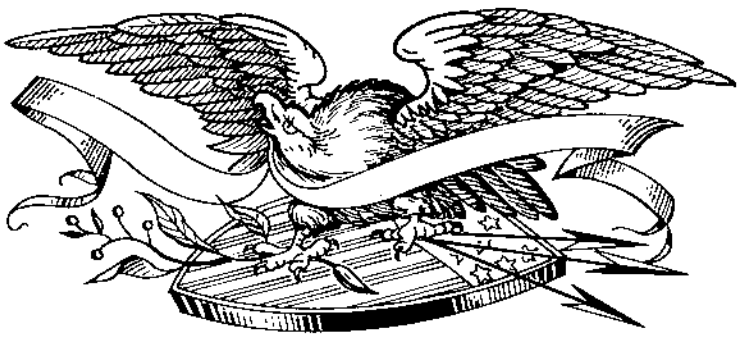

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Volcanology, Geochemistry, and Petrology

EXPERIMENTAL IGNEOUS PETROLOGY

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The 1975-1978 quadrennium was a period in which research in igneous petrology continued in many of the areas of interest of the previous quadrennium (Boettcher, 1975, sect. A) -- that is, processes of melting and phase transformations in the Earth and planetary mantles and igneous processes that are peculiar to specific tectonic regimes. The object of these studies is understanding the contribution of igneous events to the evolution of crust-mantle systems.

The references in the bibliography cover the period from the latter months of 1974 to the end of 1978. References listed are believed to reflect both the contributions of geoscientists of the United States and the interactions between U.S. scientists and their colleagues in foreign countries, in particular other countries of the Western world.

It should be noted that topics in two important areas of experimental igneous petrology, trace element partitioning and physical properties of melts, were largely ignored in light of other reports in this volume.

A. Reviews

A few articles, primarily of a review nature, that were written during the quadrennium are listed in the bibliography. The review by Green (1976) on the Australian experimental program is particularly useful. Books published by Ringwood (1975) and Yoder (1976) include much experimental work, chiefly of the Australian National University and the Geophysical Laboratory (Carnegie Institution of Washington), respectively. Many papers on experimental determinations of trace element partitioning appear in a volume edited by Drake and Holloway (1978).

B. Melting of Peridotite Without Volatiles

Petrologists and geochemists now generally accept that the great accumulations of basaltic rocks in the ocean basins and many continental basalts are ultimately derived by essentially volatile-free melting of peridotite. In view of that acceptance, and in view of still-running controversy on experimental constraints on conditions and compositions of partial melts, it is surprising that relatively little effort has been devoted in this quadrennium to resolving the controversies.

One effort that was made was the measurement by Mysen and Kushiro (1976, 1977) of the degree of melting of a fertile peridotite composition, at high pressures, as a function of temperature, and the analysis of compositions of crystals and liquids ("primary liquids"). They found that liquid compositions are largely controlled by the crystalline phase assemblage and that those liquids are, for relatively large degrees of melting (3 to 45 % melting at 20 kb and 25-45 % at 35 kb), tholeiitic. They did discover, however, that for small degrees of melting (less than 3 %), liquids were nepheline-normative (alkalic). This tholeiite-alkali basalt transition lends some credence to an idea, long espoused by Green and Ringwood (e.g., 1967), that degree of melting is as important as pressure in determining composition of primary liquids, although Green and Ringwood (1967) put the alkali basalt-tholeiite transition at about 20 % melting, rather than 3. Presnall et al. (1978a), in concluding from a literature survey that primary alkalic basalts can be formed at pressures as low as 13 kb, must have had the first few percent of melt in mind. One must talk about such a limiting pressure with some caution, however: the hard experimental data in volatile-free systems bearing on the question are not numerous nor without controversy, and minor elements (e.g., P, Ti) (Kushiro, 1974, 1975; Arculus, 1975) or volatiles (section D) in the source peridotite can have profound influence on the chemical composition of liquids produced by small degrees of melting. (It may also be noted that even in the "alkalic" system K_2O-Al_2O_3-MgO-SiO_2, model primary liquids are not alkalic below 19 Kb [Wendlandt, 1977b, sect. D].)

The reactions by which peridotite melts, and by which primary melts fractionate, have been studied by Kushiro and Yoder (1974) in the system CaO-MgO-Al_2O_3-SiO_2. They have discovered an important new reaction that is operative at pressures less than about 28 kb:

olivine + liquid =
orthopyroxene + clinopyroxene + spinel (or garnet)

A previously-known reaction operates at pressures less than about 50 kb:

orthopyroxene + liquid = clinopyroxene+ garnet

These two reaction relations permit the conclusion that at least some eclogites represent cumulates from primary magmas (Yoder, 1976, sect. A; see also Howells et al., 1975) and also bear importantly on melting reactions considered in trace-element modeling, as detailed by Mysen (1977a,b). Reaction relations among derivative liquids at lower pressures can be examined from the new study by Presnall et al. (1978a) in CaO-MgO-Al_2O_3-SiO_2. They conclude that the 1-bar "thermal divide" between theoleiitic and alkalic basaltic liquids persists to about 4 kb, whereas between 4 and at least 12 kb, alkalic basaltic liquids can fractionate to theoleiitic liquids.

Studies on basalt compositions (sect. E) also bear on the problem of melting of peridotite.

C. Volatiles and Metasomatism

The nature of the vapor (fluid) phase that may exist in the lower crust or upper mantle, or both, has been the topic of much speculation and of a little research.

Part of the research dealt with the thermodynamic properties of gases, principally H_2O and CO_2. These properties were estimated from phase-equilibria experiments (e.g., Haselton et al., 1978; Irving et al., 1977; Eggler et al., 1976) or from semi-theoretical thermodynamic functions (Holloway, 1977; Ostrovsky and Rizhenko, 1978).

Other research dealt with the solubilities of silicates and trace elements in fluids at high pressures, with processes of mantle metasomatism in mind (processes summarized by Boettcher et al., 1979). If water can move through the mantle peridotite with the speed measured by Mysen et al. (1978), on the order of 2-12 mm/hour, metasomatism must be, at least locally, very important. Relative solubilities of simple silicates in fluids were examined by Nakamura and Kushiro (1974), who discovered extensive silica solution in H_2O fluid in equilibrium with olivine-orthopyroxene, and by Eggler and Rosenhauer (1978), who discovered considerable solution of diopside in H_2O vapor but essentially none in CO_2 vapor. At high pressures rare earths are strongly partitioned into H_2O vapor (Mysen, 1978, 1979) or into CO_2 vapor (Wendlandt and Harrison, 1978) in preference to silicate liquids. Light rare earths are especially partitioned into fluids; inasmuch as such elements are enriched in alkalic basic magmas, metasomatism may be a key in generation of such magmas.

D. Melting of Peridotite with Volatiles

To understand completely the effects of volatiles on melting, it is necessary to know the magnitude of solution of volatile species in silicate melts and solution mechanisms. These parameters are largely understood for H_2O in aluminosilicate melts through the efforts of Burnham (e.g., 1975, sect. J), but are less well understood for H_2O in basic-ultrabasic melts, in spite of continued experimentation (Hodges, 1974; Eggler and Burnham, 1978; Mysen, 1976). Studies of the solution of CO_2 in basaltic melts, a possibility discovered in the last quadrennium by Hill and Boettcher (1970) and quantitatively measured by Eggler (1973), sprouted forth in this quadrennium (Eggler et al., 1974; Mysen et al., 1974; Kadik and Eggler, 1975; Mysen, 1975, 1976; Mysen et al., 1975, 1976; Rosenhauer and Eggler, 1975; Brey, 1976; Brey and Green, 1976; Holloway et al., 1976; Eggler and Rosenhauer, 1978). Many of the quantitative studies were accompanied by spectroscopic analyses of quenched glasses; spectral interpretations were mixed (e.g., Brey, 1976), but it seems generally agreed that CO_2 dissolves principally as the carbonate anion. Unfortunately, no measurements have been made that allow thermodynamic treatment of CO_2 solution, akin to models now available for H_2O. Other possible volatile species received less attention: carbon monoxide (CO) was discovered to be about as soluble as CO_2 by Eggler et al. (1977), whereas H_2 was discovered to be essentially insoluble by Nakamura (1974).

Sulfur is another species of potential significance for mantle processes (Duke and Naldrett, 1978), but primarily because it can form a transition-element-rich immiscible liquid, not because it exists in a fluid phase. Mysen and Popp (1978) have measured S_2 solubility at high pressures in silicate melts.

The two principal volatile species that are inferred to be present in the upper mantle, H_2O and CO_2, have quite different effects upon the compositions of the partial melts of peridotite at high pressures. Kushiro et al. (1968) first discovered, in the system MgO-SiO_2-H_2O, that liquid in equilibrium with peridotite minerals contained much more silica than liquid formed in the absence of volatiles and was, in fact, quartz-normative at pressures as high as 20 kb. Subsequent studies in more complicated synthetic systems have confirmed that conclusion; such studies in this quadrennium include those by Ford (1976) and Bravo and O'Hara (1975). At higher pressures (25-30 kb), H_2O-saturated liquids in equilibrium with peridotite minerals are olivine tholeiitic (Bravo and O'Hara, 1975; Howells, 1976). In addition to approaches from synthetic systems, natural peridotites can also be melted in order to determine the compositions of primary liquids. In this approach the number of components involved is more realistic, but the results are not necessarily more realistic, in large part because formidable problems can arise in quenching liquids to glass and in analyzing these quenched liquids (Nehru and Wyllie, 1975; Green, 1976) or in calculating liquid compositions from mineral compositions and estimated modes (Mysen and Boettcher, 1975b). Adherents of the quench-and-analyze school (Mysen and Boettcher, 1975a, 1975b, 1976) and the calculate-from-mode school (Green, 1976) continued their pursuits into this quadrennium, with predictably divergent results.

It is remarkable that when all the studies in synthetic and natural peridotite systems are weighed, together with liquidus studies on "primary" basalt compositions, that some agreement on the composition of H_2O-saturated primary melts does emerge: it is now accepted that partial melts of peridotite in equilibrium with H_2O vapor can be quartz-normative, the differences of opinion coming on the degree of silica saturation and the upper pressure limit for production of quartz-normative liquid (summarized by Eggler and Holloway, 1977).

The role of CO_2 in magma production has been defined nearly entirely within this quadrennium, spurred by two International Kimberlite Conferences (1973, 1977) and by such exciting discoveries as nearly-pure CO_2 fluid inclusions within phenocrysts in MORB (Delaney et al., 1978). Studies of melting of peridotite have been largely in synthetic systems. The principal discoveries have been that carbonate minerals (dolomite or magnesite) can be stable in the mantle at near-solidus temperatures and that, where dolomite becomes stable at the solidus, the peridotite solidus dramatically decreases in temperature (e.g., Eggler, 1975b, 1976a; Wyllie and Huang, 1975a,b, 1976a,b,c). This kink in the solidus has been offered as a new

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explanation of the low-velocity zone. Within the same P-T range as the kink, the composition of liquid produced near the solidus changes dramatically from basaltic at about 15 kb to kimberlitic-carbonatitic at 30 kb. These changes have been documented in the systems CaO-MgO-SiO_2-CO_2 (Eggler, 1974, 1976b, 1978a; Huang and Wyllie, 1974; Wyllie and Huang, 1975a,b, 1976 a, b,c), Na_2O-CaO-MgO-Al_2O_3-SiO_2-CO_2 (Eggler, 1974, 1978b), and K_2O-Al_2O_3-MgO-SiO_2-CO_2 (Wendlandt, 1977a). Analogous results have been observed for a natural peridotite-CO_2 composition (Wendlandt and Mysen, 1978).

The effects of CO_2 and H_2O in combination upon melt compositions might be expected to be intermediate between the effects of either volatile alone -- that is, melts could range in composition from quartz-normative to carbonatitic. That is indeed the case when relatively large amounts of volatiles are present, as demonstrated by Eggler (1975a) in MgO-SiO_2-CO_2-H_2O and by Mysen and Boettcher (1975a,b) for a natural peridotite. (Concurrently, the position of the peridotite solidus can range over a considerable P-T field, depending on vapor composition.) Fortunately, for the sake of petrologists already overburdened with divergent magma compositions, the mantle will not produce such a rainbow of primary liquids, at least not when H_2O and CO_2 are present in low concentrations. Wyllie (1977a,b,c, 1978) and Eggler (1977, 1978a,b) have theorized that the composition of H_2O-CO_2 vapor in the mantle should be buffered by carbonated peridotite or hydrated peridotite reactions. Consequently, the mantle solidus can lie at only one position (or, at worst, a very limited number of positions), and only one primary melt composition will be produced at any pressure. The vapor-buffered solidus of a natural peridotite at 30 and 55 kb was determined by Eggler and Wendlandt (1979), and Eggler (1978a) determined the solidus buffered by dolomite in CaO-MgO-SiO_2-CO_2-H_2O at 31 kb. Only one set of experiments (Wendlandt, 1977b) has been done on compositions of liquids produced near a vapor-buffered solidus. Eggler and Holloway (1977) suggest that the liquid produced at an amphibole-buffered solidus ought to be nephelinitic and Wyllie (1977c) suggests that the liquid produced at a carbonate-buffered solidus ought to be carbonatitic, even though the vapor composition is H_2O-rich. Wyllie's (1977c) suggestion may explain why Brey and Green (1975, 1977) found that an olivine melilitite, a composition about as silica-undersaturated as kimberlite, is a candidate for a primary liquid at 30 kb in equilibrium with a relatively H_2O-rich vapor. (At pressures in excess of about 30 kb, Wyllie [1978, 1979] and Ellis and Wyllie [1979] have theorized, vapor-liquid relations become more complicated because vapors contain more H_2O than liquids.) Liquid produced near a solidus buffered by both phlogopite and carbonate is carbonatitic at 30 kb and kimberlitic at higher pressures, according to Wendlandt's (1977 b) experiments in the system K_2O-Al_2O_3-MgO-SiO_2-H_2O-CO_2. Eggler and Wendlandt (1978, 1979) have confirmed, from melting a natural kimberlite composition, with added H_2O and CO_2, that kimberlitic liquids can be primary at pressures of 50 to 60 kb.

The mantle need not contain a vapor phase, of course, if all volatiles are tied up in crystalline phases. Holloway and Eggler (1976) have determined the solidus of such an assemblage, a garnet-phlogopite-dolomite peridotite, in the system K_2O-CaO-MgO-CoO-Al_2O_3-SiO_2-H_2O-CO_2.

E. Basalts and Related Rocks

Many of the very-basic rock studies in this quadrennium have been concerned with komatiites, which have seized the imaginations of many petrologists, perhaps because it seems unlikely, in modern volcano-tectonic regimes, for conditions to arise allowing extrusion of ultramafic rocks of this type. Experiments on peridotitic komatiite compositions (D. H. Green et al., 1975; Arndt, 1976; Bickle et al., 1977) demonstrate that the compositions could represent high-temperature liquids, with olivine on the liquidus. At least some investigators (Bickle et al., 1977; Arndt, 1977), however, dispute that any of the komatiites, peridotitic or basaltic, represent primary liquids derived from fertile peridotite. Their experiments, together with trace-element data (Arth et al., 1977), indicate that one-stage, large-percentage melting of the mantle did not occur and that the peridotitic komatiites result from multi-stage processes of remelting or assimilation.

Experimental studies on primitive MORB compositions (Bender et al., 1978) have not been entirely successful, either, in establishing the primacy of any observed MORB rocks, although synthetic systems (e.g., Presnall and O'Donnell, 1976) predict that MORB could separate from a peridotitic source at relatively low pressure. Relatively low pressure melting may also have been involved, according to Obata and Dickey (1976), in formation of mafic layers in the Ronda peridotite complex, and, according to Thompson (1975a), in the origin of magnesian tholeiites from the Snake River Plains. In studies on other theoleiitic basalt compositions, important roles have been discovered for amphibole (Helz, 1976) and spinel (Hill and Roeder, 1974) in crystallization sequences. The role of chromite spinel has also been investigated by Irvine (1977a,b), who has mapped the geometry of the olivine-chromite cotectic in the join Mg_2SiO_4-$CaMgSi_2O_6$-$CaAl_2Si_2O_8$-$MgCr_2O_4$-SiO_2. Irvine offers a new explanation of chromitite layers in theoleiitic stratiform intrusions: pulses of picritic liquids blend with differentiated siliceous compositions to shift the crystallization into the chromite primary phase volume. Hoover (1978) has delineated a "parental liquid" for the Skaergaard intrusion which, in experiments, crystallizes a reasonable sequence of minerals.

Experiments on alkaline rock compositions and in related synthetic systems served to place tighter limits on the conditions (P-T-X_{H_2O}-X_{CO_2}) of their origin. Compositions involved ranged from basanite (Chapman, 1976; D. H. Green and Sobolev, 1975; Merrill and Wyllie, 1975) to hawaiite (Knutson and T. H. Green, 1975) to highly potassic rocks (Edgar et al., 1976; Cundari and O'Hara, 1976; Barton, 1976; Dolfi and Raffaello, 1978; Barton and Hamilton, 1978; Ruddock and Hamilton, 1978) to carbonatite (Cooper et al., 1975).

F. Granites and Andesites

In this quadrennium proponents or opponents of the four major schools of andesite generation -- basaltic fractional crystallization involving amphibole, fractional crystallization involving magnetite, primary wet melting of peridotite, and wet melting of eclogite -- were all heard from. Details of amphibole fractionation were clarified by studies of Allen et al. (1975) and Allen and Boettcher (1978) on amphibole stability in andesitic and basaltic liquids, of Cawthorn (1976) and Cawthorn and O'Hara (1976) on amphibole-dominated fractionation paths in CaO-MgO-Al_2O_3-SiO_2-Na_2O-H_2O, and of Mysen and Boettcher (1976) on the influence of amphibole on liquid composition in wet melting of a garnet websterite composition. On the other hand, Ritchey and Eggler (1978) found that amphibole does not crystallize on the liquidus of the Crater Lake calc-alkaline series and could not have influenced differentiation. The effect of fluorine in extending amphibole stability to higher pressure and temperature was demonstrated by Holloway and Ford (1975).

Proponents and opponents of the wet-melting-of-peridotite school waged a long-running skirmish in the previous quadrennium (see Boettcher, 1975, sect. A), of which the study of Kushiro (1974a,b) represents a late entrant. Johnston (1978) has subsequently joined the opponents, as a result of enstatite-addition experiments on andesitic compositions.

Experiments of Osborn and Arculus (1975) and of Osborn and Watson (1977) are consistent with the hypothesis that high-alumina basalts may fractionate if magnetite is on the liquidus. Osborn (1978) also found an expanded spinel field in the MgO-FeO-Fe_2O_3-SiO_2-$CaAl_2Si_2O_8$ system at 10 kb.

In contrast to the support accorded that theory of origin of the calc-alkaline rocks, the theory of wet melting of eclogite in a subducted oceanic slab received no support from Stern and Wyllie (1978). They inferred, from analysis of melting relations of a gabbro and a tonalite composition, that liquids produced are silicic, but neither the liquids nor their derivative liquids have other calc-alkaline chemical characteristics.

It is generally now accepted, from geochemical evidence, that nearly all granites are generated by partial melting of the lower crust, and not by melting of peridotite or eclogite in the mantle. Experiments at high pressures by Stern et al. (1975) on rock compositions and of Huang and Wyllie (1975) in the system $NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2-H_2O support that view. It is also now accepted that the type of granite generated is dependent upon the type of material melted. In the case of S-type granites (Chappell and White, 1974), that material is pelitic sediments. Melting experiments of T. H. Green (1976, 1977) on pelitic compositions support this argument, inasmuch as he found residual minerals corresponding to minerals in S-type granites.

There can be no doubt that volatiles are present in granitic liquids. How much there are, and what they are, is another matter. Studies of Maaløe and Wyllie (1975) and Whitney (1975) bear on the amount of H_2O that can be reasonably assumed to be in a granitic magma, whereas Holloway (1976) advances the hypothesis that granitic magmas are also accompanied by a H_2O-CO_2 fluid phase that significantly changes the physical properties of the magma-fluid system.

G. Lunar Studies

It is now thought that very early melting of the Moon produced a magma ocean several hundred kilometers thick, which cooled and differentiated to a plagioclase-rich crust and an interior of mafic cumulates. Subsequent melting of the cumulates or a combination of cumulates and the primitive interior produced mare basalts. Experimental studies have provided important constraints on these processes.

Most experimental petrologic studies have some bearing on the first event, but, in particular, experiments on model Moon compositions (Kushiro and Hodges, 1974; Hodges and Kushiro, 1974; Ringwood, 1976; Kesson and Ringwood, 1977) have been used to select reasonable model compositions and to constrain the sequence of crystallization expected in a magma ocean, in which mafic cumulates sank and plagioclase floated (Walker and Hays, 1977). Details of fractional crystallization at the higher levels of crystallization of the magma ocean -- that is, within rocks of the lunar highlands -- could not have been worked out without knowledge of phase relations in the system Mg_2SiO_4-Fe_2SiO_4-$CaAl_2Si_2O_8$-SiO_2. Relevant planes through that system have been determined from microprobe analyses of glasses in experiments on KREEP basalt and highland feldspathic compositions (Walker et al., 1973; McKay and Weill, 1976, 1977; Hess et al., 1977) and from experiments in the pure system (Merrill and Williams, 1975; Lipin, 1978). A few highland basalt compositions lie near reaction points in that system at 1 bar and could represent partial melts of feldspathic crust (Walker et al., 1973) or residual liquids from the magma ocean crystallization (Lipin, 1978; Hess et al., 1977; McCallum and Charette, 1978).

There have been many experimental studies of mare basalts. Kesson and Lindsley (1976) and Papike et al. (1976) have listed and evaluated those before 1976. As with highland rocks, these experiments serve to separate liquid compositions (usually equated with certain rock compositions, a point discussed by O'Hara and Biggar, 1977) produced by near-surface fractional crystallization from possible primary liquids (e.g., Kesson, 1975; Walker et al., 1975a; Green et al., 1975). Nearly all investigators have identified two groups of primary basalts, high and low Ti. Multiple-saturation liquidus relations (e.g., Kesson, 1975; Walker et al., 1975a) suggest that the magmas of the two groups were melted at depths of at least 200-250 km but from compositionally different olivine pyroxenite cumulate sources. Walker et al. (1975a) in addition specify that the source of high Ti basalts was ilmenite-rich. Kesson and Ringwood (1976) have suggested that a more exotic process is required, involving melting of regions of the primitive interior that were hybridized by sinking ilmenite-clinopyroxene pods. Ringwood and Kesson (1976) have offered limited experimental evidence that

such pods can melt to produce Ti-rich liquids.

The distinctive Apollo 15 Green Glass and the Apollo 17 Orange Glass may have melted from olivine pyroxenite sources at depths of 400 km or more (Green and Ringwood, 1973; Walker et al., 1975a; Green et al., 1975), depths presumably within the primitive lunar interior.

Crystallization experiments by Hess et al. (1975, 1977) on mare and KREEP basalts and on lunar monzonites show that with extensive fractionation, lunar magmas did yield immiscible liquids and that one of those liquids is represented by the lunar granites and monzonites.

H. Geothermometry-Barometry of Mantle-Derived Rocks

Many experimental petrologists who might consider themselves "igneous" have ventured into the nominally "metamorphic" field of geothermometry-barometry, undoubtedly in part because they possess the requisite high-pressure apparatus for experimentation on ultramafic assemblages, but probably also in part because at high pressures, the fields of "igneous" and "metamorphic" petrology merge. The recorded geotherms of metamorphic rocks of the mantle -- peridotites and eclogites -- often reflect temperatures upset by the magmatic processes giving rise to the kimberlites or alkali basalts in which they occur,a geologic "Uncertainty Principle" (Irving, 1976).

A time-tested method of peridotite geothermometry, the compositions of two coexisting pyroxenes, that was pioneered by Davis and Boyd (1966), has received continued attention. New studies on the two-pyroxene field in the "pure" system CaO-MgO-SiO_2 (Nehru and Wyllie, 1974; Mori and Green, 1976; Lindsley and Dixon, 1976) are in substantial agreement. Orthopyroxene as well as diopsidic clinopyroxene compositions have been determined; in principle, therefore, two geothermometers are available. The effect of Fe on the two-pyroxene field has been modeled by Wells (1977) and examined experimentally by Mori (1978). Shifts in the two-pyroxene field caused by Al substitution in pyroxenes have been detected by Fujii (1977b), Mori (1977), Dixon and Presnall (1977), and Herzberg (1978a). To be sure, the effect of Al on the two-pyroxene field is debated, but among many petrologists the view of Herzberg (1978a) would probably prevail -- in the garnet peridotite facies, the contents and effects of Al in pyroxenes are small, but alumina must be considered when clinopyroxenes in spinel peridotites are involved. A new geothermometer, based on Al content of clinopyroxene, has in fact been proposed by Herzberg and Chapman (1976) and Herzberg (1978b).

Other geothermometers that have either been proposed or revived in the last four years are Fe-Mg partitioning between olivine and spinel, a thermometer calibrated from natural occurrences by Evans and Frost (1975) and from experiments by Fujii (1977a) and Engi (1978); exchange of Mn, Ca, Mg, and Al between pyroxenes, olivine, and garnet (Finnerty, 1977); Fe-Mg partitioning between garnet and clinopyroxene, partially calibrated for ultramafic compositions by Raheim and Green (1974), Mori and Green (1978), and Wood (1976); and Al-Cr partitioning between clinopyroxene and orthopyroxene (Mysen, 1976).

Geobarometry of garnet peridotites, based on Al in orthopyroxene, is now apparently well established from experiments of MacGregor (1974) and Wood (1974), although at least one group (O'Hara and Howells, 1978) would dispute some of the experimental constraints. The semi-empirical thermodynamic model of Wood (1974, 1977) appears to account well for effects of Fe, Ca, and Cr. Rigorous thermodynamic treatment of the pyroxene and garnet solid solutions involved is under way, based on phase equilibria (Hensen et al., 1975; Herzberg, 1978a; Cressy, 1978) or on calorimetry (Newton, 1977; Newton et al., 1977, 1979). Tests of the model by experimentation in complex systems appear to be very satisfactory in some cases (Akella, 1974, 1976; Akella and Boyd, 1974), although in at least one other case (Mori and Green, 1978) doubt exists. The status of a geobarometer for spinel lherzolites (isopleths representing the Al content of orthopyroxene in equilibrium with olivine and spinel), is much more in doubt, inasmuch as a variety of slopes of Al isopleths (dT/dP) has been found, from steeply positive (MacGregor, 1974) to very gently positive (Fujii, 1976; Danckwerth and Newton, 1978) to steeply negative (Presnall, 1976; Dixon and Presnall, 1977). Calculations of the isopleths from data in the garnet peridotite facies (Wood, 1975; Obata, 1976) are in substantial agreement with the experiments of Fujii (1976) and Danckwerth and Newton (1978). The implication of this majority view is that the Al isopleths may be geothermometers but not geobarometers.

Finnerty and Boyd (1978) have proposed another geobarometer, the solubility of Ca in olivine, that is applicable to garnet or spinel peridotites.

I. Liquid Immiscibility

A small slurry of papers has appeared in this quadrennium on two-liquid immiscibility, probably in part inspired by discovery of late-stage immiscibility in lunar basalts and in part by the experimental discovery (McBirney and Nakamura, 1974; McBirney, 1975) of immiscibility in melts of the Skaergaard Upper Zone compositions.

In several investigations, components have been added to Roedder's (1951) classic diagram showing immiscibility on the join leucite-fayalite-silica, a diagram that has withstood the tests of time (Roedder et al., 1977; Roedder, 1978). Components that expand the two-liquid region are P_2O_5 and TiO_2 (Watson, 1976; Freestone 1978a,b; Visser and Koster van Groos, 1978) and CO_2 at high pressures (Watson and Naslund, 1977); components that contract the two-liquid region are Na_2O (Naslund, 1976; Biggar, 1978; Cygan and Koster van Groos, 1978), MgO (Watson, 1976; Cygan and Koster van Groos, 1978), and CaO (Watson, 1976; Naslund, 1977). Decreasing f_{O_2} contracts the region (Naslund, 1976; Freestone, 1978b). Mixed results have been obtained on the effect of pressure on the two-liquid region (Kakamura, 1974; Watson and Naslund, 1977).

Liquid immiscibility has been discovered, at pressures less than 10 kb, between carbonatitic liquids and silicate liquids that range in composition from granitic to quartz syenitic (Koster van Groos, 1975) to ijolitic (Verwoerd, 1978). Wendlandt and Harrison (1978, sect. C) found that a carbonate-silicate miscibility gap persists to 20 kb in the system K_2O-Al_2O_3-SiO_2-CO_2.

J. Thermodynamics and Structure of Melts

Energetic investigations into the structure of silicate melts and into thermodynamic modeling of liquid-vapor-crystal equilibria characterized the past quadrennium, although the subject is hardly new: Bowen (1913), in presenting a phase diagram of the plagioclase feldspars, also presented a thermodynamic analysis. Recent interest may be attributed in part to the availability of high-precision P-V-T measurements and calorimetric measurements and to the realization that trace element partition coefficients depend on melt structure.

Thermodynamic formulations of melting in complex silicate systems require models for the mixing of components in the melts. Some of these models are reviewed by Fraser (1977) and Hess (1977). Burnham (1975a,b) has led the way in advocating a quasi-crystalline model. In Burnham's model of H_2O-melt interaction, developed from P-V-T measurements in the system albite-H_2O (Burnham and Davis, 1974), aluminosilicate components of melts, properly formulated, have been found to mix ideally (but see Dye and Vogel, 1978 and Burnham et al., 1978). With this model, Burnham has been able to calculate the thermodynamic properties of many mineral-like silicate components of melts from phase diagrams. In principle, precision of this method should far exceed the precision of calorimetric measurement, but difficulties arise in the formulations as non-aluminosilicate components are considered. By way of contrast, Drake (1976) has used a distinctly non-quasi-crystalline model of melt structure in calculating plagioclase-melt equilibria. Nor are X-ray radial distribution analyses of feldspar glasses by Taylor and Brown (1979) consistent with the contention that feldspar glasses are structurally similar to feldspar crystals. Bottinga and Richet (1978) have incorporated calorimetric data in their treatment of melts as Flory-Huggins regular solutions. Carmichael et al. (1977) sought to expand the calorimetric base by making high-temperature measurements of the heat content of glasses and liquids in a drop calorimeter. They combined those data with known melting curves and densities or heat contents of glasses (Bacon, 1977) to derive enthalpies and volumes of melting. A promising method of differential scanning calorimetry that combines calorimetry with dynamic phase equilibria enabled Rosenhauer (1976) to measure the enthalpy of melting of diopside with and without water to 4 kb.

In other studies structures of melts have been deduced from spectra or measurement of physical properties or phase equilibria or element partitioning. Those studies dealing with physical properties or element partitioning are treated elsewhere in this volume, but one example will be mentioned, the indication from Kushiro's (1976, 1978) measurements of viscosities of $NaAlSi_2O_6$ and $NaAlSi_3O_8$ composition melts that Al undergoes a coordination change at high pressures. This change was apparently also seen in infrared and K-radiation spectra of quenched glasses (Velde and Kushiro, 1978). Unfortunately, octahedrally-coordinated Al could not be detected by Raman spectroscopy by Sharma et al. (1978). Fraser (1977) has examined infrared spectra of alkali phosphate glasses that are analogous to silicates.

Mossbauer spectrometry helped Virgo and Mysen (1977, 1978) relate changes in Fe^{3+}-Fe^{2+} ratios to changes in polymerization in $NaAl_{1-x}Fe_xSi_2O_6$ melts as a function of composition, temperature, and pressure. In a related study, redox equilibria of Eu have been found to be largely a function of bulk composition (Lauer and Morris, 1977).

An example of the application of phase equilibria to questions of melt structure can be found in the work of Irvine (1975, 1976) in the system Mg_2SiO_4-Fe_2SiO_4-$CaAl_2Si_2O_8$-$KAlSi_3O_8$-SiO_2, in which he found substantial fields of metastable liquid immiscibility, presumably because quartzofeldspathic and mafic components of melt do not mix ideally (a concept that is not necessarily in variance with the model of Burnham [1975a,b]). Irvine (1976) argued that these fields influence liquidus boundaries and, hence, the course of major crystallization fractionation trends.

Other Studies

Studies in which rock textures have been reproduced are a recent development and even more recently have been quantified by mass transfer and kinetic considerations. Representative papers are listed in the bibliography. Other listings include studies devoted almost entirely to stability ranges of particular minerals and studies introducing new techniques or pointing out ways around old problems.

The Next Quadrennium

In the introduction to this section, it was suggested that the object of experimental studies -- an understanding of the evolution of the crust-mantle system -- has not changed significantly over the last eight years. Change can be noticed, however, in methods of study. In addition to traditional phase equilibria, newer areas have bloomed, such as trace-element partitioning and thermodynamic-structural-spectral modeling of liquid and crystalline solutions. This trend can be expected to continue and will spurt where new instrumentation is applied. Breakthroughs should also occur in areas in which field-based and geochemical studies have now forged far ahead of experiment, such as the calc-alkaline rock series and mantle metasomatism.

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THEORETICAL PETROLOGY

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The central issues in petrology have remained remarkably unchanged in the last 50 years. In igneous petrology, the focus is on understanding the nature and cause of diversity in igneous rocks: on identifying primary magma types and constraints on the compositional and mineralogical characteristics, the physical conditions, and the evolutions of their source regions and on establishing the processes by which derivative magmas evolve from primary magmas. In metamorphic petrology, the major concern is with understanding the conditions and processes experienced by a rock in reaching its present state. In both igneous and metamorphic petrology, the ultimate goal is the integration of petrological constraints with those from other branches of earth science into regional and global theories of earth history. What has changed over the years, however, is the framework within which these issues are addressed: the backdrop provided by plate tectonics and geophysical constraints, the growing sophistication of chemical and physical models of rock systems, the ever increasing inputs from trace element and isotopic geochemistry, the sophistication and complexity of experimental approaches to petrological problems, and the growing body of detailed petrological studies of specific rock suites and associations from all over the world. What I will attempt in this report is to pinpoint and briefly review those areas of growing interest and emphasis in American efforts in petrology during the 1975-1978 quadrennium and the ways in which they were shaped by this framework.

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Structure of Silicate Melts and Thermodynamics in Igneous Petrology

One area of growing interest in igneous petrology has been the characterization of the structural and thermodynamic properties of silicate melts and the application of these results to an understanding of phase equilibria and processes in igneous systems. Several approaches have been taken to understanding silicate melt structure and its response to changes in physical conditions and composition. Structural properties of melts have been inferred from theoretical considerations (Waff, 1975), from spectroscopic study of quenched glasses (Velde and Kushiro, 1978), and from variations observed in viscosities and densities of melts as functions of pressure and composition (Kushiro, 1976; Kushiro et al., 1976). Structural implications have also been drawn from the dependence of liquidus phase relations on melt composition (Eggler and Rosenhauer, 1978; Kushiro, 1975; Mysen, 1976). Studies of element partitioning between crystals and silicate liquids also yield information on the structures of silicate liquids (Leeman, 1978; Watson, 1977). These studies of melt structure can provide valuable insights into phase equilibria

and the physical properties of melts as functions of physical conditions and composition.

Several approaches have also been taken to characterizing the thermodynamic properties of silicate melts and to developing the methodology for the application of these results to both qualitative and quantitative prediction of phase equilibria. Thermodynamic properties of silicate melts, such as enthalpy, heat capacity, and heat of fusion, have been measured or estimated in a number of ways (Bacon, 1977; Carmichael et al., 1977; Hon et al., 1977; Peck et al., 1977; Rosenhauer, 1976; Yoder, 1975). Thermodynamic approaches to the prediction of liquidus diagrams were developed by several investigators: Polymer models of silicate systems provide qualitative insights into the properties of more complex systems (Hess, 1975), but are unlikely to provide a basis for their quantitative treatment. Models based on ideal mixing of appropriately chosen components in silicate melt systems have been applied to the prediction of binary and ternary liquidus diagrams (Burnham, 1975). Bottinga and Richet (1978) have developed a promising new approach to the prediction of liquidus diagrams based on a Flory-Huggins formulation. The concept of silica activity in melts continued to be developed (Nicholls, 1977) and applied to petrogenetic problems (Hausel and Nash, 1977). A number of authors carried out thermodynamic treatments of experimental studies of major and minor element exchange equilibria between crystalline and liquid silicates (Drake, 1976b; Longhi et al., 1978). The results of these studies have potential application to the calculation of fractionation trends in liquids, to geothermometry, and to the reconstruction of primitive liquid compositions (Drake, 1976a; Irvine, 1977a), and as mentioned above, provide insights into the structural properties of silicate liquids. Considerable interest focused on trace element partitioning between crystals and liquids and analysis of the results in terms of chemical models (Fraser, 1975; Hart and Davis, 1978; Mysen, 1978; O'Nions and Powell, 1977).

Kinetics and Textures in Igneous Rocks

Interest in the textures and mineral zoning patterns of igneous rocks and their interpretation in terms of the conditions under which the rocks crystallized, the transport properties of silicate crystals and liquids, and the dynamics of the crystallization process grew during the 1975-1978 quadrennium. Numerous experimental studies examined crystallization sequences and textures of natural compositions as functions of cooling rate. These studies showed that crystallization sequences depend on cooling rate as well as bulk composition and that textures depend on the presence or absence of phenocrysts in the cooling magma or the amount of superheat if no phenocrysts are present, as well as cooling rate. Overall textural characteristics and measures of crystal shape, crystal size, and nucleation density permit estimation of cooling rates above the solidus and can help to determine whether or not phenocrysts were present in the magma when it began to cool (Bianco and Taylor, 1977; Lofgren et al., 1975; Walker et al., 1976, 1978a). Other approaches have been applied to estimate cooling rates of igneous rocks at principally subsolidus temperatures: modelling of pyroxene exsolution (Miyamoto and Takeda, 1977), modelling of Zr distribution between ilmenite and ulvospinel (Taylor et al., 1975), and modelling of the homogenization of the initial zoning profiles of olivines (Taylor et al., 1977; Walker et al., 1977). Detailed analysis of cooling rates of igneous rocks has been applied primarily to extraterrestrial basic rocks. In such cases, where geological controls such as field relations are not available, cooling rate estimates can be used to infer the size of the magma body in which a rock crystallized (Brett, 1975; Walker et al., 1976, 1977). There has, however, been experimental study of textures in terrestrial basic rocks (Donaldson, 1977; Lofgren and Donaldson, 1975) and field study of the relationship between cooling history and magma body dimensions (Peck et al., 1977; Wright et al., 1976). Experimental and theoretical characterizations of mechanisms of nucleation and growth of crystals in synthetic and natural melts were based on the studies mentioned above, and others (Fenn, 1977; Gray, 1978; Kirkpatrick, 1975, 1977; Swanson, 1977).

Study of diffusion of major and trace components in silicate glasses (Magaritz and Hofmann, 1978) and silicate melts (Arzi, 1978; Hofmann and Magaritz, 1977) is a growing field of interest. This information can be used to understand crystal growth (Donaldson, 1975; Kirkpatrick, 1977) and to evaluate time scales for homogenization of isotopic and chemical disequilibrium in mantle systems (Hofmann and Hart, 1978). These studies have cast doubt on models of magma genesis invoking disequilibrium melting processes in the mantle to explain certain isotopic features of basic rocks, unless melts are generated and removed from mantle sources on a rapid time scale.

Oceanic Basalts

Major efforts were made in the 1975-1978 quadrennium to understand the genesis of basaltic rocks from the ocean floor. The interest in these rocks stemmed largely from the recognition of their importance in a global framework as the rock type produce at accreting plate margins and as one of the most abundant rock types in the earth's crust. Many of the samples for study were provided by the Deep Sea Drilling Project and the FAMOUS project.

Most ocean ridge basalts are tholeiitic and multiply saturated with olivine, high-Ca pyroxene, and plagioclase at their low pressure liquidi. This multiply saturated character suggests that the bulk of these basalts evolved by fractionation at low pressures and do not represent primary melts of the mantle. This rarity of primary magmas among erupted basalts is also observed, though to a less extreme extent, on the moon and may be a general feature of basalts on the large terrestrial planets. Detailed analysis of the petrology and chemistry of mid-ocean ridge basalts has led to the suggestion that processes more complex than simple fractional crystallization may be important in their petrogenesis. A number of studies have concluded that mixing of magmas in magma chambers beneath the mid-ocean ridge plays an important part in their evolution (Bryan and Moore, 1977; Donaldson and Brown, 1977; Dungan et al., 1978). Magma mixing in such chambers may be a reasonable consequence of the current tectonic picture of the ridge, where new pulses of primitive magma are more or less continuously injected into a differentiating magma chamber beneath the ridge. The structural, geochemical, geophysical, and thermal consequences of such a magma chamber have been examined by a number of authors (Dewey and Kidd, 1977; O'Hara, 1977; Sleep, 1978). Thus, one of the interesting developments of the last quadrennium was the notion that magma mixing, once believed to be a rare phenomenon exerting little influence on the compositions of most magmas, may have a profound influence on one of the most abundant magma types on earth. Magma mixing has also been invoked as a significant control on differentiation trends and on the origin of chromitite layers in large basic intrusions (Irvine, 1977b), on the chemical compositions of some Hawaiian magmas (Wright et al., 1975), and on the origin of certain andesitic and related magmas (Eichelberger, 1975). Its importance in triggering eruptions has been discussed by Sparks et al. (1977b).

As somewhat of an aside in the context of oceanic basalts, it should be noted that in addition to magma mixing, other alternatives to fractional crystallization as the major control on the compositions of non-primary magmas were explored during the 1975-1978 quadrennium. In particular, liquid immiscibility continues to attract a loyal following. The phenomenon has been explored by field petrologists and by a growing number of experimental petrologists, who have begun systematic exploration of its extent as a function of pressure, oxygen fugacity, and chemical composition in simplified systems (Irvine, 1976; Naslund, 1976; Philpotts, 1976; Roedder, 1978; Watson, 1976; Watson and Naslund, 1977). McBirney (1975) suggested that the granophyre in the upper level of the Skaergaard intrusion formed by liquid immiscibility, but alternative explanations of this phenomenon in large intrusions, such as melting of roof rocks (Smith and Silver, 1975), may be more attractive. The general importance of liquid immiscibility in petrogenesis remains to be established, although it is probably responsible for some features of certain rock types (e.g., lamprophyres). Assimilation is another process which can exert some influence of petrogenesis (Joesten, 1977) and which may be of considerable importance in explaining the isotopic systematics of certain continental rocks (Carter et al., 1978b).

While studies of ocean ridge basalts have led to an appreciation among many petrologists of the importance of the magma chambers beneath the ridge, studies of ophiolite complexes have provided a complementary view of the processes involved in the formation of oceanic crust and oceanic basalts at mid-ocean ridges since it is widely (but not universally; see, for example, Miyashiro, 1975) believed that most ophiolites represent cross sections of oceanic crust and upper mantle formed at mid-ocean ridge spreading centers. A variety of petrological and geochemical studies of ophiolite complexes during the last quadrennium contributed to a characterization of the dynamic igneous and metamorphic processes involved in the formation of oceanic crust (Coleman, 1977; Jackson et al., 1975; Menzies et al., 1977; Stern et al., 1976). These petrological studies also provide a framework for the interpretation of geophysical data bearing on the structure of the oceanic crust (Clague and Straley, 1977; Peselnick and Nicholas, 1978; Salisbury and Christiansen, 1978; Spudich et al., 1978) and for models of the ridge zone (Dewey and Kidd, 1977).

A variety of petrological and geochemical studies were carried out on oceanic island volcanic suites (Batiza, 1977; Bonatti et al., 1977; Sigurdsson et al., 1978). The chemical variations within these suites were generally interpreted in terms of partial melting in the mantle and low pressure fractional crystallization. The longstanding question of the origin of the Daly gap in these suites remains unresolved, although it was attributed to both fractional fusion (Chayes, 1977) and fractional crystallization (Clague, 1978) during the last quadrennium. The concepts of hotspots and mantle plumes continued to dominate perceptions of oceanic island magma genesis, but they are becoming more complex in response to increasing information: Dymond (1975) and Jackson (1976) proposed moving hotspots; Bonatti et al. (1977) inferred "hot lines" in the mantle; and Morgan (1978) discussed the possibility of "pipelines" from hotspots to nearby ridge crests. Some difficulties were discussed with the popular view that mantle plumes result from the rising of hot, fertile mantle peridotite through depleted peridotite due to the lower density of the former. O'Hara (1975) and Boyd and McCallister (1976) showed that fertile peridotite is in fact denser than depleted peridotite and will have no tendency to rise buoyantly in mantle plumes. Boyd and McCallister suggested that this difficulty could be avoided if fertile mantle were to rise as crystal plus liquid (~25%) mushes, which would be lighter than depleted peridotite. However, this may also encounter difficulties since liquids may segregate from the crystal plus liquid mush long before the peridotite is 25% molten (Walker et al., 1978b). If Boyd and McCallister's explanation is correct, it could have important implications: melting may not occur in plumes in response to buoyant rise of fertile mantle; rather, it may initiate the rise. An alternative possibility is that hotspots are initiated by the rise of mantle material which is somewhat depleted relative to its surroundings.

