

COMPARATIVE ASSESSMENT OF FIVE
POTENTIAL SITES FOR HYDROTHERMAL
MAGMA SYSTEMS: GEOCHEMISTRY*

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P R E F A C E

The object of the thermal regimes part of the Continental Scientific Drilling Program (CSDP), sponsored by the U.S. Department of Energy (DOE), is the development of a fundamental understanding of hydrothermal-magma systems through the utilization of drilling to obtain samples, data and to conduct down hole experiments. The rationale and scientific basis for this endeavour has been presented in the NAS/NRC Workshop Report on CSDP (1979). The goals are the understanding of heat and mass transfer within, and between, magma and hydrothermal regimes and the evaluation of hydrothermal-magma systems in space and time. Their attainment rests on the ability to characterize and interpret hydrothermal-magma systems at depth in terms of physical, thermal, mechanical and mineralogical properties. Both dedicated scientific drill holes and add-on experiments in existing drill holes or in holes planned primarily for other purposes can be used in achieving the program goals.

In the CSDP, the effective use of financial and personnel resources will require focusing on a particular subset of a large number of potential hydrothermal magma systems. To accomplish this purpose an Interlaboratory Working Group (IWP) comprising four DOE laboratories, Lawrence Berkeley Laboratory, Lawrence Livermore National Laboratory, Los Alamos Scientific Laboratory and Sandia Laboratory, was formed to assess various sites in a comparative fashion. IWP has selected five possible sites for detailed and comparative site analysis. These sites are The Geysers-Clear Lake Region, California, Long Valley, California, Rio Grande Rift, New Mexico, Roosevelt Hot Springs, Utah and Salton Trough, California. The comparative site assessment document prepared by IWP is divided

P R E F A C E (Cont'd)

into sections encompassing geology, geochemistry, geophysics and heat and mass transport. Each sub-report issued by an individual laboratory but including contributions by personnel of all laboratories contains a section A, an introduction and discussion of general scientific questions and a section B, a review of the information available concerning each site. Section C, which contains specific recommendations on individual sites, is being issued as a separate document.

The following document covers parts A and B of the geochemistry sub-report.

PART A INTRODUCTION

The CSDP drilling program will offer an unparalleled opportunity to obtain data to answer basic geochemical questions concerning magma/hydrothermal regimes. The final site selection will depend in part on the relative probabilities of answering these questions by drilling at specific sites. This section of the site assessment document consists of two parts: the first includes a brief discussion of the geochemical objectives and questions that must be addressed in such an evaluation, and the second is a summary of the currently published literature that is pertinent in answering these questions.

In general, the major geochemical processes associated with proposed hydrothermal sites can be categorized into three groups: 1) geochemistry of magma and associated volcanic rocks, 2) geochemistry of hydrothermal solutions and 3) geochemistry of hydrothermal alteration. The remainder of this report will be generally organized around these three categories. Data from individual geochemical disciplines such as isotope geochemistry are incorporated into each category.

I.A. Geochemistry of Magma and Associated Volcanic Rocks.

Primary magma sources in the earth's mantle are unreachable by present drilling technology. However, magma regimes which have been generated or introduced in the earth's crust at shallow depth represent more attainable targets for investigation. The five proposed drilling sites represent such targets. However, their tectonic setting and type and origin of magmatism appear to vary widely. Two of the areas, Long Valley and The Geysers-Clear Lake area, are inferred to be underlain by single, large magma chambers. One of the areas, Roosevelt Hot Springs geothermal area, may also be underlain by

such a magma chamber. The remaining two areas, the Salton Sea geothermal area and the Rio Grande rift, occur in rift settings. The Salton Sea area is located on an oceanic ridge-transform zone. It apparently is not underlain by a single large magma chamber; instead, the thermal anomaly is caused by dike injection from small spreading centers into a region of young, thin lithosphere. The Rio Grande rift is a major continental rift, related to the Basin and Range extensional province. It is the most complex and diverse of the areas, being 1000 km long and bordering several geologic and physiographic provinces. At least one area, the Jemez Mountain-Valles Caldera is probably underlain by a large, high level, silicic magma reservoir.

