

GLO1307

Geological significance of immiscibility in fused silicate systems containing tungsten and molybdenum

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Research on certain ore elements in silicate melts has been concentrated mainly on systems containing sulfur. These investigations have enabled us to determine immiscibility in such melts and to get a closer picture of the origin of so-called liquation-magmatic deposits.

Immiscibility in the liquid state during formation of deposits associated with acid magmatism is usually regarded as insignificant and this probably explains why most investigators pay particular attention to the equilibrium of melts containing volatile components.

Certain data on silicate systems show that WO_3 and MoO_3 can dissolve only to a limited extent (a few percent) in fused-alkali silicates (Fuwa, 1923; Tomas-Veltslov, 1934). Above this limit, separation as alkali tungstates and molybdates or other compounds of W and Mo is observed. The possible geological significance of this phenomenon was examined in a previous communication (Štemprók, 1969), in which the existence of immiscibility in the system $Na_2O-SiO_2-WO_3$ was experimentally confirmed.

This article deals with liquation in the systems $Na_2O-SiO_2-WO_3$ and $Na_2O-SiO_2-MoO_3$ and with the behavior of W and Mo during crystallization of silicates. These systems can serve as models of natural systems because the silicates formed during crystallization of melts have practically negligible tungsten and molybdenum contents. As regards the experimental investigations, my aim was to show possible migration paths of tungsten and molybdenum in nature — from a homogeneous silicate melt to an aqueous hydrothermal solution.

EXPERIMENTAL PROCEDURE

The systems $Na_2O-SiO_2-WO_3$ and $Na_2O-SiO_2-MoO_3$ were investigated by several methods, which enabled me to monitor attainment of

Translated from *Geologicheskoye znacheniye nesmesnosti v rasplavakh silikatnykh sistem, soderzhashchikh volfram i molibden*, AN SSSR Izvestiya, ser. geol., 1974, no. 4, p. 60-71. The author is with the Geological Institute, Prague.

equilibrium and to determine the solubility range of WO_3 and MoO_3 in silicate melts at equilibrium. These systems were investigated by high-temperature fusion with mixing during the experiment in the range from 1200 to 1500° C (method I). Some of the experiments were performed by the static method, with repeated intermediate grinding of the specimen and re-crushing and remelting (method II). The substance of the layers formed was analyzed. Crystallization of the homogeneous glasses obtained by methods I and II was then investigated in furnaces by quenching from different temperatures (method III). Equilibria of silicate glasses or crystalline phases with water were investigated in reactors with a cold seal in Tattia-type high-pressure apparatus (method IV). A more detailed description of these methods is given below.

Method I. The material for the experiments was obtained from crushed quartz sand (99.89% SiO_2), calcined soda, and sodium tungstate and molybdate of vp grade (Lahema, Brno). The components were finely crushed and sintered at 650°. The mixture was fused in an electric furnace with a "superkanthal" heater in Pt-Rh crucibles; the melt was mixed by a platinum propeller. The procedure and results are described in detail in a report by Štemprók and Voldán (1973).

Method II. The glasses were obtained from synthetic quartz (from the Institute of Single Crystals, Trnava), tungsten or molybdenum trioxide, and calcined sodium carbonate of vp grade (Lahema, Brno). Tungsten was added to certain mixtures as sodium tungstate Na_2WO_4 , and molybdenum was added as sodium molybdate Na_2MoO_4 of vp grade (Lahema, Brno). The material for experiments in the sections $Na_2O-2SiO_2-WO_3$, $Na_2O-2SiO_2-MoO_3$, $Na_2O-2SiO_2-Na_2WO_4$, and $Na_2O-2SiO_2-Na_2MoO_4$ was obtained from mixtures of recrystallized sodium disilicate and corresponding compounds of tungsten and molybdenum. The mixture was heated for 3-4 hr at 600-700° and then fused at 1200-1250°. If an inhomogeneous glass was obtained, it was recrushed and remelted. In both systems homogeneous glasses were obtained in most experiments. Mixtures containing more than 70% SiO_2 are among those which do not readily melt. They require careful treatment — repeated melting with intermediate grinding. A comparison of the

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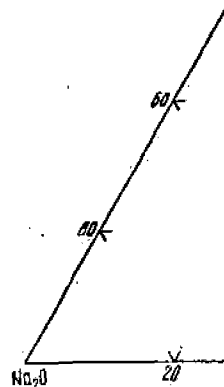


FIGURE 1. Section of (wt. %). 2L — field width

1 — experiments performed mixing of melt (method I)

* Explanations for method I
Editor.

experimental data obtained by method I showed close agreement. Mixture melting point above the experimental temperature, i. e., above 1200° C, were in small platinum envelopes. Through mixtures were placed in these and for 2-24 hr at 1200-1300°.

The homogeneity of the glasses investigated optically from the refractive indices of inhomogeneous glasses or sinters gated optically under the microscope. X-ray analysis in a diffractometer composition was determined chemically by an electron probe. Equilibrium temperatures were determined empirically from exposure times, and from all the data found in accordance with the phase diagram.

Method III. This method has been described in detail by Schairer (1959). Homogeneous glasses obtained by the first two methods were placed in small platinum envelopes. The latter were heated in a furnace with a platinum winding; the temperature was regulated to within $\pm 5^\circ$. Platinum envelopes were connected by wire to a thick wire, the ends of which

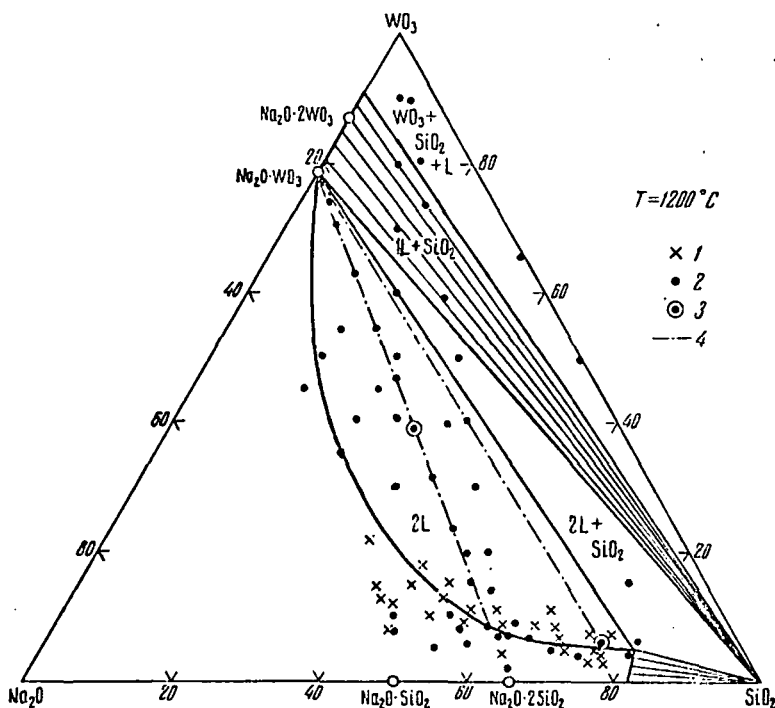


FIGURE 1. Section of phase diagram of the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{WO}_3$ at 1200°C (wt. %). 2L - field with two immiscible liquids; 1L - field of uniform liquid.

1 - experiments performed by static method (method I);* 2 - experiments with mixing of melt (method II);* 3 - composition of initial mixture; 4 - tie lines of immiscible layers.

* Explanations for methods I and II do not agree with those given in text - IGR Editor.

experimental data obtained by methods I and II showed close agreement. Mixtures with a melting point above the experimental temperature, i. e., above 1200°C , were reacted in small platinum envelopes. Thoroughly mixed mixtures were placed in these and then heated for 2-24 hr at $1200-1300^\circ$.

The homogeneity of the glasses was investigated optically from the refractive indices, inhomogeneous glasses or sinters were investigated optically under the microscope and by X-ray analysis in a diffractometer. Their composition was determined chemically and by an electron probe. Equilibrium in the mixtures was determined empirically at different exposure times, and from all the sets of data found in accordance with the phase rule.

Method III. This method has been described in detail by Schairer (1959). Homogeneous glasses obtained by the first and second methods were placed in small platinum envelopes. The latter were heated in a resistance furnace with a platinum winding; the temperature was regulated to within $\pm 5^\circ$. The platinum envelopes were connected by thin platinum wire to a thick wire, the ends of which were

brought out of the furnace. After completion of the experiment the thin wire was burnt out and the envelopes fell into a small vessel with mercury, the specimen being thus quenched from the given temperature. After the experiment the phases were investigated optically, by X-ray analysis, and by means of an electron microprobe.

Method IV. This method was used to investigate the composition of the aqueous phase in equilibrium with crystallized glasses. The composition of the aqueous phase at the junction with the crystalline material was investigated by the aqueous extract method. The phase state of the mixtures of glass and water at elevated temperatures and pressures was investigated in a Tattla apparatus by the procedure described in detail by Huebner (1971). Glass powder (about 0.3 g) was placed in gold capsules with distilled water. The pressure of the external medium was transmitted to the specimen containing water via the walls of the gold capsules. After completion of the experiment the reactor was cooled in a current of air. The capsules were opened and the liquid phase was separated from the solid phases. These products were

ly in fused silicate molybdenum

to determine the solubility and MoO_3 in silicate melts at These systems were investigated rature fusion with mixing during t in the range from 1200 to 1500°C some of the experiments were the static method, with repeated rinding of the specimen and re-melting (method II). The sub-ayers formed was analyzed. of the homogeneous glasses ob-ods I and II was then investigated quenching from different tem-ethod III). Equilibria of silicate stalline phases with water were reactors with a cold seal in h-pressure apparatus (method detailed description of these en below.

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The glasses were obtained quartz (from the Institute of , Trnava), tungsten or molyb-, and calcined sodium carbonate hema, Brno). Tungsten was n mixtures as sodium tungstate olybdenum was added as sodium oO4 of vp grade (Lahema, aterial for experiments in the $2\text{SiO}_2-\text{WO}_3$, $\text{Na}_2\text{O}\cdot 2\text{SiO}_2-\text{MoO}_3$, a_2WO_4 , and $\text{Na}_2\text{O}\cdot 2\text{SiO}_2-$ btained from mixtures of recry- a disilicate and corresponding ngsten and molybdenum. The ated for 3-4 hr at $600-700^\circ$ and $00-1250^\circ$. If an inhomogeneous ed, it was recrushed and re- systems homogeneous glasses a most experiments. Mixtures an than 70% SiO_2 are among those idily melt. They require care- epeated melting with inter- . A comparison of the

TABLE 1. Composition of demixed substance.*

Initial composition			Silicate layer			Tungstate layer			T, °C	Time, hr
Na ₂ O	SiO ₂	WO ₃	Na ₂ O	SiO ₂	WO ₃	Na ₂ O	SiO ₂	WO ₃		
27.5	33.0	39.4	34.1	60.0	6.0	21.4	1.2	77.3	1200	3
20.0	75.0	5.0	18.6	76.0	4.2	21.6	0.8	78.2	1400	4
			Molybdate layer							
Na ₂ O	SiO ₂	MoO ₃	Na ₂ O	SiO ₂	MoO ₃	Na ₂ O	SiO ₂	MoO ₃		
32.7	33.0	34.2	36.3	59.2	4.5	28.6	1.9	69.5	1170	3

*The analyses were performed by I. Červen, Chemical Laboratory of the Central Geological Institute, Prague.

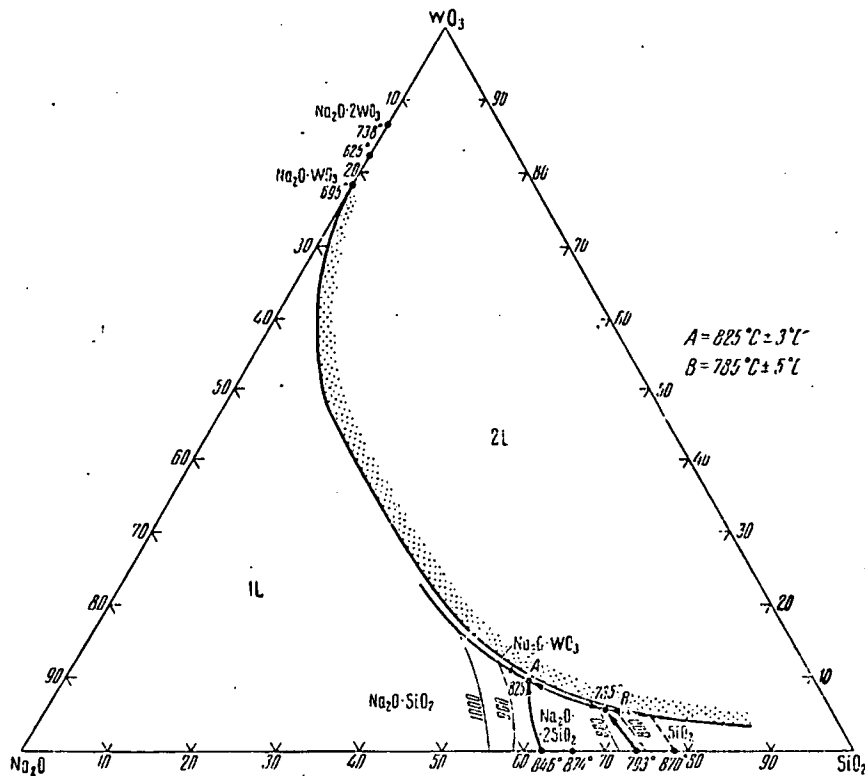


FIGURE 2. Surface of part of the liquidus of the system Na₂O-SiO₂-WO₃, determined by quenching (method III). The liquidus surface was determined in the primary crystallization fields of sodium metasilicate, sodium disilicate, and SiO₂. The invariant points in the system Na₂O-WO₃ relate to the binary system.

investigated by analytical, X-ray diffraction, and optical methods.¹

¹I thank J. Finneov for help with the experiments and would like to express my thanks to J. Kotrb for helping with the use of the microprobe. Experiments by procedures I and II-IV were performed in the Laboratory of the Central Geological Institute, those in which procedure I was employed were performed in the Institute of Glass at Gradets-Karov.

RESULTS AND INTERPRETATION

The system Na₂O-SiO₂-WO₃. The results (see fig. 1) were used to construct the ternary phase diagram at 1200°. The position of the solubility limit of WO₃ in silicate glasses at 1400° was determined previously (Štemprok and Voldán, 1973). It is practically the same as that at 1200° and shows that the slope of the demixing surface is steep. The diagram in Figure 1 shows the field of coexistence of the two immiscible liquids (2L), which is



FIGURE 3. Drops of one of the system Na₂O-SiO₂

adjacent to the side of the phase triangle which we find in equilibrium the two pyrimite as a stable modification of

The equilibria of the two immiscible liquids were also investigated by chemical analysis of both layers. These experiments also showed that the layer of silicates coexists with the layer of tungstates which contain about 1% SiO₂. Chemical analyses of the layer of silicates revealed a somewhat lower SiO₂ content than that found by other methods (about 70%). This is due to demixing of the melt during static fusion of large samples in which a zone of turbid glasses was formed at the junction with tungstate. Only two transparent glasses were analyzed.

The two-melt field disappears in the Na₂O-rich sector of the diagram, where a homogeneous liquid being formed. This sector equilibrium was investigated up to 40% Na₂O, because the high viscosity of the initial material prevents crystallization of more highly alkaline melts.

The 2L field corresponds to that of the system, in which two immiscible liquids coexist at all the experimental temperatures. In certain parts of the region of homogeneous silicate glasses (field 1L) demixing of the melt during crystallization of glasses was observed. This was expressed as the formation of drop-like segregations of silicate against the background of silicate in incipient crystals of Na₂O·SiO₂.

REVIEW

tance.*

Starting layer		T, °C	Time, hr
SiO ₂	WO ₃		
1.2	77.3	1200	3
0.8	78.2		
Residual layer		1170	3
SiO ₂	MoO ₃		
1.9	69.5		

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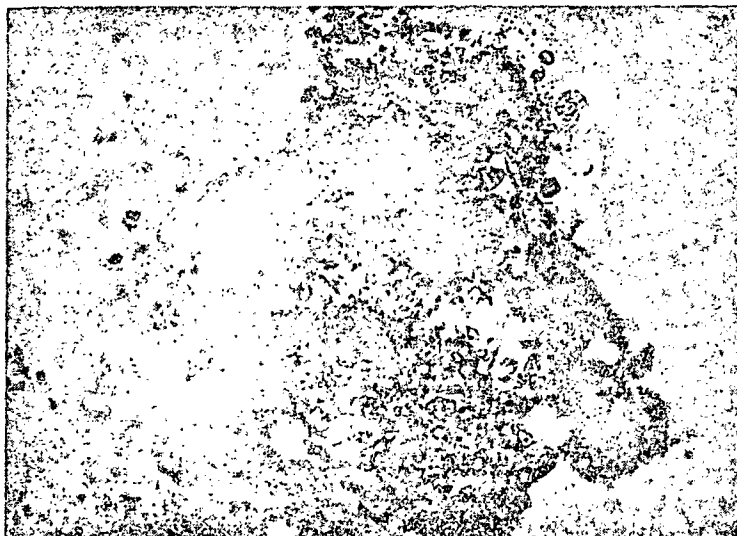


FIGURE 3. Drops of sodium tungstate in an aggregate of sodium disilicate of the system Na₂O-SiO₂-WO₃, recrystallized at 810° for 18 hr. (x 355, without analyzer.)

Adjacent to the side of the phase triangle in which we find in equilibrium the two liquids + tridymite as a stable modification of SiO₂.

The equilibria of the two immiscible liquids were also investigated by chemical analyses of both layers. These experiments and analyses showed that the layer of silicates containing tungsten coexists with the layer of sodium silicates which contain about 1% SiO₂ (table 1). Chemical analyses of the layer of fused silicates revealed a somewhat lower WO₃ content than that found by other methods (1.5% WO₃). This is due to demixing of the silicate melt during static fusion of large specimens, in which a zone of turbid glasses was formed at the junction with tungstate. Only homogeneous transparent glasses were analyzed.

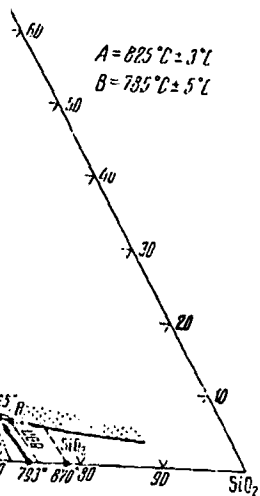
The two-melt field disappears in the Na₂O-rich sector of the diagram, only a single homogeneous liquid being formed here. In this sector equilibrium was investigated only up to 40% Na₂O, because the high hygroscopicity of the initial material prevents the preparation of more highly alkaline melts.

The 2L field corresponds to stable demixing of the system, in which two immiscible liquids coexist at all the experimental temperatures. In certain parts of the region of homogeneous silicate glasses (field 1L), demixing of the melt during crystallization of silicates was observed. This was expressed in formation of drop-like segregations of sodium tungstate against the background of silicate glass, or in incipient crystals of Na₂O·SiO₂,

Na₂O·2SiO₂, or tridymite. This phenomenon was regarded by Vogel (1959) as secondary demixing. Figure 2 shows the liquidus surface of melts of the system Na₂O-SiO₂-WO₃, which was determined by the quenching method. Two new points - A and B - were determined on the liquidus surface. Point A corresponds to the composition 56% SiO₂ and 9% WO₃, its temperature is 825 ± 3°. It represents equilibrium of sodium metasilicate and disilicate and sodium tungstate with the residual melt. Point B corresponds to the composition 67.5% SiO₂ and 5% WO₃, its temperature is 785 ± 5°. It reflects equilibrium of sodium disilicate, primary quartz, sodium tungstate, and the residual silicate melt.

It follows from the diagram that the presence of tungsten reduced the liquidus temperature of sodium silicates. The position of the invariant points in the region of higher silicate contents was not investigated in our experiments, and the experimental conditions were extrapolated to the next region.

Typical structures of the drop formation of tungstate appeared during crystallization of sodium metasilicate Na₂O·SiO₂, sodium disilicate Na₂O·2SiO₂ (fig. 3), and also during crystallization in the stability field of SiO₂ modifications (fig. 4). The primary crystallization field of the different modifications of SiO₂ is characterized by nonequilibrium crystallization, which ends in the appearance of cristobalite at temperatures below its stability.



Na₂O-SiO₂-WO₃, determined in the primary crystallization of SiO₂. The invariant points in the system.

DISCUSSION AND INTERPRETATION

in the Na₂O-SiO₂-WO₃. The results of the experiments (1) were used to construct the phase diagram at 1200°. The position of the liquidus limit of WO₃ in silicate glasses was determined previously (Štemprok 1973). It is practically the same as in the Na₂O-SiO₂ system and shows that the slope of the liquidus surface is steep. The diagram also shows the field of coexistence of two immiscible liquids (2L), which is

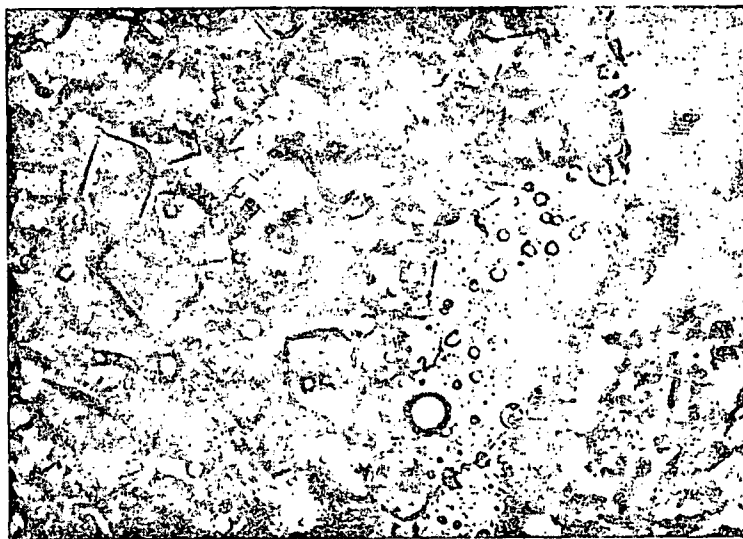


FIGURE 4. Drops of sodium tungstate in quartz crystals in partly crystallized glass of the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{WO}_3$ (temperature 730° , duration of 182 hr). (x 355, without analyzer.)

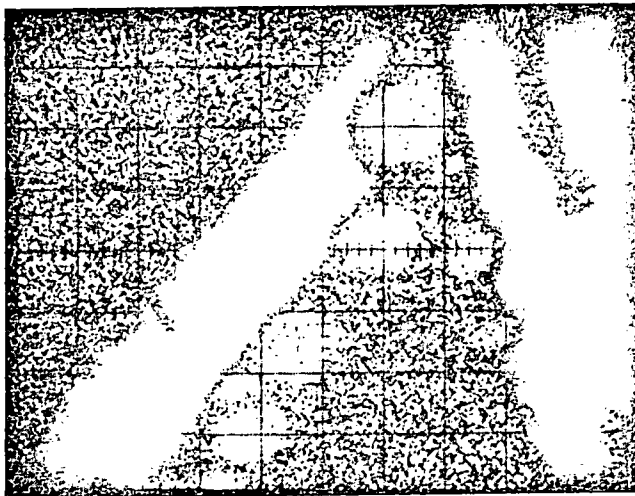


FIGURE 5. Electron probe scan of partly crystallized glass of the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{WO}_3$, similar in composition to K metasilicate ($\text{WK } \alpha_1$ radiation). The dark field corresponds to a metasilicate crystal, the light field to drop-like segregations of sodium tungstate. The residual melt of the layers containing tungsten occupied the larger part of the area. Glass composition 55% SiO_2 and 10% WO_3 , scale of square 8μ , crystallization temperature 850° , crystallization time 1 hr.

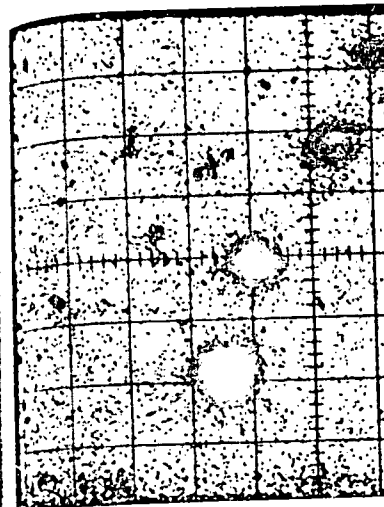
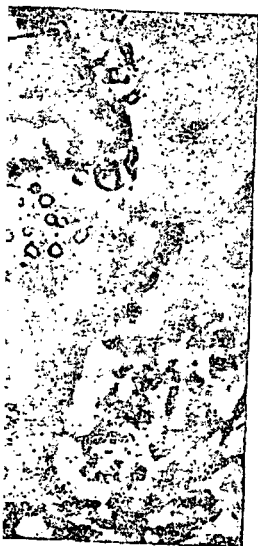


FIGURE 6. Electron probe scan of the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{WO}_3$ ($\text{SiK } \alpha_1$ radiation). The tungsten-containing silicon.

Liquation is manifested in the form of droplets on the surfaces of the crystals, in the bulk of the silicate melt, and on the cleavage of the crystallizing melt. The drop diameter varies from 0.5 to 1.5 μ . The drop composition was determined by electron probing (figs. 5 and 6), and by X-ray analysis. The sets of data obtained by these methods showed that the droplets correspond to fusion of sodium tungstate.

Microprobing of simple sodium tungstate ($\text{Na}_2\text{O}-\text{SiO}_2$ and $\text{Na}_2\text{O}-2\text{SiO}_2$) shows that they incorporate tungsten in their structure in negligibly small amounts below the detection limit of the method (for $\text{Na}_2\text{O}-\text{SiO}_2$, figs. 5 and 6). This means that gradual crystallization of the melt leads to enrichment of the residual melt with tungsten and to detachment of tungsten as drops of tungstate above the detection limit. Such conditions of gradual crystallization of the liquid with tungsten, and its incorporation in very slowly in highly viscous silicate rich melts.

The system $\text{Na}_2\text{O}-\text{SiO}_2-\text{MoO}_3$ shows an isothermal section of the phase diagram ($T = 1200^\circ$). As in the case of the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{WO}_3$, one-, two-, and three-phase equilibrium fields are distinguished. The field of coexistence of two immiscible liquids occupies a larger area than in the tungsten system. Therefore the field of coexistence of silicate melts is smaller in the tungsten system with tungsten (Štemprok and Štemproková, 1973). The solubility of MoO_3 in silicate melt in composition to sodium metasilicate is approximately 8%, in the primary crystallization field of the disilicate about



ystals in partly crystallized material at 730°C, duration of 1 hour.)



illized glass of the Na₂O-K₂O system to a metasilicate containing sodium tungstate. The tungsten occupied the largest part of the glass, 2 and 10% WO₃, crystallized at 850°C, crystalliza-

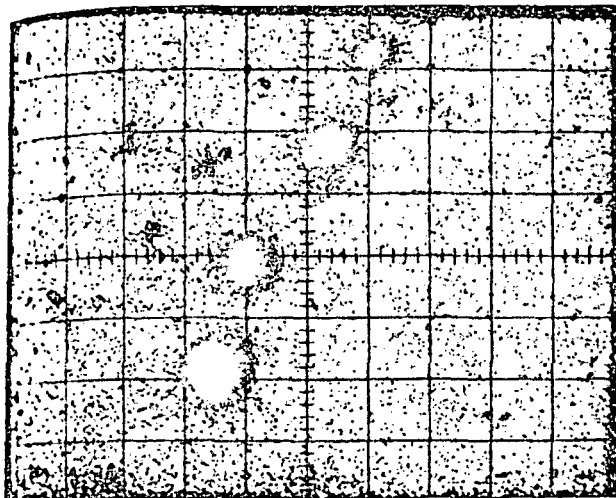


FIGURE 6. Electron probe scan of the same specimen as Figure 5 (SiK α radiation). The tungsten-containing liquid is depleted in silicon.

Liquation is manifested in the formation of droplets on the surfaces of the silicate crystals, in the bulk of the silicate melt, and along the cleavage of the crystallizing metasilicate. The drop diameter varies from 0.5 to 1 μ . The drop composition was determined by electron probing (figs. 5 and 6), and by optical and X-ray analysis. The sets of data obtained by these methods showed that the drops correspond to fusion of sodium tungstate.

Microprobing of simple sodium silicates (Na₂O-SiO₂ and Na₂O-2SiO₂) showed that they incorporate tungsten in their structure only in negligibly small amounts below the sensitivity of the method (for Na₂O-SiO₂, figs. 5 and 6). This means that gradual crystallization of silicates leads to enrichment of the residual melt with tungsten and to detachment of excess tungsten as drops of tungstate above the solubility limit. Such conditions of gradual enrichment of the liquid with tungsten, and its demixing, set in very slowly in highly viscous silica-rich melts.

The system Na₂O-SiO₂-MoO₃. Figure 7 shows an isothermal section of the system (T = 1200°C). As in the case of the system Na₂O-SiO₂-WO₃, one-, two-, and three-phase equilibrium fields are distinguished. The field of coexistence of two immiscible liquids occupies a larger area than in the previous system. Therefore the field of homogeneous silicate melts is smaller than in the system with tungsten (Štemprok and Voldán, 1973). The solubility of MoO₃ in melts similar in composition to sodium metasilicate is approximately 8%, in the primary crystallization field of the disilicate about 5%, and in

the crystallization field of the SiO₂ modifications about 4%. Chemical analyses showed that the solubility of SiO₂ in fused molybdates is about 2%. The molybdenum content of the layer of fused silicates is somewhat higher than that determined by other methods (table 1).

In contrast with tungsten, in this system the excess molybdenum is separated as drops, forming a finely dispersed cloud (fig. 8). In certain cases these drops are indiscernible, even under an optical microscope. In the field 1L + SiO₂ tridymite coexists with a liquid whose composition varies from Na₂O-2MoO₃ to fused MoO₃ (its melting point is 795°C). In the sodium-rich regions of the diagram, the break in miscibility disappears and both liquids combine to form a single homogeneous liquid.

During crystallization of homogeneous glasses, drops (up to 3 μ in diameter) distributed uniformly in the metasilicate crystals appeared in the primary crystallization field of sodium metasilicate. Like the system with tungsten, the primary crystallization field of sodium disilicate displayed drops of sodium molybdate, which covered the grains of the aggregate or appeared in the residual melt (fig. 9). Drop-like separation of sodium molybdate appeared in the primary crystallization field of the SiO₂ modifications, even in the presence of a very small amount of tridymite.

Demixing of silicate systems containing tungsten or molybdenum can be satisfactorily explained from the point of view of the atomic theory of glass structure proposed by Warren and Pincus (1940). The phenomenon of liquation in silicate systems is the result of the tendency of the individual cations to locate themselves in the most energetically advantageous manner in the environment of the oxygen anions. Experiments performed in both systems show that the region of the break in miscibility is maximal at high silicon contents and disappears in the sodium-rich part of the diagram. Differences between the structures of the (SiO₄)⁻⁴ and (WO₄)⁻² or (MoO₄)⁻² radicals are the primary prerequisite for the existence of microinhomogeneity in melts, which at a sufficient concentration of W or Mo can lead to the appearance of macroliquation. It may be assumed that the alkali cations, which both structural groups attach to themselves as alkali silicates and tungstates or molybdates, act as intermediaries and form a macroscopically uniform liquid. Volf (1961) assumes that liquation in silicate systems

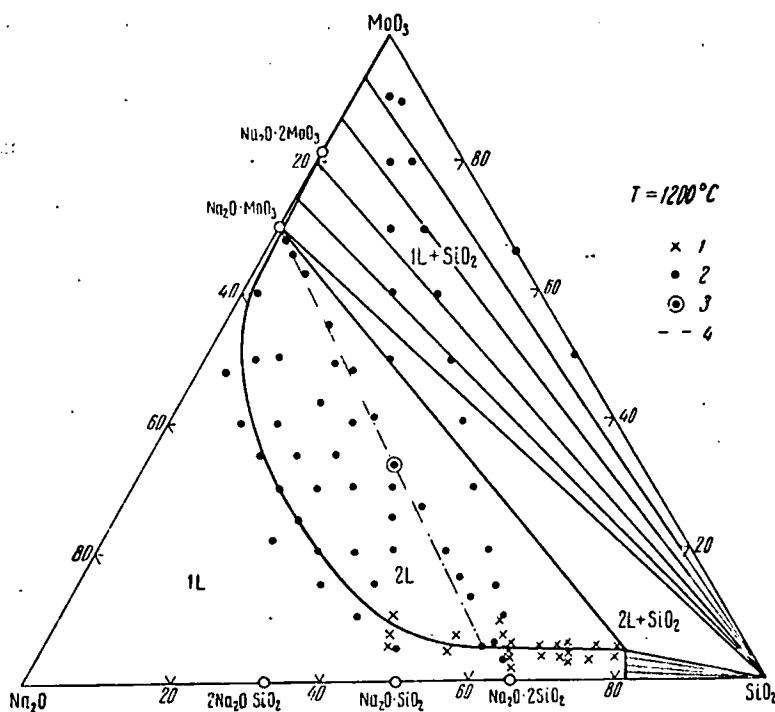


FIGURE 7. Section of phase diagrams of the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{MoO}_3$ at 1200°C (wt. %). Notation same as for Figure 1.



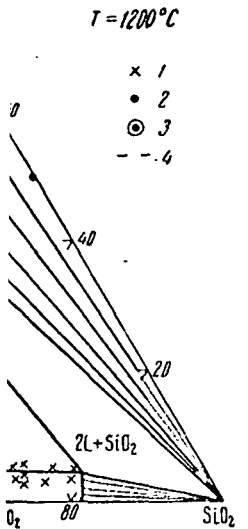
FIGURE 8. Drops of sodium molybdate in a melt containing 60.0% SiO_2 , 30.9% Na_2O , and 9.1% MoO_3 ; the melt was mixed at 1400° ($\times 355$, without analyzer). All the photographs were taken by D. Heydova.



FIGURE 9. Drops of sodium molybdate in a melt containing 60.0% SiO_2 , 30.9% Na_2O , and 9.1% MoO_3 ; the melt was mixed at 1400° ($\times 355$, without analyzer). All the photographs were taken by D. Heydova.

with tungsten or molybdenum is explained by differences in the electron structure of the d-orbitals of Si on the one hand and W or Mo on the other. Tungsten and molybdenum strongly attract oxygen and thus weaken the bond of silicon with them. Weyl (cited in 1961) denotes these relationships by the following linear scheme: $\text{O}^{2-} + \text{Si}^{4+} = \text{SiO}_2$; $\text{W}^{6+} + \text{O}_2^{2-} = \text{Si}^{4+} + \text{O}^{2-}$ [sic]. The "+" sign represents strong bonds, the "-" sign weakened bonds.

A comparison of the melting points of the simple compounds of the marginal systems $\text{Na}_2\text{O}-\text{SiO}_2$, $\text{Na}_2\text{O}-\text{WO}_3$, and $\text{Na}_2\text{O}-\text{MoO}_3$ reveals that in the general case the melting temperatures of silicates are higher than the solidification points of tungstates and molybdates (table 2). Owing to the high solubility of silicon in tungstates and molybdates in the 2L fields of these diagrams (Figure 7) we can assume that the temperatures of the eutectics coincide with the eutectic temperatures of the marginal systems $\text{Na}_2\text{O}-\text{WO}_3$ and $\text{Na}_2\text{O}-\text{MoO}_3$. The liquidus surface of the tungstate system decreases in the presence of tungsten (for tungsten see fig. 2), but this decrease does not reach the eutectic temperatures of the systems $\text{Na}_2\text{O}-\text{WO}_3$ and $\text{Na}_2\text{O}-\text{MoO}_3$. This means that during crystallization of silicates we may observe a liquid phase of the composition of tungstates or molybdates in the presence of solid crystals of silicates.



2O-SiO₂-MoO₃ at 1200°C
ure 1.



ing 60.0% SiO₂, 30.9%
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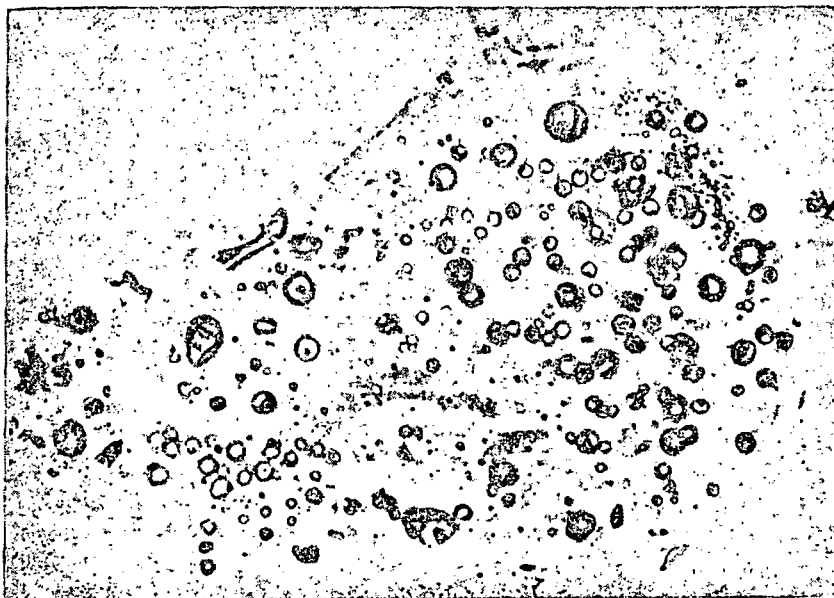


FIGURE 9. Drops of sodium molybdate in partly crystallized glass similar in composition to disilicate in the system Na₂O-SiO₂-MoO₃. Crystallization temperature 810°, time 66 hr. (x 355, without analyzer).

with tungsten or molybdenum is explicable by differences in the electron structure and the charges between Si on the one hand and W or Mo on the other. Tungsten and molybdenum strongly attract oxygen and thus weaken the bond of silicon with them. Weyl (cited by Volf, 1961) denotes these relationships by the following linear scheme: $O^{+2} \mp Si^{+4} = O^{+2} \mp W^{+6} \mp O_2^{+2} \approx Si^{+4} \mp O^{+2}$ [sic]. Here the "+" sign represents strong bonds, the "-" sign weakened bonds.

A comparison of the melting points of simple compounds of the marginal systems Na₂O-SiO₂, Na₂O-WO₃, and Na₂O-MoO₃ reveals that in the general case the crystallization temperatures of silicates are higher than the solidification points of tungstates or molybdates (table 2). Owing to the very low solubility of silicon in tungstates or molybdates, in the 2L fields of these diagrams (figs. 1 and 7) we can assume that the temperatures of the eutectics coincide with the eutectics of the marginal systems Na₂O-WO₃ and Na₂O-MoO₃. The liquidus surface of fused silicates decreases in the presence of tungsten or molybdenum (for tungsten see fig. 2), but in general this decrease does not reach the eutectic temperatures of the systems Na₂O-WO₃ or Na₂O-MoO₃. This means that during crystallization of silicates we may observe a liquid melt with the composition of tungstates or molybdates in the presence of solid crystals of sodium silicates.

It will be seen from Table 2 that, like other silicates of rock-forming systems, sodium silicates have a lower density than molybdates or tungstates. The difference is greatest for tungstates, less for molybdates. These relative differences in the densities are manifested in the liquid state of both systems and were observed in my static experiments. In the crucibles the segregated (demixed) tungstates fell to the bottom of the vessels and formed layers with distinct mutual boundaries. In the experiments with a molybdenum-containing system such sharp layer separation was observed only in certain melt compositions. A layer of sodium molybdates on the surface of the silicate melt was observed in compositions with a very high Mo content. Smaller differences in the densities of silicates and molybdates are also observed in dynamic experiments (method I), during which molybdates form a finely dispersed cloud in the glasses.

Reaction with water. The solubility of tungstates and molybdates of sodium in water is well known (Hagman, 1955). An investigation of crystallized glasses of the composition sodium metasilicate and disilicate, containing W or Mo, revealed that hydration begins in water, and drops of individual tungstates and molybdates rapidly dissolve. The whole aggregate decomposes into fine crystalline fragments of sodium and silicon hydrates. The presence of [WO₄] ions in tungsten-containing systems, and [MoO₄] ions in molybdenum systems,

TABLE 2. Certain invariant points of marginal systems of the phase diagrams of Na₂O—SiO₂—WO₃ and Na₂O—SiO₂—MoO₃

Phase	Density (s - solid phase; l - liquid phase)	Process	Temperature, °C	Reference
Na ₂ O · SiO ₂ + L	2.4 (s)	Melting	1089	Toropov et al., 1969
Na ₂ O · SiO ₂ + Na ₂ O · 2SiO ₂		Eutectic	846	"
Na ₂ O · 2SiO ₂ + L	2.5 (s)	Melting	874	"
Na ₂ O · 2SiO ₂ + Quartz + L		Eutectic	793	"
Na ₂ O · WO ₃ + L	4.18 (s)	Melting	695	Coranson, Kracek (1935)
Na ₂ O · 2WO ₃ + L		"	738	Hoerman (1929)
Na ₂ O · MoO ₃ + L	2.59 (l)	"	687	"
Na ₂ O · 2MoO ₃ + L		"	612	"
Na ₂ O · WO ₃ + Na ₂ O · 2WO ₃ + L		Eutectic	625	Gelsing et al. (1966)
Na ₂ O · MoO ₃ + Na ₂ O · 2MoO ₃ + L		"	556	Hoerman (1929)
Na ₂ WO ₄ + Na ₂ O · SiO ₂ + Na ₂ O · 2SiO ₂ + L		"	825	Author's data
Na ₂ WO ₄ + Na ₂ O · 2SiO ₂ + SiO ₂ + L		"	785	"

has been detected (only qualitatively at present) in the aqueous phase.

Investigations of tungsten-containing glasses in gold capsules under a pressure of about 1 kbar and at a temperature of 350-500° showed that they partly crystallize, forming aggregates without drop-like tungstate formations. The aqueous phase in contact with the glass is markedly enriched with tungsten. The reaction of the solution is alkaline: after evaporation of the solution, sodium tungstate was found in the solid residue in the tungsten-containing system.

GEOLOGICAL INTERPRETATION OF THE RESULTS

Immiscibility in the liquid state in these systems could shed much light on the formation conditions of tungsten and molybdenum deposits and in particular could help to solve the problem of migration of elements from a magmatic melt to a hydrothermal solution. The fact that tungsten and molybdenum deposits are linked with acid magmatic rocks is generally acknowledged (Rub, 1960; Štemprok, 1965). In most cases tungsten and molybdenum deposits are correlated with the apical sectors of granite intrusions. The residual melts of the latter are regarded as the sources of the solutions from which these deposits were formed.

The origin of granites is still disputed (Read, 1948; Kuznetsov, 1966). However, certain genetic interpretations of the origin of granites emphasize the important part played by migration of alkalis and volatile matter in various different forms in the earth's upper crust (Korzinskii, 1968). Thus relative

enrichment of a silicate melt with alkalis may occur even in the initial stage of formation of magmatic chambers. This assumption is important for subsequent interpretation of my experimental data on equilibria in Mo- and W-containing systems of the type Na₂O—SiO₂—MoO₃ (WO₃).

Investigation of these systems shows that alkalis may play an important part in concentration and migration of tungsten and molybdenum as early as the magmatic stage of development. In these systems it begins as soon as the tungsten or molybdenum concentration reaches a specific value, which depends on temperature and the chemical composition of the system in question.

The differences between the densities of fused silicates on the one hand and of tungstates and molybdates on the other enable us to assume that under certain conditions gravitational differentiation may occur, leading to sinking of the fused tungstates or molybdates until they reach the deeper sectors of the melt. Demixing can occur during crystallization of silicates. This is eventually manifested in the coexistence of silicate crystals with drops of alkali tungstates or molybdates in the residual silicate liquid.

As shown by thermodynamic calculations of Krauskopf (1965) and Ivanova (1972), transfer of volatile compounds of chlorine or fluorine with W and Mo is improbable, because these compounds hydrolyze very readily in the presence of water. On the contrary, alkali tungstates or molybdates dissolve very readily in water, and their existence in solutions in contact with crystalline aggregates

of W- and Mo-containing silicates has been proved by my experiments. It is proved as early as the stage of magmatic differentiation and Mo could exist as alkali compounds retained right up to the hydrothermal solutions.

CONCLUSIONS

1. An experimental investigation of tungsten-containing systems at 1200°, together with crystallization of silicate melts at 750-900°, has shown that in the tungsten-containing system the melt coexists with sodium tungstate. In the molybdenum-containing system the melt coexists in equilibrium with sodium tungstate. In the primary crystallization of sodium silicates and different modifications of SiO₂, liquation begins as soon as the concentration of silicates commences.

2. The experimental data show that gravitational differentiation may play an important part in the migration of tungsten or molybdenum from a magmatic melt during cooling of magmatic chambers. Another possibility is gravitational differentiation, in which drops of tungsten- and molybdenum-rich liquid descend to deeper sectors of the melt.

3. Since alkali tungstates or molybdates dissolve very readily in water, (W and MoO₄)⁻² ions, stable in an alkaline solution, are one of the probable forms of tungsten and molybdenum.

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se diagrams of Na₂O—SiO₂—WO₃

Temperature, °C	Reference
1089	Toropov et al., 1969
846	"
874	"
793	"
695	Goranson, Kracek (1935)
738	Hoerman (1929)
687	"
612	"
625	Gelsing et al. (1966)
556	Hoerman (1929)
825	Author's data
785	"

W- and Mo-containing silicates has been proved by my experiments. It is probable that as early as the stage of magmatic differentiation W and Mo could exist as alkali compounds, retained right up to the hydrothermal stage of the solutions.

CONCLUSIONS

1. An experimental investigation of these systems at 1200°, together with crystallization of silicate melts at 750-900°, has shown that in the tungsten-containing system the silicate melt coexists with sodium tungstate; in the molybdenum-containing system the silicate melt coexists in equilibrium with sodium molybdate. In the primary crystallization fields of sodium silicates and different modifications of SiO₂, liquation begins as soon as crystallization of silicates commences.

2. The experimental data show that liquation may play an important part in separation of tungsten or molybdenum from a magmatic melt during cooling of magmatic chambers. Another possibility is gravitational differentiation, in which drops of tungsten- or molybdenum-rich liquid descend to deeper horizons.

3. Since alkali tungstates or molybdates dissolve very readily in water, (WO₄)⁻² or (MoO₄)⁻² ions, stable in an alkaline medium, are one of the probable forms of transfer of tungsten and molybdenum.

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Phase composition

The problem of the phase composition of hydrocarbon (UV) at great depths becomes more and more pressing as deep-seated horizons are associated with the possibility of maintenance and increase of output of oil, gas, and condensate from the old petroleum-producing regions of the USSR, deep-seated deposits are greatly explored. Abroad, about 700-750 deep-seated hydrocarbon horizons have been revealed at depths of more than 4 km, and of these approximately 100 are located at depths of over 5 km. The greatest number of deposits has been discovered in the USA, where 350-370 wells are drilled annually to depths of more than 4.5 km, and about 30% of the wells are productive.

In this connection, a review and analysis of the global factual information on the distribution of the deposits and the hydrocarbon reserves at great depths are important. The number of joint works (1, 2, 5, 8, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100) has been recorded that in the Gulf Coast basins, the San Juan, and Western Interior basins of the USA, the greatest number of hydrocarbon deposits at depths of more than 4 km occur, and large accumulations of gas. Therefore, the search for such regions (about 40 are known in the world) is justified.

We have analyzed data on the position of the hydrocarbon deposits discovered in 1971 at depths of more than 5 km. At the present time it is possible to supplement the earlier published information about the conclusions reached, and also to investigate the petroleum occurrences at investigated depths of from 4 to 5 km. The analysis of more numerous data on the distribution of deposits of oil, gas, and condensate in this range facilitates the investigation of the distribution patterns of hydrocarbon accumulations of different phase composition at even greater depths. In the present account has also been taken of the distribution of investigated reserves of oil, gas, and condensate within the depths under consideration.

Translated from Fazovyy sostav i zapasy naftnykh i gaznykh grubinakh, Sovetskaya geologiya, no. 6, p. 106-110. Co-authors: N. A. Kalinin, L. V. Galimova, and others. They are with the Scientific-Research Institute of Foreign Geology (NILZarubezhnaya Geologiya).

Int

THE JOURNAL OF GEOLOGY

July 1973

ISLAND-ARC EVOLUTION AND RELATED MINERAL DEPOSITS¹

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ABSTRACT

In ensimatic arcs, initial submarine eruptions of island-arc tholeiites are succeeded by subaerial and submarine volcanism which is either calcalkaline or island-arc tholeiitic. Besshi-type massive stratiform sulfides develop in deep water on the submarine flanks of islands. Pluton emplacement beneath waning volcanoes is accompanied by mercury, porphyry copper, and gold mineralization. Renewed calc-alkaline or island-arc tholeiitic volcanism commonly follows arc reversal or splitting; Kuroko-type massive sulfides form in shallow-water elastic dacitic rocks and gold is concentrated around monzonites and in meta-andesites. Reef limestone deposition, block faulting, and uplift may be followed by formation of bauxite on karstic limestones, and of stratiform manganese deposits near the limestone base. Upper mantle and ocean crust rocks, emplaced as ophiolites in mélanges on the arc side of the trench and as obducted slices during arc-arc collision, contain Cyprus-type stratiform massive sulfides, podiform chromite, and nickel sulfides; nickeliferous laterites may develop on the upper mantle rocks. Increase in island-arc crustal thickness and emplacement of granitic plutons is accompanied by tin-tungsten-molybdenum-bismuth mineralization. Following arc-continent collision, massive sulfides, gold, tin, and ores associated with ophiolites are preserved.

INTRODUCTION

Island arcs, particularly those in the Western Pacific, have in the past few years attracted the interest of mining companies and state geological surveys as favorable prospects for metallic ore deposits. A number of publications have stressed the ore potential of these arcs, with varying emphasis on the origin of the ore bodies (e.g., Thompson and Fisher 1965; Liddy 1972; Stanton 1972).

Widespread acceptance of the plate tectonics hypothesis, together with increasing geological and geophysical data on island arcs, has led to new explanations of

volcanic, metamorphic, and tectonic processes and their relationship to arc evolution. The hypothesis requires that the inclined seismic plane, or Benioff zone, above which arcs are located, is the zone along which a descending rigid lithospheric slab consisting of ocean floor and upper mantle is consumed (Oliver and Isaacs 1967). This was implied by Hess (1962) and suggested by Coats (1962) for the Aleutian arc. A corollary of the hypothesis is that ancient island arcs occur within continents and interpretation of parts of orogenic belts within continents in terms of island arc and ocean floor successions is now quite commonly encountered. Suggestions that some ore deposits occurring within continents developed initially in island arcs (e.g., Stanton 1960, 1972) are thus now becoming widely accepted.

¹ Manuscript received January 4, 1973; revised March 28, 1973.

[JOURNAL OF GEOLOGY, 1973, Vol. 81, p. 381-405]

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The aims of this paper are to consider relationships between the stages of arc evolution and the formation of types of metallic mineral deposit for which an island arc forms a particularly favorable environment. Examples of most of these deposits are found in modern island arcs lying within the oceans, but a few are known only in ancient arcs now located within continents.

MODERN ISLAND ARCS AND NATURE OF UNDERLYING CRUST

Modern island arcs are separated from continents by marine basins underlain by oceanic crust. Active island arcs (Mitchell and Reading 1971) include a belt of active volcanoes, are underlain by a seismic zone, and are bordered by a submarine trench. Inactive arcs lack these features but contain older volcanic or volcanoclastic rocks (e.g., Greater Antilles, Lau Islands).

Some modern arcs contain rocks which indicate that they lay initially adjacent to, or perhaps on, a continental margin, and moved oceanward with development of oceanic crust on the continental side of the arc. Examples of these ensialic arcs are Japan, where pebbles of mid-Pre-Cambrian rock occur in a Permian conglomerate (Sugisaki et al. 1971), and New Zealand (Fleming 1969) and New Caledonia, where continent-derived sediments occur. In most other arcs the nature of the oldest exposed rocks suggests that the arcs originated on oceanic crust, and are ensimatic.

Cenozoic igneous rocks in Japan and New Zealand resemble those in many arcs which lack evidence of continental crust. This suggests that the development of initially ensialic arcs containing fragments of continental crust is similar to that of ensimatic arcs. In this paper we consider the evolution of an ensimatic arc, but in discussing ore bodies emplaced late in its development we use examples from Japan and from other arcs which could have formed initially on, or adjacent to, continental crust.

STAGE I: PRE-ARC GENERATION OF OCEANIC CRUST AND UPPER MANTLE

GEOLOGICAL EVENTS

The plate tectonics hypothesis requires that oceanic crust form above ascending upper mantle generated at ocean ridge spreading centers and in marginal basins (figs. 1A and 2A). Generation of marginal basin crust is subject to different interpretations (e.g., Karig 1971a; Matsuda and Uyeda 1971), but may resemble that of normal oceanic crust (Sclater et al. 1972).

Igneous rocks are emplaced either continuously or intermittently within a narrow axial zone along an ocean ridge crest. Tholeiitic magma, derived from the partial melting of mantle peridotite, forms layered gabbroic intrusions passing upward into dolerite sheet complexes. These intrude and are overlain by pillow lavas, hyaloclastites, and local thin pelagic sediments. "Burial metamorphism" of pillow basalts to greenschist and zeolite facies and of dolerites and gabbros to amphibolites (Miyashiro et al. 1971) probably takes place soon after emplacement in water-rich and water-deficient environments, respectively (Cann 1970); spilitization of basalts could result from post-cooling hydrothermal alteration (Cann 1969).

During lateral movement of this rock pile down the ridge flanks, it is locally intruded and overlain by alkali basalts and thinly mantled by cherts, pelagic mudstones, and limestones. Local volcanic and carbonate turbidites are derived from oceanic volcanic islands, either single seamounts or chains, which often consist of pedestals of tholeiitic or transitional basalt topped by alkali basalt and related fractionates.

FORMATION OF MINERAL DEPOSITS

The formation of mineral deposits within ophiolites, now interpreted as tectonically emplaced oceanic crust or upper mantle (table 1), is unrelated to arc formation, but exposure of the deposits may occur only subsequent to arc develop-

ment. Deposits of this type of the basaltophilic metals occur in the basaltic rocks of an early stage of geosynclinal volcanism (Smirnov 1968).

Cyprus-type massive sulfides of some massive sulfide deposits associated with submarine volcanism (e.g., Cyprus) have recently been related to environments (Pereira and Woodsworth 1972). Well-known examples of this type of setting are those of the Troodos complex in Cyprus (Sillitoe and Woodsworth 1972); we term this type of deposit "Cyprus-type deposit".