The Mantle

Efforts to understand the petrology and evolution of the earth's upper mantle were a major focus of the American petrological community during the 1975-1978 quadrennium. Views of the upper mantle have been strongly influenced by studies of the the ultramafic nodules which occur in basalts and kimberlites. They provide the basis for most estimates of its composition (e.g., Smith, 1977). Many detailed

petrological and geochemical studies of xenoliths from kimberlites can be found in papers presented at the First International Conference on Kimberlites (Ahrens et al., 1977). Paleogeotherms continued to be constructed from both garnet lherzolite nodule suites (Boyd and Nixon, 1975, 1978) and spinel lherzolite nodule suites (Mercier and Carter, 1975), but the approach has been questioned (Irving, 1976; MacGregor and Basu, 1976; Wilshire and Jackson, 1975). The potential importance of paleogeotherms spawned a wide range of studies designed to calibrate and refine techniques for estimating pressures and temperatures of equilibration in ultramafic nodules. A number of these can be found in a special issue of the American Mineralogist (Vol. 61, pp. 549-816) in which many of the papers presented to the International Conference on Geothermometry and Geobarometry are published. Pressures and temperatures of garnet lherzolites are probably valid at least in a relative sense, but the calibrations are not yet good enough to be sure of the reality of the kinked geotherm identified in the previous quadrennium. There is considerable controversy concerning spinel lherzolite geobarometry and the geotherms based on these nodules. Some of the contributors to the controversy surrounding the calibrations of the alumina isopleths of orthopyroxene in spinel lherzolites and their applications to geobarometry have been Danckwerth and Newton (1978), Mercier and Carter (1975), Obata (1976), Presnall (1976), and Wood (1975).

Synthesis of pressures and temperatures of equilibration in nodules with their mineralogical, textural, and compositional characteristics has yielded intriguing clues into the structure and evolution of the upper mantle beneath South Africa (Boyd and Nixon, 1975; MacGregor, 1975). Xenoliths from depths of greater than 150 km are strongly sheared, contain no phlogopite, and based on their major element chemistry, appear to have experienced little extraction of a basaltic component. On the other hand, the nodules from shallower depths are coarse-grained and granular, contain phlogopite, and appear, on the basis of their major element chemistry, to be depleted in a basaltic component relative to the sheared nodules from greater depth. Trace element studies, however, demonstrate that the genesis of the granular peridotites must be more complex than simple removal of a basaltic component from peridotites similar to the sheared peridotites (Shimizu, 1975). Although neither the significance nor the generality of the correlation of composition, mineralogy, and texture with depth are entirely clear, the possibility of direct petrologic mapping of the upper mantle by detailed study of ultramafic xenoliths is one of the more important developments of the last two quadrennia and is likely to continue to be actively developed in the future.

The textures of ultramafic xenoliths in basalts and kimberlites and their implications for constraining mantle processes have been explored by a number of authors (Basu, 1977; Goetze, 1975; Mercier and Nicholas, 1975; Wilshire and Pike, 1975). Other aspects of mantle processes relevant to petrology were investigated during the last quadrennium: several authors modelled the distribution and subsequent segregation of liquid from partially molten peridotite, but there is not general agreement on the geometry of the melt distribution nor on the time scale required for the segregation and escape of melts from their source regions (Arndt, 1977; Turcotte and Ahern, 1978; Waff and Bulau, 1977; Walker et al., 1978b). The flow of magma from mantle source regions to the surface in conduits was modelled by Vogt (1976) and Marsh and Kantha (1978) and the influence of crack propagation on melt rise was considered by Anderson and Grew (1977). Sparks et al. (1977a) made the interesting suggestion that ascending magmas would behave like Bingham rather than Newtonian fluids. On this basis, they suggested that magmas carry nodules from depth because of their rheology, reflecting slow ascent rates, rather than due to rapid ascent rates as is usually assumed. Their analysis, if applicable, could also undermine the widely held assumption that nodule-bearing magmas did not fractionate between the depth at which they incorporated the nodules and the surface and have thus escaped the effects of low pressure fractionation.

Melting experiments on ultramafic rocks or model mantle compositions under a range of conditions provide a framework for the interpretation of melt compositions observed in nature. If an observed magma type (or some of its critical features) can be reproduced experimentally by melting of a reasonable mantle composition, then such a magma could have been produced by melting of such a source under conditions similar to those of the experiment. During the 1975-1978 quadrennium, many experimentalists focused on studies of subsolidus phase relations and melting of model and simplified mantle compositions at various pressures as functions of volatile content and composition and constructed petrogenetic models for basic and ultrabasic magmas based on these studies (Boettcher et al., 1975; Eggler, 1975, 1978; Eggler and Holloway, 1977; Mysen and Boettcher, 1975; Newton and Sharp, 1975; Wyllie, 1978; Wyllie and Huang, 1975, 1976ab). Other petrogenetic schemes for basic magmas based largely on synthesis of high pressure experimental data relevant to mantle melting and basalt phase equilibria were presented by Mysen and Kushiro (1977), O'Hara et al. (1975), Presnall et al. (1978), Ringwood (1975), and Yoder (1976). The liquid compositions produced by small degrees of partial melting of peridotite in the presence of H_2O and/or CO_2 vary widely (depending on the experimental conditions and the investigator) and may include melts similar to andesites, kimberlites, carbonatites, olivine-melilitites, melilite-nephelinites, and other alkali-rich, silica-poor magmas. The primary magmas of the more abundant tholeiitic and alkali olivine basalts appear to form under dry or nearly dry conditions.

One of the uncertainties in problems of magma genesis which has begun to attract attention is the oxygen fugacity in mantle source regions. The oxidation states of magmatic gases (Gerlach and Nordlie, 1975) and inferred from the oxide equilibria in basalts (Haggerty, 1978) indicate

oxygen fugacities near the quartz-fayalite-magnetite buffer, but this is not necessarily a meaningful guide to mantle values, and may largely reflect hydrogen loss from magmas (Sato, 1978). Graphite-gas or diamond-gas equilibria may be the primary controls on oxygen fugacity during partial melting in the mantle (Eggler et al., 1977; Rosenhauer et al., 1977; Sato, 1978). Vesicles in ocean-ridge basalts (Moore et al., 1977), fluid inclusions in phenocrysts from these basalts (Delaney et al., 1978), and fluid inclusions in ultramafic nodules (Green and Radcliffe, 1975; Murck et al., 1978) are all CO_2-rich. This may have bearing on both the composition of a fluid phase in the mantle and whether it equilibrated with graphite, diamond, and/or a carbonate.

The implications of komatiites and their associates to mantle evolution are not entirely clear, although efforts to characterize these ultrabasic lavas continued during the last quadrennium (Arndt, 1977; Arndt et al., 1977; Arth et al., 1977; Green and Schultz, 1977). They could be produced by large degrees or by successive smaller degrees of partial melting of the mantle. The existence of Ordovician komatiites (Upadhyay, 1978) indicates that conditions required for their origin were not unique to the the Archean, although they were apparently rare in later times.

Trace Element and Isotope Geochemistry

One of the more important developments in igneous petrology over the last decade has been the growing influence of trace element and isotopic geochemistry. Trace element and isotopic analyses have become a routine part of most studies of specific rocks suites and few petrogenetic questions can be meaningfully addressed without reference to the constraints provided by these branches of geochemistry. Although these fields are reviewed elsewhere in this volume, I will here briefly mention a few of the results most important to petrogenesis.

The initial ratios of $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ and the isotopic composition of lead in basalts provide means of identifying heterogeneities in their mantle source regions. Some source regions appear to have experienced previous episodes of melt extraction and are "depleted", others appear to have experienced no previous melting and are thus "undepleted", while still others may have been enriched in a low-melting component. Modelling of the evolution of the mantle from an assumed uniform, primitive composition into this heterogeneous spectrum of mantle materials and characterization of these heterogeneities are active areas of interest with important implications for the origins of basalts and their source regions (DePaolo and Wasserburg, 1976ab; Hart and Brooks, 1977; Hedge, 1978; Hurst, 1978; O'Nions et al., 1977, 1978; Sun and Hanson, 1975; Tatsumoto, 1978). The position on the depleted to enriched spectrum occupied by a particular mantle source region plays an important role in the type of melt produced, although the degree of partial melting and the depth also play significant roles. There have been many attempts (e.g., Brooks et al., 1976ab; Tatsumoto, 1978) to attach temporal significance to the isotopic differences between basalt source regions; these have suggested on the basis of "mantle isochrons" that in oceanic regions, depleted and undepleted source regions have been isolated from each other for at least 1.5 - 2.0 AE. Carter et al. (1976b) demonstrated, however, that in some continental provinces, so-called mantle isochrons can be artifacts produced by contamination with crustal rocks and urged caution in attaching time significance to these features.

Lloyd and Bailey (1975) discussed the idea that regions of the mantle are metasomatized by upwards migrating fluids. Continued flux of volatiles ultimately results in melting of the altered mantle, producing highly alkalic, volatile-rich magmas such as the ultrapotassic lavas of the East African Rift. This concept has also been applied to the source regions of more common alkali olivine basalts and ocean floor and ocean island basalts in addition to those of bizarre ultrapotassic lavas, so the process could be of general significance (Bence et al., 1975; Boettcher et al., 1977; Carter et al., 1978a; Frey et al., 1978b). The metasomatism and light-REE enrichment of the source regions could have preceded the melting event by perhaps even billions of years (Sun and Hanson, 1975). The metasomatizing fluids could be hydrous fluids, kimberlitic melts, or simply light-REE enriched basaltic liquids generated at greater depths. The concept of mantle metasomatism is sure to be explored further in the next quadrennium. It may also require reassessment of some of the petrological inferences previously drawn from geochemical arguments; for example, strongly light-REE enriched patterns in mafic lavas need not necessarily reflect residual garnet in their source regions as is usually inferred, but may simply reflect the light-REE enrichments of their metasomatized source regions.

Calc-Alkaline Magmatism

One of the major points of impact of plate tectonic theory on petrology is in the area of calc-alkaline magmatism, where the concept of subducting oceanic lithosphere provides the framework for petrogenetic theory. A variety of processes have been proposed to explain the features of andesites and related volcanic rocks, and associated batholithic intrusions. One model is that primary calc-alkaline magmas are produced by partial melting of subducted oceanic crust composed of metamorphosed oceanic basalt (and its differentiates) plus continental and/or pelagic sediments. The amounts of sediment and seawater involved in the melting are negotiable. Alternative models involve melting of the mantle above the subducted slab, with or without the involvement of H_2O-rich fluids or partial melts derived from the subducted slab below. Other possibilities include the involvement of overlying continental crust in the melting process and in interaction with melts or other fluids evolved from below in areas where oceanic crust is subducting beneath a continent. The emphasis during the 1975-1978 quadrennium was on exploring the relative contributions of these processes to magma genesis in specific

calc-alkaline suites from a range of environments and on experimental studies aimed at determining the types of magmas which would be produced by these various processes. The message, provided particularly by trace element and isotopic studies, is that the processes leading to the development of calc-alkaline magmas are exceedingly complex, and often involve elements of several of the processes mentioned above (Arculus, 1976; Best, 1975; Church, 1976; DePaolo and Wasserburg, 1977; James et al., 1976; Kay, 1977; Lipman et al., 1978; Lopez-Escobar et al., 1977; Marsh, 1976; Meijer, 1976). In the discussion of ocean floor basalts in an earlier section, I noted that a recurrent theme in studies of basalts from the earth and other planets is the rarity of primary magmas among erupted lavas. This appears to hold for calc-alkaline lavas as well and a number of authors emphasized and modelled the fractionation which appears to be important in the development of andesites and related rocks; amphibole fractionation is considered by many to be particularly important, though other phases are also involved (Allen and Boettcher, 1978; Cawthorn and O'Hara, 1976; Frey et al., 1978; Stern and Wyllie, 1978a).

Many studies during the last quadrennium were concerned with the origins of batholiths near continental margins and granitic magmas in general. Wyllie (1977) presented a model for the genesis of granitic through granodioritic magmas near continental margins and their emplacement in batholiths which synthesized experimental, field, and tectonic constraints. Miller (1978) discussed the origin of monzonitic plutons produced in the early stages of batholith emplacement and Gastil (1975) presented models of the actual emplacement of batholiths. There were a number of studies bearing generally on the origin and evolution of granitic magmas based on experimental and theoretical data (Holloway, 1976; Huang and Wyllie, 1975, Maaloe and Wyllie, 1975; Steiner et al., 1975; Whitney, 1975). Hanson (1978) discussed the application of trace elements to modelling of the evolution of granitic melts. Thompson and Algor (1977) presented a theoretical treatment of the evolution of granitic melts by anatexis of pelitic rocks.

Metamorphic Petrology

Refinement and application of techniques for estimating equilibration conditions of metamorphic mineral assemblages constituted an important part of the American effort in metamorphic petrology in the last quadrennium. Exchange reactions (which tend to be useful in geothermometry since they are largely pressure insensitive), such as Fe-Mg distribution coefficients between coexisting phases and miscibility gaps, were calibrated experimentally or with natural metamorphic assemblages, and a variety of approaches to analytical treatment of these equilibria were applied (Evans and Frost, 1975; Ferry and Spear, 1978; Goldman and Albee, 1977; Grover, 1977; Lindsley and Dixon, 1976; Thompson, 1976). Once temperature has been estimated from an exchange reaction, pressure can often be estimated using reactions among the end-member components of phases present in the rock. Efforts have been made to develop thermodynamic characterizations of relevant reactions by analysis of the results of phase equilibrium experiments and calorimetric studies on the participating phases (Delaney and Helgeson, 1978; Helgeson et al., 1978; Navrotsky and Coons, 1976; Newton et al., 1977; Robie et al., 1978; Zen, 1977). Understanding of the mixing properties of the complex phases found in natural assemblages is necessary in order to apply the end-member reactions to quantitative estimation of equilibration conditions, and many theoretical and experimental studies were directed toward characterizing the activity-composition relations of the solid solutions involved in the reactions (papers in Fraser, 1977; Kerrick and Darken, 1975; Ulbrich and Waldbaum, 1976). The stability limits of specific phases (e.g., the aluminosilicates) and assemblages also provide constraints on equilibration conditions, and there were efforts to determine such limits (e.g., Anderson et al., 1977; Hewitt, 1975). Other approaches such as study of solid inclusions (Adams et al., 1975) can also provide constraints on P-T conditions. Despite the limitations and uncertainties of these methods of estimating metamorphic temperatures and pressures, their application to specific problems to develop local and regional constraints on metamorphic and structural evolution has become almost routine. A more general approach to the problem is to develop petrogenetic grids for model systems which can (1) be correlated with sequences of assemblages observed in the field; (2) serve as a framework for understanding regional metamorphic trends and parageneses; and (3) serve as a basis for comparison from region to region. Thompson and Thompson (1976) developed such a grid for a simplified model of pelitic rocks and roughly located important reactions in P-T-aH_2O space.

The role played by fluids in metamorphism and particularly what controls the compositions of metamorphic fluids continued to be actively studied during the last quadrennium. There seems to be no general answer to the longstanding question of whether a free fluid phase exists during metamorphism; there are clearly some cases where such a phase was present (e.g., Rice, 1977; Rumble, 1978; Trommsdorff and Evans, 1977) and others where it is likely, or at least possible, that there was not (e.g., Ferry, 1976b). The composition of the fluid phase (if present) in metamorphism can be estimated in several ways. Primary fluid inclusions can provide direct estimates (e.g., Rich, 1975; Hollister and Burruss, 1976). In some situations, stable isotopes have been used to estimate fluid compositions (Taylor and O'Neil, 1977). The presence in rocks of mineral assemblages which buffer the fCO_2 or fO_2 of the fluid phase provides the basis for the most widely applied approach to determining fluid compositions (Eugster, 1977). A number of studies in the last quadrennium dealt with analytic and experimental treatments of these buffer reactions (Kerrick and Slaughter, 1976; Slaughter et al., 1975; Skippen and Trommsdorff, 1975). Application of this approach to studies of specific metamorphic terrains has demonstrated

variations in fCO_2, fH_2O, and fO_2 on a bed to bed scale (Ferry, 1976a; Rice, 1977; Rumble, 1978), a conclusion confirmed by fluid inclusion studies (Rich, 1975). These studies support the idea that fluid compositions are often buffered by the mineralogy of the rock, reflecting its initial composition, and that fluid components are not always externally imposed, perfectly mobile components. Greenwood (1975a) discussed the buffer capacity of a mineral assemblage and its effect on the progressive changes in mineral assemblages in metamorphic sequences.

Efforts are growing to develop a dynamic picture of fluids in metamorphism. There is not simply a static fluid of unchanging composition throughout a metamorphic event. Some of the changes in fluid composition may simply be due to buffering by a mineral assemblage, where changes in P and T can produce changes in the fluid composition (Greenwood, 1975a). In other cases, emplacement of granites during regional metamorphism may affect fluid compositions by, for example, H_2O flow from the melt into the surrounding metasediments and CO_2 flow into the granite stock (Ferry, 1978). The importance of fluid interaction between magma chambers and their surroundings has long been recognized by isotope geochemists (Taylor, 1978), and is viewed as an inevitable consequence of plutonism, with important implications for heat and mass transfer (Norton and Knight, 1977). H_2O entering one region or bed may be derived from dehydration reactions in surrounding pelites (Ferry, 1976a). Olsen (1977) discussed another aspect of the dynamic evolution of metamorphic fluids: anatexis produces a granitic melt which soaks up water from surrounding metasediments, producing a gradient in fH_2O between the melt and the surrounding rocks, which in turn results in biotite breakdown, silica migration, and metamorphic differentiation.

Interest in dynamic processes in metamorphism is not restricted to fluids. The traditional approach is to characterize the "highest" grade of metamorphism as it varies on a regional scale and, where possible, to identify an overprinting of a second event or a relict of an earlier event ("polymetamorphism"). There is increasing recognition of the fact that metamorphism consists of the continuous response of a rock system to changes in externally imposed conditions. A rock is continuously chasing after an equilibrium state as the externally imposed conditions of P, T, and certain aspects of its bulk composition change. Rocks which did not reach equilibrium nevertheless contain a record of their chase, and among the developments of recent years are attempts to decipher this record. These attempts must begin with an understanding of kinetics and transport properties during metamorphism. Fisher (1977, 1978) discussed aspects of non-equilibrium thermodynamics as they apply to problems in metamorphism. He was particularly concerned with the kinetics of metamorphic processes and how they relate to the development of metamorphic structures such as metasomatic zones between incompatible assemblages. An important conclusion was that diffusion is the rate determining step in the growth of these structures rather than reaction rate or the flow of heat in the reaction zone. Metasomatic zones are an obvious place to begin to constrain kinetic factors and diffusion in metamorphic processes. Several authors presented mathematical models or general discussions relating to intergranular diffusion and the growth of metasomatic zones, primarily under constant P and T conditions (Brady, 1975ab, 1977; Frantz and Mao, 1976; Joesten, 1977; Weare et al., 1976). Studies of metasomatic zones have demonstrated the dominance of diffusion metasomatism in most cases (but Kerrick (1977) documented a case where infiltration metasomatism was dominant) and have attempted to determine the relative mobilities of components selected to describe the diffusion process by analysis of chemical potential and diffusion paths (Thompson, 1975; Brady, 1977) or of mineral zoning patterns in the reaction bands (Sack, 1977). Loomis (1977, 1978) has also applied a kinetic treatment to the analysis of metamorphic rocks.

The study of retrograde zoning and cation diffusion of Lasaga et al. (1977) introduced an approach of wide applicability which yielded a quantitative estimate of the cooling rate of a metamorphic rock ($100^{o}C/10^{6}$ years). Application of this approach to other regions and over a regional scale in a particular metamorphic terrain could yield valuable constraints on the structures, uplift rates, and heat budgets of metamorphic belts. There have been several attempts to model the heat balance and development of regional metamorphism based on constraints from metamorphic petrology. Bickle et al. (1975) and England (1978) presented thermal models of the Alpine metamorphic belt and concluded that abnormal heat flow from the mantle was not required to produce the observed metamorphism. Richardson and Powell (1976) reached a similar conclusion for the Dalradian metamorphism. Graham and England (1976) demonstrated the importance of shear heating in areas of thrust sheets in explaining inverted metamorphic zonation. They also emphasized the self-regulatory nature of this effect since the dehydration resulting from increasing temperature and the increasing temperature itself result in reduction of the shear strength of rocks, limiting the amount of shear heating possible.

Summary

While it is difficult from the vantage point of the end of a quadrennium to identify which of the developments of the last four years will be regarded as most significant on a time scale of 10 or 50 years, it is nevertheless possible to identify areas of emphasis and growing interest. In igneous petrology, studies of structures and thermodynamic properties of silicate melts and of kinetics of igneous processes are in a period of rapid growth. Plate tectonic concepts have had and will no doubt continue to have an important influence by focusing interest on specific problems and by providing a framework for the understanding of petrogenesis. The emphasis on studies of oceanic igneous processes and on the origin of calc-alkaline magmas are examples of this influence. An understanding of mantle processes and evolution through the integration of petrological, geophysical, and geochemical

constraints has been developing for the past 20 years, and will undoubtedly provide direction for future petrological studies. In metamorphic petrology, the integration of field, experimental, and theoretical studies into a framework for understanding the dynamic evolution of metamorphic systems and their interpretation in terms of the structural and thermal evolution of the crust have been important developments of the past four years and will probably be an important focus for the next quadrennium.

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KIMBERLITES AND THE MANTLE

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Introduction. During the quadriennal period 1975 to 1978 a considerable number of investigations, often closely related, have been undertaken on kimberlites, mantle xenoliths and diamonds. Much progress was made into our knowledge of specific occurrences of kimberlite and diamond in the United States. However, these works are few when compared with the large number of studies carried out on Southern African kimberlites and xenoliths, many by scientists in U.S. institutions. Since the mecca of kimberlite, xenoliths and diamonds in South Africa, particularly Kimberley, it is difficult and unwarranted to separate out the various investigations by nationality. The investigative effort of kimberlites, and associated rocks and minerals is worldwide and accordingly in this brief review of endeavors during 1974 to 1978 as much literature as possible, pertinent to the subject, has been included. Unfortunately, omissions are probable but hopefully there will be few and may perhaps be found through other references cited in the text. Especially useful and worthy of specific note are the Proceedings Volumes of the First and Second International Kimberlite Conferences (Phys. Chem. Earth, 9, 1975; Diamonds, Diatremes and Diamonds: Their Geology, Petrology, and Geochemistry; and the Mantle Sample: Inclusions in Kimberlites and Other Volcanics; Vols. I and II, Am. Geophys. Union, 1979). Also of help are the Extended Abstract volumes for these two Conferences, as well as the papers from the International Conference on Geothermometry and Geobarometry (Am. Mineral. 61, 549-816, 1976).

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Mantle Fragments

A considerable amount of indirect evidence concerning the structure and possible petrology of the upper mantle has been obtained through interpretations of various geophysical data. These interpretations generally indicate vertical and lateral inhomogeneity in mantle density, seismic velocities and thermal regimes; especially between continental and oceanic areas. Unfortunately, when compared to the extensive, and often geographically continuous area covered by the above indirect studies, the total number of known localities where mantle rocks occur is extremely sparse. Nevertheless, mantle samples from these locations have received considerable attention since they alone provide direct evidence of mantle petrology and mineralogy and serve as constraints for geophysical speculation.

Samples of the mantle occur as xenoliths and xenocrysts in diatremes (predominantly kimberlitic) and basalts in continental areas and in basaltic environments in oceanic provinces. Sequences of upper mantle rocks are also present in ophiolite complexes where they now occur as serpentinized ultramafic and mafic rocks. These rocks are believed to represent uppermost oceanic mantle whose present structural position is the result of some form of plate margin collision.

This review is primarily concerned with the progress made in our understanding of the petrology, mineralogy, and geochemistry of the upper mantle based on recent studies of mantle fragments and associated rocks obtained from kimberlitic diatremes (see also Meyer, 1977). The significance of mantle xenoliths in basalt has been discussed by MacGregor (1975a) and Wilshire and Shervais (1975) and these serve as good starting points for those interested in the subject.

Kimberlite

Kimberlite is the name given to a specific type of rock that in a previous fluidized state has transported mantle and lower crustal fragments to higher levels in the earth's surface. Unfortunately, kimberlite itself is somewhat of an enigma and although one can produce a definition of the rock type as now consolidated (Lewis, 1887; Mitchell, 1970; Dawson, 1971; Skinner and Clement, 1979) there is still a problem regarding the mineralogical and chemical nature of kimberlite at depth. This problem arises due to the petrographic nature of kimberlite, which is essentially an intrusive, inequigranular rock which contains large crystals (phenocrysts or xenocrysts) of olivine, phlogopite, pyrope-almandine, pyroxene (diopside and/or enstatite) and magnesian ilmenite set in a fine grained matrix of serpentine, phlogopite, calcite, chlorite, perovskite, spinels and monticellite (Mitchell, 1978a). In some instances the serpentinization of the groundmass minerals is not complete and one can observe small crystals of olivine. One or more of the above minerals may be absent or rare in any given kimberlite. For example, in the Murfreesboro, Arkansas kimberlite pipe garnet appears to be much rarer than diamond (Lewis, 1977; Meyer et al., 1977). Furthermore, the presence of diamond is not a prerequisite for a particular rock to be called kimberlite. In point of fact many more non-diamondiferous kimberlites are known than diamondiferous ones.

In recent years several authors have turned their attention to describing in detail the field occurrences (Hawthorne, 1975; Hawthorne et al., 1979; Clark and Mitchell, 1975; Mitchell, 1976; Meyer, 1975 and 1976, McCallum et al., 1975; Stracke et al., 1979; Svisero et al., 1979; Janse, 1975; Cornelissen and Verwoerd, 1975), mineralogy and petrology (Smith, et al., 1979; Scott, 1979; Mitchell, 1977a, 1978c and 1979; Akella et al., 1978; Ferguson and Sheraton, 1978; Emeleus and Andrews, 1975; Svisero et al., 1977; Lewis, 1977; Smith and Levy, 1976; Roden and Smith, 1979) and geochemistry (Mitchell and Brunfelt, 1975; Fesq et al., 1975; Kable et al., 1975; Frey et al., 1977; Paul et al., 1979; Brookins et al., 1979) of various kimberlites. Isotopic studies (Sheppard and Dawson, 1975; Barrett and Berg, 1975; Barrett, 1975; Kobleski et al., 1978; Basu and Tatsumoto, 1978; Tsai et al., 1979a; Kramers, 1977a and 1979), including age determinations (Allsopp and Barrett, 1975; Kramers, 1979; and Davis et al., 1976; Davis, 1977 and 1979; Naesner and McCallum, 1977) have begun to unravel some of the mysteries of kimberlite production, and it is now obvious that kimberlite activity has occurred sporadically throughout geological time (e.g. So. Africa - Precambrian, Permo-Trias., Cretaceous; Siberia - Palaeozoic, Cretaceous; United States - Palaeozoic, Cretaceous, Tertiary).

Nevertheless, there are still problems in as much as the major regional structural control of kimberlites has not yet been elucidated. Possibly this is because kimberlites are surface expressions of some deeper upper mantle fracture pattern, which is not otherwise seen in the earth's crust. In mineralogy and petrology of kimberlites it is obvious that much further work is necessary, particularly on the ground-mass minerals, as is noted later.

Isotope and trace element studies are important but need to be based on or compliment very careful petrographic investigations. The dating of kimberlites by use of zircon (Davis, 1977) is a significant step, as well as the use of fission track ages (Naesner and McCallum, 1977; Raber, 1978). Unfortunately, the Pb-U-Th, Rb-Sr, and K-Ar ages for kimberlites may also be ambiguous (or even incorrect) unless sufficient care is taken to determine the true petrographic, and hopefully genetic, significance of the particular minerals that are dated.

In an attempt to unravel the genesis of kimberlite, and correctly elucidate the evidence provided by kimberlite of mantle processes and chemistry a number of investigators have turned to study of the groundmass mineralogy (Boyd and Clement, 1977), particularly the opaque phases (Haggerty, 1975; McCallister et al., 1975; Mitchell and Clarke, 1976; Meyer and Boctor, 1975; Boctor and Meyer, 1979; Mitchell, 1977b; Raber and Haggerty, 1979). Of interest is the first terrestrial occurrence of armalcolite (FeMg) Ti_2O_5 reported by Haggerty (1975) in a kimberlite from South Africa.

Megacrysts

The major reason for identification of groundmass phases is that these minerals are most likely to be genetically associated with the "kimberlite magma". The larger crystals that are referred to as phenocrysts or xenocrysts (or both) and are a ubiquitous feature of kimberlite pose a problem with regard to genesis and genetic links. Some would consider these large crystals (olivine, diopside, enstatite, pyrope, ilmenite) as phenocrysts and maintain they are true kimberlitic minerals crystallized from and associated with the kimberlite magma at depth. In contrast, others doubt this origin and consider these large crystals as xenocrysts, derived at the latest from some very early proto-kimberlite magma whose chemistry

and initial mineralogy bear little resemblance to the currently observed surface expression of kimberlite. Diamond falls into this same category of problematic minerals (Tsai et al., 1979; Kramers, 1977; Gurney et al., 1979).

These large crystals, often referred to as megacrysts, so as not to imply genetic connotations, may occur up to 20 cm in size and yet still be single crystals (Meyer et al., 1979). In other instances these megacrysts are single phase, sometimes polycrystalline, xenoliths which have been referred to as "discrete nodules" by Boyd (1973). Although several studies have been undertaken on these megacrysts (Eggler, et al., 1979; Gurney et al., 1979; Haggerty et al., 1979; Meyer et al., 1979, Boyd and Danchin, 1974, 1979; Boyd and Nixon, 1975; Pasteris and Boyd, 1979; Boyd, 1974a; Wyatt, 1979; Mitchell, 1977b) and genesis of them is still subjective with cogent arguments being provided for both xenocrystic and phenocrystic origins.

Of major diamond exploration interest is the apparent relation between minor and trace element composition of the typical magnesian ilmenites in kimberlite and the diamond content of the kimberlite. This indicates a genetic relation only between ilmenite and diamond; although some would extend this to include kimberlite itself - thus suggesting a genetic link between ilmenite, diamond and kimberlite. In this suggestion the ilmenite and diamond are considered as phenocrysts.

Xenoliths

At this point it is appropriate to comment upon the true undisputed xenoliths that occur in kimberlites. These xenoliths include local crustal rocks, deep crustal granulites, and ultramafic and ultrabasic fragments believed to have been derived from the upper mantle by the rapid ascent of kimberlite. These ultramafic and ultrabasic xenoliths, including the megacrysts noted previously, have received considerable attention; probably more than kimberlite itself. Mineralogical and geochemical studies of the ultramafic xenoliths are numerous (Boyd, 1973; Hearn and Boyd, 1975; Boyd and Nixon, 1975; MacGregor, 1975b; Boullier and Nicolas, 1975; Harte et al., 1975; Gurney et al., 1975; Dawson and Stephens, 1975; Stephens and Dawson, 1976; Boyd, 1974b; Carswell et al., 1978; Danchin, 1979; Lawless et al., 1979; MacGregor 1979; Nixon and Boyd, 1979; Rawlinson and Dawson, 1979; Smith et al., 1979; Smith and Dawson, 1975; Mitchell, 1977a; Smith, 1977; Smith and Levy, 1976; Boyd and Nixon, 1978; Ringwood, 1975; Shimizu, 1975; Shimizu and Allegre, 1978; Nixon et al., 1978). The large amount of data now available, including textural studies, has clouded the initial simple division of the xenoliths by Boyd (1973) into granular (coarse tabular- Boullier and Nicolas, 1975) and sheared (mosaic or porphyroclastic- Boullier and Nicolas, op cit). A full discussion of textures and corresponding names has been suggested by Harte (1977).

Mineralogically these granular and sheared xenoliths are similar (i.e. lherzolite, websterite, harzburgite, etc.) but distinct chemically differences are present both in mineral and bulk rock compositions that are diagnostic for each occurrence. For example, the garnets in the discrete xenoliths (megacrysts) have a greater range in Mg/(Fe+Mg) but a very restricted range in Ca/(Mg+Fe+Ca) compared with garnets from the granular and sheared xenoliths. Also, the olivine is usually more Mg-rich in the granular than the sheared and discrete xenoliths; and, the diopside in the granular types is commonly more Ca-rich than in the other two varieties.

In bulk chemistry it appears that the granular xenoliths are depleted in Ti, Al, Fe, Ca and Na relative to the sheared xenoliths. This relative depletion has led to the terms sterile and fertile for these respective xenoliths. (O'Hara et al., 1975; Boyd and McCallister, 1976) In general, a fertile xenolith is one that upon partial melting could produce "basaltic" material. In contrast, a sterile xenolith does not have this capability and itself may be a product (residuum) of a partial melting episode.

Geotherms

A unique and major advance in mantle studies was the determination of temperatures and pressures of equilibration for the constituent minerals of the xenoliths (Boyd, 1973; MacGregor, 1974). These parameters are obtained by utilizing the results of experimental studies on the enstatite-diopside solvus (Davis and Boyd, 1966; Nehru and Wyllie, 1974; Mori and Green, 1975, 1976; Lindsley and Dixon, 1975) to determine temperature; and the Al_2O_3 content of the enstatite to calculate the pressure (Boyd and England, 1964; MacGregor, 1974).

Using these techniques it was noted that the sheared xenoliths for certain localities have generally equilibrated at higher temperatures and pressures than the granular types. For any specific locality, the trend of points on a P-T plot for several individual xenoliths were believed by Boyd (1973) and MacGregor (1974) to represent a palaeogeotherm. Perturbations in the curves of these early geotherms were at first considered to be due to frictional heating at the base of the lithosphere. At present this idea appears unreasonable (Goetze, 1975) and the deformation textures and thermal effects are not consistent with stress heating in the low velocity zone (Mercier and Carter, 1975). Other models under consideration at present to explain the palaeo-geotherms include convective movement of partially molten mantle, thermal diapers, or a combination of both (Boyd, 1976; Mitchell, 1978b).

Although Boyd's initial model was a major stimulus to petrologists, nevertheless the idea was criticized (Wilshire and Jackson, 1975; Mercier and Carter, 1975; Dawson et al., 1975; Thomsen, 1975; Mori and Green, 1976; Irving, 1976) on the basis that the perturbation (or inflection) was an artifact of the experimental data and sampling of xenoliths. However, recently using the same techniques and experimental data palaeogeotherms for mantle regions other than Lesotho have been produced. These include Kimberley, South Africa; Western U.S.; Siberia and Northern Canada. Some of these show inflections whereas others do not (Boyd, 1976; Boyd, Fujii and Danchin, 1976; Mitchell, 1977; Hearn and Boyd, 1975; Eggler and McCallum, 1976; Danchin and Boyd, 1976). Meyer and Tsai (1976a) have also applied these techniques of determining pressure and temperature to the inclusions in natural diamond.

When other techniques of geothermometry and geobarometry are applied to granulite facies xenoliths in kimberlite it is observed a P-T gap exists between the values for the granulite and associated rocks, and those of the ultramafic mantle xenoliths. By applying corrections based on thermodynamic considerations to the experimental data (e.g. Wells, 1977; Wood, 1974; Saxena, 1976; Herzberg, 1978) the P and T's of equilibration for the ultramafic xenoliths are lowered and the P-T gap diminishes. These corrections, however, are still subject to error and will undoubtedly be modified in the light of future work.

The previous discussion has been concerned with garnet-bearing periodotites. MacGregor and Basu (1974) extended the above models to include spinel and plagioclase lherzolites. Unfortunately, the experimental data (MacGregor 1974) for spinel-bearing systems are ambiguous. However, later studies (Presnall, 1976; Danckworth and Newton, 1978; Obata, 1976; Fujii, 1976) have done much to clarify the phase relations and use of data in spinel-bearing systems.

Eclogites

Eclogite (Griquaite) xenoliths, which have not yet been considered in this review, also have provided significant information about the chemistry and mineralogy of the mantle. Perhaps most notable was the first recorded "terrestrial" occurrence, other than in diamond, of coesite (Smyth and Hatton, 1977; Smyth, 1977). Although mineralogically these eclogite xenoliths are relatively simple, variations in chemistry, isotopes and major variations in texture are obvious (Lappin and Dawson, 1975; Harte and Gurney, 1975; Smith and Dawson, 1975; Reid et al., 1976; Bishop et al., 1975; Lappin, 1978; Meyer and Boctor, 1975; Robinson, 1979; Shee and Gurney, 1979; Hatton and Gurney, 1979; Tsai et al., 1979a). Unfortunately, during the last few years the ultramafic (i.e. garnet-peridotites) have received most of the attention with the griquaites (mantle eclogites) receiving scant study. Partly this is due to the early lack of experimental data enabling pressures and temperatures of equilibration to be determined. Recently, this drawback has been ameliorated (Raheim and Green, 1974; Wood, 1976) but there is much scope for further work, especially with regard to correctly sequencing the griquaites in time and place in the upper mantle and their relation to the ultramafic xenoliths. Kramers (1977) has verified the Pre-caminan age for eclogites from Roberts Victor, previously suggested by Manton and Tatsumoto (1971).

Xenolith Abundances

This latter problem is further emphasized when one considers that kimberlite pipes vary considerably in their concentration and type of xenoliths. Some kimberlites are devoid of xenoliths whereas others may contain an abundance of eclogite xenoliths or of ultramafic varieties. In other instances both eclogite and ultramafic xenoliths may occur in a single kimberlite. The significance of these differences has not been adequately addressed, other than to infer heterogeneity in lateral and vertical horizons in the upper mantle.

Kimberlite Eruption

A possible cause of the variation in xenoliths may possibly be ascribed to the mechanism of kimberlite eruption. Recent papers on this subject include Hawthorne (1975), Lorenz (1975, 1979, Woolsey et al. (1975), Clement (1975), McCallum (1976), Anderson (1979) and Mercier (1977). The concensus is that the kimberlite was emplaced by the rapid ascent of a gas charged (CO_2,H_2O) magma. Adiabatic expansion associated with breakthrough of the magma at the surface was sufficient to lower the temperature such that thermal metamorphic effects on the sedimentary xenoliths are negligible; thus coal and fossils are preserved with no alteration (Meyer, 1975a, 1976). It is also possible that the rapid ascent and subsequent quenching are the reasons for the occurrence of diamonds in kimberlite.

Role of Volatiles - Experimental Studies

The role of CO_2 in magma genesis has been the subject of several experimental studies (Eggler, 1975; Boettcher et al., 1975; Wyllie and Huang, 1976a and b; Wyllie, 1976, 1977, 1979; Eggler and Holloway, 1977; Eggler and Wendlandt, 1979, Mysen and Boettcher, 1975a and b; Brey and Green, 1975; 1976) but differences of interpretation do exist. Perhaps most noticeable is the difference between experimental studies on the solubility of CO_2 in ultramafic melts. Nevertheless, in spite of complications that occur with incorporation of Fe and Ca into the system, the above studies are extremely pertinent to understanding the genesis of kimberlite. The presence of CO_2 (or carbonates) in kimberlite led some to suggest that kimberlites are genetically associated with carbonatites, or are a mixture of silicate and carbonatite magmas. Such ideas have been refuted in detail (Mitchell, 1978a) and it is likely that the kimberlite is the result of the result of the partial melting of a periodotite - CO_2-H_2O system (e.g. Wyllie, 1979). Somewhat in contrast (Boettcher et al., 1979) would invoke anatexis and metasomatism of mantle periodotites to derive kimberlite as well as alkali basalts. Evidence cited in support of this includes K-metasomatism in certain xenoliths (Erlank, 1976; Erlank and Richard, 1977; Lloyd and Bailey, 1975). Also related to this topic are the uncertain processes in the upper mantle that cause partial melting as well as result in the kimberlite eruption at the surface. Local structural control can often be seen at the surface but the repeated occurrence of kimberlites through time and place on major continental cratons has received no solution. Such a study is important for the results may help in under-

standing plate/mantle processes, as well as being a significant aid for kimberlite prospection.

Geophysical Studies

Unfortunately, the fertile field of study of kimberlites and their xenoliths has received scant attention by geophysicists, notable exceptions being (Jordan, 1977, 1979; Goetze, 1975; Thomsen, 1975; Anderson, 1979). Anderson and Perkins (1975) developed a plate-tectonics model to account for kimberlitic, lamprophyric and other magmatic activity in the Colorado Plateau. To some extent this model has received petrologic support through the mineralogical studies of Helmstaedt and Doig (1975), Schultze and Helmstaedt (1979) and Helmstaedt and Schultze (1979) on "Franciscan-type" eclogites found in the "kimberlites" of the Colorado Plateau.

U.S. Kimberlites

Currently, several of these Colorado Plateau "kimberlites", or kimberlite-like bodies are being studied (Arculus and Smith, 1979; Ehrenberg, 1979; Smith, 1979; Roden and Smith, 1979; Switzer, 1975). In general these "kimberlites" of the Colorado Plateau differ in petrography and mineralogy from other kimberlites in the U.S. and appear to be closely associated with lamprophyric activity in the area (Meyer, 1976; Smith et al., 1979; Lewis, 1977; Lewis and Meyer, 1977; Meyer and Kridelbaugh, 1977; Mitchell, 1976).

In the last few years kimberlites in Colorado and Wyoming have proven to be diamond-bearing (McCallum and Eggler, 1976; McCallum and Mabarak, 1976a and b; McCallum, Mabarak and Coopersmith, 1979). This is the second occurrence in the U.S. of diamonds being present in kimberlite. Interestingly the initial discovery of the diamonds in Colorado was in a peridotite xenolith from kimberlite. This is a fairly unique occurrence as previously only one substantiated record of diamond in a peridotite was known (Dawson and Smith, 1975b) although Russian workers had also recognized diamond within a serpentinized rock; presumably peridotite. The discovery of diamond in Colorado has resulted in considerable commerical interest for exploration in other parts of the U.S. and Canada (e.g. Brummer, 1978; Lampietti and Sutherland, 1978).

Diamond and Inclusions

Diamond is probably the most unequivocal mantle mineral and because of its importance, both scientific and industrial, Kennedy and Kennedy (1976) redetermined experimentally the graphite-boundary curve. Fortunately, the newly determined curve differs little from the widely used curve of Bundy et al. (1961). Nevertheless, it is recommended the new curve be used in future studies, as the experimental control and corrections for pressure are currently better understood than in 1961.

A major work regarding diamond was produced by Bardet in 3 volumes who discusses the physical and chemical properties of diamond and describes the exploration and exploitation of diamond throughout the world (Bardet, vol. I, 1973; vol. II, 1974; vol. III, 1977). Orlov (1977) in a translation from Russian describes in detail the mineralogy of diamond, whereas Robinson (1978b) has provided an excellent and concise review of the characteristics of natural diamond, including an interpretation of these characters.

Geochemical research into the inclusions in diamond has continued (Meyer and Svisero, 1975; Prinz et al., 1975; Fesq et al., 1975; Meyer, 1975b; Meyer and Tsai, 1976a and b, Gurney et al., 1979; Tsai et al., 1979a and b) and the results generally confirm the earlier work of Meyer and Boyd (1972). In particular, the division of the mineral inclusions into an eclogitic suite and an ultramafic suite is well substantiated. Crystallographically, the occurrence of octahedral clinopyroxenes in diamond (Prinz et al., 1975) and the cubo-octahedral morphology of many structurally non-cubic inclusions is interesting. It is probable that these inclusions are syngenetic with the host and should provide valuable information regarding conditions of diamond growth and mantle chemistry.

The minerals occuring as inclusions are generally similar to those occurring in kimberlite, and associated xenoliths. However, in detail the chemistries of the ultramafic suite inclusions are sufficiently distinct as to cloud the genetic link between diamonds, ultramafic xenoliths and kimberlite. Recent isotope data by Kramers (1977a and b, 1979) has shown considerable age differences exist between sulfide-bearing diamonds and the host kimberlite. This and other evidence is cited (Tsai et al., 1979) as suggesting diamonds are xenocrysts in kimberlite - a view opposed by Gurney et al. (1979). In an attempt to determine the physical parameters of natural diamond genesis Meyer and Tsai (1976a) applied the pyroxene thermometer and barometers to selected suites of inclusion from diamond. Variation in P-T conditions resulted, although all were within the diamond stability field. Further study of suitable mineral suites should provide much needed insight into this subject. An independent method of determining pressure and temperatures of diamond equilibration has been attempted by Cohen and Rosenfeld (1979) using piezobirefringence techniques.