While geologic and geophysical techniques can provide information regarding the depth, size, and heat distribution of such magma bodies, igneous geochemistry is the principal method available in addressing questions concerning the origin and evolution of magmatic systems at a given site. Questions to be addressed are: From what depth, pressure and temperature is a specific magma body derived? From what materials? Has the magma interacted with the crust or with other magma bodies? What are the details of the magmatic plumbing system? Other questions can certainly be formulated.

Even with a successful drilling program, it is doubtful whether a representative magma sample can be obtained at a given site. Therefore, the answers to many of these questions will have to be derived from detailed geochemical study of the drill cores of associated volcanic rocks. For example, to answer the questions of the extent to which magmas are primitive (i.e. in equilibrium with mantle material) or evolved can be approached by relating the detailed trace and major element and isotope geochemistries of volcanic rocks to each other and to surrounding country rocks. Such data can

be interpreted by formulating quantitative models to explain relevant evolutionary processes. Significantly, geochemical techniques involving petrology and mineralogy must be applied not only to the youngest rocks at a site which may be most representative of the present magma body but to all rocks preserved in the geologic section. Such data are invaluable in defining the origin and long term evolution of the magma system.

I.B. Geochemistry of Hydrothermal Fluids

All of the proposed sites possess surface manifestations of hydrothermal activity to varying degrees. Two of the sites, The Geysers and to a lesser extent the Valles Caldera in the Rio Grande Rift, possess vapor-dominated systems. Data available from drilling indicates that all sites also possess active hydrothermal systems extending to considerable depths.

In general, the data describing the chemistry of both the aqueous and gaseous phases derived from deep drilling have two applications. One application is related to answering scientific questions in related fields. For example, chemical geothermometers can be used to estimate reservoir temperatures. Isotope data can be employed in estimating the age and origin of the hydrothermal water. Trace element and isotope data can be used to define avenues of recharge into the hydrothermal reservoir. Dissolution and aqueous equilibrium constraints can be applied to determine the effects of aqueous chemistry in controlling secondary permeability and reservoir evolution.

The second avenue of approach is to use the data to answer basic questions concerning chemical mechanisms and evolution of hydrothermal fluids. For example, the literature indicates that the hydrothermal fluids at all sites are high in certain trace elements such as As, B, Br, F and Li. What is the source of these elements? To what extent are they derived directly from

juvenile or magmatic sources and to what extent from dissolution of reservoir rocks? What is the source of the abundant sulfur associated with these hydrothermal solutions and gases? The fluid chemistries at all five sites are dominated by sodium chloride either as dilute or concentrated brines. Can such similarity in chemistry be produced by very different chemical mechanisms? For example, evaporite dissolution has been the suggested sodium chloride source in the Salton Trough as compared to rhyolite dissolution in Long Valley. Does such similarity indicate a common trend in evolution? Are vapor-dominated systems such as The Geysers underlain by concentrated sodium chloride solutions?

Another major geochemical question to be addressed is the relationship between hydrothermal solutions and formation, transport, and deposition of ore forming elements. Is mercury deposition indicative of a present or past vapor dominated system? What is the source of heavy metals in the Salton Trough and is their transport directly related to the concentrated brine chemistry? Are the sources of these elements related to a magma system or do they result from leaching of reservoir rocks? Other questions must be answered concerning the mechanisms which control the observed relationships of geothermometers such as in the Na-K-Ca system.

In order to address questions from data obtained by drilling at a specific site, an increase in understanding basic geochemical processes is needed. This includes such basic rock/water interactions as the kinetics of dissolution and precipitation at high temperatures as well as speciation of chemical elements in aqueous phases in concentrated solutions. In addition, technological advances in sampling in-situ solutions at high temperatures, pressures and great depths must be developed.

I.C. Geochemistry of Hydrothermal Alteration

Hydrothermal alteration represents the interface between the aqueous and/or vapor geochemistry and the geochemistry of the reservoir rock, either volcanic or other type. Such alteration may be controlled by the development of hydrothermal circulation. In turn, hydrothermal alteration may increase or decrease rock permeability and affect both circulation and convective heat transport. Such hydrothermal alteration also offers a record of not only present hydrothermal processes but also the past spatial, chemical and temperature regimes in such systems. Access to such a record would be important if hydrothermal alteration reduced permeability sufficiently to cause a liquid-dominated hydrothermal system to evolve into a vapor-dominated system. Spatial distribution of hydrothermal alteration is also important in evaluating geophysical anomalies associated with geothermal sites.