Cyprus-type ore bodies are typically associated with the tholeiitic pillow lavas, spilite succession—representing the oceanic crust—or between the lavas and overlying pelagic turbidites of layer 1. The Cyprus-type massive sulfides are associated with chalcopyrite, sphalerite, galena, and minor silver (Hutchinson 1972) suggested that certain land ores in oceanic tholeiitic basalt complexes (Whalesback, Little Bay, and others) are characterized by similar mineral assemblages of pyrite-pyrrhotite-chalcopyrite. Examples are those of Ergani in Turkey and Island No. 1 in California (Hutchinson 1972).

Evidence that Cyprus-type deposits are emplaced syngenetically on the ridge or marginal basin floor is provided by the Red Sea margins (Hutchinson 1966) and muds. Unless these are related to adjacent continental margins (Hutchinson 1966), their presence in the oceanic crust suggests the occurrence of concentration of metals in oceanic sediments (Anor et al. 1972) suggest that they may originate either at spreading centers on the sea floor. Alternatively, they may be epigenetic, or subsurface, deposits. Cyprus-type deposits might be associated with aquagene tuffs, pillow breccias, and volcanoclastic sediments, which

ORIGINS AND GENERATION OF CYPRUS-TYPE MASSIVE SULFIDES

the hypothesis requires that the massive sulfides form above ascending magma intruded at ocean ridges and in marginal basins. Generation of marginal basins is related to different tectonic regimes (e.g., 1971a; Matsuda and 1971) and may resemble that of the Troodos complex (Selater et al. 1972). The massive sulfides are emplaced either continuously within a narrow zone along an ocean ridge crest. They are derived from the partial melting of the mantle, forming layered mafic rocks passing upward into gabbroic complexes. These intrude pillow lavas, hyaloclastics, and thin pelagic sediments. The "island arc" of pillow basalts, gabbroic facies and of mafic rocks to amphibolites (1971) probably takes place in water-rich environments, related to the spilitization of the mantle from post-cooling contraction (Cann 1969).

The movement of this rock mass to the flanks, it is locally controlled by alkali basalts and cherts, pelagic mudstones. Local volcanic andesites are derived from the mantle, either single sea-floor basalt which often consist of mafic or transitional basalt and related

MINERAL DEPOSITS

Mineral deposits within the island arc are interpreted as tectonically related to the oceanic crust or upper mantle. They are unrelated to the tectonic evolution of the deposits subsequent to arc develop-

ment. Deposits of this type include some of the basaltophilic metals considered typical of an early stage of geosynclinal evolution (Smirnov 1968).

Cyprus-type massive sulfides.—The origins of some massive sulfide deposits associated with submarine or "eugeosynclinal" volcanism (e.g., Anderson 1969) have recently been related to oceanic ridge environments (Pereira and Dixon 1971). Well-known examples of ore bodies in this setting are those of the Troodos ophiolite complex in Cyprus (Sillitoe 1972a; Dunham 1972); we term massive sulfides located within similar ophiolite associations "Cyprus-type deposits."

Cyprus-type ore bodies lie either within the tholeiitic pillow lava, metabasalt, or spilite succession—representing layer 2 of the oceanic crust—or between the pillow lavas and overlying pelagic sediments and turbidites of layer 1. The deposits in Cyprus contain massive pyrite together with chalcopyrite, sphalerite, and marcasite, and minor galena, pyrrhotite, gold, and silver (Hutchinson 1965). Strong (1972) suggested that central Newfoundland ores in oceanic tholeiites—such as Whalesback, Little Bay, and Tilt Cove—are characterized by simple mineralogy of pyrite-pyrrhotite-chalcopyrite. Other examples are those of Ergani Maden and Kure in Turkey and Island Mountain in California (Hutchinson 1973).

Evidence that Cyprus-type deposits are emplaced syngenetically during oceanic ridge or marginal basin volcanism is provided by the Red Sea metal-rich brines and muds. Unless these originate on the adjacent continental margins (Davidson 1966), their presence in the Red Sea and the occurrence of concentrations of metals in oceanic sediments (Anon 1970; Cronan et al. 1972) suggest that some sulfides originate either at spreading centers or on the sea floor. Alternatively, possible early epigenetic, or subsurface, formation of Cyprus-type deposits might take place in aquagene tuffs, pillow breccias, and volcanoclastic sediments, which could form

traps susceptible to magmatic hydrothermal or metamorphic hydrothermal mineralization (Smitheringale 1972). A possible factor accounting for the formation of Cyprus-type deposits is high trace-metal discharge associated with periods of exceptional global volcanism resulting from active plume convection (Vogt 1972).

Massive sulfides in Hawaii-type volcanoes.—The probable formation of Cyprus-type ore bodies at ocean ridges suggests that stratiform massive sulfides might also develop near submarine vents in intra-oceanic tholeiitic shield volcanoes. Possible environments include the Hawaiian ridge, where minor quantities of iron, copper, and nickel sulfides occur within phenocrysts in subaerially erupted tholeiites (Desborough et al. 1968). Ore minerals of Hawaii-type deposits would probably be indistinguishable from those of Cyprus-type; Smitheringale (1972) suggested that the volcanic rocks and copper sulfide deposits of the early Ordovician Lush's Bight Group in Newfoundland probably formed either at an intraoceanic volcano or at an oceanic ridge.

Podiform chromite.—In island arcs, chromite or chrome spinel occurs mainly as podiform deposits within deformed Alpine-type dunites or harzburgite bodies (Thayer 1964), some of which are overlain by gabbros, basaltic lavas, and cherts. Economic chromite deposits in arcs are known only in Cuba and the Philippines.

In Cuba, refractory chromite deposits occur in the northeast of Oriente Province, where sacklike layered bodies of massive chromite within dunite pods are surrounded by peridotite and locally cut by gabbro dikes (Park and MacDiarmid 1964). In the Philippines, refractory podiform chromite ores of metallurgical grade occur in the Zambales ultramafic complex on Luzon as lenticular layered bodies within dunite, and are surrounded by saxonite and intruded by dolerite dike swarms (Bryner 1969).

Both the Cuban and Philippine deposits

TABLE 1
MINERAL DEPOSIT SETTINGS IN ISLAND ARCS

MINERAL DEPOSIT	FORMATION		TECTONIC EMPLACEMENT		EXPOSURE				
	Active Magmatic Arc	Ocean Marginal Basin Riso	Ocean Marginal Basin Floor	Within Ophiolites in Mélange	Within Ophiolites in Obducted Slices	Magmatic Arc Active	Magmatic Arc Inactive	Within Ophiolites in Mélange	Within Ophiolites in Obducted Slices
Endogenous deposits:									
Cyprus-type massive sulfides	...	1-7	?1-7	2-7	6	2-7	7
Podiform chromites	...	1-7	?1-7	2-7	6	2-7	7
Nickel sulfides	...	?1-7	?1-7	?2-7	?6	?2-7	?7
Hawaii-type massive sulfides	1-7	2-7	6	2-7	7
Island-arc tholeiite-type massive sulfides	2	5-7
Mercury	4(5, 7)	4(5, 7)	5-7
Bosshi-type massive sulfides	3(4, 5, 7)	5-7
Porphyry copper	4(5, 7)	5-7
Gold around granodiorites	4(5, 7)	5-7
Pyrometasomatic deposits	4(5, 7)	5-7
Kuroko-type massive sulfides	5, ?3, (7)	6, 7
Gold in andesites and around monzonites	5, ?4, (7)	6, 7
Tin-tungsten-wolfram-molybdenum	7	After 7
Formation and Exposure									
Exogenous deposits:									
Bauxite on karstic limestones	Commonly overlying inactive magmatic arc 5-7
Stratiform manganese	Commonly overlying inactive magmatic arc 5-7
Nickeliferous laterites	Overlying ultrabasic rocks, mostly obducted 7

NOTE.—1, 2, 3, etc. indicate stage of arc evolution with mineralization; (5, 7), etc. indicate stage of evolution with possible mineralization; ?3, etc. indicate stage of evolution with doubtful mineralization.

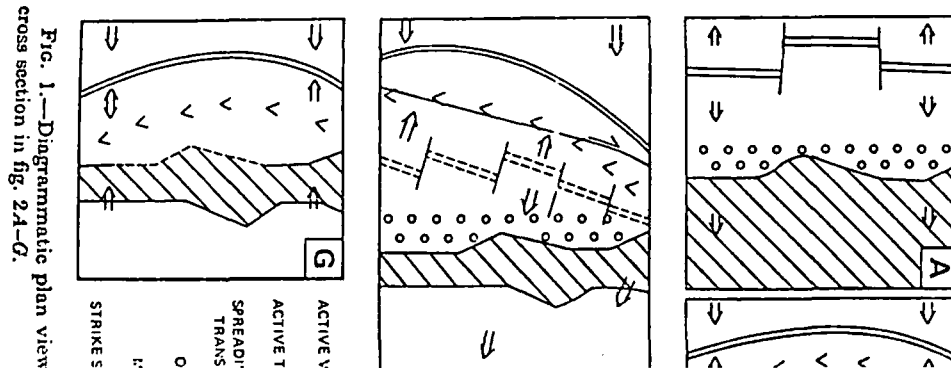


FIG. 1.—Diagrammatic plan view cross section in fig. 2A-G.

are considered to be of early origin (Guill 1947; Bryner 1959). Presence in rocks interpreted mantle slices suggests formation an oceanic or marginal basin center beneath contemporaneous abyssal tholeiites. Recent work the discovery of the incongrue of chromium diopside (Dickey 1969) indicates that chromium might from the silicate phases of mantle rock by incongruent partitioning. Ore genesis by crystal fractional magma leading to the formation of basic cumulates is favored (1969); this could occur either

are considered to be of early magmatic origin (Guild 1947; Bryner 1969). Their presence in rocks interpreted as upper mantle slices suggests formation at either an oceanic or marginal basin spreading center beneath contemporaneously erupted abyssal tholeiites. Recent work involving the discovery of the incongruent melting of chromian diopside (Dickey et al. 1971) indicates that chromium might be released from the silicate phases of lherzolitic mantle rock by incongruent partial fusion. Ore genesis by crystal fractionation of basic magma leading to the formation of ultrabasic cumulates is favored by Thayer (1969); this could occur either beneath an

ocean ridge, or beneath an oceanic volcano as shown in figure 2B.

Nickel sulfides.—Economic deposits of nickel sulfides in island arcs are known only in the Acoje Mine in the Philippines, within the ultrabasic complex on Luzon. The ore occurs with platinum sulfides as irregular blebs in serpentinized dunite, and contains pyrrhotite, troilite, pentlandite, and variolarite (Bryner 1969). Like the chromite, this ore presumably developed near the contact of upper mantle rocks with oceanic crust. Its origin probably differs from that of nickel sulfides in Archaean and early Proterozoic shield areas which are characteristically associa-

- Exogenous deposits:
- Bauxite on karstic limestones.....
 - Stratiform manganese.....
 - Nickeliferous laterites.....
- Commonly overlying inactive magmatic arc 5-7
- Commonly overlying inactive magmatic arc 5-7
- Overlying ultrabasic rocks, mostly obducted 7

NOTE.—1, 2, 3, etc. indicate stage of arc evolution with mineralization; (5, 7), etc. indicate stage of evolution with possible mineralization; 3, etc. indicate stage of evolution with doubtful mineralization.

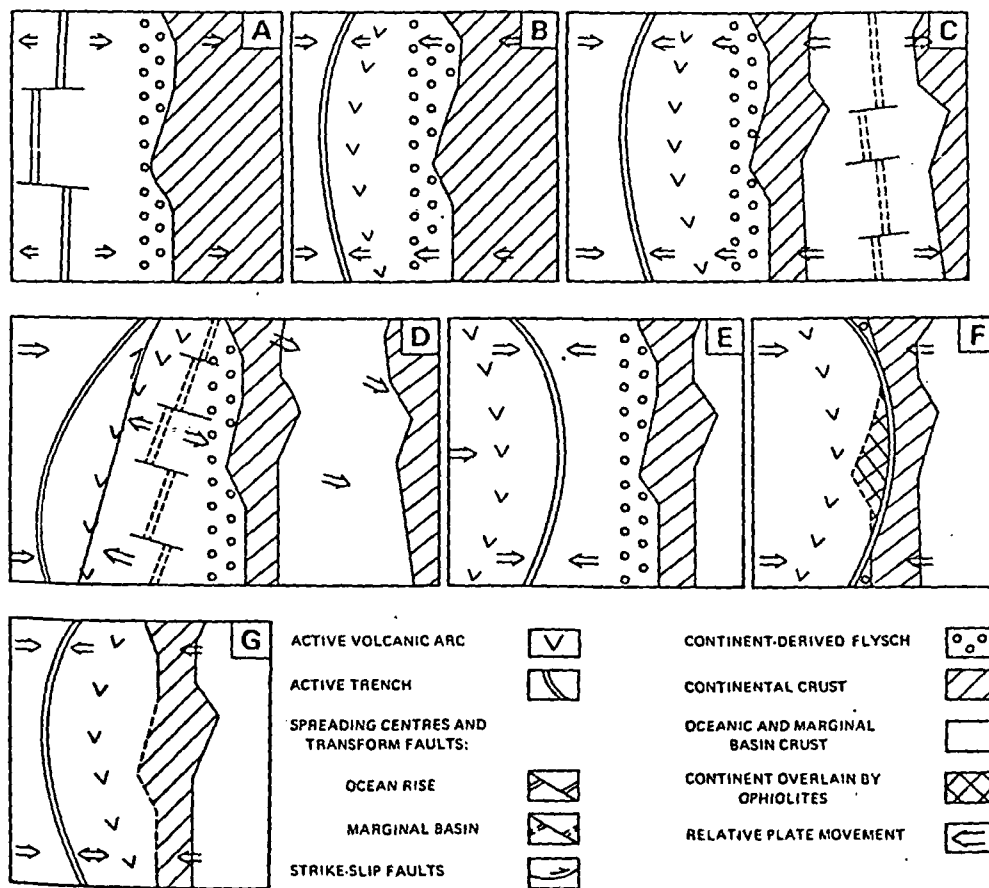


FIG. 1.—Diagrammatic plan views showing stages of arc evolution: A-G refers to corresponding cross section in fig. 2A-G.

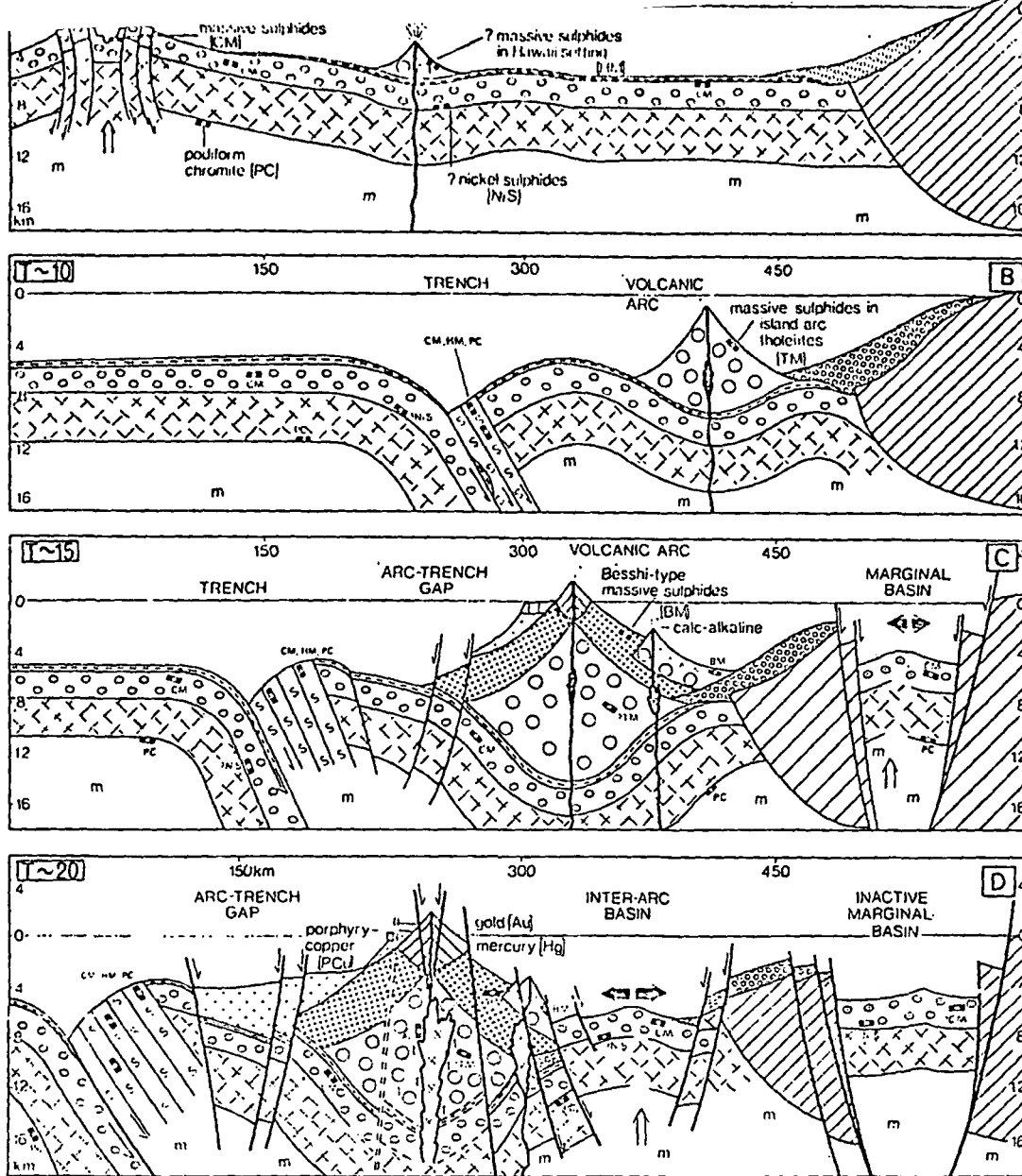
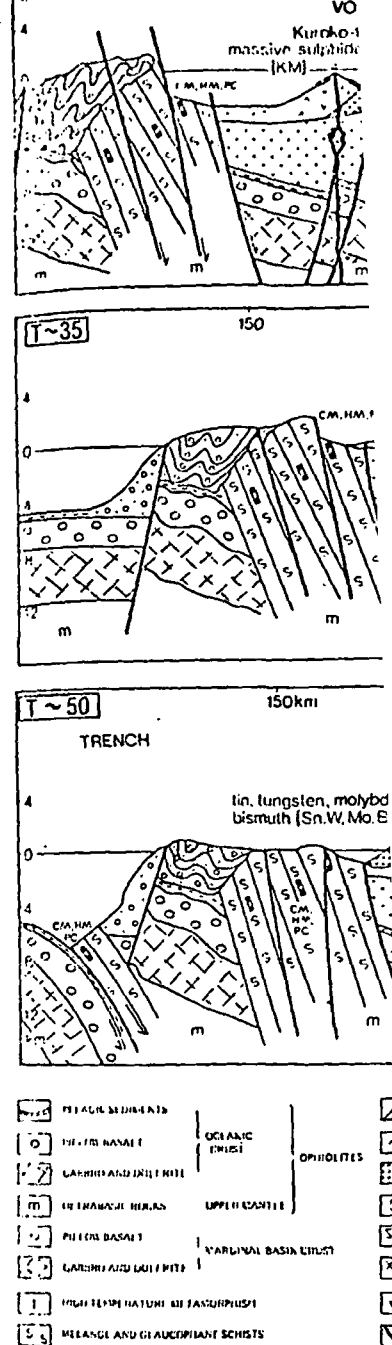
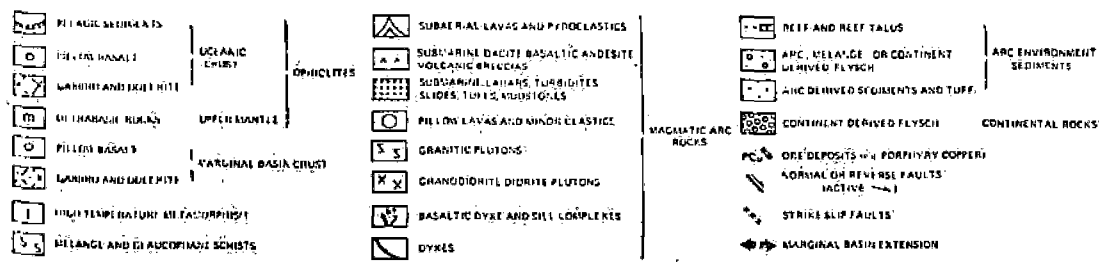
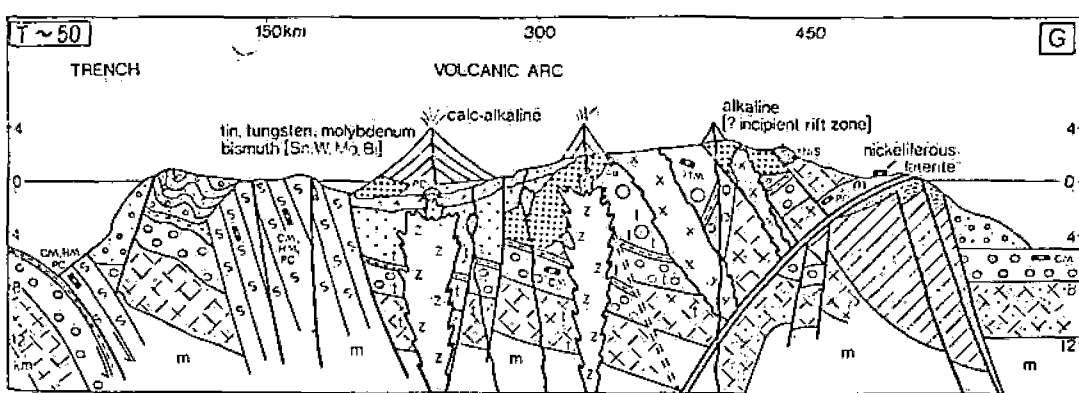
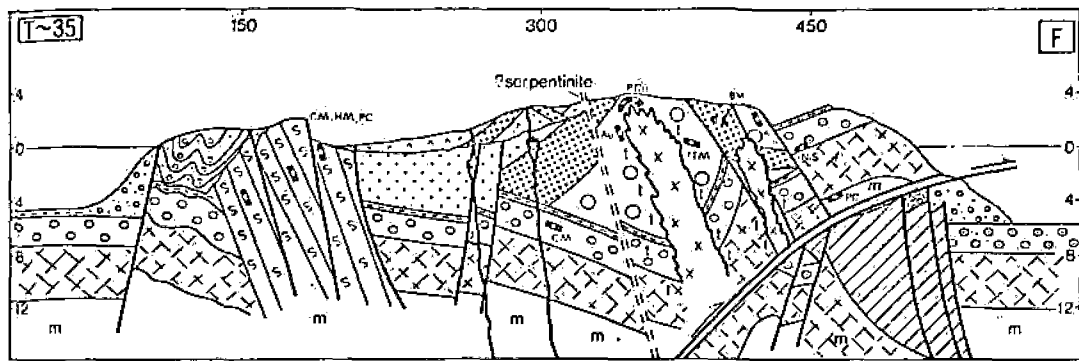
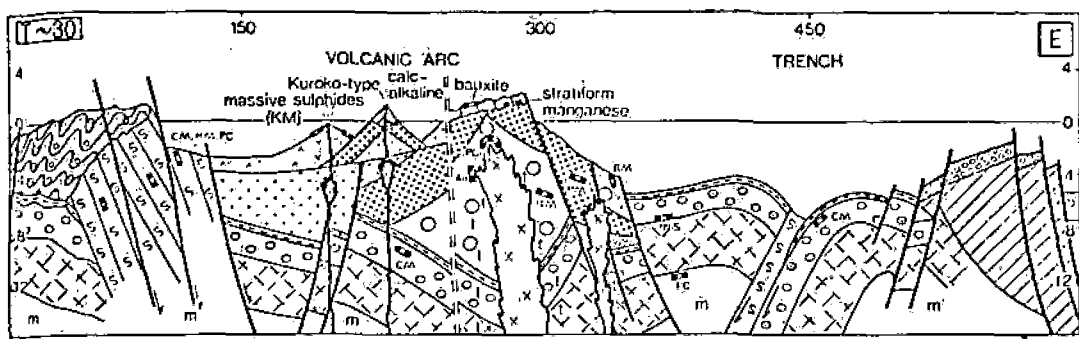
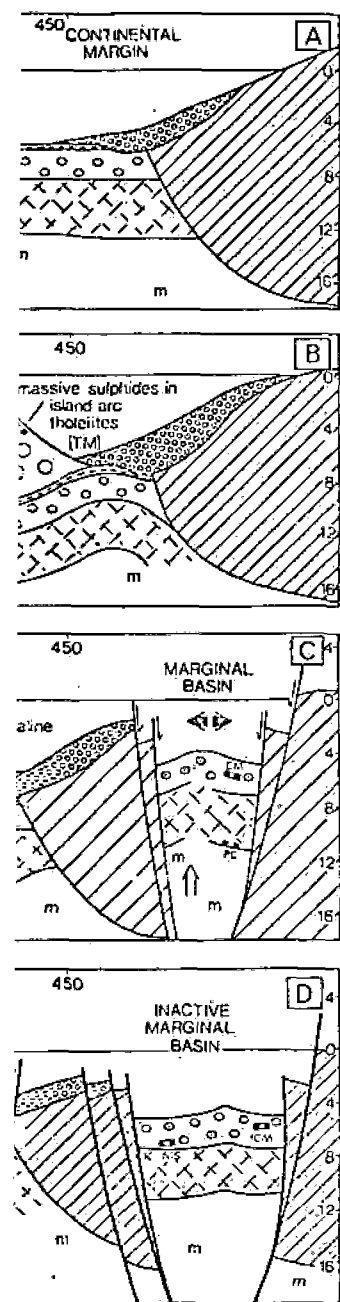


FIG. 2.—Diagrammatic cross sections through an evolving island arc; $T \sim 15$, etc. = time in m.y. since start of arc evolution: *A, Stage 1.*—Pre-arc emplacement of oceanic crust and upper mantle. Spreading ocean ridge migrates away from passive continental margin: formation of Cyprus-type and Hawaii-type massive sulfides, podiform chromite, and possibly nickel sulfides (ocean ridge after Osmaston 1971). *B, Stage 2.*—Submarine volcanism and initial arc development. Ensimatic arc develops on ocean floor near continental margin; possible massive sulfides formed in island-arc tholeiite lavas. *C, Stage 3.*—Subaerial and submarine volcanism. Volcanic arc builds up to sea level; Besshi-type massive sulfides formed on flanks of volcanic arc; rifting near continental margin and development of marginal basin with associated mineralization. *D, Stage 4.*—Plutonic activity, waning volcanism, faulting and arc rifting. Rise of granodioritic plutons in volcanic arc; caldera development with formation of porphyry copper, gold, and mercury deposits; sedimentation in arc-trench gap; development of interarc basin. (Note that porphyry copper [PCu] should be shown occurring below mercury [Hg] deposit.) *E, Stage 5.*—Arc reversal and development of new volcanic arc. Reversal of Benioff zone and loss of marginal basin crust; formation of Kuroko-type massive sulfides in dacites, and



gold mineralization; elevation of uplifted volcanic arc. *F, Stage 6.*—crust; emplacement of Cyprus-type obducted ophiolites. *G, Stage 7.*—Development of obducted ocean floor to expose arc to expose paired metamorphic and alkaline volcanism in incipient rift zone of ore body also formed in older volcanic molybdenum-bismuth mineralization shown occurring at apices of granite



T ~ 15, etc. = time in m.y. znic crust and upper mantle. formation of Cyprus-type and massive sulphides (ocean ridge after ment. Ensimatic arc develops in island-arc tholeiite lavas. up to sea level; Besshi-type marginal and development of activity, waning volcanism, caldera development with in arc-trench gap; development occurring below mercury arc. Reversal of Bonifio massive sulphides in dacites, and

gold mineralization; elevation of trench-fill deposits; bauxite and manganese deposits form on uplifted volcanic-arc. *P, Stage 6.*—Collision of arcs. Arc-arc collision follows loss of marginal basin crust; emplacement of Cyprus-type massive sulfides, podiform chromite, and nickel sulfides in obducted ophiolites. *G, Stage 7.*—Development of new volcanic arc and emplacement of granites. Erosion of obducted ocean floor to expose upper mantle rocks; uplift and erosion of melange and old volcanic arc to expose paired metamorphic belts; development of new volcanic arc and trench; shoshonitic or alkaline volcanism in incipient rift zone prior to marginal basin development; formation of some types of ore body also formed in older volcanic arc; rise of granite plutons with associated tin-tungsten-molybdenum-bismuth mineralization. (Note that this mineralization [Sn, Wo, Mo, Bi] should be shown occurring at apices of granitic plutons.)

ted with highly magnesian silicate magma (Hudson 1972).

STAGE 2: SUBMARINE VOLCANISM DURING INITIAL ARC DEVELOPMENT

GEOLOGICAL EVENTS

In some arcs, the oldest exposed volcanic rocks are basaltic (Baker 1968) with the composition of island-arc tholeiites (Jakeš and White 1972). If island-arc tholeiitic volcanism can continue intermittently for several tens of millions of years (Cill 1970), only the oldest rocks of this composition will be erupted on the ocean floor. Submarine island-arc tholeiites and ocean floor basalts cannot be easily distinguished, but there is evidence of significant differences in the proportions of Ti, Zr, and Y (Pearce and Cann 1971) and in the K/Ba and Sr^{87}/Sr^{86} ratios (Hart et al. 1972).

Stratigraphic contacts between island-arc successions and oceanic crust are rarely exposed; consequently, it is uncertain whether the oldest exposed volcanic unit in an arc represents the first episode of island-arc volcanism, or is underlain by older arc rocks. A probable example of initial arc volcanism is the Water Island Formation, the oldest stratigraphic unit in the Lesser Antilles, with a "chemically primitive" or island-arc tholeiite composition (Donnelly et al. 1971). The Water Island Formation consists of spilitic and quartz keratophyre flows and minor volcanoclastic rocks, erupted in deep water (Donnelly 1964).

Eruption of basalts and basaltic andesites on the ocean floor results in a thick succession of pillow lavas (fig. 2B). Breccias, formed by gravitational collapse of some pillows, move as mass flows down the volcano flanks and accumulate as talus cones (Jones 1969). Changes in the erupted basaltic rocks as the volcano nears sea level probably resemble those described from basalts in Hawaii (Moore 1965; Moore and Fiske 1969) and from Icelandic intraglacial olivine basalts (Jones 1966). Vesicle

size increases upward, and vitric palagonitic tuff and breccia, with pillow breccia and peperites, become abundant in rocks erupted within a few hundred meters of the surface. Within the volcanic pile, anastomosing dikes and sills form an intrusive complex which may develop into a high-level reservoir.

Figures 1B and 2B show a volcanic arc bordered by a submarine trench developing above a Benioff zone near a continental margin.

FORMATION OF MINERAL DEPOSITS

Although stratiform sulfide deposits are not known from volcanic successions interpreted as early island-arc rocks, their presence in ocean crust tholeiites suggests that they could also occur in deep-water island-arc tholeiites. Similarities in composition of the basalts erupted in the two settings suggests that the ore minerals from each setting also would be similar.

STAGE 3:

SUBAERIAL AND SUBMARINE VOLCANISM

GEOLOGICAL EVENTS

As a submarine volcano attains sea level, subaerial lava flows and tuffs are erupted, overlying predominantly clastic, shallow marine rocks (fig. 2C). Subaerially erupted successions are common in island arcs, both as stratovolcanoes in present active volcanic chains, and as block-faulted successions in active and inactive arcs (Mitchell and Reading 1971). However, conformable stratigraphic contacts between these and the oldest exposed submarine volcanic succession are rare. The examples below indicate that rocks erupted during the first subaerial episode in an arc are mostly either andesites or basalts.

In the Virgin Islands (Donnelly et al. 1971) the submarine Water Island Formation is overlain unconformably by the Louisenhoj Formation—a thick series of subaerially erupted porphyritic augite-andesite breccias similar to the pre-Robles succession in Puerto Rico. The Louisenhoj

and pre-Robles Formations have primitive characteristics, resemble the underlying Water Island

The New Hebrides islands and Espiritu Santo contain very Miocene successions of volcanic andesites (Robinson 1971). On Malekula, rocks of this facies are abundant and include tree trunks and reef limestone suggesting accumulation on the flanks of subaerially active volcanoes. Rapid erosion led to mass transport of rock debris—and submarine lahars, slides, and into deep water (Mitchell 1971). Subsequently, relatively small subaerial volcanoes become surrounded by a larger volume of submarine volcanic rocks.

The South Sandwich islands and Scotia arc consist mostly of island-arc subaerially erupted lavas from shield volcanoes and are at an early stage of arc volcanism (Baker 1968). Their slopes probably resemble those of oceanic basaltic volcanoes with foot breccias, hyaloclastites, and phreatic eruptions moving down deep water (Moore and Fiske 1969).

Subaerial and submarine volcanic successions and sedimentation in the volcanic arcs are accompanied by sedimentation in a trench gap, commonly a forearc trough, located between the passive margin and the active volcanic margin. Possible examples of these occur in the Cretaceous Melville Peninsula south of southwest Japan and in the Hokonui facies of New Zealand (Donnelly 1971), although distinction between subaerial and interisland volcanic arcs is difficult.

The distribution of the recently erupted rocks suggests that they may originate along or above a Benioff zone. Migration and probable change in the position of a Benioff zone during volcanism occurred in the Sunda arc;

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abundant in rocks
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2B show a volcanic arc
marine trench developing
one near a continental

MINERAL DEPOSITS

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FIGURE 3: SUBMARINE VOLCANISM

TECTONIC EVENTS

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2C). Subaerially erupted
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and pre-Robles Formations have chemically
primitive characteristics, resembling those
of the underlying Water Island Formation.

The New Hebrides islands of Malekula
and Espiritu Santo contain very thick early
Miocene successions of volcanoclastic basal-
tic andesites (Robinson 1969; Mitchell
1971). On Malekula, rocks of deep-water
facies are abundant and include carbonized
tree trunks and reef limestone detritus,
suggesting accumulation on the submarine
flanks of subaerially active volcanoes.
Rapid erosion led to mass downslope
transport of rock debris—as subaerial
and submarine lahars, slide, and turbidites—
into deep water (Mitchell 1970). Con-
sequently, relatively small subaerial vol-
canoes become surrounded by a much
larger volume of submarine volcanoclastic
rocks.

The South Sandwich islands in the
Scotia arc consist mostly of late Cenozoic
subaerially erupted lavas forming basaltic
shield volcanoes and arc at an early stage
of arc volcanism (Baker 1968). Submarine
slopes probably resemble those of intra-
oceanic basaltic volcanoes where flow-
foot breccias, hyaloclastites, and tuff from
phreatic eruptions move downslope into
deep water (Moore and Fiske, 1969; Jones
1969).

Subaerial and submarine volcanism and
sedimentation in the volcanic arc are
accompanied by sedimentation in the arc-
trench gap, commonly a topographic
trough, located between the trench inner
margin and the active volcanic front.
Possible examples of these successions
occur in the Cretaceous Median Zone of
southwest Japan and in the Mesozoic
Hokonui facies of New Zealand (Dickinson
1971), although distinction between these
and interisland volcanic arc deposits is
difficult.

The distribution of the recent subaerially
erupted rocks suggests that the magmas
originate along or above a Benioff zone.
Migration and probable change in slope of
a Benioff zone during volcanism may have
occurred in the Sunda arc; there is ev-

idence that the trench has been forced
oceanward as scraped-off continent-derived
turbidites (Hamilton 1972) were tectoni-
cally emplaced on the arc side of the trench
(e.g., Oxburgh and Turcotte 1971), forming
the Mentawai-Nicobar-Andaman Islands
and the Indoburman ranges. The resulting
tectonic mélange of ocean floor sediments,
high-pressure metamorphic rocks, and
upper mantle material forms a belt parallel
to the trench and is commonly partly
overlain by arc-derived sediments.

Accumulation of a thick pile of volcanic
rocks, accompanied by subsidence due
partly to isostatic adjustments (Moore
1971), results in deep burial and regional
high-temperature metamorphism of the
volcanic arc rocks and underlying oceanic
crust. Possible examples of metamorphosed
oceanic crust are the amphibolites of the
Bermeja Complex, Puerto Rico (Donnelly
et al. 1971), amphibolite rafts in serpentinite
on Pentecost Island, New Hebrides
(Mallick 1970), and "basement" green-
schists and amphibolites on Yap Island in
the Palau arc (Shiraki 1971). Meta-
morphosed submarine island-arc tholeiitic
rocks form part of the Wainimala Group
of greenschist facies in Fiji (Gill 1970).

In some arcs, the presence of rocks
typical of continents suggests that the arc
has migrated oceanward away from the
continental margin. Examples of rifted
continental fragments within active arcs
occur in New Zealand (Landis and Bishop
1972) and probably in Japan. In Figures
1C and 2C, rifting near the continental
margin is followed by development of a
marginal basin (Karig 1972) and ocean-
ward migration of the arc and continental
fragment.

FORMATION OF MINERAL DEPOSITS

Mineral deposits formed at this and
subsequent stages of arc evolution include
some copper-zinc deposits considered typi-
cal of early stages of geosynclinal develop-
ment (Smirnov 1968).

Besshi-type massive sulfides.—Many mas-
sive sulfide deposits occur in association

with andesitic or basaltic volcanic rocks together with significant thicknesses of carbonaceous mudstones, elastic limestones, quartz-rich sediments, or elastic volcanic rocks showing evidence of deep-water accumulation. These nonophiolitic components indicate deposition adjacent to a land mass, volcanic islands, or shallow-water volcanoes, rather than on an oceanic ridge.

Metamorphism and structural complexity of ores and host rocks are common features of these deposits. Both host-rock lithology and ore mineralogy are very variable and the deposits could probably be divided into subgroups. We adopt Kato's (1937) term "Besshi-type deposits," applied to bedded cupriferous iron sulfide deposits at Shikoku on Honshu Island, Japan.

Deposits at Besshi occur in the high-temperature Sanbagawa metamorphic belt of late Mesozoic age, mostly within a succession of isoclinally folded alternations of basic, pelitic, and quartzose schists (Kanehira and Tatsumi 1970). The sedimentary environment has been interpreted as a continental slope and shelf (Ernst 1972), although mafic tuffs and subsequent metamorphism suggest a volcanic arc environment. The stratiform sulfide ores are of three types: (1) compact pyrite, chalcopyrite, sphalerite, and gangue; (2) banded sulfides and silicates; and (3) copper-rich ore, containing chalcopyrite, minor pyrite, and gangue. Pyrrhotite is abundant toward the base of the deposits.

Similar massive sulfide deposits occur in the high-temperature Hida and Abukuma metamorphic belts of Japan (Kanehira and Tatsumi 1970). These have been interpreted as either volcanic sedimentary or early epigenetic deposits; evidence of slumping and mass flow of host sediments and ore (Jenks 1971) suggests a deep-water environment.

Besshi-type deposits in other arcs probably include the Hixbar and Bagacay deposits in the Philippines (Bryner 1969). In intracontinental greenstone belts, ore

bodies in the Bathurst-Newcastle area of New Brunswick and at Captains Flat in New South Wales—considered by Stanton (1960) to be strata-bound in island arc rocks—are probably of Besshi-type. Other ore bodies in similar settings occur at Stekenjokk (Zachrisson 1971) and Menstrask (Grip 1951) in Sweden, and possibly Mt. Isa in Queensland (Hutchinson 1973). In the Iberian pyrite belt, the presence of resedimented mudstones, slates, and conglomerates interbedded with massive sulfides (Sehermerhorn 1970) suggests that these are Besshi-type deposits, rather than Kuroko-type (Sillitoe 1972a) discussed below.

Besshi-type deposits include varying assemblages of ore minerals, some of which may resemble those of Kuroko type. Strong (1972) suggested that massive sulfides associated with intermediate to basic calc-alkaline volcanic rocks—for example, Betts Cove in Central Newfoundland—comprise polymetallic ores (Cu, Pb, Zn, Ag, and Au); Hutchinson (1973) and Sillitoe (1972a) considered that deposits in calc-alkaline rocks include more Pb, Zn, Ag, and Ba than those in ophiolite complexes.

Support for a syngenetic volcanic exhalative origin for deposits of Besshi-type is provided by sulfur isotope ratios in the Bathurst-Newcastle deposits (Sangster 1968, Lusk 1969). Lusk (1972) showed that the ratios of these and some similar deposits elsewhere can be explained by mixing of sulfur in rising hot igneous fluids with marine or connate sulfate below the sediment-water interface.

Deposits associated with ophiolites.—Since similarities exist between the crust and upper mantle of the oceans and of marginal basins, it is possible that mineral deposits comparable with those considered in Stage 1 may also form during generation of marginal basin crust and upper mantle in Stages 3 and 4. However, it is not yet possible to distinguish between either rocks or mineral deposits formed in these two settings.

STAGE 4: PLUTONIC A VOLCANISM, FAULTING

GEOLOGICAL

Islands in many arc gabbroic to granodioritic intruding volcanic successions. Examples are the Utuac Middle Cretaceous rock (Donnelly 1964), Upper diorites intruding Miocene in the Aleutians (Coal dioritic plutons intruding andesitic rocks in Be and Miczitis 1966; Macr Middle Miocene diorite Miocene volcanoclastic r New Hebrides (Mitchell and granodioritic plutons cene and Pliocene rock and New Georgia, Solomon and Bell 1969).

Stratigraphic relations whether the plutons were or following eruption of t canic rocks. Although calderas suggests that large lie beneath volcanic anomalies in the indicate that perched mag only a few kilometers in could consist of dike com 1970). Possibly island-arc those in anorogenic ar 1972), are underlain by se in Hawaii (Wright and Fi develop into large magma after the main volcanic act Magma ascent by stopping, batholith of Peru (Cobbin passive emplacement high pile, are probably accompanied metamorphism of the sub and sedimentary prism are levels of the rising plutons

In most arcs, intense v along any one belt during Cenozoic lasted no longer m.y. However, after an int was commonly either ren

STAGE 4: PLUTONIC ACTIVITY, WANING VOLCANISM, FAULTING, AND ARC RIFTING

GEOLOGICAL EVENTS

Islands in many arcs contain stocks of gabbroic to granodioritic composition intruding volcanic successions (fig. 2D). Examples are the Utuada Pluton intruding Middle Cretaceous rocks in Puerto Rico (Donnelly 1964), Upper Tertiary granodiorites intruding Miocene volcanic rocks in the Aleutians (Coats 1962), Pliocene dioritic plutons intruding early Miocene andesitic rocks in Bougainville (Blake and Mizitis 1966; Macnamara 1968), pre-Middle Miocene diorites intruding lower Miocene volcanoclastic rocks on Malekula, New Hebrides (Mitchell 1966), and diorite and granodioritic plutons intruding Miocene and Pliocene rocks in Guadalcanal and New Georgia, Solomon Islands (Stanton and Bell 1969).

Stratigraphic relations rarely indicate whether the plutons were emplaced during or following eruption of the overlying volcanic rocks. Although the presence of calderas suggests that large magma chambers lie beneath volcano summits, magnetic anomalies in the New Hebrides indicate that perched magma chambers are only a few kilometers in diameter, and could consist of dike complexes (Malahoff 1970). Possibly island-arc volcanoes, like those in anorogenic areas (Thompson 1972), are underlain by small reservoirs as in Hawaii (Wright and Fiske 1971), which develop into large magma chambers only after the main volcanic activity has ceased. Magma ascent by stoping, as in the coastal batholith of Peru (Cobbing 1972), and its passive emplacement high in the volcanic pile, are probably accompanied by regional metamorphism of the subsiding volcanic and sedimentary prism around the deeper levels of the rising plutons.

In most arcs, intense volcanic activity along any one belt during the Mesozoic or Cenozoic lasted no longer than about 10 m.y. However, after an interval volcanism was commonly either renewed along the

same belt, or commenced along a different belt. These variations in volcanic activity could result from stress changes accompanying arc rotation relative to the subducting plate during marginal basin opening—for example, clockwise rotation of the New Hebrides arc, during the late Cenozoic. Major strike-slip faults trending approximately parallel to the arc, as in the Philippines or Sumatra, could also result from stress changes related either to arc rotation or to changes in ocean ridge spreading direction relative to the arc. Strike-slip faults approximately parallel to complex arcs are also known in Honshu, Japan (Miyashiro 1972), Taiwan (Big 1971), and Sulawesi (Sarasin 1901).

Strike-slip faults oblique to the arc—for example, in Guadalcanal in the Solomon Islands (Coleman 1970) and in the west of the New Hebrides (Malahoff and Woollard 1969)—are possibly continuations of oceanic transform faults along which ultrabasic and basic rocks can be emplaced (Thompson and Nelson 1972). Fault slices and pods of serpentinite, commonly showing a linear distribution, such as those on Guadalcanal and the "filons" in New Caledonia (Lillie and Brothers 1969), may have been emplaced along faults of this type.

Vertical displacements along high-angle faults in volcanic arcs, common both during and following volcanism, may result either from block faulting accompanying isostatic adjustment or from vertical movements along strike-slip faults. Control of eruptive center locations by high-angle faults is indicated by the linear distribution of parasitic cones and major craters (Kear 1957; Warden 1967, 1970), by the location of major centers of eruption and calderas where two or more linear features intersect as in Hawaii (Woollard and Malahoff 1966), and by the distribution of volcanoes along an echelon fractures oblique to the arc trend as in Tonga (Bryan et al. 1972).

Figures 1D and 2D show rifting and subsequent interarc basin development

at Hurst-Newcastle area of and at Captains Flat in rs—considered by Stanton rata-bound in island arc ably of Besshi-type. Other similar settings occur at ehriesson 1971) and Men- I) in Sweden, and possibly island (Hutchinson 1973). yrite belt, the presence of udstones, slates, and con- bedded with massive sul- horn 1970) suggests that -type deposits, rather than Sillitoe 1972a) discussed

deposits include varying re minerals, some of which those of Kuroko type. suggested that massive ed with intermediate to line volcanic rocks—for ove in Central Newfound- polymetallic ores (Cu, Pb,); Hutchinson (1973) and -sidered that deposits in ks include more Pb, Zn, than those in ophiolite

- a syngenetic volcanic n for deposits of Besshi- by sulfur isotope ratios in westale deposits (Saugster). Lusk (1972) showed that ese and some similar de- can be explained by mixing ig hot igneous fluids with nate sulfate below the interface.

ciated with ophiolites.— s exist between the crust le of the oceans and of it is possible that mineral rable with those con- I may also form during arginal basin crust and Stages 3 and 4. However, ble to distinguish between mineral deposits formed in gs.

(Karig 1972) between the volcanic arc and the continental fragment. This process may explain the intraoceanic location of rafts of continental rocks or continent-derived sediments lacking a volcanic arc—for example, the Mesozoic succession on New Caledonia (Lillie and Brothers 1969).

FORMATION AND EXPOSURE OF MINERAL DEPOSITS

Mineral deposits formed at this stage and during the preceding Stages 2 and 3 can be exposed following uplift and erosion either during or subsequent to the fault movements described above.

Porphyry copper.—Porphyry copper, or copper-molybdenum and copper-gold, deposits are emplaced in island arcs and on Andean-type continental margins in the belt of andesitic to dacitic igneous activity above a Benioff zone (Pereira and Dixon 1971; Mitchell and Garson 1972; Taylor 1972; Sawkins 1972; Sillitoe 1972*b*). They occur at the summit, or around the margins, of stocks or small plutons intruded beneath contemporaneously erupted volcanic rocks.

In island arcs, the intruded host rock forms part of a thick volcanic and elastic succession which mostly accumulated below sea level, although it was probably overlain by subaerial volcanoes during mineralization. Occurrence of Miocene and younger ore bodies at a high elevation—as at Mamut in Sabah and Ok Tedi in New Guinea—suggests that a thick column of intruded host rock favors mineralization, perhaps by permitting differentiation in the rising pluton. Later uplift and erosion expose the ore body in the submarine host rocks.

Whether the volcanic host rock succession is underlain by rocks erupted in an earlier stage of arc volcanism, by oceanic crust, or by continental fragments is uncertain. Porphyry copper deposits may, therefore, develop not during the first episode of subaerial volcanism in an arc, but only during a later episode (Stage 5). Alternatively, emplacement of the deposits may be independent of the stage of

arc evolution, and occur beneath any belt of andesitic or dacitic subaerial volcanoes. It has yet to be demonstrated that porphyry coppers are associated only with calc-alkaline volcanic rocks (e.g., Sillitoe 1972*b*), and not with island-arc tholeiitic volcanic rocks of intermediate composition.

Controls on location of porphyry deposits within a volcanic belt are poorly understood. The occurrence of many active volcanoes along faults or at fault intersections suggests tectonic control of related porphyry copper mineralization. Intense shattering of the ore host rocks has been attributed to mineralization stoping (Locke 1926), pulsating magma movements (Perry 1961), fault and joint development related to strike-slip faults (Bryner 1968), and pressure release beneath a caldera (Taylor 1972)—for example, by explosive emission of nuée ardentes. The common development of both calderas and strike-slip faults toward the close of arc volcanism suggests that related porphyry copper deposits are emplaced late in the development of a magmatic arc.

Mercury deposits.—Deposits of cinnabar and minor amounts of quicksilver occur in the Philippines, Japan, and New Zealand, but are not known in the less complex arcs. Most deposits are in Cenozoic volcanic rocks and are located near either active or old volcanic centers.

Restriction of the known ore bodies to the more complex arcs is probably of genetic significance, but does not indicate whether the metal is magmatic or non-magmatic in origin. If the mercury is magma-derived, the presence of thick crust typical of complex arcs may be necessary to allow differentiation of a rising high-level pluton and concentration of volatiles. If the metal is sediment-derived, a thick stratigraphic prism including fine-grained sediments may be necessary to form a source from which mercury is expelled by magmatic heat (Moiseyev 1971). White et al. (1971) suggested that mercury, separated from less volatile metals in vapor-dominated reservoirs, could be deposited

above boiling porphyry copper mercury deposit a subaerial volca

Gold associated
—Problems in re types of gold dep ments above a discussed by Sav most important s ation in island a associated with g gold in andesitic discussed under 5

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STAGE 5: ARC DEVELOPMENT C

GEOLOG

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above boiling brine zones in which
porphyry copper deposits develop. A
mercury deposit in this position beneath
a subaerial volcano is shown in Figure 2D.

Gold associated with granodioritic plutons.
—Problems in relating the origins of some
types of gold deposit to geological environ-
ments above a Benioff zone have been
discussed by Sawkins (1972). Two of the
most important settings for gold mineraliza-
tion in island arcs are gold-quartz veins
associated with granodioritic plutons, and
gold in andesitic volcanics; the latter is
discussed under Stage 5 below.

In the Solomon Islands, and probably in
the western belt of the New Hebrides,
small quantities of placer gold have been
derived from lodes associated with the
margins of dioritic or granodioritic plutons.
Limited evidence suggests that these
magmatic-hydrothermal deposits are em-
placed at a deeper structural level than
porphyry copper ore bodies and are related
to nonporphyritic intrusions. Deposits in
this type of environment are widespread
in western North America, but the related
plutons were probably emplaced mostly in
an Andean-type igneous belt on a conti-
nental margin rather than in island arcs.

Pyrometasomatic deposits.—Pyrometaso-
matic deposits are common around plutons
in the more complex arcs, such as Japan
and the Philippines. However, deposits of
this type are neither restricted to, nor
particularly characteristic of, island arcs,
and are, therefore, not considered here.

STAGE 5: ARC REVERSAL AND DEVELOPMENT OF NEW VOLCANIC ARC

GEOLOGICAL EVENTS

In many arcs, successive volcanic belts
have not necessarily developed in the same
place. Change in volcanic arc position can
result from arc rifting and interarc basin
development (Karig 1971a, 1971b; 1972).
Thus, the relative positions of the active
Tonga arc and the Lau-Colville inactive or
remnant arc have been explained by late
Cenozoic splitting and eastward migration

of the active volcanic belt (Karig 1972;
Selater et al. 1972). Similarly, the Mariana
arc has probably migrated eastward away
from the west Mariana remnant arc (Karig
1971a).

Change in position of a volcanic arc
related to changes in Benioff zone in-
clination have been suggested in the
Peruvian Andes (J. Cobbing, personal
communication, 1972), but have yet to be
convincingly demonstrated in an island
arc. In Japan, where the distribution of
Quaternary volcanoes coincides approxi-
mately with the Miocene "Green Tuff"
volcanic belt, the two volcanic episodes
possibly resulted from intermittent descent
of lithosphere along a Benioff zone.

Changes in position of the volcanic arc,
or arc reversal, related to changes in
direction of dip of the Benioff zone
(McKenzie 1969) shown in figures 1E and
2E may have occurred in the New Heb-
rides (Mitchell and Warden 1971), the New
Ireland-Bougainville part of the Solomon
Islands arc (Mitchell and Garson 1972), and
Taiwan (Murphy 1972). Arc reversals
probably result from attempted sub-
duction of continental, island-arc, or
oceanic island crust. Changes in Benioff
zone dip may be related to emplacement of
mélanges and consequent oceanward mi-
gration of the trench, to changes in rate of
lithosphere descent, or to lithosphere drift
relative to underlying deep mantle (Hynd-
man 1972).

Development of a new volcanic arc is
probably preceded by associated trench
formation. The old inactive trench be-
comes filled with sediments and rises
isostatically as belts of thick folded and
faulted flysch-type rocks, perhaps border-
ed on the arc side by mélanges and glauco-
phane schists. The Mentawai-Nicobar-
Andaman Islands and the Indoburman
Ranges could be interpreted as trench fill
rather than mélange deposits.

The belt of flysch, glaucophane schists,
and mélanges commonly lies parallel to
uplifted and eroded rocks of an extinct
volcanic arc, showing high-temperature

metamorphism (see fig. 2F). These form the paired metamorphic belts (Miyashiro 1961) sometimes separated by a tectonic line along which major strike-slip movements may have occurred (Miyashiro 1972).

Block faulting of inactive arc segments can result in raised atolls, such as Rennell Island south of the main Solomons chain, and extensive raised carbonate platforms, as in Jamaica. Volcanic arc rocks lying between a younger active trench and volcanic arc can be elevated due to upward flexure of the arc plate above the downgoing plate (Fitch and Scholz 1971), resulting in tilted terraces, as in the western belt of the New Hebrides (Mitchell and Warden 1971), southwest Japan, and Eua in Tonga.