The problem of why the majority of kimberlites do not contain diamond is of both scientific and commerical interest. At present one may only speculate on the reasons, as this problem has not been adequately addressed by scientists. Possibly, the mechanism of eruption of the kimberlite, including such parameters as temperatures and oxygen fugacity may play important roles in either retaining or removing diamonds from the kimberlite magma. Of primary importance in producing diamonds is the amount of carbon present and the geochemistry of the original environment in which diamonds form. Evidence at present suggests that diamond is not genetically associated with the latest stages of kimberlite production, including eruption, and thus kimberlite is only the vehicle which has transported diamond to the surface. However, the effects of the vehicle on the diamond passengers are important. Rosenhauer et al. (1977) have attempted to determine the stability of graphite and diamond as a function of the oxygen fugacity in kimberlite and the mantle.

Russian Investigations

This review has been mostly concerned with the results of studies on African and American kimberlites and xenoliths. A considerable amount of parallel work has been undertaken in the U.S.S.R. and those interested in mantle petrology as revealed through studies of kimberlite and associated rocks should be aware of these studies. Of particular use is the review by Sobolev (1974) and later works (Sobolev, 1977; Sobolev et al., 1977; Galimov et al., 1978; Kaminsky, 1975).

Future Studies

During the last few years considerable progress has been made into our knowledge of the mantle as evidenced by kimberlite, diamonds, and associated xenoliths. The major thrust appears to have been in correlating the marked mineral-chemical differences within and between different localities, although the overall significance of such variations has not been the subject of interpretation. A fruitful endeavor, and one of major importance would be to examine in detail the mineralogy, chemistry (major and trace) and characteristics of kimberlite, xenoliths and diamonds from a single specific kimberlite. Surprisingly such a study has not yet been undertaken.

Future rewarding studies, to name a few, include isotope studies of the mineral inclusions in diamond, more detailed work on the eclogite xenoliths, the relation between sheared and granular xenoliths and the megacrysts, and investigation into the tectonic controls of kimberlite in space and time. If the progress made in the next quadriennum is equivalent to that of the past then the future of mantle petrology is bright.

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ULTRA-HIGH-PRESSURE EXPERIMENTAL MANTLE MINERALOGY

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Abstract. This review is focused on ultra-high-pressure mineralogical research done during the period of the quadrennium. Where possible, reference to review articles and books have been substituted for discussion. Static-pressure experiments are the theme of the review because of the breakthroughs in technique and discovery during the period. Shock-pressure experimental results during the period, of equal importance, have also contributed to the gains in understanding of the mineralogy of the mantle and core.

Static Experiments

The experimental investigation of observed minerals at ultra-high pressure (loosely defined as pressures greater than 200 kbar or 20GPa) is directed toward an understanding of the potential mineralogy of the zone in the earth that extends from the mantle, at a depth of approximately 600 km to the center of the core. There were notable achievements in this field prior to 1975, but in the time span of this review article (1975-1978), the experimental findings have been of such magnitude as to affect, and indeed reshape, the entire concept of the mineralogy and composition of the earth's mantle. There have been major breakthroughs in ultra-high-pressure experimentation utilized to produce these data and concepts, although many of them were contained in the pre-1975 technological base. Bassett (1979) recently completed a review of the development of the ultra-high-pressure field, which is a technology based on the supported, diamond-anvil, pressure-cell apparatus.

The diamond-anvil apparatus requires highly sophisticated techniques and procedures, which were developed from an early concept in high-pressure experimentation (Bridman, 1935). Many complexities involving the sample pressure distribution for awhile appeared to impede the potential application to ultra-high-pressure experimental mineralogy. What currently has emerged as a new technology is the result of (1) new designs to reduce the complexities and (2) an accurately calibrated pressure environment.

Many new supporting and analytical techniques for the diamond-anvil apparatus involve infrared radiation, gamma rays, and various types of lasers. These techniques and details of the diamond-anvil apparatus itself are thoroughly discussed in Bassett's review and need not be elaborated here. It is sufficient to note that these techniques have now resulted in the study of experimental mineralogy in the range 200 kbar-1.7 Mbar and 0-4000K. The studies range from observations of phase equilibria to accurate measurements of the properties of the phases. The findings are the subject of this review.

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Mineralogy of the Mantle

Fundamental data on the chemical compositions of the deep mantle, and on its mineral assemblages, have, in the past, been subjects of study of the field seismologist and of the shock-wave experimenter. No static experimentation had been conducted at deep mantle temperatures and pressures, and no samples are available from depths below about 200 km. If one assumes, however, the earth's upper mantle to be close in its bulk composition to eclogite or to parent (or derivative) rock types such as garnet peridotite (Yoder, 1976) it has been possible to extend available experimental data [such as data on garnet and spinel (of olivine composition)] to fit the known seismic properties. The view that at great depths the mantle is composed of a limited variety of close-packed oxide minerals was widely held because spherical packing schemes yield the most efficiently packed and dense mineral structures. Assemblages of close-packed mineral structures, in turn, seemed to meet the constraints of the density distribution and they meet the elastic constraints required for seismic modelling purposes (Birch, 1952).

Applications of the new experimental data at pressures above 200 kilobars have rendered most of these simple models invalid. Liu (1976c) found that iron-free synthetic analogues of the common mantle minerals olivine, pyroxene, and garnet transform to phases with the orthrhombic perovskite structure (plus periclase, from olivine) at pressures above approximately 250 kilobars. The value of these results in understanding the mineralogy of the earth's mantle lies in the properties of the silicate perovskite structure itself. The generalized perovskite formula, $ASiO_3$, has the same cation:anion ratio as the minerals pyroxene and garnet. Furthermore, the ratio is close to that of the bulk composition of basalt. Perovskites are known to form extensive solid solutions, so that in a way similar to the pressure stabilized basalt-eclogite reaction, where the multiphase basalt assemblage is transformed to the two-phase eclogite assemblage, one can envision a reaction at higher pressure in which eclogite will transform to the single-phase perovskite. The limit of solid solubility of each of the chemical components of basalt in the perovskite structure has proved to be a critical constraint to this hypothesis.

Perhaps the most significant and the greatest implication of the discovery of the $(Fe,Mg)SiO_3$ perovskite structure is the very high density. Perovskites of silicate composition are more dense than their constituent oxides, several of which had been proposed as predominant minerals of the lower mantle. Yagi et al. (1978) make this comparison between the volumes (per molecule) of the perovskite phase and oxide mixtures for silicates of Mg, Fe, Co, and Ni having the correct anion/cation values. Although it might have been concluded on the basis of these data alone that the entire mantle, below a depth of approximately 650 km, is composed predominantly of the single mineral $(Fe,Mg)SiO_3$-perovskite phase, further refinements of the first experimental results on perovskite form the basis of a much more complex picture of the mineralogy of the deep mantle.

For example, Liu (1976a) reported that ferrosilite, $FeSiO_3$, did not transform to the perovskite structure in his experiments, at least at pressures up to 280 kbar. Instead, ferrosilite breaks down to silicate spinel (Ringwoodite) and then to nonstoichiometric wüstite, both in equilibrium with stishovite. The diverse nature of silicate-perovskite equilibria was further revealed by the interpretation that not one, but two silicate perovskites form in equilibrium from Ca-rich compositions (Mao et al., 1977). This would lead to a predominantly bi-mineralic lower mantle. In the study of Yagi et al. (1978) on the crystal structure of synthetic perovskite of enstatite composition, the origin of many of the complexities was found to be related to the relatively large, symmetric dodecahedral site (distorted) in perovskite. The cation, Ca, with its large ionic radius, will not share the site with a significant amount of Mg. Furthermore, Yagi et al. (1978) found that symmetry and dimensional properties of the cation site result in its having a relatively low crystal-field intensity--so low, that transition metal ions such as Fe^{2+} are not greatly stabilized in the structure. Thus, the partitioning of Fe in the deep mantle will be toward oxide structures whose cation sites have relatively high crystal field stabilization energy.

Several other experimental mineralogical studies at ultra-high pressures have begun during the past quadrennium. Evidence for chemical disproportionation (Bell and Mao, 1976; Bell et al., 1977) (which in the strictest sense involves oxidation/reduction and chemical decomposition) at high pressure appear to have had a major influence in the development of theoretical models of the earth's mantle and core (Mao, 1974; Ringwood, 1977; Smith, 1977). Disproportionation reactions that involve iron must be considered in context with a mantle composed mostly of silicates with the perovskite structure plus iron-magnesium oxides, even in the original processes that formed the mantle and core (Mao and Bell, 1977).

The Core-Mantle Boundary and the Core

The experimental research at static pressures of 0.5-1.7 Mbar has only been started. The first static compressibility data on minerals to 1 Mbar included results on MgO (periclase) and on the epsilon phase of iron (Mao and Bell, 1977). Experiments at pressures equivalent to those at the core-mantle boundary and the core itself are now feasible, but to date no data in this range are reported except from schock-wave studies (several of which are referenced in the bibliography). The results of comparison of shock-wave and static high-pressure studies are expected to appear in the next quadrennium.

Static ultra-high-pressure experimentation has experienced significant advances in technique during the last four years with announcement of the first calibrated pressures to 1 Mbar. Then shortly thereafter, pressures of 1.7 Mbar were sustained. These two reports plus descriptions of the techniques for measuring the pressures, heating the samples while under pressure, and making physical measurements are summarized by Bassett (1979).

Following the mandate of this report, the most exciting results--in this case, those related to the discovery of the $(Fe,Mg)SiO_3$-perovskite structure, its properties and chemical complexities--have been the focus of this review. Important results of shock-wave experiments done in the past and recently have set the stage for mineralogical experiments under static conditions. Indeed, after reevaluation of shock-wave data on pyroxenes and olivines (Jeanloz and Ahrens, in Manghnani and Akimoto, 1977) the existence of the perovskite phase has been confirmed and there are suggestions of further transformation to denser phases or phase assemblages at higher pressures in the range 0.6-1 Mbar. It is apparent that future experiments on the mineralogy of the middle and deep portions of the earth's mantle will involve as many diverse problems, although of a different nature, as experiments on the complexities of the upper mantle have during the preceding twenty years or so.

The following bibliography is selective in that it has been assembled to cover the subject matter of this review and, to some extent, derivative areas of research. The era of static ultra-high-pressure experimentation had major advances during this quadrennium and the results are just beginning to appear in the literature. Thus, it is believed the scope of the literature is reasonably well covered. Attention is called to the book referenced above, edited by Manghnani and Akimoto, and the book edited by Strens (1976), for references to adjoining fields (i.e., shock-wave research and experimental data below 200 kbar) that are not within the scope of this review.

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*"Ultra-high pressure" is defined differently for crystallographic studies (over 1 kbar) than for other experiments (over 200 kbar). The Bibliography includes references to the text as well as general references.

PHYSICAL PROPERTIES OF MINERALS AND MELTS

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Introduction

This review summarizes measurements and theoretical developments for those physical properties of primary interest in geophysical calculations. It includes thermal properties, electrical conductivity, diffusion in minerals and melts, with only slight mention of the corresponding properties of rocks. Elastic properties and acoustic velocities are discussed; however, related work on equations of state and on plastic deformation are covered by Bell and Tullis in other reviews in this series. Knowledge of physical properties provides the basis for interpreting geophysical measurements of seismic velocities, electrical conductivity, and temperature gradients in terms of unknown quantities, such as mineralogical and chemical composition, temperature, heat flow, and fluid contents at depth in the earth and moon.

The growth of this field as a specialty is signalled by several indications, for instance: books; Physics and Chemistry of Minerals and Rocks (Strens, 1976), High Pressure Research, Applications in Geophysics (Manghnani and Akimoto, 1977), each of which reports conference results; a new journal; Physics and Chemistry of Minerals; and topical meetings; the Mineral Physics Conference, Airlie, Virginia, October 1977.

Standards of measurement and interpretation have risen considerably as the parameters affecting physical properties have become better known. Some guidelines for physical measurements were compiled by O'Connell, Shankland, and Liebermann (1976). Important questions are: first, are measurements repeatable, made under conditions where the important variables can be identified, and do they lead to a physical model for interpretation; and second, how representative are laboratory measurements of conditions of minerals in situ where grain boundaries, fluids, voids, and other mineral phases are present?

Electrical Conductivity

Electrical properties have demonstrated significant improvement in measurement quality, reproducibility, and physical understanding during recent years (cynics might attribute this change to starting rather far behind). Recent summaries of mineral conductivities are those of Shankland (1975) and Duba (1976); dielectric properties have been summarized by Olhoeft (1976). Shuey (1975) compiled an extensive treatment of the semiconducting properties of ore minerals, dominantly sulfides, for which considerable information exists in the technological literature; conductivity magnitudes, conduction mechanisms, and interpretation in terms of electronic structure of the materials are listed. Unfortunately, the oxides and silicates reviewed here are more polar compounds than are sulfides so that measurements and interpretations are more difficult. Fewer satisfactory interpretations are available outside the earth sciences literature; the most useful come from ceramics. While the technological literature continues to use the units $(\text{ohm-cm})^{-1}$, in geological applications both field and laboratory conductivities are almost universally given as $(\text{ohm-m})^{-1}$ or Siemens/M. Laboratory conductivities are more readily interpreted than resistivities because contributions from different mechanisms act in parallel and are simply additive.

To date most measured conductivities have been of mantle minerals. Reproducible data were achieved in the work of Parkin (1972) on periclase and forsterite and of Duba and Nicholls (1973) on olivine in atmospheres having controlled oxygen partial pressure or fugacity f_{O_2}. Oxygen buffering not only maintains minerals within their chemical stability fields while temperature varies [see Nitsan (1974) for olivine] but also has the experimental advantage of keeping them close to natural self-buffered defect populations so that equilibration is more rapid than it is in the case of constant f_{O_2}, for example in air or vacuum.

Recent measurements of mantle mineral conductivities are as follows: for synthetic forsterite Morin, Housely, and Oliver (1977) find highly anisotropic conduction which they assign to electronic conductivity in the b-direction and ionic in the a- and c-directions, all by extrinisic (impurity-controlled) processes. Natural single-crystal olivines have been measured by Duba, Heard, and Schock (1974) while single-crystal pyroxene conductivities are reported by Duba, Boland, and Ringwood (1973), by Duba, Heard, and Schock (1976), and by Huebner, Duba, and Wiggins (1979). The olivine samples display only slight anisotropy in contrast to the almost-pure forsterite, a probable indication of a qualitative change in conduction mechanisms at moderate iron contents as summarized by Shankland (1975). The pyroxene studied by Huebner, et al. (1979) is notable for high contents of trivalent impurities Al^{3+} and Cr^{3+}; its conductivity is higher than ordinary pyroxene and virtually independent of f_{O_2}.

Olhoeft, Frisillo, Strangway, and Sharpe (1974) measured conductivity of polycrystalline, monomineralic augite in vacuum. Also for polycrystalline olivine and pyroxene Schock, Duba, Heard, and Stromberg (1977) obtained conductivities very similar to single crystal values at pressures up to 5 GPa (50 kb), although in an unknown, presumably self-buffered f_{O_2}. These results suggest that pressure and grain boundary effects may be small, although the latter may be greater in polymineralic materials. Mao and Bell (1977) measured electrical conductivity in diamond anvil cells for polycrystalline samples across the olivine and magnesiowustite series; they observed strong and reproducible conductivity increases with pressures up to 300 kb. Further summaries, analyses, and applications of these data are to be found in these references and in Duba, Piwinski, Heard, and Schock (1976).

Data on crustal minerals are sparse. Piwinski and Duba (1974) reported conductivities of albite for which it was not possible to achieve equilibrium values in a laboratory time scale, apparently owing to the long time needed for achievement of order-disorder equilibrium. A similar problem occurs in basalt (Duba, 1976) and one suspects such time-dependent effects in other feldspar-bearing rocks. Figure 1 indicates the range of conductivity values in some minerals, rocks, and melts (Shankland and Duba, 1978).

Understanding electrical conduction in minerals--a necessity for extrapolation to in situ conditions--requires a detailed approach. Thus, Morin, et al. (1977) compared electrical and optical properties of MgO and forsterite to elucidate the forsterite electronic structure. In a series of papers (Smyth and Stocker, 1975; Stocker and Smyth, 1978; Stocker, 1978a, b, c) Stocker and Smyth have examined the defect chemistry of olivine and pyroxene. Two observations from this study are particularly significant. One is that oxidation-reduction reactions such as

$$Fe^{2+} \rightleftarrows Fe^{3+} + e \qquad (1)$$

can also involve formation of silicon defects or additions and subtractions of unit cells to the crystal, depending on the method of achieving charge balance. Another related result is the likely importance of silicon activity on olivine conductivity (which occurs with the presence of pyroxene in mantle rocks). There are both theoretical and experimental reasons to expect olivine conductivity to be different from that in isolated single crystals when excess silica governs olivine stoichiometry, as described in the references above.

A clear suggestion for future work is investigation of the activity of elements other than oxygen, especially silicon. Indeed such work is being undertaken; Cemic, Hinze, and Will (1979) have measured conductivity increases in sintered olivine exposed to buffered f_{O_2} and under high confining pressure. However, the experiment is necessarily complex and should be confirmed in other studies. If effects of silicon and other elemental activities can be determined and oxygen pressure is known, then specification of mantle mineral conductivities in situ should be possible. Another challenge is measurements of crustal mineral conductivities, particularly under high water activity, providing equilibrium can be attained. Whole classes of measurements to elucidate the nature of conduction have yet to be accomplished, for instance thermoelectric (Seebeck) coefficient to determine the sign of charge carriers or mobility to determine carrier concentration and mode of transport; although these quantities have been obtained for sulfides and transition metal oxides. A striking need is further investigation of Mao and Bell's (1972) observation of large pressure-induced conductivity changes in iron-bearing silicates that have been attributed to iron disproportionation reaction. The implications of this change are profound and have not really received adequate attention.

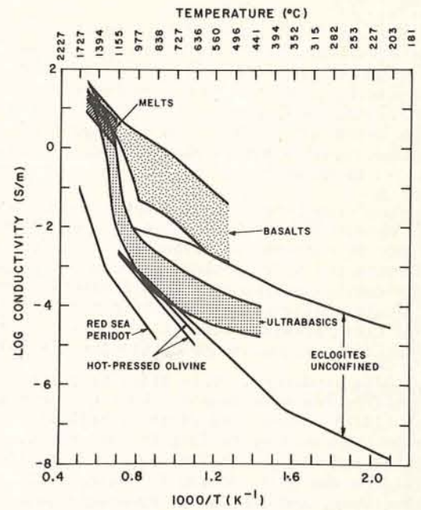

Fig. 1. Representative electrical conductivities in some rocks, minerals, and melts as adapted from Rai and Manghnani (1978).

Velocities and Elastic Moduli of Minerals

This section is a discussion of velocities and elastic moduli of minerals. The closely-related topic of equations-of-state and compression measurements in diamond cells is reviewed by P. M. Bell in another part of this series. Recent compilations of mineral elastic data have been given by Liebermann and Leitner (1979). Davies (1976), D. L. Anderson (1977), Shankland (1977), Wang (1978), Liebermann (1978), and Liebermann and Ringwood (1979) have reviewed or compiled various interrelationships of elastic properties and densities with chemical composition and crystal structure. The object of such interpretations is determination of mantle mineralogy together with pressure and temperature through use of measured seismic profiles of the Earth's interior.

A preoccupation with the Earth's deep interior is seen in the choice of mineral structures that have been investigated, mainly, olivine, pyroxene, spinel, garnet, rock salt, rutile, perovskite. Principal measurement techniques are: ultrasonic methods on both single- and poly-crystalline specimens, often under high pressure or high temperature; the same procedures applied to chemical analogs of actual and possible mantle minerals; and dynamic (shock-driven) and static compression. Of growing application are single crystal static compression in diamond

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anvil cells and Brillouin scattering from transparent specimens. The first reveals internal distortions of the unit cell as well as bulk volume changes, and the second method (Weidner and Carleton, 1977) permits the use of much smaller (∿100 μm) samples than do other techniques and usually allows the full set of elastic moduli to be determined.

Olivine structures. Wang, Gupta, and Simmons (1975) measured the complete set of nine elastic constants of chrysoberyl $Al_2Be_3O_4$. Hazen (1976, 1977a) measured bulk moduli and thermal expansion of coordination polyhedra within forsterite crystals, while cell-edge changes, bulk modulus K_T, and its first pressure derivative K_T' were obtained in compression measurements by Olinger (1977a).

Pyroxene structure. Velocities in polycrystalline diopside were measured by Liebermann and Mayson (1976). Hazen and Finger (1977) measured internal compressions in fassaite at pressures to 52 Kb, and Olinger (1977a) reports both linear compression and bulk modulus for enstatite. Weidner, Wang, and Ito (1978) used Brillouin scattering and, independently, acoustic velocities to obtain the nine elastic constants of synthetic orthoenstatite with good agreement.

Spinel and β-olivine structures. H.-P. Liu, Schock, and D. L. Anderson (1975) used a new technique, light-scattering from transducer-driven sound waves, in $MgAl_2O_4$ to obtain velocities, elastic constants, and their temperature derivatives to high precision. Velocities of variety of polycrystalline silicates and germanates in olivine, β-olivine, and spinel structures were reported by Liebermann (1975). Further measurements on stannate and titanate spinels and their high-pressure disproportionation products (Liebermann, Jackson, and Ringwood, 1977) showed noticeable differences in velocity-density relations and their changes on disproportionation depending on whether the spinels were normal or inverse. Finger, Hazen, and Yagi (1979) examined internal compression of bond lengths in spinel polymorphs of Fe_2SiO_4 and Ni_2SiO_4.

Garnet structure. Static compression data have been reported by Weaver, Takahashi, and Bass (1976) for grossular, by Sato, Akaogi, and Akimoto (1978) for synthetic pyrope and almandine, and by Hazen and Finger (1978b) for pyrope and grossular. Wang and Huang (1975), Isaak and Graham (1978), and Bonczar, Graham, and Wang (1977) used acoustic measurements to obtain complete elastic constants and their temperature and pressure derivatives for single crystals of pyrope and almandine-spessartine. While bulk moduli measured by Hazen and Finger are lower, other garnets have values of the order of 1.7 Mb with very slight dependence on composition.

Rock-salt structures. Different measurements of compression and velocities in NaCl which is widely used as a pressure standard were evaluated by Birch (1978) using finite strain theory. For MgO Meier and Ahrens (1977) used dynamic compression to 360 kb to estimate elastic moduli and pressure derivatives, while Jackson, Liebermann, and Ringwood (1978) give velocities for the series MgO-FeO determined on synthetic polycrystalline specimens.

Rutile-structure. In whatever mineralogy it takes place, the change of silicon from four- to six-fold coordination is the most profound structural change in the mantle; it is most directly studied in silica polymorphs and their chemical analogs. Chang and Graham (1975) measured the six elastic constants of rutile-structure SnO_2 along with temperatures and pressure derivatives. For the fluoride analog MnF_2 Davies (1977) obtained the six elastic constants as a function of pressure. In stishovite itself static (Olinger, 1976; Sato, 1977) and dynamic (Olinger, 1977b) measurements seem to give higher bulk moduli, about 2.9 Mb, than do acoustic measurements on polycrystalline samples, about 2.5 Mb (Liebermann, Ringwood, and Major, 1976). A consistent value of 2.7-2.8 Mb yields calculated mantle bulk modulus too low to satisfy seismic models and appears to make stishovite an unlikely phase in the lower mantle (Liebermann and Ringwood, 1977).

For the intermediate silica phase coesite (Weidner and Carleton, 1977) determined the 13 elastic constants of the complete elastic tensor by means of Brillouin scattering, a measurement that probably would not be possible by other methods.

Ilmenite and Perovskite Structures. As a highly probable phases in the mantle (e.g., Liu, 1977) materials having these structures have received an increasing degree of study. Liebermann (1976a) measured velocities in polycrystals of $MgTiO_3$ and $CoTiO_3$ and found sufficient agreement with previous work on materials having this structure to estimate bulk sound speed in $MgSiO_3$. Using similar data on perovskite $CdTiO_3$, Liebermann (1976b) and Liebermann, Jones, and Ringwood (1977) predicted bulk velocity and bulk modulus for the perovskite polymorph of $MgSiO_3$. Jones (1979) measured both temperature and pressure variations of the complete set of elastic constants of single crystal perovskite $KMgF_3$.

Crustal minerals. Static linear and volume compressibilities of α-quartz were measured to 120 Kb by Olinger and Halleck (1976) and compared to dynamic properties. Using the technique of time-of-flight powder neutron diffraction, Jorgensen (1978) obtained internal deformations as well as linear and volume compressibilities in α-SiO_2 and GeO_2. Though the volume compressibilities were about the same the deformation mechanisms were different: relative rotation of Si tetrahedra in one case and changes of the O-Ge-O bond angles within a tetrahedron for the other. Weidner, Swyler, and Carleton (1975) measured most of the quartz elastic constants using Brillouin scattering. By the same technique Vaughn and Weidner (1978) obtained the nine elastic constants of andalusite and sillimanite polymorphs of Al_2SiO_5 and were able to relate differences in the constants to crystal structural differences. For zircon Özkan and Jamieson (1978) obtained the complete elastic constants as well as their temperature and pressure derivatives, while Hazen and Finger (1979) measured linear, bulk, and internal compressibilities. They also obtained the same data from single crystal structure refinements of ruby (Finger and Hazen, 1978). Velocities in polycrystalline anorthite were determined by Liebermann and Ringwood (1976). X-ray compression measurements (Hazen and Finger, 1978) of the layer minerals fluorophlogopite and chlorite show a pronounced anisotropy of 5:1 and 3:1, respectively, in different directions and extremely low bulk moduli of the order 0.5 Mb. Other x-ray compression measurements have been made on hematite (Wilburn, Bassett, Sato, and Akimoto, 1978) and show good agreement between data collected in both diamond anvils and a cubic press.

The expansion in quantity of elastic data on minerals has complicated interpretations of systematic relations that can be applied to interpretations of systematic relations. It is desirable to distinguish between possible changes of chemical composition and changes of crystal structure within a planetary interior. Thus, for the relationships $K_S V_m = \text{const.}$ or $v_b \bar{m}^{1/2} = \text{const.}$ that roughly apply for chemical substitutions within a given crystal structure, e.g., perovskites (Jones, 1978) or rutile structure (Liebermann, Ringwood and Major, 1976), there are deviations in the case of Fe-Mg substitutions; this is suggested in the compilation of Jackson, Liebermann, and Ringwood (1978). (V_m = molar volume; $\bar{m}$ = mean atomic weight; $v_b = (K/\rho)^{1/2}$; and ρ = density.) Calculations by Ohnishi and Mizutani (1978) indicate that crystal field effects on ferrous iron can at least partly account for the constant or rising bulk modulus with molecular volume. The other principal systematic relationship connects velocity changes to density changes with crystal structure changes at constant chemical composition. While the relations of Mao (1974) using Poisson's ratio are adequate for the polymorphs of SiO_2 and spinel as in Fig. 2, Liebermann (1978) has summarized the complexity of other phase transitions. He distinguishes between phase transitions involving decrease of ionic distances where changes of velocity with density are large from those involving changes of cation coordination where velocity changes more slowly with density. This distinction agrees with earlier conclusions that no change of Fe/(Fe+Mg) is needed to explain the seismic discontinuity at 650 km depth. O. L. Anderson (1976) pointed out yet another systematic relationship, namely that the bulk modulus itself is quite diagnostic of crystal structure since it is relatively independent of iron content; this result agrees with other formulations of systematics (Wang, 1978).

A promising theoretical approach has been the relation of elastic properties to optical properties through models of crystal vibrational modes. These have been accomplished for α-quartz (Striefler and Barsch, 1975a), the rutile-structure oxides GeO_2, TiO_2, SnO_3 (Striefler and Barsch, 1975b), and stishovite (Striefler and Barsch, 1976). From classical dielectric theory, O. L. Anderson (1975) compiled relationships of mineral refractive index to density and velocity.

The systematic trends in mineral properties have mainly been used for inferring Fe/(Fe+Mg) ratios and dominant mineralogy. To infer Mg/Si stoichiometry it has been necessary to use the forward calculation of possible mantle elastic properties from mineral properties. The present result favors a dominant olivine stoichiometry

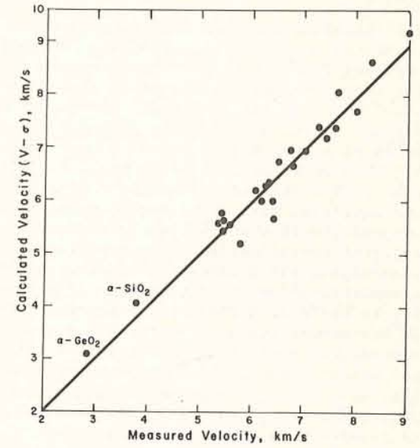

Fig. 2. Predicted vs. measured bulk sound velocities in a variety of minerals as calculated by the method of Mao (1974), from Shankland (1977).

Mg/Si ≈2 (Graham and Dobrzykowski, 1976; Watt and O'Connell, 1978). This effort has seen increasing application of the elastic theory of composites, a topic reviewed by Watt, Davies, and O'Connell (1976).

Challenges for future work are many. Experimentally there is the application of new methods using diamond pressure cells together with Brillouin scattering (Bassett and Brody, 1978) and energy-dispersive x-ray analyses, in addition to further acoustic measurements on single- and poly-crystalline specimens. Both of the latter would be aided by an expansion of the stock of high-quality synthetic minerals, particularly of end-member compositions. Point defects in alkali-halides affect velocities and attenuation (Shaw, 1978), and it is desirable to determine if similar effects occur in silicates. The systematics of internal and external variations of atomic configurations is only beginning to be investigated for effects on elastic properties (Hazen, 1977b; Hazen and Prewitt, 1977). Theoretically, both a priori calculations of elastic properties (Cohen, Gordon, 1975; Bukowinski and Knopoff, 1977) and the detailed approaches of Striefler and Barsch are needed. Finally, measurements of melted minerals and rocks together with temperature- and pressure-effects would be useful. As yet there is no compilation of systematic variations of melt elasticity and anelasticity to aid in interpretations of low velocity zones or the core.

Thermal Properties

Despite a large number of measurements on rocks (previously compiled by Desai, et al., 1974), thermal properties of minerals have seen fewer measurements than have other physical properties. Here we discuss thermal conductivity and thermal expansion. For thermal conductivity, SI units are only slowly being adopted. Conversions for various frequently used units are: 4.18 $Wm^{-1}K^{-1}$ = 0.0418 W cm^{-1} = 0.01 cal cm^{-1} s^{-1} K^{-1} = 10 heat conductivity units (HCU). These values are of the order of conductivity in dense minerals.

Individual mineral conductivities were last assembled by Horai (1971). Kieffer, Getting, and Kennedy (1976) have since measured thermal diffusivity and conductivity as a function of pressure to 35 kb for rock salt, quartz, silica glass, and teflon and used the data for testing theories of pressure dependence of heat conduction. This work was applied by Kieffer (1976) to calculation of lattice thermal conductivity in the mantle as well as to investigate the volume dependence of the Grüneisen parameter. Theoretical consolidations have been important. Thus, Roufosse and Klemens (1974) observed that the proportionality of lattice thermal conductivity to recipricol absolute temperature should apply for temperatures up to the melting point as a consequence of the distribution of vibrational modes in the complex crystal structures of most minerals. In a comprehensive review of vibrational modes of minerals, Kieffer (1979a, b, c) related them to thermal energy and developed predictive models for heat capacity. The effect of alloying iron with silicon, a possible core composition, is to decrease the lattice conductivity (Taylor and Fowler, 1978). Holt's (1975) measurement of thermal diffusivity in polycrystalline olivine agree reasonably well with values calculated from Schatz and Simmons (1972) despite uncertainties of oxidation state introduced by heating in air. Radiative heat transfer has received some attention. Shankland, Nitsan, and Duba (1979) calculated the radiative contribution K_R to total heat conductivity from measured optical absorption in olivine at temperatures to 1400°C and found K_R to be lower than previous calculations. On the basis of optical absorption measurements at pressures to 420 kb in shock-compressed MgO, Goto, Ahrens, Rossman, and Syono argue that high conductivities, of the order of 0.01 cal/cm-5-K, are possible in the lower mantle. As an aid to estimating the scattering contribution to opacity and K_R Nitsan (1976) determined the magnitude of grain boundary scattering from both Monte Carlo calculations and experiment, finding strongly forward scattering and therefore only weak impedance to radiative transfer in mantle conditions. On the other hand, rhyolitic glasses had strong, presumably isotropic scattering giving rise to virtually temperature-independent spectra (Stein and Shankland, 1978); the extrapolated K_R in these materials increases strongly with temperature so that K_R becomes comparable with the "lattice" contribution at crustal magmatic temperatures.

Measurements of thermal expansion have substantially increased as a result of high temperature x-ray analysis of single crystals, e.g., Smyth (1975). Combined effects of temperature and pressure on internal atomic configurations permitted not only calculation of mineral volume expansion but also linear expansions of internal coordination and bond lengths polyhedra (Hazen, 1977b; Hazen and Prewitt, 1977). Lager (1978) devised methods to calculate volume expansion from changes of size, shape, and rotation of internal bond lengths and angles.

Despite an apparent lull in measurement of mineral thermal conductivities some interesting problems remain. Especially needed are conductivities at high temperature and pressure where measurement is quite difficult. If accomplished at high pressure, the technique of Schatz and Simmons (1972) for separately evaluating the combined effect of radiative and lattice contributions at high temperature would be highly useful for calculation of conductivity in the deep earth. Thermal conductivity of melts has received little attention. Interpreting conduction in composites has not been simple. Unlike electrical conductivity or permeability where the good transport path is in fluid-filled void space, the crystals in a rock are the good conductor. Hence, Robertson's (1979) concept of "solidity" $\equiv$ (1 - porosity) should prove helpful in estimating rock thermal conductivity from mineral conductivities.

Diffusion in Minerals and Melts

Diffusion is frequently the rate-governing process for a variety of chemical and physical transformations involving mass transport. This section treats recent work in laboratory measurements and theory that can be applied to problems from zoning in minerals to long-term strength of rocks. Previous and comprehensive theoretical and experimental papers are to be found in the volume by Hofmann, Giletti, Yoder, and Yund (1974). Anderson (1976) has considered atomic models of diffusion, and Hofmann (1979) has recently reviewed work on diffusion in silicate melts.

In theoretical developments Brady (1975a) elaborated the importance of careful definition of the reference frames in which diffusion constants are evaluated. He distinguished which frames are most important for different problems, e.g. when volume changes take place, and showed the different results obtained for ionic and metallic crystals when interdiffusion behavior is calculated from self-diffusion coefficients. Brady (1975b) also demonstrated how chemical components could be chosen to simplify solutions of multicomponent systems through appropriate component transformations. By means of eigenvector analysis, Loomis (1975a) developed a method of computing diffusion profiles in multi-component systems with allowances for cross coefficients of diffusion and demonstrated the importance of cross-coefficients in garnets (Loomis, 1975b).

The ion microprobe has provided a valuable method for measuring low diffusion rates. Giletti, Semet, and Yund (1978) obtained oxygen self-diffusion constants varying less than an order of magnitude between adularia, albite, and anorthite and found good agreement with earlier work. The effect of water pressure to 4 kb is to enhance oxygen diffusion (Yund and Anderson, 1978); the apparent negative activation volume presumably results from activity of "water" in the lattice. In phlogopite mica oxygen self-diffusion is strongly anisotopic with diffusion normal to the layering. By contrast, though it is also anisotopic, potassium self-diffusion in mica parallel to the layers is greater than that normal to the layering by two to four orders of magnitude (Hofmann, et al. 1974), presumably because the oxygen layers provide a barrier to cation motion. Argon self-diffusion (Giletti, 1974) shows the same kind of anisotropy in phlogopite and only weak pressure dependence (Giletti and Tullis, 1977).

As mentioned above, Hofmann (1979) has recently reviewed diffusion studies for melts where diffusion constants are roughly six orders of magnitude greater than in silicate crystals. Hofmann and Hart (1978) compiled diffusion data and argue that even in the presence of melt only very local (kilometer-scale) equilibrium can be established by diffusion in geologic time. Cationic diffusion in basaltic melts (Hofmann and Magaritz, 1977) is far less dependent on the particular cation than is the case in obsidian (Magaritz and Hofmann, 1978a). This may reflect the different degrees of polymerization in the two kinds of melts. For predicting cation diffusivities D_c in melts, Hofmann demonstrated a linear relationship between log (D_c) and Z^2r where Z is the charge on a cation having ionic radius r. Water diffusion in obsidian has been studied by Shaw (1974), Friedman and Long (1976), Jambon, Carron, and Delbove (1978), Arzi (1978a) in connection with melting, and by Laursen and Lanford (1978) who used nuclear resonance of ^{15}N with ^{1}H to profile hydrogen concentration. In another method involving nuclear particles, Hoffman and Brown (1976) demonstrated that fast deuterons could be used for in situ emplacement of tracer ions in silicate glass. Oh, Reddy, Major, and Cooper (1979) used α-particles emitted during proton irradiation to obtain oxygen self-diffusion in forsterite. While the activation energy of 89 kcal/mole is noticeably less than values used in studies of presumably diffusion-controlled strain in olivine, there is good agreement in magnitude with diffusivities inferred by Goetze and Kohlstedt (1973).

A number of unsolved problems await solution. Hofmann (1979) pointed out the lack of measurements on the chain-forming elements Al and Si. Deformation of minerals is probably diffusion controlled which provides further inducement for Al and Si measurements. The intriguing "plateau" in temperature dependence of diffusion of Eu and Gd in basalt partial melt (Magaritz and Hofmann, 1978b) that parallels the plateau in melting basalt (Rai and Manghnani, 1977) merits further investigation. Finally, there are relatively few measurements of pressure effects on diffusion in either minerals or melts.

Physical Properties of Melts

Since the comprehensive work of Murase and McBirney (1973) covering density, velocity, electrical and thermal conductivities, viscosity, and surface tension of several melts, subsequent work has been more specialized.

In contrast to a neglect of velocity and thermal measurements, electrical conductivity of melts has received a satisfying amount of attention. A conductivity increase of about two orders of magnitude occurs on melting. Waff and Weill (1975) established that melt conductivities are relatively independent of chemical composition to within a half order of magnitude and almost totally independent of oxygen fugacity. Because of low activation energy, the temperature dependence is also relatively weak. These results were confirmed by Rai and Manghnani (1977, 1978; Manghnani and Rai, 1979) who extended their measurements to temperatures below the solidus and obtained agreement with rock measurements in most cases. Similar results for partly melted peridotite were obtained by Murase, Kushiro, and Fujii (1977b). Higher rock conductivities were measured in samples of high alkali and glass content. Ultramafic rocks contained little glass and thus readily attained equilibrium and produced more consistent results. Good agreement is also achieved with magmatic conductivities measured in the field (Mathews, 1969), so that electrical conduction in melts at zero pressure has become one of the better-known physical parameters. By contrast, when pressure is included there are contradictory results with some measurements showing a positive pressure coefficient and thus a negative effect. The effect may depend on composition and is an important topic for further study.

The decrease of melt viscosity with pressure for many compositions has been a striking result. On the basis of pressure-induced coordination changes of Al^{3+} Waff (1975) predicted this effect which was observed by Kushiro (1976, 1978) and Kushiro, Yoder, and Mysen (1976). The viscosity decrease is strongest in the most alumina-rich compositions. However, since some Al-free melts also show pressure-induced viscosity decreases (Kushiro, 1978) and Raman spectra show no evidence of Al coordination changes (Sharma, Virgo, and Mysen, 1978), other interpretations are needed. Virgo, Mysen, Scarfe, and Sharma (1979) point out that highly polymerized melts have the greatest viscosity decreases as pressure alters 3-dimensional linkages, while structures of low polymerization have more ordinary pressure behavior. Another strong effect is the substantial increase of density of basalt melt with pressure (Fujii and Kushiro, 1977); the resulting high compressibility is slightly lower than that of Murase and McBirney (1973). Murase, Kushiro, and Fujii (1977a) demonstrated abrupt velocity changes on partial melting of peridotite.

In further work on melts it would be valuable to extend pressure effects on density, velocities, electrical, and thermal conductivities to better interpret geophysically anomalous zones attributed to the presence of magma chambers or partial melt.

Application to geophysical and geochemical problems of physical data on melts depends critically upon assumptions about the configuration and interconnections of partial melt. Two questions have arisen: what is the equilibrium texture--defined as an invariant melt shape independent of changes in grain size--of partial melt in a rock; and how long does it take to be achieved? The topic was discussed by Goetze (1977) who pointed out the rather small effect of minor melt fractions on mantle rheologies as illustrated by Stocker and Gordon's (1975) work on equilibrium melts of alloys. Arzi (1978b) indicated a critical melt fraction necessary for melt to alter rheology. Melt shape is also important because a well-interconnected melt fraction readily flows through a partial melt zone (Turcotte and Ahern, 1978; Walker, Stolper, and Hays, 1978). Waff and Bulau (1979); Bulau and Waff (1979) found that the equilibrium texture for a few percent partial melt in peridotite is interconnected prismoidal tubules at triple

grain intersections; the more commonly observed interfacial melting appears to be a transient that does not persist for large periods (Waff and Holdren, 1979). Since times of the order of days are needed to attain textural equilibrium even in fine-grained sintered powders, it seems likely that textures seen in laboratory-melted rocks of normal grain sizes are not readily observed even in low-viscosity basaltic materials, let alone silicic rocks of higher viscosity and slower melt diffusion. Partial melt textures observed in the field due to adiabatic decompression (Padovani and Carter, 1977) or melting under stress (Boudier and Nicholas, 1977) are dynamic configurations although the latter may also occur during steady state deformation. A tubular configuration is sufficient to explain electrically anomalous zones (Shankland and Waff, 1977), but flatter melt shapes are needed to provide low velocities and high attenuations (O'Connell and Budianski, 1977; Mavko and Nur, 1975). Waff (1979) has further argued from considerations of surface and gravitational energies for stratification of partial melt configuration.

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TRACE ELEMENT GEOCHEMISTRY: APPLICATIONS TO THE IGNEOUS PETROGENESIS OF TERRESTRIAL ROCKS

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Introduction

Trace element geochemistry, like the entire field of geochemistry, has applications in many earth science problems. In a brief contribution, it is not possible to report on recent advances in all aspects of trace element geochemistry; thus, I focus on applications in determining the origin and evolution of terrestrial igneous rocks. Important advances in trace element geochemistry arising from lunar and meteorite studies are reviewed in the sections on meteorites and planetology. This report primarily reviews progress from 1975 through 1978, but a few important 1973-1974 papers are included as are significant foreign contributions.

Although trace element geochemistry was established by early geochemists such as Goldschmidt and Clarke, it is only during the last ten years that this speciality has made important contributions to an understanding of igneous rock petrogenesis. Moreover, significant advances have been made since the last U.S. report to IUGG on trace elements (Murthy, 1971). As an indication of the increasing importance of trace element geochemistry a special issue (vol. 38, No. 1, 1978) of Earth and Planetary Science Letters, Trace Elements in Igneous Petrology, a Volume in Memory of Paul W. Gast (also available in book form, Elsevier, 1978) has been published to review recent advances in the field.

Major advances in trace element geochemistry have arisen because significant improvements in analytical techniques (e.g., ion exchange separations) and equipment (e.g., mass spectrometers and semi-conductor detectors for use in neutron activation) have led to a rapidly growing data base of accurate and precise trace element abundances. Simultaneously, there has been increased understanding of the complexities involved in trace element modelling, and significant progress in development of techniques for experimental determination of trace element partition coefficients as a function of pressure, temperature and composition. Therefore, it is convenient to divide this review into sections on Theory and Modelling and Experimental Determination of Trace Element Partition Coefficients followed by summaries of trace element applications to various igneous rock types.