Deep drilling also offers an opportunity to observe alteration assemblages and specific hydrothermal solutions at known temperatures and pressures. These data will provide much needed tests of existing mass transfer codes and permit evaluation of the feasibility of inferring the thermodynamic properties of hydrothermal fluids from alteration assemblages. In addition, it should be possible to evaluate the lower temperature limits for fluid/rock chemical equilibrium. Such data will also answer the question of the effect of reservoir rock type on the observed alteration sequence and the influence of temperature on this relationship. Drilling in a vapor dominated regime will furnish much needed information on vapor-rock interaction.

Use of mass transfer models for quantitative characterization of hydrothermal processes requires a major increase in the chemical/mineralogical data

for alteration phases and the corresponding reactant assemblages. Solid solution variations and substitutional order/disorder phenomena must be explicitly accounted for in analysis of alteration mineral assemblages and coexisting hydrothermal fluids. Determinations must be made of weight percent modes for altered and unaltered rocks. In addition, the thermodynamic data base must be expanded to describe mineral equilibria at temperatures and pressures encountered at proposed sites.

PART B Review of Existing Information

This summary is intended for use in selection of a site for continental scientific drilling and as a basis for research proposals from the scientific community. It is not meant to be an exhaustive review nor an interpretive synthesis of available information. As will become apparent, a considerable variation exists in the amount of information available at different sites. In geochemistry, as in other scientific endeavors, an increase in the amount of information concerning a given subject generally leads to an increase in the number of proposed questions. In a sense, the skewness in site information tends to prejudice the assessment in favor of sites with the greatest available information simply because these sites appear to raise the greatest number of scientific questions. However, another way of assessing the importance of available information lies in the fact that probability of selecting a limited number of drill sites that can lead to meaningful scientific information increases with an increase in definition of known parameters.

I. THE GEYSERS - CLEAR LAKE REGION

The Geysers - Clear Lake Region lies in the northern part of the California Coast Ranges in Lake, Mendocino, Napa and Sonoma Counties. The Geysers steam field, currently the world's largest commercially developed geothermal resource, is located near the crest of the Mayacmas Mountains, a northwest trending highland composed of a series of steep linear ridges and canyons. The reservoir rock is a massive Franciscan graywacke which is dense and virtually impermeable. Steam flow occurs only in open fractures. The Clear Lake basin lies northeast of the Mayacmas Mountains. This topographically low area contains many volcanic domes and lava flows, some very recent (10,000 Y.B.P.). Geophysical surveys suggest a large heat source, consisting of a shallow (3-5 km) magma body underlies Mt. Hannah located between Clear Lake and the Geysers.

I.A. Geochemistry of Primary Volcanic Rocks

I.A.1 Petrology and primary mineralogy

Volcanic rocks of the Geysers -- Clear Lake area are divided into two main sequences: the northern part of the Sonoma Volcanics, which are older than 2.9 m.y., and the Clear Lake Volcanics, which range in age from 2.1 - 0.01 m.y. The northern Sonoma Volcanics consist primarily of pyroclastic rocks (about 80%), with about 15% rhyolite and 5% andesite flows.

The Clear Lake Volcanics consist of four distinct age groups, with lavas ranging from basalt to rhyolite, and have been related to extrusion above a major (1430 km³), evolving magma chamber (e.g., Hearn et al., 1980). These age groups are:

Group 1	0.2 - 0.01 m.y.
Group 2	0.65 - 0.30 m.y.
Group 3	1.2 - 0.8 m.y.
Group 4	1.3 - 2.1 m.y.

Lavas of group 4 consist mainly of basalt, basaltic andesite, and andesite. Hearn et al. (1980) conclude that evidence for a major magma chamber for these rocks is lacking. The small amount of andesitic to rhyolitic lavas could have been derived from a small -- now cool -- magma chamber. Lavas of group 3 consist of andesite, dacite, and rhyolite. Group 2 consists mostly of dacite. Group 1 lavas again consist of basalt, basaltic andesite, andesite, dacite, and rhyolite.