The younger volcanic arcs may develop on oceanic crust, on submarine sediments derived from an older arc (e.g., the active Central Chain in the New Hebrides), or on a subaerial or submerged erosion surface of older arc deposits and plutons (e.g., the Japanese "Green Tuff" succession). These younger volcanic successions may resemble either the subaqueous or subaerially erupted successions of Stages 2 or 3 described above.

The composition of these later volcanic rocks varies widely both within an arc and between different arcs. In many late Cenozoic volcanic arcs, the potash content increases with increasing depth to the Benioff zone (Kuno 1966; Hatherton and Dickinson 1969). In some arcs (e.g., Honshu), tholeiites nearest the trench pass laterally into calc-alkaline rocks and finally into shoshonites (Jakeš and Gill 1970). Variations from calc-alkaline to tholeiitic volcanism along the length of the arc are known in the Central Islands of the New Hebrides (Mitchell and Warden 1971) and also in the Lesser Antilles (Donnelly et al. 1971), where calc-alkaline rocks are associated with under-saturated basaltic lavas (Sigurdsson et al. 1973). Ignimbrites are common in the late Cenozoic calc-alkaline belt of some complex arcs

because the islands are larger and the lava more acidic than in arcs at earlier stages of development.

Figures 1E and 2E show arc reversal with "flipping" of a Benioff zone, and development of a related volcanic arc.

X FORMATION AND EXPOSURE OF MINERAL DEPOSITS

The endogenous Kuroko-type massive sulfide and gold deposits described below may be exposed during the subsequent Stages 6 and 7 of arc development. Deposits formed in the older magmatic arc during Stages 2, 3, and 4 may be exposed during Stages 6 and 7, and also during tilting and faulting described above.

Kuroko-type massive sulfides.—Among the best-known massive sulfide ore bodies in a modern island arc are those at Kuroko in northeast Japan. They are all associated with predominantly clastic dacitic or more rarely andesitic volcanic rocks interpreted as shallow near-shore marine deposits. The host rock therefore differs considerably from that of both Cyprus-type and Besshi-type deposits. Massive sulfides associated with clastic andesitic or more acidic rocks emplaced mostly in shallow water are here termed "Kuroko-type" deposits.

In the Kosaka deposits (Horikoshi 1969; Horikoshi and Sato 1970), the stratiform ore bodies are vertically layered with an upper zinc-rich layer of black (= Kuroko) ore and a lower zinc-poor yellow layer. The main minerals are pyrite, chalcopyrite, sphalerite, galena, and minerals of the tetrahedrite group. The ores have been interpreted as volcanic exhalative deposits formed by hydrothermal activity during the last stages of volcanism. This activity followed phreatic explosions which accompanied emplacement of dacite domes and flows and formed lenticular units of lithic dacitic fragments. Graded bedding in the upper levels of the ore bodies indicates a syngenetic sedimentary origin for at least part of the deposit.

Examples of Kuroko-type ore bodies are probably fairly common in orogenic belts

now lying within Archaean Kewatin. Hutchinson et al. (1971) association of mass ores with felsic extr. Possible examples (Sinclair 1971) and in the Noranda are just possible that related with earlier, it should be included for example, deposits in Ethiopia (Anon. 1963) chalcopyrite-sphalerite Precambrian rocks (Anderson and Nash 1963).

The Kosaka deposits "Tuff" belt of intense volcanic activity in dacitic rocks predominate (1963). This succession of Mesozoic age or older on the east by an older belt. It therefore possible of island-arc volcanism though Kuroko-type expected within calc-alkaline episode of shallow Stage 3; a possible deposit at Undua (personal communication).

Gold associated with volcanites.—Gold deposits with quartz veins and successions of andesitic sedimentary rocks in example, in the Hauraki Zeland, gold occurs in propylitized andesitic overlain by Pliocene (1963).

Host rocks in deeply commonly metamorphosed but necessarily cut by metamorphism indicate burial and suggests the overlain by younger volcanic arc facies. Concentration of gold to probably accompanied

arger and the lava
at earlier stages of

show are reversal
Benioff zone, and
d volcanic arc.

EXPOSURE OF DEPOSITS

Kuroko-type massive
sulfides described below
show the subsequent
arc development.
Older magmatic arc
deposits may be exposed
and also during
orogenesis above.

Sulfides.—Among
sulfide ore bodies
are those at Kuroko
type are all associated
with dacitic or more
acidic rocks interpreted
as epithermal deposits. The
Kuroko type differs considerably
from the Besshi-type and Besshi-
sulfides associated
with more acidic rocks
in which low water are here
deposits.

(Horikoshi 1969;
Sawada et al. 1970), the stratiform
Kuroko type is layered with an
upper black (= Kuroko)
pyrite, chalcopyrite, and
pyrite, chalcopyrite, and
pyrite and minerals of the
Kuroko type have been
deposited during
volcanic activity during
orogenesis. This activity
is associated with accom-
panying dacite domes and
similar units of lithic
bedding in the
ore bodies indicates a
volcanic origin for at least

type ore bodies are
found in orogenic belts

now lying within continents. In the
Archean Keewatin lithofacies of Canada,
Hutchinson et al. (1971) have stressed the
association of massive pyrite-base metal
ores with felsic extrusives and pyroclastics.
Possible examples are the Horne Mine
(Sinclair 1971) and the Delbridge deposit
in the Noranda area (Jenks 1971). It is
just possible that certain deposits associ-
ated with earlier, more mafic, extrusives
should be included within the Besshi-type,
for example, deposits near Asmara in
Ethiopia (Anon. 1971), and the pyrite-
chalcopyrite-sphalerite massive sulfides in
Precambrian rocks at Jerome, Arizona
(Anderson and Nash 1972).

The Kosaka deposits lie in the "Green
Tuff" belt of intense early Miocene vol-
canic activity in which andesitic and
dacitic rocks predominate (Sugimura et al.
1963). This succession overlies a basement
of Mesozoic age or older, and is bordered
on the east by an older paired metamorphic
belt. It therefore postdates the first period
of island-arc volcanism in Honshu, al-
though Kuroko-type deposits might also be
expected within calc-alkaline rocks of the
first episode of shallow marine volcanism
of Stage 3; a possible example is the
deposit at Undua in Fiji (H. Colley,
personal communication, 1973).

**Gold associated with andesites and mon-
zonites.**—Gold deposits, mostly associated
with quartz veins, are common in thick
successions of andesitic lavas and meta-
sedimentary rocks in complex arcs. For
example, in the Hauraki Peninsula in New
Zealand, gold occurs in early Tertiary
propylitized andesitic and dacitic flows
overlain by Pliocene lavas (Lindgren
1933).

Host rocks in deposits of this type are
commonly metamorphosed and folded but
not necessarily cut by intrusions. The
metamorphism indicates relatively deep
burial and suggests that the succession was
overlain by younger rocks, possibly of
volcanic arc facies. Migration and con-
centration of gold together with quartz
probably accompanied metamorphism and

deformation of the andesites (e.g., Helge-
son and Garrels 1968). We therefore place
the origin of gold occurring within ande-
sites or meta-andesites in this stage of arc
evolution.

Gold deposits at Vatukoula in Fiji occur
in brecciated andesitic rocks of Pliocene
age, closely associated with a caldera
boundary fault. Infilling of the caldera
with sedimentary rocks and andesites was
followed by intrusion of trachyandesite
and monzonite plugs. Tellurides and
auriferous sulfide mineralization followed
plug emplacement (Denholm 1967). The
more basic Vatukoula rocks are island-arc
alkali basalt or shoshonites (Dickinson et
al. 1968; Gill 1970), and locally lie un-
conformably on older rocks of calc-alkaline
or island-arc tholeiite composition which
form much of the island. Hence they were
erupted subsequent to the first major
volcanic episode in Fiji.

Deposits broadly similar in structural
setting and mineralogy to those at Vatu-
koula occur at Antamok and Acupan in the
Philippines (Bryner 1969; Callow and
Worley 1965).

Bauxite.—Economic deposits of bauxite
on elevated limestones in island arcs are
known in Jamaica and on Rennell Island
(De Weisse 1970) south of the Solomon
Chain; minor deposits occur in the Domini-
can Republic, Haiti, and the Lau Islands.

In Central Jamaica, large gibbsitic
bauxite deposits occur in solution pockets,
sinkholes, and troughs on a karstic surface.
The limestone, of Oligocene and early Mio-
cene age, overlies upper Eocene carbonates
and accumulated after the final major
volcanic episode in the island. The bauxite
developed in post-Miocene time, following
mid-Miocene faulting and uplift, in well-
drained areas at elevations of 700–1,000 m.
The hypothesis that the ore is a residual
deposit resulting from weathering of several
hundred feet of limestone (e.g., Hose 1963)
is supported by trace element data (Sin-
clair 1967). Some authors (Zans 1954;
Burns 1961) favored derivation from
weathered volcanic rocks above the lime-

stone, a hypothesis now coming back into favor.

Stratiform manganese.—Manganese deposits associated with raised limestones are largely restricted to recently elevated areas in or near the tropics. These deposits are distinct from raised ocean floor manganese nodule deposits which are not currently economic. Economic deposits associated with raised limestones occur only in the New Hebrides and Cuba, although other types of occurrence are known, for example on Hanesavo island in the Solomon Islands (Grover et al. 1962).

In the New Hebrides, manganese occurs at or near the contact of raised late Cenozoic reef limestone with clastic volcanic rocks—as, for example, in Erromango, the Torres Islands, and Malekula. The Erromango deposits are probably syngenetic, but those on the other islands are considered to be largely or entirely epigenetic. The recently exploited Forari deposits on Efate Island, which mostly occur at the contact of laterites or limestones with underlying Pliocene volcanoclastic rocks, were possibly precipitated from solutions leached from volcanic rocks (Warden 1970).

In Cuba, economic deposits of manganese are largely restricted to the southwest of Oriente Province. The ores occur near the top of an Upper Cretaceous to Middle Eocene thick marine volcanoclastic and sedimentary unit, and are concentrated within a few tens of meters of the contact between pyroclastic rocks and an overlying limestone member. Psilomelane, pyrolusite, and wad are the chief ore minerals. Simons and Straczek (1958) considered the deposits to be syngenetic and related to hot submarine springs.

STAGE 6: COLLISION OF ARCS

Reversal of arcs and loss of marginal basin crust along a younger Benioff zone can result in approach of the active and remnant arc and their eventual collision.

GEOLOGICAL EVENTS

Collision of arcs in the late Oligocene or

early Miocene probably took place in New Caledonia (Dewey and Bird 1971; Karig 1972), where blueschist metamorphism accompanied southwestward thrusting of peridotites (Avias 1967) over older rocks including Permian-Triassic greywackes (Lillie and Brothers 1969). Derivation of these greywackes from the Australian continent presumably preceded late Mesozoic rifting and northeastward drift of the New Caledonia ridge. Attempted subduction of the ridge, perhaps beneath the Loyalty Islands, resulted in thrusting or "obduction" (Coleman 1971) of the Loyalty Island plate margin onto the New Caledonia plate.

In the Philippines, Tertiary arc collision is suggested by the discontinuous arcuate belt of layered ultrabasic rocks and diabase-gabbro dike swarms exposed on Palawan and western Luzon. These rocks were possibly emplaced during attempted subduction of the Palawan-western Luzon arcuate ridge along a Benioff zone which dipped east beneath an island arc, since fragmented by opening of the Sulu sea and by tectonic movements in western Luzon.

In the Solomon Islands, the ultrabasic rocks, basic lavas, and folded pelagic sediments of the northeastern Pacific Province (Coleman 1970) may be remnants of a late Mesozoic-early Cenozoic marginal basin thrust or obducted southwestward onto the Central Province during the Oligocene.

In the Oriente Province of Cuba, an ultrabasic complex interlayered with gabbroic rocks lies at the eastern end of a belt of northward-thrust ultrabasic slices of probable late Jurassic age (Meyerhoff and Hatten 1968). To the south, Cretaceous quartz diorite and granitic plutons (Khudoley 1967) were probably intruded beneath a volcanic arc. Upper mantle and ocean crust forming the layered complex were either emplaced in a mélange or obducted northward onto the Bahama Bank carbonate platform during southward subduction of a marginal basin. Emplacement of the layered complex may thus have

involved collision of a arc with the Bahama margin (M. Iturza-Gomara, personal communication, 1973).

Figures 1F and 2F show a reversed arc with the continental fragment. Obduction over continent-derived arcs resembles that inferred for

EMPLACEMENT AND EMPLACEMENT OF MINERAL DEPOSITS

Mineral deposits formed in oceanic crust, or are tectonically emplaced in island arcs; they occur in slices, in mélanges, and in elevated blocks. Mineral deposits known from serpentinitized rocks, perhaps mantle-derived, were emplaced along strike-slip faults, or only obducted ophiolites; during collisions, we can expect emplacements of mineral deposits in these settings.

Cyprus-type massive sulfides.—Cyprus-type massive sulfides could occur in oceanic crust, or within mélanges (Silliman 1967). Presently, no deposits are known in mélanges; those in New Caledonia, for example, probably occurred in slices later deformed by arc collision.

Podiform chromite.—The chromite in upper mantle rocks in the Philippines were probably emplaced together with their host rocks during collision of arcs, with, respectively, a continental arc and another arc. Exposed chromite followed erosion or tectonic uplift of the overlying oceanic crustal rocks. Chromite within upper mantle rocks also occur in mélanges, or in diapirs emplaced along major faults. No deposits are known in tectonically emplaced slices.

Nickel sulfides.—Nickel sulfides in the Philippines were presumably emplaced together with the chromite

took place in New Bird 1971; Karig st metamorphism ward thrusting of) over older rocks greywackes (Lillie orivation of these Australian continent le Mesozoic rifting ift of the New tted subduction of each the Loyalty hrusting or "ob- l) of the Loyalty to the New Cale-

riary arc collision ontinuous arcuate basic rocks and arms exposed on uzon. These rocks during attempted an-western Luzon enioff zone which island arc, since of the Sulu sea and n western Luzon. ds, the ultrabasic d folded pelagic theastern Pacific may be remnants Cenozoic marginal d southwestward ince during the

nence of Cuba, an layered with gab- tern end of a belt rabasic slices of o (Meyerhoff and outh, Cretaceous granitic plutons robably intruded pper mantle and layered complex a mélange or ob- he Bahama Bank g southward sub- in. Emplacement may thus have

involved collision of a Cretaceous island arc with the Bahama Bank continental margin. (M. Itturalde-Vinent, personal communication, 1973).

Figures 1F and 2F show collision of the reversed arc with the previously rifted continental fragment. Obduction of ophiolites over continent-derived greywackes resembles that inferred for New Caledonia.

EMPLACEMENT AND EXPOSURE OF MINERAL DEPOSITS

Mineral deposits formed on the ocean floor, in oceanic crust, or in upper mantle are tectonically emplaced within ophiolites in island arcs; they occur in obducted slices, in mélanges, and possibly in fault-elevated blocks. Mineral deposits are not known from serpentized ultrabasic rocks, perhaps mantle-derived, which are locally emplaced along strike-slip faults. Although only obducted ophiolites are emplaced during collisions, we consider here the emplacement of mineral deposits in any of these settings.

Cyprus-type massive sulfides.—Deposits of Cyprus-type could occur in ocean floor basalts emplaced either as obducted slices or within mélanges (Sillitoe 1972a). At present no deposits are known from mélanges; those in Newfoundland, for example, probably occur in obducted slices later deformed by continent-continent collision.

Podiform chromite.—The podiform chromites in upper mantle rocks in Cuba and the Philippines were probably emplaced together with their host rocks as obducted slices during collision of the island arcs with, respectively, a continental margin and another arc. Exposure of the ore followed erosion or tectonic removal of overlying ocean crustal rocks. Podiform chromite within upper mantle rocks could also occur in mélanges, or in fault slices or diapirs emplaced along major faults, but no deposits are known in these settings.

Nickel sulfides.—Nickel sulfides in the Philippines were presumably emplaced together with the chromite with which they

are associated. Like podiform chromites, they are likely to be exposed only at deep structural levels, probably in obducted ophiolites.

Formation of nickeliferous laterites.—In southeast Sulawesi, nickel-bearing laterites overlie partly serpentized harzburgite and lherzolite possibly emplaced as mélange during early Tertiary westward descent of lithosphere (Hamilton 1972). The ore is best developed as nickeliferous serpentine in the lower level of the laterite profile (PT International Nickel Indonesia 1972), which presumably formed during late Cenozoic weathering. Economic deposits of nickeliferous laterites on rocks possibly emplaced in mélanges also occur on Obi and Gube Islands in the Moluccas (Anon. 1972).

In Burma, nickeliferous laterite deposits approaching economic grade overlie ultrabasic rocks in the early Tertiary flysch belt forming the Chin Hills (Gnau Cin Pau, personal communication, 1972). These and other elongate ultrabasic bodies exposed along the eastern margin of the Indoburman Ranges are probably related to eastward subduction of lithosphere prior to late Cenozoic sedimentation in the Central Valley of Burma.

The nickeliferous laterites of the Dominican Republic also probably belong to this environment (F. J. Sawkins, personal communication, 1973).

STAGE 7: DEVELOPMENT OF COMPLEX ARCS AND CHANGES IN MAGMA COMPOSITION WITH TIME

GEOLOGICAL EVENTS

Repeated arc riftings, marginal basin spreading, and arc reversals lead to development of successive magmatic arcs, flysch belts, and paired metamorphic belts (fig. 1G). Arc collisions and strike-slip fault movements result in juxtaposition of tectonic blocks of different age and lithology. An original simple arc thus becomes increasingly complex with magmatic and tectonic addition of younger arcs. For

example, the late Cenozoic simple Scotia arc might progress through an arc reversal to the stage of the New Hebrides arc; collision with remnant arcs, obduction of ophiolites, and major strike-slip movements would result in an arc with the complexity of the Philippines. Alternatively, with intermittent loss of lithosphere and no reversal, an arc of Andaman-Nicobar type could eventually reach the complexity of Honshu Island in Japan.

As stated earlier, the development through time of a complex arc involves changes in magma composition. Jakeš and White (1972) considered that initially tholeiitic, predominantly basaltic, lavas are overlain by both tholeiites and minor calc-alkaline andesitic and dacitic rocks, and that finally tholeiitic, calc-alkaline, and shoshonitic rocks are erupted. Although such changes in composition with time have been described from Puerto Rico (Donnelly et al. 1971) and Viti Levu in Fiji (Gill 1970), they are evidently not universally found. In the Japanese "Green Tuff" belts, thick Miocene successions of largely dacitic and andesitic rocks (Sugimura et al. 1963) are overlain by Quaternary, predominantly tholeiitic, basalts. In the southern Kitakami Massif of eastern Honshu, late Palaeozoic and Cretaceous high-alumina basalts are overlain by Quaternary low-alkali tholeiites (Sugisaki and Tanaka 1971). In the new Britain-Schouten Islands, andesitic clastic rocks of probable early Tertiary age are cut by porphyries (Thompson and Fisher 1965) and overlain in the north by predominantly tholeiitic Quaternary lavas lacking contemporaneous calc-alkaline rocks (Jakeš and White 1969; Lowder and Carmichael 1970). Moreover, evidence that alkaline or shoshonitic rocks in arc environments are related to extensional tectonics typical of marginal basins (Martin and Pwinski 1972) suggests that they are unrelated to this stage of arc evolution.

There are several possible controls on changes in composition of island-arc magma with time. Donnelly et al. (1971)

suggested that island-arc tholeiites result from partial melting of primitive upper mantle prior to development of a Benioff zone; they considered that later calc-alkaline rocks originate from partial melting of tholeiites metamorphosed to amphibolite or eclogite along a Benioff zone, and that as the arc develops descent of increasing volumes of arc-derived sediment would contaminate the tholeiitic layer. Armstrong (1971) suggested that descent of continent-derived ocean floor sediments and mixture with partially melting tholeiite, could explain the lead isotope ratios and high proportion of Pb, Ba, Th, K, Rb, and Cs in some calc-alkaline arc magmas.

The composition of arc magma may be related to rate of lithosphere descent (Sugisaki 1972) which could control the inclination of the Benioff zone (Luyendyk 1970). Benioff zones beneath active arcs erupting tholeiitic magma—such as the Marianas, Izu Islands, and Scotia arcs—mostly dip at more than 40°, while those beneath some arcs erupting predominantly calc-alkaline magma—such as the western Honshu arc and the Aleutians—are less steeply inclined. Marginal basin crust is not developing above the shallow dipping zones which underlie the Peruvian Andes and Central America; in the Marianas arc system, the generation of marginal or interarc basin crust may be dependent on the dip of the Benioff zone which possibly varies cyclically (Bracey and Ogden 1972).

There is a possibility that calc-alkaline magmas may be generated above a Benioff zone. Rise of volatiles from the descending plate into the zone of isotherm inversion above the descending cold slab of oceanic lithosphere could reduce melting points below the ambient temperature (McBirney 1969), facilitating partial melting of wet peridotite to produce liquids of calc-alkaline composition (Yoder 1969). Consequent magma compositions would be largely independent of the nature of the descending lithospheric plate, and would change with time due either to depletion

in the low-temperature addition of dc material to the upper crust (Curran 1972). Mag also be determined by thickness of crust (Hamilton 1972), with degree of differential melting around, rising.

The composition partly to the stage Quartz diorite and relatively simple moderate thickness (Islands, Puerto Rico, bodies of alkali granite been described only Japanese arcs where some of late Cretaceous (kami 1970). The gran highly differentiated p melted mantle or they from partial melting lower part of the island difference of 40 m.y. bet of diorites and granite strated in a calc-alkal Palaeozoic age at Yeo Wales (Gulson and Boff

FORMATION OF MINE

Successive volcanic a the same or adjacent lo be accompanied by for ore bodies—for examp perhaps Besshi-type mas phyry coppers, and mere . As the thickness of the increases, emplacement of granitic plutons may be mineralization associated particularly, soda gran believed to be largely res nental crust. This mineral deposits of the granite; sometimes considered to in the crust together with granitic plutons (Smirnov) later stages of geosync (McCortney and Potter 196

e tholeiites result primitive upper ment of a Benioff that later calcite from partial metamorphosed to along a Benioff develops descent are-derived sedite the tholeiitic) suggested that rived ocean floor e with partially explain the lead proportion of Pb, Cs in some calc-

e magma may be hosphere descent could control the F zone (Luyendyk neath active arcs ma—such as the and Scotia arcs— a 40°, while those ing predominantly ch as the western leutians—are less al basin crust is e shallow dipping e Peruvian Andes the Marianas arc of marginal or be dependent on ne which possibly and Ogden 1972). that calc-alkaline ed above a Benioff om the descending sotherm inversion id slab of oceanic e melting points erature (McBirney al melting of wet liquids of calc-oder 1969). Con- sitions would be the nature of the plate, and would ither to depletion

in the low-temperature melting fraction or to addition of descending ocean crust material to the upper mantle (Arculus and Curran 1972). Magma composition may also be determined partly by the increasing thickness of crust as the arc develops (Hamilton 1972), which could control the degree of differentiation of, and partial melting around, rising magma.

The composition of plutons is related partly to the stage of arc development. Quartz diorite and granodiorite occur in relatively simple arcs with crust of moderate thickness (such as the Solomon Islands, Puerto Rico, and Fiji), but large bodies of alkali granite or adamellite have been described only from the complex Japanese arcs where they form batholiths, some of late Cretaceous age (e.g., Murakami 1970). The granites could either be highly differentiated products of partially melted mantle or they could have resulted from partial melting or anatexis of the lower part of the island-arc crust. A time difference of 40 m.y. between emplacement of diorites and granites has been demonstrated in a calc-alkaline association of Palaeozoic age at Yeoval in New South Wales (Gulson and Bofinger 1972).

FORMATION OF MINERAL DEPOSITS

Successive volcanic arcs developing in the same or adjacent localities may each be accompanied by formation of similar ore bodies—for example, Kuroko and perhaps Besshi-type massive sulfides, porphyry coppers, and mercury deposits.

As the thickness of the island-arc crust increases, emplacement of adamellite and granitic plutons may be accompanied by mineralization associated with alkali and, particularly, soda granites, commonly believed to be largely restricted to continental crust. This mineralization includes deposits of the granitophile elements, sometimes considered to have originated in the crust together with palingenetic granitic plutons (Smirnov 1968) during the later stages of geosynclinal evolution (McCartney and Potter 1962).

Tin - tungsten - molybdenum - bismuth.— These are of economic importance only in Japan, occurring mainly around batholiths in southwest Honshu (Shunso 1971). However, tin ores are also known in the Philippines (Bryner 1969). Fluorine, invariably present with tin and tungsten deposits (e.g., Rub 1972), may originate in the upper mantle or lower crust, or it may be derived with other volatiles from down-going oceanic crust at depths of 200–400 km (Mitchell and Garson 1972).

ANCIENT ARCS ON AND WITHIN CONTINENTS

Continued addition to an island arc of igneous rocks and of tectonically emplaced ophiolites results in development of crust with a thickness approaching that of continents. However, before an arc complex can grow to continental thickness it usually becomes attached to, and forms part of, an older continental mass. Tectonic, and less common sedimentary, accretion of arcs and related ore bodies to a continental margin have been discussed elsewhere (e.g., Dewey and Bird 1971; Mitchell and Garson 1972).

Island arc-continent accretion may eventually be followed by collision with another continent, resulting in further orogeny and deformation of the arc succession. Thrust movements exceeding 100 km during collision have been explained by crustal "flaking" whereby continental crust on the descending plate splits into an upper overriding and lower underriding slab (Oxburgh 1972). Late rifting of the continent over a spreading center may take place in a zone different from that of the collision, resulting in continental fragments each containing arc complexes lying between older shields.

Many orogenic belts of Palaeozoic and Proterozoic age within continents contain metamorphosed greenstone belts. Parts of these resemble in lithology and chemistry the successions in Cenozoic island arcs, with submarine volcanic rocks of calc-alkaline and island-arc tholeiite compo-

sition, and calc-alkaline plutons. Examples are the late Precambrian Harbour Main, Conception, and Hollywood rock groups of the Avalon Peninsula Newfoundland (Hughes and Bruckner 1971).

Archaean shield areas also include low-grade metamorphic greenstone belts with volcanic rocks broadly resembling those of island arcs in composition and, in some cases, in lithology. Examples include the igneous rocks of the Slave Province in the Yellowknife area of Canada (Folinsbee et al. 1968), part of the Kalgoorlie System in Western Australia (Glikson 1970), and the Onverwacht Group in South Africa (Viljoen and Viljoen 1969). Despite minor chemical differences between some of these successions and modern island arcs (Glikson 1971; Jakeš and White 1971; Hart et al. 1970), many recent workers consider that tectonic accretion of island arcs to continental margins has continued for at least 3.5×10^9 years (e.g., Engel and Kelm 1972).

Although the formation of some types of massive sulfide deposits may be characteristic of certain periods of the earth's development (Hutchinson 1973), we consider that similarities between ancient and modern arc rocks together with similarities in associated mineral deposits suggest that ore-forming processes in arcs have changed little during the last 2×10^9 years.

CONCLUSIONS

Major mineral deposits in island arcs can be divided into three main groups according to their environment of formation: (1) deposits formed in magmatic arcs, (2) deposits formed in oceanic crust or upper mantle and tectonically emplaced within ophiolites, and (3) exogenous deposits formed in or on raised limestones and on ultrabasic rocks.

Magmatic arc deposits consist of stratiform massive sulfides and deposits related to plutons. Stratiform massive sulfides of Kuroko-type form in a shallow nearshore

marine environment together with acidic volcanoclastic rocks; those of Besshi-type form in a deep-water environment together with sediments and minor amounts of intermediate to basic volcanic rocks; possibly massive sulfides also form in submarine island-arc tholeiites. Magmatic hydrothermal porphyry copper, gold, and some mercury deposits form around the upper margins of dioritic and granodioritic plutons emplaced beneath volcanoes. Gold mineralization also occurs around monzonitic intrusions and in andesites.

Deposits formed in or on oceanic crust comprise stratiform massive sulfides of Cyprus-type, and similar deposits may form on Hawaii-type oceanic volcanoes. Near the mantle-crust boundary, podiform chromites and possibly nickel sulfides develop. These are emplaced tectonically with the host rocks in mélanges or in obducted slices.

Exogenous deposits include bauxites developed on karstic raised limestones, stratiform manganese deposits formed near limestone-tuff contacts, and nickeliferous laterites developed on tectonically emplaced upper mantle rocks.

Ore deposits likely to be preserved in island arcs now within continents are magmatic arc deposits of deeply eroded porphyry copper and of gold and in some cases tin and tungsten deposits, and island-arc tholeiite-type, Besshi-type, and Kuroko-type massive sulfides; preserved deposits in ophiolites within arcs include chrome deposits, Cyprus-type massive sulfides, and possibly nickel sulfides.

ACKNOWLEDGMENTS.—We thank Dr. H. G. Reading and Mr. E. Eadie of Oxford University, Dr. M. S. Garson of the Institute of Geological Sciences, London, and Dr. Frederick J. Sawkins for critically and constructively reviewing the manuscript. The first author is grateful to the Rio Tinto Zinc Co., Ltd. for permission to publish the paper.

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INTERNATIONAL CLASSIFICATION OF MINERAL RESOURCES

The Committee on Natural Resources of the United Nations Economic and Social Council will this month be considering recommendations of the Expert Group on Definitions and Terminology for Mineral Resources at a meeting in Ankara, Turkey. The latter group had put forward certain recommendations about this at the U.N. Headquarters in New York between January 29 and February 2, this year. The essence of its findings is presented below.

THE Expert Group on Definitions and Terminology For Mineral Resources, convened by the Secretary-General of the United Nations and organised by the Centre for Natural Resources, Energy and Transport at U.N. Headquarters on January 29-February 2, 1979, has recommended an international classification system for mineral resources.

Three basic resource categories, R-1, R-2 and R-3, are distinguished according to the level of geological assurance. Each of these categories can further be subdivided into those considered to be exploitable under the prevailing socio-economic conditions (sub-category E) and other resources (sub-category S). These categories can either refer to *in situ* quantities of metals or minerals or to recoverable metal or mineral.

The Group of Experts recommends the adoption of this classification system. It further recommends that the system be adapted to the needs of individual commodities; that the classification system, if adopted, be reviewed periodically; and that the system be employed not only for further work by the United Nations but also to encourage the expansion of and internal improvement in resource estimation by individual countries.

The Group recognised the advantages that might follow international acceptance of a system of resource classification, including definitions and terminology, particularly as the basis for the compilation of world-wide information. It is also recognised, however, that any system should be used with caution. Thus, while recommending a system, the Group also draws the attention of the Committee on Natural Resources to some of the difficulties that may be associated with its use.*

*The Group based its work on a background paper prepared by J. J. Schanz, on request from and in co-operation with the Centre for Natural Resources, Energy and Transport, which drew on other papers, notably those by I. Bondarenko and J. Zwartendyk.

General guidelines

The Group sought a classification system that used terms, definitions and resource categories that would be compatible to the maximum extent possible with those already in use and with current assessment techniques. It was also thought important that the system should be simple to make possible its use in all countries.

After discussing general principles, the Group agreed that the classification system should:

(a) facilitate the international exchange of data, particularly by enhancing their comparability. This, it was felt, might be a step towards better world-wide understanding of mineral resource issues;

(b) ideally, be suitable for all mineral resources, or be readily adaptable to the specific needs of particular mineral commodities. For practical reasons, the Group considered oil and gas only to the extent necessary to ensure universal applicability;

(c) take account of measurement and collection procedures to the extent necessary to ensure that the system will be of practical value;

(d) provide for the inclusion of estimates concerning all mineral resources that are known or surmised to exist with varying degrees of assurance, as well as resources that are as yet undiscovered;

(e) make provision for both *in situ* and recoverable resources;

(f) allow separate estimates of economic and sub-economic resources within those categories where such subdivision is feasible; and

(g) be primarily concerned with estimates of resources that are of economic interest over the foreseeable period of the next few decades. However, provision should be made for recognition of estimates or descriptions of mineral occurrences that fall outside of the major resource categories as defined.

The Group reviewed present basic terminology. The terms "resources" and "reserves" give rise to confusion because in a number of languages (among them English, French and Spanish), they have general as well as technical meanings. In some languages only one term is available, while in Russian both terms have virtually the same meaning. Furthermore, it is not uncommon for the terms to be used interchangeably, as synonyms, by non-specialists. For example, the Economic and Social Council's resolution itself refers to "reserves" where, in line with the established technical definitions in many English-speaking countries, "resources" would have been more appropriate. The Expert Group therefore recommends that the term "resources" be used exclusively for general classification purposes.

The Group emphasises the need to understand that the extent of mineral resources is a dynamic concept, but estimates for each mineral commodity and for each country must be made at a fixed point in time. It is stressed therefore that all estimates are static representations of a dynamic picture; prospecting, technical improvements and changes in market prices alter them.

While all countries find it useful to gather information about their short-term mineral supply potential, the Expert Group questions the value of estimating the total amount of mineral commodities that will ultimately become available from the earth's crust for mankind's use. To try to estimate very long-term resource potentials in detail would be an expensive process of limited usefulness, it is asserted.

The Group is aware that, even with ideal definitions for the different categories of resources, the information received from countries cannot be expected to be fully homogeneous. The basic information available to any resources estimator is not exhaustive, varies in detail, and interpretation for most categories involves subjective judgement.

Thus, the ability to assemble resources estimates and store them in a computer could create a false impression that the computer output will provide definitive answers to mineral policy issues. Even with the best resource information, policy-making must rely upon the continuing participation of specialists familiar with each commodity. They are able to interpret as well as recognise the limit of original or processed data, to correct for any apparent over- or under-estimation, to make assumptions or adjustments to provide for the ever-present gaps in the data base, to account for future price trends, and to draw conclusions as to the amount of each commodity that appears

likely to be available within stated limits of error.

Although each category described in the simplified classification system recommended is defined as clearly as possible, it is recognised that some countries will probably have difficulties applying the definitions to their specific circumstances. For example, it must be appreciated that even if a reporting system is agreed upon as desirable, some countries will not provide data for some categories or will find it necessary to aggregate the data for two or more categories. These aggregations may then hide differences in the accuracy and reliability of the individual components used to derive the aggregate data. §

Thus the adoption of a satisfactory classification system for international use cannot, by itself, solve all problems of compilation and evaluation. Non-specialists, including planners and decision-makers, should be made aware of the pitfalls inherent in the application of the resulting data to purposes for which they are not suitable.

Resource categories

The Group proposes that for the international classification of mineral resources, three basic categories of resources should be provided, identified as R-1, R-2 and R-3. These categories are differentiated according to the level of geological assurance that can be assigned to each category. They include all of the *in situ* mineral resources that might be of economic interest over the foreseeable period of the next few

§The subjective nature and varying reliability of resource estimates suggest that it may eventually prove useful to request countries to provide broad regional or world estimates in addition to their own national data. Not only would this provide an interesting cross-section of judgements about total resource availability, it would establish benchmarks for identifying variations in outlook or assessment methodologies among countries that are also reflected in their national data.

decades. For the present purpose, foreseeable economic and technical conditions are limited to the next two or three decades. This will vary to some extent according to the commodity being estimated. The limit of economic interest may be further established by the use of various economic or physical criteria suitable for that individual mineral commodity.

Category R-1: This encompasses the *in situ* resources in deposits that have been examined in sufficient detail to establish their mode of occurrence, size and essential qualities within individual ore bodies. The major characteristics relevant to mining and processing such as the distribution of ore grade, the physical properties that affect mining, the mineralogy and deleterious constituents, are known mainly by direct physical penetration and measurement of the orebody, combined with limited extrapolation of geological, geophysical and geochemical data.

Quantities have been estimated at a relatively high level of assurance, although in some deposits the estimation error may be as high as 50%. The primary relevance of such estimates is in the planning of mining activities.

Category R-2: This provides for estimates of *in situ* resources that are directly associated with discovered mineral deposits but, unlike the resources included in Category R-1, the estimates are preliminary and largely based upon broad geological knowledge supported by measurements at some points. The mode of occurrence, size, and shape are inferred by analogy with nearby deposits included in R-1, by general geological and structural considerations, and by analysis of direct or indirect indications of mineral deposition. Less reliance can be placed on estimates of quantities in this category than on those in R-1; estimation errors may be greater than 50%. The estimates in R-2 are relevant

mostly for planning further exploration with an expectation of eventual reclassification to Category R-1.

Category R-3: Such resources are undiscovered but are thought to exist in discoverable deposits of generally recognised types. Estimates of *in situ* quantities are mostly on the basis of geologic extrapolation, geophysical or geochemical indications, or statistical analogy. The existence and size of any deposits in this category are necessarily speculative. They may or may not actually be discovered within the next few decades. Estimates for R-3 suggest the extent of exploration opportunities and the somewhat longer range prospects for raw material supply. Their low degree of reliability should be reflected by reporting in ranges.

Any additional material with a lower economical potential, estimates of which would fall outside of the boundaries of "resources" as here defined, should be referred to as "occurrences" and should be reported separately along with some clarification as to the derivation and meaning of the estimates.

Each of the categories can be further sub-divided as follows:

E — Those *in situ* resources that are considered to be exploitable in a particular country or region under the prevailing socio-economic conditions with available technology.

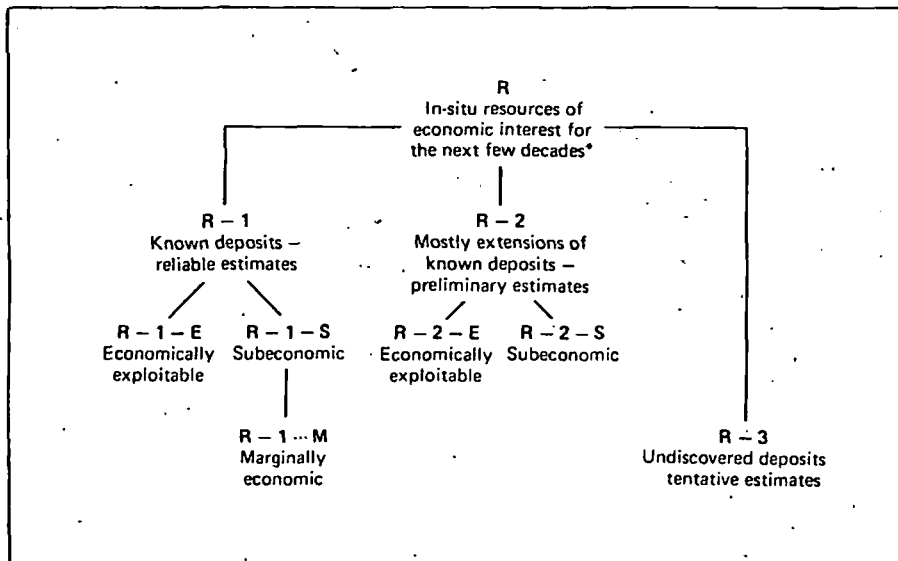
S — The balance of the *in situ* resources that is not considered of current interest but may become so as a result of foreseeable economic or technologic changes.

The sub-classifications "E" and "S" are seen as particularly useful for subdividing resource category R-1 and perhaps R-2, but the Group does not expect that R-3 will generally be subdivided in practice.

Some countries may wish to further sub-divide "S" to provide for an estimate of resources "M" that may become exploitable in the more immediate future as a result of normal or anticipated changes in economic or technical circumstances.

The categories and sub-categories are all specified as referring to estimates of *in situ* quantities of metals or minerals. The Group was fully aware that resource estimates for some minerals, such as oil and gas or uranium, are more commonly reported as estimates of recoverable metal or mineral. In the Group's judgement, *in situ* estimates are important but the recoverable content of metal or mineral more closely approximates the quantity that may appear as mineral supply.

Therefore, the Group recommends the establishment of a parallel set of categories and definitions for recoverable quantities in addition to the above categories and sub-classifications.



This will provide for the opportunity of using either one of both sets depending on what is most suitable. To distinguish between the two sets of parallel data, it is proposed that R-1, R-2 and R-3 should be used for the *in situ* categories, while the recoverable quantities should be shown as r-1, r-2 and r-3. The sub-classification notations E, S and M can be used for both. However, there can be no general definition of recoverability, or of the point in the mining and processing sequence at which it should be measured. These must be established for each commodity.

The letter-number combinations have been chosen to be different from any now in use in the better-known

national classification systems. The Expert Group strongly recommends that they should be used rather than descriptive terms. The use of word identifiers was rejected because of the tendency of the user to assume, often incorrectly, that the desired definition would be identical to his own. The Group's strategy is apparent: if the categories bear no name or commonly used letter-number combination, both the estimator and the user of this data will be required to read the definitions. An added advantage is that the relationship of letters and numbers to one another is simpler to recall than words that do not have such an orderly arrangement.

The Group was well aware that there will still be an inclination to equate the proposed categories with familiar terms. Despite the risk in violating its own caveat, the Group lists some of the more common terms that, to varying degrees, have been used for the proposed categories:

R-1 — established, demonstrated, reasonably assured, explored

R-2 — inferred, estimated additional, possible

R-3 — potential, undiscovered, hypothetical, speculative, prognostic

E — economic

S — subeconomic

M — marginal

Further recommendations

It is recommended that expert assistance be sought to design individual questionnaires. If this classification system proposed here is placed into common use for international reporting of resource information, it will be only the first step toward general harmonisation of resource classification. The collection, aggregation and dissemination of resource estimations on a worldwide scale are at present only carried out regularly by the International Atomic Energy Agency for uranium and the World Energy Conference for other energy resources. If it is to be used for a reporting system, this classification system will have to be adapted to the specific requirements of individual commodities. For example, levels of assurance may have to be defined and recovery levels established. It is also recommended that both the definitions and the questionnaires to be used for individual commodities should be tested carefully before actual use.

If a set of standard definitions and classifications is adopted for general use throughout the United Nations or as a part of a reporting system, then it is recommended that provision be made for periodic review of the classification system.

It is recommended that the classification system be employed not only to further the work of the United Nations on resources, but also to provide a means of encouraging the expansion of and internal improvement in resource estimation by individual countries, both for their internal use as well as for international purposes.

The Expert Group notes that it did not address the problems of production and consumption data classification, definition, and terminology. It recommends that an intergovernmental group, selected for its particular expertise in this kind of terminology, be convened to complete the work specified by ECOSOC resolution 1954 (LIX), Part B.

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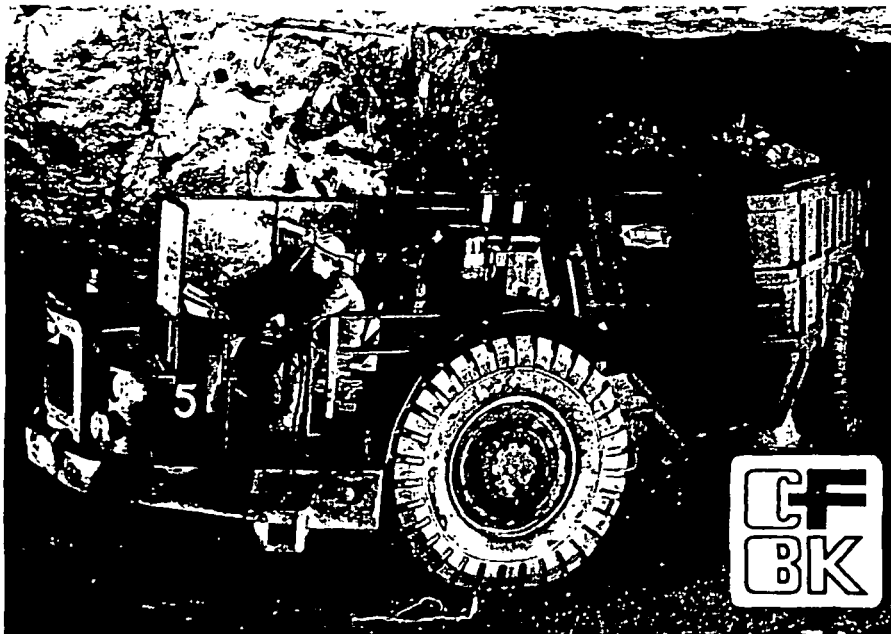
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Magnetite-apatite intrusions and calc-alkaline magmatism, Camsell River, N.W.T.

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Received 22 October 1974

Revision accepted for publication 31 October 1975

The Camsell River area comprises a roof pendant of volcanic rocks within an Aphebian (~1800 m.y.) orogenic belt. Magnetite-apatite intrusions and related bodies are common and are closely associated with plutons of intermediate composition. The magnetitic intrusions are interpreted as immiscible liquids that separated from a magma of intermediate composition. The immiscible fractions were predominantly crystalline when they reached their present higher levels, and final emplacement was facilitated by volatile-streaming and fluidization. Their presence in the orogenic belt is taken as further support for the hypothesis that the orogen was of Andean type.

La région de la rivière Camsell comprend un pendant du toit de roches volcaniques à l'intérieur d'une ceinture orogénique aphébiennne (~1800 Ma). Les intrusions de magnetite et apatite et d'autres qui leur sont apparentées sont communes et étroitement associées à des plutons de compositions intermédiaires. Les intrusions de magnetite sont interprétées comme étant des liquides immiscibles séparés d'un magma de composition intermédiaire. Les fractions immiscibles étaient en majeure partie cristallines au moment d'atteindre leurs niveaux actuels et leur emplacement final fut facilité par des processus de transport en phase gazeuse et fluidisation. Leur présence dans la ceinture orogénique est interprétée comme étant un argument supplémentaire pour un orogène de type andin.

Introduction

The Camsell River area is occupied by part of the Great Bear batholith (Fraser *et al.* 1972), which has been interpreted as the orogenic belt of the Wopmay Orogen (Fig. 1) (Badham 1973a; Hoffman 1973), and which evolved between ~2100 and 1700 m.y. ago. The area is fairly typical of an 'Andean' calc-alkaline batholith and has been described as such in some detail (Badham 1973a,b). The geological history of the area and the nature of the magmatism have been documented (Badham 1972, 1973a); details of many individual features, including magnetite intrusions, metasomatic bodies and hydrothermal mineralisation are available in Badham (1973b). This paper will describe one of these features, namely the magnetite intrusions. The data are taken principally from the thesis of one of us (J.P.N.B.), which was carried out under the supervision of the other (R.D.M.).

Regional Geology

The area consists of a volcano-sedimentary

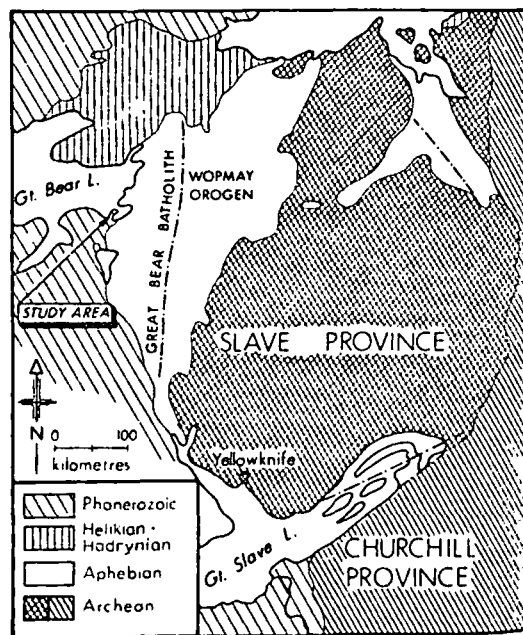


FIG. 1. Location map for the Camsell River area, N.W.T.

complex intrud (Fig. 2). The ob antly volcanic. S in abundance, I canic rocks are: tuffs and breccia and andesite th entirely volcani fluvial and sha sequence was lai of 'positive' rell The basement to in the Camsell I were at first vol; sedimentary and These were the had fed the voler sions were clust alkaline stocks; were intruded bodies (Fig. 3). 7 cal continuum f final intrusive pl

All the intrusi porphyry dykes, and hydrotherm around 1400 m. terminated by th sills. Details of t will be presentec

Many authors Bear batholith ha alteration around (see especially elements involve Cu, Pb, and Zn, fested in the form magnetite, apatit or close to, the intrusions are su which metamorp hornfels facies w minerals, which and tuffaceous re after the thermal Again there is a be generalized as

1. Metamorp
2. Fe infiltrat
3. Cessation
4. S introduc
5. Base metal

complex intruded by a suite of granitic rocks (Fig. 2). The oldest known rocks are predominantly volcanic. Sedimentary components increase in abundance, higher in the sequence. The volcanic rocks are predominantly andesite-rhyolite tuffs and breccias, with minor, intercalated basalt and andesite flows. The sediments are almost entirely volcanoclastic and were deposited in fluvial and shallow water environments. The sequence was laid down in a basin, between areas of 'positive' relief, now occupied by intrusions. The basement to the sequence is nowhere exposed in the Camsell River sector. The 'positive' areas were at first volcanic highlands (from which the sedimentary and volcanic rocks were derived). These were then intruded by the magmas that had fed the volcanoes. The earliest of these intrusions were clusters of small, intermediate calc-alkaline stocks (Badham 1973a). These in turn were intruded by larger granite-granodiorite bodies (Fig. 3). There was a temporal and chemical continuum from the initial extrusions to the final intrusive phases.

All the intrusions are surrounded by aplites, porphyry dykes, contact metamorphic aureoles, and hydrothermal veins. The latter persisted until around 1400 m.y. (Robinson 1971) and were terminated by the intrusion of diabase dykes and sills. Details of the hydrothermal mineralization will be presented elsewhere (Badham 1975a).

Many authors who have discussed the Great Bear batholith have noted extensive metasomatic alteration around earlier, intermediate intrusions (see especially Furnival 1939b). The principal elements involved were Cl, Fe, Si, P, B, F, Ti, S, Cu, Pb, and Zn, and metasomatism was manifested in the formation of tourmaline, scapolite, magnetite, apatite, actinolite, and sulphides in, or close to, the margins of the intrusions. The intrusions are surrounded by narrow aureoles in which metamorphism up to the hornblende-hornfels facies was observed. The metasomatic minerals, which occur most often in calcareous and tuffaceous rocks, were apparently developed after the thermal peak of contact metamorphism. Again there is a continuum of events that may be generalized as follows:

1. Metamorphism
2. Fe infiltration → Fe silicates
3. Cessation of silicate reactions and development of Fe oxides
4. S introduction → Fe sulphides
5. Base metal introduction → sulphides.

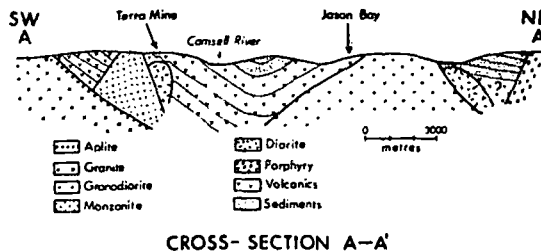


FIG. 2. Diagrammatic cross section from A to A', as indicated on Fig. 3.

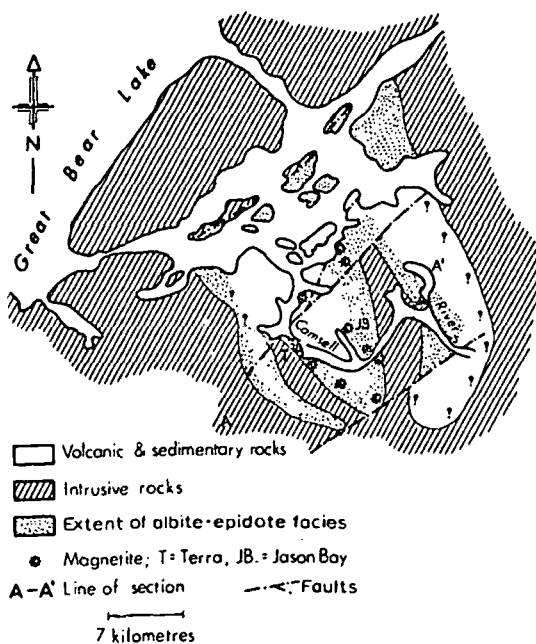


FIG. 3. Sketch map of the Camsell River sector, illustrating the disposition of the volcanic and sedimentary rocks and their metamorphosed equivalents, relative to the intrusions of the Great Bear batholith complex.

The intrusions are characteristically porphyritic and bear hornblende. They are also commonly hydrothermally altered and locally carry small amounts of 'porphyry' type sulphide mineralization (Pyrite ± chalcopyrite, sphalerite, and galena). The margins of the intrusions are often highly sheared and altered. Apatite is usually developed in these zones, especially where there are skarns nearby.

All these data attest to the enrichment of these early plutons in volatiles, Fe, P, S, and base metals, and to the escape of these materials from the intrusions during their cooling.

In a number of localities in the Camsell River area magnetite-rich bodies, ranging from veins and disseminations to small plutons, occur within

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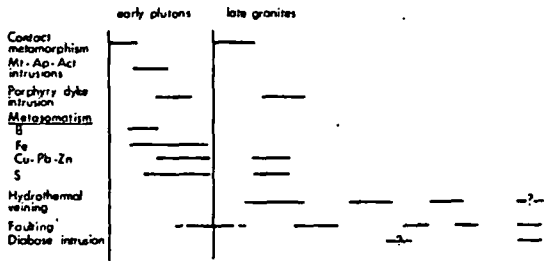


FIG. 4. Paragenetic diagram relating the various phases of intrusion, metamorphism, and veining within the Cam-sell River sector.

the inner parts of contact metamorphic aureoles. They are easily located by strong airborne magnetic anomalies, in the range 3000-5000 γ compared with background values of around 2900 γ (unpublished information, Department of Indian Affairs and Northern Development, Yellowknife, 1972). One such body has already been described briefly (Badham 1972), and it and another one will be described in more detail in the following sections. A paragenesis of events around the cooling intrusions is presented in Fig. 4.

The Terra Magnetite Intrusion

Some 800 m to the SE of the Terra Mine portal, there is a plug and replacement zone of magnetite-apatite-actinolite (Fig. 5). In the field, both intrusive and replacive relations are clearly visible. The intrusive plug has a sharp contact with a narrow chill zone, and contains numerous angular, rotated xenoliths of the local tuff and lava sequence, which is transected by the intrusion. Metamorphism at the contacts cannot be distinguished from the hornblende-hornfels facies aureole of a sodic monzonite (analysis 16, Badham 1973a), which outcrops 200 m to the south and within which this plug lies. The plug is cut by veinlets of coarse, fractured magnetite and apatite, and by thin pegmatitic seams of magnetite, apatite, and actinolite.