Developments in Theory and Modelling

In 1975 most trace element data for igneous rocks were interpreted by utilizing straightforward models of equilibrium, incremental, or fractional fusion and/or similar models for crystallization. Arth (1976), in a short review for nonspecialists, has summarized these trace element models. More recent reviews by Shaw (1977) and Allegre and Minster (1978) discuss problems and complexities that are too frequently ignored in trace element models for partial melting and fractional crystallization. An important and previously neglected approach in understanding trace element abundances in basalts is the study of multiple samples from single flows. Haskin et al. (1977) found that random compositional variability among samples from a single flow exceeded analytical uncertainties, and noted that such variability must be understood before trace element abundance data can be used to narrowly constrain melting and crystallization models or to define source heterogeneity. Lindstrom and Haskin (1978) showed that such random compositional variations in undifferentiated lava flows can be explained by short-range (few cm) unmixing of phenocrysts, residual liquid and average in-situ crystallized minerals.

In many cases the simple fractionation and melting models fail to explain the variety of trace element data for a given igneous rock suite. For melting models these failings commonly lead to two alternatives: postulating several compositionally distinct sources or development of more complex petrogenetic models. Examples of the former are explanations for geochemical trends in basalts along the Reykjanes Ridge-Reykjanes Peninsula transect (Schilling, 1973). In such models mixing of magmas and mantle sources may be important and Langmuir et al. (1978) have thoroughly discussed the effects of mixing on trace element abundances. An example of more complex models is disequilibrium melting which is commonly invoked to create special trace element abundances and isotopic ratios in a melt. Disequilibrium melting was proposed (O'Nions and Pankhurst, 1974) to account for geochemical differences between basalts from the Mid-Atlantic Ridge (MAR) axis and islands such as Iceland, but the model was later abandoned (O'Nions et al., 1976) because it could not account for the full range of isotopic and trace element abundance variations in these basalts. Consideration of diffusion rates also argues against disequilibrium models (Hofmann and Hart, 1978), but such models are still favored by some researchers (e.g., Beswick and Carmichael, 1978).

Another example of a complex melting model is the "dynamic melting" concept developed by Langmuir et al. (1977) to account for the range of trace element abundances in basalts from the Mid-Atlantic Ridge at ∿ 37°N. In this model a variety of liquids with distinct trace element contents are derived from compositionally homogeneous, upwelling mantle by considering that different melting processes occur simultaneously, but to different degrees throughout the uprising mantle source; for example, one region may melt in a batch equilibrium manner while another region may melt in a fractional fusion manner provided that there is incomplete segregation of melt from the residue. Multi-stage, incremental melting is an important aspect of the dynamic melting

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concept; thus, late-stage melts are derived from different source compositions than early melts. An important but poorly known parameter in this melting model is the quantity of melt trapped in the residue when melt segregation occurs. An equally important parameter key to all trace element melting models is the amount of liquid required for melt segregation (Arndt, 1977; Turcotte and Ahern, 1978; Waff and Bulau, 1979).

Additional important advances in trace element modelling are the application of matrix inversion techniques for quantitatively modelling rock suites related by fractional crystallization (Allegre et al., 1977; Minster et al., 1977) and partial melting (Minster and Allegre, 1978). Also, improvements for modelling trace element abundances during crystal fractionation are models for closed system fractionation (Haskin and Korotev, 1977) and for fractionation in a periodically refilled magma chamber (O'Hara, 1977).

It is apparent that the number of unknown parameters in complex petrogenetic models which include mixing, open system fractionation, dynamic melting and mantle heterogeneity are sufficient so that these parameters can be adjusted to accurately model any set of trace element abundances. As one looks to the future of trace element geochemistry the selection of realistic models will require: (1) careful selection of samples for detailed study, (2) acquisition of a large and accurate data base for abundances of trace elements with different geochemical characteristics, and (3) model constraints from other types of data ranging from stable and radiogenic isotope data to field geology, petrography and petrology.

Experimental Determination of Trace Element Partition Coefficients

Trace element modelling of igneous rock systems usually requires apriori knowledge of trace element partition coefficients. In 1975 almost all trace element partitioning data came from studies of natural materials such as coexisting minerals or phenocryst-matrix pairs (see summary by Arth, 1976). These natural system studies have usually yielded systematic results indicating that crystal structure is a major factor controlling trace element partitioning (Jensen, 1973; Matsui et al., 1977; Philpotts, 1978). Although the majority of partition coefficients used in trace element modelling are derived from studies of partitioning in natural systems, it is apparent that these natural system data are inadequate for understanding the effects of pressure, temperature, and composition (P, T, X) on trace element partitioning. At present, a major obstacle in trace element modelling is our poor knowledge of trace element partition coefficients as a function of P, T, and X; before modelling can be markedly improved, experimental studies of trace element partitioning are required. A testament to the recognition of this need is the special issue of Geochimica et Cosmochimica Acta (vol. 42, No. 6a, 1978) containing papers presented at the AGU-sponsored meeting on Experimental Determination of Trace Element Partition Coefficients.

A variety of elements and phases have been studied experimentally and some important compositional and temperature effects have been identified (see review by Irving, 1978); e.g., partition coefficients of some trace elements such as rare-earth elements, are highly dependent on silicate liquid composition (Watson, 1976; Ryerson and Hess, 1978). However, no trace element has been studied in sufficient detail to accurately define the P-T-X dependence of all major mineral/liquid partition coefficients. In addition, very few researchers have convincingly demonstrated that their experiments reached equilibrium. Not surprisingly, at this early stage there is little unanimity of results. Moreover, there is considerable disagreement (Drake and Holloway, 1978; Mysen, 1978; Navrotsky, 1978) regarding the concentration regions where Henry's Law behavior is followed. Encouragingly, the early experimental results are in qualitative agreement with natural system studies, thereby supporting petrogenetic inferences made from models using natural system partitioning data. However, many more experimental studies must be done before a new level of sophistication can be reached in quantitative trace element modelling. Ideally, a few key trace elements in important systems will be studied in enough detail to obtain a thermodynamic understanding of trace element partitioning so that we can accurately predict partition coefficients for other trace elements and other phases as a function of P, T, and X.

Another application of research on experimental, trace element partitioning, results from study of trace elements, such as Cr and Eu, that exist in more than one oxidation state at oxygen fugacities typical of igneous rock petrogenesis (Sun et al., 1974; Morris et al., 1974; Morris and Haskin, 1974; Drake and Weill, 1975; Schreiber and Haskin, 1976; Schreiber, 1977). In particular, Eu partitioning has been used as an indicator of oxygen fugacity (Drake, 1975).

APPLICATIONS OF TRACE ELEMENT GEOCHEMISTRY TO THE PETROGENESIS OF TERRESTRIAL IGNEOUS ROCKS

Ultramafic Rocks:

Many ultramafic rocks in the earth's crust have coexisting mineral compositions which reflect equilibrium at upper mantle pressures and temperatures. Trace element studies of these rocks provide insight into igneous processes within the upper mantle and they are a basis for inferring upper mantle compositions. Alpine peridotites form the largest masses of ultramafic rock exposed in the crust. Several researchers (Loubet et al., 1975; Menzies, 1976, 1977; Dickey et al., 1977; Menzies et al., 1977; Suen and Frey, 1977) have found that compatible and incompatible[1] trace element abundance trends in alpine peridotites correlate well with major element indexes such as Mg/Mg + Fe. The straightforward interpretation is that these peridotites are residues from partial melting processes that yielded basaltic magmas.

[1] Compatible elements are preferentially incorporated into the bulk solid during solid-liquid partitioning whereas incompatible elements are preferentially incorporated into the liquid. Note that the mineralogy of the solid is important in defining an element's compatibility or incompatibility.

Another important ultramafic rock type derived from the upper mantle are ultramafic xenoliths in basalts and kimberlites. Trace element studies of lherzolite-harzburgite xenolith suites from basalts demonstrate that compatible trace elements vary systematically as a function of Mg/Mg + Fe, but incompatible trace elements do not (e.g., Frey and Green, 1974; Frey and Prinz, 1978). There are several suites of xenoliths from single localities where the samples most depleted in basaltic constituents (relatively high MgO and low CaO and Al_2O_3 contents) have the highest contents of incompatible elements such as light rare-earth elements (REE), U and K. Similar discrepancies between major element trends and incompatible element abundances occur in garnet lherzolite xenoliths from South African kimberlites (Shimizu, 1975a,b; Shimizu and Allegre, 1978). These data for ultramafic inclusions in basalts and kimberlites have led to complex models for the lherzolite-harzburgite xenolith suite. One of the most intriguing models involves migration of trace element-rich fluids within the mantle (e.g., Frey and Green, 1974). Recent high pressure experiments (Mysen, 1978; Wendtlandt and Harrison, 1978) of REE partitioning between minerals and CO_2-H_2O fluids suggest that significant amounts of REE are incorporated into the fluid phase; fluid mobility may therefore be an important cause of compositional heterogeneity within the upper mantle. Several types of isotopic data are also consistent with mantle "metasomatism" (e.g., Boettcher et al., 1979) and combined trace element and isotopic studies of xenolith minerals (e.g., Basu and Murthy, 1977) are required to understand the complex geochemical history of ultramafic xenoliths. It is puzzling that alpine peridotites show little evidence of this "metasomatic" process. This distinction between alpine peridotites and ultramafic xenoliths in basalts and kimberlites must reflect different mantle histories; possibly, the xenolith compositions reflect a mantle metasomatic process that is a prerequisite for alkalic volcanism.

Precambrian Basic and Ultramafic Volcanics:

During the last four years an important exciting research area in trace element geochemistry has been the study of komatiites. In particular, the trace element characteristics of spinifex-textured, MgO-rich komatiites, presumably derived by high degrees of melting, provide insight on trace element abundances in the Precambrian mantle beneath eastern Canada, South Africa, and western Australia; therefore, study of such rocks provides information on key questions such as, how upper mantle composition has evolved with time (e.g., Jahn et al., 1974; Hart and Brooks, 1977; Sun and Nesbitt, 1977, 1978; O'Nions and Pankhurst, 1978; O'Nions et al., 1978). Interpretations of geochemical data for these ancient rocks must recognize that they are commonly altered and metamorphosed (e.g., Condie, 1976; Condie et al., 1977; Sun and Nesbitt, 1978; Whitford and Arndt, 1978). However, abundances of elements believed to be relatively immobile during alteration, such as REE, have been extensively used to conclude (Herrmann et al., 1976; Whitford and Arndt, 1978) that the sources of ultramafic komatiite lavas were depleted in incompatible elements similar to the oceanic mantle source of recent mid-ocean ridge basalts (MORBS). Because Nd isotope data for komatiites (Hamilton et al., 1977) are consistent with a source having a chondritic Nd/Sm ratio, the lower Nd/Sm ratio inferred in the source region of some Archean komatiites must have been created shortly before melting or possibly by an incremental (multi-stage) melting process (Arth et al., 1977; Arndt, 1977). Nevertheless, an important observation is the occurrence $\geq 3.5 \times 10^9$ years ago of mantle with relatively low incompatible element abundances similar to the modern oceanic mantle (Herrmann et al., 1976).

Basaltic komatiites and geographically associated tholeiites have a wide range of trace element abundances (e.g., Condie, 1976; Sun and Nesbitt, 1978) usually distinct (e.g., higher La/Sm) from those of associated ultramafic rocks. This wide abundance range is not explainable by alteration effects or fractional crystallization, and consequently, such data have led to models of incremental melting and/or compositional heterogeneity of the Archean mantle (e.g., Arth et al., 1977; Sun and Nesbitt, 1978). Although the trace element abundance levels of Archean basalts fall within the range of modern oceanic basalts (O'Nions and Pankhurst, 1978; Sun and Nesbitt, 1978), several researchers (Jahn et al., 1974; Hart and Brooks, 1977; Sun and Nesbitt, 1977, 1978; O'Nions and Pankhurst, 1978) have argued that in detail, Archean mantle compositions were richer in incompatible trace elements than the present mantle source of normal MORBS.

Alkalic Basalts:

Because compatible trace element contents of peridotites are rather constant, modelling of elements, such as Ni, (e.g., Sun and Hanson, 1975; Hart and Davis, 1978) has been useful in identifying primary basalts that have been unaffected by major fractional crystallization of mafic phases. Sun and Hanson (1975) reviewed the trace element and isotopic characteristics of primary alkalic basalts and concluded that these basalts originate in the mantle below the level of present-day convection. Furthermore, the similar and systematic trace element abundances in most alkalic basalts from diverse areas constrain the major and minor mineralogy of the mantle residue remaining after melt segregation. For example, studies of alkalic suites from specific areas (Hawaii, Navajo-Hopi Buttes region, Arizona, and Leucite Hills, Wyoming, Kay and Gast, 1973; Grenada, Shimizu and Arculus, 1975; Arculus, 1976; Ross Island, Antarctica, Sun and Hanson, 1975; southeast Australia, Frey et al., 1978) consistently conclude that these basalts are generated by small degrees < 15% of melting of garnet peridotite. Important conclusions have also been reached on the role of phlogopite and apatite during melting. For

example, Sun and Hanson (1975) and Frey et al. (1978) concluded that the nearly constant ratio of P_2O_5/Ce in alkalic basalts precludes residual apatite, but an opposite view is advocated by Beswick and Carmichael (1978).

Although the similar trace element characteristics of most primary alkalic basalts imply comparable similarity in source compositions and subsequent petrogenesis, there is no unaminity concerning trace element concentrations in the mantle source of such basalts. For example, Sun and Hanson (1975) and Minster and Allegre (1978) argue for a source relatively enriched in light REE compared to chondrites, Kay and Gast (1973) and Shimizu and Arculus (1975) utilize a source with relative REE abundances as in chondrites, while Nd isotopic studies (e.g. De Paolo and Wasserburg, 1976; Evensen et al., 1977) of some alkalic suites require a source with long-term Nd/Sm depletion compared to chondrites. In an effort to further define the composition and mineralogy of mantle sources for basalts, Frey et al. (1978) evaluated the interrelationships between basaltic major and trace element compositions, experimental petrological data and the compositions (major and trace elements) of mantle sources for basalts.

Trace elements have continued to be sensitive monitors for evaluating and modelling fractional crystallization processes in alkalic rock suites. Most geochemical features of alkalic basalt to phonolite or trachyte suites are apparently controlled by fractional crystallization (e.g., Gregory Rift Suite in Kenya, Baker et al., 1977; McMurdo volcanics, Antarctica, Sun and Hanson, 1976); however, variation of trace element partition coefficients during fractionation is an important but poorly understood variable in such models.

Continental Tholeiitic Basalts:

Studies of continental tholeiites from the Columbia River (Nathan and Fruchter, 1974; McDougall, 1976) and Snake River (Leeman, 1976) suites provide evidence that these basalts are are derived from a mantle source compositionally distinct from that of most ocean floor tholeiites. Nevertheless, there is considerable trace element abundance heterogeneity in continental tholeiites. For example, eastern U.S. Triassic diabases vary systematically in trace element content from south to north (Smith et al., 1975; Bryan et al., 1977). Undoubtedly, fractional crystallization has been important during the evolution of continental tholeiites, but the relative roles of mantle compositional heterogeneity and crustal contamination in causing trace element abundance variations are ambiguous (e.g., Mark et al., 1975). However, Nd and Sr isotopic studies of Tertiary tholeiites from Scotland indicate that some of these basalts have been significantly contaminated by continental crust (Carter et al., 1978).

The large geochemical variations occurring within some continental tholeiite suites (Steens Mountain, Oregon, Helmke and Haskin, 1973; Snake River Plain, Leeman et al., 1976) have been modelled by extensive fractional crystallization of the phenocryst phases. The Skaergaard intrusion continues to be a classic example for modelling fractional crystallization, but with increased sampling and more sophisticated geochemical approaches this example is becoming more complex. For example, Paster et al. (1974) showed that trapped liquids have a major affect in determining trace element contents of cumulate gabbros in the Skaergaard intrusion.

Tholeiitic Basalts from the Oceanic Floor and Oceanic Islands:

Tholeiitic basalts derived from the oceanic mantle have been intensively studied in recent years because of (1) the important geochemical gradients (most obviously seen in trace element abundances and radiogenic isotope ratios) found in basalts dredged from the spreading ridge axes in the north Atlantic Ocean (e.g., Schilling, 1973; White and Schilling, 1978), and (2) the dramatically increased sampling of ocean floor, particularly significant penetrations of old oceanic crust, provided by the Deep Sea Drilling Project (DSDP) initiated in 1968 and continuing since 1975 as the International Phase of Ocean Drilling. The recent emphasis on trace element studies of ocean floor basalts is apparent from the large number of references.

Kay and Hubbard (1978) reviewed the trace element characteristics of ocean floor and island basalts and discussed the implications for mantle evolution with time. Within the ocean basins, major geochemical differences in basalt composition occur on two distinct geographic scales (hundreds of km and meters to a few km). Most oceanic island tholeiites have significantly higher incompatible element abundances than ocean floor basalts distant from oceanic islands (e.g., Bryan et al., 1976). This distinction in incompatible element abundances is accompanied by different radiogenic isotope ratios, and commonly large-scale vertical and horizontal mantle compositional heterogeneity is invoked to account for these geochemical differences. The best documented example of this large-scale (∿ 400 km) heterogeneity is the Reykjanes Ridge-Iceland transect (Hart et al., 1973; Schilling, 1973; O'Nions and Pankhurst, 1974; Sun et al., 1975; O'Nions et al., 1976), but it is also well established that central and northern (29-64°) Mid-Atlantic Ridge axial basalts have systematic variations in trace element abundances and radiogenic isotopic ratios as a function of latitude (Schilling, 1975; White and Schilling, 1978). Distinct mantle sources (mantle plume for Iceland tholeiites and low velocity zone for Reykjanes Ridge tholeiites) have been proposed and extensively tested by Schilling and coworkers. However, the data are not easily explained by only a two-component model (Langmuir et al., 1978), and recent evidence suggests at least two independent mantle sources (both distinct from the Reykjanes Ridge source) beneath the Reykjanes Peninsula (Zindler et al., 1979). Detailed but different models for the petrogenesis of Icelandic tholeiites are presented by Schilling et al. (1978) and Zindler et al. (1979).

Progess has also been made in understanding the petrogenesis of other tholeiitic island suites, such as Reunion (Zielinski, 1975; Ludden, 1978) and Hawaii (Leeman et al., 1977, 1979; Murali et al., 1979). There is no evidence that garnet equilibrated with Icelandic and oceanic floor tholeiites, but it is apparently required as a residual phase during generation of Hawaiian and Reunion tholeiites (if the mantle source is assumed to be light REE depleted or nearly chondritic in relative REE abundances). A garnet-bearing source for Hawaiian and Reunion tholeiites is consistent with the thicker lithosphere expected at their intraplate locations. Each Hawaiian tholeiitic shield has distinctive trace element abundances (Leeman et al., 1979) which are closely coordinated with differences in Pb^{206}/Pb^{204} (Tatsumoto, 1978). However, preliminary comparison by Clague and Frey (1979) of modern Hawaiian tholeiites with tholeiites recently drilled on the Emperor seamounts show that there is no correlation of trace element abundances with age in tholeiites formed at the Hawaiian "hot spot" over the last 65 x 10^6 my.

On a smaller scale, some localized areas along the Mid-Atlantic Ridge (∿ 37°N e.g., Blanchard et al., 1976; Langmuir et al., 1977; White and Bryan, 1977), the Faeroe Islands (Schilling and Noe Nygaard, 1974), and Iceland (Zindler et al., 1979) have tholeiitic basalts in close (m to few km) proximity with very different abundances of incompatible elements and, in some cases, different isotopic ratios (Zindler et al., 1979). These different trace element abundances cannot be easily explained by varying degrees of fractional crystallization or partial melting. Some authors interpret these localized variations in terms of fine-scale mantle heterogeneity and several independent primary magmas are called for even within a single 580 m drill core (e.g., Blanchard et al., 1976). However, others have used more complex petrogenetic models to explain such data; e.g., disequilibrium melting (O'Nions and Pankhurst, 1974), volatile transfer of incompatible elements during fractionation (Bryan and Moore, 1977), open system fractional crystallization (O'Hara, 1977), dynamic melting (Langmuir et al., 1977), and mixing(Schilling and Noe-Nygaard, 1974; Dungan et al., 1978, Rhodes et al., 1979).

Increased sampling and study of the oceanic lithosphere is required to evaluate these disparate models. During the last four years, the Deep Sea Drilling Project has recovered igneous rocks from many sites in all major oceans and, especially in the Atlantic, several sites have penetrated hard-rock to depths of 100-600 m. Study of these cores already demonstrates that the large majority of ocean floor basalts are "normal MORBS"; that is, tholeiites depleted in incompatible elements compared to continental and island tholeiites. However, there is considerable compositional variation among these "normal MORBS" and several drill sites have also recovered tholeiitic basalts relatively enriched in incompatible elements. In addition, fine-scale combined dredging-submersible programs such as FAMOUS are providing geologic control and detailed sampling not previously possible (Bryan and Moore, 1977; Langmuir et al., 1977). Undoubtedly, further study of ocean floor rocks recovered in these programs will provide significant advances in our understanding of oceanic tholeiite petrogenesis.

A relatively new and promising area of trace element research is the determination of volatile trace element abundances in the quenched glassy margins of MORB (e.g., Dymond and Hogan, 1973; Fisher, 1975; Craig and Lupton, 1976; Unni and Schilling, 1978) and in fluid inclusions (Delaney et al., 1978). Although there are several complexities (Dymond and Hogan, 1978) these studies provide information about the volatile content of the mantle. Such data are important to a variety of geochemical problems ranging from development of the atmosphere to mantle metasomatism.

Ophiolites:

Kay and Senechal (1976) showed that the ubiquitous alteration and metamorphism of ophiolite suites causes great difficulty in utilizing isotopic and trace element abundance data to infer the tectonic setting of ophiolites. Because the effects of alteration and metamorphism on trace element abundances must be understood before trace element abundances of ophiolite rocks (also, Archean greenstones and altered ultramafics) can be used to infer petrogenesis, there have been several studies of trace element abundances in rocks with local variations in degree of alteration or metamorphism (Frey et al., 1974; Wood et al., 1976; Condie et al., 1977; Hellman et al., 1977; Humphris et al., 1978; Ludden and Thompson, 1978; Muecke et al., 1979). Although abundances of all elements are mobile in some situations, there is a general consensus that Ti, Y, Zr, Hf, Nb, Ta, and heavy REE form a relatively immobile group whose relative abundances are generally invariant during alteration or metamorphism of basic rocks. As a result, the abundances of these elements in altered and/or metamorphosed basic rocks have been utilized to infer the type (alkalic vs. tholeiitic) of precursor basalt (Floyd and Winchester, 1978) and attempts have been made to infer the original tectonic setting of the altered and/or metamorphosed basalts (Pearce and Cann, 1973; Pearce, 1975).

The pillow lavas and diabases of most ophiolite suites have trace element abundance features (such as relative light REE depletion) similar to ocean floor tholeiites and ophiolite gabbros have cumulate geochemical characteristics similar to ocean floor gabbros (e.g., Kay and Senechal, 1976; Menzies, 1976; Menzies et al., 1977). However, these features are not diagnostic for a deep-ocean lithosphere because recent studies of basalts from mid-ocean ridges, marginal basins, island arcs and ophiolites have significantly increased the variety of basalt compositions found in these environments. In fact, in the Betts Cove ophiolite, Newfoundland, Coish and Church (1979) found that within a volcanic pile with no tectonic breaks the Ti-Zr abundance criteria established by Pearce and Cann (1973), identify the upper basalts as MORBS, the intermediate basalts as island arc basalts and the lower basalts fit neither category.

The relationship of ultramafic rocks to the overlying volcanics in ophiolite suites is ambiguous. Most lherzolites have REE abundances suitable for generating the REE contents of the overlying volcanics by partial melting (e.g., Menzies et al., 1977), but the harzburgites, presumed melting residues, have REE abundances inconsistent with model residues. Simple models which purportedly account for the harzburgite

REE content (Figure 34 of Coleman, 1977) utilize unrealistic (> 1) light REE partition coefficients for spinel/liquid. Because most ultramafic rocks in ophiolites are extensively altered, trace element studies of unaltered minerals in ophiolite and ocean floor ultramafics are required to understand the relationship of the ultramafics to the volcanics, and to directly characterize samples of oceanic mantle.

Andesites and Associated Rocks:

Gill (1978) reviewed the usefulness of trace elements in determining andesite petrogenesis, and concluded that "no general model of andesite petrogenesis accounts for all the trace element characteristics of orogenic andesites...." Modelling trace element characteristics of andesites is difficult because most andesites have probably undergone fractional crystallization and there are several possible parental magmas and source regions for these parental magmas. Furthermore, many trace element partition coefficients may vary significantly during andesite petrogenesis. Nevertheless, it has been possible to show that single-stage melting of subducted oceanic crust in an eclogitic mineralogy is inconsistent with trace element abundances in most andesites (e.g., Gill, 1974; Noble et al., 1975; Lopez-Escobar, et al., 1977). However, two-stage models (ascent and reaction of a low percent partial melt derived from a subducted slab forms modified mantle peridotite which melts to form orogenic basalts and andesites) can successfully account for most trace element abundances in orogenic basalts (Kay, 1977).

Although satisfactory models have not been developed, new data sets for andesitic suites (e.g., Whitford, 1975; Dostal et al., 1977) continue to show that incompatible element abundances increase with perpendicular distance from the plate boundary. Furthermore, in some regions of complex subduction along strike of the plate boundary (e.g., the Andes) there are variations in trace element abundances that correlate with variations in subduction parameters such as dip of the Benioff Zone (Lopez-Escobar et al., 1977). In contrast, the large compositional variations from north (tholeiitic) to south (alkalic) along the lesser Antilles axis are not correlated with subduction conditions (Brown et al., 1977). Gill (1978) noted the variety of processes that may be important in andesite petrogenesis, and he emphasized that in order to develop realistic models future trace element studies must be accompanied by thorough sampling plus field, petrographic, and isotopic research. Indeed, a similar statement is valid for using trace element geochemistry to infer the petrogenesis of any igneous rock suite.

Granitoids:

Hanson (1978) thoroughly reviewed the application of trace element geochemistry to the petrogenesis of granitoids. Compared to contributions in basalt petrogenesis, applications of trace element geochemistry have had limited success in understanding granitoid petrogenesis. The difficulties arise in part from the larger number of possible source rocks, the likely role of volatiles, rapidly changing partition coefficients as a function of composition and temperature, and the more important role of accessory phases (e.g., zircon, sphene, apatite). In an important conceptual paper, McCarthy and Hasty (1976) considered that granitoid rocks may not represent liquid compositions, but that they may, in part, be cumulate rocks. This model contrasts with the interpretation (White and Chappell, 1977) that many granitoids contain residual material that did not segregate during melting. In both models granitoids are believed to be liquid-solid mixes, and this complexity is important in trace element modelling.

Most recent trace element research has focussed on Precambrian suites (e.g., Arth and Hanson, 1975; Condie and Hunter, 1976; Anderson and Cullers, 1978; Arth et al., 1978; Condie, 1978; O'Nions and Pankhurst, 1978). Many Precambrian granitoids have been modelled by partial melting of silicic lower crustal rocks followed by varying amounts of fractional crystallization. In contrast, models developed for the early Precambrian greenstone-granite complex of northeastern Minnesota by Arth and Hanson (1975) utilized partial melting of quartz eclogite to account for the very low heavy REE abundances in the trondhjemite-dacite suite. However, subsequent study of trondhjemitic suites (Arth and Barker, 1976; Arth et al., 1978) showed that hornblende, as a fractionating or residual mineral, is important in controlling heavy REE abundances in silicic melts; consequently, an eclogite source is not required by the REE data.

Trace element abundances in younger granitoid suites are also generally consistent with partial melting of lower crustal silicic rocks (e.g., Albuquerque, 1977, 1978; Price and Taylor, 1977). Some of the most interesting trace element results are for the voluminous batholiths of the western U.S. (Kistler and Peterman, 1973; Gromet and Silver, 1977; Frey et al., 1978). In particular, the Sierra Nevada and Peninsular Range batholiths have strong geochemical gradients coordinated with geographic location (southeast-northwest, and east-west trends respectively). These compositional gradients are interpreted as resulting from a systematically changing source composition, but the Tuolumne Intrusive Series in the Sierra Nevada batholith exhibits many of the same systematic trace element abundance variations but in a much smaller ($\sim$ 1000 km^2) region (Frey et al., 1978; Bateman and Chappell, 1979). More geochemical studies of these batholithic rocks are required to differentiate the effects of source composition on trace element abundances from variations caused by different degrees of melting and subsequent processes such as fractional crystallization, assimilation, etc.

An indication that trace element behavior may be complex in a silicic magma chamber results from Hildreth's (1979) study of the Bishop Tuff. He found that large systematic variations in trace element abundances (more than a factor of 10 for some elements) could not be explained by solid-liquid partitioning, and he suggests that the trace element abundance variations resulted from a compositionally-zoned rhyolitic magma that differentiated in an essentially all-liquid state by convection-driven thermogravitational diffusion processes.

Anorthosites:

Interest in the trace element content of anorthosites has been rekindled by analogies of early terrestrial crust development with the lunar highlands (e.g., Griffin et al., 1974; Morgan et al., 1976). Trace element abundances of terrestrial anorthosites clearly establish their cumulate origin, and trace element modelling has been used to define the parental liquids and the role of fractional crystallization in producing associated rocks such as the granitoids. However, there is no unanimity concerning the parental magma. Simmons and Hanson (1978) studied northeastern North America anorthosites and concluded that these anorthosites are cumulates from basic melts rich in feldspar components (SiO_2, 50-54 wt.%; Al_2O_3 > 20 wt.%) derived by partial melting of tholeiitic basalt at 15-20 Kb. In contrast, Henderson et al. (1976) concluded that anorthosites from the Fiskenasset Complex of West Greenland accumulated from a partial melt of a garnet-bearing source. Furthermore, Duchesne and Demaiffe (1978), who reviewed trace element data for massif anorthosites and studied south Norway anorthosites in detail, concluded that a variety of parental liquids are required for different anorthosites, but that the abundant andesine-type massifs formed from jotunitic magmas (Ti-rich, low Si-andesites with low Al_2O_3 contents of 12-14%). At this time it is probably valid to conclude that a variety of parental liquids are required for anorthosite massifs, but it is important to note that inferred geochemical features of the parental liquids are very model dependent and subject to refinements with new data, especially trace element data for minerals coupled with more sophisticated modelling procedures.

Future Prospects

Because most elements in rocks are trace elements and there is a wide range of trace element abundances, leading to a large signal/noise ratio, trace element geochemistry has and will continue to provide significant constraints on petrogenetic models for all types of igneous rocks. Continued acquisition of accurate trace element abundance data, especially when combined with isotopic, petrologic, and field data, will be a major future activity because there are many problems in igneous petrogenesis where the present trace element data base is inadequate. However, it is evident that petrogenetic constraints are required from a variety of geologic, petrologic and geochemical data in order to distinguish the trace element abundance variations caused by complex petrogenetic processes from those inherited from compositionally heterogeneous source regions. Although isotopic research is reviewed elsewhere, combined isotopic and trace element abundance data provide especially strong constraints on petrogenetic models. A relatively new isotopic research area with exciting early results (e.g., DePaolo and Wasserburg, 1976; Richard et al., 1976; O'Nions, et al., 1978) is that of Nd isotopes. Determination of Nd isotopic ratios along with REE abundances is a powerful approach to igneous petrogenesis because the geochemical behavior of the parent-daughter-system (Sm-Nd) are similar and well understood. A particularly intriguing result is that several basalts with relative light REE enrichment compared to chondrites have been derived from a mantle source with a long-term light REE depletion (e.g., De Paolo and Wasserburg, 1976; O'Nions et al., 1977; Carlson et al., 1978; Carter et al., 1978).

In the immediate future advances in several research areas of trace element geochemistry are required for improvements in petrogenetic modelling.

The first is experimetal determination of a few trace element partition coefficients as a function of pressure, temperature and composition in a relatively small number of carefully selected experimental systems. These results must be followed by development of predictive models for trace element partitioning in a variety of compositional systems. Such models will require a knowledge of element partitioning between different coordination sites in multisite mineral structures (Burns, 1973; Morris, 1975) and improved knowledge of silicate liquid structure. Also, past utilization of trace element geochemistry in petrogenesis problems has been dominantly concerned with partitioning between minerals and a silicate liquid, but increasing attention must be given to the role of CO_2 and H_2O - rich fluids. Preliminary experiments (Flynn and Burnham, 1978; Mysen, 1978; Wendtlandt and Harrison, 1978) show that at high pressures (> 20 kb) fluid phases may be important in determining the trace element content of alkali-rich basalts, kimberlites and some granitoids. Shaw (1978) has developed equations for modelling such systems.

Trace element geochemistry will also be markedly advanced by development of new analytical techniques, such as the proton and ion microprobes (Bosch et al., 1978 and Lovering, 1975, respectively), which enable in situ determination of trace element abundances. By defining the heterogeneity of trace elements within phases, such data provide key information regarding the role of kinetic and diffusive processes in trace element partitioning, (e.g., Shimizu, 1978) and in turn, these data will lead to development of more realistic petrogenetic models for igneous rocks.

Comments on Reference List

The reference list includes the majority of trace element-oriented papers published by U.S. scientists in English language journals from 1975-1978. Note, that I include some key papers published in 1979 and earlier important papers published in 1973-1974 as well as significant foreign contributions. Inevitably, there are some accidental omissions.

For convenience, the references are divided into the following categories. Note, that some references are pertinent to more than one category, but they are listed only under one category.

Models of Trace Element Partitioning in Igneous Systems
Trace Element Partitioning Between Phases in Natural Systems
Experimental Studies of Trace Element Partitioning
Site Occupancy of Trace Elements in Minerals

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GEOCHRONOLOGY AND RADIOGENIC ISOTOPE RESEARCH

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Introduction

During the four year period 1975-1978 research activity in the fields of geochronology and radiogenic isotopes has been alive and quite healthy. Geochrondlogical laboratories have added greatly to our knowledge of time relations and patterns in the crust and others have applied studies of radiogenic isotopes to problems of the sources, genesis, and history of terrestrial and extraterrestrial materials. In this paper we will review progress in areas that are, in our judgment, the most exciting and that represent the greatest advances in earth science through application of isotopic studies. Much of the paper will be devoted to the development of the Sm-Nd system and to the discovery of long-term heterogeneity in the mantle. Other topics discussed include the new decay constant conventions, the application of Sr and Pb isotopes to understanding of continental and continent-marginal igneous activity, advances in technique in U-Pb geochronometry in zircons, the discovery of rocks with ages close to 3.7 b.y. and isotopic constraints on the evolution of the crust, and progress in extraterrestrial chronology.

New Decay Constant Convention

One major problem in geochronology over the past two decades has been a lack of unanimity with regard to certain physical constants, particularly the half-life of ^{87}Rb. This problem became compounded recently by proposed revisions or new determinations of half-lives and isotopic abundances for geochronologic systems. Thus, recent literature contains results based on various sets of physical constants, with attendant systematic differences in ages. A Subcommission on Geochronology of the IUGS was formed under the direction of R. H. Steiger and E. Jäger to evaluate various alternatives and to decide upon a "best" set of constants. After considerable study, the subcommission reached a consensus in 1976 at the 25th IGC in Sydney with the results published shortly thereafter (Steiger and Jäger, 1977). There is currently a strong tendency for general adoption of these recommended values. Furthermore, systematic differences between different parent-daughter systems will also be small (on the order of 1 percent or less). To be sure, there may still be some refinements in the exact values of interest, but such revisions will probably be minor and entail less than a 1 percent change in absolute ages, making it not worthwhile to change from the set of adopted values. Such remaining uncertainties are more than offset by the advantage of having all data reported on a uniform basis.

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Sm-Nd Dating

Probably the most important advance in the field of geochronology and related isotopic geochemistry in the past four years has been the development and application of the Sm-Nd technique. Until recently the long half-life of ^{147}Sm (α - decay to ^{143}Nd, 1.06×10^{11} years) and the generally low Sm/Nd ratio in nature (~ 0.3) have precluded application of this system. These problems are compounded by the similar geochemical behavior of these rare earth elements, so that ranges in Sm/Nd ratios are also generally small. Thus, radiogenic enrichments in $^{143}Nd/^{144}Nd$ are commonly only 1-2 percent over the age of the solar system.

With the use of the high-precision mass spectrometry developed over the past several years, Lugmair (1974) reported the first successful determination of the Sm-Nd age of a rock: the basaltic achondrite (eucrite) Juvinas (internal mineral isochron, 4.56 ± 0.08 b.y.). This study was also important because the sample chosen represents a system that crystallized very soon (< 50 m.y.) after the formation of the solar system and has basically a chondritic (flat) rare earth pattern. As a result, the isotopic parameters defined by Juvinas for the Sm-Nd method now provide the principal reference to which other results may be referred (see below).

These techniques have been adopted by several other laboratories, but this has also resulted in a problem not covered by the IUGS Subcommission on Geochronology report (see above): What values of the Sm and Nd isotope ratios are "best", and which should be adopted as principal reference values? For example, data reported from La Jolla (Lugmair, 1974; Lugmair et al., 1975b, 1976) are normalized to the equivalent of $^{142}Nd/^{146}Nd = 1.5817$; Caltech (DePaolo and Wasserburg, 1976a, b; 1977) has used the equivalent of $^{150}Nd/^{142}Nd = 0.2096$; and Lamont-Doherty (O'Nions et al., 1977; Carter et al., 1978a; Hamilton et al., 1977) has used $^{146}Nd/^{144}Nd = 0.7219$. The Caltech normalization is not equivalent to the others and results in a value of 0.50598 for the isochron intercept value of Juvinas whereas the La Jolla and Lamont-Doherty value for this intercept is 0.50677 (Lugmair, 1974; Lugmair et al., 1976). This isochron intercept represents our best estimate of the initial Nd isotopic composition at the time of planet formation. So long as appropriate care is taken to normalize data from various labs to the same base, no systematic errors will result in age interpretations based on Sm-Nd isochrons. However, because radiogenic enrichments of Nd are small, extreme care must be taken to be sure that all inter-laboratory bias is removed; Nakamura et al. (1976) have discussed this problem in more detail. Clearly, one major step that remains for Sm-Nd dating is agreement on a common base for normalization of data or consistent use of ε (Nd) values (DePaolo and Wasserburg, 1976a). On the other hand, based on intercomparison of coexisting

Rb-Sr, K-Ar, and Sm-Nd ages for a variety of lunar basalts and meteorites (Papanastassiou et al., 1977), there does not appear to be a major uncertainty in the half-life of ^{147}Sm. The review of Sm-Nd dating below will use the normalization base used by Lugmair et al. (1975b, 1976) where specific values are cited.

One major advantage for Sm-Nd dating of lunar and meteoritic basalts and related rocks is that the mineral phases used as primary control on an isochron are both major constituents: plagioclase (lower Sm/Nd ratio) and pyroxene (higher Sm/Nd ratio). Thus, the system is much less sensitive to disturbance than Rb-Sr, U-Pb, or K-Ar, and more nearly correct ages of crystallization can be obtained. For relatively undisturbed systems concordant ages result (Papanastassiou et al., 1977), but Lugmair and Scheinin (1975a) were able to show that the crystallization age of the disturbed eucrite Stannern is essentially the same as for Juvinas and other eucritic basaltic achondrites, about 4.55×10^9 years. In addition, Nakamura et al. (1977a) were able to show from Sm-Nd data that the 1.3 b.y. age commonly obtained for the nakhlite achondrites probably represents a crystallization age, indicating an unusual history for these meteorites. For lunar chronology, Lugmair et al. (1976) were able to show that the troctolite 76535 has an age of 4.26 ± 0.06 b.y., failing to confirm the 4.61 ± 0.07 b.y. Rb-Sr age determined by Papanastassiou and Wasserburg (1976). Thus, it is clear that Sm-Nd techniques, along with the Rb-Sr, U-Pb, K-Ar methods, will play a considerable role in deciphering the complex history of lunar highland samples and certain meteorites in the coming years.

Few Sm-Nd mineral isochrons have been reported for old terrestrial samples, perhaps due in large part to problems with alteration. However, Hamilton et al. (1978) obtained a Sm-Nd isochron age of 3.77 ± 0.04 b.y. for the supracrustal rocks at Isua, Greenland, and Hamilton et al. (1977) were able to obtain a reasonable Sm-Nd whole-rock age of 2.64 ± 0.14 b.y. for altered Rhodesian greenstones. Thus it is clear that terrestrial Sm-Nd isochron studies are feasible for old rocks and also that alteration apparently affects the Sm-Nd system to a much smaller degree than others, such as Rb-Sr.

In addition to straight chronologic applications, the Sm-Nd method has added a new tool for the geochemical study of petrologic systems, including the evolution of the crust and mantle of both the Earth and Moon (Lugmair et al., 1975, 1976; DePaolo and Wasserburg, 1976a, b, 1977; O'Nions et al., 1977; Carter et al., 1978a, b; McCulloch and Wasserburg, 1978). In these treatments the principal reference is the composition of $^{143}Nd/^{144}Nd$ as a function of time in a reservoir of chondritic (e.g., primitive) $^{147}Sm/^{144}Nd$ ratio, from the time of planet formation to the present. The parameters for this reference growth curve are currently defined by the study on Juvinas (Lugmar, 1974; revised data reported in Lugmair et al., 1976) and are: $^{147}Sm/^{144}Nd = 0.1936$, $T = 4.56 \pm 0.08$ b.y., $I\ (^{143}Nd/^{144}Nd) = 0.50677 \pm 0.00010$, and present $^{143}Nd/^{144}Nd = 0.512636 \pm 0.000040$.

For any rock that forms at some later time from a reservoir that has always had a chondritic Sm/Nd ratio, the initial $^{143}Nd/^{144}Nd$ of that rock should fall on the chondritic growth curve. Lugmair et al. (1975, 1976) found, instead, that individual initial $^{143}Nd/^{144}Nd$ values for lunar basalts did not fall on a chondrite evolution line, clearly indicating that Apollo 17 mare basalts were formed from a reservoir with non-chondritic Sm/Nd ratio. Additional results by Papanastassiou et al. (1977) and Nakamura et al. (1976, 1977) have shown that this phenomenon is characteristic of the lunar basalts in general. The details of this problem are discussed by Papanastassiou et al. (1977), who point out that the available Sm-Nd data do not allow precise definition of the initial lunar Sm/Nd ratio, the exact time of lunar differentiation (inferred as 4.42 b.y. from U-Pb results; Tera and Wasserburg, 1974), the Sm/Nd ratio in the source regions of mare basalts, or the degree of Sm/Nd fractionation during mare basalt genesis. Thus, although the details remain to be worked out, it is clear the Sm/Nd system in the Moon was fractionated at some early stage as compared to Sm/Nd systems in primitive (chrondritic) reservoirs.

In contrast to the lunar case, DePaolo and Wasserburg (1976a, b) showed that the source regions for most terrestrial mantle-derived igneous rocks may have had chondritic Sm/Nd ratios for the entire history of the Earth. The principal exceptions are young midocean ridge basalts and alkali basalts which have initial $^{143}Nd/^{144}Nd$ ratios up to 0.1 percent greater than expected from a chondritic uniform reservoir (CHUR: DePaolo and Wasserburg, 1976a), indicating a certain degree of mantle heterogeneity, Sm/Nd differentiation of the mantle during the last 1.0 b.y. or so, crustal contamination of mantle-derived magmas, or some combination of these (DePaolo and Wasserburg, 1976b, 1977; O'Nions et al., 1977; Carter et al., 1978a, b). The fact that the earth had a chondritic Sm/Nd over its early history (first 3 b.y. or so; DePaolo and Wasserburg, 1976b), in contrast to the early differentiation of the Moon, may be due to the more dynamic state of the early Earth (Papanastassiou et al., 1977).

Although much has been learned from Sm-Nd results over the past four years, it is clear that many problems remain. As more data become available in the next several years, we can look for resolution of some problems and finer-scale definition of others.

Long-term Heterogeneities in the Mantle

The discovery that the mantle is geochemically heterogeneous is of fundamental importance, not only to our understanding of such problems as the origin of various basalt types, but to our knowledge of the nature of the earth and major events in its history. Earlier, such workers as Gast (1968) showed that the mantle must be chemically heterogeneous on the basis of trace element distributions in basalts. In the last four or five years, study of Rb-Sr, U-Pb, and Sm-Nd isotopic systematics in basalts from various parts of the oceanic crust have not only proved the existence of such heterogeneities, but have shown that they came about 1 to 2 billion years ago. Many workers have contributed to this growing knowledge, but major data and ideas have come from work of S. R. Hart, C. Brooks, D. E. James, A. W. Hofmann, R. K. O'Nions, R. J. Pankhurst,

M. Tatsumoto, S. S. Sun, D. J. DePaolo, and G. J. Wasserburg in the United States and C. J. Allegre and his associates in France.