Petrographically, basalts and basaltic andesites contain 1-10% phenocrysts of olivine; plagioclase phenocrysts may be present. Andesites typically contain phenocrysts of plagioclase, orthopyroxene and clinopyroxene; rarely, olivine, hornblende, or ilmenite may be present. Dacite ranges from abundantly to sparsely porphyritic. Phenocrysts of plagioclase, clinopyroxene, orthopyroxene, and quartz are always present in the dacite. Biotite with or without hornblende may be present; olivine is only rarely present. Abundantly porphyritic varieties of dacite contain sanidine phenocrysts. Rhyolites are of two modal types: those in which biotite is abundantly present (0.5-5%) and those which are nearly biotite-free (0-0.5 vol. %). Biotite rhyolites contain 15-30% phenocrysts of quartz, plagioclase, sanidine, and biotite. Those rhyolites that lack or nearly lack biotite phenocrysts generally contain less than 3% phenocrysts.

I.A.2 Elemental Chemistry

The major and minor element chemistry of the Clear Lake Volcanics has been summarized by Hearn et al. (1980). In general, the Clear Lake Volcanics show a broad Cascade-type reference trend, but tend to be lower in FeO and higher in MgO than average Cascade lavas. Major and minor element variation diagrams for the basalts and basaltic andesites show considerable scatter, indicating that the basalts and basaltic andesites are not related, as groups, by fractional crystallization of a single parental basalt. They are

probably derived from several parental mafic lavas independently generated from deep mantle sources.

Within each period of volcanism incompatible elements such as K, Rb, Cs, Ta, Hf, Th and total rare earth elements (REE) tend to increase with increasing SiO₂ and to reach about the same maximum values in rhyolites of each period. Similarly, compatible elements such as Cr, Co, Zn, and Sc systematically decrease from mafic to silicic rocks; these values scatter considerably in the basalts, but are more uniformly low in the rhyolites. These uniform values for the rhyolites suggest that the magma system lost its silicic fraction to the surface when these elements had reached a particular enrichment in the upper part of the magma chamber.

I.A.3 Petrogenesis

Hearn et al. (1980) have related the Clear Lake Volcanics to eruption above a major upper crustal magma chamber. The general lack of very evolved rocks in the older (group 4) lavas and their widespread distribution suggests this earlier phase is not related to a single, large magma chamber. However, by the time of the group 3 volcanics (1.2 - 0.8 m.y. ago), volcanism was tightly concentrated in space and compositions were very evolved, as though eruption was derived from a single, large magma chamber. Group 2 volcanism was shifted slightly to the north, but was still tightly clustered and very silicic. The group 1 volcanics have shifted further to the north, away from the geophysically-inferred present magma chamber (see Geophysics Section), to the area near the southeastern arm of Clear Lake and northeast of the lake. Most of the lavas during this period were basalt, basaltic andesite, and andesite. Hearn et al. (1980) suggest that lavas of groups 2 and 3 represent differentiated magmas from a single, large chamber, whereas group 1 lavas

were derived again from deep, presumably mantle, sources. They suggest that this shift to the northeast signals a new cycle of magma generation with consequent heating of the crust and development of new magma chambers.

The REE patterns indicate that the Clear Lake basalts are derived from a relatively unfractionated source. Most basalts and basaltic andesites of the Clear Lake Volcanics show no Eu anomaly, which suggests that plagioclase has not played a role either in the source area or as a fractionating phase in these magmas.

I.B. Fluid Chemistry

I.B.1. Vapor dominated thermal water

These steam condensate waters represent a classical example of a vapor dominated geochemical system (Table 1, col.1). As discussed by White (1967) and White et al. (1971) vapor dominated surface springs have very low discharge, are very acid (pH 2 to 3) and are low in chloride. H_2S , that evolves with the steam, reacts near the surface with oxygen to form sulfuric acid, thus accounting for the high sulfate contents and low pH. The acid condensed water dissolves available cations from the surrounding rocks which are adequate sources for the reported constituents. As reported by Goff et al (1977), vapor dominated water at The Geysers is generally undersaturated with amorphous silica. As discussed by White et al. (1971), the geochemistry of chloride is critical in understanding the differences between coexisting chloride-containing waters and the vapor dominated waters. Most metal chlorides are highly soluble in liquid water and the low content of Cl in most rocks can be selectively dissolved at high temperature. The common metal chlorides, however, have negligible volatility and solubility in low pressure steam. Therefore the vapor dominated waters at the Geysers are

characteristically low in chloride relative to sulfate. White et al. (1971) also described young mercury deposits that have formed in the upper parts of the vapor-dominated system at The Geysers. Mercury has high volatility in steam which provides an attractive mechanism for separation and concentration. White et al. (1971) proposed that Hg and H₂S dissolve in the steam condensate and precipitate as HgS as the temperature decreases and the pH of the condensates increases from the reaction with silicates.