Much of the clearly intrusive plug is surrounded by a replacement zone that has been arbitrarily divided into areas of strong and weak replacement, for mapping purposes. Replacement has taken place preferentially in tuffaceous calc-argillite and volcanic breccia. Replacement has often been intense enough that unreplaced

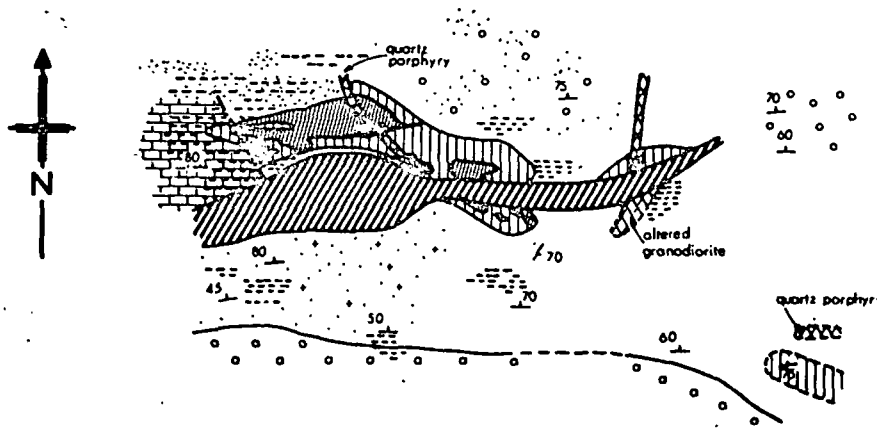
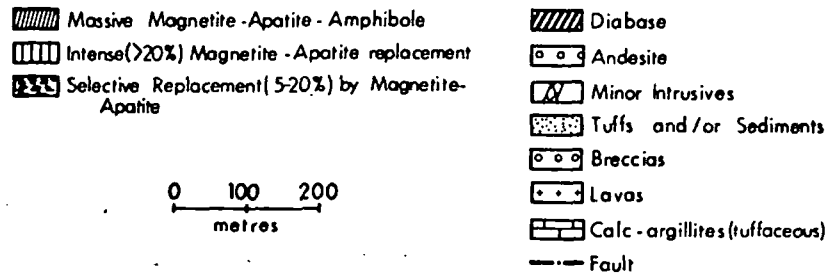


FIG. 5. Sketch map of the principal magnetite-apatite occurrences adjacent to the Terra Mine.

areas appear to be distinct from the... that they are not... are also cut by p... ate-apatite-actin...

The magnetite-quartz-porphyry margins, by small... ate-hematite vein... ected by a consi...

Field studies show... ment zone consist... (60-70%) and a... polished-section s...

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residual liquid frac... Minerals identifi... magnetite, hematit... carbonate, pyrite, g... and monazite. The... rite are clearly ad...

younger quartz-c... A paragenetic sche... X-ray diffraction... and V contents in... ical analyses have... amounts in weight...

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 $Ti =$
The apatite has a... ratio ranging betw... The magnetites... tatively analyzed... microprobe. Phen... chemically indistin... contents of the m...

areas appear to be xenoliths: these areas are distinct from the true xenoliths in the plug, in that they are not rotated. The replacement zones are also cut by pegmatitic stringers of magnetite-apatite-actinolite.

The magnetite-bearing rocks are cut by a quartz-porphry dyke that has strongly chilled margins, by small faults and by quartz-carbonate-hematite veins. All these features are transected by a considerably younger diabase dyke.

Field studies show that both plug and replacement zone consist predominantly of magnetite (60-70%) and apatite (30-40%). Thin- and polished-section studies reveal the existence of two generations of magnetite and apatite. Fractured remnants of large phenocrysts of both minerals are contained within a matrix of fine fragments and second generation of magnetite and apatite. It is this second generation that becomes fine-grained in the chill-zone. The phenocrysts make up over 60% of the rock and it is inferred that the intrusion apparently reached its present level as a crystal 'mush', carried by a low viscosity, residual liquid fraction. Subsequently, pulses of this liquid were intruded into dilatant zones to form the pegmatitic lenses in which the phenocryst fragments are often abraded and have been 'streamed-out' in the matrix. In places there are flow bands of apatite phenocrysts in the magnetite. In our opinion, these features attest to the volatile nature of the residual liquid fraction.

Minerals identified in the intrusion include magnetite, hematite, apatite, actinolite, quartz, carbonate, pyrite, goethite, chalcopyrite, chlorite, and monazite. The hematite, goethite, and chlorite are clearly alteration products caused by younger quartz-carbonate \pm sulphide veining. A paragenetic scheme is shown in Fig. 6.

X-ray diffraction studies indicate very low Ti and V contents in the magnetite, and wet chemical analyses have shown that the actual average amounts in weight percent are:

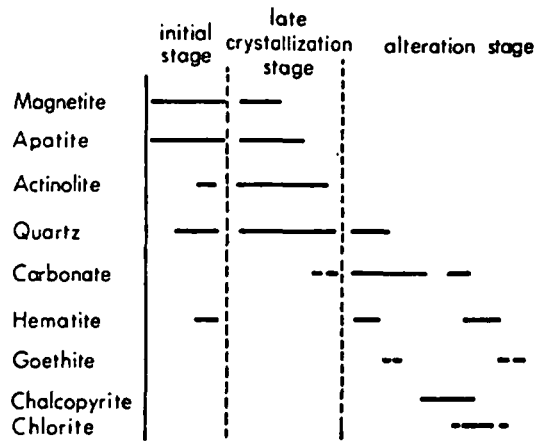
$$V = 0.12\% \pm 0.03\%$$

$$Ti = 0.55\% \pm 0.03\%$$

The apatite has a fluorine to chlorine weight ratio ranging between 0.867 and 0.133.

The magnetites and apatites were also qualitatively analyzed, using an ARL-EMX electron microprobe. Phenocryst and matrix material are chemically indistinguishable. The low Ti and V contents of the magnetite were confirmed, and

TERRA INTRUSION



JASON BAY INTRUSION

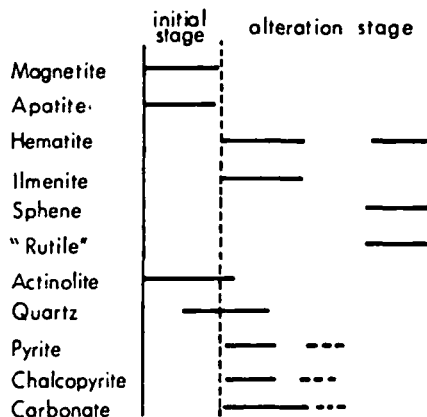


FIG. 6. Paragenetic diagrams for the mineral constituents of the magnetite-apatite bodies adjacent to the intrusion near the Terra Mine and that on Jason Bay.

only minute amounts of Mn were detected. As well as being fluorine-rich, the apatites contain trace amounts of Y and Ce (La was not analyzed). These results are analogous to those of Parak (1973), who noted Y, Ce, and La in the Kiruna apatites and observed that they are often concentrated in minute monazite inclusions. The actinolite is not a major constituent of the intrusion, but occurs most frequently in the pegmatitic veins. It was identified optically and by X-ray diffraction. Electron microprobe studies show that it is a variety very rich in Fe.

The intrusion of the magnetite plug has had no noticeable effect upon the country rocks and it must be concluded either that both were at similar temperatures during the intrusive event,

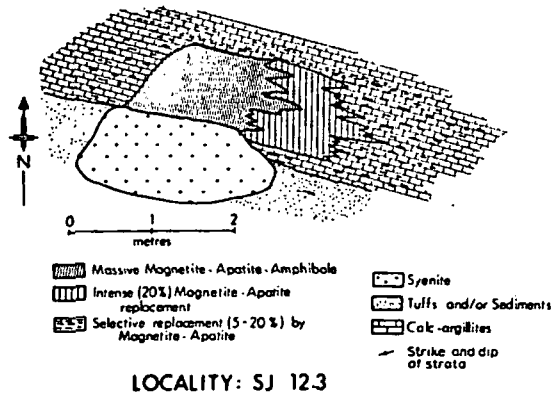


FIG. 7. Sketch map of the minor magnetite-apatite body at locality SJ 12.3, near Terra Mine.

or that the intrusion was relatively cool. Badham (1973b) estimated that the country rocks reached a maximum temperature of about 550 °C after the intrusion of the monzonite. Presumably the magnetite plug was intruded shortly after the monzonite, and it is felt that the temperature of the intrusion is unlikely to have exceeded 600 °C, as is argued below.

In addition to this main intrusion, some 800 m to the NW there is a very small occurrence of magnetite-apatite associated with a minor plug of altered syenite (Fig. 7). Both have intruded and replaced country rocks, and they appear to be intimately associated. This magnetite-apatite body is petrographically indistinguishable from the larger one. The syenite contains 5-10% apatite.

Finally, as was mentioned previously, the borders of the intermediate plutons are often highly enriched in apatite; this is the case for the monzonite at Terra Mine. The outer 5-10 m of the intrusion from level with locality SJ 12.3 to beyond the eastern end of the main magnetite intrusion are hydrothermally altered and contain up to 30% apatite, again suggesting a close connection between the monzonite and the magnetite-apatite intrusions.

The Jason Bay Magnetite Intrusions

The three lenses that occur at Jason Bay, ~5 km ENE of Terra Mine (Fig. 8), are somewhat different in character. They occur within well-bedded andesitic tuffs which have been metamorphosed to the upper albite-epidote facies of contact metamorphism by a granodiorite intrusion (Fig. 3). Each lens is roughly con-

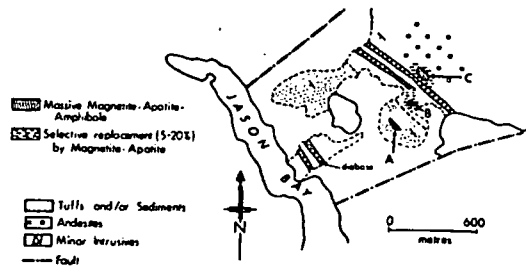


FIG. 8. Sketch map illustrating the disposition of the magnetite-apatite bodies at Jason Bay.

formable with the bedding and is surrounded by a hematitized zone and by numerous actinolite veinlets, which commonly contain quartz and pyrite. The lenses are clearly intrusive and are not flows.

Lens A measures 60 by 4 m. Actinolite crystals up to 15 cm long project perpendicularly inwards from a very sharp contact. The central zone consists of pegmatitic magnetite, apatite, and actinolite with younger interstitial quartz, carbonates, and pyrite. There is no noticeable effect of the intrusion on the country rocks. Lens B is similar but smaller (10 by 1 m).

Lens C is more complicated, having been cut by a younger diabase dyke. There are a number of pods of magnetite, apatite, and actinolite, containing quartz, carbonate, and pyrite within an area of 200 by 20 m. The pegmatitic pods have been recrystallized at the diabase contact, making it appear as if the diabase represents the parent magmatic phase.

Thin- and polished-section and electron microprobe studies reveal a similar paragenesis to that at Terra Mine (Fig. 6), but the proportion of actinolite is far greater at Jason Bay. In all the lenses, magnetite has been severely altered (usually to hematite). However, there are numerous lamellae of ilmenite, attesting to a relatively high original Ti content. In places this ilmenite-hematite-magnetite mixture has been further altered by reaction with silica and lime to form a complex intergrowth of rutile and titanite. This alteration was apparently coeval with the introduction of sulphides.

Other Magnetite Bodies

Other similar bodies observed within the Cam-sell River Block, but not studied in detail (Fig. 2), include: (a) biotite-magnetite-apatite-actinolite skarns, (b) magnetite-apatite-actinolite veins, (c) magnetite-apatite-actinolite-pyrite-chalco-

pyrite lenses and disseminated actinolite veinlets. A continuum in these magmatic to infiltrative events is inferred that the Jason Bay lenses at the top of an intrusion, more pegmatitic nature, and for the greater events in them.

Origin

Phillipotts (1967) noted the magnetite:apatite mixture in the system and concluded that it was miscible with an alkali magma. He thus inferred that the mixture could separate a differentiating parent magmatic residue well the observed relations at Terra Mine (1967, p. 303) notes that the diorite and apatite could form three immiscible phases: an apatite-rich one, a silicate melt." Here for the observed enrichment at the margin of the Terra Mine.

Thus, all the magnetite-apatite bodies in the Jason Bay area are considered to be related to the parent magmatic phase. The observed continuum in these events represents a range in immiscibility with the magma. Kidd and Hill (1939a,b) reached similar conclusions for the logous bodies in other batholiths. Robinson (1935, 1937, and 1938) proposed logous hypotheses for the veins near Echo Bay. The veins, 1435, 1370, and 1415, contain amphiboles and could be related to, and defined by, sills that cut the veins. The U-Pb dating of the U-Pb veins (Thorpe 1967) presumed that they were related to the K-Ar system. One of the principal applications of Phillipotts' work to natural systems

pyrite lenses and disseminations, and (d) apatite-actinolite veinlets. It is concluded that there is a continuum in these from purely intrusive-magmatic to infiltrative replacements. Further, it is inferred that the Jason Bay lenses must represent the top of an intrusion similar to that at Terra Mine, a relationship that would account for the more pegmatitic nature of the Jason Bay lenses and for the greater evidence of 'late' paragenetic events in them.

Origin and Significance

Phillpotts (1967) proposed that a 2:1 magnetite:apatite mixture constitutes a eutectic mixture in the system magnetite-fluorapatite, and concluded that such a eutectic mix is immiscible with an alkaline, intermediate magma. He thus inferred that a magnetite-apatite fraction could separate as an immiscible phase from a differentiating parent magma, leaving an alkaline magmatic residuum. Such an hypothesis fits well the observed lithologies and paragenetic relations at Terra Mine. Further, Phillpotts (1967, p. 303) notes that "mixtures of magnetite, diorite and apatite containing apatite in excess of 30% form three immiscible liquids on melting: an apatite-rich one, a magnetite-apatite melt and a silicate melt." Here, then, is a possible source for the observed enrichment in apatite at the margin of the Terra Mine monzonite intrusion.

Thus, all the magnetite bodies in the Camsell River area are considered to have been derived from the parent magma of the early plutons; the observed continuum in varietal variations simply represents a range in the derivative process, from immiscibility with, to infiltration from, this magma. Kidd and Haycock (1935) and Furnival (1939a,b) reached similar conclusions for analogous bodies in other parts of the Great Bear batholith. Robinson (1971), who forwarded analogous hypotheses concerning magnetite-actinolite veins near Echo Bay, obtained K-Ar ages of 1435, 1370, and 1415 m.y. (all \pm 60 m.y.) for the amphiboles and concluded that the veins must be related to, and derived from, those diabase sills that cut the veins. Since these diabases caused updating of the U-Pb systems in nearby mineralized veins (Thorpe 1971; Badham 1973b), it is presumed that they may have had a similar effect upon the K-Ar systems of the amphiboles.

One of the principal problems inherent in the application of Phillpotts' (1967) experimental work to natural systems is that of temperature.

His data indicate that magnetite-apatite mixtures of eutectic composition do not melt below 1400 °C. Even with certain provisos, he suggests temperatures in the 1000 °C range. The country rocks adjacent to the plug at Terra show no evidence of reheating due to the plug, and had previously been heated to a maximum temperature of 550 °C. It might be argued that the country rocks could have reached temperatures of around 500 °C without there being obvious effects, and application of Jaeger's (1957) theoretical calculations would permit a magmatic temperature of around 1000 °C. However, it has been shown that the intrusions were 60% crystalline during final emplacement, and that the transporting fluids were highly volatile. These data, coupled with the lack of any noticeable thermal effects in the country rocks, suggest that far lower temperatures pertained in the magma; we feel that estimates of around 600 °C are more in keeping with the data.

Estimates of temperature of crystallization of the magnetite using the Ti and V content (Buddington and Lindsley 1974; Lister 1966) are difficult to make because of the low amounts of these elements in the Terra Mine intrusion and because of the apparent alteration in the Jason Bay intrusions. Temperature estimates from fluid inclusion work and from O¹⁸ partition between magnetite and apatite are presently being attempted.

Park (1972) noted that magnetite bodies of various types were "distributed throughout the highly deformed rocks bordering the Pacific Ocean". Included in this group of bodies are both pyrometamorphic deposits and apatite-amphibole-magnetite intrusions. Descriptions of these are indistinguishable from those of the Camsell River bodies. Park emphasizes the association of the magnetitic bodies with intermediate, calc-alkaline magmatic activity within continent-margin orogenic belts and concludes that they are typical of these environments and possibly even diagnostic.

Magnetite-apatite bodies also occur in anorthositic and alkaline provinces, but there is no similarity between such deposits and those in the Camsell River area; nor is there any similarity in the regional geology.

The presence of magnetite-apatite intrusions in the Camsell River area is thus presented as further evidence that the Great Bear batholith represents the core of an 'Andean' orogen devel-



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oped on the margin of the Slave craton during Aphebian times. Such a proposal has been previously discussed by Badham (1972, 1973a,b; 1975b).

Acknowledgments

The Terra Mine intrusion was briefly investigated by R.D.M. in 1969 and was mapped in detail by J.P.N.B. in 1970; the cooperation of Terra Mining and Exploration Ltd. during these programs is gratefully acknowledged. The Jason Bay and other bodies were investigated by J.P.N.B. in 1971, while employed by Vestor Explorations Ltd.

The advice and help of Dr. D. G. W. Smith, Mr. D. A. Tomlinson, and Mrs. R. Bliss were invaluable during the electron microprobe work. Much of the laboratory work was supported by NRCC grant A4242 to R.D.M. and NRCC grant A4254 to D. G. W. Smith.

Finally, Mr. J. D. Murphy, D.I.A.N.D., Yellowknife, who also mapped the Terra intrusion in 1972 for an undergraduate research project at Queen's University, most generously made his resulting paper available.

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Modern electron microscopy in geological research

G.S. Gritsaienko, et al.

The fundamental problems of geology — both theoretical and applied — cannot be solved without the aid of exact up-to-date methods. One of the most important problems of geology is to translate its laws into the language of figures and formulas.

Present progress in general physics and the development of physical methods of solid-state research is now enabling us to make a fresh, more profound approach to the study of minerals — the initial state of the components of the earth's crust. Precise methods (X-ray structural analysis, electron microscopy, microprobes, etc.) make it possible to study the composition and structure of each mineral separately and to clarify the laws connecting them with the processes of formation and evolution of the crust.

We consider that mineralogy is entering a new phase — the investigation of the microcosm of minerals (micromineralogy), in which minerals are studied not in averaged form, but with all the micromineral impurities and inclusions which are regularly associated with their processes of formation. Such investigations open avenues for a new approach to the fundamental problems of genetic mineralogy, enable us to ascertain new signs of the genesis of minerals, and from them to make sounder judgments on the nature of geological processes. The reconstruction of mineral, ore, and rock forming processes with the aid of instrumental investigation is one of our contemporary problems. Development of diagnostic criteria for geological processes on the basis of modern progress in the study of minerals by a combination of exact physical methods will be of great value for the solution of many practical problems, especially in the study of mineral deposits and their laws of occurrence and formation.

In this direction, many possibilities are opened up by electron microscopy (EM), which has been added to the complex of geological,

lithological, and geochemical methods in the development and extension of research on Precambrian sedimentary-metamorphic rocks. Minerals of the sedimentary-metamorphic strata of the Precambrian have a complex geological history due to the integration of a number of geological processes of endogenous and exogenous character; they have undergone the longest development and are suitable material for study by all contemporary physical methods, particularly electron microscopy.

The electron microscopy of minerals has recently made marked strides, due to various factors, including: 1) industrial production of high-quality microscopes (transmission and scanning) and supply of many attachments which can greatly widen the scope of experimental conditions; 2) introduction of combined methods corresponding to the specific requirements of the specimens and problems; 3) improved trustworthiness of the data and extension of the diagnostic possibilities of a method thanks to the use of microdiffraction in transmission microscopy and microanalysis in scanning microscopy; 4) training and growth of a force of specialists capable of using the method and fruitfully applying and developing it. It is also important that EM is a method which can relate the morphological, structural, and chemical characteristics not to averaged volumes of a specially selected substance, but to particular individuals or particles (even single particles) which are too small or few to be within the limits of resolution or threshold sensitivities of other methods. It is noteworthy that in EM there are not only existing trends, but also new ones, including for example electron petrography, which has arisen in connection with the study of moon rocks.

In the present stage of development of EM the question is not whether to use it or not, but how to choose the most important problems from all those which can be solved with its aid. It is necessary that EM shall be an organic component of research on the fundamental science of the earth and other bodies in space. This does not, of course, exclude EM from research in particular problems of science and technology.

In this article we shall consider the prospects opened up by transmission and scanning electron microscopy in geological research,

Translated from *Vozmozhnosti sovremennoy elektronnoy mikroskopii pri reshenii geologicheskikh zadach*, Sovetskaya Geologiya, 1973, no. 11, p. 9-23. Co-authors with Gritsaienko are A.V. Sidorenko, O.I. Luneva, M.I. H'in, Sv.A. Sidorenko, and T.L. Petrova. They are with the Geological Institute, USSR Academy of Sciences.

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taking as examples the applications of EM in mineralogy, lithology, and (partly) petrography. The contemporary state and fundamental problems of mineralogy (11) and lithology (10), like the prospects for transmission EM in mineralogical research (6), have already been discussed in the literature, so we can here invoke these data only as far as they are required for completeness of the exposition.

All the scanning electron micrographs in this article are original, and were taken in the Laboratory of the Lithology of Ancient Sedimentary-Metamorphic Strata, using a Steroscan instrument.

The authors take this opportunity of thanking Prof. Shaw for the specimens of Precambrian rocks from South Africa.

Transmission electron microscopy (TEM). Transmission electron microscopy is at present developing in two main directions — TEM at ordinary accelerating voltages, and high-voltage EM (HVEM) at accelerating voltages of up to 3000 kv. In laboratory practice, ordinary voltages have found the widest range of applications. Use has already been made of HVEM in various countries, and interest in it is continually increasing, but the high cost, large size, and complicated procedures required create considerable barriers against its introduction. With the aid of HVEM, interesting data have been obtained on the minerals studied in moon-rock specimens (22).

The achievements of TEM are well known from many publications including specialized monographs and symposia. The most significant results of TEM have been obtained by using microdiffraction both for diagnostic purposes and to solve independent structural problems, and also by means of the decoration method, which enables us to study minerals at the atomic or near-atomic level (9). Powerful aspects of TEM have been clearly manifested in the solution of problems on the homogeneity and inhomogeneity of minerals (7).

The decoration method, which has long been successfully used in crystallography and solid-state physics, has for some time been regarded as of no practical use in geology, and its use has been regarded as a pursuit of mere methodological novelty. Certainly this method is finicky and laborious and requires expert application of preparation techniques and a deep knowledge of the objects studied. However, if used skillfully and with careful reasoning, especially in conjunction with microdiffraction, it can yield remarkable results. The unique feature of the decoration method lies in the possibility of fixing the moment of formation of new phases, which cannot be done by other methods. We can establish not only

the actual fact of formation of a new phase, but also its orientation relative to the mineral from which it develops; the new material may be only a few monolayers thick, and its dimensions less than a micron.

The mineralogical value of the decoration method has been convincingly demonstrated by recent work on supergene changes in feldspars (16, 18). Unlike other investigators, who studied the final or remotely past stages in the replacement of primary minerals by secondary ones, we directly established the formation of new phases and the initial stages of their appearance (16, 18). We showed that kaolinite is formed directly from microcline, without any intermediate compounds (16), and halloysite from oligoclase (18). In oligoclase-microcline perthites, the oligoclase alters first during weathering, and we can fix a stage in which it is almost completely replaced by halloysite, while some of the microcline is preserved and the kaolinite which replaces it forms local inclusions. The conclusions we drew concerning the influence of primary minerals on the character of the new material formed from them go beyond the original scope of the research and agree with a similar thesis which was stated in a study of the processes of metamorphism — that the degree of metamorphism and the resulting mineral associations depend on the composition of the original rocks (13).

Work on the use of TEM to study rocks began very recently in the USSR, but interesting results have already been obtained. Thus for liparite rocks, by means of replicas it has been shown that the glassy part of the rock, which appears isotropic under the optical microscope, shows clear inhomogeneity under the EM. In a mass of hummocky and porous glass were seen spherulites, the number of which increased from the top to the depths of the current. The EM data revealed that the spherulites are of a liquation nature and that, since the glass was formed from a strongly supercooled effusive melt, its structure fixes a stage of development of the melt at the moment of a sudden change in conditions (10).

The electron microscope has been successfully used to investigate the microstructures of siliceous rocks (17). Microstructural types have been distinguished, and a number of their transitions have been noted, reflecting the main line of development of the siliceous substance (from globular to highly crystallized); present ideas on the mechanism of conversion of the opal of the siliceous skeletons to quartz have been refined and augmented; the difference between the microstructures of phthanites and jaspers has been clearly revealed; it has been shown that sedimentary siliceous rocks show signs not only of the process of formation of a crystallomorphic structure but also of the

process of its breakdown; that the microstructure of can be used as an additional cl

A noteworthy scheme of forming minerals was developed for specimens (22). They were graphically in standard thin sections. The most interesting parts were studied by ultrasound and reduced resolution. And when each mineral was studied under a transmission electron microscope. In the principal cases, plagioclase, clinopyroxene, plagioclase, and complex substructures were studied. The decay structures of solid solution (slip, domains, etc.) revealed and structural inhomogeneity was studied by microdiffraction. Investigation of the pyroxenes was attributed to platelets of solid solution. It decomposed, to pigeonite simultaneously with decomposition in the distribution of the pyroxenes which has a marked effect on the properties of the minerals. It is noted that during mineral decomposition occurred plastic deformation at temperature. Detailed investigation of lunar pyroxenes revealed platelets separating from the glass about 250 Å thick and the presence of such fine structure under the optical microscope would appear perfect. The presence of such fine structure suggests that the rock contains

All experience of the use of TEM to study minerals, rocks, and the present transmission method of investigation of finely-dispersed natural materials. Many features of the mineralogical macro-objects are small or few to be distinguished by other methods.

Scanning electron microscopy. Although TEM can show the microstructure of phases in a specimen, it has certain limitations as follows. a) It is limited in scale between studies of bulk specimens and thin sections. b) It is difficult to make even an indirect measurement of the depth of focus and optical resolution when they are small (9).

Scanning electron microscopy using the television principle

process of its breakdown; it has been concluded that the microstructure of siliceous rocks can be used as an additional classificatory sign.

A noteworthy scheme for studying rock-forming minerals was developed for moon-rock specimens (22). They were first studied petrographically in standard thin sections; then the most interesting parts were separated by means of ultrasound and reduced by electron bombardment, and when each mineral attained the required degree of "transparency" to the electron beam it was studied under a megavolt electron microscope. In the principal minerals — clinopyroxene, plagioclase, and ilmenite — complex substructures were found (microtwins, slip, domains, etc.) revealing their material and structural inhomogeneity. On the basis of microdiffraction investigations, the matrix of the pyroxenes was attributed to augite, and the platelets of solid solution which separated when it decomposed, to pigeonite. It was shown that simultaneously with decomposition there occurs ordering in the distribution of iron atoms, which has a marked effect on the magnetic properties of the minerals. These features suggest that during mineral formation there has occurred plastic deformation and change in temperature. Detailed investigations of the lunar pyroxenes revealed that the pigeonite platelets separating from the augite matrix are about 250 Å thick and therefore cannot be seen under the optical microscope, where the pyroxene would appear perfectly homogeneous. The presence of such fine structural decomposition suggests that the rock crystallized very rapidly.

All experience of the application of TEM to minerals, rocks, and ores shows that the present transmission method is now a fundamental method of investigation, not only of finely-dispersed natural formations, but also of many features of the detailed structure of mineralogical macro-objects which are too small or few to be distinguished by traditional or other methods.

Scanning electron microscopy (SEM).

Although TEM can show up and diagnose all phases in a specimen, including single ones, it has certain limitations. The main ones are as follows. a) It is impossible to make direct studies of bulk specimens. b) There is a discontinuity in scale between details observed under the optical and electron microscopes. c) It is difficult and sometimes impossible to make even an indirect study of specimens with coarse microrelief, both because of the shallow depth of focus and owing to breakage of the replicas when they are separated from such surfaces (9).

Scanning electron microscopy, based on the television principle of scanning a thin elec-

tron beam over the surface of the specimen, enables us to study surfaces of any type; they are shown as if in three dimensions on the screen (15).

The chief advantages of SEM for geological objects are as follows. 1) The great depth of focus, which enables us to use SEM to study surfaces with "dissected" relief and to obtain three-dimensional images of microcrystals of very varied habits, from isometric to filamentary, both present on the same surface. 2) The possibility of investigating large sections of the surface (up to a few centimeters) with gradually increasing magnification between the optical and the electron-microscope scales. 3) Simplicity of preparation: the test surface is covered with a thin (50-200 Å) conducting layer of metal, which prevents accumulation of charge on the surface. 4) The high throughput and the possibility of bulk inspection of specimens in given observation conditions.

Scanning electron microscopy is being introduced into geological practice so rapidly that already we can distinguish several principal trends in which the method has proved fruitful: 1) micropaleontology and microphytology; 2) engineering geology and soil science; 3) electronic petrography (primarily of the moon rocks); 4) ontogeny of minerals.

The first investigators to use SEM to study the earth's crust were paleontologists, with the purely practical aim of correlating oil-bearing sedimentary rocks. Rotor drilling with its high speeds practically annihilates large indicator forms, but microscopic residues are well-preserved and can be studied. It is well known that correlation of rocks by microforms is based on their combinations of grouped signs, which are stratigraphic age indicators. Until the last decade, micropaleontologists could study organic residues only with least dimensions of 0.2-0.1 mm, whereas the use of SEM permits this level to be reduced to microns. The study of such groups of microorganisms is exceedingly difficult owing to the great similarity of many forms and the brittleness of their skeletons, which can easily be broken during separation by special preparation methods. Therefore to reliably clarify the finest details and establish group signs of microfossils, it is necessary to preserve the morphology and examine a large number of specimens. Both these conditions are satisfied by SEM (26).

A second field of practical importance in which SEM is highly effective is the study of the nature of the strength of soils and rocks for engineering-geological purposes (23). Comparison of the results obtained in soil studied by various methods including SEM has revealed that SEM enables us to directly elucidate and study features of the rocks which can

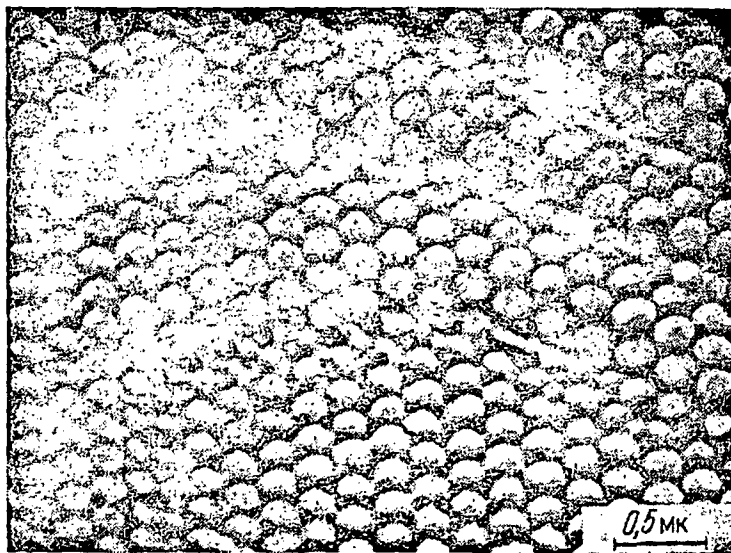


FIGURE 1. Regular structure of packed silica particles in precious opal.

only be indirectly established by other methods. We refer primarily to the pore space and the shear zone under compression for soils, and the character of the microfissuration and grain contacts in ledge rocks. It was also found that to preserve the primary porosity and fissuration of the rocks we need special methods of preparation, in particular freeze-drying, which does not cause changes in the textural-structural features of the rock (unlike air drying). The copiousness and variety of the information obtained by SEM leads us to the conclusion that we must not confine ourselves to subjective ("manual") methods of processing the results. Systems and algorithms have been devised for solving the problems of determining the statistical distributions of the dimensions of microdetails and their means and dispersions, directly from the photographic images (2, 3).

Electron microscopy was widely used to study rocks in connection with moon research (1). It was at this time that the term "electronic petrography" arose and is now firmly established in the scientific literature. From the first, this investigation was of a combined character involving all the methods necessary for an exact study of a substance, with an important place occupied by electron microscopy (TEM and SEM), microdiffraction, and electron microprobes. Comparative study of lunar and terrestrial rocks is of interest not only from the viewpoint of scientific conclusions regarding their similarities and differences and the inferences drawn therefrom, but also as an example of a modern methodological approach to the study of rock-forming minerals and rocks at a new level. This approach is very promising for research in the lithology of sedimentary

and metamorphic rocks. In these investigations SEM is an important method for direct study of the structures and textures of the rocks with simultaneous determination of the elementary compositions of the minerals and automatic recording of the results.

Recently much attention has been paid to the ontogeny of minerals (5) — the nucleation and growth of individuals (layered growth, zonality, sectoriality, mosaicity, cleavage during growth, etc.), changes in mineral individuals (deformation, recrystallization, chemical changes, etc.), and genesis of mineral aggregates (combined growth of individuals, geometrical sorting, formation of spherulites, etc.). The genesis of individuals and aggregates has been established from signs which are recorded in the minerals themselves.

SEM is the most "ontogenous" of all the physical methods, because it permits direct study of the finest features of microindividuals and microaggregates in all their variety of spatial relations. Let us consider some examples.

Everybody knows the play of colors on a precious opal, but the cause of this has been obscure, and only by means of EM has it been possible to explain the origin of this remarkable phenomenon. From replicas of chips etched in hydrofluoric acid it has been found that the remarkable range of colors is due to diffraction of light from a regular three-dimensional structure of regularly arranged spherical particles of amorphous silica with diameters near the wavelength of visible light (1500-4000 Å). Disturbance of the regular packing of spheres

impairs the play of colors and disappears altogether when the structure is disordered (in common opal).

Structures of regularly packed particles have been observed by using electron microscopy in natural opal, but the three-dimensional structure has been most clearly observed by the SEM (24). In these studies have been observed screw and dislocation boundaries, twinning, packing defects, and other boundaries, i. e., the same as in true crystals. We have observed similar patterns in precious opal (fig. 1).

A clear example of the possibilities of SEM is afforded by the study of synthetic millerite, obtained by the process of its hypergrowth. We found that acicular microcrystals forming radial concretions in low tubes; we observed the splitting of microcrystals into subspherulites (fig. 2). In other typical forms, inclusions of millerite in the interspherulite gaps, which are displayed in the SEM in vivid relief in large ore specimens observed by the eye.

The possibilities of electron microscopy in the study of minerals can be even further extended in the cathode luminescence example, in this way in the study of cassiterite we found that it showed that with the aid of SEM one can display hetero-

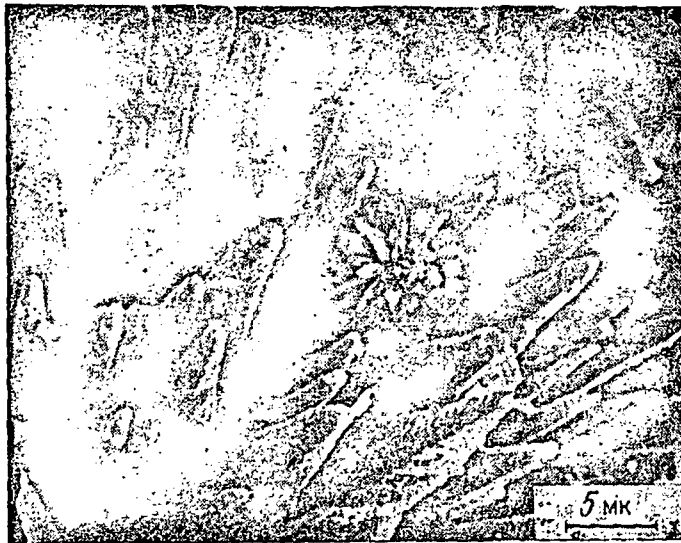


FIGURE 2. Microaggregate of synthetic millerite.

impairs the play of colors in an opal, and it disappears altogether when the packing becomes disordered (in common opals) (27).

Structures of regularly arranged silica particles have been observed by all investigators using electron microscopy to examine precious opal, but the three-dimensionality of these structures has been most clearly revealed by the SEM (24). In these structures there have been observed screw and edge dislocations, twinning, packing defects, and small-angle boundaries, i. e., the same structural features as in true crystals. We have seen similar patterns in precious opal (fig. 1).

A clear example of the ontogenic possibilities of SEM is afforded by the results of a study of synthetic millerite, obtained by simulating the process of its hypergene formation. It was found that acicular microcrystals of millerite forming radial concretions are sometimes hollow tubes; we observed the phenomenon of splitting of microcrystals to form second-order subspherulites (fig. 2), growth trillings, skeletal forms, inclusions of elementary sulfur in the interspherulite gaps, and other features, which are displayed in the scanning electron microscope in vivid relief, as if they were large ore specimens observed with the naked eye.

The possibilities of SEM for the study of minerals can be even further extended by working in the cathode luminescence mode. For example, in this way in optically homogeneous cassiterite we found very fine zonality and showed that with the aid of cathode luminescence one can display heterogeneity for a lower im-

purity concentration and in more detail than by means of microprobes (25). Cathode luminescence was also used to make SEM observations of quartz from Pleistocene sands, in particular, to display hidden fissuration in the grains (23).

Combined use of TEM and SEM. For all the importance of the problems which can be solved by means of transmission electron microscopy or scanning electron microscopy, it is more effective to use them in combination, getting the best out of both methods. We shall discuss the combined use of TEM and SEM for the case of study of representative rocks of the Precambrian with marked geological characteristics, which have been previously investigated by traditional methods.

Many of the minerals in the earth's crust are associated with complexes of sedimentary rocks and processes. Among the sedimentary formations both of the Phanerozoic and the Precambrian we find almost all types of minerals, often forming large deposits. Electron microscope investigations of sedimentary and sedimentary-metamorphic rocks from the Archean to the Recent not only enable us to refine our characterization of the processes of rock and ore formation in the crust and their evolutionary development over almost four billion years, but also bridge the gap between endogenous and exogenous processes which have formed and are forming the earth's crust, and which are historically and genetically associated via the processes of metamorphism and ultrametamorphism.

This link between exogenous and endogenous rock and ore formation requires a thorough

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detailed investigation, in which EM methods should play an important part. Solution of this problem will enable us to reconsider the questions of the sources of ores and to assess the prospects of ore occurrence in various geological formations, and this in turn will help us to refine prospecting criteria and methods of study of geological processes and clarify the history of formation and geological evolution of the earth's crust as a whole.

Though paying much attention to the evolutionary development of the crust, investigators do not always take enough notice of one of the principal factors in changes in the sedimentary envelope of the earth throughout its geological history. This factor is organic material in its broadest sense, as discussed by V. I. Vernadskiy. At present a very close correlation has been established between the processes of sediment deposition (including weathering, transport, and deposition of material) and the development of organic matter with its rapid evolution and reactivity (14). The broad development of carbonaceous material in various Precambrian rocks and its finely dispersed state require the use of electron microscopy, because traditional methods can give only scanty information here.

To determine the information capacity of each of the methods, we took specimens of Precambrian rocks which had been carefully studied and described in the non-Soviet literature — the dense black siliceous rocks of the hornstone type in the Fig-Tree series (3.1-3.2 b. y.) and Onverwacht series (3.5-3.7 b. y.) from South Africa, which are considered to be the oldest almost unaltered sedimentary rocks still bearing traces of life on earth (20, 21, 28).

In the study of these rocks the greatest interest was occasioned by the nature of the organic material and the elucidation of organogenic structures. The insoluble organic material, owing to the lower probability of its migration, can be regarded as contemporaneous with the rock itself, whereas sources of contamination by soluble mobile organic compounds can be much younger formations than those in which they are found. In rocks of both series there have been found spheroidal organic particles with reticulate surface structures; their mean diameter is 18 μ , which is 2-6 times larger than the individual grains of the siliceous matrix in which they are included. In dimensions, shape, and general structure these spheroids are comparable with certain representatives of modern blue-green algae. The photosynthetic nature of these organisms has been confirmed by the authors cited above by means of data on the carbon isotopes and determinations of the chlorophyll composition of the organic material.

Our data (fig. 3a-b) entirely agree with the literature and show that the structures possess characteristic forms and well-defined sizes, and are found in many specimens. We can confidently conclude that the good preservation, dimensions, and relations of the microfossils with the matrix exclude the possibility that they might have migrated through the inter-grain spaces, and show that they are syngenetic formations.

Despite the clarity of the photographs taken by SEM, they have not enabled us to explain the nature of the black, tarry coloration of the African specimens: here TEM came to the rescue. By taking replicas and extraction it was shown that the carbonaceous substance is present in the form of dispersed particles, aggregated in places, and often so fine that it is difficult to resolve them on the screen of the microscope. The microdiffraction patterns confirmed that they are of carbon with a very small degree of structural ordering. The presence of organic material was confirmed by means of infrared spectrometry. X-ray diffractograms revealed only alpha-quartz.

An example of the particulate form of the carbonaceous manifestations in the sedimentary metamorphic rocks of the Precambrian in the USSR (14) is afforded by the kyanite schists of Keyv (Kola peninsula). The black coloration of the rock-forming minerals is here also due to the presence of dispersed carbonaceous particles, but they are larger than those from the South African specimens (fig. 4a) and structurally more ordered (graphite with mosaic structure). In the kyanite the graphite forms spherical inclusions, which had previously been found by TEM (4) and confirmed by our SEM data (fig. 4b).

There is much interest in shungites as primordially coarse aggregates of organic material (14). Microdiffraction showed that the carbonaceous substance of shungites is either amorphous or weakly ordered; however, together with these there are specimens containing graphite with either mosaic structure or with a high degree of structural ordering. In shungites there are many microinclusions, of which the most characteristic is pyrite. It is distinguished by the great multiplicity of morphological types of its individuals: the most widespread microcrystals are octahedral, sometimes slightly blunted at the vertices by poorly-developed cube faces (fig. 5a); sometimes on these small faces there are autoepitaxial growths of tiny pyrite crystallites; skeletal forms, etc., are also found. By means of SEM (19) the importance of the crystal-morphological description of the microcrystalline minerals had been shown earlier. The SEM method, which enables us to obtain three-dimensional images of the microcrystals,

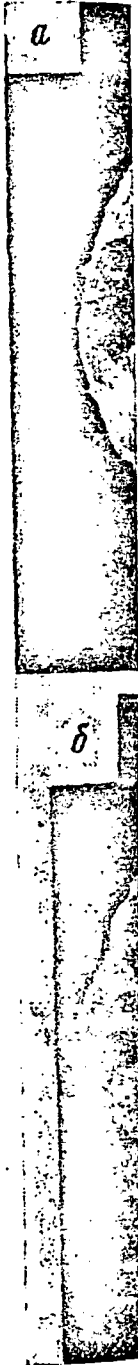


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FIGURE 3. Organic structures found in black siliceous shales of the Onverwacht series (S. Africa)

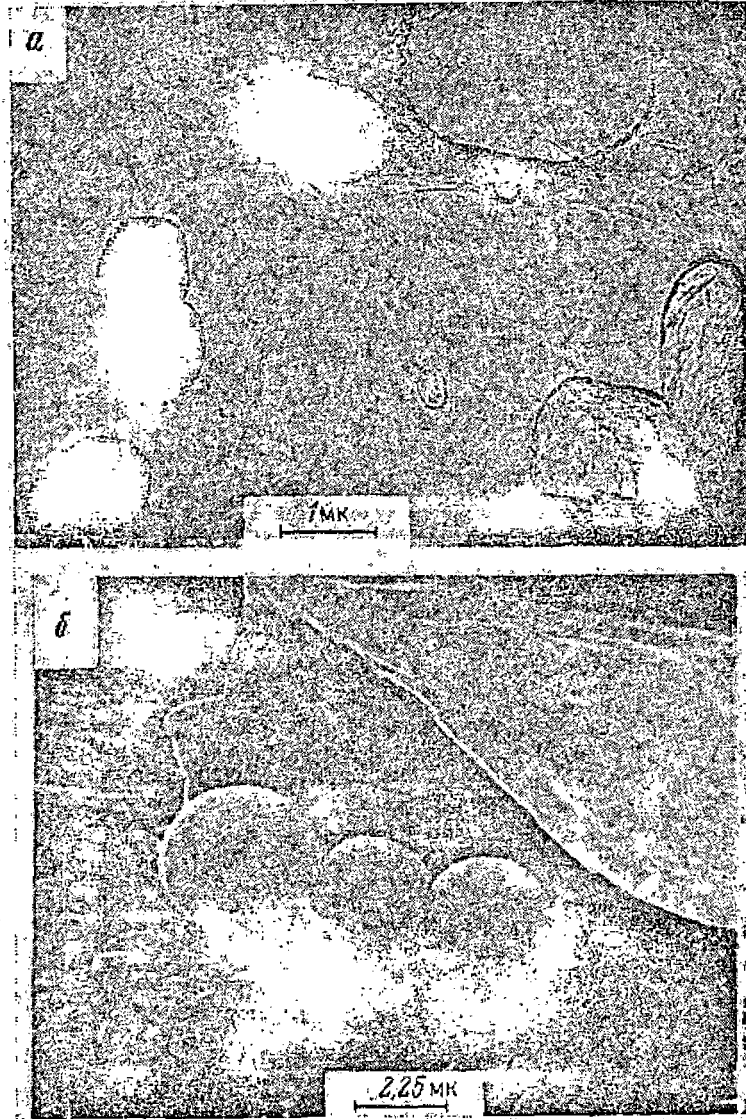


FIGURE 4. Black minerals from Keyv schists.

a - quartz; replica with extracted carbonaceous particles (black); transmission photograph, x 12,000. b - Spherical particles of graphite in kyanite; SEM photograph.

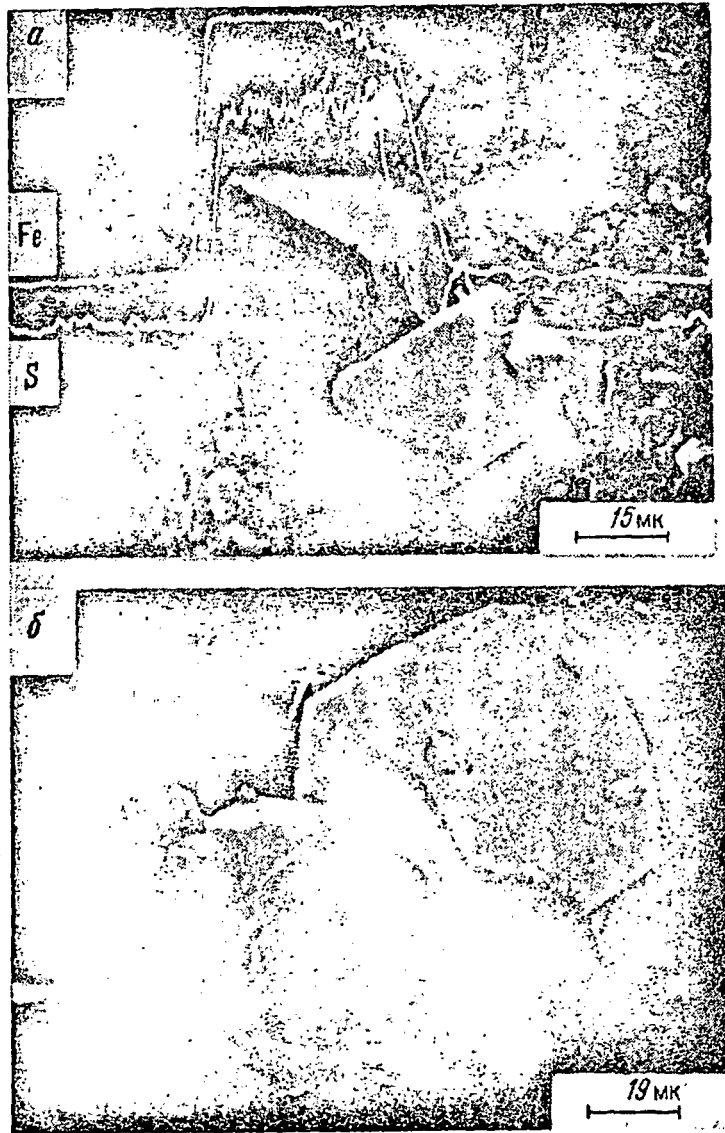


FIGURE 5. Microcrystals of pyrite.

a - in shungite; b - in quartzite.

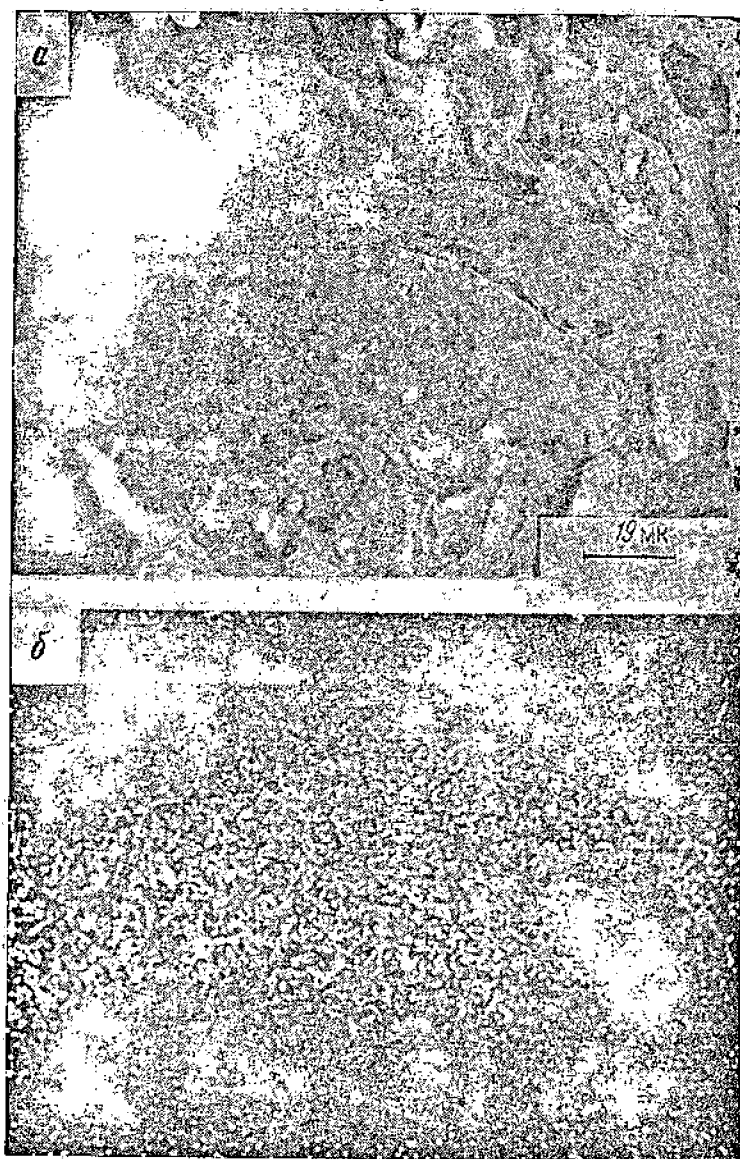


FIGURE 6. Clastic zircon in quartz-micaceous cement of quartzite.

a - Image in secondary electrons; b - distribution of Zr in the same section.

creates very favorable conditions for such a description, especially if stereoscopic photography is used.

As well as carbon-containing rocks, we investigated quartzites from the metamorphic complexes of the Kursk series of the Kursk magnetic anomaly (KMA). They are primarily of interest as a rock which contains clastic quartz, one of the end-products of sedimentary differentiation, and a cementing material consisting of chemogenic silica, argillaceous

material (with all its microimpurities), and a variety of finely detrital grains of minerals of the heavy fraction.

The first results of our study of the KMA quartzites by the TEM and SEM methods were extremely interesting. In a cement of quartzites we found fine (0.06-0.1 mm) rounded grains of zircon, fragments of sulfides, and fine neogenic crystals and irregularly-shaped inclusions of anatase, chalcopyrite, etc. (see fig. 5b). In contrast to the pyrite microcrystals

observed in the shungites (in the quartzites is characteristic development of the cubation with the octahedron and hexahedron faces. In investigation it also seemed possible to the structures of accessory could not be seen by optical microscope. For example, in a rounded zircon (6) we can clearly see cracks closed by the cement (quartz) and another remains open. The disturbances occurring at different stages to repeated deformation of

Very encouraging results promise of the method, obtained in the first stages of application of TEM and SEM to topographical reconstructions (8).

The material accumulated during which EM has been that this method is a reliable method on those features of rocks which we must know many problems at the construction as well as those mentioned above following problems: a) study of chemical and structural history of rocks. b) Tracing phase transitions under the influence of the other factors. c) Investigation of phenomena between the grains of different minerals and the cement. d) To establish the degree of metamorphism and its influence on the conditions of formation of minerals and its forms of incorporation of incorporated elements in carrier rocks. To refine our knowledge of the conditions of decomposition of solid rock-forming minerals, etc. series.

We must emphasize that in the study of metamorphism this method has not yet been applied in the USSR. The promise of this method to the following factors: a) study of magmatic rocks, basaltic and sedimentary rocks; in the conditions of metamorphism, endogenous and exogenous (tectonic, magmatic, and epigenetic) processes in rocks. b) During regional metamorphism of sedimentary rocks also study of rocks and minerals, their composition and structural features of the rocks are responsible for their properties (density, porosity, etc.) regional metamorphism

observed in the shungites (fig. 5a), the pyrite in the quartzites is characterized by preferential development of the cube faces in combination with the octahedron and rhombic-dodecahedron faces. In investigating the quartzites it also seemed possible to observe details of the structures of accessory minerals which could not be seen by optical petrography methods. For example, in a rounded grain of zircon (fig. 6) we can clearly see cracks, one of which is closed by the cement (quartz and mica), while another remains open. This may be due to disturbances occurring at different times owing to repeated deformation of the rock.

Very encouraging results, showing the promise of the method, have already been obtained in the first stages of a combined application of TEM and SEM to problems of paleogeographical reconstructions of the Precambrian (8).

The material accumulated over the years during which EM has been used in geology shows that this method is a reliable source of information on those features of minerals, ores, and rocks which we must know in order to solve many problems at the contemporary level. As well as those mentioned above, we can cite the following problems: a) study of the degree of chemical and structural homogeneity of minerals. b) Tracing phase transitions of minerals under the influence of thermal, dynamic, and other factors. c) Investigation of boundary phenomena between the grains of identical or different minerals and their interreactions. d) To establish the degree of structural ordering of minerals and its functional dependence on the conditions of formation. e) To study the forms of incorporation of rare and scattered elements in carrier minerals. f) To refine our knowledge of the boundaries of limits of decomposition of solid solutions in ores and rock-forming minerals, including isomorphic series.