Their research has shown that there are distinct differences in the isotopic compositions of Sr, Pb, and Nd between the basalts of oceanic islands and midoceanic ridge basalts (MORB). Basalts of the oceanic islands have $^{87}Sr/^{86}Sr > 0.703$, $^{206}Pb/^{204}Pb > 18.7$, and $^{143}Nd/^{144}Nd < 0.51305$, whereas in MORB $^{87}Sr/^{86}Sr < 0.703$, $^{206}Pb/^{204}Pb < 18.7$, and $^{143}Nd/^{144}Nd > 0.51305$ (normalized to $^{146}Nd/^{144}Nd = 0.72190$; $\epsilon_{Juv.} = +8$). These isotopic variations suggest that island basalts are derived from a mantle source region that is less depleted in Rb and U, and presumably other large-ion lithophile (LIL) elements as well, than are the MORB; the mantle source regions from which MORB are derived are relatively depleted in Rb, U, and the LIL, and are depleted in Nd relative to Sm. The Sm-Nd relationship occurs because Sm is a smaller ion than its daughter Nd; thus in "depleted" mantle sources Sm/Nd will be greater than in non-depleted sources, and through time the ratio $^{143}Nd/^{144}Nd$ will become greater.

Tatsumoto (1966) noted that there was a correlation between the U/Pb ratios of basalts from oceanic crust and their Pb isotopic composition. He concluded that if this correlation were inherited from the mantle source region, U/Pb heterogeneities must have existed in such mantle regions for at least a billion years. Later Hart (1971a), Allegre (1972), James and others (1976), and Sun and Hanson (1975) observed that the same correlation existed for $^{87}Sr/^{86}Sr$ and Rb/Sr. Brooks and others (1976) have argued that both the isotopic composition of Pb and Sr and the ratios U/Pb and Rb/Sr in tholeiites are probably representative of their mantle sources because of derivation by processes involving rather large degrees of partial melting; alkali basalts, widely believed to originate through much smaller amounts of partial melting, appear to be enriched in Rb and U relative to the source region.

Brooks and others (1976a) further argue that these correlations may be interpreted as mantle isochrons, that is, that the relationships between parent-daughter ratios and isotopic compositions of daughter elements have a time significance, suggesting isolation of parts of the mantle in the past over much of the present oceanic area. They offer two models: (1) the mantle was differentiated into a rather large number of subsystems on a scale larger than that sampled by various island basalt magmas. In this case the "mantle isochrons" represent a sampling of a number of such subsystems, and indicate that the differentiation occurred 1.6 ± 0.2 b.y. ago; (2) the mantle is divided into essentially two parts. One of these is "depleted" and has low U/Pb and Rb/Sr ratios and is the source of tholeiites; the other is undepleted, has higher U/Pb and Rb/Sr, and may be the source of island basalts. Mantle "isochrons" result from mixing of melts from these two regions during basalt genesis, and thus have age significance only if the material from which the two parts were derived was originally of uniform isotopic composition. Brooks and others believe that the general agreement of Rb-Sr and U-Pb data for the time of mantle segregation argues against random mixing (Model 2) as the mechanism of producing the "isochrons".

Island arcs tend to exhibit considerable variability in the isotopic compositions of both Sr and Pb. Many basalts of island arcs show apparent contamination by continental crust, seawater, or sediment, but others show no effects of such contamination. Commonly island arcs show large isotopic variations along their lengths (e.g., Pb in the Marianas and Kermadecs; Meijer, 1976; Oversby and Ewart, 1972) but others (e.g., Pb in Tonga Arc, Oversby and Ewart, 1972; Hawkesworth et al., 1977) are isotopically uniform. Presumably this depends upon the scale of mantle domains and the location of plate boundaries that determine the position of the island arcs. DePaolo and Wasserburg (1977) have studied Nd isotopic abundances in island-arc lavas from New Britain and the Marianas, finding that their data are compatible with derivation of the lavas from a light REE-depleted reservoir.

Rb/Sr versus $^{87}Sr/^{86}Sr$ plots of basalts from many island arcs yield "mantle isochrons" indicating that the melts erupted were derived from mantle sources whose Rb-Sr and U-Pb systems were isolated about 1.6 b.y. ago; such mantle presumably has had a history similar to that of most of the rest of the oceanic mantle. Some island arcs, however, yield "intra-arc" isochrons indicating "ages" as low as 500 m.y. (Oversby and Ewart, 1972). The meaning of such mantle isochron ages is difficult to determine; the ages may be only the result of averaging of continuously changing mantle characteristics or they may indicate that real segregations of the mantle, on a local scale, occurred within the last 500 m.y.

Brooks, James, and Hart (1976b) have also proposed that "pseudoisochrons" determined for suites of continental volcanic rocks, notably those of the western United States, indicate the age of isolated portions of the sub-continental lithosphere. Arguing convincingly against contamination of magmas with older crust, they attribute the greater range of initial $^{87}Sr/^{86}Sr$ ratios observed in continental volcanic rocks to the development, through time, of a subcontinental mantle enriched in Rb, and other LIL, relative to Sr. Carter and others (1978a, b) have studied Rb-Sr and Sm-Nd relationships in Tertiary volcanic rocks from northwestern Scotland and concluded that many of the magmas, although mantle-derived, were contaminated with much older continental crustal material. Noting that a plot of $^{87}Sr/^{86}Sr$ versus Rb/Sr yields a "pseudoisochron" indicating an age of 1.6 b.y., they suggest that it is the result of chemical mixing of Rb and Sr from mantle and continental crust, and has no time significance. Sm and Nd also yield a "pseudoisochron" indicating an age of 6.2 b.y.

Relations Between Ultramafic Rocks and Basalts

Isotopic studies have been undertaken in conjunction with trace element work in attempts to place constraints upon what ultramafic rocks might be the sources of basaltic magmas. Isotopic measurements have been particularly effective in distinguishing whether particular ultramafic rocks are potential sources of basalt, residua left after the extraction of basaltic liquids, or cumulates from the fractional crystallization of basaltic magma. Samples for these studies have come from alpine periodotites (ophiolites), nodules in alkalic basalts, and nodules in kimberlites.

A major difficulty in isotopic and trace element analyses of peridotite samples is contamination. Menzies and Murthy (1976, 1978) approached this problem by studying separated and purified minerals from unaltered lherzolite portions of alpine perodotites from Beni Bouchera, Morocco; Ronda, Spain; Lanzo, Italy; and Othris, Greece. They calculated the $^{87}Sr/^{86}Sr$ ratio of whole rocks by combining data from olivine, orthopyroxene, and clinopyroxene in proportion to their modal abundances. The resulting ratios, 0.7025 to 0.7028, are compatible with modern MORB. However, lherzolites from alpine periodotites have abundances of K, Rb, and Sr that are too small for them to be the source of basalt magmas if the magmas were derived by reasonable degrees of partial melting. Thus these peridotites appear to be residual from earlier partial melting episodes in which a small amount of an alkaline liquid was removed.

The petrology and mineralogy of nodules in alkalic basalts resembles that of the alpine peridotites. Although the suite is diverse and the samples may represent both cumulates and true fragments of the mantle, the dominant rock type is spinel lherzolite. Recent studies on mineral separates from these nodules (e.g., Stueber and Ikramuddin, 1974; Dasch and Green, 1975; Burwell, 1975; Basu and Murthy, 1977a) indicate that there is considerable variability in $^{87}Sr/^{86}Sr$ between minerals, such that olivine and orthopyroxene commonly have higher ratios than coexisting clinopyroxene; these variations between minerals from the same rocks must reflect the isotopic history of the samples.

Stueber and Ikramuddin (1974), Dasch and Green (1975) and Basu and Murthy (1977a) have shown that such heterogeneities in $^{87}Sr/^{86}Sr$ are commonly correlated with $^{87}Rb/^{86}Sr$ and indicate that the minerals in the nodules have been closed systems for long but variable times. The nodules, like the alpine perodotites, are too depleted in trace elements to be the source of basalts. Thus, the upper lithosphere appears to be depleted in lithophile trace elements and has apparently had a long and complex history of melting and formation of residua.

The other major source of ultramafic rock samples that might be the source of basalts is the nodules in kimberlites. Studies of mineral separates from such nodules indicates a range of $^{87}Sr/^{86}Sr$ ratios, again suggesting derivation from a mantle region with a complex history of melting. Trace element studies show that many nodules from kimberlites are probably residual from small degrees of partial melting and cannot be the direct sources of basaltic magmas.

It is agreed that the source material from which basalt magmas are derived must be aluminous peridotites, but the available samples of mantle rocks are all too depleted in K, Rb, Sr, and Ba to yield basaltic liquids with the appropriate trace element distributions. It is interesting that, excluding the basalts of the midoceanic ridges, both alkali basalts and tholeiites commonly have similar $^{87}Sr/^{86}Sr$ and $^{206}Pb/^{204}Pb$ ratios, although tholeiites usually have smaller U/Pb and Rb/Sr ratios. These results strongly suggest that the isotopic compositions of Sr and Pb in these basalts reflect the source regions, but that alkali basalts are enriched in Rb and U relative to the source region. Brooks and others (1976a) and Menzies and Murthy (1978) suggest that the Rb and Sr relationships depend upon the presence of phases such as amphibole and phlogopite in the source region that are capable of fractionating Rb and Sr during partial melting. If tholeiites are formed by relatively large amounts of partial melting, amphibole and phlogopite may not be left behind in the residue. In this case the Rb/Sr ratio of the melt (basalt) should be essentially the same as that of the source region. If, however, alkali basalt results from small amounts of partial melting and amphibole and phlogopite are residues, Rb may be enriched in the melt relative to Sr. Basu and Murthy (1977b) have suggested that kaersutitic amphibole may be what is necessary to modify lherzolitic compositions so that partial melting will yield liquids with trace element concentrations and distributions like those in basalts. They suggest that small quantities of kaersutitic melt may rise from the asthenosphere beneath ridges, mixing with partial melts of anhydrous lherzolite.

Degassing of the Earth

A major application of the gaseous radiogenic isotopes such as ^{4}He, ^{40}Ar, ^{129}Xe, and ^{136}Xe is their use as monitors of degassing of the earth. Attention was focused on such applications during a recent conference in Japan (Alexander and Ozima, 1978, and papers therein). A number of workers addressed the question of the degree of degassing of the earth, its time dependence, and the bulk K content of the earth. The consensus was that answers to these questions are highly model-dependent: if the earth has undergone continuous and extensive degassing, then the K content is on the order of 100 ppm. On the other hand, if the atmosphere formed by an early (> 4.0 b.y. ago) major pulse of degassing followed by subsequent degassing at reduced rates, then permissible K concentrations for the earth may range up to 800 ppm or more. The results depend upon the models used by the various authors (see especially the papers by Hart and Hogan, 1978; Bernatowicz and Podosek, 1978; Hamano and Ozima, 1978; Fisher, 1978; and Schwartzman, 1978). The current sentiment seems to favor an early, major degassing period; thus, for the time being, the K content of the mantle is best considered poorly constrained (100 to > 400 ppm) by degassing models.

Isotopic Studies of Continental and Continent-Marginal Rocks

Whereas most igneous rocks of the oceanic areas have isotopic compositions that suggest long-term heterogeneities in their mantle source regions, continental and continent-marginal igneous suites have isotopic signatures that indicate significant contamination by older continental crust. Important and careful studies of isotopic abundances in the major batholiths of the western United States, underway for the last ten years or so, have yielded results of considerable interest in the last four years.

L. T. Silver and H. P. Taylor and their students, working in the Southern California Batholith (Early and Silver, 1973; Taylor and Silver,

1978); R. W. Kistler and Z. E. Peterman, working in the Sierra Nevada Batholith (Kistler and Peterman, 1973); and R. L. Armstrong and his coworkers, working in Washington, Oregon, and Idaho (Armstrong and others, 1977) have shown that there is an abrupt break, or "step", in $^{87}Sr/^{86}Sr$ ratios between batholithic rocks on the western, or oceanic side, and those on the eastern, or continental side. The boundary, between rocks with $^{87}Sr/^{86}Sr < 0.705$ on the west and those with $^{87}Sr/^{86}Sr > 0.706$ on the east, is regular and can be demonstrated in both plutonic and volcanic rocks. In the Southern California Batholith, Taylor and Silver (1978) have demonstrated that this boundary also divides rocks with high $\delta^{18}O$ values on the east from those with low $\delta^{18}O$ values on the west. These data suggest that rocks in the western parts of the batholiths were derived, either primarily or through more complicated mechanisms, from normal mantle sources due to melting at a consuming plate boundary. Rocks in the eastern parts have evidently interacted in some way with older continental rocks.

Zartman (1974) has also shown that Mesozoic and Cenozoic rocks and ore minerals within 100-300 km of the Pacific coast are characterized by Pb that is isotopically distinct from that in rock and ores of similar ages farther inland. The Pb in the inland samples is less radiogenic ($^{206}Pb/^{204}Pb = 16.2-18.8$; $^{208}Pb/^{204}Pb = 36.5-39.9$) than that from the coastal samples ($^{206}Pb/^{204}Pb = 18.7-19.4$; $^{208}Pb/^{204}Pb = 38.2-39.1$), suggesting that it was derived from ancient continental rocks with depleted U/Pb ratios.

Terrestrial Geochronology

Advances in Techniques for U-Pb Studies of Zircons

An important advance in technique was published by Krogh (1973), two years prior to the four year period covered in this review. We mention it here because application of Krogh's methods has made it possible to routinely and easily obtain U-Pb data from zircon samples of only a few milligrams. Briefly, Krogh devised a microchemical method for dissolution of small zircon samples in teflon bombs and separation of U and Pb for mass spectrometric analysis on small ion exchange columns. These methods, which use only a few ml of reagents, and typically yield analytical blanks on the order of a few picograms, have made possible the analysis of very small zircon samples. Krogh's methods have been adopted by most geochronological laboratories, with two major advantages. First, the relative simplicity of the method has made zircon geochronology much more common than previously. Secondly, it has become possible to obtain high quality age data from such small samples that U-Pb ages are now routinely obtained from small cores or from cuttings returned from deep drilling in areas where basement rocks are covered by sedimentary material.

Dating of the Most Ancient Rocks and Studies of Crustal Evolution

There has been great interest in locating and studying very ancient continental crust since the first report of 3.3 b.y. rocks in the Minnesota River Valley by Catanzaro (1963). Interest has intensified following the report that rocks at least 3.7 b.y. old occur in the Archean craton of western Greenland (Black and others, 1971; Moorbath and others, 1972; Baadsgaard, 1973, 1976a, b; Moorbath and others, 1975a); it is now clear that rocks of similar age occur in eastern Labrador (Hurst and others, 1975; Barton, 1975). Hickman (1974), Hawkesworth and others (1975), and Moorbath and others (1977) have shown that basement granitic gneisses in the Rhodesian craton are 3.5 to 3.6 b.y. old, and it seems likely that rocks of similar age occur in the Barberton Mountain Land in Swaziland, southern Africa (Hurley and others, 1972; Sinha, 1972; Jahn and Shih, 1974). Goldich and Hedge (1975) have reported a Rb-Sr age of 3.6 b.y. for gneisses in the Minnesota River Valley; although there is still some controversy regarding the age of these rocks (Goldich and Hedge, 1974; Farhat and Wetherill, 1975) they are at least 3.3 b.y. old.

The availability of such ancient rocks has made possible studies of the evolution of Sr and Pb isotopes from the earth's early history. Moorbath (1975b, 1976) has shown that the initial $^{87}Sr/^{86}Sr$ ratios of many ancient granitic rocks with ages from 3.7 b.y. to as low as 1.8 b.y. are essentially equal to that expected from growth in the mantle from original primordial values. He has argued that the data indicate that major reworking of older sialic material is not responsible for most gneissic terranes and that they were derived from the mantle during major crust-forming events. Pb isotopic data are mostly consistent with these interpretations (Moorbath, 1975a, 1975b) and suggest derivation of gneiss terranes from sources with rather homogeneous U/Pb ratios such that the Pb isotopic data approximate single-stage evolution from the formation of the earth to the age of the gneisses. It is interesting that the formation of deep-seated ancient crust has evidently produced rocks depleted in U relative to Pb (Black and others, 1971; Zartman, 1964) so that their Pb is relatively unradiogenic. Pb from the Amitsoq gneisses of west Greenland is the most unradiogenic ever measured on the earth (Moorbath, 1977). Hurst (1978) has argued that the Sr data from the west Greenland-Labrador area require an early differentiation of the earth with respect to Rb, since the initial $^{87}Sr/^{86}Sr$ ratios of the gneisses are elevated relative to the $^{87}Sr/^{86}Sr$ growth curve of a chondritic mantle. Moorbath (1978), however, has disagreed with the interpretation, suggesting that a period of relatively rapid growth of $^{87}Sr/^{86}Sr$ may have occurred during differentiation of newly accreted crust.

K-Ar Geochronology

K-Ar dating continues to be a major approach to many problems, especially the chronology of extraterrestrial samples (Turner, 1977; Turner et al., 1978) and young terrestrial volcanic rocks. It is clear, however, that $^{39}Ar-^{40}Ar$ dating of terrestrial samples is still beset by many difficulties (e.g., Dalrymple et al., 1977). On the other hand, Dallmeyer (1975a, b, c; 1977; 1978; Dallmeyer et al., 1975; Dallmeyer and Sutter, 1976) has been able to use $^{39}Ar-^{40}Ar$ techniques on a variety of problems involving metamorphic rocks.

One major advance in understanding incremental heating spectra for $^{39}Ar-^{40}Ar$ dating was reported by Huneke and Smith (1976), who were able to demonstrate that recoil transfer of ^{39}Ar during irradiation can significantly affect thermal release patterns, depending on the relative retentivity of the phase into which the ^{39}Ar is transferred. The problem is most significant for samples in which K is in fine-grained phases.

Extraterrestrial Chronology

Over the past few years the data base for ages of lunar rocks has expanded considerably. Much of this represents filling in of details related to lunar mare volcanism over the interval 3.1-3.9 b.y. ago and will not be reviewed here (see Nyquist, 1977, for a partial summary). One interesting conclusion based on U-Pb studies (Tera and Wasserburg, 1974, 1975) is that there was a major lunar differentiation about 4.4 b.y. ago.

Much of the effort on lunar samples over the past few years has concerned attempts to identify the age of the primordial lunar crust and to find the oldest lunar igneous rocks. Many investigators have found ages in the range 4.0-4.2 b.y. for highland rocks, and Papanastassiou and Wasserburg (1975, 1976) have reported Rb-Sr ages of 4.55 $\pm$ 0.10 b.y. for a dunite clast in boulder 72417 and 4.61 $\pm$ 0.07 b.y. for troctolite 76535. As mentioned earlier, however, Sm-Nd results on the troctolite (Lugmair et al., 1976) only yielded an age of 4.26 $\pm$ 0.06 b.y., indicating that the two systems may be recording different events (Papanastassiou and Wasserburg, 1976), or there may yet be unresolved problems in trying to accurately date ancient lunar material. Concordant Rb-Sr, U-Pb, and Sm-Nd ages of about 4.36 b.y. were, in fact, obtained on lunar norite 77215 (Nakamura et al., 1976), so there are at least some rocks that represent very ancient sources. Further comment is provided by Nakamura and Tatsumoto (1977b). Resolution of the antiquity of lunar crust and lunar differentiation will continue to be a major line of investigation over the next few years.

There has also been considerable activity in dating meteorites over the past four years, with major contributions based on Pb-Pb and Sm-Nd results. In general, the primordial ages of chondritic meteorites have not changed significantly, with the best estimates for primary condensation and accretion ages being provided by Pb-Pb results on Allende (Chen and Tilton, 1976; Tatsumoto et al., 1976) with an age of 4.56 $\pm$ 0.01 b.y. Recent studies on basaltic achondrites have generally confirmed the original results of Papanastassiou and Wasserburg (1969) for Rb-Sr data (e.g., Birck and Allegre, 1978), and Pb-Pb data on basaltic achondrites (Mahnes et al., 1975; Wasserburg et al., 1977; Tatsumoto et al., 1973; Unruh et al., 1977a) indicate an age of 4.54 $\pm$ 0.02 b.y. for these earliest of solar system igneous rocks.

A very exciting development in extraterrestrial geochronology has been the discovery of radiogenic ^{26}Mg produced from the decay of ^{26}Al (0.7 m.y. half-life) in the Allende meteorite (Lee and Papanastassiou, 1974; Lee et al., 1976) and, most recently, radiogenic ^{107}Ag produced from the decay of ^{107}Pd (6.5 m.y. half-life) in the Santa Clara ion meteorite (Kelly and Wasserburg, 1978). These results clearly show that condensation and planetary accretion occurred on a time scale of $\sim 10^6$ years, and the cosmologic implications have been well summarized by Schramm and Clayton (1978), along with attempts to reconcile the $\sim 10^6$ year time scale required by ^{26}Al and ^{107}Pd with the $\sim 10^8$ year time scale suggested by ^{129}I and ^{244}Pu (Reynolds, 1977; Wetherill, 1975).

Conclusions

The past four years have seen tremendous and exciting developments in geochronology and radiogenic isotope geochemistry, including cosmochemistry and cosmochronology, and we eagerly look forward to the further developments coming in the next quadrennial.

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STABLE ISOTOPE GEOCHEMISTRY

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INTRODUCTION

There has been an explosion of stable isotope data in the literature over the past few years. Establishment of routine analytical techniques and advances in mass spectrometry have made entrance into this field far less formidable than in former years. Today there are about 150 laboratories throughout the world where research in stable isotope geochemistry is conducted. In August, 1976 a conference devoted entirely to stable isotope investigations was held at the New Zealand Institute of Nuclear Sciences in Lower Hutt, New Zealand. The titles of the sessions at this conference are an indication of the scope of the discipline: Oceanography; Paleoclimatology; Hydrology and Atmospheric Studies; Geothermal and Volcanic Studies; Petrology; Ore Deposits; Experimental and Theoretical Equilibrium Studies; Techniques. Twenty-three papers including two review articles that were presented at this conference appear in a hard-cover book entitled "Stable Isotopes in the Earth Sciences" (DSIR Bulletin 220; Editor, B. W. Robinson). Another conference devoted exclusively to isotope geology was held in August, 1978 in Aspen, Colorado. Many excellent papers presented at that meeting appear in a volume entitled "Short Papers of the Fourth International Conference on Geochronology, Cosmochronology, and Isotope Geology (USGS Open-File Report 78-701; Editor, R. E. Zartman).

Inasmuch as stable isotope measurements have been applied to almost every problem in geology, it is impossible to report on all the research that was carried out by scientists from the U.S.A. during the years 1975-1978. The following discussion summarizes the kinds of problems that scientists are attempting to solve with the use of stable isotope measurements.

EXPERIMENTS AND THEORY

A few review articles have summarized and evaluated many experimental and theoretical investigations. Friedman and O'Neil (1977) compiled all known measurements and calculations of equilibrium fractionation factors of geochemical interest. This uncritical presentation of all these data has called attention to several serious disagreements that require resolution. O'Neil (1977) has summarized the results of laboratory investigations, analyses of natural materials, and theoretical considerations that bear on the importance of temperature, pressure, chemical composition, and crystal structure to the isotopic properties of minerals. Deines (1977) has critically evaluated the regularities observed in the oxygen isotope compositions of mineral triplets from about 400 igneous and metamorphic rocks. By comparing experimental and calculated fractionation factors, he points out which mineral associations are likely to have attained and retained an equilibrium distribution of oxygen isotopes.

Until recently, the measurement of rates of isotopic exchange has been virtually ignored in favor of securing equilibrium data. Many important geologic questions are left unresolved because of the lack of detailed knowledge of isotopic exchange rates and the factors that influence them. Because rates of exchange involving a solid phase are usually quite low, it is difficult to obtain meaningful data in reasonable times. O'Neil and Kharaka (1976) measured the extent of hydrogen and oxygen

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isotope exchange between clay minerals and water in the temperature range 100°-350°C for bomb runs of up to two years. Hydrogen isotope exchange between water and the clays was clearly demonstrable at 100°C; this result means that such exchange must occur at this temperature and lower in nature. Negligible oxygen isotope exchange occurred in these low-temperature experiments, and the great disparity in D and ^{18}O exchange rates indicates that hydrogen isotope exchange between clays and water occurs by a mechanism of proton exchange that is independent of the slower process of ^{18}O exchange. Sakai and Dickson (1978) measured the rates of sulfur isotope exchange between sulfate and sulfide in solutions that had values of pH and sulfur content similar to those found in natural hydrothermal solutions. With these data, the authors were able to postulate that residence times of sulfate and sulfide were not longer than 1000 years in Kuroko ore fluids and that ^{34}S equilibrium could be reached in 300 years at 300°C at the Wairakei geothermal system. Muehlenbachs and Shaeffer (1977) determined oxygen diffusion coefficients in vitreous-SiO_2 fibers by measuring the rate of ^{18}O exchange between O_2 gas and SiO_2 glass at temperatures of 1150° to 1430°C. The calculated activation energy of oxygen diffusion in the silica is about 20 kcal/mole, a value much lower than observed in complex silicate melts. This fact implies that the oxygen atoms move by different mechanisms in the glass and silicate melts. Giletti and Anderson (1975) measured the self-diffusion of oxygen in phlogopite, and by use of an ion microprobe, Giletti and others (1978) studied the diffusion of oxygen in feldspars. Yund and Anderson (1978) showed that oxygen isotope exchange rates between feldspar and water increased with increasing water pressure (125 to 4000 bars). Increases in isotopic exchange rates with increases in non-hydrostatic pressures were also observed by Clayton and others (1975), who showed in addition that there were no detectable changes in the equilibrium distribution of ^{18}O between calcite and water at 500°C upon increasing the pressure from 1 to 20 kbar.

Matsuhisa and others (1978) introduced a new technique in which both $^{18}O/^{16}O$ and $^{17}O/^{16}O$ fractionations are measured between two substances. Use of this novel "three-isotope" exchange method results in increased confidence in the estimation of equilibrium oxygen isotope fractionations from partially exchanged samples. Suzuoki and Epstein (1976) found that the chemical composition of the octahedral site in hydrous minerals is the dominant factor controlling their relative hydrogen isotope compositions. An unusual result of the work of these authors is that all mineral-mineral fractionations have the same temperature coefficient and, consequently, hydrogen isotope fractionations among coexisting minerals cannot be used for geothermometry.

Equilibrium oxygen isotope fractionations were measured between carbon dioxide and water (O'Neil and others, 1975), illite and water (James and Baker, 1976), and kaolinite and water (Kulla and Anderson, 1978). Stewart and Friedman (1975) measured the deuterium fractionations between aqueous salt solutions and water vapor. Theoretical treatments of the ^{18}O fractionation between quartz and water are given in Becker and Clayton (1976) and Kawabe (1978). The Kawabe calculation yields fractionations considerably smaller than previous estimates but in good agreement with the empirical scale of Knauth and Epstein (1976). Moderately serious discrepancies still exist among the various laboratory determinations, calculations, and empirical stable isotope fractionation curves.

EXTRATERRESTRIAL MATERIALS

The most significant development in this field has been in the measurement of nitrogen isotope ratios of lunar materials. Kerridge (1975), Becker and Clayton (1975), Becker and others (1976) and Kerridge and others (1977) have shown that (1) the $^{15}N/^{14}N$ ratio in lunar rocks and soils varies by more than 200 permil, (2) there is a ^{15}N-rich component derived from cosmic-ray spallation and, most importantly, (3) there has been an increase with time in the $^{15}N/^{14}N$ ratio of the nitrogen that has been implanted in the soil. The $\delta^{15}N$ values of this nitrogen have increased from at least -125 to about +120 in 4 x 10^9 years for reasons not understood. Becker and Clayton (1977) have proposed that the nitrogen isotope ratios in lunar soils are a good measure of cosmic-ray exposure and regolith history. Nitrogen isotope measurements have also been made of a number of stony meteorites by Kung and Clayton (1978). These authors recognized four isotopic groups of meteorites, found a range of $\delta^{15}N$ values of -10 to +50, and discussed the implications of these measurements to the isotopic homogeneity of the nebular gas from which the meteorites condensed.

The heterogeneous distribution of oxygen isotopes in the solar nebula has provided a valuable means of "finger-printing" meteoritic materials. Clayton and Mayeda (1975; 1978a, b) and Clayton and others (1976) have been able to classify meteorites according to their oxygen isotope composition, and to draw inferences concerning the genetic relationships among the various classes and with the moon.

H, C, O and Si isotopic analyses of samples from later lunar missions are very similar to those obtained earlier (Epstein and Taylor, 1975; Mayeda and others, 1975). Kerridge and others (1975) have used sulfur isotope analyses to identify indigenous and meteoritic sulfur in the lunar soils and showed that the amount of meteoritic sulfur correlates with inferred surface exposure times. DesMarais and others (1975) presented arguments that the ^{13}C content of soils is correlated with the degree of maturity of the soil. There are several detailed studies of the stable isotope variations in lunar and meteoritic samples that are published in the Proceedings of the 9th Lunar Conference, but these were not available at the time of this writing.

GEOTHERMAL STUDIES

Thousands of stable isotope analyses of materials, chiefly fluids, from geothermal areas have been made during the last few years in an attempt to identify fluid origins, water/rock

ratios, and reservoir temperatures, among other things. Although most of these measurements are not yet published, a considerable amount of data is given in the Open-File Reports of the U.S. Geological Survey. McKenzie and Truesdell (1977) have shown that dissolved sulfate and water are probably in oxygen isotope equilibrium in all large reservoirs that have temperatures above 140°C and that little re-equilibration takes place during ascent to the surface. The sulfate-water geothermometer yields estimates of 360°, 240°, and 140°C for the deep reservoirs at Yellowstone Park, Wyoming, Long Valley, California, and Raft River, Idaho, respectively. In this same paper, methods to calculate the effects of boiling and dilution are described. Truesdell and others (1977) made a detailed study of the effects of subsurface boiling and dilution on the isotopic compositions of thermal waters from Yellowstone Park. They considered both single-stage and continuous steam separation from the reservoir and showed that such processes can result in significant differences in the D and ^{18}O contents between surface and deep waters.

One of the more exciting new developments in geothermal research in the last few years has been the identification of mantle-derived helium in the fluids of several geothermal areas. Craig and others (1978) have discovered large ^3He enrichments relative to atmospheric and crustal helium in volcanic gases from Lassen Park and Yellowstone Park. Of particular interest is their observation of extremely high helium isotope ratios, 15 times atmospheric and greater, in the Mud Volcano area of Yellowstone Park. Such high ratios, observed also at Kilauea and in Iceland, are probably indicative of the presence of deep-mantle plumes under hot-spots. The presence of this unusual helium at Yellowstone indicates that at least in certain areas the continental crust is apparently transparent to mantle volatiles.

ORGANIC GEOCHEMISTRY

Kaplan (1975) has reviewed the literature and discussed the use of the stable isotope ratios of H, C, N, O and S as guides to the identification of biogeochemical processes both on Earth and on extraterrestrial bodies. Low-temperature reactions, particularly those mediated by organisms, are generally controlled by kinetic factors, and reduced products of metabolism are enriched in light isotopes. Regular patterns of biological enrichment factors have been recognized on Earth, but not as yet in lunar or meteoritic samples. Carbon isotope analysis has rapidly become one of the most important techniques used in organic geochemistry. Fuex (1977) has reviewed the use of carbon isotope ratios in hydrocarbon exploration and points out that the full potential of this method is realized only when used in conjunction with good geologic control and additional geochemical data.

The isotopic ratios of H, C, and N appear to be useful indicators of marine and nonmarine sources of organic matter, although hydrogen isotopic compositions can be influenced by factors other than a fresh-water or sea-water source (Hoering, 1975). Stuermer and others (1978) measured the stable isotope ratios of H, C and N in addition to elemental compositions and electron spin resonances of humic acids and proto-kerogens from 12 widely varying locations of well-defined environments. They concluded that a combination of $\delta^{13}C$ values and H/C ratios is a simple and reliable source indicator that allows differentiation of marine-derived from terrestrially-derived organic matter. They also concluded that $\delta^{15}N$ values are useful indicators of nitrogen nutrient source and that δD values appear to reflect variations in deuterium content of local meteoric waters and are thus unreliable source indicators. Fry and others (1977) showed that organic carbon from sediments collected in Texas seagrass meadows is enriched in ^{13}C by an average of 6.6 permil relative to organic carbon from offshore sediments. They were thus able to use carbon isotope data to estimate the relative contributions of seagrasses and plankton to sedimentary organic matter.

A number of laboratory-controlled experiments have been made on organic systems. Sackett (1978) has measured the carbon and hydrogen isotope fractionations associated with the pyrolysis of normal octadecane as a function of time, temperature, and catalysis. At 400° and 500°C there are carbon isotope fractionations of 27.9 and 25.4 permil, respectively, during methane production. Deuterium depletions in the methane of 170 permil at 400°C and between 140 and 178 permil at 500°C were observed. If the pyrolysis is carried out in the presence of a clay mineral, little or no carbon isotope fractionation takes place. This remarkable effect is probably due to the operation of a carbonium ion mechanism induced by the clay mineral rather than to a thermal free-radical mechanism operative in the other experiments.

DeNiro and Epstein (1977) have shown that the low carbon isotope ratio of lipids results from isotopic fractionation during the oxidation of pyruvate to acetyl coenzyme A. Their in vitro analyses of the kinetic isotope effects of this reaction indicates that there will be a large, temperature-dependent difference in the carbon isotope ratio between the methyl and carbonyl carbon atoms of acetyl coenzyme A and between those carbon atoms of lipid components that derive from them.

ORE DEPOSITS

It was clear several years ago that stable isotope analyses of H, C, O and S in ore minerals, gangue minerals and fluid inclusions are powerful indicators of (1) the origin of water, sulfur and carbon in the ore fluid, (2) the temperature history of deposition, and (3) the water/rock ratios that prevailed during the development of hydrothermal deposits. The major general observations were made prior to the time of the last report and attention is now directed toward elucidating details of development of individual deposits (Casadevall and Ohmoto, 1977; Batchelder, 1977; Addy and Ypma, 1977; Ripley and Ohmoto, 1977; Kamilli and Ohmoto, 1977; Hall and others, 1978; Rye and others, 1978).

IGNEOUS ROCKS

Variations in the stable isotope compositions

of igneous rocks are controlled by factors that are pertinent to several classical problems of igneous petrology. Much attention has been directed toward the identification of the source materials of both plutonic and volcanic rocks. Taylor and Turi (1976) reported $\delta^{18}O$ values between 11.2 and 16.4 for rocks from the Tuscan Magmatic Province in Italy. The Tolfa rhyolites and quartz latites have the highest $\delta^{18}O$ values ever reported for primary volcanic rocks. These magmas undoubtedly formed by melting or large-scale assimilation of high ^{18}O argillaceous sediments. The S and I granitoid rocks from southeastern Australia are readily distinguished by their oxygen isotope ratios and, in addition, a good correlation exists between the δD values and water contents of these rocks (O'Neil and Chappell, 1977; O'Neil and others, 1977). The andesites of the Banda arc of Indonesia have high initial $^{87}Sr/^{86}Sr$ ratios and relatively high $^{18}O/^{16}O$ ratios. Cordierite-bearing lavas there have very high $\delta^{18}O$ values of ~15. Magaritz and others (1978) conclude from these data that sediments or continental crustal material can be carried down subduction zones to great depths. Kyser and O'Neil (1978) note that fresh alkali basalts are generally enriched in ^{18}O by 0.5 to 1.0 permil relative to tholeiites and that isotopically distinct sources in the mantle are responsible for this effect. Taylor and Silver (1978) have found a remarkably systematic west-to-east increase in the ^{18}O content of plutons from the Peninsular Ranges batholith of Southern and Baja California. The patterns correlate very well with increases in $^{87}Sr/^{86}Sr$ ratios and are independent of rock type. The authors conclude that the western part of the batholith was generated dominantly from a primitive source material from the upper mantle and that eastward migration of the axis of magmatism involved increasing access to heavy ^{18}O reservoirs like metasedimentary rocks or altered upper portions of an oceanic lithospheric slab. Craig and Lupton (1976) have identified a primordial neon and helium component to certain deep-sea tholeiitic glasses by their ^{20}Ne anomalies and high $^{3}He/^{4}He$ ratios. δD values of such materials are ~-77 and may represent values characteristic of juvenile hydrogen in the mantle.

Several studies were made of Precambrian igneous suites. Barker and others (1976a) were able to delineate different source materials for the trondhjemites of southwestern Colorado by their $\delta^{18}O$ values. The stable isotope variations in other trondhjemitic suites are discussed in Barker and others (1976b) and Arth and others (1978). Unusually low δD values ranging from -90 to -120 were observed in the Pike's Peak batholith by Barker and others (1976c). From analyses of composite samples, Shieh and Schwarcz (1977, 1978) have estimated an average $\delta^{18}O$ value of 8.1 for a large segment of the Canadian Shield. Oxygen isotope compositions of Archean igneous rocks from the Lake Despair area of Ontario are given by Longstaffe and others (1977).

The phenomenon of ground-water interactions with magmas and cooling intrusions was identified by stable isotope analyses and has continued to pique the interest of the geologic community. Extensive review articles of the subject have been written by Taylor (1977, 1978a, b). On the basis of oxygen isotope evidence, Lipman and Friedman (1975) postulated that major interactions between ground water and batholithic-sized bodies of silicic magmas occurred prior to the eruption of the ash flows in southern Nevada. Forester and Taylor (1976, 1977) made detailed studies of the ^{18}O and D depleted rocks from the Isles of Mull and Skye in Scotland. Magaritz and Taylor (1976a, b) presented hydrogen and oxygen isotope evidence for meteoric-hydrothermal alteration of plutonic rocks on a massive scale in their studies of the Yakutat Bay and Skagway areas in Alaska and the Coast Range batholith of British Columbia. ^{18}O and D measurements provide evidence of low-temperature, meteoric-hydrothermal alteration of the Precambrian granite-rhyolite terrane in the St. Francois Mountains, Missouri, and that the late Precambrian oceans may have been isotopically similar to the modern ocean (Wenner and Taylor, 1976).

METAMORPHIC ROCKS

Estimates of temperatures of formation, origin and direction of flow of fluids and tests for equilibrium were made in studies of regionally metamorphosed rocks in the Esplanade Range of British Columbia (O'Neil and Ghent, 1975), at Naxos, Greece (Rye and others, 1976), and in the Monte Rosa Granite, Western Alps (Frey and others, 1976). In the latter study, comparison of radiogenic and stable isotope relations indicated that the radiogenic isotopes in the interlayer positions of micas can be mobilized without recrystallization, that is, without breaking Al-O or Si-O bonds. Oxygen and hydrogen isotope measurements of eclogites and associated rocks from the Sesia zone in the Western Alps of Italy indicate attainment of a high degree of isotopic equilibrium, and the average oxygen isotope temperature of 540°C implies subduction of the precursor rocks into the upper mantle in order to achieve the high pressures required (Desmons and O'Neil, 1978). Longstaffe and Schwarcz (1977) evaluated the use of ^{18}O measurements in distinguishing metasedimentary or metavolcanic gneisses from those of plutonic origin in the Superior Province of Canada. Taylor and O'Neil (1977) examined the stable isotope relations in metasomatic skarns and related rocks in the Osgood Mountains of Nevada and used oxygen isotope variations to estimate CO_2/H_2O ratios in the metamorphic fluids. Becker and Clayton (1976) estimated temperatures of burial metamorphism of around 300°C for the Precambrian banded-iron formations in the Hamersley Range of Western Australia and evaluated relative susceptibilities of the various minerals to isotopic exchange with the pore fluids.

Several studies have shown that oxygen isotope equilibrium is often not attained in lower-temperature environments. Yeh and Savin (1977) showed that shales from the Gulf of Mexico are not isotopically equilibrated systems even at depths where temperatures are as high as 170°C, and Clayton and others (1978) demonstrated the resistance of quartz silt to isotopic exchange under burial and intense weathering conditions. Analyses of rocks and minerals from the Franciscan Formation in the Coast Ranges of California indicate that metamorphism produces no change in the $\delta^{18}O$ values of the graywackes (11 to 14), but that igneous rocks become enriched in ^{18}O by 2-6 permil and the cherts depleted by 5-10 permil (Magaritz and Taylor, 1976c).

Murata and others (1977) determined the oxygen isotope composition of silica polymorphs in three diagenetic zones, (1) biogenic opal, (2) disordered and ordered cristobalite, and (3) microcrystalline quartz, in two areas of California. They found that the ^{18}O content remains fairly constant in each zone and changes substantially at zone boundaries. The phase transformations at the boundaries probably take place by a solution-deposition mechanism but the progressive structural ordering of cristobalite within zone 2 must proceed by a solid-state reaction not involving water. Isotopic and other geochemical evidence for modern low-temperature serpentinization has been found in three new localities: New Caledonia, Oman, and Yugoslavia by Barnes and others (1978). These authors postulate that the ^{18}O content of such serpentine may be inherited in part from the precursor pyroxene and olivine. For a deep-sea sediment 2.7 m.y. old, only 4-9 percent of the oxygen in the clay minerals has exchanged with ocean water (Yeh and Savin, 1976). Also, no significant hydrogen isotope exchange between clay minerals and sea water takes place in 2-3 m.y. (Yeh and Epstein, 1978). Therefore information concerning the provenance and mode of formation of detrital clay minerals can be obtained from the oxygen and hydrogen isotope compositions of deep-sea sediments younger than a few million years.

Many oxygen isotope analyses have been made of materials from the DSDP cores (Muehlenbachs, 1976, 1977a, b; Anderson and Lawrence, 1976; Anderson and others, 1976; Lawrence and others, 1975, 1976). These studies show that basalts are commonly weathered to various extents by reactions with seawater at low temperatures. The formation of high ^{18}O clays results in altered basalts with $\delta^{18}O$ values that vary typically between 6 and 10 permil. During such alteration the pore waters become concomitantly depleted in ^{18}O. The intrusive rocks are relatively depleted in ^{18}O due to exchange with seawater at high temperatures (>300°C). Muehlenbachs and Clayton (1976) have shown that if estimates are correct of the volumes of materials involved in the formation and alteration of the oceanic crust, cycling of water through the mantle, and weathering of the continents, the oxygen isotope composition of the ocean may be held at its present value as a consequence of the ^{18}O enrichments balancing the ^{18}O depletion. They calculate a time constant of 200 or 300 m.y. for approach to the present isotopic ratio in the ocean.

PALEOTEMPERATURES AND PALEOCLIMATOLOGY

Stable isotope geochemistry has its origins in oxygen isotope studies of ocean paleotemperatures and this is an area of research that continues to receive considerable attention (Margolis and others, 1975; Savin and others, 1975; Anderson and Cole, 1975; Herman and O'Neil, 1975; Douglas and Savin, 1975; Durazzi, 1977; Shackleton and Matthews, 1977; Williams and others, 1977; Emiliani and others, 1978). An excellent comprehensive review of this subject was written by Savin (1977). New approaches to the study of ocean paleotemperatures involve the measurement of (1) oxygen isotope variations in silica-bearing organisms (Mikkelsen and others, 1978) and (2) the oxygen and carbon isotope fractionations between the calcite and aragonite of pairs of benthic foraminifera (Sommer and Rye, 1978). The latter method is somewhat limited and requires high precision analyses, but has the advantage of being independent of the isotopic composition of the water in which the shells grew. Excellent materials are now available from the deep-sea cores, and with the advances being made in stratigraphic correlations and the increase in the number of stable isotope laboratories in the world, even further sophistication is expected in exploiting isotopic methods of determining ocean paleotemperatures.

The factors that determine climatic regimes on land are complicated, but temperature is certainly the most important. The well-known temperature dependence of the hydrogen and oxygen isotopic compositions of meteoric waters has been used in a variety of novel new methods. Ages of successive layers of speleothems can be dated by the $^{230}Th/^{234}U$ method. On the assumption that the fluid trapped as inclusions in ancient speleothems is an unaltered sample of the seepage water, one can extract and analyze it as well as the host calcite and estimate the temperature of formation from the ^{18}O fractionation between calcite and water (Schwarcz and others, 1976; Thompson and others, 1976). Inasmuch as cave temperatures are long-term averages of surface temperatures, these measurements are indicative of ancient continental or island surface temperatures. From measurements of the oxygen isotope compositions of pedogenic and groundwater carbonates, Cerling and others (1977) postulated a dramatic climatic change in East Africa during the Pleistocene. The data suggest that meteoric water of the earlier, more humid climate was 2-4 permil lower in ^{18}O content than modern waters of these regions. Hanshaw and Hallet (1978) discussed the paleoclimatic implications of the oxygen isotope composition of subglacially precipitated calcite.