I.B.2 Thermal ground waters.

Many of the hot water springs in the Geysers area reflect mixtures of the regional groundwater chemistries. (White et al. 1973). These groundwater chemistries can be classified as follows:

I.B.2a Surface and shallow groundwater

Mg⁺²-CO₃⁼ rich waters constitute most of the surface and shallow groundwater discharged from both serpentinites and ultramafics in the Geysers area (Barnes et al. 1967). In general, HCO₃⁻ concentrations (Table 1 col.3) are high and the dissolved CO₂ can vary from 0.003 to greater than one atmosphere. Such waters are thought to reflect the hydrolysis of serpentine (Barnes 1970). At high PCO₂ Barnes et al. (1973) showed experimentally that serpentine dissolves incongruently to yield silica-rich secondary minerals. Such alteration by groundwater in The Geysers area is closely associated with mercury deposition. Some of the post-cinnabar quartz contains fluid inclusions that yield filling temperatures of less than 100°C suggesting alteration by low temperature groundwater.

I.B.2b Water reflecting serpentinization.

A rarer water type, classified as a Ca⁺²-OH⁻ type (Barnes and O'Neil, 1969),

TABLE 1

Examples of Water Compositions Associate with Geothermal Systems^{a)} in ppm

	1	2	3	4	5	6	7	8	9	10	11
	Geysers- Clear Lake, Vapor Dominated System	Geysers- Clear Lake, Water Reflecting Serpenti- zation	Geysers- Clear Lake, Water Reflecting Weathering of Serpen- tine	Geysers- Clear Lake, water from Great Valley Sequence	Long Valley Thermal water	Long Valley Shallow Water system	Rio Grande Rift Valles Caldera Thermal Water	Rio Grande Rift Ground- Water	Roosevelt Hot Springs Thermal Water	Salton Trough Brine	Salton Trough Surface Water
SiO ₂	225	0.4	170	190	110	58	170	96	639	400	41
Al	14	0.2	0.66	-	-	-	-	-	1.86	-	>0.5
Fe	63	-	0.22	-	-	-	-	-	.016	2000	>0.3
Mn	14	-	0.02	-	-	-	-	-	-	1370	1
As	-	-	-	-	0.74	0.02	-	-	-	-	-
Ca	47	40	30	1.4	50	5.1	7.3	160	31	28800	435
Mg	281	0.3	238	58	0.6	5.9	13	6.6	.26	10	69
Na	12	19	162	9140	410	23	4800	510	2072	53000	5430
K	5	11	26	460	30	40	180	63	403	16500	334
Li	-	-	-	14	2.8	0.04	-	-	-	210	12
NH ₄	1400	0.19	-	303	0.40	0.13	-	-	-	-	52
HCO ₃	0	0	1258	7390	416	90	-	773	25	682	630
CO ₃	-	0	0.2	-	-	0	-	0	-	-	-
SO ₄	5710	0.4	6.3	23	96	8.1	1600	290	48	96	414
Cl	0.5	63	272	11000	200	5.7	2600	300	3532	155000	8920
F	-	0	-	1.1	8.4	0.5	16	4.4	-	-	-
Br	-	-	2	15	-	-	14	3.0	-	-	9.1
NO ₃	-	-	9.2	-	-	-	-	-	-	-	-
B	3.1	.02	19	293	10.6	0.37	26	7.4	-	390	62
H ₂ S	-	-	-	-	2.3	0.1	-	-	-	-	-
pH	1.8	11.54	6.17	7.2	6.5	6.8	7.7	6.6	5.0	5.2	6.33
Temp	100	20	52	57	79	11	-	-	92	>300	34