We must emphasize the great value of EM in the study of metamorphic rocks, to which this method has not yet been applied in the USSR. The promise of EM in this case is due to the following factors: a) during metamorphism, magmatic rocks behave differently from sedimentary rocks; in the same conditions of metamorphism, endogenous mineral associations of magmatic rocks are transformed differently from exogenous (argillaceous, chemogenic, and epigenetic) minerals of sedimentary rocks. b) During regional metamorphism, sedimentary rocks also give different series of rocks and minerals, according to their primary composition and the textural and structural features of the original rocks, which are responsible for their different physical properties (density, porosity, etc.). c) During regional metamorphism, genetically different

rocks of similar chemical composition can give identical mineral associations and correspondingly similar metamorphic rocks. d) During regional metamorphism of sedimentary rocks, metamorphic differentiation of the material is very limited (not exceeding the finest layers in the original rock), and despite the recrystallization, the primary structure of the rocks and strata are not eliminated, even under a very high degree of metamorphism.

This is why it is so important to use modern, exact methods to study metamorphic strata, with their great variety of compositions, original rocks, and formation processes. Exact methods are also necessary for reliable reconstruction of paleogeographic situations in the remote past and, in conjunction with geological observations, in deducing the geological histories of regions in the earliest stages of development of the earth's crust.

Without disparaging the value of separate use of transmission and scanning electron microscopy (in conjunction with traditional methods), it must be acknowledged that the best results are obtained by combined use of TEM (including microdiffraction) and SEM with simultaneous microanalysis. The more systematically and rigorously we choose the rock material from the viewpoint of geological and mineralogical study, the more complete and trustworthy will be the interpretation of the electron microscopy data. To solve large-scale problems we need not single results, but statistics of large numbers of specimens; thus a place will be found for machine processing, including transfer of information directly from the instruments to computers.

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VOL. 73

JANUARY-FEBRUARY

No. 1

1978

Magmatic Vapor Plumes and Ground-Water Interaction in Porphyry Copper Emplacement

R. W. HENLEY AND ALEX McNABB

Abstract

Porphyry copper deposits, all showing similar geological characteristics, occur in Tertiary and older orogenic-volcanic belts around the world. Recent isotope and fluid inclusion studies have shown that in a number of deposits the development of the characteristic ore alteration pattern, at some stage, involved the interaction of meteoric ground waters with saline fluids evolved from a magma. A fluid dynamic model is proposed for porphyry copper emplacement which focuses on the interaction of a buoyant low-salinity magmatic vapor plume with surrounding ground water. As the magmatic vapor rises and cools, high-salinity liquid condenses in a two-phase plume core, drains under gravity, and is diverted to vertical lower salinity stream lines tangential to the two-phase core boundary. Cool ground water is entrained into the rising fluid, giving rise to a buoyant dispersion plume. The potassic core and inner part of the phyllic alteration envelope of the porphyry copper system is regarded, in compliance with isotopic data, as the remnant imprint of the plume on the ground-water regime.

Although the model may be modified to a ground-water source for the "magmatic fluid," the authors favor an orthomagmatic hypothesis by which water and essential ore components are derived from a cooling magma column convecting lighter, more volatile components from a deeper level. The temperature profile of the steady-state plume is calculated using empirical data for permeability and heat input from the active Wairakei and Broadlands geothermal systems. Chemical implications of the physical model are in accord with the observed alteration-mineralization patterns and available high-temperature solubility data. Metals enter the system as hydroxyl or chloride complexes in the low-salinity magmatic gas precipitating in response to ground-water entrainment, temperature, and wall-rock induced pH and f_{O_2} variations. Some transport analogies are tentatively drawn with the observed chemistry of volcanic gases.

The plume model also provides an interpretation of the characteristics of the deep portion of active geothermal systems and may be extended to other ore-forming systems such as epithermal veins and massive sulfides. In the majority of such hydrothermal systems, if ore formation occurred below around 350°C, the magmatic input may be marked by the then predominant entrained ground-water component.

Introduction

SINCE the initial operations in the southwestern United States, porphyry copper deposits have been discovered throughout the Circum-Pacific region and, more recently, in some parts of the Caribbean and Alpine-Himalayan orogenic belts. These deposits are associated with Mesozoic and Tertiary calc-alkaline intrusive and volcanic suites, but deposits with essentially similar characteristics have subsequently been recognized in some much older orogenic belts

(Hollister et al., 1974; Kirkham, 1972). The geology of these large tonnage disseminated deposits (commonly 50-500 million tons at greater than 0.4% copper) has been particularly well documented through a number of excellent detailed studies of individual deposits, such as El Salvador, Chile (Gustafson and Hunt, 1975), and only the briefest of reviews is warranted in this paper. The reader is referred to the following authors for comprehensive reviews: Titley and Hicks, 1966; Lowell and Guil-

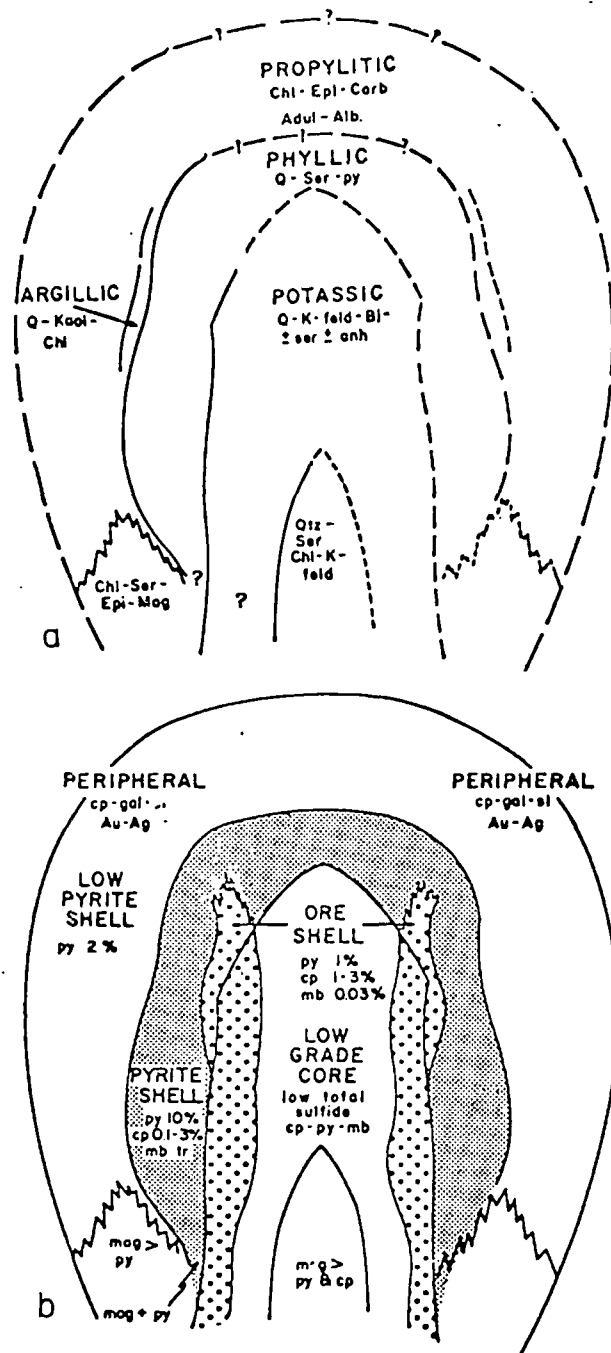


FIG. 1. Primary ore and alteration zones in an idealized porphyry copper deposit (reproduced with permission from Guilbert and Lowell, 1974).

a. Schematic drawing of alteration zoning in a typical porphyry ore deposit. Closure of the phyllic and propylitic envelopes at the apex is by inference alone.

b. Schematic drawing of mineralization zoning in a typical porphyry ore deposit. The ore "shell" indicated is typical of San Manuel-Kalamazoo while in other deposits no such distinct shell is always recognized.

bert, 1970; Rose, 1970; James, 1971; Sillitoe, 1973, 1976; Guilbert and Lowell, 1974; Titley, 1975; Sutherland Brown, 1976. The hydrothermal deposits

are all associated with calc-alkaline and alkaline plutons and while some, such as in the Highland Valley of British Columbia, occur in bodies of batholithic proportions, the majority are associated with smaller epizonal and mesozonal intrusives. Sillitoe (1973) has stressed the subvolcanic environment of formation although evidently at greater depth of erosion the deposits appear to be more closely related to larger batholithic intrusives. The reviewers cited above have drawn attention to the common concentric pattern of alteration and mineralization which characterizes the porphyry copper deposits and which is recalled in Figure 1. Most frequently copper is primarily associated with potassic core and inner part of the sericite alteration envelope. A pyrite shell commonly mantles the copper ore and, as at El Salvador, appears to overprint the primary distribution of copper sulfides. Individual variations on this normative character appear to be interpretable on the basis of local geological variables (Guilbert and Lowell, 1974) or the superimposition in time of a sequence of geochemical events.

Perhaps the most fascinating aspect of these deposits is the very high frequency by which deposits of such similar geological character have been generated in the crust, and this frequency in turn implies the common reproduction of a special physicochemical environment of formation through geological time.

A number of authors have used generalized genetic models to account for this, concepts falling into two broad groups depending on the genetic role assigned to magmatism in the ore-forming environment.

There is little doubt that during emplacement calc-alkaline magmas can, and do, exsolve a magmatic vapor phase which may subsequently become involved in ore deposition (Burnham, 1967; Holland, 1972). Recently, Whitney (1975) has related the phase chemistry of an isolated crystallizing granitic system containing 3 percent water, to the thermal profile of a cooling pluton and has derived an elegant model for the evolution of a magmatic vapor phase. Burnham (1967) and Phillips (1973) have discussed the release of such accumulated aqueous vapor by a retrograde boiling mechanism which leads to hydraulic fracturing of the crystalline envelope. Magmatic fluid generated and released in this manner has been considered to transport the ore components to the depositional area in the orthomagmatic models (Fig. 2b) of a number of recent authors (e.g., Nielsen, 1968; Rose, 1970; Fournier, 1972; Phillips, 1973; Whitney, 1975). In contrast, with the accumulating evidence for ground-water involvement at some stage during porphyry copper formation, an alternative model (Fig. 2a) has been developed by Norton and others in which convective ground-water flow through a cooling subsolidus pluton leads to ore for-

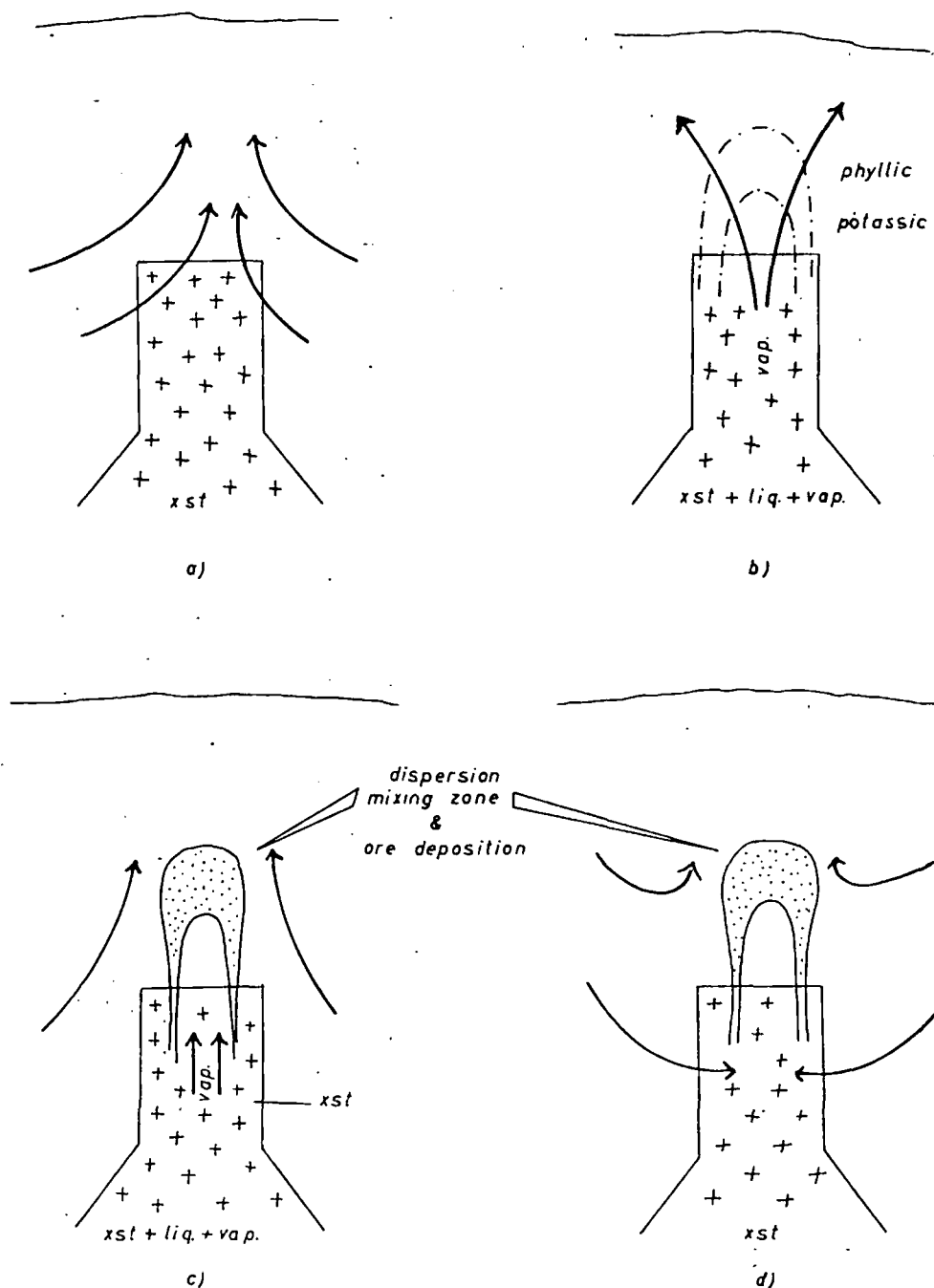


FIG. 2. Comparison of flow schemas of ore genesis models proposed for porphyry copper deposits.

a. Ground-water convection through subsolidus pluton (cf. Norton and coworkers).

b. Exsolution of magmatic fluid which subsequently "migrates" into country rock developing characteristic alteration assemblages (cf. orthomagmatic models of Rose, 1970, and others).

c. This paper. A plume of low-salinity magmatic gas exsolved from the crystallizing pluton penetrates and interacts with a preexisting ground-water convection system.

d. Modification of the plume model c) to allow for generation of "magmatic" vapor by boiling of ground water in contact with the cooling subsolidus pluton. Little data support this model.

mation, the role of the intrusive being simply that of the energy source to drive the ground-water system (Norton, 1972; Gerlach et al., 1975; Norton and Cathles, 1976).

One of the most significant features to emerge from the intensive studies to which porphyry coppers have recently been subjected, has been that *two* independently evolved fluids appear to be involved

in the development of the characteristic alteration assemblages and ore zones (White, 1974). Combination of fluid inclusion and isotopic evidence (Sheppard et al., 1969, 1971; Roedder, 1971; Moore and Nash, 1974; Hall et al., 1974; Taylor, 1974; Gustafson and Hunt, 1975; Eastoe, 1976) strongly suggests that the development of the outer phyllic, argillic, and prophylic alteration envelopes occurred at temperatures around 350°C and involved isotope exchange with *ground waters* which were dominantly meteoric in origin. In contrast the assemblages of the potassic core developed by reactions involving denser (up to 1.3 gm/cm³), higher salinity fluid. In the core, fluid inclusion homogenization temperatures range from 350°C in some to 700°C in a much larger proportion (some lower temperatures are also encountered but these probably relate to much later waning stages of the hydrothermal activity). The coexistence of liquid and vapor-rich (respectively, high- and low-salinity), often CO₂-bearing, inclusions also show that a two-phase (so-called "boiling") relationship was common and perhaps continuous in the core fluid which the isotopic evidence indicates included a substantial proportion of "magmatically" evolved fluid.¹

These data give no evidence whether the magmatic and ground-water hydrothermal activity were synchronous or diachronic but demand that effective genetic models must describe the physical and chemical behavior of *both* fluids in the ore-forming environment. Intuitively any ground-water system will continue to operate long after the freezing of the magmatic system and the termination of any supply of exsolved fluid, and Gustafson and Hunt (1975) have stressed the activity of ground-water convection in redistributing ore minerals during the post-igneous-hydrothermal stage. Otherwise little attention has been afforded the physicochemical characteristics of ore-forming environments in which two independently derived fluids may be active.

In the model developed here (Fig. 2c), we consider the nature of the interaction between a low-density and salinity magmatic vapor and cooler ground water in an essentially hydrostatic environment. The magmatic vapor carrying copper, molybdenum, sulfur, and other ore components sustains a discrete high-temperature buoyant thermal *plume* penetrating and interacting with the ground-water system. We regard the copper ore and alteration

pattern as the result of this interaction and the *remnant imprint* of this vapor plume on the ground-water system which, as the pluton crystallizes, invades the region earlier occupied by the plume. The essential differences between this and the earlier genetic models of other authors are schematically illustrated in Figure 2. White et al. (1971) tentatively compare the environment of porphyry copper formation to that of the so-called vapor-dominated hydrothermal systems. Their model has only superficial similarity to that presented here and does not involve a magma-generated thermal plume. Sillitoe (1973) rejects their model on the basis of a number of factors which we believe to be well satisfied by the plume model discussed in this paper.

In some deposits the interpretation of ore-alteration assemblages has suggested to some authors that magmatic fluid at lithostatic pressure may have actively penetrated the crust above porphyry intrusions in an essentially ground-water-free environment. Rose (1970) discussed the alteration and heat transfer characteristics of such a model in which outward flow of metal-bearing magmatic fluid from a source near the core of the deposit leads to the potassic and phyllic alteration and mineral deposition. He experienced some problems with the magnitude of the heat loss required by the model although recognizing that mixing with cooler solutions provided a possible qualitative resolution. In our model temperature decrease in the rising magmatic fluid is shown to result from mixing with the cooler external ground-water system by fluid dispersion at the margins of the buoyant magmatic plume.

General Aspects of Magmatic Vapor-Ground-water Interaction

Porphyry copper and related deposits appear to be restricted to the upper few kilometers of the earth's crust, within which vapor exsolution from magmas may occur and in many cases within which ground-water convection systems can be established and maintained. Such systems, which operate at hydrostatic pressure, can only occur where a fracture system open to the surface exists and this in turn is related to the intrinsic strength of the rocks. It has commonly been observed in deep drilling and inferred from studies of a number of low-grade metamorphic terranes that the condition $P_{fluid} < P_{load}$ may be maintained in the crust to depths of six to eight kilometers (Hubbert and Rubey, 1959; Bredehoeft and Hanshaw, 1968; Norris and Henley, 1976). As depth increases, the difference between hydrostatic and lithostatic pressure increases until induced deviatoric stresses about the contact zones of rock faces forming fissures exceed the elastic limits of the rock. This does not necessarily imply that cavities cannot

¹"Magmatic water is an H₂O rich solution that has thoroughly exchanged chemically and isotopically at magmatic temperatures with a magma system or igneous rock body. The ultimate origin of the water, either juvenile in the sense that it is coming from degassing in the lower crust or upper mantle, or recycled meteoric or sedimentary-rock H₂O that has subsequently exchanged both chemically and isotopically with the magma system, is not inherent in this definition" (Sheppard et al., 1969).

exist in any given rock substance below a certain critical depth. Once a material has fractured or deformed plastically, a new stress state develops which may reduce the deviatoric stresses below their critical limit and maintain a cavity of reduced size. Given an elastic material of a certain strength, it is possible to enclose within it a cavity of zero pressure by a succession of concentric spheres in such a way that the pressure on the outer spheres is as high as desired and the deviatoric stresses remain below the critical limit. In a volcanic zone which has been subject to high local stress levels, it is clear that, as the stresses decay at depth due to falling temperatures and magmatic pressures, a state will be created where fractures can exist to greater depths than usual in the crust thus allowing the penetration of ground water to deeper levels and, by the same token, easing the escape of late-stage magmatic fluids along a zone of enhanced vertical permeability.

Hydraulic fracturing occurs when $P_{fluid} > P_{lithostatic} + \text{tensile strength of rock}$ and is the most likely mechanism whereby magmatic vapor or fluid from deep-level plutons may penetrate upward to the higher levels of the crust (Phillips, 1973) where P_{fluid} tends to $P_{hydrostatic}$. The model discussed here applies to vapor evolution from plutons emplaced within 10 kilometers of the surface or to a flux of magmatic vapor from greater depth entering the base of a ground-water system.

We believe the close spatial and temporal relationships between ore formation and magmatism are prima facie evidence for a magmatic source for the fluids and ore components.²

We consider a steady flux of low-density vapor at submagmatic temperatures around 750°C establishing a stable buoyant thermal "plume" (fluid dynamic terminology of Turner, 1969) as it enters a homogeneous porous medium saturated with ground water, itself convecting due to magmatic heat. The plume contains a low-salinity aqueous gas mixture which, with cooling, *condenses* a small proportion of a high-salinity liquid. (This is compatible with the fluid inclusion data mentioned above previously ascribed to a boiling relationship.) The sodium chloride content of fluids exsolved from magmas is unknown, but Carmichael et al. (1973, p. 317) reason that "generation of a chloride-rich aqueous fluid, together with an immiscible sodium chloride liquid, would seem to be the normal product of crystallization of chloride-rich magmas of

² It is worthy of passing note that the vapor plume characteristics discussed here may also be applicable to the ground-water convective models of Norton and Cathles (in press) (cf. Cathles, 1976) subject to some depth and ground-water salinity constraints. Isotope data do not, however, favor this model (Nielsen, 1976).

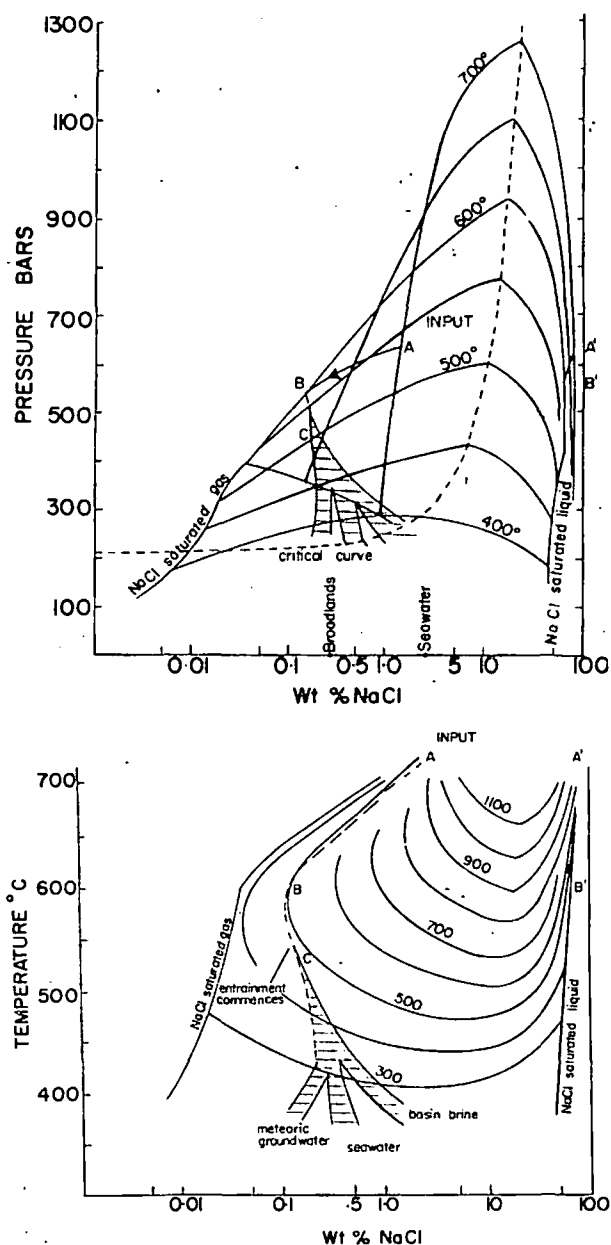


FIG. 3a and b. Isotherms, 400° to 700°C, and isobars, 300 to 1,100 bars, of coexisting gases and liquids in the system NaCl-H₂O (redrawn from Sourirajan and Kennedy, 1962). ABC represents the compositional changes of the magmatic vapor as it rises vertically through the plume and A'B' represents the composition of the coexisting liquid. In the portion BC at very high temperature gradients the vapor phase may become supercritical. Salinity variations due to entrainment of ground water are shown by the ruled ornament representing input of meteoric, sea-water, or high-salinity basin brines respectively.

high silica activity," and this has been confirmed experimentally by Ryabchikov and Hamilton (1971) and by Kilinc and Burnham (1972). Hydrogen chloride contents of volcanic gases are compatible with this viewpoint, e.g., Showa-shinzan, Japan

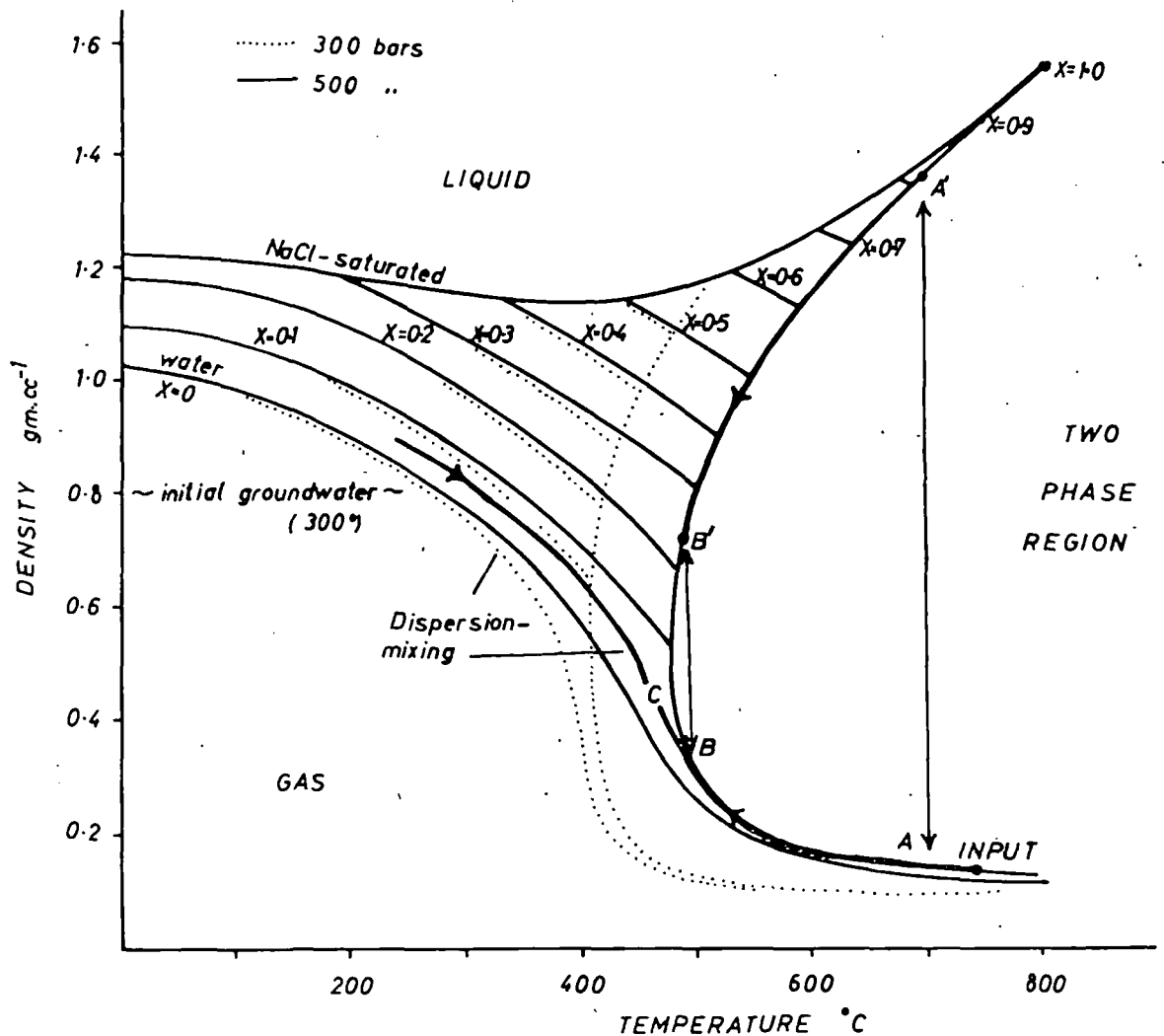


FIG. 4. Density-temperature relations in the system NaCl-H₂O at 500 bars and 300 bars fluid pressure. Data from Ellis and Golding (1963) and Urasova (1975). Explanation of A through C as for Figures 3 and 5. X = mole fraction of NaCl.

(Carmichael et al., 1973), and Ruapehu, New Zealand (Giggenbach, pers. commun., 1975), and fluid inclusions from the Ascension Island granite (Roedder and Coombs, 1967) provide direct evidence of an immiscible high-salinity liquid coexisting with a granitic melt.

At pressures above 500 bars and temperatures above 600°C compositions in the system NaCl-H₂O are subcritical (Sourirajan and Kennedy, 1962) and occur as two phases with salinities of 0.05 to 5 weight percent and about 40 to 50 weight percent, respectively (Fig. 3). NaCl and KCl predominate in inclusion fluids so that data for the simple binary system (H₂O-NaCl) are a reasonable approximation to the phase relations in a magmatic gas containing low concentrations of other salts. Data for phase relations in the system NaCl-H₂O-CO₂ show that, at

a given temperature, the onset of critical phenomena occurs at somewhat higher pressures than for equivalent salt contents in the CO₂-free system (E. V. Franck, pers. commun., 1975). Consequently any saline fluid which evolves at a total pressure of less than about 1,500 bars within a pluton must generate two discrete phases volumetrically dominated by the low-density gas phase,³ which feeds the plume.

In an actively convecting magma column, a continuous supply of saline fluid would be transferred from a lower batholithic portion toward the effervescent upper levels of the pluton and expelled through its subsolidus roof as a magmatic vapor plume. Phase separation in such a system occurs through the greater buoyancy of the gas relative to

³ The terms "gas" and "vapor" are used interchangeably.

the high-salinity coexisting liquid and the gas (at a concentration in the vicinity of A, Figs. 3a and b) would migrate out of the pluton through available fractures in the subsolidus envelope and country rock, displacing ground water and producing the discrete thermal plume. Passing from quasi-lithostatic pressures in the pluton to hydrostatic pressures in the ground-water regime, magmatic vapor undergoes irreversible isenthalpic expansion and cooling through at least 50°C (Toulmin and Clark, 1967). Intermittent choking of exit fractures by mineral deposition may lead to repetitive thermal stressing and hydraulic fracturing. Occasional explosive vapor release may result in hydrothermal breccia formation.

Figure 4 has been constructed from available data for the densities of solutions in the system NaCl-H₂O at the elevated temperatures and pressures of concern here. On the basis of the phase relations and the densities of the NaCl-H₂O system and the analysis presented in the next section Figure 5 illustrates the calculated thermal profile of a buoyant magmatic-vapor plume penetrating a superadjacent cold ground-water system. The two-phase region is limited in maximum depth by the onset of critical conditions in the multicomponent system. For the simple binary NaCl-H₂O system this pressure limit would be around 1,200 bars at magmatic temperatures and at higher pressures higher salinity fluid would occur. The composition of the gas phase as it rises through the plume may be traced using the data of Sourirajan and Kennedy (1962) reproduced in Figure 3. As vapor carrying 1 to 2 percent salt rises through point A and cools within the plume, a small fraction *condenses* to higher density and salinity liquid. In this region fluid inclusions would preserve evidence of a two-phase "boiling" relationship. After this dense phase has filled about one-third of the pore space, the permeability of the medium to the dense liquid rises above zero and tends to such a value that the liquid condensate is able to drain under gravity as fast as it accumulates. Because of the isobaric solubility minimum in the NaCl-H₂O system (Fig. 3), further cooling of the plume vapor as it rises produces a single-phase region (B-C) above and marginal to the two-phase region. The high salinity phase is diverted toward the margins of the two-phase region where refluxing occurs, into the vapor streaming upward along vertical stream lines tangential to the two-phase region.

Observations of laboratory thermohaline systems (Turner, 1965) and of geothermal systems such as Wairakei, New Zealand (Wooding, 1963; Elder, 1966), indicate that, except at extreme Reynold's numbers, fluids of differing density and viscosity do not rapidly intermix but tend to maintain relatively sharp boundaries. Through lateral dispersion in this

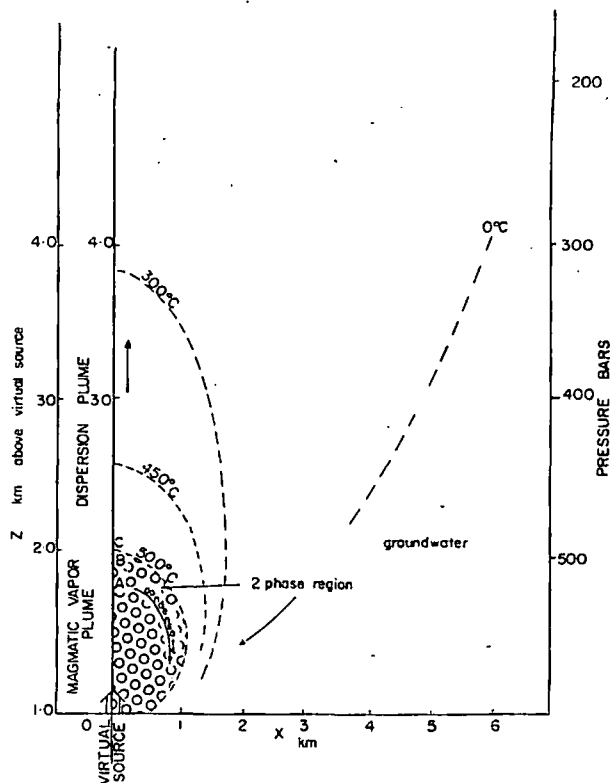


FIG. 5. Thermal profile of a magmatic vapor-dispersion plume couple, calculated through the analysis presented in the text. Selected boundary conditions are virtual source depth = 7 km, vapor input at 700°C and ground-water input at 0°C.

boundary region (Saffman, 1959; Wooding, 1963) ground water would be progressively entrained into the *magmatic vapor plume*. The proportion of ground water incorporated in the plume increases with plume height eventually subordinating the magmatic component. The latter contributes its heat content to the then *ground-water-dominated dispersion plume* as well as enriching it in metallic components, sulfur, halogens, etc. This also results in the steady addition of a proportion of magmatic vapor to the overall geothermal system contributing to the characteristic isotope shifts which have been determined in the case of porphyry copper and other ore-forming systems as well as some present-day geothermal waters. Fluid mixing occurs as a result of complexities in the flow along fissures and at fracture intersections (Richardson, 1961) so that the diameter of the dispersion plume would be a function of fracture density and tortuosity. Salinity changes in the plume due to dispersion are clearly related to the salinity of the surrounding ground-water system (Fig. 3, B-C).

The magmatic vapor plume, its core of condensed high salinity liquid, and the ground-water-domi-

nated dispersion plume constitute the essential elements of the geothermal environment of porphyry ore formation. The metal zonation and alteration pattern of these deposits follow the development and subsequent collapse of the magmatic vapor plume.

The following sections are concerned with an analysis of heat and mass transfer in this mixing environment, the thermal profile of the dispersion plume, and the implications of these with respect to metal transport and deposition and to rock alteration. No previous studies have attempted the complex analysis of hydrothermal dispersion phenomena in porous media in which a point source of high-temperature subcritical vapor buoyantly penetrates a superadjacent groundwater environment, although White (1957) has discussed the origin of some thermal waters in terms of interaction of waters of meteoric and volcanic origin.

Quantitative aspects of the plume model

In this section we attempt to quantify the heat and mass balances implied by the plume model outlined above. The thermal pattern of the ground-water system is likely to be similar to that of a water-dominated system of the Wairakei type. These are high Rayleigh number systems (Elder, 1966) for which the deeper upflow portions may be modeled as buoyant hot-water plumes (Wooding, 1963; McNabb, 1975) with near-vertical isotherms and large transverse thermal gradients. Since certain essential parameters are virtually unobtainable for the ore-forming system itself, by analogy we shall use values which pertain empirically to the New Zealand geothermal regions.

The macroscopic permeability of porphyry copper systems in their prime active states is probably dominated by the distribution of fissures and not by the local permeabilities of laboratory-sized specimens. D. T. Snow (pers. commun., 1971) and Putnam (1975) have noted high fracture densities in certain porphyry ore systems suggestive of very high macro-permeabilities. Villas (1975), from a study of fracture abundance of the Mayflower mine in Utah, estimated permeabilities in the range 10^{-11} to 10^{-13} m². In ore-forming and geothermal systems, fissures are continually being closed through mineral deposition and regenerated by intermittent tectonism, hydraulic fracturing, stress corrosion cracking (Grew, 1976), and thermal stress fracturing (McNabb, 1975), so that permeability fluctuates locally but on the large scale can be assumed constant. Such factors operate in the Wairakei and Broadlands geothermal systems where heat and mass transfer data lead to estimates of large-scale effective permeabilities of the order of 5×10^{-15} m². We take this figure as applicable to

the time-averaged large-scale permeability of our porphyry copper model.

If p is the fluid pressure in the medium and μ the fluid viscosity, then V , the vector describing the flux of fluid per unit area per second, is given by Darcy's law:

$$V = \frac{-k}{\mu} (\text{grad } p - \rho g) \quad (1)$$

where ρ is the fluid density and g is the gravitational acceleration vector.

If a liquid and a gas phase are jointly present where conditions of temperature and pressure are subcritical, we assume each phase satisfies an expression analogous to equation (1) but with k modified by a permeability reduction factor $F(e)$ which depends on the fraction e of the pore space ϵ per unit volume which is occupied by the liquid phase.

Let the suffix l refer to the liquid phase and g to the vapor phase. Then, in regions where two phases exist:

$$V_l = \frac{-k}{\mu_l} F_l(e) (\text{grad } p - \rho_l g),$$

$$V_g = \frac{-k}{\mu_g} F_g(e) (\text{grad } p - \rho_g g) \quad (2)$$

For want of experimental data relevant to fractured porous media, we assume $F_l(e)$ and $F_g(e)$ are given by the curves of Wyckoff and Botset (1936).

The mass of water M_w per unit volume of porous medium is given by

$$M_w = \epsilon \rho \chi_w \quad (3)$$

in the single-phase zone and by

$$M_w = \epsilon [e \rho_l \chi_w^l + (1 - e) \rho_g \chi_w^g] \quad (4)$$

in the two-phase zone. Here ϵ is the porosity, e the fraction of pore space occupied by liquid, ρ the fluid density, and χ_w the mass fraction of water present in the fluid; l and g superscript or subscript the relevant phase.

The mass of salt M_s per unit volume is given by analogous expressions. Thus, in the two-phase zones,

$$M_s = \epsilon [e \rho_l \chi_s^l + (1 - e) \rho_g \chi_s^g], \quad (5)$$

where χ_s^l and χ_s^g are the mass fractions of salt in the liquid and vapor phases, respectively.

The local energy content E per unit volume, ignoring potential energy contributions, is given by the expression

$$E = \rho_m U_m + \epsilon [e \rho_l U_l + (1 - e) \rho_g U_g], \quad (6)$$

where ρ_m is the density of the rock medium and U_m , U_l , and U_g are the internal energies per unit mass of

the solid medium, liquid phase, and vapor phase, respectively.

The mass flux vector for water F_w we assume to be given by an expression of the form:

$$F_w = \chi_w^l \rho_l V_l + \chi_w^g \rho_g V_g - [K(\rho_l V_l) : \text{grad } \chi_w^l + K(\rho_g V_g) : \text{grad } \chi_w^g] \quad (7)$$

where $K(\rho V)$ is a dispersion tensor dependent on the local fluid mass flux vector. Similarly, the salt flux vector F_s and energy flux vector F_E are assumed to be given by the relevant equation of the pair:

$$F_s = \chi_s^l \rho_l V_l + \chi_s^g \rho_g V_g - [K(\rho_l V_l) : \text{grad } \chi_s^l + K(\rho_g V_g) : \text{grad } \chi_s^g] \quad (8)$$

$$F_E = h_l \rho_l V_l + h_g \rho_g V_g - [K(\rho_l V_l) : \text{grad } U_l + K(\rho_g V_g) : \text{grad } U_g] \quad (9)$$

In the last equation, enthalpy h occurs in the first terms instead of just internal energy U in order to account for the work flux contributions. The diffusive contributions to the various flux vectors have been ignored on the grounds that they are probably so much smaller than the dispersive terms.

The equations governing the behavior of the system are three concerned with the conservation of water, salt, and energy:

$$\frac{\partial M_w}{\partial t} + \text{div } F_w = \frac{\partial M_s}{\partial t} + \text{div } F_s = \frac{\partial E}{\partial t} + \text{div } F_E = 0 \quad (10)$$

and various equations of state describing the distribution of salt and water between the liquid and gaseous phases (one of equilibrium at the local temperature and pressure) and the densities and viscosities of the two phases as a function of temperature pressure and salt concentration.

Saffman (1959) derived an expression for the effective transverse thermal diffusivity K_t :

$$K_t = \frac{3}{16} ul \quad (11)$$

in terms of the average fluid velocity u and the average "pore" length l of the medium, and so we assume the components of K_t are proportional to relevant components of V .

In the following section we describe some approximations which enable us to derive a workable system of equations intended to portray the broad features of a steady plume in its ground-water environment.

We first assume the system is in a steady dynamic state and that the ground water imposes a pressure

distribution on it approximately of the form

$$P = P_0 + \rho_0 g z. \quad (12)$$

The coordinate z measures distances vertically and upward from an origin point O acting as the virtual source of the plume. The plume is assumed symmetrical about the vertical axis through O , and r measures horizontal radial distances from this axis.

The mass of magmatic steam rising from the source O is assumed to carry about 2 percent salt as it enters the two-phase core of the plume. Since the liquid phase away from the bounding critical surface of the two-phase zone is about 50 percent salt, only about 2 percent of the magmatic fluid can be carried out of the inner regions of the two-phase zone as a liquid phase. We assume, therefore, that for the purposes of conserving fluid mass and energy, we can treat the whole plume approximately as a single fluid system which assumes the vapor properties in the two-phase zone.

Next, the vertical velocities are assumed to be generated by buoyancy forces created by fluid densities differing from ρ_0 and the radial velocities and temperatures to be such that mass and energy are conserved. Only the transverse or radial component of the dispersion terms generated by the vertical fluid fluxes is assumed to be significant. Moreover, we choose to ignore the dispersion term in the mass conservation equations on the grounds that $\text{grad } \chi_w$ is small almost everywhere. Let u be the radial component and w the vertical component of ρV and suppose $\chi_s + \chi_w = 1$, so that from equations (7), (8), (10) we have:

$$\frac{1}{r} \frac{\partial}{\partial r} r \mu + \frac{\partial w}{\partial z} = 0. \quad (13)$$

Now w is given by equations (1) and (12) as

$$w = \frac{k\rho}{\mu} (\rho_0 - \rho)g$$

and the temperature T is described in terms of the dimensionless function θ by the expression

$$T = T_0 + (T_1 - T_0)\theta \equiv T_0 + \Delta T \theta$$

where T_0 is the cold ambient ground-water temperature and $(T_1 - T_0)$ is representative of the temperature changes on entering the plume. The density ρ may be assumed to vary roughly linearly with temperature except perhaps in a narrow zone on the boundaries of the two-phase region. We assume this region has only a small perturbing effect on the global temperature and velocity picture and write

$$w = \frac{k\rho}{\mu} g \alpha \Delta T \theta = \beta \theta; \quad \rho = \rho_0 + \alpha \Delta T \theta \quad (14)$$

and

$$-\frac{1}{r} \frac{\partial}{\partial r} r u + \beta \frac{\partial \theta}{\partial z} = 0. \quad (15)$$

In the energy conservation equation we again retain a bare minimum of terms. We assume

$$\begin{aligned} \operatorname{div} \rho V h &= \rho V \operatorname{grad} h = \operatorname{div} [K(w) : \operatorname{grad} U] \\ &\simeq \frac{1}{r} \frac{\partial}{\partial r} r K w \frac{\partial}{\partial r} (h) \end{aligned}$$

and a linear dependence of h on T , thus arriving at an energy equation of the form:

$$\begin{aligned} u \frac{\partial \theta}{\partial r} + w \frac{\partial \theta}{\partial z} &= u \frac{\partial \theta}{\partial r} + \beta \theta \frac{\partial \theta}{\partial z} \\ &= \frac{K}{r} \frac{\partial}{\partial r} r w \frac{\partial \theta}{\partial r} = \frac{K \beta}{r} \frac{\partial}{\partial r} r \theta \frac{\partial \theta}{\partial r}. \end{aligned} \quad (16)$$

A simple change of coordination scales reduces equations (15) and (16) to a parameterless form. Let $r = K\beta x$, $z = K\beta^2 t$, so that

$$\frac{1}{x} \frac{\partial}{\partial x} x u + \frac{\partial \theta}{\partial t} = 0 \quad (17)$$

$$u \frac{\partial \theta}{\partial x} + \theta \frac{\partial \theta}{\partial t} = \frac{1}{x} \frac{\partial}{\partial x} \left(x \theta \frac{\partial \theta}{\partial x} \right). \quad (18)$$

These equations are invariant under the similarity transformation:

$$x \rightarrow \alpha x, \quad t \rightarrow \alpha^2 t, \quad \theta \rightarrow \theta/\alpha, \quad u \rightarrow u/\alpha^2, \quad (19)$$

and moreover, this transformation leaves invariant the expression

$$J = \int_0^\infty x \theta^2 dx$$

which is proportional to the vertical energy flux through the horizontal plane at z . Thus any solution satisfying these invariance properties should have some relevance to our plume problem. We search for a suitable solution of equations (17) and (18) by expressing θ and u in terms of the invariants of equation (19) thus:

$$y = \frac{x}{\sqrt{t}}, \quad \theta = \frac{f(y)}{\sqrt{t}}, \quad u = \frac{g(y)}{t}; \quad (20)$$

and substituting into equations (17) and (18) to obtain

$$2 \frac{d}{dy} (y g) = y \frac{d}{dy} (y f) \quad (21)$$

$$4 y g \frac{df}{dz} = \frac{d}{dy} (y^2 f^2) + 2 \frac{d}{dy} \left(y \frac{df^2}{dz} \right). \quad (22)$$

By adding $2f$ times equation (21) to equation (22) we get

$$4 \frac{d}{dz} (y g f) = 2 \frac{d}{dz} (y f)^2 + 2 \frac{d}{dy} \left(y \frac{df^2}{dy} \right)$$

which integrates to give:

$$g = \frac{df}{dy} + \frac{y f}{2} \quad (23)$$

since f and g are required to vanish as x goes to infinity or y gets large.

This result, inserted in equation (21) gives rise to the linear Bessel equation of zero order:

$$y^2 \frac{d^2 f}{dz^2} + y \frac{df}{dy} + \frac{y^2}{2} f = 0, \quad (24)$$

with solution

$$f = A J_0(y/\sqrt{2}). \quad (25)$$

The function g is given explicitly by equation (23).

In this solution, the negative values of J_0 are unattractive and we imagine a plume consisting of only the positive values inside the parabola $y = \sqrt{2} y_1$, where y_1 is the first zero of J_0 . We imagine these values of θ and u associated with $\theta = 0$ outside the parabola and u on the bounding parabola giving the local rate of entrainment of cold ground water into the plume. The integral J is given by the expression

$$J = \frac{A^2}{t} \int_0^{y_1 \sqrt{2t}} x J_0^2(x/\sqrt{2t}) dx = \frac{A^2 y_1^2}{4} J_1^2(y_1). \quad (26)$$

The flux of energy Q_E up through the plume is given by

$$Q_E = 2\pi \int_0^\infty r w (h - h_0) dr$$

and since we assume

$$w = \beta \theta, \quad h - h_0 = h^* \theta, \quad (27)$$

then

$$Q_E = 2\pi \beta h^* K^2 \beta^2 \int_0^\infty x \theta^2 dx = 2\pi h^* K^2 \beta^3 J. \quad (28)$$

Equations (26) and (28) enable us to relate the constant A to the total energy output Q_E of the plume. Thus,

$$Q_E = A^2 (2\pi y_1^2 J_1^2(y_1)) h^* \beta^3 K^2 = A^2 \lambda^2 h^* \beta^3 K^2.$$

The central temperature T_c in the plume along $r = 0$ is given by

$$T_c = T_0 + \Delta T \frac{f(0)}{\sqrt{t}}$$

so that

$$T_c - T_0 = \frac{B}{\sqrt{z}}, \quad B = \frac{\Delta T}{\lambda} \sqrt{\frac{Q_E}{h^* \beta K z}}$$

$$\lambda^2 = 2\pi y_1^2 J_1^2(y_1). \quad (29)$$

The quantity $h^* \beta K / \Delta T$ plays the role of an apparent transverse thermal conductivity K_t . The boundary of the plume is given by $x = y_1 \sqrt{2t}$, or $r = y_1 \sqrt{K 2z}$.

From the formula for the central temperature T_c we have the rate of increase of T_c with z that satisfies

$$\frac{dT_c}{dz} = - \frac{(T_c - T_0)}{2z}$$

Thus z , the depth to the virtual source, is given by

$$z = - \frac{(T_c - T_0)}{2dT_c/dz}$$

and knowing z , we estimate K from the radius of the plume using

$$K = r^2 / 2zy_1^2.$$

For the Wairakei field, T_c is observed to increase with depth underneath the two-phase zone where $T_c \approx 250^\circ\text{C}$ at about 20°C per kilometer, giving $z \approx 7$ km below surface, and since the area of the field is about 15 km^2 , $K \approx 6 \times 10^8 \text{ cm}$.

In the next section we estimate the distribution of salt in the system. The preceding analysis assumes a pressure distribution

$$P = P_0 - \rho_0 g z \quad (12, 30)$$

where P_0 is the pressure at the virtual source and ρ_0 is a constant taken here to be 0.9 gm/cm^3 since cold ground water must flow down toward the plume source to replace the entrained fluid convected by the plume out through the ground surface as hot springs and steaming ground. P_0 will be taken here as 600 bars, on the assumption that the virtual source is at depth close to 7 kilometers.

The temperature distribution was found to be given approximately by the equation

$$T - T_0 = \frac{1}{\lambda} \sqrt{\left(\frac{Q_E}{dT} \frac{dw}{dT} \right)} J_0(r/\sqrt{2Kz}) / \sqrt{Kz} \quad (31)$$

where w is given by equation (14), λ by equation (29), and K is taken as about 60 meters.

The temperature profile is essentially governed by two physical parameters, the dispersion constant K which affects the width to depth aspect of the plume and the ratio Q_E/k which affects its hotness. Again, for definiteness, we assume the axial plume tempera-

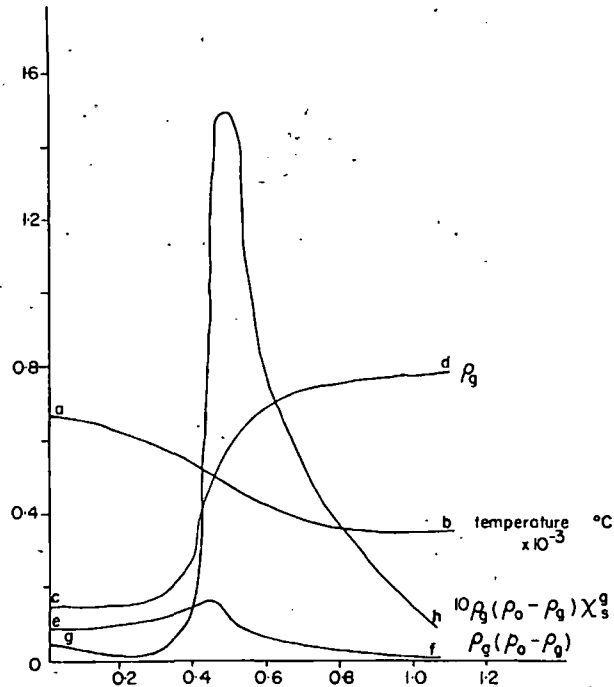


FIG. 6. Temperature, fluid density, and salt flux relations through a plane horizontal section of the plume at $P_{11014} = 500$ bars; for explanation see text. Abscissa gives dimensionless radius from the plume axis and is correlated with the temperature profile; in general, units show approximate kilometers. Ordinate units are those c.g.s. units appropriate to each function represented.

ture T_c , given by

$$T_c = 700/\sqrt{z}$$

where z is the distance in kilometers above the virtual source (at 7 km depth).

Figure 5 shows the calculated thermal profile of a dispersion plume originating from magmatic vapor rising from a virtual source at 7 km into a cold ground-water environment. Where the vapor plume penetrates a hot convecting ground-water system, the profile will be modified due to the entrainment of hotter water such that isotherms become stretched in the vertical sense. For example, where ambient temperatures in the deep ground-water system reach 400°C , the 500°C plume isotherm closes at about 4 km above the virtual source.

From critical data of Sourirajan and Kennedy we see there is a central region in the plume bounded by a surface coinciding with the 500°C isothermal at virtual source and intersecting the central axis close to the 470°C isotherm. Outside this surface conditions are single phase, except for a low-pressure zone near the ground surface.

We consider a flux of magmatic steam entering the plume at about 700°C providing, say, 100 kg/sec of water, about 2 percent NaCl, equilibrium propor-

tions of HCl, some CO₂, various sulfur compounds, and perhaps 1 part in 10⁶ copper.

Consider the fluid rising along the plume axis. As it rises and cools to 600°C, the concentration of salt falls to 0.1 weight percent in the gas and a liquid phase containing 60 to 70 percent by weight of salt condenses. Since the density of this fluid is 1.2 gm per cc or more, it drains back toward the source and eventually out toward the plume margins.

The proportion e of liquid to gaseous phase adjusts itself so that $F_1(e)$ is of such a value the liquid phase flows away at the same rate it is deposited from the gas. As the temperature of the rising gas on the plume axis falls farther from 600° to 500°C it is undersaturated in salt and, as the only source is via dispersion from outer regions of the plume, the

concentration rises only slowly above 0.1 weight percent.