Analyses of the isotopic composition of H, C, and O in dated tree rings appear to be useful indicators of paleoclimates (Libby and others, 1976; Epstein and Yapp, 1976, 1977; Yapp and Epstein, 1977; Libby and Pandolfi, 1977; Long and others, 1978). Epstein and others (1976) demonstrated that the D/H ratio of C-H hydrogen in the cellulose of plants is non-exchangeable and maintain that only the isotopic composition of this hydrogen is systematically related to that of the water incorporated by the plants.

New measurements have been made which bear on the important fact that marine limestones and cherts become progressively depleted in ^{18}O with age. Knauth and Epstein (1976) have analyzed the oxygen and hydrogen isotopic compositions of a suite of nodular and bedded cherts from the U.S. and interpret their data in terms of changing climatic temperatures. They suggest that Earth

surface temperatures may have reached about 52°C at 1.3 b.y. and about 70°C at 3 b.y. Osyarek and Perry (1976) and Perry and others (1978) measured ^{18}O contents of many ancient cherts from Greenland and discuss the temperature limits of the early Archean oceans as well as the possibility of changing isotopic compositions of the oceans. These important questions still remain unresolved.

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COMPUTER MODELING IN LOW TEMPERATURE GEOCHEMISTRY

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During the 1975-78 quadrennium, the field of low-temperature geochemistry advanced greatly from a synergistic relation combining increasing utilization of computer science with other endeavors in geochemistry. The rapid growth in computer programming and its applications to modeling and predictions of natural phenomena has generated a rapid growth of sophisticated experimental methods to check the validity of the computer models and increased the data base necessary for calculation and comparison of the models. Evolution of this relation can be seen as an extension of trends that had been developing during the past decade. Application of thermodynamics to the interpretation of natural geochemical systems (Garrels and Christ, 1965) was enhanced by use of computers, enabling more complex and relevant systems to be investigated. This early period was characterized by a series of papers that applied thermochemistry to complex natural systems using computers (Helgeson, 1968; Helgeson, 1969; and Helgeson, Garrels and Mackenzie, 1969). The program PATHCALC alluded to above was based primarily on equilibrium thermodynamics and was followed by two other equilibrium-oriented computer programs, SOLMNEQ (Kharaka and Barnes, 1973) and WATEQ (Truesdell and Jones, 1974). These computer programs were then used for a wide variety of purposes--some intended by the programmers and some not. As the use of these programs became more extensive, it was apparent that there were some discrepancies between the observed and the calculated equilibria (Miller et al., 1977; Nordstrom and Jenne, 1977; Potter et al., 1978). These discrepancies could be attributed to several possible causes: (1) a data base that was thermochemically inconsistent, (2) reactions controlled by kinetics, (3) incomplete understanding of the mechanisms involved in natural processes, and (4) irreversible reactions.

As a first attempt to correct the discrepancies the researchers began to improve the equilibrium programs. For example, PATHCALC was extensively altered to produce the HH program (Miller et al., 1977), WATEQ was upgraded to form WATEQF (Plummer et al., 1976) and later, WATEQ2 (Ball et al., 1978) was written. Most of the improvements have been intended to increase the running speed of the programs, improve the data base, and expand the capacity of the programs to handle a greater number of elements and compounds. In addition to improving the existing programs, new ones were developed to deal with special problems: MIX2 (Plummer et al., 1975) SYSTAB (Smith and MacCarthy, 1978), GEOCHEM (Mattigod and Sposito, 1978), REDEQL2 (Harriss et al., 1978), EQUIL (Fritz, 1975), EQ3 (Wolery, 1978), IONPAIR (Thrailkill, 1970), MINEQL2 (Westall et al., 1976) MIRE (Holdren, 1977), SEAWAT (Lafon, 1969), WATSPEC (Wigley, 1977), and SIAS/COMIC (Perrin and Sayce, 1967). One of the conclusions derived from the application of these models to natural systems was the need for an internally consistent data base that would be far more comprehensive than those available at that time.

There were two basic types of problems with the data bases of the programs: (1) absence of data for many phases and aqueous species, and (2) lack of internal consistency for the thermochemical properties used in the data base. The absence of data for many pertinent minerals, chemical compounds, and aqueous species led to attempts to estimate the necessary thermochemical properties (Tardy and Garrels, 1976 and 1977; Langmuir, 1978; Brookins, 1975; Chen, 1975). New direct measurements of the thermochemical properties of minerals and related aqueous species were developed (Hemingway et al., 1977 and 1978; Charlu et al., 1975 and 1978; Robie et al., 1976; Krupka et al., 1977; Potter, 1977; Herr and Helz, 1976; Hemley et al., 1976 and 1977; Eberl and Hower, 1977; McGee and Hostetler, 1975 and 1977; and Reardon and Langmuir, 1976).

However, no one addressed the fundamental underlying difficulty, which was the lack of consistency between thermochemical properties of a single phase or several phases. This difficulty arises primarily from the limited scope of most experimental studies that measure the thermochemical properties of a phase or group of related phases. Usually most studies involve the measurement of only one thermochemical property such as the heat capacity, enthalpy, or equilibrium constant of a reaction. The computer utilizes all properties of the phases included in the program and, if all the various parameters are not internally consistent to begin with (usually they are not) errors quickly develop with the computer calculations.

Such problems have been effectively addressed by the program PHAS20, written to produce thermochemical data that are internally consistent (Haas, 1974; Haas and Fisher, 1976). Extensive work has gone into the development of this program. PHAS20 sets up simultaneous regression equations for all available thermochemical properties for 201 different components and then solves the equations so as to yield consistent data sets for all the properties of the 201 phases. The program also allows the user to evaluate the various types of data and identify data sets having serious discrepancies. Thermodynamically consistent data bases for fluorite have been obtained with the coexisting aqueous species expected in geothermal fluids (Nordstrom and Jenne, 1977), and an internally consistent thermochemical data set for the stable and metastable phases in the system copper-sulfur (Potter, 1977) has been produced employing this approach.

Early in the development of the equilibrium programs, it was recognized that many reactions are kinetically controlled rather than by only equilibrium (Helgeson, 1971). This realization generated an abundance of kinetic studies. For example, the kinetics of dissolution of feldspars, calcite, and orthopyroxenes have now been examined extensively (Petrovic et al., 1976; Petrovic, 1976; Plummer and Wigley, 1976; Plummer et al., 1978; Sjoberg, 1976; Busenberg, 1978; Busenberg and Clemancy, 1976; Grandstaff, 1977). Many of these kinetic studies illustrate the synergistic relations that exist between computer programs and low-temperature geochemical studies. For example, the chemical speciation in the aqueous phase was calculated by programs from experimental measurements of concentration and pH. In addition, to distinguish some of the predicted behavior, the controlling mechanisms had to be experimentally elucidated and quantified, so new methods and new instrumentation were introduced for examining the surfaces of mineral phases, delineating the controlling alteration products, or quantifying the diffusion mechanisms (Petrovic et al., 1976; Houser et al., 1978). A further use of kinetic studies was to gain insight into natural processes such as precipitation, crystallization, and sorption phenomena (Dayal, 1977; Eberl and Hower, 1976; Emerson and Widmer, 1978; Hurd et al., 1978; Hurd and Theyer,1975; Lerman et al., 1975; Maynard, 1975; Stain and Kirkpatrick, 1976; Weichers et al., 1975). The rapid growth in availability of kinetic data and an increase in the studies of the reaction mechanisms have allowed for the consideration of kinetic controls on solution composition of a fluid interacting with rock (White and Claassen, 1978). In addition, studies of the controlling mechanisms have begun to yield information about the coupled nature of reactions that occur in the low-temperature environment (Churchman and Jackson, 1976; Potter et al., 1978).

The geochemical details of the processes by which low-temperature coupled reactions occur in a natural system still pose problems in our ability to calculate them. The advent of equilibrium models that could be used to calculate speciation in natural waters and interacting minerals helped define the relations between natural waters and host rocks. This was accomplished, in part, by detailed field studies of the observed minerals in equilibrium with the natural waters. These measurements required an Eh buffer, such as Zobell's solution, which although known for some 30 years, was not readily applicable because its Eh as a function of temperature was unknown. Hence, such data (Nordstrom, 1977) were measured experimentally to fill this vital gap. In addition, the need to obtain reliable data for low concentrations of various elements led to increased efforts in developing more sensitive laboratory and field methods. For example, one of the critical components for modeling natural waters is the concentration of aluminum in solution as well as the speciation of aluminum. Methods for obtaining concentrations to ppb levels and for distinguishing speciation were developed, so that many equilibria between aluminosilicates and aqueous solutions could be more accurately calculated and verified by field data (Barnes, 1975). Recent studies now apply not only more sensitive field and laboratory procedures but also combine the data with one or more of the equilibrium programs to discern the controls on ground-water compositions (Miller and Drever, 1977).

The application of the programs to more concentrated solutions such as those encountered in evaporite sequences or concentrated geothermal brines has proved to be difficult (Miller et al., 1977). The fundamental reason is that the codes are designed for dilute fluids rather than for concentrated solutions, where various extrapolations of infinitely dilute solution behavior are valid. Some interesting approaches dealing with the thermochemistry of more saline fluids have begun to develop. Most of the work is directed at seawater and seawater concentrates (Millero, 1976 and 1977; Millero et al., 1976; Millero and Leung, 1976; Atlas and Pytkowicz, 1977; Sayles and Mangelsdorf, 1977; Bodine, 1976; Byrne and Kester, 1976; Pytkowicz and Hawley, 1975; Watson et al., 1975 and Wood, 1975). A few studies were directed toward more concentrated brines such as those in geothermal systems and evaporite sequences (Potter and Haas, 1978; Marcus, 1977; Van Luik, 1978); less is known about these types of fluids. Modeling of concentrated salt solutions is developing also in a parallel manner in Europe, primarily in the United Kingdom (Whitfield, 1975). It is obvious from the few modeling studies done to date that this field of investigation is an area for much future effort and growth.

In connection with the problems of studying the more concentrated fluids, there has been extensive research on the diagenesis of marine sediments and the geochemistry of their interstitial waters. These studies are noted for combining data bases of detailed field studies employing the most sensitive analytical methods, kinetic data, redox equilibria based on the thermochemical models, and absorption and ion-exchange reaction data (Anderson and Graf, 1978; Berner, 1975 and 1976; Bischoff et al., 1975; Donnelly and Merrill, 1977; Gardner, 1978; Goldhaber, et al., 1977; Goldhaber and Kaplan, 1975; Kastner and Keene, 1975; Lerman, 1977; Merion, 1975; Murray, et al., 1978; Walls et al., 1977; Wong and Brewer, 1977). However, there has been little effort to reduce these

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data into comprehensive numerical models of the type applicable to a computer program, aside from a few attempts to construct some viable models of the diagenetic environment and its complex geochemistry (Graf and Anderson, 1975; Lasaga and Holland, 1976). Undoubtedly this lack of activity results from the complexity of the phenomena involved and the need for more detailed work.

Corresponding to the studies of the diagenesis of marine sediments there have been active investigations of the diagenesis of fresh-water sediments and their chemistry of interstial waters (Elder, 1975; Emerson, 1976; Emerson and Widmer, 1978; Lahann, 1977; Robbins and Callender, 1975). The intermediate environment between fresh water and marine water has also received attention, particularly in the area of trace-metal contamination (Boyle et al., 1977; Elderfield and Hepworth, 1975; Evans et al., 1977; Helz et al., 1975; Holdren et al., 1975; Lafon, 1975; Long and Angino, 1977; O'Connor and Kester, 1975). These studies of trace metals in the estuarine environment have been modeled thermodynamically as well as on an adsorption basis (e.g. Whitfield, 1975; Long and Angino, 1977). The diagenesis of metals in organic-rich areas such as those encountered in swamp and peat environments have also been investigated (Casagrande and Erchull, 1976 and 1977; Casagrande et al., 1977).

Considering the direction the field of low-temperature geochemistry has taken during the past four years, it is unlikely that there will be any radical change in the next four years. Extensive research directed toward the thermochemistry and kinetics of natural systems has begun to define those areas that have significant problems to be solved. Although it may sound pessimistic, it should be remembered that each problem solved in the past has raised many new dilemmas and additional problems to be solved.

Present programs are all based essentially on equilibrium thermodynamics. For these codes to become truly predictive, they must begin to incorporate kinetic and sorption phenomena. The models also need to become more comprehensive, incorporating data on trace elements and minor phases. Detailed studies cross-checking the various models would be quite useful. In addition, the modelers will need to develop an understanding of the processes and mechanisms of the many irreversible reactions frequently observed in nature. By addressing these problems, the programs produced in the next four years may become sophisticated enough to be used in practical endeavors such as tailoring lixiviants for solution-mining operations or modeling the interactions of nuclear wastes and host rocks.

The thermochemistry of minerals and aqueous species will continue to be an area of active research, particularly in producing internally consistent data sets and in the thermodynamic processes involved in the study of concentrated solutions. The difficulty in producing internally consistent data is a result of problems associated with aqueous species in conjunction with solids and the thermodynamic properties of solutions. The main effort during the next four years should be in improving experimental procedures for obtaining data for those phases where little work has been done and the application of more sophisticated techniques in the study of the thermodynamic properties of stable and metastable phases.

We can expect to see a continued increase in the number of investigations in the field of kinetic geochemical reactions. In order for these studies to provide more than just dissolution or precipitation rate data, they must begin to address the questions related to the mechanisms involved in reactions and improve numerical representation of these phenomena. This approach requires an increasing sophistication in experimental technique, along with better representation of the phases involved in the experiments.

In field studies, the primary emphasis will be to obtain better descriptions of the chemical and mineralogical states of the geochemical environment being studied. As this degree of sophistication increases and the subtlety of the controls of the observed natural phenomena are understood, more critical tests should be applied to the computer models to improve the quality of data in both areas. In order to progress rapidly in these areas during the next four years, active integration between the modelers and the field-oriented geochemists will be required.

As a subset of the field studies, investigations into the geochemistry of diagenesis and interstitial waters in marine, estuarine, and fresh waters have perhaps the best potential for rapid progress in reaching a comprehensive understanding of the processes involved. However, this progress is dependent on the degree to which such work is integrated with the modeling of other types of geochemical environments by use of the computer. An essential part of the marine-related problems and, to a lesser extent, the estuarine environments relates to the thermochemistry of trace metals in concentrated solutions. Impressive beginnings have been made in this area, and if continued in an increasingly sophisticated manner, we can assume rapid progress in our ability to model and predict these complicated systems that have such an important ecological significance.

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EXPERIMENTAL METAMORPHIC PETROLOGY

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Introduction

Since Bowen and Tuttle's pioneering study of the system MgO-SiO_2-H_2O in 1949, advances in experimental metamorphic petrology have occurred steadily rather than in "leaps and bounds". The number and quality of papers published during the past quadrennium, 1975-1978, attests to the health of the science. Although the purpose of this report is to focus international attention on the U.S. effort in experimental metamorphic petrology, some papers published by foreign experimentalists have been included, especially where their contributions complement those made in the U.S. To keep the review current, abstracts of papers read at national meetings of the Geological Society of America and the American Geophysical Union in 1978 are included.

Coverage is generally limited to papers reporting experimental data acquired at pressures below 10 kbar and temperatures between 200°C and the solidus for the system in question. Several papers reporting calorimetric and experimental data for pressures and temperature outside these limits were included to demonstrate how experimental metamorphic petrology interfaces with calorimetry, low temperature geochemistry, and experimental igneous petrology.

Papers are grouped into nine categories and are cross-referenced where necessary. Papers reporting experimental data for silicates have been subdivided according to the structural group of the dominant phase or phases whereas papers dealing with non-silicates are grouped together regardless of structure or composition. Papers dealing with multicomponent chemical systems are grouped under the heading "Rock Systems". Papers dealing with experimental techniques or with the calculation of thermochemical parameters of minerals are grouped under the headings "Experimental Techniques" and "General Physical Chemistry", respectively.

Paper number 9R0608.

Discussion

With the realization that many important equilibria could not be investigated in the laboratory, experimentalists turned to thermodynamic theory in order to extrapolate experimentally determined equilibria to conditions not amenable to experiment, to calculate the effects of additional components, and to evaluate the consequences of varying intensive parameters. Unfortunately, many of the early experimental data are not sufficiently accurate for such calculations. In order to be useful for thermochemical calculations, phase equilibrium data must be reversed, activities of components in the fluid phase must be determined, and solid phases must be thoroughly characterized chemically, mineralogically, and structurally (order-disorder, vacancies, polytypism, etc.).

Several techniques developed or refined during the past quadrennium will aid the experimentalist in controlling fluid composition in hydrothermal experiments. The "Shaw apparatus" was redesigned [Frantz et al., 1977] because H_2-equilibration times in the original design resulted in f_{O_2} values lower than the equilibrium values [Hewitt, 1977]. Chou [1978] recalibrated the (FMQ), (MH), ($MnO-Mn_3O_4$), (NNO), and (Co-CoO) oxygen fugacity buffers; Hewitt [1978] recalibrated (FMQ). Although Hewitt's recalibration differs from Chou's by no more than 0.5 log units, the discrepancy must be resolved if the phase equilibrium data generated using (FMQ) are to be used for thermochemical calculations. The Ag + AgCl acid buffer was recalibrated by Chou and Frantz [1977]; Frantz and Popp [1977] modified this buffer technique in order to determine speciation in hydrothermal fluids. Hallam and Eugster [1976] developed a method for buffering fluids in the system N-O-H by combining the (Cr + CrN) nitrogen buffer with conventional hydrogen buffers. Modifications of a chloride electrode and a flow-cell calorimeter by Popp et al. [1978] allow accurate and precise measurement of chloride ion in the concentration range 0.01 to 0.0001 m in microvolume samples (1-10 μℓ).

Ziegenbein and Johannes [1977] designed a device which aids in the extraction and gaschromatographic analysis of fluids present in high pressure experiments. Schmid et al. [1978] developed a sensitive method for determining reaction direction in experiments where one of the reacting phases is a solid solution of two components. Navrotsky [1978] designed a microcalorimeter which can accept a cold-seal pressure vessel and is using the apparatus to measure enthalpies of aqueous solutions at pressures to 2 kbar and temperatures to 800°C.

During the past quadrennium, experimental studies were initiated to determine the compositional limits of micas [Hazen and Wones, 1978; Franz and Althaus, 1976], phlogopite [Robert, 1976a, b], brittle micas [Olesch, 1975], kornerupine [Werding and Schreyer, 1978], viridine [Abs-Wurmbach and Langer, 1975], and sapphirine [Bishop and Newton, 1975]. Successful synthesis of clinoptilolite [Goto, 1977], spodumene [Drysdale, 1975], carpholite [Mottana and Schreyer, 1977], and a triple chain silicate [Tateyama et al., 1978] was achieved.

Among the dehydration equilibria whose locations in P_{H_2O}-T space have been refined are reactions involving anthophyllite [Ravior and Hinricksen, 1975; Chernosky, 1976], phlogopite [Wones and Dodge, 1977], tremolite [McKinstry and Skippen, 1978], sillimanite + biotite + quartz [Hoffer, 1976], clinochlore [Staudigel and Schreyer, 1977], clinochlore + quartz [Chernosky, 1978], portlandite, and brucite [Irving et al., 1977]. Experimentalists have successfully reversed equilibria involving bicchulite [Gupta and Chatterjee, 1978], margarite [Chatterjee, 1976], lizardite [Chernosky, 1978], gehlenite [Huckenholz, 1977], and antigorite [Evans et al., 1976].

Considerable effort has been expended in determining the stabilities and phase relations of crystalline solutions. Such studies require that the compositions of the coexisting phases be determined. Determinative curves relating the unit cell parameters of a phase to its composition have been experimentally calibrated for piemontite [Anastasiou and Langer, 1977], Fe-Mg orthoamphiboles [Popp et al., 1976], orthoamphibole [Maresch and Langer, 1976], Fe-Mg-Al biotites [Hewitt and Wones, 1975], Mg-Al serpentines [Chernosky, 1975], nepheline-kalsilite [Ferry and Blencoe, 1978], OH-F amblygonite [Loh and Wise, 1976], edenite-pargasite [Hinricksen and Schürmann, 1977], pargasite-richterite [Braue and Seck, 1977], and grandidierite [Olesch and Seifert, 1976].

Among the crystalline solutions whose stabilities and phase relations have been determined are nepheline-kalsilite [Ferry and Blencoe, 1978], pyrope-grossular [Hensen, 1976], uvarovite-andradite and uvarovite-grossularite [Huckenholz and Knettel, 1976], grossularite-spessartine [Hsu, 1978], pargasite-richterite [Braue and Seck, 1977], richterite-ferrorichterite [Charles, 1975, 1977], actinolite-cummingtonite [Cameron, 1975], hastingsite [Charles, 1978], grunerite [Forbes, 1977], Fe-Mg amphiboles [Popp et al., 1977a], chlorite [McOnie et al., 1975; Fleming and Fawcett, 1976; James et al., 1976], serpentine [Moody, 1976], cordierite [Holdaway, 1976; Holdaway and Lee, 1977; Lee and Holdaway, 1976], calcium brittle micas [Olesch and Seifert, 1976], and pyroxenes [Warner, 1975; Lindsley and Dixon, 1976; Ikeda and Yagi, 1977; Herzberg, 1978; and Wood, 1978].

Experimental calibration of the temperature, pressure and compositional dependence of major and trace element distribution coefficients may enable them to be used as geothermometers and geobarometers. The partitioning of Fe and Mg between biotite-garnet [Ferry and Spear, 1978], garnet-phengite [Krogh and Råheim, 1978], olivine-spinel [Engi, 1978], and biotite-salt solution [Schulien, 1975] were determined experimentally. Rajamani [1976] investigated the distribution of Fe, Co, and Ni between sulfide and orthopyroxene. Jacobson and Usdowski [1976] investigated the partitioning of Sr between calcite and dolomite, Suvorva and Tenishev [1976] determined the distribution of sulfur isotopes between Mo, Pb, Zn and Sn sulfides, and Fournier [1976] studied the exchange of Na^+ and K^+ between water vapor and feldspar. Fluorine-hydroxyl exchange was experimentally investigated for topaz [Rosenberg, 1978], muscovite [Munoz and Ludington, 1977], and amblygonite [Loh and Wise, 1976].

Experimental data for reactions involving a C-O-H fluid phase have been obtained for sphene [Hunt and Kerrick, 1977], andradite [Taylor and Liou, 1978], grossular, and wollastonite [Shonulovich, 1977], rhodochrosite [Candia et al., 1975], siderite [Chou, 1978], and zeolites [Ivanov and Gurevich, 1975]. Novgorodov [1975, 1977] investigated the solubility of quartz in H_2O-CO_2 mixtures. Locations of key equilibria in multicomponent systems involving C-O-H fluids were experimentally determined by Slaughter et al. [1975], Hewitt [1975], Metz [1976], Zharikov et al. [1977], and Puhan [1978]. Devolatilization equilibria in graphitic systems were discussed by Ohmoto and Kerrick [1977].

The stability relations of scapolite received considerable attention from experimentalists; Orville [1975] and Goldsmith and Newton [1977] investigated scapolite-plagioclase phase relations, Ellis [1978] investigated chloride and carbonate bearing scapolites, Newton and Goldsmith [1975] investigated the stability of meionite, and Goldsmith [1976] discussed the role of scapolite as a reservoir of CO_2 and sulfur in the lower crust.

Natural metamorphic fluids contain acids, salts, ions, and complexes as well as gases. The composition of a fluid in equilibrium with a particular metamorphic mineral assemblage can in principle be determined provided the assemblage contains fugacity indicators and appropriate buffer and exchange reactions [Eugster, 1977]. The success of this approach is limited because thermodynamic data for aqueous species at high temperatures and pressures is often unavailable. Although laboratory calibrations of equilibria involving multicomponent gases and aqueous electrolytes are uncommon, solubility studies continue to provide valuable information on the stabilities and thermochemical parameters of minerals and solutions. Solubilities of iron [Popp and Frantz, 1977], fluorspar [Malinin, 1976], wollastonite [Gunter and Eugster, 1978], mullite [Ostapenko et al., 1975], talc, antigorite, forsterite, chrysotile, brucite, and

enstatite [Hemley et al., 1977a, b] were measured. Frantz and Popp [1978] investigated speciation of aqueous $MgCl_2$ in the system $MgO-SiO_2-H_2O-HCl$ and found that at a total pressure of 2 kbar, associated $MgCl_2$ is the dominant magnesium species in the fluid at temperatures above 550°C whereas Mg^{2+} ions were dominant at temperatures below 400°C. Experimental data for solution-rock equilibria have been obtained for seawater-basalt [Mottl and Holland, 1978], seawater-peridotite [Seyfried and Dibble, 1978], seawater-andesite [Liou and Dickson, 1978], NaCl solution-carbonate rock [Radtke et al., 1978], and aqueous chloride solution-two mica schist [Vidale, 1975].

Textural relations in metamorphic rocks and ore deposits suggest that sulfides, silicates, and oxides often coexist stably. Experimental studies on sulfide-silicate phase relations remain uncommon despite the economic importance of sulfide deposits. A notable exception is the study of amphibole-magnetite-pyrrhotite phase equilibria by Popp et al. [1977] which hopefully will pave the way for future experimental work on sulfide-silicate phase relations. We must understand how and to what extent metals and sulfur dissolve and are transported in order to understand the ore deposition process. Experimental studies on the replacement of marble by sulfides [Howd and Barnes, 1975], on the mobility of metals in aqueous solutions [Govett et al., 1976; Giblin, 1978], on the solubility of chalcocite [Crerar and Barnes, 1976], scheelite [Foster, 1977], iron [Popp and Frantz, 1977], barite [Blount, 1977], and pyrite + pyrrhotite + magnetite [Crerar et al., 1978] provide the type of information required to understand ore genesis.

The processes of nucleation and growth (including diffusion and reaction rates) require further investigation before mechanisms by which metamorphic reactions proceed can be fully understood. Laboratory studies which enhance our understanding of diffusion and reaction rates include those of Hoffman et al. [1975], Wyart [1975], Kalinin and Shapovalova [1975], Seifert and Virgo [1975], Sipling and Yund [1976], McCallister and Yund [1977], Kay [1973], Sakai and Dickson [1978], Ildefonse and Gabis [1976], Lagache [1976], and Grandstaff [1976].

Methods for calculating reaction entropies and enthalpies from reversed phase equilibrium data were proposed by Gordon [1977] and Chatterjee [1975, 1977]; Anderson [1976, 1977] discussed uncertainties involved in such calculations and suggested that errors could be evaluated using a Monte Carlo method. Techniques for calculating and extrapolating equilibria in $P-T-X_{CO_2}$ space have been discussed by Skippen [1975], Skippen and Carmichael [1977] and Kerrick et al. [1976] and have been compared by Kerrick and Slaughter [1976] and Kerrick and Jacobs [1978].

Thermodynamic parameters for diaspore, margarite, pyrophyllite, zoisite, wairakite [Chatterjee, 1976], bicchulite [Gupta and Chatterjee, 1978], hydrous phlogopite [Wones and Dodge, 1977], talc, anthophyllite, enstatite, chrysotile [Zen and Chernosky, 1976], and andradite [Taylor and Liou, 1978] were extracted from phase equilibrium data. Thermodynamic properties of mullite [Ostapenko et al., 1975], barite [Blount, 1977], talc, antigorite, anthophyllite, chrysotile [Hemley et al., 1977a, b], and supercritical aqueous $CaCl_2$ [Gunter and Eugster, 1978] were extracted from solubility data.

The relationship between activity and composition for rock-forming crystalline solutions is required to calculate equilibrium conditions in complex natural systems using thermodynamic principles. Activity-composition relations for pyrope-grossular [Hensen et al., 1975], almandine-grossular [Cressey et al., 1978], muscovite-paragonite [Chatterjee and Froese, 1975], magnetite-ilmenite [Lindsley, 1978; Spencer and Lindsley, 1978], high albite-sanidine [Blencoe and Merkel, 1978] were extracted from phase equilibrium data using various solution models.

Procedures for estimating thermodynamic properties of minerals have been proposed by Chen [1975], Saxena [1976], Tardy and Garrels [1976, 1977], Tardy and Gartner [1977], Tardy and Vieillard [1977], Dibble and Dickson [1978], and Helgeson et al. [1978]. Ulbrich and Waldbaum [1976] emphasized the need for considering structural contributions to the third-law entropies of silicates. The thermodynamics of metamorphic fluids was discussed by Ryzhenko [1976], Eugster [1977], and Holloway [1977]; an equation of state for aqueous species at infinite dilution has been predicted by Helgeson and Kirkham [1976]. Fugacity coefficients for CO_2 have been calculated by Shmulovich and Shmonov [1975].

Among the minerals investigated calorimetrically are garnets [Kiseleva, 1976b; Kiseleva and Topor, 1976; Perkins et al., 1977; Kolesnik et al., 1977; Kiseleva, 1977; Newton et al., 1977; Charlu et al., 1975, 1978], pyroxenes [Navrotsky and Coons, 1976; Newton et al., 1977; Thompson et al., 1978; Charlu et al., 1975], spinel [Navrotsky and Kasper, 1976], gedrite [Kolesnik et al., 1976], sapphirine [Kiseleva, 1976a], gibbsite [Hemingway and Robie, 1977; Hemingway et al., 1977], kaolinite [Hemingway et al., 1978], muscovite [Robie et al., 1976], low albite [Hemingway and Robie, 1977], anorthite [Robie et al., 1978] and alkali feldspar [Hovis and Waldbaum, 1977]. Comprehensive computer programs designed to evaluate and correlate calorimetric and phase equilibrium data were written by Haas and Fisher [1976] and Helgeson et al. [1978]. During the quadrennium, two internally-consistent compilations of thermodynamic properties of rock-forming minerals were published; one is based on calorimetric data [Robie et al., 1978] whereas the other is primarily based on phase equilibrium data [Helgeson et al., 1978]. Although the thermochemical properties for many minerals in these compilations are similar, there are significant differences which the experimentalist is challenged to resolve.

The Future

One of the chief goals of the modern metamorphic petrologist is to determine the physiochemical conditions prevailing at the time a given metamorphic rock was recrystallized. Toward this end, experimentalists have explored the role of intensive parameters such as total pressure, water pressure, temperature, and oxygen fugacity in detail. Until recently, however, the nature, composition, and role of the supercritical metamorphic fluid has not received much attention from experimentalists. Now that techniques for studying acid-base, dissociation, and solubility reactions at elevated temperatures and pressures have been developed, experimental work on the solution chemistry of metamorphic supercritical fluids will flourish.

The petrologic community is in need of experimental data for a wide range of topics: activity-composition relations for most rock-forming crystalline solutions need to be determined; diffusion coefficients for aqueous species and ions at metamorphic conditions are virtually unknown; the distribution of major and trace elements among most important metamorphic mineral pairs remains to be calibrated experimentally. Unfortunately, the current funding picture and the paucity of academic positions for scientists trained in experimental petrology preclude radical changes in the level of activity. Consequently, equilibria which provide the most useful information must be identified in order to maximize efficient use of equipment and time.

In the past decade it has become evident that phase equilibrium data can be used as input for thermochemical calculations. Consequently, considerable effort will be directed toward investigating relatively simple equilibria involving key phases even though such reactions may not be observed to occur in rocks. Although the traditional approach which involves mapping out the stability field for a particular mineral or assemblage will be retained, experimental techniques must and will be sharpened to the point that brackets 5-10°C wide will be routinely obtained. Narrow brackets are necessary if the thermochemical parameters of minerals are to be refined. Precise and accurate techniques for determining the composition of fine-grained material must be developed. The discovery of triple chain silicates in natural and synthetic phases [Veblen et al, 1978], for example, emphasizes the need to evaluate starting materials more critically. Interlaboratory calibration of hydrochemical equipment is necessary to insure internal consistency among data obtained in different laboratories.

The ability to measure high temperature heat capacities of relatively small synthetic samples with a differential scanning calorimeter is a major development. High temperature heat capacity data for many rock-forming minerals and crystalline solutions will become available during the next quadrennium. The possibility of routinely measuring the high temperature heat capacities of phases used in starting materials for hydrothermal experiments now exists!

The development of computer programs for correlating and extrapolating phase equilibrium and calorimetric data challenges the experimentalist to insure that new experimental data are consistent with the corpus of existing phase equilibrium and thermodynamic data.

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VOLCANOLOGY

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Volcanology in the 1970s has expanded greatly in both size and scope. Comparison of the references listed here with those of the U.S. National Report to IUGG for 1963-6 (by R. W. Decker) and 1967-70 (by T. L. Wright)* illustrates many of these changes. The number of references has doubled, reflecting increased interest in active volcanoes as well as the overall increase in scientific literature. Kilauea has been at least twice as active as any other oceanic volcano during the last decade, and its references (48) continue to dominate work on individual U.S. volcanoes. Alaskan volcanoes, 33 of which have erupted in the last 100 years, continue to be the most neglected of U.S. volcanoes (total of 24 references). On the other hand, those of the western conterminous U.S., only one of which is known to have erupted in the last 100 years, have received far more attention in the 1970s (21% of the references here, compared with 14% and 7% in the '67-70 and '63-66 reports, respectively). Much of this increased attention stems from the search for geothermal power, and heightened awareness of volcanic hazards.

The most striking volcanological advances of the 1970s, however, have been in the investigation of deep sea volcanism. The recognition that most of the world's volcanic activity is submarine, matched with technological advances in marine exploration, have led to exciting new discoveries on the sea floor. Continental segments of the world's rift systems have also benefited from increased volcanological attention. Additional recent expansion in 1970s volcanology has come with interdisciplinary approaches: the application of physics and chemistry to eruptive processes, the meteorological effects of explosive eruptions, the geophysical delineation of subsurface magma bodies, and the increasing interaction with archeological problems.

Previous U.S. National Reports to the IUGG have reviewed volcanological findings at Hawaiian, Alaskan, and western U.S. volcanoes, and provided tabular summaries of the volcanic activity at each region during the report periods through 1970. The years since 1970, however, have all been reviewed in each January issue of Geotimes, and additional chronologic detail can be found in several references cited below (under "Surveillance"). U.S. volcanoes have produced an average of 3.4 eruptions per year (σ=1.8) during the last two decades, with no remarkable variation in the 1970s. Consequently, this review will carry no chronologic summary, although outstanding volcanic events will be woven into the review. The review will be organized around the main subject areas of volcanologic research, but the accompanying bibliography contains a letter code to facilitate rapid identification of references in major geographic areas. In a general way, the review will move from effusive rift volcanism, through intraplate activity, to the explosive volcanism of island arcs and continental margins, before treating meteorological and socioeconomic aspects of volcanoes.

*Volcanology was not reviewed in the 1971-4 report. Several important references appearing during this period, if not listed in the author's subsequent work, have been included in this bibliography and the 1970's are reviewed as a whole in the text.

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Subaerial lava: flood basalts, flows, forms, & lava lakes

Flood basalts must be one of the most dramatic forms of volcanism, but they have never been witnessed by man. The most recent known are those of the Columbia Plateau, northwestern U.S., most of which erupted 15 million years ago. Recent work by Swanson, Wright, and others has shown that single flows measuring 700 km^3 have spread over 10^3 km^2 in a few days. This eruption rate (1 km^3/day per km of active fissure) is 2-3 orders of magnitude greater than sustained rates observed on Hawaii. The largest historic lava eruption was from the 10 km Lakagigar fissure in Iceland, when 10 km^3 covered 370 km^2 during 50 days in 1783 (Thorarinsson, 1969). Iceland also now holds the record for the smallest, historic lava eruption known, after 1 m^3 of magma was extruded from a Krafla drill hole in 1977.

Hawaii's largest and longest historic flank eruption ended in 1974, and provided many opportunities for the study of moving lava. The full course of the 5 year eruption is reviewed by Peterson et al. (1976) and its vigorous first 17 months, including dramatic lava falls into pit craters and the construction of the small shield volcano Mauna Ulu, is described in detail by Swanson et al. (1979). The formation of lava tubes was observed by Peterson and Swanson (1974) who emphasised the importance of tubes in transporting large volumes of lava 12 km down the south flank. The formation of new lava deltas, where these flows met the sea, has been described by Moore et al. (1973) and Peterson (1976).

Recent studies of lava rheology include those by Sparks and Pinkerton (1978) and, with special attention to pahoehoe/aa surfaces, by Peterson and Tilling (1979), Fink and Fletcher (1978), and Swanson (1973). But the most striking illustration of lava fluidity came in the 1977 eruption of Nyiragongo, Zaire. In less than one hour, at least 20 x 10^6 m^3 of molten melilite nephelinite drained from this famous lava lake and spread over 20 km^2 of Nyiragongo's flank (Tazieff, 1977). Flow velocities up to 100 km/hr were estimated and the highly fluid lava left coatings only milimeters thick near its vents (and on unburned vegetation).

Lava lakes are valuable natural laboratories for the study of many petrologic and volcanologic problems. Kilauean eruptions over the last 20 years have flooded pit craters to form lava lakes in a variety of sizes, and the U.S. Geological Survey's Hawaii Volcano Observatory has carried out an immensely valuable drilling and sampling program there (summarized by Wright et al., 1976). Recent papers show how lava lakes can be used to obtain information on diverse subjects such as plagioclase growth rates (Kirkpatrick, 1977), Curie temperatures (Zablocki and Tilling, 1976), gravity differentiation (Wright and Okamura, 1978), vesiculation (Peck, 1978), and the cooling history of a magmatic body (Shaw et al., 1977). The 111 m thick lake at Kilauea Iki, formed in 1959, had developed a 44 m thick crust when drilled in 1975 and had largely solidified by 1979. Its still-molten interior, believed to be about 10 m thick in 1975, was mapped and characterized by seismic (Aki et al., 1978) and electrical VLF induction (Zablocki, 1978) techniques.

Subsurface magma: chambers, intrusions, & rifts

Geophysical techniques such as those used on the known, shallow magma body at Kilauea Iki have also been used on larger, deeper bodies. Certainly one of the outstanding advances in recent years has been the delineation of subsurface magma chambers and, in several important situations, the careful monitoring of subsurface magma migration using multiple geophysical techniques.

Surface deformation, ground tilt, techniques (see Kinoshita et al., 1976) have previously been used to infer a 1-4 km depth to Kilauea's summit magma chamber (Dieterich and Decker, 1975). The results of a 1,262 m drill hole in 1973 (Zablocki et al., 1974) are consistent with a 4 km depth if directly below the hole or somewhat shallower if horizontally displaced. By studying the arrivals of distant earthquakes in the Kilauea area, Ellsworth and Koyanagi(1977) found a 2-4 km deep summit chamber underlain by a deeper one at 27-42 km. This teleseismic technique (Iyer and Stewart, 1977) has been effectively used to locate molten magma beneath Yellowstone Park (Eaton et al., 1975, Iyer, 1979), Long Valley (Bailey et al., 1976), Clear Lake (Hearn et al., 1976), and elsewhere. Seismic reflection profiling has been used with high resolution in the Rio Grande Rift to delineate a magma body 18-22 below Soccoro, New Mexico (Rinehart et al., 1979).

Within 22 days of each other in 1975, an Hawaiian earthquake and an Icelandic eruption began two separate sequences of events that have brought exciting new information on the subsurface movement of magma in rifts and on the nature of sea-floor spreading. Hawaii's 29 November earthquake, its largest since 1868, resulted in seaward displacement (locally as much as 3.5 m) of Kilauea's entire south flank (Tilling et al., 1976), a movement previously predicted by Swanson et al. (1976). During the following 22 months, the volcano was quiet at the surface, but underwent 3 major intrusive events in which movement of magma into the East Rift was documented by seismic, geodetic, gravimetric, and electrical self-potential techniques. These movements are interpreted by the Hawaii Volcano Observatory staff (Dzurisin et al., 1979) as reflecting constant supply of magma from depth to the summit chamber, punctuated by intrusive events feeding magma laterally toward, and into, fractures created by the 1975 earthquake. After the available space had been filled, magma again appeared at the surface in the September, 1977, eruption. Although an atypical eruptive cycle for Hawaii, the magma budget for this period matches the careful monitoring of the events, and offers a fascinating example of tectonic influence on volcanism.

Similar activity in northern Iceland has followed the December, 1975, eruption in Krafla Caldera, but in this situation the tectonic influence is that of global sea-floor spreading and not at all atypical (Bjornsson et al., 1977). Since 1975, slow and steady inflation of the Krafla chamber has 10 times reached critical levels resulting in 3 eruptions, intrusions up to 40 km along the rift zone, and horizontal rift separations of the order of 1 meter. Seismic studies indicate a magma chamber of 1-2 km horizontal diameter 3-7 km below Krafla Caldera, and intrusion velocities around 2 km/hr (Einarsson, 1978). Similar episodes in the past have resulted in 70 km lateral intrusions and caldera collapse such as the 1875 event at Askja (Sigurdsson and Sparks, 1978). Sea-floor spreading in this, and no doubt other, rift areas apparently proceeds episodically, every 100-150 years, with events such as those now taking place in Iceland.

Submarine magmatism: rift volcanism on the sea floor

Increased use of submersibles, deep tow instrument packages, deep-sea drilling, and other techniques has recently opened the sea-floor spreading rifts to detailed study. The Mid-Atlantic Ridge at 37° N has been investigated by Project FAMOUS (see Ballard et al., 1975, Bryan and Moore, 1977, and Ballard and Moore, 1977). This region had previously been the site of the first major penetration of the oceanic crust when DSDP Leg 37 cored 583 m into the crest of the ridge (Aumento, Melson et al., 1977). Additional deep coring of oceanic crust and sampling of abyssal glass from the ocean ridge system (Melson et al., 1977) have resulted in valuable characterization of the globe's most voluminous young volcanic products. Detailed studies of the Cayman trough

show, in addition to fresh glass at 5 km depths, a 1.8 km section through oceanic crust (CAYTROUGH, 1979), and Lonsdale (1977), surveying the East Pacific Rise at 3° S, finds broader, higher axial shield volcanoes than those at slower spreading ridge crests.

An ocean spreading center that has received much recent attention is that paralleling the equator just north of the Galapagos Islands. The marine geology of the ridge has been summarized by Johnson et al. (1976), the tectonic setting by Hey et al. (1978), and striking petrologic variations (apparently related to the Galapagos Hot Spot) by Byerly et al. (1976) and Schilling et al. (1976). A segment at 86° W, that has been studied in great detail, has revealed remarkable hot springs 17° C above ambient with extraordinary organisms inhabiting these thermal oases 2½ km below the surface. This setting has been recently reviewed by Corliss et al. (1979), and local volcanism has been described by van Andel and Ballard (1979). Additional dives are taking place at the time of this writing.

Hawaiian rift volcanism, as emphasised above, has close similarities to spreading center volcanism, and Fornari et al. (1978) have made useful observations of Kilauea's East Rift Zone from a submersible 2 km below the surface (and 70-80 km east of the caldera). Near-vertical "walls" of pillow lavas, to 30 m high, mark the ridge crest, and these have also been observed on spreading centers. It was not until early 1971 that the formation of pillow lavas was first observed, by divers off Hawaii (Moore, 1975), and subsequent work by Moore and co-workers, de Witt and Stern (1978), and others has greatly increased understanding of what must be the most abundant volcanic rock on earth.

Ocean islands, hot spots, & intraplate volcanism

Understanding of oceanic island growth has been advanced by the concept of mantle hot spots, relatively fixed with respect to each other, feeding surface volcanoes through the overriding crustal plate to form island/seamount chains or aseismic ridges. Hawaii, and the Hawaiian-Emporer chain, have been emphasised in the development of this concept in a series of papers by E. D. Jackson, H. R. Shaw, G. B. Dalrymple, and co-workers. Hot spots closer to spreading centers have been studied by J.-G. Schilling and co-workers, P. R. Vogt, and others, with particular emphasis on their petrologic, trace element, and isotopic characteristics. More ancient chains have been investigated by Houghton et al. (1977), Duncan (1978), and others. In the South Pacific, however, problems in the progressive age relations of some chains (see Jarrard and Clague, 1976) led Bonatti et al. (1977) to propose the "hot line" concept: linear mantle upwelling producing broadly contemporaneous volcanism at several points along a line thousands of km long. Although mentioned here for their obvious bearing on oceanic volcanism, these investigations are more thoroughly reviewed in accompanying chapters on tectonics, petrology, and DSDP.

In addition to the work cited above, understanding of Hawaiian shield volcano growth has been advanced by Fiske and Jackson (1972) and Lipman (1979) emphasising the importance of rift development, and by S. C. Porter's Mauna Kea studies of a shield's final stages of growth. The development of steeper-sided Galapagos shields by circumferential venting (Simkin, 1972) rather than radial dike distension (Nordlie, 1973) has received support from Lonsdale and Spiess's (1979) work on similarly steep-sided volcanoes of the East Pacific Rise. Detailed deep tow studies show circumferential vents, calderas, and pit craters on two symmetrical volcanoes 35 km from the rise crest and 1½ km below the surface. Another valuable contribution to island growth studies is that of Batiza (1978) on a young island directly on the ridge crest in the Gulf of California. Additional comments on volcano growth are below under "explosive volcanism: characteristics and processes".