Now consider fluid conditions near the almost vertical sections of the critical surface bounding the two-phase zone. We see from the 500-bar curve of Figure 3 that, as the critical temperature of about 460°C is approached, the concentration of salt in the two phases approaches a common value of about 5 weight percent, and the densities from Figure 4 approach a common value of about 0.5 gm per cm³. In fact, both liquid and gaseous phases have densities less than 0.9 gm per cc for temperatures outside the 500°C isotherm. Thus the salt rises through the plume primarily along vertical stream lines which are tangents to the critical surface bounding the hot core of the plume. The hot central core is a reflux zone, condensing hot salty fluid and generating a secondary

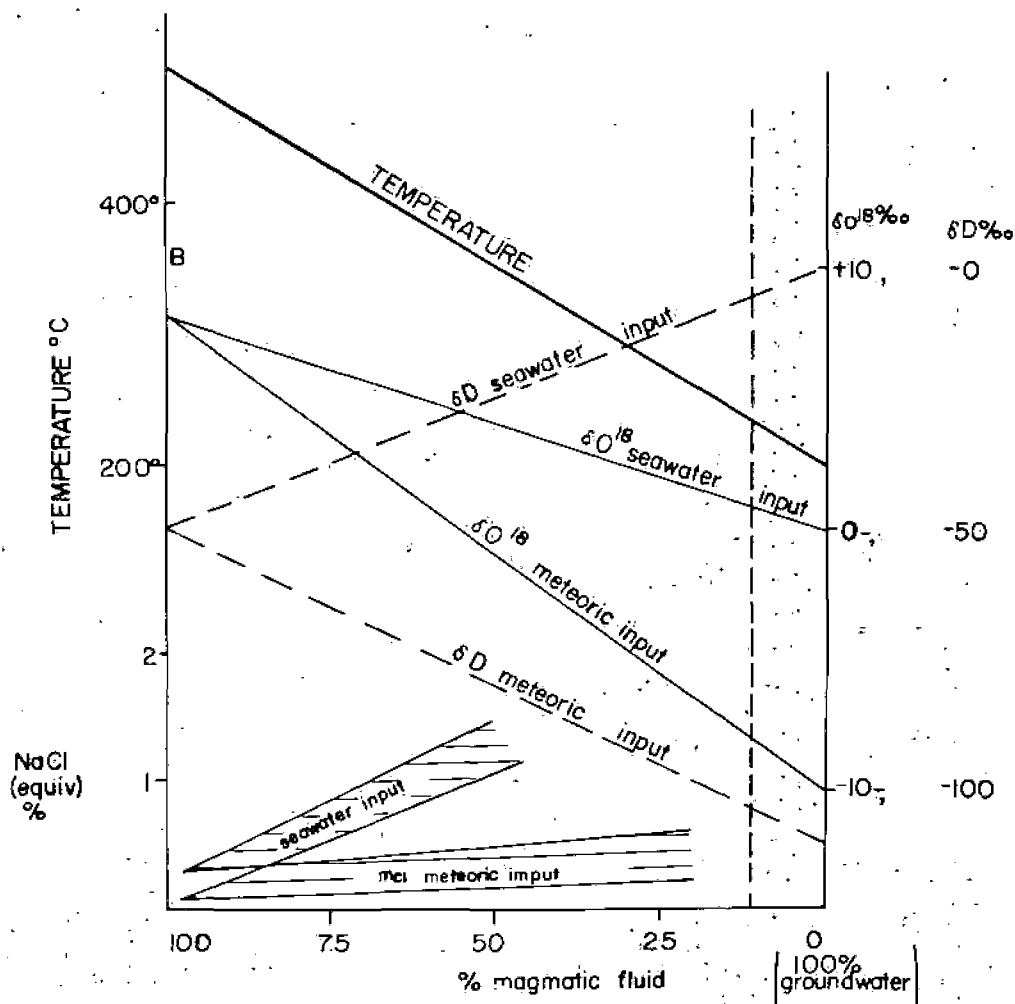


FIG. 7. Correlation of temperature, isotope composition, and salinity of fluid on a vertical section through the dispersion plume above the two-phase region. The linear relations are based on a simple lever rule. The stippled region, bounded at 10 percent magmatic fluid, is a conservative estimate of the range of temperature, salinity, and isotope analysis within which a magmatic contribution may not be detected other than by inference.

flow transporting the salt to the outer edges of the plume. If copper and other magma-derived metals are preferentially partitioned to the liquid phase, this reflux mechanism focuses metals to the outer streamlines enhancing the metal content of this region and may in part account for the formation of the cylindrical ore shell which occurs in a number of deposits.

Note from Figure 4 that when $x > 0.4$ the fluid will not convect vertically upward and it is possible for the hot salty fluid to form a stably stratified near-horizontal hot plate for the ground-water convection system.

In Figure 6, curve ab is the temperature distribution across the plume at the 500-bar pressure level, cd is a plot of corresponding values for ρ_R obtained from Figure 4 assuming x_s^g constant at 0.05 below $T = 470^\circ\text{C}$ and saturation values above this. The curve ef is a plot of $\rho_R(\rho_0 - \rho_R)$ and, ignoring viscosity, is an index of the potential for convecting water mass vertically via the gas phase. The curve gh, the function $\rho_R(\rho_0 - \rho_R)x_s^g$, represents the potential for convecting salt mass vertically via the gas phase and illustrates how the system channels the vertical flow of salt along the vertical tangents of the

two-phase boundary, where conditions are near critical.

In consequence the horizontal salt profile at this level is strongly bimodal. Higher in the plume where the higher harmonics are reduced due to dispersion, the temperature and salt concentrations become highly correlated because both are determined by the same dispersion-mixing process (Fig. 7). Ore metals whose rate of deposition is a function of salt concentration will precipitate in a bimodal fashion modified by temperature and consequent pH, $f_{\text{H}_2\text{S}}$, etc. controls. Those which are dependant on temperature and/or the proportion of admixed ground water will be deposited with profiles closely approximating the isotherm distribution.

The isotope composition of the mixed fluid in the plume itself becomes linked to the thermal and salinity profile (Fig. 7). This behavior may account for the frequency of ground-water-induced isotope patterns determined for many ore-forming environments and also lends support to the possible utility of total chloride concentration as a prospecting tool in some environments (Stollery et al., 1971).

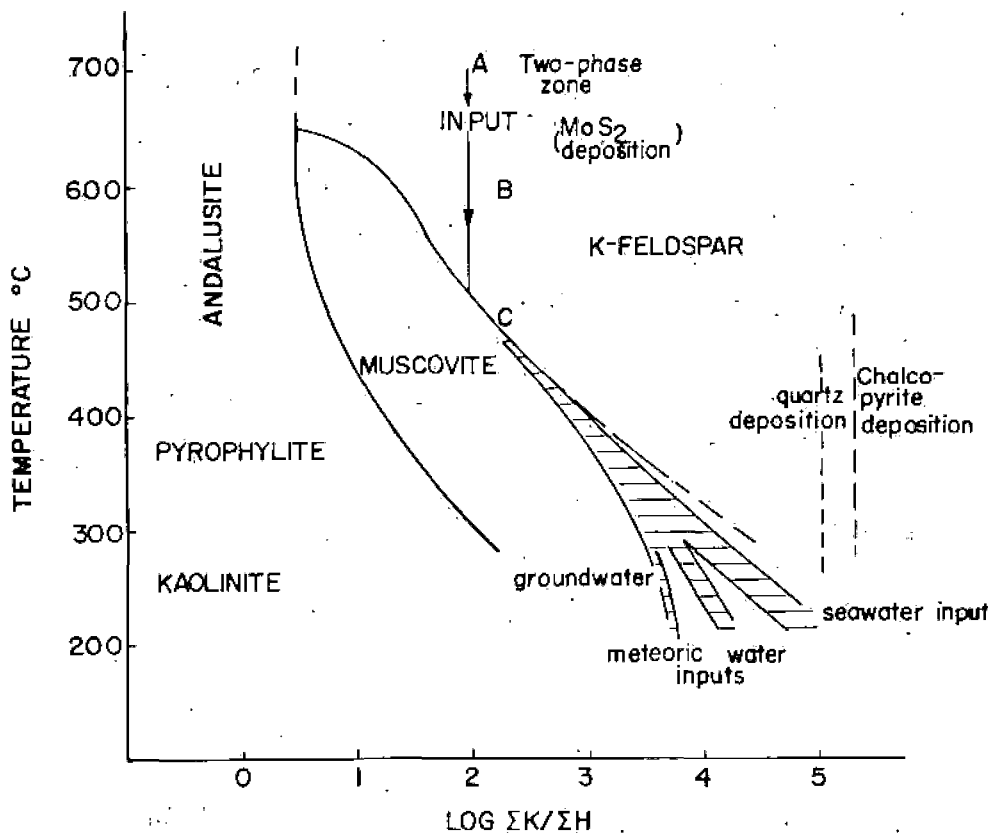


FIG. 8. Stability relations of the aluminosilicates, kaolinite, muscovite, and K-feldspar in chloride solutions with respect to temperature and $(\text{KCl} + \text{K}^+)/(\text{HCl} + \text{H}^+)$ ratio (after Hemley, 1959). The temperature path ABC into the ruled area is consistent with Figures 3 and 4. See text for explanation.

Chemical Aspects of the Plume Model

The physical model described above has several implications with regard to metal and sulfur transport, mineral deposition, and rock alteration which must be compatible with the observed field relations. Each of these is discussed below.

In uniform rocks the distribution of potassic and phyllic alteration zones is dependent upon the temperature and salinity profile of the plume and the surrounding ground-water envelope. Figure 8 reproduces the $m\text{KCl}/m\text{HCl}$ temperature data for the relevant assemblage, K-feldspar, muscovite, quartz (Henley, 1959). The plume gas (see discussion above and Rose, 1970) has a low initial $m\text{KCl}/m\text{HCl}$ ratio; for a 5 percent salinity gas ($10^{-2.2}$ molal), $m\text{HCl}$ has the value $10^{-2.2}$ at 650°C and this remains constant through cooling into the sericite stability field (see Rose, 1970, fig. 13). In contrast in ground waters of low salinity (e.g., Broadlands type) $m\text{KCl}/m\text{HCl}$ at 300°C would be around 10^4 . For unmodified higher salinity ground waters (e.g., sea water) $m\text{KCl}/m\text{MCl}$ at this temperature would be around 10^7 , so that clearly salinity and concomitant pH variation would exercise a powerful, possibly dominant, control on ore deposition in the region peripheral to the plume. Figure 8 illustrates the variation of $m\text{KCl}/m\text{HCl}$ in this region and is the basis for the alteration zones shown on Figure 9. Figure 8 also indicates the solution behavior of quartz as implied by the plume model. It may be assumed that the solubility of quartz in the magmatic gas is a simple function of that in supercritical water under the same pressure-temperature conditions (Styřichovich et al., 1960). Quartz experiences a solubility reversal at around 375°C in water at 500 bars (Kennedy, 1950), but this disappears at higher pressures. In all cases quartz will be deposited as temperature decreases below 400°C , but in systems operating at hydrostatic pressure below about 700 bars, precipitation would not occur within the two-phase core of the plume or its margins. At higher pressures choking of microfractures in the core would severely limit the time-averaged permeability of the system, although Fournier (1967), discussing silica transport in the case of alteration at Ely, speculated on the possibility of solutions becoming supersaturated with respect to silica through the slow nucleation of quartz even at high temperatures. This suggestion has been substantiated by experiment (Carr and Fyfe, 1958) and indicates that fracture choking by silica precipitation would be far less severe than otherwise anticipated above 700 bars fluid pressure.

Transport of ore metals into the ore-forming environment is considered to occur as molecular complexes in the hot low-salinity magmatic gas. This

mode of metal transport has received little attention since Krauskopf (1957) argued that metal chloride volatility was an inadequate mechanism, but his thermodynamic calculations could take no account of possible complex halide interactions or hydration or hydroxylation of the monomeric or polymeric species (e.g., CuCl , Cu_3Cl_3) in the H_2O - HCl -rich gas mixture transported through the plume. Such interactions greatly enhance the volatility of the ore metals so that the saline gas mixture, derived from a melt of low initial metal content, would be greatly undersaturated with respect to the metal or metal sulfides. In the industrial TORCO copper segregation process, which involves the reaction of copper ore with coal and aqueous sodium chloride at 750° to 850°C , vapor-phase copper transport occurs as mixed halide complexes CuNaCl_2 and Cu_2NaCl_3 rather than Cu_3Cl_3 (Brittan, 1970; Gross and Stuart, 1972). Gold is also transported in the magmatic gas and in low-density chloride solutions at 500°C and has been shown to form solvation complexes such as Au_2Cl_6 , 6HCl , $n\text{H}_2\text{O}$ (Henley, 1971), while mixed halide complexes may also occur (Henley, 1971, 1973; Hastie, 1975). Vapor-phase transport of molybdenum occurs probably as hydroxy-species such as $\text{Mo}_7\text{O}_{18}(\text{OH})_6$ (Glemser and Wendlandt, 1963).

The chemistry of metal deposition in any high-temperature hydrothermal system is complex. Within the plume copper deposition is unlikely directly from the undersaturated gas except through stability decrease of the complex molecular species. For the system NaCl - H_2O - MCl_2 at 650°C and 500 to 1,000 bars, reconnaissance data (unpub. data, Henley, 1976) have confirmed the general rule proposed by Styřichovich et al. (1960), that the partition coefficient of metal between coexisting phases is a function of the density ratio of the two phases. These data also suggested that the metal content of the low-density phase may positively deviate from this rule. For a gas input containing, say, 20 ppm copper the coexisting liquid would contain in excess of 1,000 ppm copper.

A high molybdenum content of the condensate along with destabilization of its solution complex may account for the deposition of molybdenum preferentially in the core region while copper and other metals migrate at high concentration in the condensate toward the core margin. As described above, condensed brine from the core flows toward the plume margin and is subsequently refluxed into the single-phase marginal flow and thence into the ground-water-dominated dispersion plume, both becoming enriched in metal ion. In the system SO_2 - H_2O , SO_2 predominates over H_2S above 550°C (Barnes and Czamanske, 1967) so that SO_2 would be the predominant sulfur species in the vapor plume.

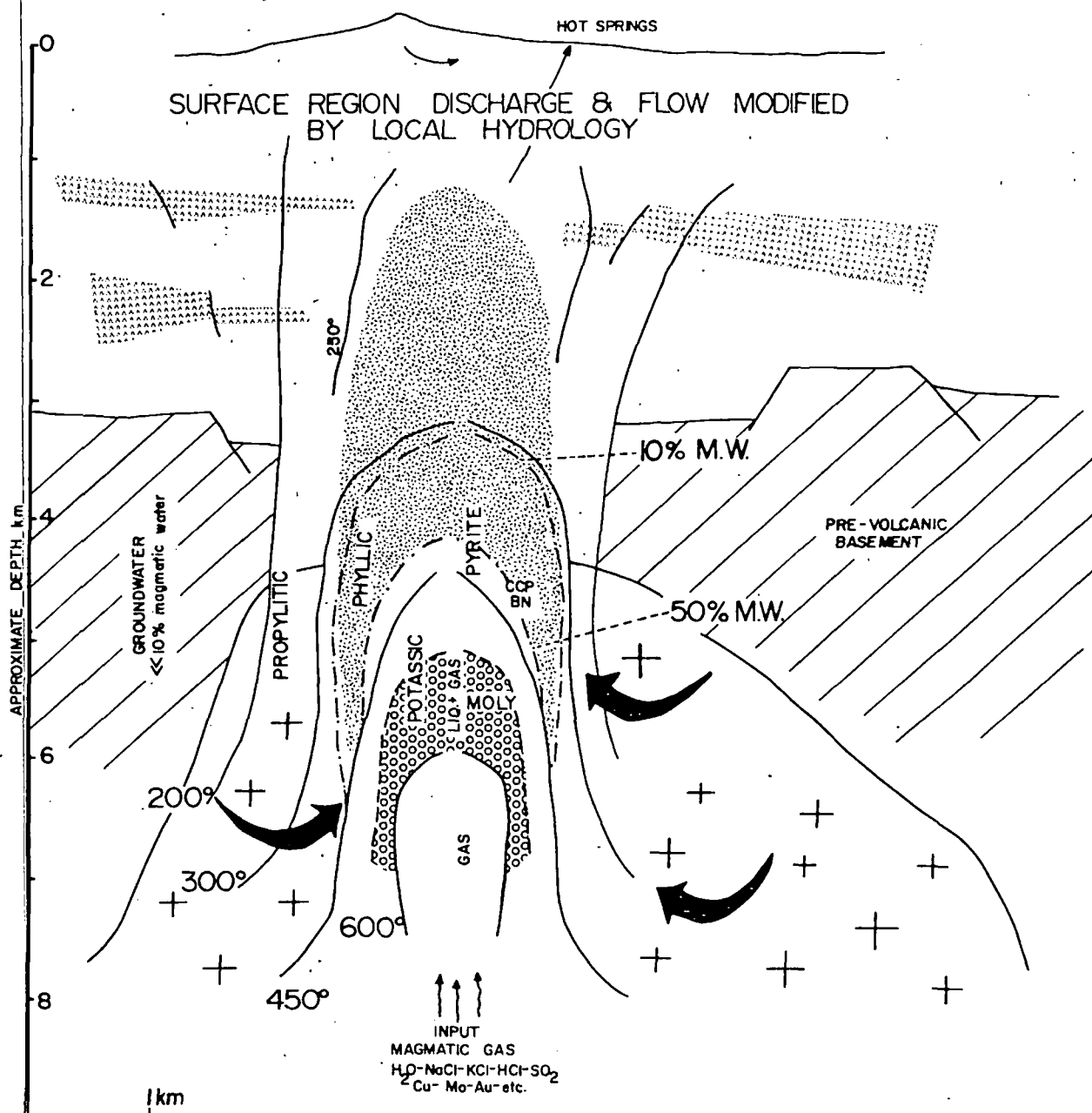


FIG. 9. Schematic summary of the plume model described in the text for a developing porphyry copper deposit. Temperature profile is similar to Figure 5 and alteration zones consistent with Figure 8. The thermal profile in the surface zone depends on the local permeability characteristics; mushrooming of the isotherms occurs only if the system undergoes little discharge through the surface or multiple symmetrical relatively high power discharge (cf. Elder, 1966). The dispersion plume is shown by the flecked ornament but its boundaries have been arbitrarily chosen to outline a region characterized by enhanced metal content. Direct discharge from this region may locally produce a metalliferous hot-spring precipitate or epithermal vein deposit. Note the small volume of the whole-rock volume in which isotope data would indicate predominance of magmatic fluid and, in contrast, the large volume of the dispersion plume dominated by the ground-water input. The distribution of pyrite and bornite may depend on late-stage dissolution and reprecipitation of primary chalcocite by encroaching ground water. Localized boiling may occur in the surface region.

With decreasing temperature, f_{H_2S} increases and metal sulfide deposition may be an indirect consequence.

At the plume margin, where the highest mass flux occurs, temperature decrease below 450°C into the field of dominant ionic complexing may lead to metal

deposition. Crerar and Barnes (1976) report the results of a solubility study of the assemblage pyrite-chalcopyrite-bornite up to 350°C and suggest that $(\text{CuCl})_0^+$ is the predominant copper species unless the solution is sulfur rich, when copper thiosulfide complexes occur. Their discussion of depositional mechanism is oriented toward the porphyry copper environment and need not be repeated here, but the reader is referred to pages 785 to 790 of their paper. They show that the most significant depositional mechanisms for both copper and iron involve either decrease of acidity by about 1 pH unit or decrease of salinity in the temperature regime 250° to 350°C. Entrainment of cooler, lower salinity ground water, with consequent temperature, salinity, f_{O_2} , and pH variation, would clearly be an effective process leading to sulfide deposition in the dispersive region marginal to and above the two-phase zone.

The salinity of ground water entrained into the rising plume does not modify the buoyancy-dominated plume picture but certainly affects the behavior of ore metals. The above discussion of ore transport highlighted decreasing salinity as one of a number of interrelated factors likely to lead to ore deposition within the dispersion zone. By contrast in an environment where sea water becomes the entrained component, salinity increases rapidly with height through the dispersion plume (Figs. 3 and 7).

To date only the porphyry ores of the Guichon Creek batholith, British Columbia, have yielded isotope data suggestive of sea-water circulation at some stage during ore formation (Osatenko and Jones, 1976), but it is to be anticipated that sea-water involvement will be recognized in those deposits which are associated with alkalic plutons emplaced within coeval submarine volcanics. In such cases ore deposition will result largely from temperature and f_{O_2} variations. Outside a potassic core, phyllic and propylitic alteration may pass imperceptibly into zeolite, prehnite-pumpellyite, or greenschist facies metamorphic assemblages. In submarine environments, high-power discharge to the sea floor of a metal-enriched sea-water-dominated dispersion plume leads to polymetallic (Cu-Fe-Zn-Pb-A-Ag) massive sulfide ore formation. The geothermal characteristics of such submarine systems and their discharge behavior are discussed at length elsewhere (Henley and Thornley, in prep.).

Discussion—An Analogy with Volcanic Discharges and the Broader Picture

No two-ore-forming systems are ever identical, each varying in its fabric through local geological variables and the *precise* sequence of geochemical events which lead to ore formation, but we believe

that the plume model described in this paper satisfactorily accounts for the gross similarities in mineral distribution, formation temperature, fluid inclusion, and isotope data and geologic setting of the porphyry copper deposits. This is a single-stage model not incorporating a succession of magmatic vapor pulses or renewed magmatism in the ore environment. With the collapse of the vapor plume, encroachment of the ground-water system onto the primary alteration mineralization pattern may lead to redistribution of early-phase copper in the inward-developing pyrite and bornite assemblage and to overprinting of early-phase potassic alteration by ground-water-dominated phyllic alteration as has occurred at El Salvador (Gustafson and Hunt, 1975) and elsewhere.

The temperature profile of the dispersion plume, discussed above refers to conditions of isotropic permeability. While this picture may hold true in a number of crustal environments (e.g., where plutons penetrate fractured crystalline basement material), it clearly requires modification in anisotropic environments. In young volcanic terranes stratification is generally subhorizontal so that plume development is constrained to the relatively low component of vertical permeability or induced zones of high vertical permeability such as fracture zones or late-stage collapse features. Where horizontal ground-water flow is restricted, early-phase phyllic or propylitic (low-grade metamorphic) assemblages may be overprinted first by higher temperature and later by waning-stage lower temperature assemblages to produce a telescoped alteration pattern.

With the recognition of the shallow subvolcanic environment of porphyry ore formation it is possible to follow Sillitoe (1973) and others (e.g., Lindgren, 1933) in drawing a useful analogy between the chemistry of the plume vapor and the observed chemistry of atmospheric pressure fumarolic gases from present-day volcanoes. Such data are notoriously difficult to obtain free from atmospheric contamination, but they do provide some useful guidelines. Volcanic gases are predominantly $\text{H}_2\text{O}-\text{CO}_2-\text{SO}_2$ mixtures, dominated by H_2O and containing small but significant HCl contents (White and Waring, 1963; Gerlach and Nordlie, 1975). In the porphyry ore environments the magmatic steam may contain up to 11 percent CO_2 (Roedder, 1971; Gustafson and Hunt, 1975) and substantial quantities of SO_2 are fixed as sulfate-anhydrite in the core alteration assemblages (Norton, 1972). The porphyry metal suite, i.e., Cu, Mo, Sn, etc., is also found in fumarolic gas precipitates (White and Waring, 1963) although this in itself by no means indicates a juvenile origin for the metals.

The complexity of the ore-forming system and the paucity of volcanic gas data only allow a general

but informative mass balance comparison to be made between the volcanic gas compositions and a hypothetical ore transporting solution, but perhaps significantly the Cu/SO₂ ratio of the gas from Showa-shinzan volcano in Japan is very close to that of the hypothetical ore solution calculated by Norton (1972). Stoiber and Jepsen (1973) attempted the very difficult task of estimating the SO₂ emission from some basaltic and andesitic volcanoes and obtained a range of estimates from 200 to 420 metric tons per day. Anderson (1975) suggested that such high outputs were explicable if the gas were derived by the outgassing of some subsurface magma reservoir—precisely the situation envisaged here for porphyry copper formation. Combining the data of Stoiber and Jepsen with that from Showa-shinzan allows a rough estimate to be made of the time required to form a 50-million-ton copper orebody averaging 0.5 percent copper. At Showa-shinzan the fumarole gas contains 427 ppm SO₂ and 0.03 ppm Cu. At a mean flux of 2.1×10^8 gm SO₂/day⁻¹, 5×10^{11} gm of copper would be transported in about 10⁵ years. Even allowing an order of magnitude error on the raw data, this calculation is in keeping with the volcanic analogy, yielding reasonable time spans for ore formation. Stoiber and Jepsen's SO₂ output data applies to active volcanoes, whereas for porphyry ore systems the ore flux occurs in the waning stages of volcanism. Reported copper contents of fumarole gases may only be distantly related to the original concentration in the deep system and some authors (e.g., Rose, 1970) have considered possible much higher copper concentrations. These would imply correspondingly shorter, but still geologically reasonable, depositional times for orebodies of the size considered above. Thus at 20 ppm dissolved copper the formation time would be around 8×10^3 years for a 100 kg/sec water flux in the plume. The thermal structure of the plume itself requires in excess of 10⁴ years to establish and destroy. The New Zealand geothermal systems have been estimated by a variety of methods to have been in existence for over 10⁵ years.

For a 100-million-ton orebody the formation of the potassic alteration would involve the addition, on a constant volume basis, of around 10^{11} gm H⁺, using the average figure 2.9 gm equivalents per 1,000 cc given by Nielsen (1968) for the Santa Rita deposit. Reestimated entirely as HCl, the figure is 3.7×10^{12} gm. The HCl/SO₂ ratio of the Showa-shinzan gas is about 3, so that the HCl output of a volcano would be 2×10^{15} gm over 10⁴ years; more than adequate to account for the alteration assemblage. Calculations such as these are of course by no means definitive, but at least they show that, at the order of magnitude level, chemical transport models based on

the chemistry of volcanic gases are compatible with field observation.

As is the case with volcanic processes, the chemical and physical model discussed above is only part of the larger scale framework. Solution compositions and mass flux estimates in the present discussion suggest a "source volume" of calc-alkaline magma of the order of 10³ km³ at some depth. For the orthomagmatic model favored by these authors and by Sillitoe (1972, 1973), Lowell (1974), and Nielsen (1976) metal and water transport occurs from the zone of magma generation, a free vapor phase exsolving from the magma during its convective rise toward the surface. During active volcanism exsolved vapor is expelled directly via the magma column to the surface, but when volcanic eruption is dormant, vapor release from a subvolcanic magma reservoir may feed a magmatic vapor plume—which in turn transports metal to the environment of ore formation.

Recently some attention has been focused on the source and role of water in calc-alkaline melt formation with suggestions that the partial melting environment is open with respect to water (Kushiro, 1974). Thus both Fyfe and McBirney (1975) and Best (1975) suggest that water evolved by dehydration reactions in subduction zone sediments and volcanics may migrate upward into the overlying wedge of upper mantle or lithosphere where it may initiate and control melt formation. Such suggestions are speculative but if verified could become extremely powerful as a means to account for the very large quantities of water and metals which are channeled through the crust via active or, indeed, solidified magma conduits into igneous-hydrothermal ore-forming systems.

We cannot see or remotely sense the root zones of present-day geothermal systems. The remains of old geothermal systems—ore deposits—exposed by erosion may prove the only effective means of achieving this. The inference of the model presented here is that porphyry copper-type and epithermal-type ore deposits may be currently forming in the deep levels of the active geothermal systems beyond the present reach of deep drilling. Eventually it may be possible to penetrate to these depths by inclined drilling through the cooler less-corrosive zones of these convection systems. Metal sulfides are found in some currently active systems (e.g., Broadlands, New Zealand; Browne, 1970), but these may offer only a glimpse of possible mineralization at greater depth. In our modeling, the dispersion plume is doped with magma-derived metals, although the water isotope composition will generally be dominated by the ground-water component. Hence at shallower intrusive levels than shown on Figure 9 or in different

permeability regimes, the dispersion plume may extend closer to the surface, its discharge via fracture systems accounting for some epithermal vein-type deposits and for the locally high metal concentrations observed in some hot-spring precipitates. Examples are the Au-Ag-As-Sb precipitates of the Champagne Pool, Waiotapu, and high tungsten precipitates of the Frying Pan Lake, Waimangu, New Zealand (Weissberg, 1969). A related possibility is that such highly differentiated metal suites result from redistribution of primary base metal-dominated porphyry ores during late-stage geothermal activity following plume collapse (Henley and McNabb, in prep.).

Summary

A fluid dynamic model has been derived for the generation of porphyry ore deposits. The salient features of this model are as follows:

(a) Evolution of a low-density "magmatic" vapor phase whose gross composition may be represented by the system $\text{NaCl-H}_2\text{O-CO}_2$. Cu, Mo, S, and other ore components are transported in this gaseous mixture as complex halide-hydroxyl species at temperatures in excess of 500°C . Water and metal components are derived ultimately from the zone of magma generation, reaching the upper crust by transport in a convecting magma column and subsequent exsolution as a free fluid phase.

(b) Forceful or passive emergence of the vapor from the pluton establishing a subvertical buoyant thermal plume in the permeable country rock or the cooled outer shell of the pluton. With cooling during upward flux, saline liquid condenses in the plume until the vapor phase reaches its minimum salinity at the ambient pressure of the system. If the plume penetrates a preexisting ground-water convection system, the magmatic vapor plume retains its discrete character in the axial portion, while entrainment of ground water and dispersion of plume components generates a dispersion plume marginal to and above the core and penetrating higher into the ground-water system.

(c) Metal precipitation occurs in response to decreasing temperature and salinity as well as induced f_{O_2} , pH, $f_{\text{H}_2\text{S}}$ variation within the dispersion plume. Later redistribution of metals (chalcopyrite \rightarrow bornite + pyrite) and inward growth of the phyllic alteration zones may be consequent on collapse of the magmatic vapor plume and the encroachment of the ground-water system.

(d) The plume model appears to satisfy heat transfer constraints when modeled on the basis of the physical parameters (permeability, diffusivity, etc.) which relate to active geothermal systems such as Wairakei, New Zealand.

(e) The individual alteration-mineralization characteristics of any ore deposit may be accounted for by modifying the general chemical-physical implications of the plume model to incorporate different ground-water salinities, depths of emplacement, renewal of magmatism, successive pulses of magmatic vapor, etc.

(f) The hydrothermal environment described by the plume model represents but one stage in the overall sequence of geochemical processes by which metals are concentrated from their source region (subducted oceanic crust, upper mantle peridotite, or heterogeneous lithosphere) via magma and fluid transport into an ore deposit in the upper crust.

(g) The plume model provides an interpretation of the characteristics of the deep zone of active geothermal systems and, with modification, may find application in the genetic interpretation of other families of ore deposit such as epithermal veins and submarine massive sulfides. The magmatic input to such systems is obscured in the upper levels at temperatures less than about 550°C by the predominant entrained ground-water component of the hydrothermal fluid.

Acknowledgments

The critical comments of the following sharpened our thinking and hopefully improved the clarity of the final manuscript: L. B. Gustafson, Jahn Malpas, R. J. Norris, Denis Norton, Edwin Roedder, Richard Sillitoe, David Strong, and the anonymous reviewers of an early version of the manuscript. Correspondence with these workers revealed the great diversity of viewpoints concerning the generation of porphyry ore formation so that the views expressed in this paper are the responsibilities of the authors alone.

R. W. Henley acknowledges financial support from the New Zealand Universities Research Committee and from the National Research Council of Canada (Grant No. A3798). Alex McNabb acknowledges publication permission from the Director, Applied Maths Division, D.S.I.R., Wellington, New Zealand.

J. D. Lowell kindly allowed us to reproduce Figures 1a and b from his work, and permission was kindly granted by the American Journal of Science for the use of the emended Figures 3a and b. We thank Mrs. D. King for diligently drafting the diagrams and all those involved in typing successive versions of this paper.

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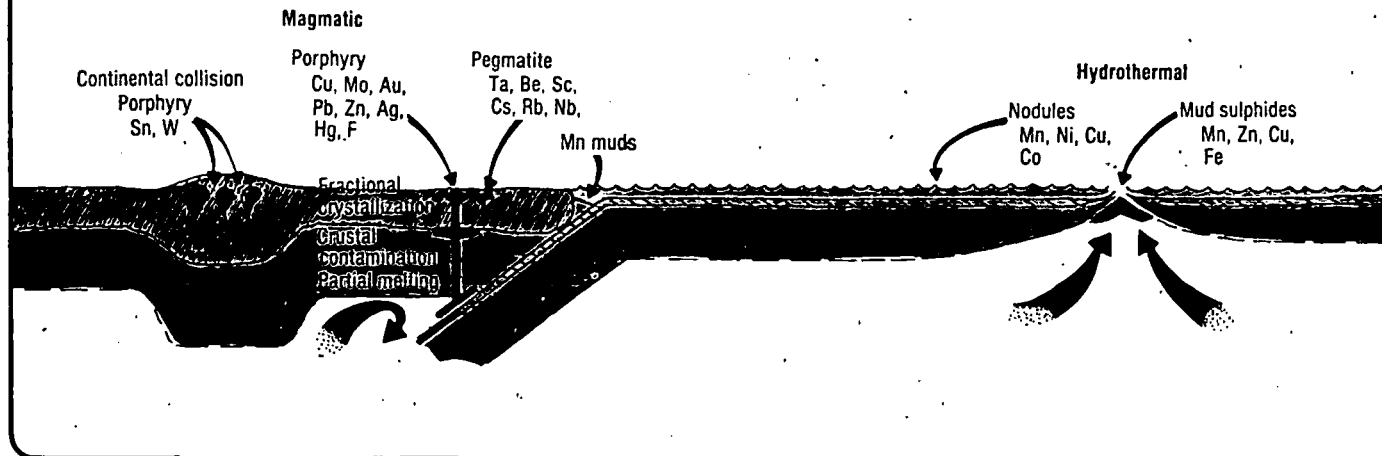
April 28, 1976, March 2, 1977

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Summary sketch of the plate tectonic settings of common ore deposits



ORE DEPOSITS RESEARCH

THE SEARCH FOR CONCEALED OREBODIES IS PROMPTING RESEARCHERS TO LOOK MORE CLOSELY AT THE ENVIRONMENTS IN WHICH ORE DEPOSITION OCCURS

Alvin Lewis, Associate Editor

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The declining frequency of ore deposit discoveries has forced the minerals industry to look deeper into the earth in its search for ore. To do this, the industry is looking to increasingly sophisticated prospecting methods and improved geologic concepts, both of which employ the latest advances in geochemistry and geophysics.

The increasing importance of exploration tools such as groundwater geochemistry and remote sensing are reviewed here, as well as the current thinking about the processes that generate the following types of ore deposits: Mississippi Valley, sedimentary copper and uranium, porphyry copper-gold-moly, porphyry tin-tungsten, and Kuroko-type volcanic massive sulphides. The role of plate tectonics in forming ore deposits is also mentioned.

The developments presented here were discussed at a "Minerals Review for Industry" conference sponsored by the Ore Deposits Research Section of Pennsylvania State University (see box). Held March 16-18, 1981, the meeting was attended by 60 delegates from major mining and exploration firms from the US and Canada.

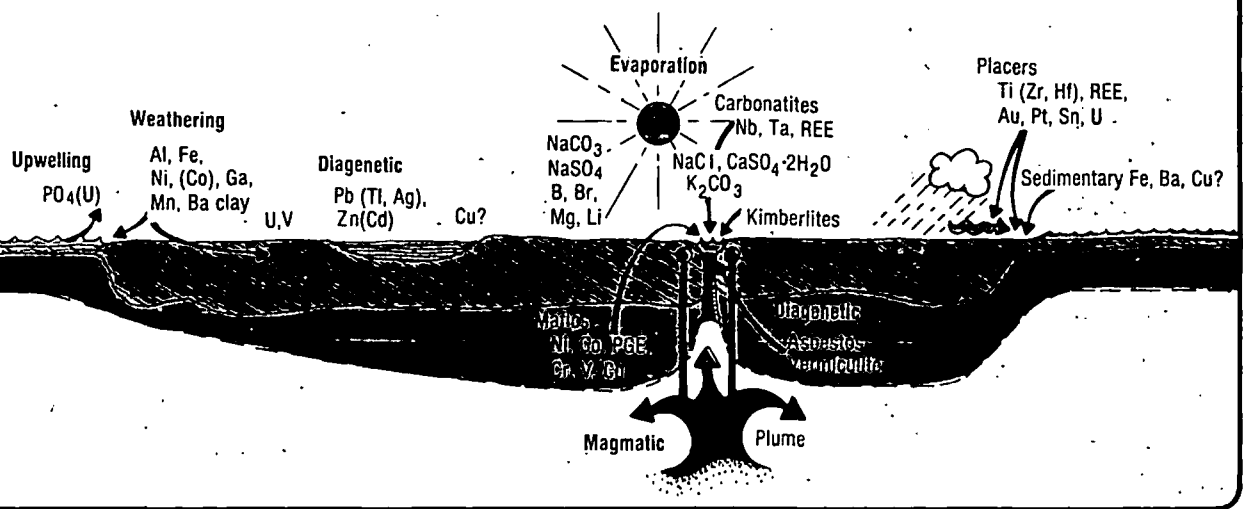
EXPLORATION DEVELOPMENTS

Groundwater geochemistry.¹ As exposed orebodies in accessible regions become exhausted, exploration geologists seek out subsurface deposits that are much more difficult to detect. Advances in detecting these hidden orebodies lie largely in the future developments in groundwater geochemistry—a discipline involving the inspection of anomalous signals from concealed orebodies.

Groundwaters may circulate through a concealed orebody, where they can pick up anomalous values of certain metal species. These waters can then be sampled by wells, seepages, streams, or vegetation.

The intensity and extent of a groundwater anomaly is determined by the volume of fluid flow through the deposit, the solubility of the ore, the precipitation and adsorption of metals along the flow path, and the dilution of the groundwater by other constituents.

Thermodynamic and solubility data of relevant minerals and of aqueous species can be used to make solubility estimates. Computer programs, such as Penn State's "SOLUPLOT" program, can help to analyze a wealth of possible chemical reactions (up to 5,000 simultaneous equations) and draw the corresponding Eh-pH diagram, showing the solid and dissolved species, respectively (Fig. 1). Small changes in the concentrations and elements considered can



Courtesy of L. M. Cathles

give interesting insights into new stability fields for minerals and complexes. For example, if a small amount of phosphorous is added to the Eh-pH relations for lead, a large stability field for pyromorphite develops (Fig. 1). Pyromorphite is very insoluble, and its presence may explain lead's well-known immobility in many environments. Researchers have not yet looked into this specific problem, but the value of perfecting the "SOLUPLLOT" program is obvious.

Another interesting concept illuminated by the program dealt with the use of arsenic as a pathfinder in gold exploration. These two elements are frequently associated with each other, and one would expect to see arsenic mobilized in groundwaters as a gold deposit weathers. But, if there is any goethite in the subsurface, arsenic will be adsorbed over a wide range of conditions and may not show up as an anomaly in the groundwater analysis.

The "saturation index" is another future direction in groundwater exploration. This measurement, recently applied to exploration for uranium, gives a better definition to the groundwater anomaly by accounting for the interrelationships of the concentrations of various species in solution.

A computer analyzes the data and then plots the extent of the saturation of waters with various minerals.

A possible complication in groundwater studies is adsorption and complexing. For instance, uranium is known to adsorb on iron oxides in neutral to basic solutions. In the presence of air and CO₂, however, uranium is complexed in basic solutions and is not adsorbed. Because of this, uranium deposits may be formed in arid carbonate regions with basic groundwaters.

Metastable sulphur species, such as sulphite, thiosulphate, and polysulphide, may play a major role in groundwater geochemical exploration of the future. These species have been shown to be anomalously high in groundwater flow from some uranium and Mississippi Valley lead-zinc deposits. Originating from the dissolution and oxidation of various sulphides, these species may possibly be used to distinguish the sulphur species of interest (those derived from the oxidation of sulphides) from the unimportant sulphate species (those derived from evaporites).

Knowledge of the background values for various metals in groundwaters can assist in recognizing anomalies. In order to

Penn State's Ore Deposits Research Section seeks to improve communications with the minerals industry

The ore deposit and exploration concepts described in this story were based on a Penn State University conference entitled "Minerals Research Review for Industry." The Research Section, an institute of the university's College of Earth and Mineral Sciences, plans to hold these reviews annually as part of a drive to increase its interaction with the minerals industry.

In the coming years, federal allocations to universities and their research programs will be drastically cut, and mineral departments in several institutions are looking to the private sector to secure funding. Funding for graduate programs by the minerals industry would be of mutual benefit, as research areas common to both parties would be explored.

Penn State's plan is to seek industrial assistance to support a graduate-level project of interest to the sponsoring company as well as to the university's Research

Section. In return for its support, the sponsor would obtain research results on a confidential basis for an agreed-upon period of time before possible publication. The company would be able to enjoy preferential consulting privileges by faculty members involved in the project. The college is equipped with an impressive variety of up-to-date analytical facilities, which would be used to gather data for the studies.

About 60% of the geological science graduates from schools such as Penn State will seek professional careers in industry. To counter a tightening-up of government spending in the coming years, universities are hoping that the private sector will help to pick up some of the tab to train graduate students and to maintain high standards at academic research facilities. Address any inquiries to H.L. Barnes, Chairman, Ore Deposits Research Section, Penn State University, University Park, Pa. 16802.

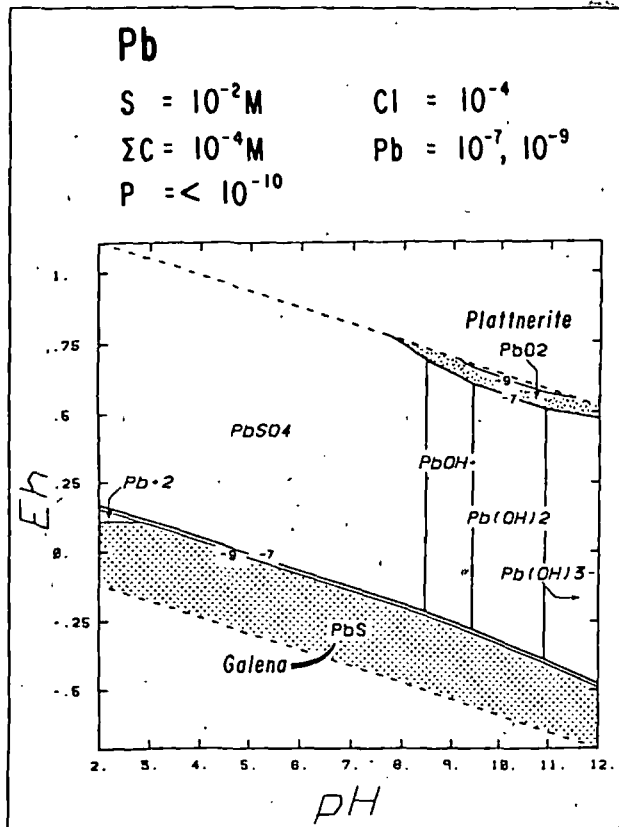
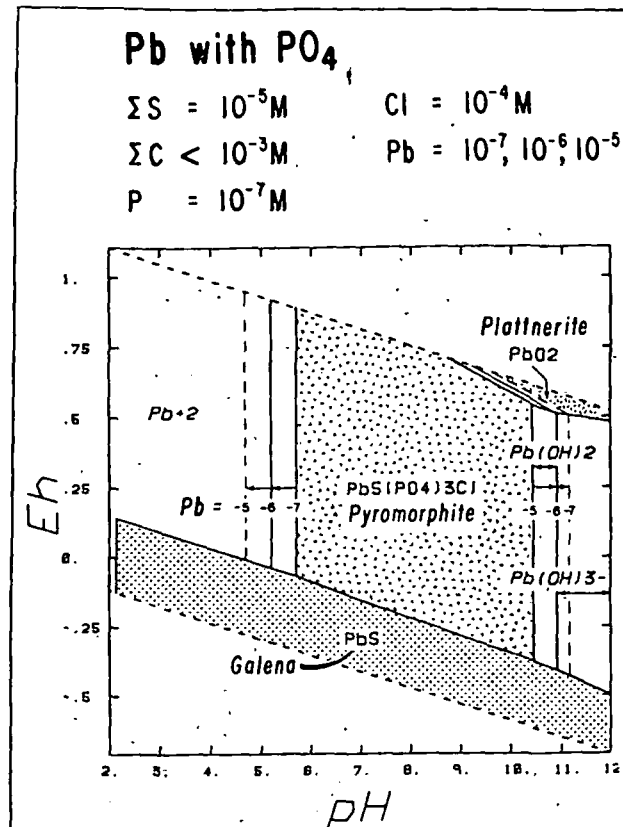


Fig. 1—Eh vs. pH diagram for lead as computed by Penn State's "SOLU-PLOT" program. Note that a small amount of phosphorous (above right)



results in a large pyromorphite stability field, which may explain lead's well-known immobility in many environments.

decrease scatter, metal values, as functions of either specific conductivity or total dissolved solids, are being researched. Factor analysis is also being used to try to sort out sources of variability.

Groundwater technicians should be advised to watch out for sampling errors and contamination in their studies. For example, tests show that before a water sample is taken from a well, the water should be flushed for a good 30 min to eliminate zinc contamination from pipes and galvanized storage tanks. Landowners may not be too enthusiastic about this procedure, especially in arid regions, but it is necessary in order to get a representative sample of the zinc content of the groundwater.

Remote sensing.² Remote sensing refers to the gathering of information at a distance (Fig. 2). The technique combines photogeologic and spectral information and has been shown to be useful in deciphering morphology, structure, and lithology. Remote sensing has the potential for being a useful tool for mineral exploration, but it should not be considered an end in itself.

Massaged and contrast-enhanced data taken over the mineralized East Tintic district in Utah demonstrated the ability of the technique to discriminate quartz-lattice, quartz-monzonite, and hydrothermal and argillically altered rocks. General rock-type separations and identification of alteration zones have been successful in the Silver Bell and Safford porphyry copper districts. Remote sensing is now finding its way into uranium exploration in the Colorado Plateau and in oil-field basin evaluations.

A comprehensive summary of the technique, including data acquisition and processing methods, interpretation of

*Goetz, F. H., and Lawrence C. Rowan, SCIENCE, 1981, pp 781-791.

Fig. 2—Special features of the "Multispectral Resource Sampler," designed by NASA for the remote sensing of the Earth's resources.

regional structural features, and lithologic information, was recently published in SCIENCE.*

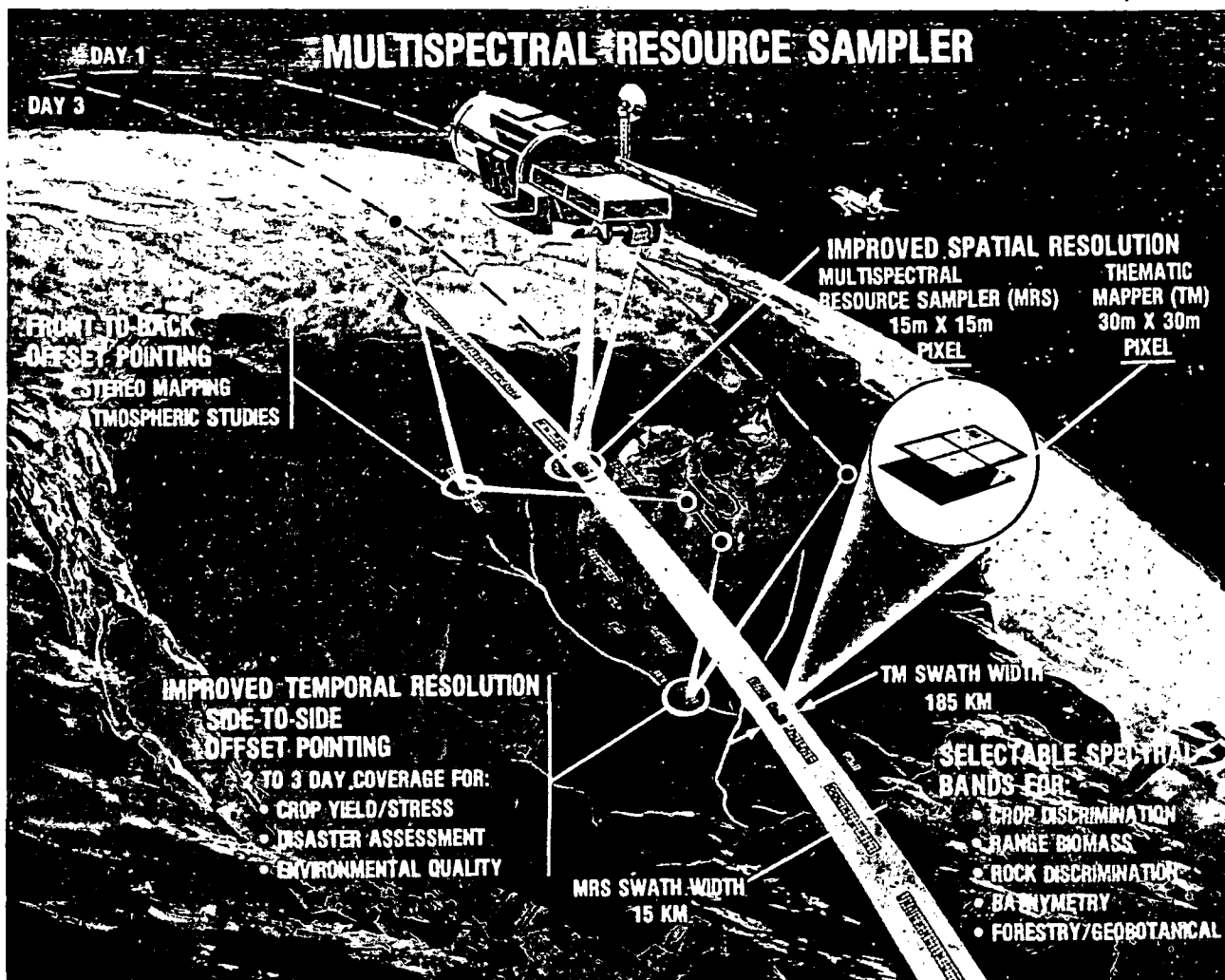
Future trends in remote sensing include the development of a new generation of equipment for Landsat: a narrow-wave band-pass system at 2.2 μm in the infrared with improved detection capabilities, pointing systems for stereo coverage, and the development of heat-capacity mapping systems. Progress in correlating spectral absorption anomalies to specific minerals, rock-types, and geobotanical anomalies is critical to remote sensing's future role in mineral exploration.

FINDING SPECIFIC DEPOSIT TYPES

Mississippi Valley-type deposits.³ These deposits account for the majority of the world's reserves of lead and zinc. Examples of some of the major districts include southeast Missouri, central Tennessee, southwest Wisconsin, and the southern Illinois Fluorite districts in the US; Bleiberg in Austria; Laisvaal in Sweden; Raibl in Italy; Mirgalimsai in the southern Kazakhstan region of the USSR; and the Pine Point district in the Northwest Territories of Canada.

Geologists now believe that they have established a framework within which they can begin to understand Mississippi Valley-type deposits. The research goal today is to try to improve the genetic models. Some major points of contention still remain, mostly centered around the types of complexing agents that are capable of transporting metals in the ore-forming fluids.

Mississippi Valley deposits are genetically related to mio-



geosynclines, and the key processes that are currently thought to be responsible for generating them are described here. The first stage is the filling in of a basin with a mixture of carbonate, evaporite, clay, sand, and silty sediments. The importance of evaporitic material has been known for some time, but researchers have only recently begun to realize the critical role that the organic contents of the sediment play.

During deposition, sediment loading and thermal contraction cause the basement under the basin to subside. The earlier-deposited sediments begin to transform from hydrostatic to lithostatic conditions at depths of approximately 3-5 km. The drastic loss of sediment porosity, as much as 50% at these depths, is accompanied by the squeezing-out of a tremendous volume of pore fluids. These fluids will eventually act as the transporting medium for the trace metals deposited in the ore zone.

Both temperature and the geothermal gradient (in °C/km) of the basin increase with depth. Fluid inclusion data from Mississippi Valley-type ores reveal that temperatures $\geq 150^{\circ}\text{C}$ are necessary for ore deposition. Oil field data from the Gulf Coastal sediments indicate that these temperatures are obtained at sediment depths of about 3 km. Data from the Gulf Coast are used to formulate Mississippi Valley-type models because the area has been thoroughly drilled and studied for its petroleum potential.

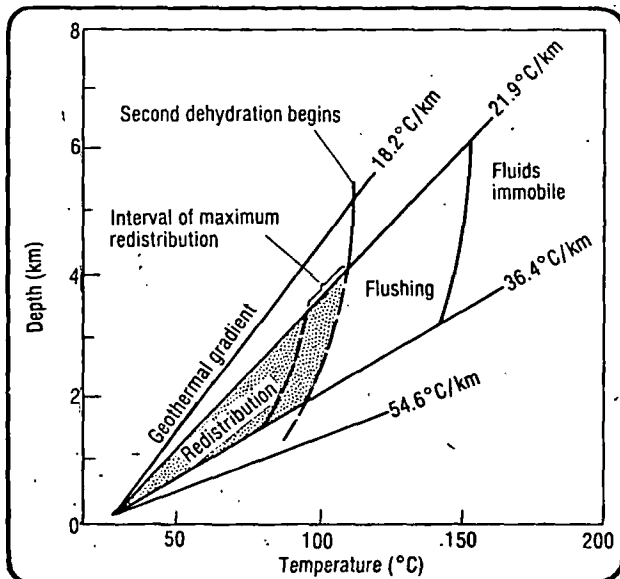
Sediment loading studies in the Gulf Coast and on Sable Island off the coast of Nova Scotia bracket a maximum time interval of 40-80 million yr to achieve the needed 3 km of depth. At this time, water will begin to be expelled from the

basin. Fig. 3 illustrates the depth-temperature relations in regard to dewatering the basin. Most of the water is lost in the "zone of flushing," where the water content is believed to drop to 10% by volume. Only the higher-temperature part of this zone and the "fluids immobile zone," where there is a slower release of water with time, have temperatures adequate enough to generate Mississippi Valley-type ore deposits of interest.

Similar depth-temperature conditions prevail in other young basins of the world. For example, the average geothermal gradient in the young Pannonian Basin of Hungary intersects the 150°C contour at 3 km.

The pathways that enable the basin to dewater are thought to be along permeable basal sands or along growth faults, the latter commonly developing during basinal subsidence. Seismic sections in the Gulf Coast off Texas, as well as in the oil fields of Alberta, Canada, and in the North Sea reveal that growth faults are common at a depth of 3 km. Oil companies routinely discover such structures while searching for new petroleum deposits.

Mississippi Valley-type deposits can be subdivided into three systems, categorized according to structural setting: 1) The ore-forming fluids may migrate up growth faults and deposit metals on the basin floor. Examples of these syngenetic and bedded "basinal" sulphide deposits are found in Bleiberg, Austria, and in Mirgalimsai, USSR; 2) The fluids follow aquifers through the craton, where they are deposited after encountering cooler groundwaters. Examples of these "cratonal types" are the 5,000-mi² mineral district of south-



Modified from Burst (1969), Am. Assoc. Petrol. Geol. Bull., Vol. 53, p 91.