Explosive volcanism: products

The recent volcanological emphasis on the sea floor has resulted in extensive new information on the distribution of tephra from major explosive eruptions. Marine tephra coring programs by D. Ninkovich, N. D. Watkins, H. Sigurdsson, S. N. Carey, and others have sought and found widespread records of specific eruptions. The deeper sediment cores of DSDP have also been used to trace the eruptive history of major belts back millions of years. Important cautionary notes have been raised concerning the effects of bioturbation (Ninkovich and Ruddiman, 1977), plate motion (Ninkovich and Donn, 1976), and single-layer heterogeneity (Jezek, 1976). However, there seems to be substantial evidence that volcanism has been episodic on a global basis (Kennett et al., 1977, Vogt, 1979), as well as at major belts (e.g. McBirney et al., 1974, Scheidegger and Kulm, 1975, Scholl et al., 1976), and this observation is significant to the discussion of climate below. Valuable petrographic studies of marine tephra include Huang's (1976) explosivity index based on micro-features, Hein and Scholl's (1978) work on diagenesis, and the continuing investigation of sea-floor fragmental volcanic material by Honnorez and Kirst (1975).

Detailed tephra study has also been successful on land, and provides additional reason for caution in interpretation of far-traveled ash deposits. The Glacier Peak tephra of northern Washington, for example, has been separated into progressively more units (Lemke et al., 1975; Smith et al., 1977; Westgate and Evans, 1978; Porter, 1978) so that this prominent Early Holocene marker, once thought to represent a single explosive eruption, is now recognized as the product of as many as 9 distinct events over at least 1,000 years and with marked changes in magma composition during that time. The eruption leading to the formation of Crater Lake, Oregon, 6700 years ago is now known, by pollen studies in western Montana (Mehringer et al., 1977), to have taken place in the autumn with substantial tephra fall continuing for at least 3 years. Petrographic work on the products of terrestrial explosions includes that by Heiken (1974), Duffield et al. (1977), Sheridan and Ragan (1977), and the manual of tephrochronology by Steen-McIntyre (1977).

During the report period, nuees ardentes were photographed and timed in Alaska (Stith and Hobbs, 1977) and New Zealand (Nairn and Self, 1978). In Guatemala, Rose et al. (1976) described a 1973 nuee ardente from the growing dome at Santiaguito, and valuable sedimentologic studies were made on the deposits left by the 1974 nuees ardentes at Fuego (Davies et al., 1978). Notable recent pyroclastic flows were described from Alaska (Miller and Smith, 1977), Arizona (Moore and Wolfe, 1976), and California (Miller, 1978). Base surge deposits were described from Hawaii (Fisher, 1977; Swanson and Christiansen, 1973), California (Crowe and Fisher, 1973), Germany (Schmincke et al., 1973), and Mexico (Gutman, 1976). The April, 1977, formation of two new maars in Alaska is documented by Kienle et al. (1979) and others.

Major ash flows, however, have not taken place in historic time, and understanding of this important form of volcanism must come from careful geologic reconstruction of Cenozoic ash-flow tuffs such as those of the western U.S. Examples of these continuing studies include the work of Smith (1979), Hildreth (1979), Ekren and Byers (1976), Christiansen et al. (1977), and Steven and Lipman (1976).

Explosive volcanism: characteristics & processes

Explosive eruptions make up three-fourths of all historic eruptions and 97% of eruptions causing fatalities. Much effort, therefore, has gone into the study of this form of volcanism. Specific recent papers have dealt with eruptive ballistics (Chouet et al., 1974), clouds (Wilson et al., 1978; Settle, 1978), and noise (Woulf and McGetchin, 1976), while broader work on eruption dynamics includes that of Sparks (1978), Kieffer (1977), McBirney (1973), Self et al. (1979), and Bennett (1976). The concept of magma mixing has received considerable attention (e.g. Condie and Hayslip, 1975; Anderson, 1976; Sparks et al., 1977; Carey and Sigurdsson, 1978, Eichelberger, 1978; and Johnston, 1978) with the addition of basic magma to a strongly differentiated chamber being suggested as the triggering device of major explosive eruptions.

As with rift volcanism reviewed above, tectonism is an important influence on explosive volcanism at destructive plate margins. Different aspects of this influence are explored by Dickinson (1975), Fyfe and McBirney (1975), Berg and Sutton (1975), Marsh (1976, 1979), and Kay (1978). The work of M. J. Carr and R. E. Stoiber in Central America is particularly interesting in relating volcanic behavior to tectonic setting. Vogt (1974) has correlated volcano spacing with lithosphere thickness, Mohr and Wood (1976) have extended this to East Africa, and Heiken (1976) has discussed spacing of northern California volcanoes as a possible reflection of an underlying batholith. Wood (1979) has reviewed the growth of cinder cones, and Crowe et al. (1978) have emphasised the importance of intrusions in developing a composite volcano from a cinder cone. Pike (1978) has statistically analyzed all volcano morphologies with dimensions tabulated for 655 individuals.

Explosive volcanism: climate effects

Meteorological interest in the effects of major explosive eruptions has increased greatly in the 1970s with some assistance from the October, 1974, eruption of Volcan Fuego in Guatemala (Rose et al., 1978). Although it provided only 1/5th the material erupted by Mt. Agung in 1963, the largest explosive eruption of recent decades (Cadle et al., 1976), twilight glow was soon apparent (Meinel and Meinel, 1975; Volz, 1975) and atmospheric effects were measured by a variety of modern techniques including lidar (Hirono et al., 1977), ground-based spectrometry (Crafford, 1976; Rose, 1977), and balloon-borne instrumentation showing that sulfuric acid droplets dominated ash particulates in the volcanic aerosol (Hofmann and Rosen, 1977). Fifteen months later, Alaska's Augustine eruption (Kienle and Forbes, 1976) again offered the opportunity of tracking a cloud trajectory across the U.S. (Meinel et al., 1976) and flying through the cloud to measure its aerosol (Schell and Delany, 1976; Hobbs et al., 1977). The first extensive airborne analyses of volcanic clouds, however, were in early 1978 over small Central America eruptions, and this successful program formed the basis for a symposium on the subject (Cadle and Rose, 1978).

Apart from these direct observations, most investigations into the effect of widespread volcanic dust veils on climate have centered on the recent historic record and theoretical interpretations of it (Baldwin et al., 1976; Barbera and Self, 1978; Cadle et al., 1976; Hamner, 1977; Hoyt, 1978; Oliver, 1976; Roosen et al., 1976; Shaw, 1976; and Volz, 1975). Uncertainties in the data, both meteorological and volcanological, are large enough to keep many competing interpretations alive, but it seems certain that several major historic eruptions have indeed lowered global temperatures for the few years required for the fine aerosol to settle out (e.g. Mass and Schneider, 1977). The magnitude of the temperature drops, however, are not large when compared with normal variation in global temperature, and major explosive eruptions have been too infrequent during the last few centuries to have had a long-term effect on world climate. The geologic record, though, shows episodes of unusually vigorous global volcanism, and investigation of oceanic tephra layers by J. P. Kennett and co-workers suggests that such an increase in the Quaternary may have been a significant contributor to Pleistocene glaciation. However, other hypotheses for the causes of glaciation (e.g. Beaty, 1978) are also supported by increasing evidence, and the answer is most likely a complex interaction of many influences. Unfortunately for volcanology, analysis of the historic record has been clouded by some circular reasoning - gauging eruption magnitude by assumed meteorological effect and then using the correlation to demonstrate a volcanism-climate link. Detailed work on major historic explosive eruption is urgently needed.

Volcanic hazards, surveillance & prediction

During the last 8 years, an average of 2 eruptions per year have claimed lives, and only two of these have produced more than 10 fatalities (15-30 in the 1971 Villarrica eruption and 60-300 in the 1977 Nyiragongo eruption). However, an-

other 2 eruptions per year have led to evacuation of 1000 or more people, and a succession of events has focused increasing attention on volcanic hazards. In April, 1971, the venerable Etna Observatory was destroyed by lava (Guest and Skelhorn, 1973), and 6 months later a dome grew in the summit crater lake of St. Vincent's Soufriere volcano (Aspinall et al., 1973; Sigurdsson, 1977), reviving memories of its tragic 1902 eruption. In 1973 the eruption of Heimaey, Iceland (Thorarinsson et al., 1973) attracted global media coverage as over 300 buildings were destroyed and the islanders fought to control the lava flow (Williams and Moore, 1976). Increased thermal activity on Ecuador's Cotopaxi caused alarm in late 1975 and led to preparation of a valuable volcanic risk map (Miller et al., 1978), but this dangerous volcano did not erupt. Similar activity at Washington's Mt. Baker in early 1975 (Frank et al., 1977) reminded a broader public of the dangers posed by Cascades volcanoes, and Mauna Loa's summit eruption that July, its first in 25 years, raised the specter of a later flank eruption threatening major population centers on Hawaii (Lockwood et al., 1976). It was the West Indian volcano La Soufriere, however, that most clearly focused attention on volcanic hazard. In late 1976, increased thermal and seismic activity on Guadeloupe, combined with phreatic explosions, led to the evacuation of 74,000 residents of the volcano's lower slopes. No substantial eruption took place, and the citizens returned home after several months and great socioeconomic loss. Debate over the volcanologist's role in this affair (Allegre, 1976; Tazieff, 1977) has been acrimonious, but the issues raised (see editorial columns of the Journal of Volcanology and Geothermal Research for late 1978 and early 1979) are important, and we are fortunate that they are being raised by an event that did not cause fatalities.

Volcanoes commonly show individualistic behavior, and crises usually emphasise the value of cool-headed appraisal of hazards made long before the crisis atmosphere develops. This means careful attention to the deposits of the last several thousand years, the development of a chronology that helps attach probabilities to the likelihood of various events, and the designation of areas particularly vulnerable to hazards. This approach has been pursued by the U.S. Geological Survey team of D. F. Crandell, D. R. Mullineaux, J. F. Hyde, C. D. Miller, and co-workers, who have built highly valuable hazard assessments for many Cascade volcanoes, and by M. J. Roobol and A. L. Smith in the West Indies. It is the good records of recent historic eruptions, however, that give valuable clues to aid in the interpretation of premonitory events. These clues, plus a knowledge of the breadth of historic volcanism, are important elements to the volcanologist who must assess the seriousness of irregular activity at a specific volcano. The International Association of Volcanology and Chemistry of the Earth's Interior (IAVCEI) has met the need for summaries of historic volcanism by a series of regional Catalogs, a world list of dangerous volcanoes (Shimozuru, 1974), and tables of post-Miocene volcanic centers (for U.S. volcano lists, see Smith and Soule, 1975, and Smith et al., 1978). Updating of these catalogs has come from the Volcanological Society of Japan, from the Smithsonian Center for Short-lived Phenomena (1968 to 1975), and from its Smithsonian successor, the Scientific Event Alert Network (SEAN). Data from all these sources have been compiled by the Smithsonian Institution into a data bank of historic volcanism from which tabular summaries have been extracted to aid in regional, historical, or behavioral volcanic studies (Simkin et al., 1979; Morris et al., 1979).

The historic record, however, spans only a few tens to thousands of years and, as Smith et al. (1978) point out, individual volcanoes may be intermittently active over 10 million years with repose periods as long as a hundred thousand years. Therefore, accurate identification of all potentially active volcanoes requires careful study of the late Cenozoic record. Toward this end, Luedke and Smith (1978, and following) have prepared a valuable series of maps covering Late Cenozoic volcanism in the western U.S.

While the past record of a volcano is important in evaluating its future behavior, careful surveillance is needed to guide these assessments when it threatens to erupt. These techniques have been reviewed by Decker (1973) and Simkin (1977) and chapters contributed to Civetta et al. (1974) provide more detail. Wider use of portable seismographs, surface deformation studies (by precision leveling and geodimeter), and gas monitoring techniques have been important recent advances in volcano surveillance. Although well-monitored volcanoes continue to surprise their monitors, the 1975 eruption of Plosky Tolbachik, Kamchatka's most important historic flank eruption (Fedotov et al., 1976), was so successfully predicted by P. I. Tokarev that television crews were on hand for its start. Recent discussion of prediction and risk include the Panel of Geophysical Prediction (1978), Macdonald (1975), Scheidegger (1975), and Warrick (1975). White and Haas (1975) and Burton et al. (1978) deal specifically with the oft-neglected sociological aspects of natural hazards.

Miscellaneous: Planets, Archeology, Publication, & Meetings

Recent studies of volcanism on other planets include giant shield volcanoes on Mars (Carr et al., 1977), a vigorous volcanic history on Mercury (Dzurisin, 1978), an 80 km caldera on Venus (Malin and Sanders, 1977), and current eruptions on one of the moons of Jupiter (see Smith et al., 1979). Lunar volcanism has been reviewed by Head (1975) and Taylor (1975). Somewhat closer to earth, satellite monitoring of terrestrial eruptions has been described by Heiken and Pitts (1975), Jayaweera et al. (1976), and Friedman et al. (1976).

Volcanological contributions to archeology include Hay's (1976) elegant tephrastratigraphy of Olduvai Gorge, Ninkovich et al. (1978) on the hominid-bearing tephra of Indonesia, and both Watkins et al. (1978) and Sparks and Sigurdsson (1978) on the famous "Minoan" eruption of Santorini. A full volume edited by Sheets and Grayson (1979) is devoted to the interrelationship of volcanoes and early man.

The new Journal of Volcanology and Geothermal Research began in 1976 under the editorship of A. R. McBirney, and has been a valuable (but expensive) medium for volcanological communication. Textbooks by U.S. workers that have appeared since the last IUGG review of volcanology include those by Bullard (1976), Carmichael et al. (1974), Green and Short (1971), Macdonald (1972), Oakeshott (1976), Wyllie (1976), and Yoder (1976). Westgate and Gold's book (1974) is particularly noteworthy for Steen-McIntyre and Wilcox's 67 page bibliography of U.S. tephrochronology, and several U.S. volcanologists contributed other sections to this valuable, cross-referenced bibliography. The February, 1973, issue of the Geological Society of America Bulletin should also be mentioned for its volcanological papers dedicated to Aaron Waters by his many outstanding students.

IAVCEI met in Moscow (8/71), Santiago (9/74), and Durham (8/77) with over 100 volcanological papers being presented at the latter meeting. In March, 1978, an informal association of North American volcanologists gathered at the Cordilleran Section meeting of the Geological Society of America in Tempe, Arizona. The meeting was well attended, 60 volcanological papers were presented, and many local field trips offered. The same arrangement is planned for the September 18-19, 1979, NW Region meeting of the American Geophysical Union in Bend, Oregon.

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References

To assist readers searching for references dealing with a specific region or setting, a letter code has been added at the lower right margin of each reference (see first page of text). No code follows references of global extent or general process orientation.

OCEAN BASINS

H = Hawaii

O = Other (islands & sea-floor)

CONTINENTS (and island arcs)

A = Alaska

W = Western U.S.

L = Latin America (& West Indies)

P = Pacific Margin (South & West)

E = E. Hemisphere (Europe, Africa, E. Indies)

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GEOTHERMAL SYSTEMS AND THEIR ENERGY RESOURCES

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Introduction

Geothermal systems have not been reviewed comprehensively in previous IUGG Quadrennial Reports, although thermal aspects of the shallow crust were considered by Diment (1975). Nearly all types of geothermal systems are reviewed in this report, with emphasis on U. S. systems that are most likely to be utilized as energy sources. Active volcanism and the generation and evolution of magma are not considered in detail.

Outstanding advances in geothermal resource utilization include: (1) Rapid growth in electrical generation from hydrothermal convection systems. All installed capacity in the U. S. to date (610 MW_e in February, 1979) is from the huge vapor-dominated system at The Geysers, California. Rapid expansion of capacity to ~1200 MW_e is expected by 1982; this includes at least 200 MW from several hot-water systems, now that the most serious technological, environmental, and Federal leasing problems seem to have been solved; (2) Increasing interest in low-temperature geothermal waters for non-electrical (direct) uses; (3) Recognition of the resource potential of the geopressured environment of the Gulf Coast for geothermal and methane energy.

Major advances in the understanding of geothermal systems have resulted from several new developments. (1) A variety of chemical and isotopic geothermometers and mixing models were developed and are being widely used for predicting subsurface temperatures of hydrothermal convection systems. (2) High $^3He/^4He$ ratios are now recognized as reliable indicators of mantle or deep crustal contributions to the hydrosphere and atmosphere. (3) Many geophysical techniques have been tested in exploration of hydrothermal convection systems and delineation of reservoir extent. (4) Teleseismic P-wave delays and attenuation of seismic energy imply huge volumes of magma under Yellowstone National Park (Wyoming), The Geysers - Clear Lake (California), and Long Valley (California). (5) The long duration and continuity indicated for submarine convection near spreading ridges has broad significance to continental systems. (6) Fossil geothermal systems (largely hydrothermal ore deposits) provide insight on temperatures, salinities, and origins of different waters that are likely to participate in active systems.

Geochemistry

Geochemical techniques for exploration and development of hydrothermal convection systems have been reviewed by White (1970), Truesdell (1976a), and Ellis and Mahon (1977). The chemical compositions of subsurface waters and the controlling reactions were reviewed by Barnes and Hem (1973). Truesdell and Singers (1974) developed a computer method to calculate the chemical compositions of reservoir fluids prior to production and decompression. Nehring and Truesdell (1978) documented the relation between hydrocarbon gases and the general nature of subsurface rocks of convection systems. The origin of some gases in geothermal fluids and the effect of production on gas contents were discussed by Truesdell and Nehring (1978).

Chemical geothermometers are useful for estimating subsurface temperatures from compositions of surface waters, if careful attention is given to the fundamental assumptions (Fournier and others, 1974). Recognized weaknesses in the Na/K geothermometer were partly rectified through development of the Na/K/Ca geothermometer (Fournier and Truesdell, 1973), which was further refined by correcting for Mg (Fournier and Potter, 1978). The quartz geothermometer was refined by better understanding of amorphous silica solubility (Fournier and Rowe, 1977). Mixing of hot and cold waters previously introduced errors in geothermometers, but development of mixing models and enthalpy-chloride relations now permit the extension of geothermometry to higher temperatures (Fournier and Truesdell, 1974; Truesdell and Fournier, 1976, 1977; Fournier, 1977a, 1977b, 1979; Fournier and others, 1979). A geothermometer based on the fractionation of ^{18}O between water and dissolved sulfate (McKenzie and Truesdell, 1977; Sakai, 1977) is now being widely applied (Brook and others, 1979). The effects of

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dissolved salts and steam loss or gain on isotopic composition of water have also been considered (Truesdell, 1974; Truesdell and others, 1977).

Light stable isotopes are widely used as tracers of the origin of fresh and altered rocks and of fluids (Taylor, 1975). The dominant source of water in most active geothermal systems (excluding submarine systems) is meteoric, with some exceptions noted by White and others (1973). Abundant ^{3}He relative to ^{4}He in geothermal fluids reliably indicates a mantle or deep crustal contribution (Craig and others, 1975; Craig and Lupton, 1976; Lupton and others, 1976, 1977a, 1977b; Craig and others, 1978; Jenkins and others, 1978). Low $^{3}He/^{4}He$ ratios characterize fluids from shallow crustal environments where ^{4}He is generated from U-Th series decay; the atmosphere and meteoric waters have intermediate ratios.

Geophysics

Geophysical methods in exploration and research of geothermal systems were reviewed by Combs and Muffler (1973) and Combs (1976). Major growth in applying geophysics to U. S. systems has occurred since the early 1970's.

In general, the most successful techniques for defining drilling targets are directly related to temperature. These include direct temperature measurements in drillholes as well as all electrical resistivity techniques, but the latter are also strongly affected by porosity and salinity of pore fluids (Moskowitz and Norton, 1977). Thermal infrared methods (Marsh and others, 1976; England and Johnson, 1976; Del Grande, 1976) are responsive to surface temperatures and other non-geothermal noise, which commonly exceed the earth's natural heat flow by three orders of magnitude. Thermal model studies involving three or more samples per diurnal cycle greatly reduce non-geothermal effects (Watson, 1974) and may have future applications. Thermal inertia of the earth's surface can be used in geologic mapping by modeling multiple radiation temperature measurements through a diurnal cycle (Kahle, 1977).

Seismic noise surveys initially seemed promising in recognizing and defining geothermal reservoirs, but are commonly ambiguous and difficult to interpret (Iyer and Hitchcock, 1976a; Whiteford, 1976). Microearthquake surveys of geothermal areas seem certain to yield useful and diagnostic information in natural heating and cooling environments and for production-induced changes (Knapp and Knight, 1977; Gilpin and Lee, 1977; Bufe and others, in press).

The large young silicic volcanic systems are becoming better understood through study of teleseismic P-wave delays (Iyer, 1975a, 1975b; Steeples and Iyer, 1976a). The Yellowstone anomaly is especially impressive in its magnitude and depth range (near-surface area ~40 x 80 km extending down greater than 200 km). Magnetotelluric methods are being used increasingly to recognize deep crustal layers with low electrical resistivities, useful in regional geothermal assessments (Hermance and others, 1976; Stanley and others, 1977).

All of these and other techniques have been applied to specific systems, cited in later sections.

Igneous Systems and Associated Hydrothermal Convection

Young silicic igneous sytems were evaluated as present thermal anomalies by Smith and Shaw (1975, 1979). Most high-temperature hydrothermal convection systems of the U. S. (Renner and others, 1975; Brook and others, 1979) are associated with young silicic volcanic systems, but many other convection systems occur in regions of high conductive heat flow with no clear igneous affiliations. The relation between cooling igneous bodies and hydrothermal convection has been modeled by numerical simulation (Cathles, 1977; Norton, 1977, 1978; Norton and Knight, 1977; Peck and others, 1977; Shaw and others, 1977). Lister (1974, 1976) presented a conceptual model of the downward penetration of water into hot rocks by a process of cooling and cracking.

Most hydrothermal convection systems are dominated by liquid water, but a few have subsurface reservoirs dominated by vapor (White, Muffler, and Truesdell, 1971). Experimental studies of two-phase hydrothermal convection in porous media were made by Sondergeld and Turcotte (1977). Most exploration and research efforts have focused on the large high-temperature systems.

Yellowstone National Park, Wyoming

Yellowstone National Park contains a huge natural igneous-centered system undisturbed by exploitation (Keefer, 1971; Eaton and others, 1975), with enormous convective and conductive heat flow and total stored heat (Renner and others, 1975; Fournier and others, 1976; Morgan and others, 1976, 1977; Lachenbruch and Sass, 1977, p. 649; Brook and others, 1979). Chemical and isotopic geothermometers and mixing models indicate subsurface temperatures as high as 337°C (Fournier, 1979) and 370°C (Truesdell, 1976a). Research drillholes provided depth-temperature-pressure relations (White and others, 1975) and better understanding of near-surface conductive heat flow (White, 1978). Drill cores permitted study of hydrothermal alteration and chemical self-sealing (Keith and Muffler, 1978; Keith and others, 1978). Physical data from these drillholes clarified interrelations of geysers and hot springs (Marler and White, 1975), vapor-dominated and hot-water convection systems (White and others, 1971; Zohdy and others, 1973), and hydrothermal explosions (Muffler and others, 1971), including the largest yet recognized (Richmond, 1976; Wold and others, 1977). Soils and spring deposits of thermal areas are high in mercury, but the anomalies extend outward only a few hundred meters from discharging thermal fluids (Phelps and Buseck, 1978). Studies in and around Yellowstone Lake clarified late Pleistocene and recent history (Richmond, 1976; Otis and others, 1977).

A huge anomalous mass below the Yellowstone caldera with roots at least 200 km deep that extend far into the mantle is indicated by teleseismic P-wave delays (Iyer, 1975a, in press; Hadley and others, 1976). Yellowstone gases have anomalously high $^{3}He/^{4}He$ ratios, including the highest ratio yet recorded for continental samples (Craig and others, 1978). Earthquake epicenters

decrease in depth toward the caldera (Trimble and Smith, 1975; R. B. Smith and others, 1977). An M=6 earthquake near the rim of the caldera showed strong attenuation of seismic energy through the caldera, and aftershocks were limited to the upper 6 km (Pitt and others, 1979). The caldera is a major gravity low and has relatively low magnetic intensities (Eaton and others, 1975; R. B. Smith and others, 1977) and a shallow calculated Curie-point isotherm (Bhattacharyya and Leu, 1975). Magnetotelluric sounding indicated a deep conductive zone decreasing in depth from about 18 km in the Snake River Plain to about 5 km beneath the Yellowstone caldera (Stanley and others, 1977). These data indicate a huge, probably molten, near-surface mass about 40 x 80 km in area and a tapering root at least 200 km deep.

The Geysers - Clear Lake, California

The Geysers steam field is adjacent to the predominantly silicic, 0.01 to 2.1 m.y. old Clear Lake volcanic field (Hearn and others, 1976, in press; Donnelly and others, in press; Futa and others, in press). Active tectonism in the region is related to crustal plate movements (McLaughlin and Stanley, 1976; McLaughlin, in press). Teleseismic P-wave delays of about one second (Iyer and others, 1978, in press), the great attenuation of seismic energy (Young and Ward, in press), a large compound negative gravity anomaly (Isherwood, 1976, 1977, in press), and the absence of deep earthquake hypocenters relative to surrounding areas (Bufe and others, in press) are best interpreted as indicating a molten chamber about 14 km in diameter with its top about 7 km beneath the volcanic field and with a tapering root extending to the mantle. Geochemical studies (Goff and others, 1977; Thompson and others, in press) and gravity surveys (Harrington and Verosub, in press) imply that a distinct hot-water convection system to the northeast of The Geysers underlies the main volcanic field. Chemical analyses of gases from both the volcanic and steam fields do not indicate a magmatic origin for most of the gases (Nehring, in press; Brook, in press). Fault-controlled mercury mineralization is related to hydrothermal alteration of serpentinite (Ciancanelli, in press). Very high conductive heat flows and high, nearly linear thermal gradients at The Geysers confirm the dominance of conductive heat flow between the reservoir top and the surface (Urban and others, 1976). Seismic-reflection techniques tested at The Geysers may be useful in exploration for similar systems (Denlinger and Kovach, in press).

Long Valley, California

Long Valley, California, is a 700,000-year-old caldera with associated ash-flow tuffs, a resurgent dome, younger lava flows, and an extensive hot-water convection system (Bailey and others, 1976). Various chemical geothermometers indicate subsurface temperatures of 200° to 250°C (Mariner and Willey, 1976; Sorey and Lewis, 1976; Brook and others, 1979); mixing models and enthalpy-chloride relations predict 282° ± 10°C (Fournier and others, 1979). The near-surface hydrothermal regime has been studied by heat-flow holes less than 300 m deep (Lachenbruch and others, 1976a). A generalized conceptual and mathematical model of heat and fluid flow was developed by Sorey and others (1978). The caldera structure was studied by gravity and magnetic methods (Kane and others, 1976; Williams and others, 1977) and seismic refraction (Hill, 1976). Deep electrical resistivity measurements (Stanley and others, 1976) indicate fault-controlled hydrothermal activity, but a significant hot-water reservoir less than 2 km deep was not clearly defined. Microearthquakes within the caldera are relatively scarce (Steeples and Pitt, 1976). A deep residual magma chamber beneath the western part of the caldera is indicated by thermal models (Lachenbruch and others, 1976a, 1976b) and teleseismic P-wave delays (Steeples and Iyer, 1976b). An exploratory well 2110 m deep was drilled east of the resurgent dome; the lower 1410 m was entirely in ash-flow tuffs that accompanied caldera collapse (Smith and Rex, 1977). Temperatures are too low for generation of electricity, but the resurgent dome is still an attractive drilling target. Shallow thermal gradients, seismic noise (Iyer and Hitchcock, 1976b), self-potential (Anderson and Johnson, 1976), and audio-magnetotelluric (Hoover and others, 1976, 1978) techniques were found to be unreliable in assessing the deep geothermal resources.

Salton Sea - Imperial Valley, California

The structural trough of Imperial Valley-Gulf of California formed by rifting of the North American plate; the continental crust is being thinned by extension, and conductive heat flows are high (Elders and others, 1972). At least five convection systems related to the very high conductive heat flow are identified with characteristic temperatures near 160°C to 250°C (Brook and others, 1979); a sixth system has been suggested (Harthill, 1978). The volcanic-centered convection systems of Salton Sea (Robinson and others, 1976) and Cerro Prieto, Mexico (Truesdell, 1976a) have temperatures near 350°C.

The Salton Sea system is remarkable for its extreme temperatures, salinity (~26% in situ), high metal contents, and recent exploitation rate. The reservoir fluids are not well mixed; the brines vary in ^{18}O by at least 4‰ (Olson, 1976). The thermodynamic properties of brines (Potter and others, 1975; Haas, 1976a, 1976b; Potter and Brown, 1977; Potter and Haas, 1978) differ greatly from dilute waters, with important consequences. Swarms of shallow microearthquakes occur in the geothermal system to depths of ~3.5 km, probably with aseismic creep in deeper parts (Gilpin and Lee, 1977; Hill, 1977). Shallow temperature holes seldom extrapolate to deeper reservoir temperatures (Lee, 1976).

The East Mesa field, now being actively developed, is a moderate-temperature convection system (~180°C) with no surface manifestations. Geophysical results were reviewed by Combs and Muffler (1973) and Swanberg (1976). Temperature and heat-flow measurements indicate that hydrologic effects extend at least to 150 m (Urban and others, 1978). A seismic noise survey (Iyer, 1975b) was dominated by cultural noise and did not support an earlier survey. The hot anomalous mass attenuates high-frequency P-waves, and the source

of the heat is deeper than 2 km (Combs and Jarzabeck, 1978). In the past, the system was hotter and more saline than now (Hoagland and Elders, 1977).

The nearby Heber field, also being actively developed, is nearly circular in area (≈20 km^2), with a maximum measured temperature of 182°C (Tansev and Wasserman, 1978). Other industry-generated data are not yet released. Even less is available for the Brawley field, which may be a southern extension of the Salton Sea field (Brook and others, 1979). Brawley's earthquake swarms (Weaver and Hill, 1978) may be related to local crustal spreading and intrusion of dikes at depth.

U. S. scientists have cooperated extensively with Mexico in studying the nearby Cerro Prieto field (most U. S. work not yet formally published). Temperatures range up to 350°C and salinity to 20,000 ppm (Reed, 1976). Hydrothermal mineral zonation (Hoagland, 1978), isotopic geochemistry (Olson and Elders, 1978), and practical applications of these studies (Elders and others, 1978) have been summarized.

Other Volcanic-centered Systems

The Coso geothermal area lies within the 40,000 to 4,000,000-year-old Coso volcanic field at the western margin of the Basin and Range Province adjacent to the southern end of the Sierra Nevada (Duffield and others, 1979). Active fumaroles are associated with Quaternary faulting (Roquemore, 1979) at the eastern margin of a young field of rhyolite domes and flows, partly surrounded by coeval basaltic vents (Bacon and others, 1979). The geothermal area is characterized by high conductive heat flow (Combs, 1979), low apparent resistivity (Jackson and O'Donnell, 1979; Towle, 1979), and high seismic activity (Combs and Rotstein, 1976; Walter and Weaver, 1979; Weaver and Walter, 1979). Chemical and isotope analyses of fluids recovered from two bore holes indicate a hot-water geothermal system with temperatures of 205 to 240°C (Fournier and others, 1979). Circulation of geothermal fluids is controlled by fractures that allow groundwater access to rock probably heated by underlying silicic magma (Duffield and others, 1979). Shallow magma has not been detected at Coso by aeromagnetic and gravity surveys (Plouff and Isherwood, 1979). However, teleseismic P-wave delay studies (Reasenberg and others, 1979) and other data are consistent with a relatively small, deep (greater than or equal to 10 km), silicic magma reservoir presumably sustained by basaltic magma responding to crustal extension (Weaver and Hill, 1978; Bacon and others, 1979).

A 1,262-m-deep hole was drilled in 1973 in the summit caldera of Kilauea Volcano, Hawaii, where a hot-water convection system overlies a magma chamber (Zablocki and others, 1974). The hole was sited in part on an electromagnetic sounding (Jackson and Keller, 1972) and a self-potential survey (Zablocki, 1976, 1978). Self-potential data also strongly influenced the siting of a geothermal test well at Kapoho on Kilauea's East Rift, where a hot-water system of high temperature (up to 358°C), modest salinity, and relatively low permeability has been discovered (Chen and others, 1978). Kilauea Iki was partly filled with a lava lake during Kilauea's 1959 eruption, providing exceptional opportunities for studying a cooling magma body (Wright and Peck, 1978) and testing feasibility of extracting energy directly from magma (Colp and Okamura, 1978).

The Valles caldera of New Mexico contains a hydrothermal convection system beneath an area of at least 130 km^2, with depths exceeding 2 km and temperatures generally near 260°C, but ranging to 330°C (Dondanville, 1978). Experiments in extracting thermal energy from hot impermeable rocks are being carried on a few kilometers west of the caldera, where the thermal gradient is about 65°C/km (M. C. Smith and others, 1976; Smith, 1978). A deep, electrically-conductive layer underlies the caldera area (Jiracek and others, 1976), which is on the west side of the Rio Grande rift near its northern end. To the south, the rift is characterized by high heat flow (Decker and Smithson, 1975; Reiter and others, 1975; Edwards and others, 1977) and other geophysical anomalies (Cordell, 1978). The conducting layer in the rift near Socorro is 18 to 20 km deep (Chapin and others, 1977) and is interpreted as magma, in part from response to microearthquakes (Sanford and others, 1977).

The Roosevelt geothermal area of Utah is near the northeastern edge of the Basin and Range Province and is associated with young silicic extrusions 0.5 to 0.8 m.y. old (Lipman and others, 1978). Many geologic, geophysical, and geochemical techniques have been applied to this hot-water system (Ward and others, 1978); dipole-dipole resistivity survey and a heat-flow survey in holes from 40 to 200 m deep were especially useful in defining the subsurface reservoir (≈20 km^2 in area), where temperatures are near 260°C (Brook and others, 1979).

Steamboat Springs, Nevada, has been studied extensively in the past; near-surface acid alteration was studied recently (Schoen and others, 1974). The complex history of activity started at least 2.5 m.y. ago, and activity was perhaps most intense 1.1 m.y. ago (Silberman and others, in press).

Submarine Hydrothermal Convection Systems

Studies of submarine convection systems developed from discoveries of the hot Red Sea metalliferous brines, from concepts of plate tectonics, and especially from anomalous measured vs. computed conductive heat flows near spreading ridges. Only the very recent work by U. S. scientists is emphasized here. Three active hydrothermal fields had been found near ocean spreading centers by 1977 (Rona and Lowell, 1978): (1) Red Sea hot brines; earlier work was reviewed by Shanks and Bischoff (1977); (2) the so-called TAG field of the mid-Atlantic Ridge crest near 26°N latitude (Rona, 1976; Rona and others, 1976; Scott and others, 1976); and (3) the Galapagos spreading axis and the related Mounds field 18 to 25 km south of the axis (Williams and others, 1974; Lonsdale, 1977; Corliss and others, 1978, 1979).

In the TAG field, nearly pure hydrothermal Mn crusts form rapidly near spreading centers and are followed by slowly-deposited Fe-Mn crusts (Scott and others, 1976); the early activity starts (or becomes obvious) in 0.4-m.y.-old basalts and

continues vigorously for approximately 0.3 m.y.; decreasing Mn-Fe deposition occurs for another 0.4 m.y. In the Galapagos axis and Mounds field, convection has probably been continuous and still persists in crust at least 0.7 m.y. old. Thermal-stress cracking in the oceanic lithosphere may progress downward with time and distance from spreading ridges (Epp and Suyenaga, 1978), perhaps continuing even in basalts as old as 100 m.y. Some studies support large scale convection of seawater without specifically identified thermal discharge (Dymond and Veeh, 1975; Bonatti and others, 1976a, 1976b; Bischoff and Rosenbauer, 1977; Bonatti, 1978; Humphris and Thompson, 1978a, 1978b). Lowell (1975) emphasized the relation between convective flow rate and fracture width; a fracture only 1 mm wide could discharge convective heat at roughly 200 times conductive, but with no thermal anomaly detected in adjacent seawater. Hydrothermal activity with metal deposition is occurring below sea level off the west coast of Baja California (Vidal and others, 1978). Basalt-seawater interaction experiments have documented extensive chemical exchange; water-rock ratios and temperatures affect pH and specific chemical changes (Hajash, 1975; Seyfried and Bischoff, 1977; Bischoff and Seyfried, 1978). Experimental rhyolite-seawater interaction relates to Kuroko-type base-metal deposits (Dickson, 1977; see below). Observed chemical gains and losses in oceanic basalts at both high and low temperatures were compared by Thompson and Humphris (1977). The thermal and geochemical consequences and required flow rates of such extensive convection is now becoming evident (Williams and others, 1974; Wolery and Sleep, 1976; Sleep and Wolery, 1978; Corliss and others, 1979).

Anomalously high ^3He concentrations, first measured near ocean spreading ridges, constitute a much-needed tracer for identifying fluids with mantle or deep crustal components (geochemistry). ^3He is being utilized to estimate hydrothermal heat flux and oceanic gains and losses of individual constituents (Corliss and others, 1979); these estimates may be seriously in error if spreading-ridge volcanism discharges abundant CO_2-rich vapor phase with ^3He, even at considerable depths.

Conductive Regimes and Associated Hydrothermal Convection Systems

Much thermal energy is transported in the upper crust by conduction (Diment and others, 1975). Conductive heat flow varies on a regional scale with large tectonically active areas of the western U. S. having high heat flow (Lachenbruch and Sass, 1977; Blackwell, 1978; Sass and Lachenbruch, 1979). Hydrothermal convection not directly associated with igneous systems can be sustained by regional conductive heat flow transferred to deeply circulating groundwater along fault planes and fractures.

The Basin and Range Province, covering Nevada and parts of adjoining states, is an area of extensional tectonics and localized Cenozoic volcanism, with numerous hydrothermal convection systems and thermal springs (Brook and others, 1979; Sammel, 1979). Conductive heat flow in this region is very high and variable; the "Battle Mountain High," extending across north-central Nevada and the Rio Grande rift in New Mexico and southern Colorado are subregions of exceptionally high heat flow. Lachenbruch and Sass (1978) suggest that these variations in heat flow result from differences in the extensional strain rate of the lithosphere (with corresponding variations in the vertical transfer of heat from the mantle into the deep crust by solid and molten phases) rather than anomalous conductive heat flow from the asthenosphere.

The Gerlach-Hualapai Flat area (1300 km^2) of northwest Nevada lies within the Battle Mountain High and is representative of Basin and Range geothermal systems without associated volcanism (the youngest volcanism is approximately 23 m.y.). Intermontaine basins with up to 2 km of thermally-insulating sedimentary fill and fractured bedrock contain 175-200°C fluids at depths of 2 to 3 km (Anderson, 1978; Grose, 1978; Grose and Sperandio, 1978; Keller and others, 1978a). This may be the most extensively studied area of high temperatures related to regional conductive heat flow (>2-1/2 HFU) and thermally-insulating cover. Geophysical studies include electrical exploration (Morris, 1978; Pires, 1978; Zeisloft and Keller, 1978; Keller and others, 1978b; Rodriguez, 1978), shallow ground temperatures (Crewdson, 1978a), thermal infrared (Lee, 1978), microearthquakes (Kumamoto, 1978), seismic reflection (Callaway, 1978) and gravity (Crewdson, 1978b).

The Raft River Valley near the southern edge of the Snake River Plain in southeast Idaho has relatively high heat flow and a moderate-temperature (≈150°C) hydrothermal system. Geophysical and other techniques and drilling have indicated that water, circulating deeply in bedrock fracture zones, is heated in a regional conductive environment, spreading laterally in basin sediments (Brott and others, 1976; Hoover and Long, 1976; Williams and others, 1976; Mabey and others, 1978; Brook and others, 1979). The regional thermal anomaly may be related to a low-resistivity layer at ≈7 km depth (Stanley and others, 1977) that extends northeast under the Snake River Plain to Yellowstone National Park, Wyoming.

Conductive heat flow is higher along the margins of the Snake River Plain than in the center; in the eastern plain this is due to disturbance by shallow hydrologic conditions (Brott and others, 1976). Discharge of thermal waters occurs primarily along the margins of the plain, but the size of individual reservoirs is not well known (Brook and others, 1979). Thermal models by Brott and others (1978) suggest the heat-flow distribution of the plain may be related to thermal refraction by a low-conductivity sedimentary layer and to a large transient deep-crustal heat source related to the eastward progression of silicic volcanism.

A hydrothermal convection system with no surface manifestations was first indicated by heat-flow studies near Marysville, Montana (Blackwell and Baag, 1973; Blackwell and Morgan, 1976). High heat flows near Klamath Falls, Oregon, are influenced by local convection and do not represent heat flux at depth (Sass and Sammel, 1976). The geologic setting and chemistry of hot springs in west-central Alaska were summarized by Miller and others (1975).

Parts of the Gulf Coast are characterized by high conductive thermal gradients and geopressured pore fluids, as a result of sedimentary loading and retardation of fluid flow in sedimentary rocks (Papadopulos and others, 1975; Jones, 1976; Wallace and others, 1979). Chemical and isotopic data indicate evolution of the pore waters from original seawater (Kharaka and others, 1977a, 1977b, 1978a).

Fossil Geothermal Systems

Geothermal systems have formed hydrothermal ore deposits in the past which provide insights not yet available from active systems. Epithermal gold-silver deposits formed from relatively dilute waters dominated by local meteoric water; temperatures were near 200° to 250°C, and magma bodies provided the thermal energy and possibly some of the fluids (Taylor, 1973, 1974; O'Neil and Silberman, 1974; Silberman and others, 1976). This class of fossil systems has many similarities to active systems such as Wairakei and Broadlands, New Zealand, and Steamboat Springs and Yellowstone National Park, U. S. A. (White, 1974).

Some mercury deposits of California formed from mixtures of metamorphic, evolved connate, and meteoric water (White and others, 1973; White, 1974). The large Sulphur Bank mercury mine probably formed continuously over the past 34,000 years; significant mercury and some antimony are still being deposited today at temperatures of 80° to 150°C (Sims and White, in press). Other hot springs are also depositing small amounts of mercury (Dickson and Tunell, 1968).

Epithermal base-metal deposits formed dominantly from saline brines at temperatures near 250° to 320°C and at depths of less than several thousand meters. Meteoric water was dominant, especially in post-ore stages, but some "deep-seated" water is also indicated (Bethke and others, 1976; Barton and others, 1977; Casadevall and Ohmoto, 1977; Bethke and Rye, in press).

The Kuroko base-metal deposits of Japan were formed on or near the seafloor, intimately associated with silicic seafloor extrusions (extensive Japanese literature not reviewed). Seawater was dominant in the ore fluids, but meteoric and possibly magmatic waters were also involved (Ohmoto and Rye, 1974). Chemical precipitation on the seafloor was probably accompanied by diagenetic reconstitution and redistribution of constituents (Barton, 1978).

Porphyry copper and molybdenum deposits indicate pre-ore dominance by magmatic fluids of extreme salinity, followed by increasing proportions of meteoric water during ore and post-ore stages (Hall and others, 1974; Sheppard and Gustafson, 1976; Batchelder, 1977). Temperatures ranged downward from about 600°C. The heat and much fluid, sulfur, and metals were probably derived from underlying igneous sources, not the local porphyritic rocks.

The effects of isotopic exchange between meteoric water and igneous rocks are becoming widely recognized in fossil convection systems other than ore deposits (Taylor, 1974, 1977; Forester and Taylor, 1976; Magaritz and Taylor, 1976). Zones of strong ^{18}O depletion in rocks are narrower and more sharply defined than the broad zones of deuterium depletion. Muehlenbachs and Clayton (1976) recognized isotopic signatures of seawater convection in seafloor basalt. Igneous rocks deficient in ^{18}O have been explained by direct entry of meteoric water into molten magma and by magma engulfment of rocks previously depleted in ^{18}O by meteoric convection (Friedman and others, 1974; Muehlenbachs and others, 1974; Lipman and Friedman, 1975; Taylor, 1977).