Fig. 3—Temperature vs. depth relations in the dewatering of a basin.

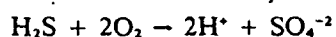
western Wisconsin and the Laisvaal, Sweden, lead-zinc deposits; 3) The most common sites of deposition are above growth faults in "hinge zones," especially reefs, or gravity-faulted areas. The central Tennessee and southeast Missouri districts, Pine Point in the Northwest Territories of Canada, Mezica in Yugoslavia, and Raibl in Italy are examples.

After the fluid is generated from the basin, its chemistry must be such that it can transport metals in the aqueous phase, and precipitate them at some later place and time to form the deposit. Based on fluid inclusion analysis, basin analysis, and thermodynamic calculations, the composition of the transporting fluids is on the order of 2-3 molal NaCl, 0.0X molal SO_4^{-2} , 20 per mil $\delta^{34}\text{S}$, neutral or slightly alkaline pH, and they contain approximate trace metal concentrations as follows: X,000 ppm Fe; X00 ppm Zn, Pb; X ppm Ni, Co, Ag, Hg; and 0.X ppm Cu. It is interesting to note that the $\delta^{34}\text{S}$ and pH values are similar to or match those of seawater.

In carbonate host-rock environments, the neutral to slightly alkaline fluids must undergo a drastic pH change to dissolve enough carbonate rock at the "Y-structure." Solution breccias that have been in-filled with contemporaneous sulphides are observed and must be explained by the influx of acidic solutions. The oxidation of sulphide in solution could be the reaction by which the required acidic solutions are generated. An electrochemical reaction between the brine plume and groundwater has been proposed to achieve the acidic solutions, where oxygen is extracted from the water to oxidize sulphide to sulphate as follows:



It would be difficult for the groundwaters, which contain only a few ppm of oxygen, to oxidize aqueous sulphides and to decrease the pH significantly. If there is an excess of oxygen from the hydrolysis of water, the pH of the solution will be lowered by the release of H^+ by the following equation:



The metals in solution that are complexed by bisulphides

or organics will, upon oxidation, precipitate as metal sulphides according to the following reaction:



This reaction also produces acid and is a contributing factor in the digestion of the carbonate-bearing host rocks at the deposit.

In Laisvaal, Sweden, ore deposition occurs within a sandstone host rock instead of the carbonate hosts just described. This indicates that deposition need not be caused by reaction with the host rock, but by the oxidation of the hydrothermal solution as:



A problem revealed by experimental work is that neither chloride nor bisulphide complexing is adequate to transport the quantities of lead or iron that are found in Mississippi Valley lead-zinc environments. Research is now turning to the possible role of organics (i.e., mercaptans, etc.) in complexing significant quantities of the metals found in these ores. The basis for suggesting organic complexing is that the lead content of oil field brines is fairly high, higher than can be explained by inorganic complexing. Zinc complexing by inorganics may be barely adequate to form a good deposit, but organic complexing may be important in transporting zinc, too. Answers to the chemical problems of metal transport in these environments should be found in the near future.

Sedimentary copper deposits.⁴ Sedimentary copper deposits contain approximately 30% of the world's copper reserves. Well-known deposits are located in Zambia, Zaire, the Kupferschiefer in Europe, Adalaidan in Australia, and the Belt and White Pine districts in the US.

Some of these deposits have very high concentrations of other metals. For example, the Zambian copper deposits contain about 60% of the world's cobalt reserves. Silver, lead, nickel, and uranium are other common accessory metals.

Sedimentary copper deposits can occur in shales, carbonates, and sandstones. Several features common to most of these deposits are worthy of mention: 1) the deposits are stratiform or stratabound; 2) they are often found at the margins of basins where sediments are deposited rapidly; 3) transgressions of marine sediments overlie continental sediments at the larger deposits; 4) biogenic sulphur and evaporites are common; 5) there is no evidence of contemporaneous igneous activity, although some deposits are located in rift environments (i.e., White Pine); 6) the larger deposits are common in the late Proterozoic era.

Nearly all sedimentary copper deposits are associated with hematitic red beds, although the ore is located in the pyritic-organic reducing horizon. Vertical and lateral mineralogical zoning, from hematite-copper-chalcocite-bornite-chalcopyrite-galena-sphalerite-pyrite, is common.

Fluid inclusion and mineralogical studies bracket the depositional temperatures at 25-100°C. The Eh-pH relations for copper at 25°C indicate that significant amounts of copper cannot be dissolved by ordinary groundwaters or river waters (Fig. 4a). But copper solubility increases dramatically in chloride systems, such as with seawaters (Fig. 4b). A cuprous chloride complex, CuCl_2^- or CuCl_3^{-2} , opens up in Eh-pH space and is capable of dissolving and transporting significant amounts of copper in the aqueous phase at 25°C. The cuprous chloride complex permits the dissolution of copper in neutral waters where the Eh is intermediate in value.

The implications of the above for sedimentary copper

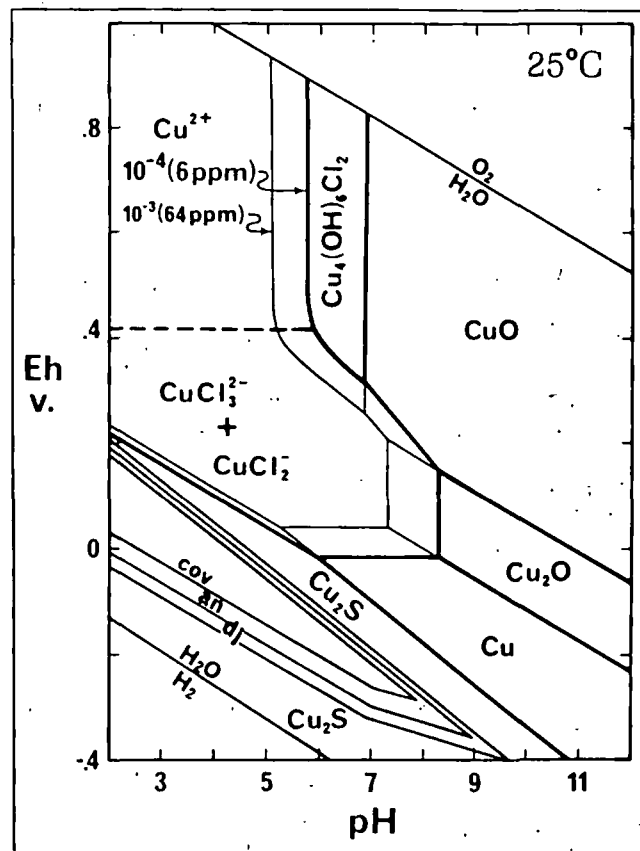
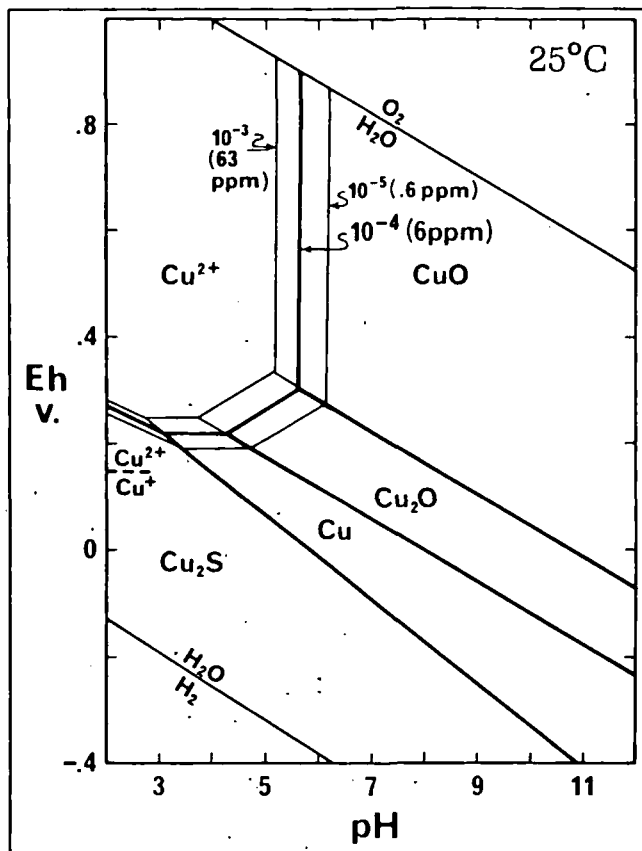


Fig. 4—The Eh vs. pH relations for copper at 25°C without chloride (4a) and with chloride (4b).

deposits are that when red beds are contacted with brine solutions, copper will be leached out and accumulated in a fluid phase. The metals will be rapidly deposited if the fluids enter a reducing environment.

At White Pine, the Nonesuch shale is the host of ore mineralization, and it overlies the Copper Harbor red bed conglomerate. Various geologic models have been proposed for introducing and moving brines through the conglomerate, leaching its copper contents, and precipitating ore from the fluids in the reducing Nonesuch shale.

In Europe, the poorly consolidated Kupferschiefer member is sandwiched between underlying red beds and overlying limestones and evaporites. Models have been proposed to circulate marine waters down and into the red beds, where they can pick up metals, and then have them come up into the Kupferschiefer, where the metals are deposited.

Sedimentary uranium deposits.⁴ These deposits appear to be derived from the leaching of relatively enriched source rocks and subsequent transport to the sedimentary basin. Possible source rocks from which significant quantities of uranium can be extracted are arkoses, tuffs, and granitic rocks.

One of the main areas of sedimentary uranium research today is the interpretation of U/Th relationships. Uranium is soluble in various environments, but thorium, a common associate in fresh igneous source rocks, is highly insoluble and remains behind. Somewhere downstream, the uranium may precipitate in the aquifer. The leaching of uranium from source rocks, and its eventual precipitation, can be detected by changes in U/Th.

The uranium content of the source area can be approximated by the analysis of uranium in its zircons. For example,

when a uranium-rich alkali granite is eroded, the highly physio-chemically resistant detrital zircons will retain their anomalous uranium values. Given clues from zircon analysis, the exploration geologist can use other reconnaissance techniques to pursue the anomaly.

Diagenetic sulphide formation.⁵ Ore deposits that are related to the diagenetic environment include the Mississippi Valley and Black Shale types. Examples of the Black Shale types are White Pine (replacement type) and the Kupferschiefer (syngenetic type) deposits.

The factors that seem to control the amount of sulphide precipitation in these environments include: 1) the availability of dissolved sulphate, 2) the rate of sulphate reduction, 3) the concentration and reactivity of iron compounds, 4) the sedimentation rate, 5) the amount of decomposable organic matter, and 6) bioturbation. The last two are limiting factors.

Marine sedimentary pyrite commonly occurs with several hundred to several thousand ppm of copper, nickel, cobalt, lead, and molybdenum. Nearly all of the moly and 50% of the copper in the Black Sea deposits occur in the pyrite.

The pyrite is thought to form by the following process: After photosynthesis at the surface of the ocean, a trickle (<0.10%) of the oceanic organic matter is buried on the sea floor. This material decomposes and oxidizes in the sedimentary column and quickly uses up the available oxygen and nitrate. Anoxic bacteria act to reduce sulphate and oxidize the organic matter to produce sulphides. The sulphides can reduce iron to its ferrous state, enabling it to react to produce fine-grained black iron sulphide as mackinawite $(Fe,Ni)_{1.1}S$ and greigite (Fe_3S_4) . Finally, zero-valent sulphur from the

oxidation of sulphide and from the reduction of iron can react with the black FeS to form pyrite.

In a bioturbated sediment, sulphur is introduced to the pore water by the following:

$$\Sigma S = \frac{32}{24} \frac{kN_o}{\alpha w} [1 - e^{-\alpha L}]$$

where N_o = decomposable organic carbon in wt %
 k = sulphate reduction rate constant in yr^{-1}
 w = sedimentation rate in cm/yr
 L = depth of bioturbation zone in cm
 α = $[(w^2 + 4kD_B)^{1/2} - w] / 2D_B$
 D_B = biodiffusion coefficient in cm^2/yr

The equation above shows that more sulphur can be introduced to the system by increasing the amount of decomposable organic matter, the sulphate reduction constant, and the biodiffusion coefficient.

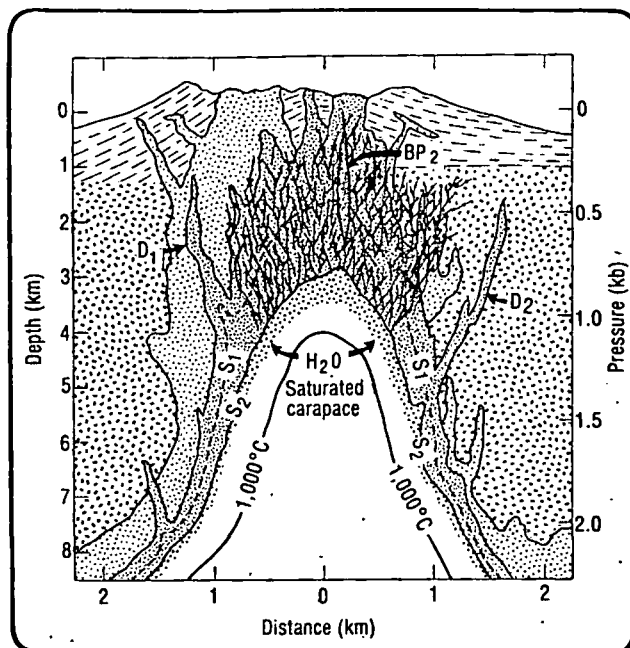
The relationship is simpler for a non-bioturbated sediment, where the amount of total sulphur is solely proportional to N_o , the amount of decomposable organic carbon. Finally, if sulphate is depleted in the pore waters, the sulphur content of the sediment will be dependent on the concentration of sulphate in the overlying water.

These relationships suggest that explorationists looking for diagenetic sulphides should concentrate their searches in near-shore environments containing high levels of organic carbon and the life forms necessary to stir up the sediment-water interface. Inland sea areas of high heat flow, such as the Gulf of California, are favorable environments for later replacement of diagenetic sulphides.

Porphyry type deposits.⁶ Porphyry deposits are related to intrusive igneous bodies, and mineralization is usually disseminated in and adjacent to the igneous body. Such deposits can be enriched in copper-molybdenum (e.g., Santa Rita, Bingham, Climax), copper-gold (e.g., Panguna, Bougainville), tungsten (e.g., Yangchuling, China), and tin (e.g., Bolivia).

All porphyry-type deposits have several features in common: 1) They are all associated with felsic plutons, 2) they have extensive systems of steeply dipping fractures concentrated on the apical parts of the pluton as well as in the adjacent wall rocks, 3) the hydrothermal alteration assemblages in their fracture systems are distributed centro-symmetrically, 4) the alteration halos are commonly zoned from potassic to phyllic (or sericitic) and then to propylitic, from the core to the margins, respectively, and 5) the primary ore minerals are also centro-symmetrically distributed in the fracture system, roughly coinciding with the alteration halo. For example, in porphyry Cu-Mo systems, the potassic core zone is Mo-rich, the transition zone is Cu-rich, and pyrite increases near the margins.

It is now pretty well accepted that the composition of the magma source rocks and the environment of magmatic emplacement are the critical factors that determine the type of mineralization in the porphyry system. It has been proposed that the so-called "I-type magmas," which are thought to be derived by the partial melting of pre-existing igneous rocks or arkoses, produce the granodioritic and quartz monzonitic plutons, which are associated with Cu-Au and some of the Cu-Mo porphyries. The "S-type magmas," which are thought to be derived by the partial melting of muscovite-bearing metasediments, are believed to produce the felsic-alkalic peraluminous porphyries, which are associated with tin-tungsten mineralization.



From "Geochemistry of Hydrothermal Ore Deposits," H. L. Barnes, ed., 2nd edition, John Wiley & Sons, 1979, p 111.

Fig. 5—Schematic cross-section through a hypothetical granodioritic porphyry stock, showing the minimum temperature at a given pressure where silicate melts can exist at initial stages of porphyry copper development.

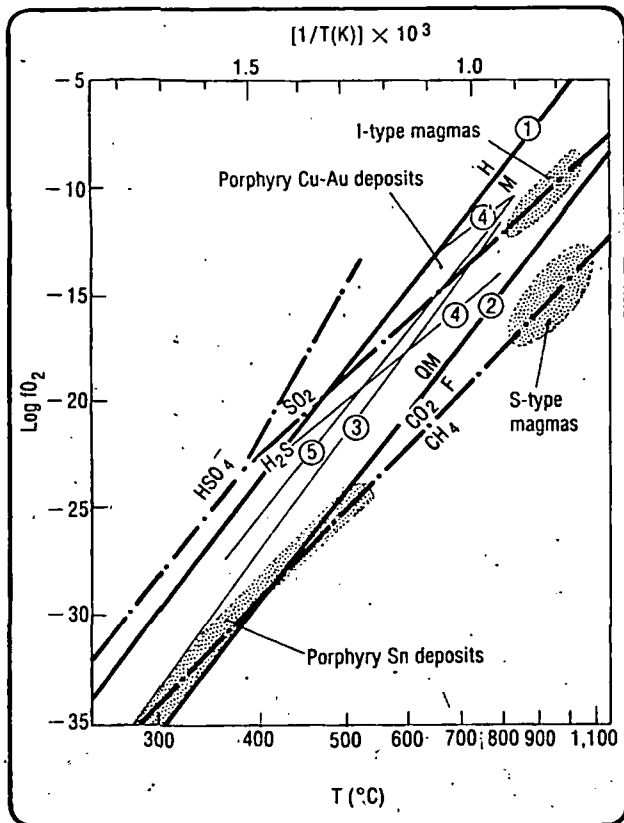
Given the magma types above, there are several major constraints in the magmatic system that will determine the degree of mineralization within a porphyry system. The most important constraint is the water content of the magma. The T-H₂O relations of magmas associated with porphyry systems govern such variables as the depth of emplacement, extent of fracturing, concentrations of metals of interest in the melt, mineralogy, texture, water saturation in different parts of the pluton, the occurrence of a "second boiling," etc., and are unique for the different types of source rocks melted. These relationships are too detailed for this review, but interested readers are referred to *Geochemistry of Hydrothermal Ore Deposits*,* 2nd edition.

Here, it is sufficient to say that the water content of the magma must be high enough to produce extensive fracturing at a depth of 1-6 km but low enough to keep the magma temperature at levels sufficient for emplacement at <5 km (Fig. 5).

The metal content of the magma is inversely proportional to the degree of source rock melting and is therefore related to the T-P_{H₂O}-depth relations. At the onset of partial melting, the concentration ratio of metals in the melt to the source rocks is high but decreases as melting progresses. Experimental work has shown that melting only 20% of an average mafic-basaltic amphibolite containing 80 ppm copper would produce a melt with approximately 400 ppm copper. This is why some experimenters maintain that there is no problem in obtaining a copper-rich magma from an average mafic-basaltic amphibolite.

The metal content of the aqueous phase that separates from the magma in the water-saturated carapace is strongly dependent upon the partition coefficient between the fluid and the melt. With the notable exception of molybdenum and tungsten, the metals of concern form neutral chloride complexes under these conditions, so their partition coefficients are functions of chloride concentrations of the fluids. Molybdenum and tungsten, which do not form chloride complexes, are thought to form stable molybdic and tungstic

*Barnes, H. L., editor, Chapter 3, John Wiley and Sons, 1979.



From Burnham and Ohmoto (1980), *Mining Geology (Japan) Special Issue, No. 8*, pp 1-11.

Fig. 6—Oxygen fugacity vs. temperature relations for the predominant sulphur and carbon species in aqueous fluids, with the approximate fields for porphyry copper-gold and porphyry tin mineralization.

acids in magmatic aqueous fluids.

The sulphur partition coefficient must be high enough to form sulphides, and it is strongly dependent upon the oxidation state (fO_2) of the magma. When the fO_2 is low, the dominant sulphur species is H_2S , which is soluble in the melt and tends to precipitate sulphides upon crystallization of the magma. But at higher fO_2 values, SO_2 , which is insoluble in the melt, becomes the dominant sulphur species, making it possible for hydrothermal fluids to transport large quantities of metals and sulphur. Precipitation of sulphides from these fluids is promoted by hydrolysis of the SO_2 at lower temperatures. The higher magmatic fO_2 conditions are thought to be responsible for generating the high-sulphur copper porphyries.

Hydrothermal tin and tungsten deposits.⁷ The granitic rocks containing tin and tungsten mineralization have distinctly different geochemical characteristics from those holding copper and moly values. Some of these characteristics (i.e., trace-element and isotopic composition) can be used as an exploration tool for these deposits.

The major mineralogical feature of the tin-tungsten "S-type" granites is the presence of muscovite and ilmenite, rather than the hornblende, sphene, and magnetite assemblages common to the copper-moly "I-type" granites. These minerals, and the lower ferric/ferrous ratio for these plutons, can be used as an exploration tool. The oxygen and sulphur isotopic compositions are significantly different and can also be used in exploration.

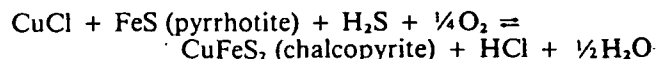
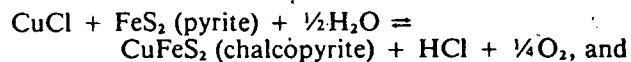
Solubilities of important copper, moly, tungsten, and tin minerals are studied to understand the transport and precipitation processes necessary to form a major mineral deposit.

The mineral solubilities of interest are strongly dependent upon the fO_2 of the ore-forming fluids. Oxidized fluids are more favorable for transporting copper, moly, and gold, while more reducing fluids can transport tin and tungsten (Fig. 6).

Tungsten solubility is likely to be controlled by:



Copper transport is however, likely to be controlled by fO_2 as in the following equations:



$\log fO_2$ - T (Fig. 6) and $\log fO_2$ - $\log \Sigma S$ plots can be drawn to show the chemical and mineralogical differences between these ore deposit types.

The solubility of cassiterite has been shown to increase as fO_2 decreases. It may be that tin is transported in its more reduced +2 oxidation state rather than as +4, possibly by chloride complexing.

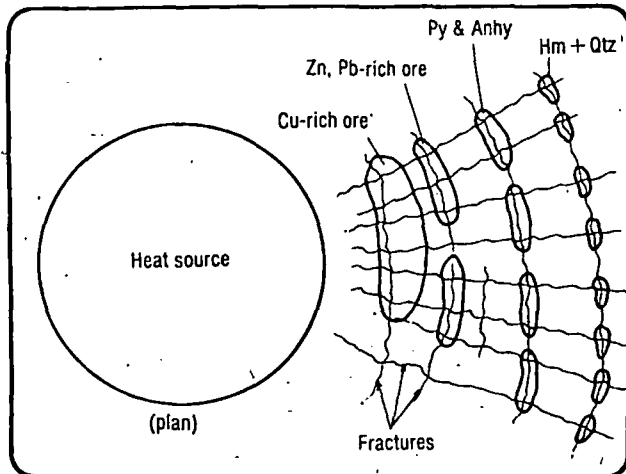
The differences between tin-tungsten and copper-moly-gold porphyry systems are thought to be the result of melting different source materials, rather than a function of differential crystallization. The melting of carbonaceous sediments, such as shales and schists, is believed to form the tin-types. Metavolcanics are believed to be the source for copper porphyries, and the molybdenum and tungsten porphyries are believed to be intermediates. Of the intermediates, the tungsten-bearing magmas have a greater contribution from the melting of carbonaceous sediments.

Kuroko-type volcanogenic massive sulphides.⁸ Volcanogenic massive sulphides contain high grades of copper, lead, and zinc, with significant quantities of gold and silver. They can be associated with basaltic volcanism (as in the Red Sea, East Pacific Rise, and Cyprus), andesitic volcanism (as in Raul, Peru), or felsic volcanism (as in the Archean deposits at Timmins and Noranda, and the Kuroko deposits of the Hokuroko district of Japan). Other Kuroko-type deposits occur in Bathurst, N.B., Mt. Lyell and Rosebury in Tasmania, and Broken Hill in New South Wales, Australia.

Favorable settings for Kuroko ores include deep-sea and extensionally tectonic environments with volcanics and caldera structures. Gravity and magnetic surveys can help to define these areas. Some of the more important characteristics of Kuroko-type deposits are summarized in Table 1.

An extensional tectonic setting is revealed by evidence of rapid subsidence accompanied by numerous high-angle faults and grabens, which occurred prior to volcanism. Mineralization temperatures in the range of 150-350°C are indicative of a strong heat source, probably capable of powering fluid circulation systems.

A current view of the ore-forming process suggests the leaching of metals by interacting hot seawater with large quantities of fractured country rock, and then convecting the ore-forming hydrothermal solutions back up to the sea floor, where they are quenched and deposit the ore. Oxygen isotopic data support the role of seawater, and lead isotopic data suggest that copper is leached from basalts and basement rocks, and that lead and zinc are derived from felsic volcanics and sediments.



Courtesy of H. Ohmoto.

Fig. 7—Plan view of mineralogically zoned assemblages in Kuroko-type deposits, showing that the higher-temperature "yellow ore" (chalcopyrite) and lower-temperature "black ore" (sphalerite & galena) distributions are governed by the distances of ore-forming fluids from the heat source.

Table 1—Some important characteristics of Kuroko-type volcanogenic massive sulphide deposits

- 1) Association with marine sediments and submarine volcanism.
- 2) Geometry and configuration:
Stockwork vs. massive ores
Stratabound, lenses, beds
- 3) Formation of massive ores on the sea floor (syngenetic) with sedimentary textures.
- 4) High temperature of mineralization (150-350°C).
- 5) Zoning of the ores and alteration assemblages.
- 6) Restriction in time with one major mineralization epoch within a volcanic belt:
All ores formed within several million years over a 100 x 1,000-km area
All ores formed within 1 million years over a 50 x 50-km area
- 7) Non-uniform spatial distribution of ore deposits:
Several major ore districts occur within a volcanic belt
The ore clusters within the district are spaced 5-15 km apart
- 8) Association with "basin" (caldera?) structures.
- 9) Ore occurrences on lineaments (basement fractures).
- 10) Prior to the onset of active submarine volcanism, the area subsided rapidly and developed grabens and high-angle normal faults (i.e., extensional tectonics).
- 11) Ore mineralization took place during waning stages of an explosive and felsic volcanism which created calderas of 5-20 km dia.
- 12) Ores are often associated with small (approx. 200-m) dacite lava domes.
- 13) Ores are often overlain by basalt flows.
- 14) Bimodal volcanism and several episodes of resurgent caldera activity continued.
- 15) The area gradually uplifted.

The characteristic single-mineralization epoch that produced the zoned assemblages, in conjunction with fluid inclusion studies, provide information about the temperature gradients within the fluid system. The "yellow" chalcopyrite ore was deposited by higher-temperature fluids than the "black" sphalerite and galena ore. These relationships are thought to reflect the distance of the ore-forming fluids from the heat source (Fig. 7).

Mineralogical and geochemical halos in Kuroko ores are critically important to explorationists. From the ore zone to the periphery, the alteration mineral assemblages go from a sericitic and chloritized zone to a montmorillonitic zone, and then to a zeolitic zone. In the latter two zones, characteristic minerals go from calcic- to sodic-rich toward the periphery. Other zoning features are the increasing K_2O values and decreasing Na_2O , CaO , Sr , $\delta^{18}O_{wrr}$, and magnetic susceptibility values toward the ore zone.

The $\delta^{18}O$ chemistry is proving to be an extremely important exploration tool. The $\delta^{18}O$ values correlate with alteration zoning and have a unique advantage in that they are unlikely to be disturbed by regional metamorphism. Mineralogic assemblages, on the other hand, can be modified by metamorphism.

PLATE TECTONIC INFLUENCE

In porphyry systems, the type of rock melted and the environment of magmatic emplacement govern the chemistry of mineralization. For volcanogenic massive sulphide systems, a heat source may drive a fluid convection system and concentrate metals hydrothermally. In diagenetic sedimentary uranium, copper, and Mississippi Valley-type deposits, the sedimentation processes and subsequent squeezing-out of pore solutions from a basin seem to be responsible for concentrating the metals. Only in the last 15 years or so have these ore-forming processes been considered in terms of the global dynamic concepts of plate tectonic theory.

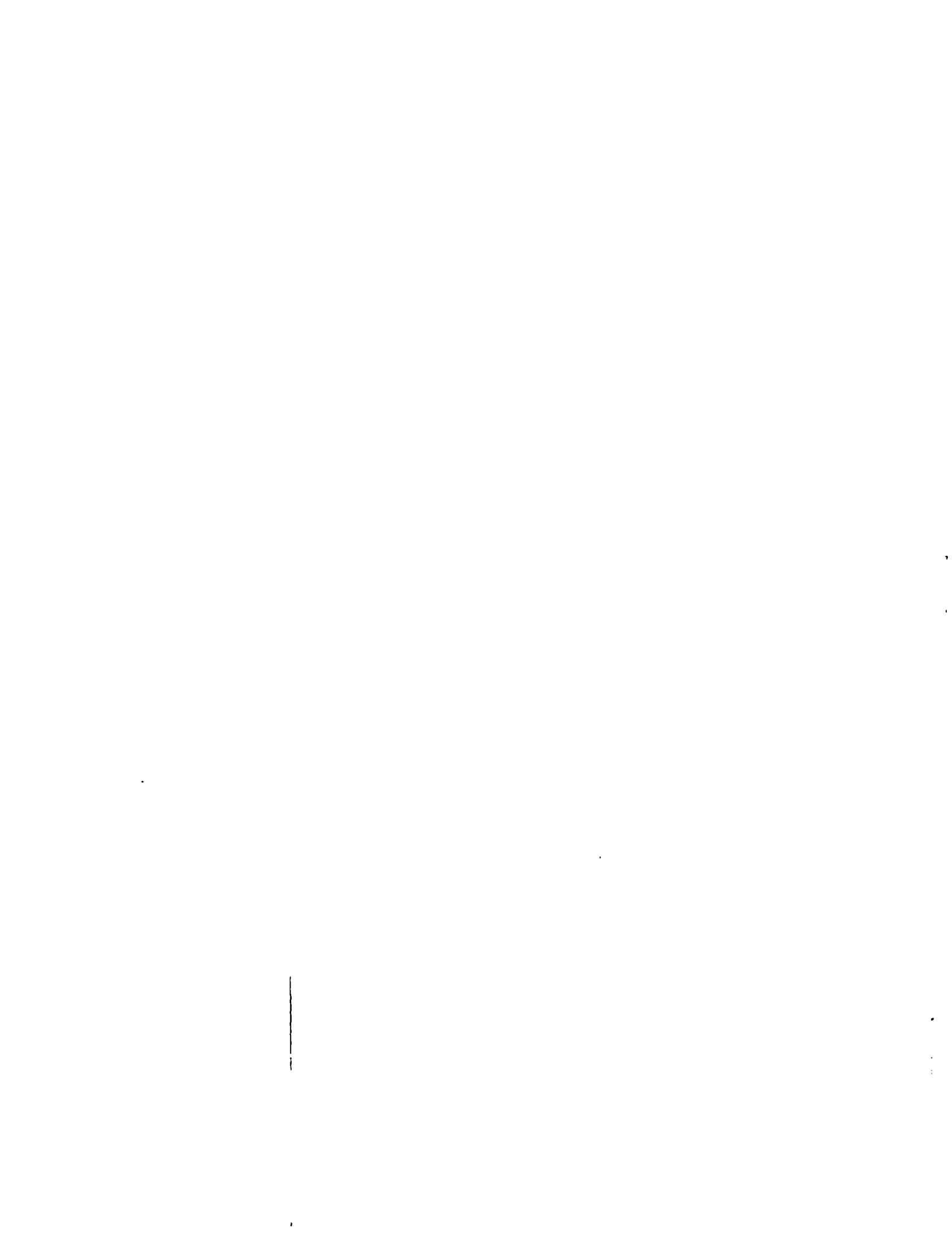
Proponents of the interpretation of ore deposits in terms of plate tectonics believe that by looking at the earth as functions of time and tectonics, one can get a better understanding of the sequence of events responsible for ore genesis and the probabilities of occurrence in various geologic settings. (A summary sketch of the plate tectonic setting of common ore deposits is found across the opening two pages of this article.)

A current plate tectonic explanation for Japan's Kuroko massive sulphides held by some researchers is the "failed rift" model. A failed attempt to rift an arc and form a marginal basin can account for some of the peculiarities of these deposits. The non-uniform mineralization distribution can be related to spreading structures and transform faults. The observed pre-mineralization subsidence and post-mineralization uplift can be explained via a dynamic loss of "fluid head" during the attempt at rifting, resulting in a depression that provides the site for submarine mineralization.

The important exploration ramification is that the existence of a submarine volcanic pile is not sufficient for generating Kuroko-type deposits. Geologists should look for evidences of rifting and then search for strata similar in age to the rifting episode. In Japan, gravity studies have been successful in identifying evidences of rifting. Reconnaissance studies should be carried out in other areas of similar tectonics.

Good places to look for porphyry tin-tungsten deposits are in areas of continental collisions. These environments provide double thicknesses of sialic material and the organic recycling that is necessary to generate the "S-type" magmas discussed previously.

The interrelationships between mantle plumes and flood



Rift evaporites—80% certain in low-precipitation belts, 40% probability overall

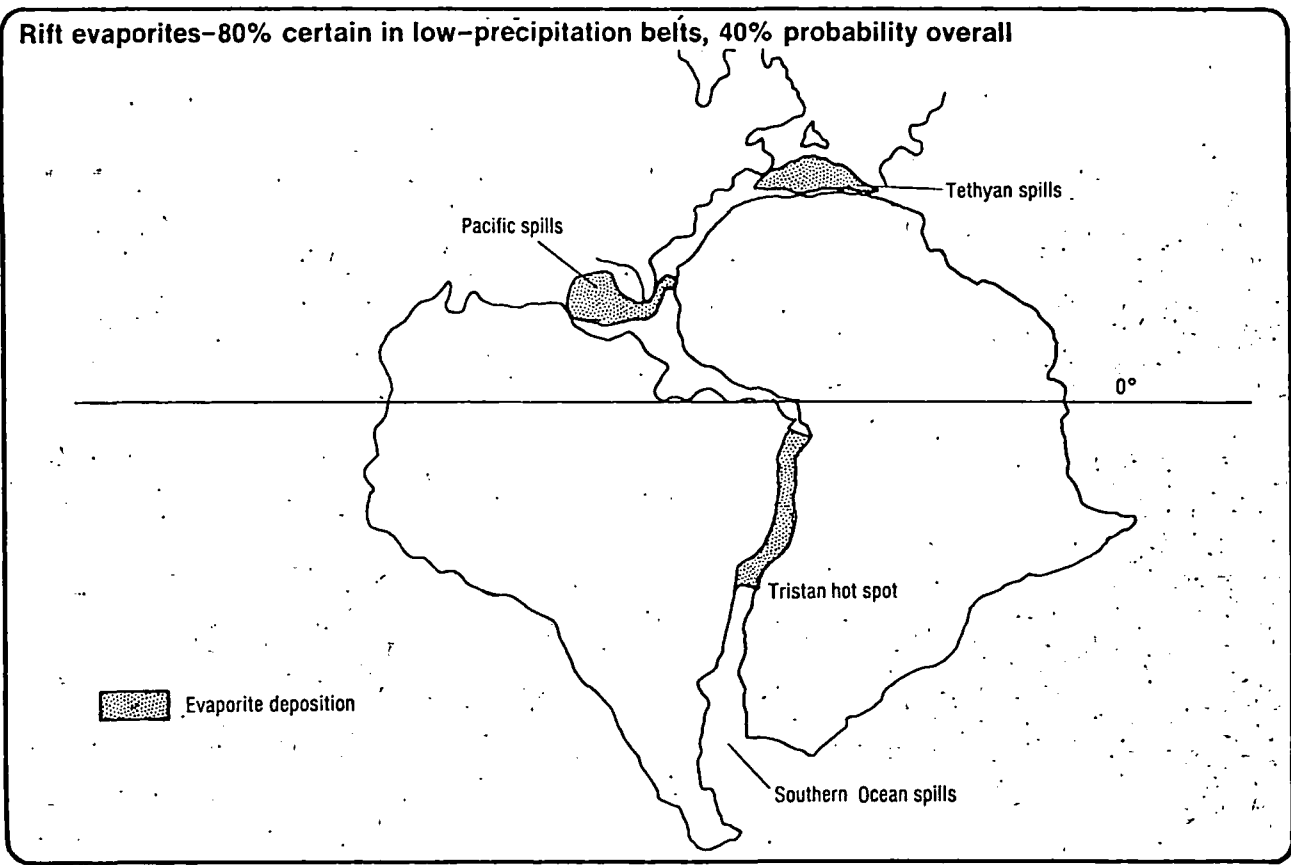


Fig. 8—Evaporites formed in the narrow seas that existed between Africa and North and South America in the early stages of opening of the present Atlantic

Ocean. The figure is based on Burke (Geology, 1975); the probability of evaporite formation was calculated by Kinsman (NATURE, 255, 1975).

basalt volcanism are being studied, as in the Snake River of the US, the Karroo district of South Africa, and the Noril'sk district in the USSR. The massive Ni-, Cu-, Pt-rich deposits in Noril'sk are thought to be formed in traps of feeder zones.

Plume tracks create zones of weakness along which continents may split (i.e., both sides of Greenland, part of Africa from South America, and Madagascar from east Africa and then from India).^{*} Continental rifting in the Oslo Rift is believed to be responsible for generating the hydrothermal activity that lead to Pb-Zn mineralization in the area.

In arid environments, there is an 80% probability that evaporites will develop in areas of continental rifting (Fig. 8). If hydrothermal activity is significant in these areas, the hot brine fluids should be capable of transporting and precipitating lead and zinc ores in basinal features. Examples of ore deposits that are thought to have formed this way are the McArthur River, Broken Hill, and Sullivan deposits. This process is going on today in the Red Sea.

As the advances in ore deposit research continue, geologists must keep open minds and continually challenge existing ideas and models. The Kuroko ores were previously thought of in terms of subduction and calc-alkaline volcanism. Now, re-evaluations using new and pre-existing data suggest that extensional tectonics are critical in generating these ores. This new tectonic understanding should help in the search for Kuroko-type ores in new locations. Updating and re-evaluating current ideas will help in the search for hidden ore deposits. ■

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This feature was based on presentations by the following faculty of Penn State's Ore Deposits Research Section:

- 1) A.W. Rose, Prof. of Geochemistry
- 2) D.P. Gold, Prof. of Geology
- 3) H.L. Barnes, Prof. of Geochemistry and Director of ODRS
- 4) A.W. Rose, Prof. of Geochemistry
- 5) A.C. Lasaga, Assoc. Prof. of Geochemistry
- 6) C. Wayne Burnam, Prof. of Geochemistry
- 7) H. Ohmoto, Prof. of Geochemistry
- 8) Ibid.
- 9) L.M. Cathles, Assoc. Prof. of Geosciences

^{*}As shown by Dr. Morgan at Princeton University.

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One hundred million years of geomagnetic polarity history

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ABSTRACT

Since 1968, absolute ages have been assigned to the Late Cretaceous–Cenozoic geomagnetic reversal time scale by fixing the ages of two or more calibration points in a composite marine magnetic-anomaly profile and interpolating between or extrapolating beyond these points, assuming constant spreading rates in each interval. Previously, no more than 4 calibration points were used, but it is now possible to specify 11 calibration points, in addition to the 0 m.y. datum. This improvement is based on magnetostratigraphic studies in Italian pelagic limestones; these studies closely tie the geomagnetic reversal sequence to the foraminiferal and coccolith zonations. Absolute ages of calibration points are provided by the best available dates on stage boundaries, which are located from the biostratigraphic zonation. The greatest changes from previous scales come in the late Paleocene–early Eocene, where the new ages are as much as 3 m.y. younger than in the 1977 scale of LaBrecque and others, and as much as 1.8 m.y. younger than in the 1980 scale of Ness and others.

INTRODUCTION

A major goal of geochronology is to tie together the three principal time scales, which are based on evolutionary changes recorded by fossils, on "absolute age" determined from radioactive decay, and on the sequence of geomagnetic reversals recorded by spreading oceanic crust and in stratigraphic sequences. The compendium of papers edited by Cohee and others (1978), dealing largely with absolute-age calibration of the paleontological time scale, is still up to date. Absolute ages have been applied to the reversal sequence principally by fixing the ages of two or more calibration points in a composite marine magnetic-anomaly profile and interpolating between or extrapolating beyond these points, assuming constant spreading rates in each interval. Ness and others (1980) gave a valuable review of the successive versions of this type of time scale for the Late Cretaceous and Cenozoic and offered a revised version as an "up-to-date but temporary synthesis."

At this point it is possible to make a further substantial revision of the Late Cretaceous–Cenozoic magnetic-polarity time scale on the basis of new magnetostratigraphic information from

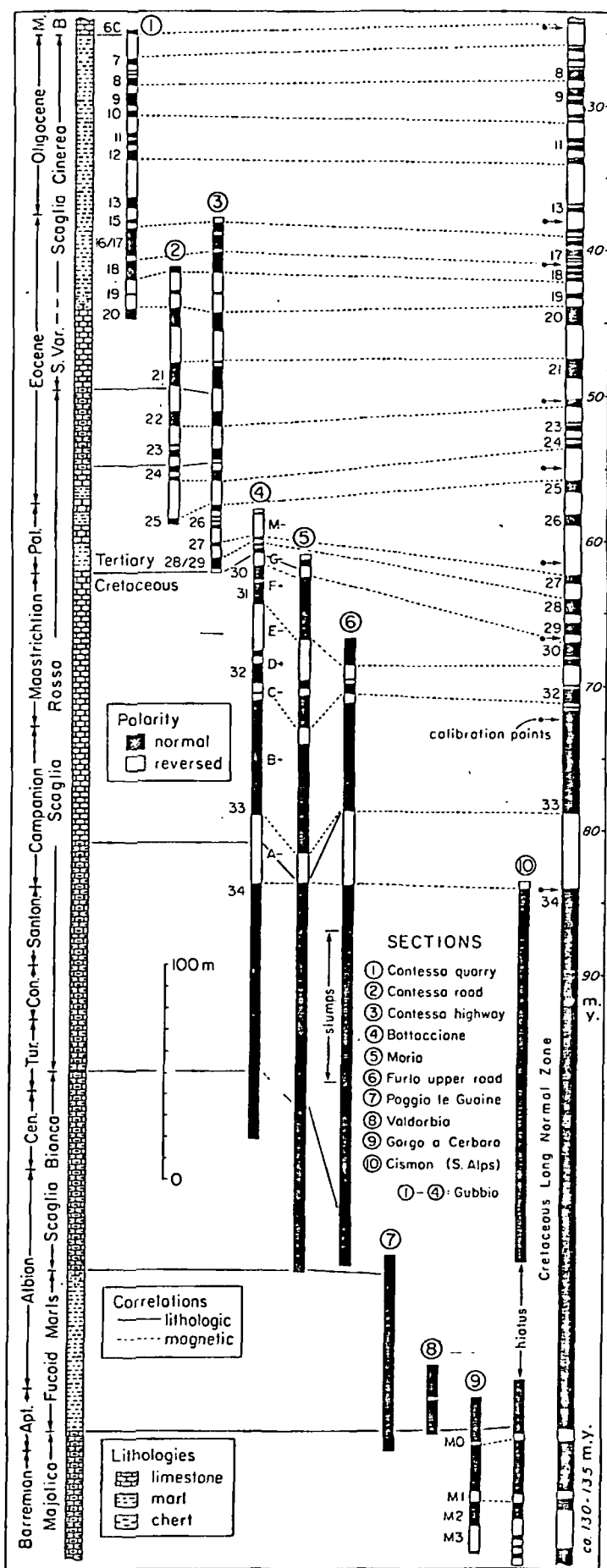
pelagic limestones in Italy. This revision provides a very close tie between the reversal sequence and the planktic foraminiferal biozonation. The widely used time scale of LaBrecque and others (1977) was based on two calibration points, and that of Ness and others (1980) employed four, but it is now possible to fix the biozonal positions, and thus indirectly the absolute ages, of 11 calibration points in the reversal sequence. (The present is an additional calibration point in all cases.)

Magnetostratigraphic studies in Italy have yielded a reversal sequence with a fingerprint of long and short polarity zones which almost exactly matches the marine magnetic-anomaly sequence of LaBrecque and others (1977) and which has been paleontologically dated on the basis of abundant foraminifera, with coccoliths employed in certain intervals. This paleontological information fixes the positions in the reversal sequence of chronologic boundaries to the stage level in the Late Cretaceous and the Tertiary. Using the currently accepted absolute ages for these boundaries, we are able to fix the ages of 9 calibration points in the magnetic polarity sequence from the base of the Campanian to the Oligocene–Miocene boundary; for Miocene and younger we use the previously established calibration points of Ness and others (1980). The polarity sequence of LaBrecque and others (1977) has been adjusted to these dates using linear interpolation between calibration points.

MAGNETOSTRATIGRAPHY

The pelagic limestones and marls of the Umbrian sequence in northern peninsular Italy have yielded excellent records of magnetic polarity and foraminiferal evolution. These records can be precisely linked because for each stratigraphic level the magnetic and paleontological information both come from the same small sample.

Figure 1 shows the Umbrian and southern Alpine sections for which detailed magnetic stratigraphy has been measured. The Cretaceous results have been reviewed by Lowrie and others (1980b). Details have been presented in the following papers: Contessa Quarry, Road, and Highway: Lowrie and others (1981); Bottaccione: Premoli Silva and others (1974), Lowrie and Alvarez (1975, 1977a, 1977b), Roggenthen and Napoleone (1977), Alvarez and others (1977), G. Napoleone and others (in prep.); Moria: Alvarez and Lowrie (1978), Vandenberg and others (1978); Furlo Upper Road: W. Alvarez and W. Lowrie (in prep.); Poggio le Guaine, Gorgo a Cerbara: Lowrie and others (1980a); Valdorbia: Vandenberg and others (1978), Lowrie and others (1980a); Cismon, in the southern Alps: Channell and others (1979). The Umbrian magnetic stratigraphy has been confirmed by work on Deep Sea Drilling Project (DSDP) Legs 73 (Tauxe and others, 1980) and 74 (Chave, 1980).



BIOSTRATIGRAPHY

The Umbrian sections have been zoned with planktic foraminifera by Premoli Silva (1977; and *in* Lowrie and others, 1980a, and *in* G. Napoleone and others, in prep.); Premoli Silva and others (1976), and Premoli Silva and Toumarkine (*in* Lowrie and others, 1981). Nannoplankton zonations have been made by Moneschi (1979; and *in* Lowrie and others, 1980a) and by Perch-Nielsen (*in* Lowrie and others, 1981). The southern Alps section was zoned on the basis of foraminifera and nannoplankton by Medizza (*in* Channell and others, 1979).

The result of these magnetostratigraphic and biostratigraphic studies has been to fix the positions in the magnetic-polarity sequence where various appearances and extinctions of planktic foraminifera and coccolith taxa occur. The most significant relocation concerns the Paleocene-Eocene boundary. This was located by Heitzler and others (1968) within anomaly 21 by extrapolation from present spreading rates in the South Atlantic. It was relocated within anomaly 23 by interpolation in the time scale of LaBrecque and others (1977), and readjustment of the age of the boundary placed it at the base of anomaly 24 (Ness and others, 1980). None of these locations was done directly. However, recent magnetostratigraphic results from Italian pelagic limestones (Lowrie and others, 1981) and in vertebrate-bearing continental sediments (Butler and others, 1981) locate the Paleocene-Eocene boundary within the negative polarity zone just younger than anomaly 25. As a result of this shift of the boundary location toward higher anomaly numbers and revision of the date of the boundary, sea-floor spreading rates and the timing of major events related to sea-floor spreading changes in early Tertiary time have been altered substantially (Coney and Butler, 1980; Butler and Coney, 1981).

ABSOLUTE-AGE CALIBRATION

After discussions with colleagues actively working on biostratigraphic and radiometric questions, we have decided to follow Ness and others (1980) in accepting the ages given for the late Tertiary by Berggren and Van Couvering (1974), for the early Tertiary by Hardenbol and Berggren (1978), and for the Late Cretaceous by Obradovich and Cobban (1975). These ages have been corrected by Ness and others (1980) for the new decay and abundance constants used in K-Ar dating, so our time scale from the base of the Cenomanian to the present is identical to the right-hand column of their Table 1. For the Early Cretaceous, where absolute age calibration is much more uncertain, we use the time scale of Lanphere and Jones (1978), but unfortunately the Barremian, the most critical stage for our purposes, cannot yet be dated with any certainty. The chronologies we have chosen differ from some other available systems, notably those of Van Hinte (1976) and Odin (1978). A discussion of the relative merits of the various proposed chronologies would be out of place here; we justify our choices on the basis of arguments presented by

Figure 1. Correlation of magnetostratigraphic sections in Umbrian Apennines and southern Alps with sea-floor magnetic anomalies. Left-hand columns: age (from foraminiferal zonation), formation names, and lithology (M. = Miocene, S.Var. = Scaglia Variegata, B. = Bisciaro). Columns 1-10: detailed magnetostratigraphic sections (references given in text). Column 4 has been extended upward to anomaly 18 in recent work by G. Napoleone and others (in prep.). Numbers are standard magnetic-anomaly identification; letters in column 4 give Gubbio magnetic zonation (Alvarez and others, 1977). Right-hand column: magnetic-reversal sequence determined from sea-floor magnetic anomalies by LaBrecque and others (1977) and redated in this paper by interpolation between the nine paleontologically controlled calibration points marked by arrows. Absolute ages of M-sequence reversals are uncertain.

Berggren and others (1978), Lanphere and Jones (1978), and Ness and others (1980). The set of boundary ages used in this paper is given in Table 1.

CONSTRUCTION OF THE NEW TIME SCALE

The polarity sequence in the magnetic time scale of LaBrecque and others (1977) assumes a constant rate of sea-floor spreading in the South Atlantic during the Tertiary and in the North Pacific during the Maastrichtian and Campanian. The stage and substage boundaries used as calibration levels (Table 1) were located in the polarity sequence of LaBrecque and others (1977) on the basis of the Italian magnetostratigraphic studies, and their ages were specified as in Ness and others (1980, Table 1). The revised ages of polarity-zone boundaries were then obtained by linear interpolation between calibration points, using the reversal spacings from LaBrecque and others (1977). Our revised time scale is thus related to previous time scales as follows:

- (1) for $O \leq t_R \leq 10.30$, ($O \leq t_N \leq 10.30$),
 $(O \leq t_L \leq 9.74)$, $t_R = t_N$;
 (2) for $10.30 \leq t_R \leq 84.02$, ($10.30 \leq t_N \leq 85.86$),
 $(9.74 \leq t_L \leq 79.65)$, $t_R = t_R(Y)$
 $+ [t_R(O) - t_R(Y)] [t_L - t_L(Y)] / [t_L(O) - t_L(Y)]$,

where t_L , t_N , and t_R are ages (m.y.) in the LaBrecque and others (1977), Ness and others (1980), and present revised time scales, respectively. Note that upper-case O and Y refer to the older and younger calibration points that bound the interval of interest, whereas lower-case o and y used in Table 1 and in Ness and others (1980) refer to the older and younger limits of polarity intervals. Table 2 gives the revised ages for all polarity-zone boundaries.

The apparent precision of 0.01 m.y. in the revised time scale (Table 2) is not the absolute accuracy of the scale but is necessary to portray correctly the relative durations of short polarity intervals. LaBrecque and others (1977) included polarity intervals shorter than 40,000 yr in their Table 1, but they omitted these from their figures. "Tiny wiggles" on anomaly profiles can be due to short duration reversals or to geomagnetic intensity fluctuations (see LaBrecque and others, 1977, for a discussion of the problem). Because of this ambiguity, we have omitted all polarity intervals shorter than 40,000 yr from our Table 2 and from the graphical representations of the new magnetic time scale for the Cenozoic (Fig. 2) and Late Cretaceous (Fig. 3). For completeness, the scale has been extended down into the Cretaceous for those stages whose boundaries are reasonably well dated. The Late Cretaceous stage-boundary ages shown are those recomputed by Ness and others (1980) from the radiometric dates of Obradovich and Cobban (1975).

We have restricted our revision of the magnetic time scale to the Cenozoic and Late Cretaceous. At present there are not enough reliable radiometric dates for the Early Cretaceous and Late Jurassic stage boundaries to justify presenting a new magnetic time scale for these times. A tentative comparison of geomagnetic polarity sequences in the Cretaceous as derived from magnetostratigraphic sections and oceanic magnetic anomalies was made by Lowrie and others (1980b). This used the proposed numeric time scale of Van Hinte (1976), which, like other time scales preceding it, was largely intuitive for the Early Cretaceous stages. However, magnetostratigraphic studies in Italian pelagic limestones have firmly correlated the long normal-polarity zone prior to the Campanian (Fig. 3) with the Cretaceous magnetic smooth zone in the oceanic magnetic anomalies (Lowrie and Alvarez, 1977a, 1977b; Alvarez and others, 1977) Channell and others, 1979). The youngest of the *M*-sequence anomalies pre-

TABLE 1. CALIBRATION LEVELS FOR THE NEW MAGNETIC TIME SCALE

Calibration level	Location in anomaly sequence*	Previous [†] age (m.y.)	Revised age (m.y.)
Present	--	0.00	0.0
Pliocene (reversal boundary)	2.3'(o)	3.32	3.4 [§]
Early late Miocene (reversal boundary)	5.5(o)	9.74	10.3 [§]
Miocene/Oligocene boundary	Below 6C	24.2	24.6
Oligocene/Eocene boundary	13-15	36.4	38.0
Late/middle Eocene	Below 18(y)	41.5	41.0
Middle/early Eocene	Below 22(y)	52.5	50.3
Eocene/Paleocene boundary	24-25	58.2	54.9
Late/early Paleocene [#]	26-27	61.8	61.5
Tertiary/Cretaceous boundary	29-30	65.0	66.7
Maastrichtian/Campanian boundary	33	72.5	72.3
Campanian/Santonian boundary	33-34(o)	79.7	84.1

* Anomalies are numbered as in Ness and others (1980); (o) and (y) refer to the reversals at the older and younger ends of a polarity interval.