Utilization

Present utilization of geothermal resources for electricity and direct use is restricted to hydrothermal convection systems, but the huge resources of geopressured reservoirs and hot impermeable rock are attractive for future use. Recent trends in exploration and development of convection systems in the western U. S. were summarized by Koenig and others (1976) and Rex (1979). Methods of assessing geothermal resources on a regional basis were outlined by Muffler and Cataldi (in press). The economic aspects of geothermal development were reviewed by Barr (1976), and legal and institutional problems by Anderson (1976). Many aspects of specific reservoirs, production technology, modeling, and engineering are included in Proceedings of Workshops on Geothermal Reservoir Engineering (Stanford University, 1975-8). Nathenson (1976) considered recovery and some other factors not treated elsewhere, and Armstead (1976a, 1976b) summarized papers on electrical generation and direct uses.

The resources of U. S. hydrothermal convection systems to a depth of 3 km and at temperatures >90°C have been assessed (Nathenson and Muffler, 1975; Renner and others, 1975; Muffler and Christiansen, 1978; Brook and others, 1979). The most recent estimates indicate that about 23,000 megawatts of electricity (MW_e) for 30 years may be obtainable from 215 identified systems greater than 150°C. Systems at temperatures of 90° to 150°C could produce 42 x 10^{18} joules of heat for direct uses. Sammel (1979) tabulated data on low-temperature (<90°C), shallow (<1 km) geothermal waters and indicated areas favorable for direct uses.

Present electrical generation from geothermal systems in the U. S. is still entirely from The Geysers, California, but production from hot-water fields is starting in 1979. Reservoir characteristics and performance of The Geysers field were considered by Chasteen (1976), Lipman and others (1977), Ramey (1976), and Ramey and Gringarten (1976). Ground subsidence, dominantly due to steam production, has been documented by precise land-leveling surveys (Lofgren, in press), and seismicity has increased in production areas (Bufe and others, in press). Isherwood (1977) reported a gravity decrease related to net mass produced that implies recharge into the reservoir is slight. A tritium tracer experiment indicated that at least 18% of injected steam condensate was revaporized to steam (Gulati and others, 1978).

Isotope geochemistry is becoming increasingly useful in reservoir studies (Truesdell and Frye, 1977). Radon enrichment in produced fluids may yield data on effectiveness of artificial fracturing techniques (Stoker and Kruger, 1976; Kruger and others, 1977).

Truesdell and White (1973) explained the thermodynamic and production characteristics of exploited vapor-dominated reservoirs. Bodvarsson (1974, 1976) and Nathenson (1975) presented physical models for the extraction of heat from hot-water systems by circulating fluids, and flow and production characteristics of flashing hot-water wells were analyzed by Nathenson (1974).

Environmental aspects of geothermal development were summarized by Armstead (1976c). Axtmann (1975) analyzed the environmental impact of a geothermal power plant in New Zealand, where precautions were initially ignored. Mercury emissions from two geothermal power plants were measured by Robertson and others (1977). The problems of injecting spent fluids into geothermal reservoirs were discussed by Lipmann and others (1977) and Messer and others (1978).

Geopressured pore waters in the northern Gulf of Mexico basin are potential sources of electricity, direct heat, and methane (Isokari and Knapp, 1976; Jones, 1976; Wilson and others, 1976; Randolph, 1977). Wallace and others (1979), using the recoverability analysis of Papadopulos and others (1975), estimated that 23,000 to 240,000 megawatts of electricity for 30 years might be obtained from thermal energy stored in pore fluids to depths of 6.86 km; the thermal energy equivalent of recoverable methane ranges from 158 x 10^{18} to 1640 x 10^{18} J. Injection of spent fluids could clog pore spaces by chemical precipitation (Kharaka and others, 1978b).

The concept of extracting thermal energy from "hot dry rock" (hot crystalline rock without sufficient fluid and permeability for natural hydrothermal convection) has received much attention. Scenarios call for artificially fracturing the rocks and establishing a confined circulation system between two wells (Gringarten and Witherspoon, 1973; Bodvarsson and Reistad, 1976; Hunsbedt and others, 1976; M. C. Smith and others, 1976; Smith, in press). Although a vast quantity of thermal energy is contained in crustal rocks at temperatures high enough for electrical generation, depths are commonly too great for near-future economic production; igneous-related systems with high thermal gradients provide attractive targets for "hot dry rock" technology (Muffler, 1979a). The feasibility of extracting energy directly from deep magma sources is also being studied (Colp, 1976; Colp and Brandvold, 1976), but the problems are formidable (Peck, 1975).

Important Open Questions, Applied and Basic

(1) Will hydrothermal convection systems that lack obvious surface expression be discovered? (2) Can better pre-drilling techniques be developed for defining reservoir extent, temperature, and permeability? (3) Will geopressured fluids become competitive energy alternatives in the near future? (4) Can all major environmental hazards of geothermal utilization be solved or ameliorated?

(1) Can geophysical techniques that have recognized large, deep magma chambers be further refined to identify small, shallow magma bodies? (2) Will suggested relations between fossil ore-generating convection systems and the roots of active convection systems be confirmed? (3) Can D/H and $^{18}O/^{16}O$ ratios be utilized to distinguish meteoric (cool) zones of recharge from the hot upflow zones (the focus of most interest, both in ore deposits and active systems)? (4) Will $^{3}He/^{4}He$ ratios become critical in distinguishing between volcanic-centered and regional conductive environments? (5) Are durations of continental igneous-centered convection systems limited to $\sim 10^{4}$ to 10^{5} years (indicated by present models of cooling plutons), or may durations be far longer, as suggested by submarine convection systems?

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GENESIS OF METALLIFEROUS ORE DEPOSITS

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Introduction

During the quadrennial period beginning in 1975, the major topic of interest regarding genesis of metallic mineral deposits has been the extent and consequences of fluid flow within the shallow earth crust. Although certain advances have been made in understanding formation of metallic minerals from the liquid (magmatic) state (cf., Irvine, 1975a; Naldrett and Watkinson, 1978), the most abundant harvest of information concerning metal genesis has been derived from studies focusing on sources, compositions, and physico-chemical characteristics of H_2O-rich fluids, the nature of their movement, and the processes responsible for removal and localization of the materials which they transport. The extent and importance of hydrothermal fluid circulation relating to the formation of mineral deposits has been predicted and reasonably documented by complementary field and laboratory analyses of fossil and active geothermal systems. The following brief discussion will attempt to provide an overview of research efforts originating, for the most part, from centers within the USA as well as a summary of results and insights obtained which contribute to our understanding of the generation of metallic mineral deposits.

H_2O-Rich Fluids and Their Movement

Fluids circulating in the earth's crust are derived from and participate in magmatic, metamorphic and meteoric processes. Fluids from each of these environments can be reasonably recognized, although not necessarily uniquely, using hydrogen and oxygen isotopic criteria (see review by O'Neil, this vol.). In addition to these fluid sources, another recently recognized and readily documented reservoir consists of moderately saline solutions from the oceans (Ohmoto, 1978; Shanks and Bischoff, 1977). Identification of generative processes as well as types and sources of fluids associated with mineral deposition has been made possible through use of temperature dependent mineral-H_2O isotope partition coefficients, and by extraction and analysis of ore-forming fluids trapped in minute structural defects in ore and gangue. For the most part, hydrogen and oxygen isotope characterization of fluids is deduced from the imprint they have left on rock-forming minerals. Regular decreases in δD and $\delta^{18}O$ of minerals and rocks have been recognized with increasing distance from intrusive centers, and such systematic patterns have been interpreted to represent either mixing of ore-forming fluids with groundwater, or widespread convective circulation of groundwaters about plutons (Taylor and Magaritz, 1977; Criss and Taylor, 1978). A characteristic inverted L-shaped pattern shown on a δD vs. $\delta^{18}O$ diagram by hydrogen and oxygen isotopes of feldspar and biotite has recently been ascertained by Taylor (1977) as a quantitative means of estimating minimum water-to-rock ratios in fossil geothermal systems.

Numerical simulation of convective fluid circulation in response to thermal anomalies has enabled quantification of heat and mass transfer associated with fluid flow about hot plutons. Such studies have shown that convective circulation provides for extensive redistribution of fluids in and about cooling magmas (Norton and Knight, 1977; Cathles, 1977; Norton, 1978; Parmentier and Spooner, 1978; Norton and Taylor, 1978), a suggestion which substantiates the stable isotope patterns described above. Predicted consequences of convective circulation in and around a fractured, cooling pluton are a rapid upward migration of steep thermal gradients (Cathles, op. cit.), and smoothing of thermal anomalies above the intrusive (Knight, 1977). This phenomena has been observed by means of fluid inclusion studies at Red Mountain, Arizona, where a temperature gradient of 70°C/km has been established over a 1.5km interval in pre-intrusive volcanic cover (Bodnar and Beane, 1977).

Convective circulation of hydrothermal fluids in response to thermal anomalies is most pronounced in rocks whose permeability is structurally enhanced by fracturing. Such conditions have long been observed to occur in conjunction with epizonal plutons, but within recent years similar settings have also been widely recognized in association with calderas (cf., Bethke et al., 1976; Lipman et al., 1976; Ohmoto, 1978), oceanic spreading centers (cf., Bonatti, 1975; Bonatti et al., 1976; Shanks and Bischoff, 1977; Corliss et al., 1978), intracontinental rifts (Van Alstine, 1976; Beane and Allmendinger, 1977; Weiblen et al., 1977; Sawkins, 1977), and plate boundaries (Titley and Heidrick, 1975; Mitchell and Garson, 1976; Gair and Slack, 1978). Convective circulation has also been caused by decay of radioactive materials in crystallized intrusives (Fehn and Cathles, 1976) and by heating of saline brine circulating at great depths in structural basins (Lange and Murray, 1976). Additionally, low temperature fluids flowing in weathering and diagenetic environments may be correlated empirically or inferentially with mobilization and deposition of metals under a variety of conditions (Armstrong and MacKevett, 1975; Cannon, 1976; Klein and Bricker, 1977; Adams et al., 1978; Titley, 1978; Zantop, 1978). Finally, metamorphic processes of varying intensity have been suggested as a means of initiating localization of materials originally dispersed through a pre-existing rock mass by inducing flow of hydrothermal fluids (Squiller and Sclar, 1976; Stein and Kish, 1978).

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Sources of Ore-Forming Materials

Although Norton (1978) indicates that convective flow about hot plutons is dominated by fluids from relatively high-permeability host rocks adjacent to and above the central intrusive, the question still remains of the relative importance of exogenous fluids or ones of magmatic parentage in the transport and deposition of ore minerals. Based on isotope studies in the Andes, Rye et al. (1975) indicate magmatic water was nearly always present at some stage in the development of hydrothermal deposits of Tertiary age. Burnham and Ohmoto (1978) discuss current concepts of orthomagmatic mineral deposits which originate by separation of a hydrothermal chloride-rich fluid transporting relatively large amounts of metals and sulfur from a crystallizing magma. Such an origin is advocated, for example, for K-silicate alteration and main-stage copper mineralization at the El Salvador porphyry copper deposit (Gustafson and Hunt, 1975; Sheppard and Gustafson, 1976). However, while experiments have shown that magmatic processes may proceed to generate ore-forming fluids, evidence for such fluids in hydrothermal mineral deposits is largely permissive. Cloke et al. (1978) feel they have recognized hypersaline magmatic fluids in inclusions, but little conclusive evidence exists to relate such fluids directly to ore genesis (cf., Nash, 1976). One of the reasons for this uncertainty is the fact that more than one type of fluid may be present and leave its isotopic and fluid inclusion signature during the protracted history of a given mineral deposit. Numerous fluid inclusion studies have defined two fluids as having been present in single hydrothermal ore deposits, one of which is commonly hypersaline (>30 wt. % NaCl equivalent) while the other is more dilute (cf., Nash, 1976; Bodnar and Beane, 1977; Kamilli and Ohmoto, 1977; Cloke et al., 1978). Inclusions showing diverse salinities within a single mineral deposit may show similar or different overall homogenization temperatures, and appear in either of the two possible chronologic sequences.

The source of metals and accompanying anions found in mineral deposits has been a subject of considerable debate for many years. Stable isotope systematics for sulfur and carbon permit use of anions of these elements in ore and gangue minerals to define their potential source rocks or regions. Among the sources suggested for sulfur and carbon in metalliferous deposits of hydrothermal origin are seawater (cf., Ripley, 1975; Shanks and Bischoff, 1975), marine evaporites (Beane and Allmendinger, 1977; Casadevall and Ohmoto, 1977), wallrock sulfides and carbonates (Trammel, 1975; Hagni and Gann, 1976; Rose, 1976), and a deep-seated, possibly magmatic source (cf., Field and Gustafson, 1976; Wetlaufer, 1978). Evidence is also emerging which indicates that assimilation or other chemical interaction of sulfur-bearing country rocks may have significant bearing on formation of metal sulfides from magmas (Naldrett and Watkinson, 1978; Ripley, 1978; Tyson and Chang, 1978). Both magmas and marine evaporites are compatible with generation of saline fluids associated with many ore deposits (see above discussion), as well as metals (Burnham and Ohmoto, 1978; Thiede and Cameron, 1978). The only metal which can be directly traced with isotopes is Pb, and to do this successfully, one must be able to interpret past isotopic abundances and concentrations of U-Th parents (Casadevall and Ohmoto, 1977; Stuckless and Nkomo, 1978). Rare earth element (REE) patterns and strontium isotope ratios serve as potential tracers for ore-forming materials (Flynn and Burnham, 1978; Drake, 1975; Farrell et al., 1978). For example, characteristic REE patterns in different ore types in a massive sulfide deposit have been used to define different wallrock sources for copper and lead+zinc (mafic- and rhyolitic-volcanic rocks, respectively) by Graf (1977).

Numerous experimental studies have been designed to investigate leaching of trace metals from shale (Long and Angino, 1977) and basalt (cf., Mottl and Seyfried, 1977; Mottl and Holland, 1978) using a variety of thermochemical conditions, water/rock ratios, and brine types. In the case of the former rock type, copper was found to be mobilized by potassium-rich brines, while lead and zinc were removed by calcic solutions. At temperatures $\geq$300°C reactions between seawater and basalts were found to produce a variety of alteration silicates including sodic plagioclase, actinolite, zeolites, quartz, talc and smectite which were accompanied variously by magnetite, hematite, pyrite, pyrrhotite and possibly chalcopyrite (Mottl and Holland, op. cit.; Hajash, 1977). The minerals produced in such experiments compare well with those observed in veins and stockworks found along the mid-Atlantic spreading center containing pyrite, chalcopyrite and sphalerite (Bonatti et al., 1976; Hajash, 1975; Humphris and Thompson, 1978). Interestingly, Robertson (1975) also reports similar sulfide minerals in vescicles and flow tops in andesites and basalts, respectively, on the Michigan peninsula. Comparable alteration silicates are also seen in the basalts, but the observed silicates there predate sulfides and comprise a regional metamorphic assemblage.

Environments of Transport and Deposition

Information concerning the physical and chemical character of mineralizing fluids may be derived by direct and indirect analysis of fluid inclusions and by calculations using mineral stability relations. Mineralization temperatures are obtained from fluid inclusion homogenization measurements using standardized procedures (see review by Roedder, 1976), from mineral-composition geothermometers, and by interpretation of invariant or divariant mineral assemblages. Freezing tests with dilute fluid inclusions provide information concerning gross salinities, and if daughter minerals are present in more concentrated inclusion fluids, identification of these provide definite evidence of appropriate chemical components within the aqueous phase. Two new analytical procedures have been introduced since 1975 which greatly facilitate identification of daughter minerals in fluid inclusions. Rosasco et al. (1975, 1976) employed laser-excited Raman spectroscopy to positively identify anhydrite in unopened fluid inclusions, and Metzger and coworkers (1977) succeeded in chemically analyzing daughter minerals in opened fluid inclusions using scanning electron microscopy which also provided excellent morphologic imagery of these product phases. In addition to these techniques which may be used only on saline inclusions, another new development makes use of the laser microprobe to vaporize inclusion fluids and obtain a partial chemical analyses of cation ratios in the fluids (Tsui et al., 1975). In a slightly different manner, Norman et al. (1976) used spectrometry to measure relative masses of H_2S and H_2O evolved by fluid inclusion decrepitation and thus obtained H_2S concentrations in fluids associated with sulfide mineralization. Studies have also coupled fluid inclusion crushing and leaching with gross fluid salinity measurements and mineral stability considerations to define chemical compositions of mineralizing solutions (Barton et al., 1977; Beane, 1977; Casadevall and Ohmoto, 1977).

It is a well-known fact that the capability of aqueous solutions to transport metals may be greatly enhanced by chemical association or complexing. Analyses of natural waters and fluid inclusions, and materials introduced into mineralized rocks provide the data bank of chemical species in solution. Experimental studies are necessary, however, to establish the degree to which various chemical species interact or associate. Using available data, various modes of transport have been proposed for iron (Lougheed and Mancuso, 1975; Chou and Eugster, 1977; Crerar et al., 1978), additional base and precious metals (Crerar and Barnes, 1976; Giordano and Barnes, 1976; Rose, 1976; Barnes et al., 1978), uranium (Capuano, 1977; Barnes et al., 1978; Langmuir, 1978; Romberger, 1978) and the alkali and alkali earth metals (Crerar and Barnes, 1976; Herr and Helz, 1978; Johnson and Pytkowicz, 1978).

Understanding of environments and controls of mineralization are facilitated by experimental studies of gangue and ore-mineral stability relations (cf., Montoya and Hemley, 1975; Burton and Taylor, 1976; Hsu, 1977; Luce et al., 1977; Myers and Gunter, 1978). Depositional mechanisms for metal-bearing minerals in nature are obtained in a variety of ways of diverse certainty. For example, textural observations and mineral stability considerations of sedimentary uranium and copper have received considerable attention recently (Nash, 1975; Tourtelot and Vine, 1976). Various studies indicate deposition by reduction (cf., Rawson, 1975; Rose, 1976; Capuano, 1977) and replacement (LaPoint, 1975; Trammell, 1975; Hagni and Gann, 1976; Rose, 1976). Numerical simulations provide predictions of depositional controls of ore minerals as a consequence of water-rock interaction (cf., Knight, 1977; Gerlach et al., 1975; Capuano, 1977). Such calculations can be now extended to 600°C and 5kbars pressure (Helgeson, 1978) using recently published data for minerals (Helgeson et al., 1978; Robie et al., 1978) and aqueous species (Helgeson and Kirkham, 1976). These calculations must then be tested for accuracy against the accumulating bank of a quantitative abundance and paragenetic data for mineral deposits (cf., Gustafson and Hunt, 1975; Reid, 1976; Einaudi, 1977; Brimhall, 1978). An excellent example of comparative analyses of numerical modeling and mineral abundance data is provided by Villas and Norton (1977).

Where Now?

The understanding of processes responsible for and associated with genesis of metallized rock systems will benefit from both laboratory and field studies. Critical experimental data should focus on replicating natural environments as much as possible. Emphasis should be placed on dynamic (flow-through) studies of water-rock interaction and should combine both ore and gangue mineral considerations. Attempts should also be made to examine fundamental gaps in our knowledge of the thermochemical behavior of minerals, solutions, and magmas, such as properties of salt-saturated liquids in the system $NaCl-H_2O$ at elevated temperatures and pressures. In the field, paragenetic relations, and detailed compositional and mass abundance data should be determined for both minerals and fluids in recognized ore deposits. These may then be compared with numerical models and/or active metallogenic and geothermal systems to interpret the mode of formation of the fossil systems. And finally, the most desirable strategy for both field and laboratory studies should focus, as excellently stated by Cathles (1978), "...on a scale that encompasses the entire formative system, not just the ore deposit."

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METEORITE RESEARCH

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Meteorites contain a record of events and processes in the three earliest stages of solar system history: (1) formation of the raw material that was to become the solar system; (2) processing of the condensable component of this material in a nebular disk that circled the protosun; and (3) processing of condensed material after it had accumulated into planetesimals of asteroidal dimension. To test our acumen, the record has been written in cryptic rather than plain language. Progress toward breaking the cipher, made in the U.S. during the period 1975-1978, is summarized below.

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Much of the record in meteorites is contained in patterns of isotope abundances. This particular field of research is admirably reviewed by Podosek [1978].

Pre-solar System Material

The simplest raw material for the solar system would be ancient, well-mixed, homogeneous interstellar matter. However, there is clear evidence by now that the material ancestral to our system did not have these properties. Isotopic anomalies in meteorites due to the decay of ^{129}I and ^{244}Pu (half-lives 16×10^6 and 82×10^6 yr, respectively) were discovered more than a decade ago. These nuclides must have been synthesized in supernovas and added to the solar system raw material shortly (relative to the geologic time scale) before the solar system was formed. More recently, evidence of the existence of ^{26}Al ($t_{\frac{1}{2}} \simeq 0.7 \times 10^6$ yr) and ^{107}Pd ($t_{\frac{1}{2}} = 6.5 \times 10^6$ yr) in condensed solar system material has drastically shortened the permissible interval between the last addition of newly synthesized nuclides and solar system formation [Lee et al., 1976, 1977a; Papanastassiou et al., 1977; Bradley et al., 1978; Hutcheon et al., 1978; Kelley and Wasserburg, 1978].

More controversial is the question of the presence in carbonaceous chondrites of a superheavy element ($Z > 112$), presumably short-lived, fission of which could account for the anomalous levels of heavy Xe isotopes in these meteorites. Isolation of a Cr- and C-rich mineral fraction in which this Xe component is enriched by ∿200x [Lewis et al, 1975; Anders et al., 1975; Lewis et al., 1978; see also next section] narrowed the search, but did not conclusively prove the existence of a superheavy element [e.g. Fraundorf et al., 1977]. A search for light rare earth isotope anomalies which should accompany Xe isotope anomalies introduced in the Cr-rich mineral fraction by superheavy element fission might resolve the question [Flynn and Loubet, 1977].

Thus the solar system raw material was not all ancient, and in the last decade discoveries of heterogeneities of Ne and O isotope compositions among the meteorites showed that it was not well mixed either. Most conspicuous is the variability of isotopic composition of O among meteorites. This is interpreted as due to incomplete mixing of two pre-solar system components in the nebula: "normal" (≃ terrestrial) oxygen, and ^{16}O-enriched oxygen [R.N. Clayton et al., 1977]. Two Ca,Al-rich inclusions from the Allende meteorite, dubbed C1 and EK 1-4-1, contain oxygens that are blends of "normal" O with ^{16}O-rich components that had been chemically fractionated before mixing [R.N. Clayton and Mayeda, 1977].

The two inclusions mentioned appear to be totally anomalous in their isotopic makeup relative to other known solar system materials. Anomalous ratios of stable isotopes of Si [R.N. Clayton et al., 1978; Yeh and Epstein, 1978], Ca [Lee et al, 1978], Mg [Wasserburg et al., 1977; Lee et al., 1977b], Sr [Papanastassiou and Wasserburg, 1978], Ba and Nd [McCulloch and Wasserburg, 1978a], and Sm [McCulloch and Wasserburg, 1978b] have been observed. Anomalous ratios of Hg isotopes have been reported in several unequilibrated chondrites [Jovanovic and Reed, 1976a, b].

A discrete Xe isotope component (enriched in masses 128-132), presumably sited in refractory phases in the Murchison carbonaceous chondrite and possibly generated by nucleosynthetic processes in pre-solar system red giant stars, has been reported by Srinivasan and Anders [1978].

These stable isotope anomalies are a record of complex migrations and intermingling of pre-solar system materials which are far from being understood. It must be kept in mind, however, that the anomalies constitute exceptions to a much more general state of the solar system materials we have access to (Earth, Moon, meteorites), which is an exceptional degree of isotopic homogeneity.

The evidence seems clear that one or more supernovas contributed freshly synthesized nuclides to the parent material of the solar system shortly before the latter came together. Cameron and Truran [1977] and Cameron and Cowan [1978] have attempted to rationalize the early solar system's stable isotope components and content of short-lived radionuclides in terms of the contamination of "normal" interstellar material by debris from a single supernova. They also suggest that the shock wave from the supernova triggered gravitational collapse of the interstellar cloud that was to produce the solar system.

Is it possible that some solid components of the chondrites condensed in the expanding envelope of one or more pre-solar system supernovas instead of in the solar nebula? Lattimer et al. [1978] and Falk et al. [1978] explore the possibility that Ca,Al-rich inclusions in carbonaceous chondrites had this origin, though it is uncertain that grains so formed could survive in the post-supernova environment. Boynton [1978b], however, points out that the high Ce content of practically all Ca,Al-rich inclusions is inconsistent with their condensation in the H_2-poor environment of a supernova. Anomalous inclusion C1, mentioned above, is a possible exception, being depleted in Ce.

One interpretation of the O and Ne isotope anomalies is that they were preserved in solid grains during the nebular and accretion stages of meteorite formation [e.g., R.N. Clayton, 1977a]. D.D. Clayton [1975, 1977a, b, c] has gone farther than this, arguing that isotope patterns attributed to decay of short-lived radionuclides also were established before solar system formation, in interstellar grains, and not disturbed by the process of solar system formation. This proposal is considered controversial, however; Drozd et al. [1977] have argued specifically for the presence of live ^{244}Pu, not merely ^{244}Pu fission products, in the early solar system.

As an alternative to multiple pre-solar system sources, Heymann and Dziczkaniec [1976] have proposed that irradiation of the nebular gases by MeV protons from the protosun produced the observed Mg and Ne isotopic anomalies. Similarly, Müller and Schaeffer [1978] have proposed that the anomalous Xe (and also Kr) ratios in carbonaceous chondrites, discussed above, were produced by fission induced by the bombardment of early solar system material by C, N, and O flare particles from the protosun. It appears unlikely that the first of these processes could have operated, however, without producing other isotopic anomalies that are not observed [D.D. Clayton, 1977d; D.D. Clayton et al., 1977a; Dwek, 1978].

Improved determinations of B (an x-process element) abundances in carbonaceous chondrites permit an estimation of the history of irratiation of pre-solar system materials by galactic cosmic rays [Weller et al., 1977, 1978].

Nebular Processes

For the most part cosomochemists have interpreted their observations in terms of a hot, integral solar nebula which at first vaporized pre-solar system dust it incorporated, then permitted the metallic and oxide vapors to recondense as the

nebula cooled. This nebula model, first advanced by A.G.W. Cameron fourteen years ago, has continued to be used in spite of the fact that Cameron himself [1978a, b, c] has disavowed it in favor of a nebula that is little heated by collapse and that promptly subdivides into protoplanetary masses as a result of gravitational instability. Wasson [1978] has summarized evidence that condensation in a hot nebula appears necessary to account for the properties of the meteorites.

The refractory Ca,Al-rich inclusions in Allende and other carbonaceous chondrites are generally considered to be the most compelling evidence that condensation from hot gases occurred in the early solar system. Inclusions are classified by several schemes (Table 1). Grossman [1975], Mason and Martin [1977], McSween [1977e], and Taylor and Mason [1978] summarize the petrography and compositions of these objects. The mineralogy of particular inclusions of exceptional interest is described by Fuchs and Blander [1977], Hutcheon [1977], Fuchs [1978], Haggerty [1978b], Davis et al., [1978], and Macdougall and Carlson [1978]; the trace element chemistry of classes of inclusions is developed by Grossman et al. [1977a, b], Nagasawa et al. [1977], and Grossman and Ganapathy [1976a, b]. Amoeboid olivine aggregates are discussed by Grossman and Steele [1976].

Exactly how the Ca,Al-rich inclusions formed is not yet understood, however. Three possibilities are currently advocated. (1) They are the result of condensation directly from vapor to solid, followed by grain aggregation and possibly metamorphism [e.g., Grossman et al., 1975; Ganapathy and Grossman, 1976; Allen and Grossman, 1978; Blander et al., 1978]. A cosmothermometer based on the valence state of Ti in inclusion minerals, developed by Haggerty [1978a], yields results consistent with vapor → solid condensation. Boynton [1978c] concludes from the depletion of the least volatile REE in some of these supposedly refractory condensates that they condensed from a nebular region already depleted in the most refractory elements by earlier episodes of condensation. (2) The igneous textures and REE partitioning among constituent minerals suggest that many inclusions have been molten at one time [Blander and Fuchs, 1975; Philpotts et al., 1975; Nagasawa et al., 1976; Nagasawa and Jahn, 1976]. (3) Refractory inclusions may be the residues after distillation during temperature rises rather than early condensations during epochs of cooling [Chou et al., 1976].

The mechanism of nebular condensation has been investigated both theoretically and experimentally. Wagner and Larimer [1978] are attempting to compute the stability of liquid as well as solid phases during condensation. De [1977] considers condensation from a system in which grain temperatures are consistently much lower than the embedding gas temperature, although Boynton [1975] has concluded that the REE patterns in Ca,Al-rich inclusions exclude such a mechanism. Experiments on the evaporation (by laser) and condensation of solids in a controlled environment are being carried out [Kothari and Stephens, 1977; Stephens and Kothari, 1978; Arnold, 1977]. Nucleation theory and experiments indicate to Donn [1978] and Day and Donn [1978] that condensation in the postulated nebula would produce submicroscopic amorphous particles, not the relatively coarse,

Table 1. High-temperature Components of Carbonaceous Chondrites

(1)	(2)	Principal minerals	REE pattern, relative to mean chondritic
Type A Ca,Al-rich inclusions	Group I	Melilite-rich; coarse-grained	unfractionated
Type B Ca,Al-rich inclusions	Group II	Spinel plus fassaite aggregates	fractionated
	Group III		unfractionated
Amoeboid olivine aggregates	Group IV	Olivine-rich chondrules and aggregates	unfractionated

(1) Original taxonomy of L. Grossman
(2) Mason and Martin [1977]

stiochiometrically correct minerals in chondrite inclusions.

Condensation of the major components of ordinary chondrites is more easily understood in systems where the (condensable elements)/(nebular gas) ratio has been enhanced by several orders of magnitude [Herndon and Suess, 1977; Wood and McSween, 1977]. Such a fractionation is not called for in the case of the enstatite chondrites [Herndon and Suess, 1976]. Attempts have been made to relate apparent condensation fractionation effects in the meteorites to positions of condensation in the nebula (chondrites: Wasson [1977b], Wasson and Kallemeyn [1978]; irons: Wasson and Wai [1976], Wai et al. [1978], Scott [1978c], Wai and Wasson, [1978]).

The fractionation of actinide elements and Pb during condensation of the chondrite components is discussed by Boynton [1978a] and Stapanian and Burnett [1978].

The basic nature of the temperature fractionation mechanism in the nebula has been debated by two groups. Wai and Wasson [1977] and Wasson [1977a] see a monotonically increasing element depletion with decreasing condensation temperature in chondrites, and postulate progressively less efficient condensation and/or accretion at lower temperatures. Anders [1977] sees several element groups, each with a characteristic depletion factor, and identifies these with discrete structural components in the chondrites that have had different thermal histories and are present in varying proportions (see for example Takahashi et al. [1978a]).

A component dubbed "mysterite," which is greatly enriched in the more volatile trace elements, has been isolated in several chondrites. This is believed to represent a late condensate from the nebula, which incorporated volatiles left behind by earlier epochs of chondrite condensation [Higuchi et al., 1977; Davis et al., 1977].

Chondrules are still an enigmatic component of chondritic meteorites. Petrographic and chemical studies of chondrules in particular meteorites were carried out by Grossman et al. [1978a, b], Lux et al. [1978], Gooding et al. [1978a], O'Nions et al. [1978], and Fredriksson et al. [1978].

Gooding et al. [1978b] report on the physical properties of chondrules. Blander et al. [1976] and McSween [1977d] argue for their origin as liquid condensates from the solar nebula; Dodd [1976, 1978a, b] believes they were formed by impact processes on a differentiated planetary surface. Snellenburg [1978] relates many of the variable properties of chondrules to differences in f_{O_2} of their environments of formation. Kerridge and Kieffer [1977] reject impact processes in a planetary regolith as the source of chondrules because of the absence of glassy agglutinates (analogous to those in lunar soils) in chondrites; however, Noonan et al. [1978] report the presence of such agglutinates in several chondrites. Kieffer [1975] proposes that chondrules were formed by impacts between small rocky objects orbiting in space, but Wilkening et al. [1978] find no evidence of charged-particle tracks under the surfaces of chondrules, such as would be produced by the solar wind if chondrules had a protracted independent existence in space.

The properties of carbonaceous chondrites have been collected into a comprehensive volume by Nagy [1975]. Carbonaceous chondrite matrices are discussed by McSween and Richardson [1977] and Kerridge [1977]. Formative processes in the C1 parent body (or bodies) are pictured by Richardson [1978] and Houseley [1978]. Phyllosilicate minerals, or semi-amorphous substances similar to phyllosilicates [Day, 1976], are the principal constituent of C1 and C2 chondrites. There is a growing feeling that this material was not formed by nebular condensation, but by hydrous alteration in the carbonaceous chondrite parent bodies [Kerridge, 1976; Bunch and Chang, 1978]. Magnetite in these meteorites may have had a similar origin [Herndon et al., 1975].

McSween [1977a] and Richardson and McSween [1978] present evidence that isolated olivine crystals in carbonaceous chondrites had an igneous origin, and are fragments of chondrules; Olsen and Grossman [1978] hold to their original view, that they are primary vapor→solid condensations from the nebula.

It has been found that most of the primordial noble gases in chondrites reside in a component comprising <0.5% of the host meteorite, which can be isolated by dissolution of the remainder of the meteorite in acids [Lewis et al., 1975; Alaerts et al., 1977; Srinivasan et al., 1977; Lewis et al., 1977]. Retentivity of this component is so great that gases are held during the metamorphism experienced by ordinary chondrites. The above authors further decompose this gas-rich component into "Q," a HNO_3-soluble fraction that contains most of the gases of planetary isotopic composition, plus an insoluble fraction that contains gases of anomalous isotopic composition, presumably of fission origin. The latter is the Cr- and C-rich fraction discussed in the first section of this article. Gros and Anders [1977] and Srinivasan et al. [1978] identify Q as a mixture of Fe,Ni- and Fe,Cr-sulfides. Frick and Chang [1977, 1978], Frick and Moniot [1977], and Reynolds et al. [1978], on the other hand, present evidence that both noble gas components-- planetary and anomalous-- are contained in thermally stable kerogen-type carbonaceous matter.

Hennecke and Manuel [1977] have found, in iron meteorites, noble gases with isotopic compositions complementary to those of the anomalous noble gas component mentioned above. They suggest that planetary noble gases are mixtures of these two end-members.

Macdougall and Kothari [1976] and Macdougall [1977] have measured fission track densities on crystal surfaces in C1 and C2 meteorites, and determined that the latter cannot have been as compactly aggregated as they are now for all geologic time. Compaction times $4.2 - 4.4 \times 10^9$ yr ago are derived.

Comprehensive examinations of the C3(V) and C3(O) chondrite subclasses were carried out by McSween [1977b, c]. McSween and King et al. [1978] see metamorphic effects in both subclasses.

The following groups of organic compounds were studied in carbonaceous chondrites: purines and triazines [Hayatsu et al., 1975]; amino acids [Pollock et al., 1975; Pereira et al., 1975; Cronin and Moore, 1976]; alcohols and carbonyl compounds [Jungclaus et al., 1976]; and organic polymers [Bandurski and Nagy, 1976; Hayatsu et al., 1977].

Parent Meteorite Planets

Major events that occurred in or on the parent meteorite planets were: metamorphism of the ordinary chondrites; melting and differentiation, which produced achondrites, irons, and stony-iron meteorites; and regolith production.

Heyse [1978] has related mineralogical properties of a variably metamorphosed suite of LL-group chondrites to positions in a parent planet. The effects of metamorphism on matrices of unequilibrated ordinary chondrites have been examined by Huss et al. [1978].

A major effort has been made to determine the mobility of trace elements in chondrites at metamorphic temperatures by means of laboratory experiments [Ikramuddin and Lipschutz, 1975; Ikramuddin et al., 1976; 1977a, b; Matza and Lipschutz, 1977, 1978; Bart et al., 1978]. Collateral studies of the mobility of C, S, and noble gases were made by Gibson [1976] and Herzog et al. [1978]. Comparison of residual element abundances with abundances in metamorphosed meteorites indicates to Lipschutz and Ikramuddin [1977] that trace element depletions in the enstatite chondrites are a metamorphic effect, while those in L-group chondrites were established during nebular condensation. Cripe and Larimer [1976] and Takahashi et al. [1978b], however, reject the idea that any chondrites suffered volatile element losses during metamorphism. Taylor et al. [1978] have criticized the metamorphism experiment for the dissimilarity of petrographic and mineralogic changes wrought, relative to those observed in naturally metamorphosed chondrites. A recently developed technique for observing the microdistribution of Bi in meteorites [Woolum et al., 1977, 1978] may help us better understand the migration of volatile trace elements during metamorphism.

Attention has recently fallen on the Shaw chondrite, which has been so severely heated as to be partially melted and differentiated [Dodd et al., 1975; Rambaldi and Larimer, 1976, 1977; Berkley et al., 1976]. Effects of late reheating (as by impact) on chondrites are reported by Fruland [1975] and Smith and Goldstein [1977].

Recent careful descriptive work has greatly enlarged our knowledge of achondrites and stony-irons, particularly the relatively rare subclasses.

Eucrites: petrographic and chemical descriptions are provided by Wilkening and Anders [1975], Steele and Smith [1976], Takeda et al. [1976], Harlow et al. [1977], Prinz et al. [1977], Duke [1978], and Garcia and Prinz [1978]. Eucrite chronology is discussed by Tatsumoto and Unruh [1975], Lugmair and Scheinin [1975, 1977], Unruh et al. [1977], and Hamet et al. [1978]. An experimental petrology investigation of eucrite compositions was carried out by Stolper [1977]. Hostetler and Drake [1978] and Walker et al. [1978a] comment on the kinetics of eucrite crystallization. The nature of the eucrite parent body is divined from element abundance considerations by Consolmagno and Drake [1977] and Morgan et al. [1978]. Its dimension is inferred from crystal settling rates by Walker et al. [1978b].

Howardites: Bunch [1975] and Hewins and Klein [1978] discuss petrography, and Huneke et al. [1977] discuss chronology of this subclass. The origin of howardites as polymict breccias of magmatically differentiated rock types is treated by Dymek et al. [1976], Bunch [1976], Fukuoka et al. [1977], and Mittlefehldt [1978].

Diogenites and Chassigny: Johnstown, a diogenite, is described by Floran et al. [1977]; Chassigny by Mason et al. [1975] and Floran et al. [1978].

Shergotty: McSween and Stolper [1978a] and Smith and Hervig [1978] describe this meteorite, which was shocked heavily enough $<\sim 165 \times 10^6$ yr ago to isotropize plagioclase and homogenize Sr isotope compositions [Nyquist et al., 1978]. Experimental petrology of this composition was investigated by Stolper and McSween [1978] and McSween and Stolper [1978b].

Nakhlites: members of this subclass are described by Bunch and Reid [1975] and Boctor et al. [1976]. Wasserburg and Papanastassiou [1976], Nakamura et al. [1977], and Bogard and Hussain [1977] concur on the young (1.3×10^9 yr) age of nakhlites. The igneous history of these meteorites is discussed by Reid and Bunch [1975].

Petrogenetic schemes relating all the above achondrite types, in various combinations, are presented by Stolper [1975], Fukuoka et al. [1977], and Stolper et al. [1978].

Consortia of investigators have reported on concerted studies of two particularly interesting achondrites: Angra dos Reis (Keil [1977] and contiguous articles), and the Kenna ureilite (Keil [1976] and contiguous articles). The genesis of ureilites is discussed by Higuchi et al. [1976] and Berkley et al. [1978].

Pallasites: descriptive surveys are presented by Buseck [1977] and Scott [1977a]. The relationship of pallasites to iron meteorites is addressed by Scott [1977c], pertinent planetary fractionation processes by Davis [1976], and the formation of pallasite textures by Scott [1977b]. Wood [1978a] asserts that the pallasite texture would not have been stable (while the metal fraction was still molten) in parent bodies of $>\sim 10$ km radius.

Mesosiderites: petrographic descriptions are provided by Weigand [1975], Nehru et al. [1978], and Floran [1978b]. Murthy et al. [1977, 1978] have obtained Rb/Sr and $^{40}Ar/^{39}Ar$ ages of the Estherville mesosiderite. Mittlefehldt [1977] and Simpson and Ahrens [1977] argue that mesosiderites are not as closely related to howardites as previously supposed. The origin of some mesosiderite textures via impact melting is expounded by Floran [1978a]. Estimates by several techniques of the cooling rates of mesosiderites [Kulpecz and Hewins, 1978; Crozaz, 1978] appear consistent with the extraordinarily slow rate ($\sim 0.1°C/10^6$ yr) derived from the Ni distribution in its metal alloys.

Lodran: this unique meteorite was studied by Bild and Wasson [1976], Fukuoka et al. [1978], and Prinz et al. [1978].

Bencubbin and other unusual metal-rich meteorites are described by Newsom and Drake [1977], Kallemeyn et al. [1978], and Bild [1975].

The classification and properties of subgroups of iron meteorites are summarized by Scott and Wasson [1975], and supplemented by Scott and Wasson [1976], Scott [1977d], and Scott [1978a]. Pertinent metallurgical processes are explored by Clarke and Goldstein [1976] and Lin et al. [1977]. Solid/liquid element partitioning in iron meteorite systems has been investigated by Kelley [1976], Bild and Drake [1978], and Goldstein and Friel [1978]. On the other hand vapor/condensate partitioning (i.e., nebular fractionation) is more likely to be responsible for compositional differences between the iron subgroups according to Scott [1978b]. New and improved techniques of estimating the cooling rates of iron meteorites have been developed by Moren and Goldstein [1976] and Randich and Goldstein [1978]. Whether or not Group IVA cooling rates are highly variable is debated by Willis and Wasson [1978a, b] and Moren and Goldstein [1978]. Bild [1977b], Wlotzka and Jarosewich [1977], Fukuoka and Schmitt [1978], and Niemeyer [1978] report on aspects of silicate inclusions in iron meteorites. The parent bodies and genesis of iron meteorites are discussed by Scott [1977e], Kelley et al. [1977], and Kracher [1978].

At least nine parent bodies are indicated for the meteorites on the basis of the discrete isotopic compositions of oxygen associated with various meteorite classes [R.N. Clayton et al. 1976; R.N. Clayton, 1977b; R.N. Clayton and Mayeda, 1978]. The parent bodies may still have been quite small (a few km) when most of the properties of their meteoritic substance were established [Wood, 1978b].

Uncertainties in the relationship between meteorites, asteroids, and comets are summarized by Delsemme [1977]. The apparent association between Apollo/Amor asteroids and stony meteorites is treated by Wetherill [1976, 1977, 1978] and Levin et al. [1976]. Anders [1975, 1978] argues that Apollo/Amor asteroids must be derived from the main asteroid belt, though the mechanism of orbital modification is still not well understood.

Photometric studies that allow particular asteroids and meteorite types to be matched with some confidence have been carried out by McCord and Chapman [1975a, b], Johnson et al. [1975], Zellner [1975], Gaffey [1976, 1978], Gaffey and McCord [1977], Zellner et al. [1977], Leake et al. [1978], and McFadden and Gaffey [1978]. Collisional models and other aspects of an asteroid belt source for the meteorites are examined by Chapman [1976, 1977].

Polymict brecciated meteorites are the products of mixing in parent-body regoliths. Numerous papers describing exotic clasts (often carbonaceous) in these breccias have been published [e.g., Wilkening, 1976, 1977; Fodor and Keil, 1976; Noonan and Nelen, 1976; Bild, 1977a]. Impacts and regolith evolution on asteroids, and their relationship to brecciated meteorites, are discussed by Anders [1975, 1978], Chapman [1978], and Housen et al. [1978].

Of the many topics that proved difficult to fit into the chronologic framework of this review, two cannot be passed over. First, Brownlee et al. [1977] found it possible to collect interplanetary dust from the stratosphere by scooping air into special collectors during long-duration flights of U2 aircraft. The particles collected are of generally cosmic composition, but different morphologically from any known component of meteorites. Their content of solar wind ^4He confirms their extraterrestrial source [Rajan et al., 1977]. Presumably they are cometary dust particles. As such, they constitute a new source of extraterrestrial material.

Second, Antarctica has turned out to be a bountiful source of new meteorites. Meteorites that fall on the ice cap are preserved for long periods of time under very clean conditions, as the glacial flow carries they toward the continental margins. If the host ice encounters a barrier it cannot pass, it tends to dissipate by ablation, leaving an accumulation of meteorites on the surface [Cassidy et al., 1977; Olsen et al., 1978]. Collecting expeditions are now being sent to the Antarctic on a regular basis by the U.S. and Japan. Finds by the U.S. are described and stored under clean conditions at the NASA Johnson Space Center [Duke, 1976; Annexstad and Yanai, 1978].

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