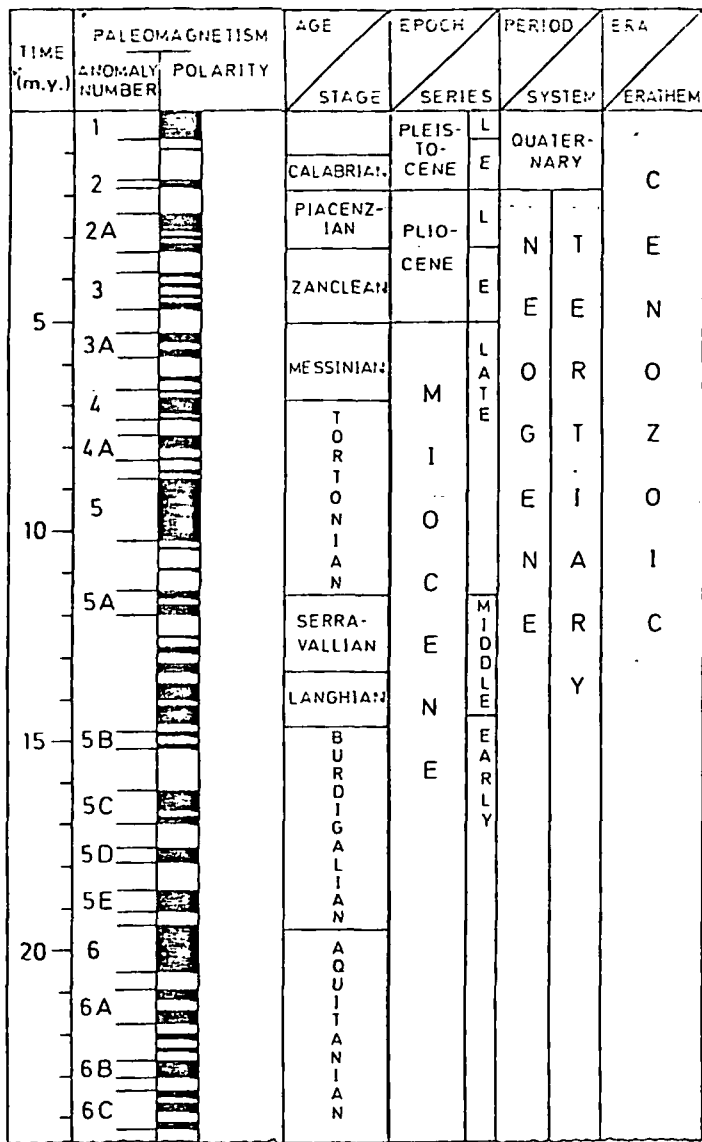
† In the LaBrecque and others (1977) time scale.

§ Revised ages from Ness and others (1980).

Taken as the *angulata/uncinata* boundary (Hardenbol and Berggren, 1978).

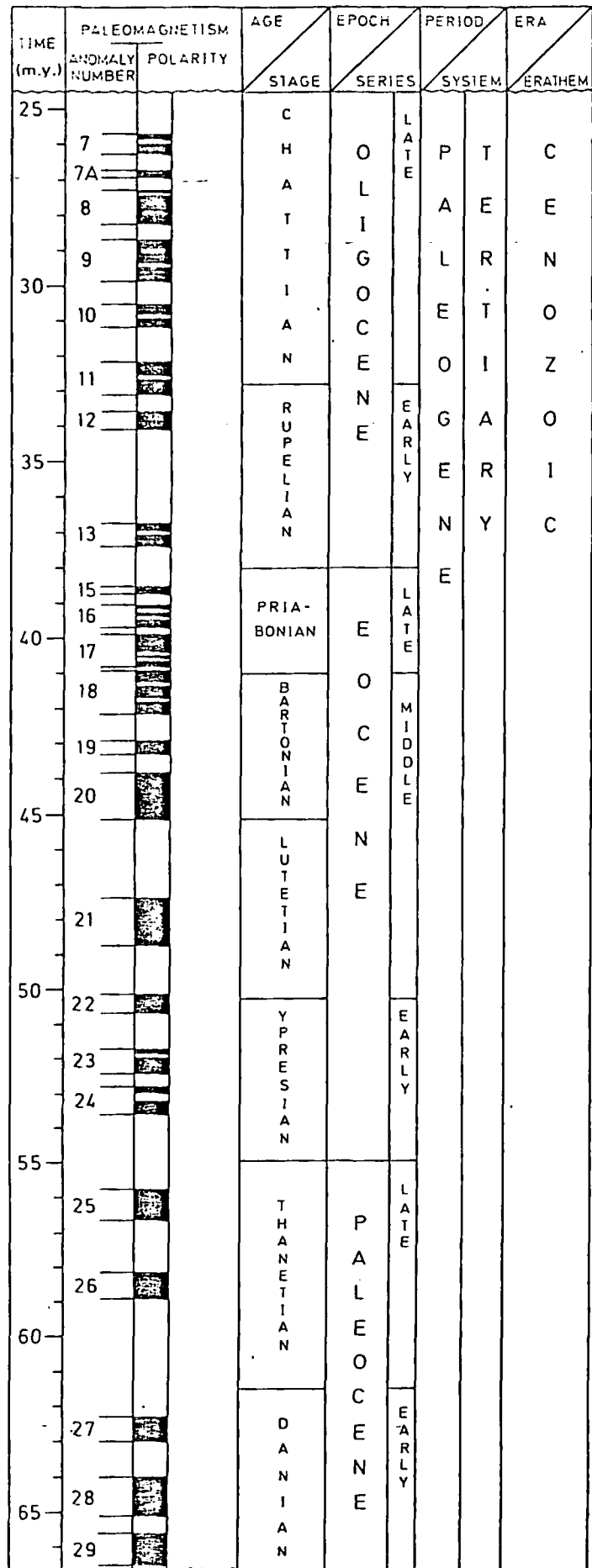
TABLE 2. DURATIONS OF NORMAL POLARITY INTERVALS

Time interval (m.y.)	Anomaly	Time interval (m.y.)	Anomaly
0.00 - 0.72	1	25.74 - 25.86	7
0.91 - 0.97		25.94 - 26.27	7
1.66 - 1.87	2	26.73 - 26.94	7A
2.47 - 2.91	2A	27.27 - 27.36	8
2.98 - 3.07	2A	27.44 - 28.27	8
3.17 - 3.40	2A	28.73 - 29.39	9
3.87 - 3.97	3	29.45 - 29.92	9
4.10 - 4.24	3	30.50 - 30.84	10
4.39 - 4.46	3	30.90 - 31.18	10
4.56 - 4.76	3	32.19 - 32.59	11
5.33 - 5.52	3A	32.65 - 33.12	11
5.67 - 5.87	3A	33.57 - 34.07	12
6.34 - 6.47		36.75 - 36.96	13
6.68 - 6.75	4	37.03 - 37.41	13
6.83 - 7.25	4	38.51 - 38.77	15
7.32 - 7.38	4	39.02 - 39.16	16
7.77 - 8.09	4A	39.26 - 39.43	16
8.29 - 8.38	4A	39.47 - 39.71	16
8.59 - 8.68		39.88 - 40.42	17
8.80 - 10.30	5	40.46 - 40.59	17
10.42 - 10.47		40.63 - 40.84	17
10.91 - 10.98		40.94 - 41.30	18
11.46 - 11.64	5A	41.36 - 41.74	18
11.76 - 12.03	5A	41.79 - 42.17	18
12.50 - 12.54		42.92 - 43.32	19
12.76 - 12.94		43.83 - 45.14	20
13.14 - 13.40		47.37 - 48.75	21
13.63 - 14.04		50.14 - 50.70	22
14.16 - 14.62		51.74 - 51.87	23
14.83 - 14.93	5B	51.91 - 52.42	23
15.10 - 15.23	5B	52.79 - 52.97	24
16.21 - 16.73	5C	53.21 - 53.61	24
16.80 - 16.99	5C	55.76 - 56.66	25
17.59 - 17.92	5D	58.15 - 58.95	26
18.60 - 19.13	5E	62.31 - 63.00	27
19.41 - 20.52	6	64.00 - 65.12	28
20.96 - 21.24	6A	65.63 - 66.54	29
21.47 - 21.79	6A	66.98 - 68.01	30
21.99 - 22.15		68.07 - 68.62	31
22.35 - 22.44		69.84 - 70.01	32
22.66 - 23.07	6B	70.17 - 71.18	32
23.37 - 23.54	6C	71.43 - 71.46	
23.66 - 23.90	6C	71.64 - 78.82	33
24.15 - 24.32	6C	84.02 -	34



 normal polarity
  reversed polarity

Figure 2. Revised magnetic-polarity time scale for Cenozoic, prepared by locating Paleocene, Eocene, and Oligocene stage and substage boundaries in oceanic magnetic-anomaly reversal sequence by magnetostratigraphic correlations (Fig. 1). Revised radiometric ages (Ness and others, 1980) were then associated with 9 Cenozoic calibration points (Table 1), and intervening anomalies were dated by interpolation.



ceding this quiet zone have been tied into the Early Cretaceous biostratigraphic framework in Italian sections: anomaly N10 occurs at the base of the Aptian and anomaly N11 in the middle of the Barremian. These dates are about half a stage older than the corresponding ages estimated by Larson and Hilde (1975).

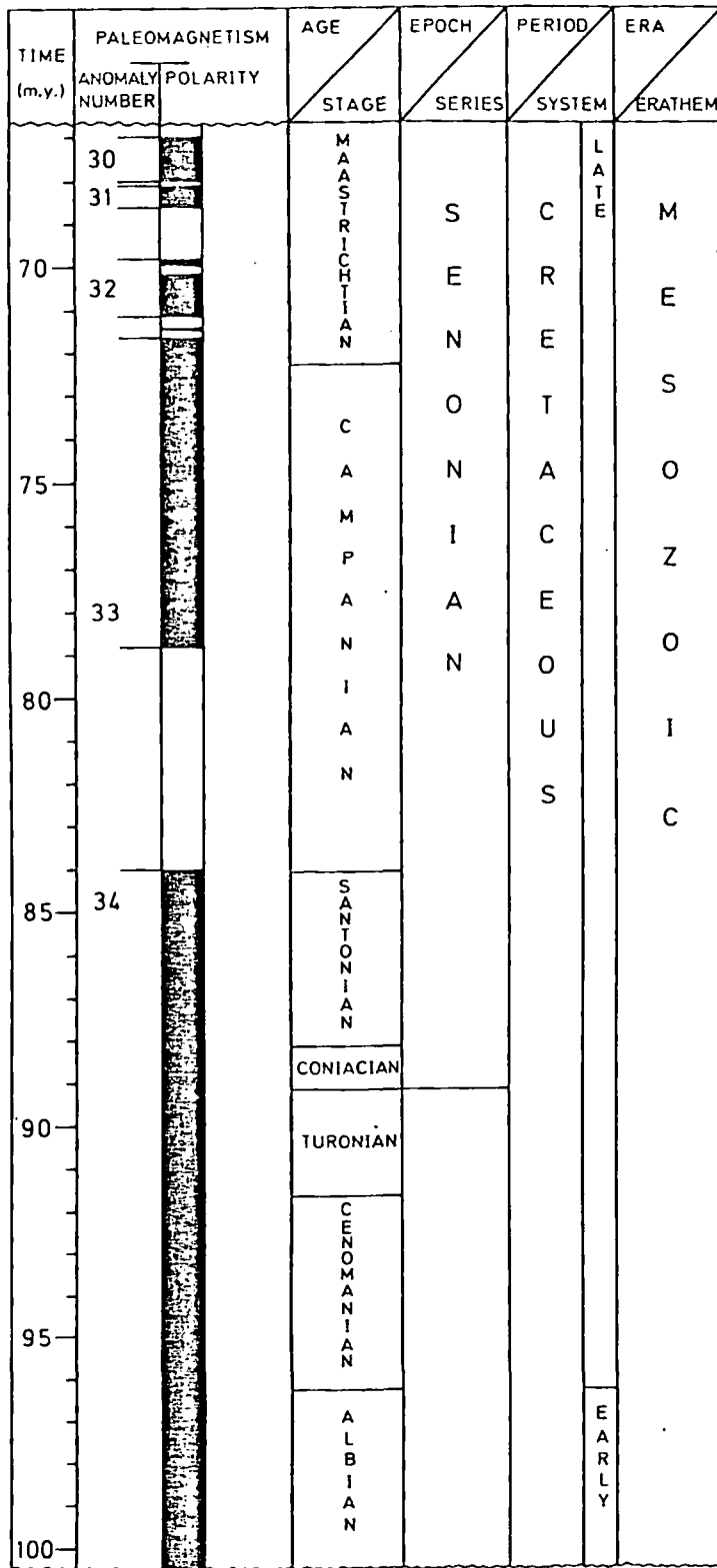


Figure 3. Revised magnetic-polarity time scale for Late Cretaceous, prepared similarly to Figure 2. Maastrichtian and Campanian reversal sequences have been interpolated between appropriate calibration points (Table 1). Ages of Albian to Santonian stage boundaries in Cretaceous quiet interval correspond to dates of Obradovich and Cobban (1975), as revised by Ness and others (1980).

Unfortunately, there are no reliable dates for the boundaries of these critical stages. Lanphere and Jones (1978) cited two dates closely straddling the Hauterivian-Barremian boundary at 136 m.y. and two further dates at 114 and 120 m.y. for levels within the Albian.

COMPARISON TO DSDP DATING

LaBrecque and others (1977) tested their time scale by plotting, in their Figure 4, the paleontologically determined age of the sediment found immediately above basement in various DSDP holes against the age of the crust predicted on the basis of the magnetic anomaly at the drill site, with the anomalies dated according to their proposed time scale. The observed ages agreed fairly well with the predicted ages, with divergences, as they noted, in the late Paleocene-early Eocene and in the middle Miocene. In Figure 4 here, we give a similar plot, adding three recent DSDP sites (408, 410, 442), and using our new dating of the anomalies. Comparison of this figure with Figure 4 of LaBrecque and others (1977) shows the improvement resulting from revision of the time scale. The Paleocene-Eocene discrepancy has been eliminated. The remaining problems are with Miocene sites 15, 36, and 396, in the only part of the anomaly sequence that has not yet been calibrated by magnetostratigraphic studies.

As LaBrecque and others (1977) stressed, a plot of this kind does not test the validity of the absolute ages assigned to the magnetic anomalies, because these age assignments are based on acceptance of one particular set of dates for the paleontological stage boundaries. What Figure 4 demonstrates is that DSDP information agrees with the correlation between foraminiferal biostratigraphy and polarity zones determined in Italian limestones. This was previously demonstrated for the Late Cretaceous and Paleocene by Larson (1976).

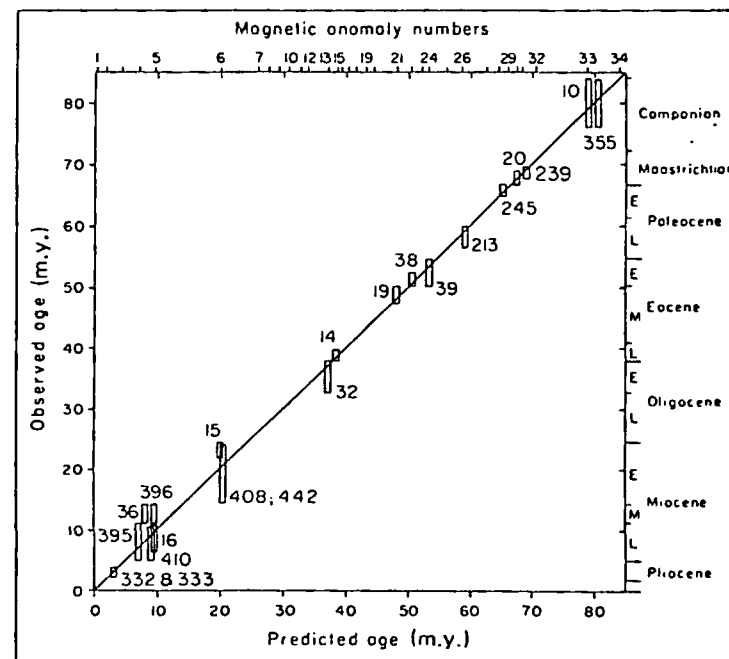


Figure 4. Comparison of paleontological ages of basal sediments in DSDP holes with basement ages predicted from magnetic anomalies. Sites intersected by 45° line show agreement between predicted and observed age. Comparison of this plot with Figure 4 of LaBrecque and others (1977) shows that discrepancies in Paleocene-Eocene have been removed. As discussed in text, this plot tests correlation of magnetic-reversal sequence to foraminiferal biostratigraphy, not absolute ages assigned to polarity zones.

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ACKNOWLEDGMENTS

Reviewed by R. F. Butler, Roger L. Larson, and John LaBrecque. In our Italian stratigraphic studies since 1973, we have been stimulated by cooperation and friendly competition with colleagues whose names are given in this paper, and we thank them for their many contributions. We are particularly indebted to Isabella Premoli Silva, Fabio Medizza, Monique Toumarkine, and Katharina Perch-Nielsen, whose micro-paleontological studies provided the calibration points we have used. Roger Larson has frequently contributed information on the marine magnetic-anomaly sequence. We thank the following colleagues for discussion of the current status and critical problems of biostratigraphic correlation and absolute-age calibration of paleontological events: W. A. Berggren, G. Ness, R. L. Armstrong, J. D. Obradovich, W. A. Cobban, and D. L. Jones. We also thank Allan Cox, Jim Channell, and Friedrich Heller for reviews of the manuscript and for helpful discussions. Alvarez has been supported by the Geology Program of the National Science Foundation. Institut für Geophysik, ETH-Zürich Contribution No. 330.

MANUSCRIPT RECEIVED MARCH 23, 1981

REVISED MANUSCRIPT RECEIVED MAY 15, 1981

MANUSCRIPT ACCEPTED JUNE 11, 1981

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A large intrusive complex of alkaline gabbro and related felsic and ultramafic rocks is exposed in the West Humboldt Range southeast of Lovelock, Nevada. Correlative gabbros occur to the east in the adjacent northerly trending Stillwater and Clan Alpine ranges, thereby indicating an easterly dimension of the complex of at least 35 miles.

Most of the complex in the West Humboldt Range is composed of hornblende gabbro and hornblende leucogabbro. Minor anorthosite is gradational with these gabbros. Hornblende picrite and strongly foliate hornblende leucogabbro form tabular bodies along the periphery of the intrusion. Later dolerite, keratophyre, and gabbroic pegmatite are widely spread.

The age of the gabbroic complex is in the range Early Jurassic-Miocene. Structural relations of the igneous rocks and the wallrocks suggest that emplacement occurred during regional deformation of the intruded terrane. Contact metamorphism by the intrusive rock produced a thin aureole of hornfels in the albite-epidote hornfels facies.

Rocks of the complex are characterized chemically by a high ratio of Na/K (> 5) and low bulk iron (3-9.5 per cent as FeO). Sequence of mineral assemblages and rock analyses indicate that differentiation of the parent basaltic magma followed an extreme ferro-gabbro trend. Progressive retention of Fe, Ti, Na, and volatiles produced late magmatic kaersutite magnetite, minor titanobiotite, and analcite which are interstitial to the earlier magmatic labradorite, diopsidic augite, forsterite, and bronzite. Veins of magnetite which were contemporaneous with ductile sodic scapolitization and albitization were formed from iron-bearing fluids residual from magmatic consolidation.

1964 GSA Abs p. 1

Association of Gabbroic Complex and Mesozoic Thrusts, West-Central Nevada

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The marginal parts of the Humboldt gabbroic complex intrude plates of Paleozoic and Mesozoic sedimentary rocks which are thrust over Mesozoic strata along the periphery of the intrusion. The complex consists of gabbroic, dioritic, albitic, and basaltic rocks which crop out in an elliptical area of 500 sq mi in the West Humboldt and nearby Stillwater and Clan Alpine ranges of west-central Nevada. Gabbroic rocks along the margin of the complex occur mostly as tabular bodies within, or on top of, upper-plate strata; in places, however, gabbros form the sole of the upper plate. The central part of the gabbroic complex consists of apparently continuous gabbro and overlying comagmatic mafic extrusive rocks.

The virtual restriction of gabbroic rocks to the upper plates and the fact that gabbro does not cut across the thrust planes indicate that intrusion occurred before or during thrusting. Structural and petrologic relationships suggest that the gabbros were liquid, at least in part, during emplacement of the thrust blocks. According to these relationships, the age of the gabbroic complex should approximately date the thrusting. A potassium-argon age of primary biotite from the complex is $(150 \pm 3) \times 10^6$ years; consequently, the probable date of intrusion and thrusting is Late Jurassic. The thrust plates overlie rocks containing Early Jurassic fossils. If these time relationships are correct, thrusting in this area occurred near the onset of the widespread Jurassic-Cretaceous orogeny in northwestern Nevada.

1966 GSA Abs p. 1

Mechanics of Emplacement of a Gabbroic Lopolith, Northwestern Nevada

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A gabbroic lopolith, which underlies about 450 square miles east of Lovelock, Nevada, intrudes and is circumscribed by Jurassic sandstone which had been deposited in a local marine basin shortly before emplacement of the igneous rocks. The lopolith and sandstone occur largely in thrust plates which moved radially about 5 miles from the magma conduit over older Mesozoic slates. The motion occurred before solidification of the intrusion was complete.

Magmatic pressure in the initial conduit apparently produced sufficient shear stress along the sandstone-slate contact to move the sandstone out onto the flanks of the sedimentary basin. Low effective normal stress was produced by elevated pore-water pressure (Hubbert and Rubey, 1959) due to magmatic heating. Wall-rock solids reached 450-500° C; sea water heated to these temperatures should have an equilibrium vapor pressure between 250 and 425 bars depending on sandstone permeability. Overburden pressure at the sandstone base was 300-400 bars so that only slight magma pressure was required to cause radial thrusting.

Pore water in the impermeable slates of the lower plate should have reached high pressures near the magma conduit and assisted the propagation cracks through which the magma could proceed toward the surface. Pore water in the shallow, permeable sandstone, however, would have distributed magmatic heat to a large, nearly isothermal reservoir in which water pressure could buoy up the containing medium but would not have been sufficient to rupture the overburden extensively. Magma could thus follow a lateral path above the slate-sandstone contact.

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Pore water in the impermeable slates of the lower plate should have reached high pressures near the magma conduit and assisted the propagation cracks through which the magma could proceed toward the surface. Pore water in the shallow, permeable sandstone, however, would have distributed magmatic heat to a large, nearly isothermal reservoir in which water pressure could buoy up the containing medium but would not have been sufficient to rupture the overburden extensively. Magma could thus follow a lateral path above the slate-sandstone contact.

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SPEED, ROBERT C., *Stanford University, Palo Alto, Calif.*

A large intrusive complex of alkaline gabbro and related felsic and ultramafic rocks is exposed in the West Humboldt Range southeast of Lovelock, Nevada. Correlative gabbros occur to the east in the adjacent northerly trending Stillwater and Clan Alpine ranges, thereby indicating an easterly dimension of the complex of at least 35 miles.

Most of the complex in the West Humboldt Range is composed of hornblende gabbro and hornblende leucogabbro. Minor anorthosite is gradational with these gabbros. Hornblende picrite and strongly foliate hornblende leucogabbro form tabular bodies along the periphery of the intrusion. Later dolerite, keratophyre, and gabbroic pegmatite are widely spread.

The age of the gabbroic complex is in the range Early Jurassic-Miocene. Structural relations of the igneous rocks and the wallrocks suggest that emplacement occurred during regional deformation of the intruded terrane. Contact metamorphism by the intrusive rock produced a thin aureole of hornfels in the albite-epidote hornfels facies.

Rocks of the complex are characterized chemically by a high ratio of Na/K (> 5) and low bulk iron (3-9.5 per cent as FeO). Sequence of mineral assemblages and rock analyses indicate that differentiation of the parent basaltic magma followed an extreme ferro-gabbro trend. Progressive retention of Fe, Ti, Na, and volatiles produced late magmatic kaersutite magnetite, minor titanobiotite, and analcite which are interstitial to the earlier magmatic labradorite, diopsidic augite, forsterite, and bronzite. Veins of magnetite which were contemporaneous with ductile sodic scapolitization and albitization were formed from iron-bearing fluids residual from magmatic consolidation.

1964 GSA Abs p1

Association of Gabbroic Complex and Mesozoic Thrusts, West-Central Nevada

p 278

SPEED, R. C., *Jet Propulsion Lab., California Institute of Technology, Pasadena, Calif.* and B. M. PAGE, *Dept. Geology, Stanford University, Stanford, Calif.*

The marginal parts of the Humboldt gabbroic complex intrude plates of Paleozoic and Mesozoic sedimentary rocks which are thrust over Mesozoic strata along the periphery of the intrusion. The complex consists of gabbroic, dioritic, albitic, and basaltic rocks which crop out in an elliptical area of 500 sq mi in the West Humboldt and nearby Stillwater and Clan Alpine ranges of west-central Nevada. Gabbroic rocks along the margin of the complex occur mostly as tabular bodies within, or on top of, upper-plate strata; in places, however, gabbros form the sole of the upper plate. The central part of the gabbroic complex consists of apparently continuous gabbro and overlying comagmatic mafic extrusive rocks.

The virtual restriction of gabbroic rocks to the upper plates and the fact that gabbro does not cut across the thrust planes indicate that intrusion occurred before or during thrusting. Structural and petrologic relationships suggest that the gabbros were liquid, at least in part, during emplacement of the thrust blocks. According to these relationships, the age of the gabbroic complex should approximately date the thrusting. A potassium-argon age of primary biotite from the complex is $(150 \pm 3) \times 10^6$ years; consequently, the probable date of intrusion and thrusting is Late Jurassic. The thrust plates overlie rocks containing Early Jurassic fossils. If these time relationships are correct, thrusting in this area occurred near the onset of the widespread Jurassic-Cretaceous orogeny in northwestern Nevada.

1966 GSA Abs p.1

p 208

Mechanics of Emplacement of a Gabbroic Lopolith, Northwestern Nevada

SPEED, ROBERT C., *Geology Dept., Northwestern University, Evanston, Ill.*

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Humboldt Gabbroic Complex, Nevada 1962 GSA Abs.

SPEED, ROBERT C., *Stanford University, Palo Alto, Calif.*

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A possible volcanic-exhalative origin for lenticular nickel sulfide deposits of volcanic association, with special reference to those in western Australia

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Received 6 May 1975

Revision accepted for publication 8 December 1975

Archean lenticular nickel sulfide deposits of volcanic association bear a striking resemblance to volcanic-exhalative Cu-Zn massive sulfide deposits. They have similar morphologies, show well developed mineralogical layering, and exhibit close stratigraphic relationships with intimately associated volcanics and intra-volcanic sediments of greenstone belts. The nickel sulfide deposits are associated with early ultramafic/mafic volcanics, and massive Cu-Zn sulfide deposits with intermediate to silicic volcanics that formed later in volcanic-sedimentary cycles.

It is suggested that a magmatic volcanic-extrusive origin does not explain features of massive nickel sulfide deposits as well as an alternative volcanic-exhalative origin, which provides a direct link between sulfide ores and intimately associated exhalative sediments. It also satisfactorily accounts for a number of important features, including mineralogical layering, a relative enrichment in pyrite, and the local abundance of millerite.

Outpouring of extremely hot ultramafic lavas across top surfaces of deposits would partially melt the Ni-Cu sulfides, thereby generating the igneous textures observed. Later regional metamorphism has modified these earlier features.

Les gisements archéens et lenticulaires de sulfure de nickel associés à du volcanisme ressemblent beaucoup aux gisements de sulfures massifs de cuivre et zinc d'origine d'exhalation volcanique. Ils sont semblables morphologiquement, ils montrent des couches bien développées de minéraux et leurs relations stratigraphiques avec les volcaniques associées, les sédiments intra-volcaniques des ceintures de roches vertes sont parfaites. Les gisements de sulfure de nickel sont associés aux volcaniques basiques et ultrabasiques précoces, et les gisements de sulfures massifs de cuivre et nickel sont associés aux volcaniques acides à intermédiaires qui sont arrivées plus tard dans les cycles volcaniques et sédimentaires.

Nous suggérons qu'une origine magmatique extrusive n'explique pas les caractéristiques des gisements de sulfure de nickel massif aussi bien qu'une origine d'exhalation volcanique qui fournit un lien direct entre les sulfures et les sédiments intimement reliés à l'exhalation.

Elle tient compte aussi de façon satisfaisante d'un bon nombre de caractéristiques importantes, telles les couches de minéraux, un enrichissement relatif en pyrite, et une abondance locale de millérite.

Les épanchements de laves ultrabasiques extrêmement chaudes à la surface des dépôts fusionneraient partiellement les sulfures de cuivre et de zinc produisant les structures éruptives observées. Le métamorphisme régional subséquent a modifié ces premières caractéristiques.

[Traduit par le journal]

Can. J. Earth Sci., 13, 451-458 (1976)

Introduction

Naldrett (1973) attempted to classify nickel sulfide deposits with the aim of contributing to an understanding of genesis, and to guiding exploration for volcanic-association nickel sulfide deposits, which may become increasingly important in the future. He concluded that a possible volcanic-extrusive origin should be borne in mind for volcanic association deposits and their ultramafic associates.

Derivation of this class of deposit through deposition from immiscible oxy-sulfide liquids introduced together with ultramafic host mag-

mas has also been invoked by others (e.g. by Nesbitt 1971; Hancock *et al.* 1971; and Ewers and Hudson 1972, for W Australian deposits). A sulfurization hypothesis involving copper and nickel derived from ultramafic magmas and sulfide sulfur derived from chemical sediments and basaltic lavas was suggested by Prider (1970) for the same deposits.

The present contribution attempts to show that a volcanic-exhalative origin should be considered seriously, as a possible alternative for lenticular nickel sulfide deposits of volcanic association.

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Classification, Setting, and Distinguishing Characteristics of Lenticular Nickel Sulfide Deposits of Volcanic Association

Kilburn *et al.* (1969), Naldrett and Gasparrini (1971), and Naldrett (1973) attempted to classify Ni sulfide deposits, primarily on the basis of geological setting of associated ultramafic and related mafic rocks. Kilburn *et al.* subdivided Canadian nickel sulfide deposits into layered intrusive, orogenic, and volcanic associations. Their *orogenic* association includes deposits located along or adjacent to major crustal sutures separating geological provinces, whereas their *volcanic* association includes deposits distributed randomly throughout thick volcanic-sedimentary sequences. Naldrett and Gasparrini grouped Canadian Archaean ultramafics and associated deposits into two broad categories; namely, those in *orogenic* and those in *non-orogenic* or *intracratonic* environments. Naldrett followed this scheme with respect to his orogenic volcanic association deposits, but expanded the overall classification to include other classes of nickel sulfide deposits as well. Within his volcanic association, he recognized ultramafic sill (I(i)) and lens (I(ii)) classes, both of which are represented in Archaean greenstone belts of the Canadian, South African, and Australian shields (Naldrett 1973). Of these, class I(ii) deposits appear at present to be overwhelmingly important economically and in terms of frequency of occurrence.

The geological settings of Naldrett's volcanic association nickel sulfide deposits appear to be seafloor volcanic or shallow sub-volcanic marine environments featuring ultramafic to mafic volcanics with tholeiitic affinities (Naldrett and Gasparrini 1971). Demonstration of the shallow emplacement of these volcanics is afforded by pillow and pahoehoe-like developments, and by spinifex textures at the tops of multiple thin sheets, or at the margins of intrusive lenses and their connecting feeders (Naldrett 1973). Volcanics of the lens (I(ii)) association are largely conformable with stratigraphy and show little or no differentiation, in contrast to many examples of the sill (I(i)) association (Naldrett 1973). The extensive volcanics are accompanied by sediments, including chemical varieties that accumulated during periods of quiescence.

Nickel sulfide deposits of the ultramafic lens (class I(ii)) association tend to be small, to occur toward the bottoms of ultramafic lenses, and are

distinguished from other classes of nickel deposits by their relative enrichment in nickel and sulfur (Naldrett and Gasparrini 1971). The size of deposits, as judged by numerous Canadian examples, is generally small, ranging from a few tens of thousands up to a maximum of around four million tonnes for the Texmont deposit. They occur variously between and toward the tops(?), but most often as massive and disseminated sulfides toward the bottoms of lenses. Although nickel values vary considerably (5.7% at Alexo to 35% at Marbridge), nickel is most enriched relative to copper (*i.e.* lowest Cu/(Cu + Ni) ratios, approximating 0.025) in this class of deposit, and millerite can be an abundant mineral. Their higher sulfur content is inferred from the qualitative observation that pyrite, which may occur as layers or schlieren in massive pyrrhotite-pentlandite ore, is appreciably more abundant in this type of nickel sulfide deposit. There appears to be a paucity of quantitative data that would enable proper testing of this observation.

Comparison with Features of Archaean and Other Volcanic-Exhalative Cu-Zn Sulfide Ores

Comparison of features of class I(ii) nickel sulfide deposits with volcanic-exhalative massive Cu-Zn sulfide deposits seems justified on the basis of shared lenticular form, banded character of their massive sulfide ores, a common enrichment in Cu and S, and their mutual intimate relationship with volcanic/sedimentary rocks that accumulated in similar submarine settings. Although similar settings are inferred, there appears to be a clear-cut temporal and spatial separation between the deposits. Class I(ii) deposits are associated with abundant early ultramafics in older volcanic-sedimentary cycles, whereas volcanic-exhalative Cu-Zn deposits tend to be associated with intermediate to silicic volcanics that developed later during individual cycles, and tended to become more abundant in younger cycles (Anhaeusser 1971; Goodwin 1971). The Abitibi orogenic zone in the Superior Province of Eastern Canada affords an example in which both kinds of deposit occur within the same Archaean greenstone belt, and the Cu-Zn sulfide deposits of Cyprus serve as much younger examples that are associated with mafic rather than intermediate or silicic volcanics.

Volcanic-exhalative Cu-Zn deposits in the

Noranda area of the typical of their class, in association with rhyolite form part of a near-circular more than 10 km across the latter, the deposit upper and lower contact with rhyolite formations (Sangster) remarkable stratigraphic horizon is also marked by chemical sediments, concretion iron formation and chert as the regional stratigraphic sulfide deposits (Sangster) volcanic-exhalative origin products.

While the volcanogenic deposits of Cyprus exhibit graphic control, the late containing them bear resemblance to the mafic containing Archaean deposits. The Cypriot contact between a 900 m thick low basalts and an underlying more mafic basalts, sheet gabbro, and serpentinized pillow development (Sangster) of Fe- and Mn-rich sulfide bands overlies the young Searle (1972), abnormality of As, Co, Bi, Se, Mo, the shales and sulfide ore in the lavas.

Lens-shaped bodies of Cu-Zn sulfides may have and diffuse lower contact to cylindrical-shaped altered disseminated and stringer more copper-rich: see Sangster 1972; Searle 1972; and Goodwin 1971). Examples of this to be common among deposits occurring in brittle (Sangster 1972), but are more subtly developed in footwall rocks, and footwall sharp. Only one occurrence of Cyprus deposits, the strong alteration and steep underlying pillow lavas (Sangster) While lenticular nickel

Noranda area of the Abitibi orogenic zone are typical of their class, in that they occur in close association with rhyolites and andesites that form part of a near-circular volcanic complex more than 10 km across (Sangster 1972). Within the latter, the deposits are restricted to both upper and lower contacts of only one of five rhyolite formations (Sharpe 1968), thus showing remarkable stratigraphic control. This favorable horizon is also marked by an association of chemical sediments, comprising various facies of iron formation and cherts, which are regarded as the regional stratigraphic equivalents of the sulfide deposits (Sangster 1972). A common volcanic-exhalative origin is implied for all these products.

While the volcanogenic Cu-Zn sulfide deposits of Cyprus exhibit similar close stratigraphic control, the late Mesozoic volcanic rocks containing them bear a closer compositional resemblance to the mafic/ultramafic successions containing Archaean lenticular nickel sulfide deposits. The Cypriot deposits occur at the contact between a 900 m succession of younger pillow basalts and an underlying pile comprising more mafic basalts, sheeted intrusive diabase and gabbro, and serpentinitized ultramafics showing pillow development (Searle 1972). A thin veneer of Fe- and Mn-rich shales containing cherty bands overlies the younger basalts. According to Searle (1972), abnormally high concentrations of As, Co, Bi, Se, Mo, and Sb are common to the shales and sulfide ores, but were not detected in the lavas.

Lens-shaped bodies of delicately banded Cu-Zn sulfides may have sharp upper contacts and diffuse lower contacts, which overlie funnel- to cylindrical-shaped alteration zones containing disseminated and stringer ore (characteristically more copper-rich; see, for example, Sangster 1972; Searle 1972; and Tatsumi and Watanabe 1971). Examples of this kind of deposit appear to be common among Archaean Cu-Zn deposits occurring in brittle rhyolitic wall rocks (Sangster 1972), but are relatively scarce or much more subtly developed among Phanerozoic deposits, where metasediments commonly form the footwall rocks, and footwall contacts are also sharp. Only one occurrence among the numerous Cypriot deposits, the Limni Mine, shows strong alteration and stockwork development in underlying pillow lavas (Searle 1972).

While lenticular nickel sulfide deposits differ

notably from Cu-Zn massive sulfide deposits in being nickel-rich and having ultramafic host or wall rocks, there is increasing awareness that these ultramafic lenses appear to be largely if not entirely volcanic, and that the nickel deposits tend also to be located in stratigraphic horizons shared by iron-rich chemical sediments. These characteristics are well illustrated by nickel mineralization associated with the Kambalda Dome in Archaean greenstones of the Eastern Goldfields of Western Australia (see Figs. 1a and 1b). Here, at least ten areas of Cu-Ni mineralization, aggregating some 19 million tonnes of ore, occur at the contact or within the lower part of a 600 m thick, ultramafic lava sequence that overlies pillowed tholeiitic basalt (Ross and Hopkins 1973). According to Ross and Hopkins, approximately 75% of the mineralization occurs as banded stratiform massive sulfide bodies located at the base of the ultramafics, and most of the balance is located within 100 m of the lower contact, typically in close proximity to the contact ores. Thin conformable horizons of sulfide-bearing shales and chert occur at interfaces between extrusive units, particularly at the lower contact and within the lower half of the ultramafic sequence. However, Ross and Hopkins reported that these are conspicuously absent in close proximity to contact orebodies. Nevertheless, their presence and overlapping spatial relations with sulfide mineralization show a close parallel with volcanic-exhalative Cu-Zn mineralization.

The Windarra deposits in the Eastern Goldfields afford an excellent example of lenticular nickel sulfide mineralization showing stratigraphic control on a larger scale and overlapping spatial associations with developments of chemically precipitated magnetic iron formation. As shown in Fig. 1c, the Windarra deposits with their associated magnetic iron formation occur some 15 km apart, and are stratigraphically located at or near the footwall of a sheeted ultramafic complex (Robinson *et al.* 1973). Massive and disseminated ores are represented, and thin ore lenses show intimate relationships with the banded iron formation. The F shoot at Mt. Windarra is associated with a discontinuous metasedimentary horizon within ultramafics, and a minor ore development at South Windarra reputedly occurs within banded iron formation (Robinson *et al.* 1973).

Another feature common to class I(ii) nickel

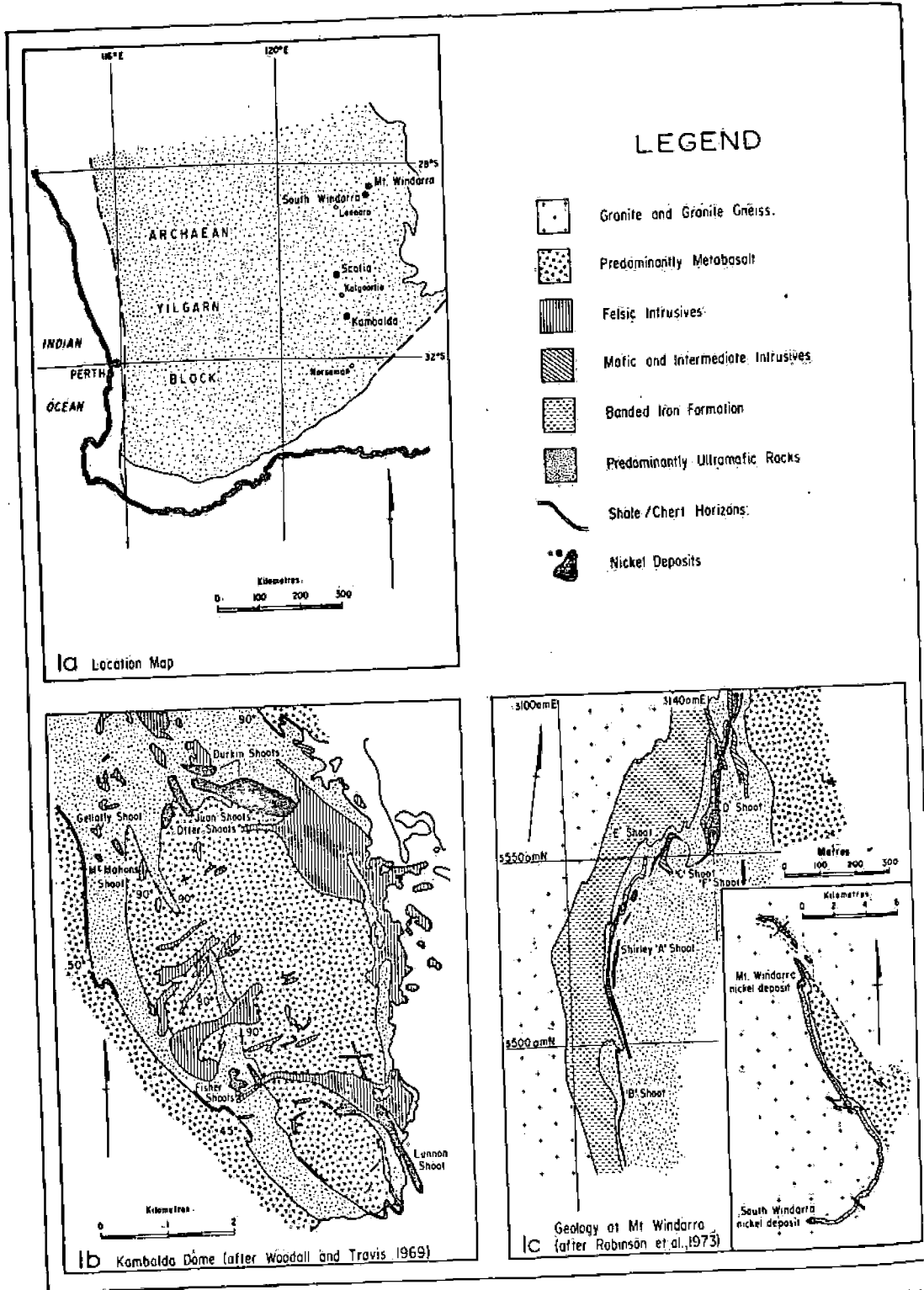


FIG. 1. a. Location Map; b. Kambalda Dome (after Woodall and Travis 1969); c. Geology at Mount Windarra (after Robinson et al. 1973).

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sulfide deposits and volcanic-exhalative Cu-Zn sulfide deposits is that they appear to occur close to either margins of associated principal volcanic units (Naldrett 1973; Sangster 1972). The complexly deformed Marbridge No. 3 deposit in the Abitibi greenstone belt serves as an example where disseminated and stringer-type nickel mineralization is interpreted to occur toward the stratigraphic top of an ultramafic lens (Graterol and Naldrett 1971). In this deposit, stringers of massive nickel-bearing ore occur along fractures in the ultramafic body close to the contact, but grade into disseminated mineralization with increasing depth into the host (Graterol and Naldrett 1971). Pyrite with subordinate pyrrhotite occurs in amounts up to 5% in volcanic rocks throughout the area, and up to 70% within a thin sulfide-rich band in the vicinity of the deposit. The latter shows distinct mineralogical zonation, grading downward from a pyrite-pyrrhotite-pentlandite zone (Zone 1—Naldrett and Gasparini 1971), into a millerite-pyrite-pentlandite ore zone (Zone 2). Below the latter and toward the centre of the peridotite, there occur small amounts of heazlewoodite, pentlandite, and minor millerite contained in late-stage green serpentine veinlets.

The Scotia deposit in the Eastern Goldfields (see Fig. 1a for location) is of special interest here, because metasediments immediately underlying the deposit contain high nickel values and show development of bleach zones suggestive of hydrothermal alteration (Christie 1972). Christie noted that the deposit consists of a small lens at the base of a 600-m thick ultramafic pile, separated from an underlying sequence of basic volcanics by a thin (~15 m thick) veneer of metasediments, comprising graphitic slates and quartz-biotite schists intercalated with probable basic tuffs. Notably within these metasediments below the orebody there occur pods of 'buff-grey, textureless' rock—up to 20 m long and 3 m wide—that Christie interpreted as hydrothermally altered rock. The latter contains fine impregnations of nickel sulfides, which yield nickel values up to 7 wt%.

The Marbridge and Scotia examples variously illustrate the variable stratigraphic location of class 1(ii) nickel sulfide mineralization with respect to ultramafic lenses, the development of both mineralogical zoning and of stringer ore grading downward into disseminated mineralization, the persistence of disseminated sulfides in

adjacent metasedimentary wall rocks, and of possible hydrothermal alteration in rocks underlying the deposits. All of these features are observed in volcanic-exhalative Cu-Zn deposits.

A Re-examination of the Features of Class 1(ii) Nickel Sulfide Deposits in the Light of a Possible Volcanic-Exhalative Origin

Any attempt to explain the genesis of a given class of deposit runs the risk of misadventure if it does not adopt an overview approach, at least in the initial stages. This kind of error was made in the case of volcanic-exhalative massive sulfide deposits up until about 1960 (see Stanton 1972, pp. 31–35), and perhaps is being repeated for the lenticular nickel sulfide deposits of volcanic association considered here. This is evidenced by recent preoccupation with only certain aspects of class 1(ii) nickel sulfide deposits, namely: (1) the consistently close association with ultramafic rocks that are enriched in nickel, and whose magmas are capable of dissolving some Fe-Ni-Cu sulfides; (2) a tendency for heavy massive sulfides and their overlying disseminated zones to occur near the stratigraphic bottoms of ultramafic units; (3) location in foot-wall bulges of ultramafic units, believed (though generally not proven) to be pre- or syn-emplacment structural downwarps; and (4) textural features—particularly in disseminated ores—that clearly indicate crystallization from melts. Consideration of these factors, alone constitutes strong evidence for the existence of a genetic link between the ores and ultramafic magmas and, by implication, a magmatic origin for both.

In a narrow sense, the principal recurring difficulties confronting a magmatic origin for lenticular nickel sulfide deposits appear to be the lack of consistency for (2) above, and their unusual enrichment in sulfur, reflected by the relative abundance of pyrite, which can exist as small scale schlieren or discrete layers paralleling mineralogical layering and contacts in massive ores. The increasing recognition of ultramafic lenses as comprising a succession of thin lava flows with interlayered sulfide lenses and chemical sediments in places is a less important difficulty. Nevertheless, it poses transportation and sulfide/silicate volume problems, requiring separate sulfide and silicate rest magmas that can be selectively "tapped" (Naldrett 1973, p. 60). While the ubiquitous association of mineralogical banding in massive class 1(ii) nickel sulfide de-



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posits presents a problem for a magmatic origin in general terms, its generally strong development in these ores cannot be regarded as a serious criticism, as banding exists locally in some Sudbury ores (*e.g.*, some contact ores in the Strathcona deposit).

In an overview sense, a magmatic origin is at a loss to directly link the deposits to spatially associated volcanic-exhalative units occurring at similar levels, or to satisfactorily explain other features shared by them and volcanic-exhalative Cu-Zn deposits described previously. Indeed, these close similarities between both classes of deposit suggest a common volcanic-exhalative origin that can provide a direct genetic link between massive sulfides and iron-rich chemical sediments. Consequently, it is necessary to ask whether a submarine volcanic-exhalative origin is feasible for class I(ii) nickel sulfide deposits.

A submarine volcanic-exhalative origin implies that hydrothermal fluids containing metal- and sulfur-bearing compounds are discharged through sea floor fumaroles, around which metal sulfides precipitate as lenticular accumulations of banded chemical sediments. Associated hydrothermal activity in the vicinity of vent walls close to the sea floor produces the disseminated/stockwork mineralization and alteration observed in some deposits.

The prerequisites for a volcanic-exhalative origin include the heat source provided by volcanism, aqueous fluids of igneous or hybrid origin, and a supply of metals and reduced sulfur, which could be igneous or leached from wall rocks by hot circulating fluids. The existence of plumbing connections (*e.g.*, fumarolic vents, fractures, permeable rocks, *etc.*) between sea floor and high level ultramafic magma reservoirs—possibly largely liquid, with temperatures around 1450 °C (Nesbitt 1971; Naldrett 1973)—may have permitted escape of juvenile saline fluids, and/or promoted convective circulation of heated hybrid, connate, or sea water above such reservoirs. These fluids may have contained adequate concentrations of dissolved Fe, Ni, Cu, and S, and/or leached some or all of these elements from existing ultramafic or tholeiitic lavas. However, the uniquely low Cu/(Cu + Ni) ratios shown by the deposits tentatively favour an association with ultramafic parents (Cameron *et al.* 1971; Naldrett 1973).

Because there is no reason for supposing that the above-mentioned prerequisites could not

have been satisfied, it is suggested that submarine fumarolic activity probably yielded the massive nickel sulfides, and certainly contributed to the formation of the intimately associated and more widely distributed Archaean cherts and iron-rich sediments that are similar to exhalative deposits presently forming on the crest of the East Pacific Rise (Bostrom and Peterson 1966). The latter are notable in being relatively enriched in Fe, Mn, Cu, Cr, Ni, and Pb, with Fe oxide accounting for up to 60 wt% of the sediments. Accordingly, consistently close spatial and temporal relationships between exhalative sulfides and iron-rich chemical sediments might be expected, but consistent stratigraphic relationships between sulfide ores and extrusive volcanic wall rocks would not necessarily follow.

In addition to offering a satisfactory explanation for the lenticular shapes and banded character of the massive ores, a volcanic-exhalative origin can also account for other features, including the presence of millerite and the relative abundance of pyrite in these ores. Nickel, like Fe and Cu, can precipitate from low temperature aqueous solutions as the monosulfide (Zaritskiy 1972), and exist as millerite in Ni-rich assemblages below about 300 °C (Kullerud *et al.* 1969). Layered pyrite forms diagenetically through reaction of iron sulfide with elemental sulfur (possibly by the mechanism suggested by Roberts *et al.* 1969, and others), which may have formed through oxidation of volcanic H₂S (Lusk 1972). Consequently, a relative abundance of pyrite probably reflects an excess of precipitated volcanic sulfur, and marked changes in pyrite/pyrrhotite proportions across the mineralogical layering in volcanic-exhalative ores attest to the variability of the sulfur-generating mechanism. Thus, a volcanic-exhalative origin offers a reasonable explanation for the occurrence of millerite and for the development of pyrite-rich layers in massive pentlandite-pyrrhotite ore.

The rapid extrusion of an ultramafic lava sheet across the top surface of a chemically precipitated nickel sulfide deposit on the sea floor should succeed in melting at least some of the upper portion of the deposit, thereby yielding magmatic textures and the disseminated ores observed. The intensity of contact effects would depend on a number of factors, of which magmatic temperature, and the thickness and composition of massive sulfides are probably the most important. Rapid heating by an ultramafic lava with a

temperature around 1000 °C should present no difficulty in locally melting Ni-Cu (± magnetite) sulfides, and in generating a liquid phase around 1000–1100 °C (Yoder 1963) and in generating a liquid phase from pyrite breakdown at temperatures (≥ 743 °C: Craig 1963) thus at some distance from the source. The migration of a sulfur-rich fluid should be particularly rapid because of its anticlockwise changes at the contact. Because of its anticlockwise migration, sulfur-rich fluid should be particularly abundant at the bottom of an overlying magma chamber (Yoder 1963) with the liquid oxy-sulfide phase. This would then favor a gradient in temperature to produce disseminated sulfides.

Subsequent regional metamorphism modified the massive ores to a type comparable to that of massive Cu-Zn deposits. The ores, together with deformational features during metamorphism, adjustments tending to produce morphic banding. The ores, both kinds of deposit

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The present contrast shows that Naldrett's deposits have many features of volcanic-exhalative origin. The origin in the light of exhalative origin suggests only feasible, but an explanation for many of

The likely possibility of origin suggests that the occurrence and distribution of sulfide deposits should be explored for further deposits. In particular, control, and possibly deposits around larger small felsic intrusions (Sangster 1972), are:

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temperature around 1450 °C should encounter no difficulty in locally melting pyrrhotite-rich Ni-Cu (\pm magnetite) ore with a melting point around 1000–1100 °C (Craig and Kullerud 1969), and in generating a sulfur-rich fluid resulting from pyrite breakdown at much lower temperatures (\geq 743 °C: Craig and Kullerud 1969), and thus at some distance from the contact. Generation of a sulfur-rich fluid from pyrite breakdown should be particularly effective in promoting changes at the contact and near-contact area. Because of its anticipated lighter density, any sulfur-rich fluid should rise upward through the bottom of an overlying ultramafic lava and engage in sulfurization reactions (see Kullerud and Yoder 1963) with the silicate magma to yield liquid oxy-sulfide globules, whose formation would then favor a gravitational settling process to produce disseminated ores above the massive sulfides.

Subsequent regional metamorphism(s) has modified the massive nickel ores in a manner comparable to that observed in volcanic-exhalative Cu-Zn deposits. The effects of dislocation together with deformation and recrystallization during metamorphism have resulted in fabric adjustments tending to obliterate the premetamorphic banding. These effects are common to both kinds of deposit.

Conclusion

The present contribution has attempted to show that Naldrett's class I(ii) nickel sulfide deposits have many features in common with volcanic-exhalative Cu-Zn deposits. Their examination in the light of an alternative volcanic-exhalative origin suggests that this origin is not only feasible, but appears to offer a better explanation for many of the features exhibited.

The likely possibility of a volcanic-exhalative origin suggests that lessons learned from the field occurrence and distribution of Cu-Zn massive sulfide deposits should be borne in mind when exploring for further lenticular nickel sulfide deposits. In particular, the close stratigraphic control, and possible clustering of Cu-Ni deposits around larger volcanic centres containing small felsic intrusions and favorable fault linears (Sangster 1972), are among the more important.

Acknowledgments

The generous assistance given by Mr. W. Steel, General Manager, and by Messrs. K.

Schultz and D. Christie of Great Boulder Mines, Limited, is gratefully acknowledged. Thanks are also extended to the Geological Staff of Western Mining Corporation, and to Mr. J. Ross in particular.

I am grateful to Dr. D. Durney for reading and commenting on the manuscript, and to many individuals involved in research and exploration for western Australian nickel deposits who gave freely of their time to discuss problems and research projects. However, any errors, misinterpretations, and personal ideas suggested herein are entirely my responsibility.

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