a) Reference

- | | | | |
|---|---|--|--------------------------------------|
| 1. Table 1, White (1970) | 4. Wilbur Springs (Table 1) Barnes 1970 | 7. N4 (Table 1) Trainer and Lyford (1979) | 10. N02 11D Helgson (1968) |
| 2. Table 2, Barnes & O'Neil (1969) | 5. 3S/28E-13ES3 (Table 1) Mariner & Willey 1976 | 8. H17 (Table 1) Trainer and Lyford (1979) | 11. Table 1, Muffer and White (1968) |
| 3. Seigler Spring, Barnes and others (1973) | 6. 2S/28E-25AS1 (Table 1) Mariner & Willey 1976 | 9. Sample #3 Parry et al. (1980) | |

issues only from incompletely serpentized peridotite. (Table 1 col 2). Experimental data indicate that compositions are apparently controlled by reaction of primary phases (olivine and pyroxene) to yield secondary phases (serpentine and brucite). The pH is generally high (11 to 12). The $\text{Ca}^{++}\text{-OH}^-$ water type is thought to be derived from the $\text{Mg}^{+2}\text{-HCO}_3^-$ type.

I.B.2c Groundwaters of the Great Valley Sequence

Barnes et al. (1973a) showed that in the Clear Lake region, 50 km east of the Geysers geothermal area, the groundwater is related to structure and type of underlying rock. The principal structural control is the Coast Range fault which separates the eastern Great Valley sequence from rocks in the western Franciscan sequence. West of the fault the waters are generally of the $\text{Mg}^{++}\text{-HCO}_3^-$ type previously discussed. East of the fault the chemical composition is characterized by relatively high chloride and low bicarbonate compositions. In some locations, high chloride waters which issue from Franciscan metasedimentary rocks have been explained by the existence of underthrust Great Valley rocks at depth. Goff et al. (1977) used such relatively chloride-rich waters to outline the concealed extent of the Great Valley sequence beneath the Clear Lake volcanic field east of the Geysers area.

Hydrocarbon gases are produced in large quantities from Great Valley sequence rocks. These waters are chemically and isotopically similar to the oil field and gas field waters of the Central Valley of California but are generally enriched in bicarbonates and boron (Barnes et al. 1973a). These waters probably evolved from connate sea water in the pores of marine sediments but may be affected to some extent by low grade metamorphism at depth. White et al. (1973) recognized an additional water type at Sulphur Bank that was similar in isotopic composition to the oil field type water but was lower in Cl and

higher in B. The water was interpreted as a product of more extensive metamorphism of marine sediments.

The abundance of NH_3 and high Br/Cl and I/Cl ratios of both types of waters suggest their involvement at some time with sea water, marine sediments, and activity of marine organisms (White et al. 1973). High I/Cl ratios have been ascribed to decomposition of marine biologic remains (Barnes 1970). The B concentrations have been explained by recrystallization of marine clays with release of B back into solution (Barnes 1970).

Goff et al. (1977) found that waters high in chloride, reflecting an origin in the Great Valley sequence, had higher calculated reservoir temperatures, based on the Na-K-Ca geothermometer than waters emerging from the Franciscan assemblage. These anomalous temperatures lead Goff et al. (1977) to conclude that concentrations of Na, K, and Ca in thermal waters in the Clear Lake region are controlled by rock composition as well as temperature.

I.B.3 Isotope geochemistry

A sizable amount of isotopic data is also available for this system and nearby areas. D and ^{18}O values indicate that water involved in producing carbonates associated with ultramafics (O'Neil et al. 1977) and water involved in the serpentinization of these ultramafics (Wenner et al, 1973) were meteoric in nature. The meteoric waters sampled in the Geysers Clear Lake region contained oxygen-18 values of -5 to -9 per mil and deuterium contents of -35 to -65 per mil. All are close to Craig's meteoric water line. Oil field waters cluster around an oxygen-18 value of +3 per mil and deuterium value of -20 per mil. Some thermal and mineral waters sampled (Grizzly Spring and Abbott Mine) fall on a mixing line which represents a mixture of meteoric water with water evolved originally from waters of the Great Valley sequence.

I.C. Hydrothermal alteration

The Geysers geothermal area is underlain by the Franciscan assemblage, an assemblage that is lithologically heterogeneous, consisting of tectonically and positionally juxtaposed bodies of graywacke, shale, altered mafic rocks, tuffs, breccias, cherts, ultramafic rocks, serpentinites, and limestones. Medium grade blueschist occurs widely throughout the Franciscan, and occasional high-grade blueschist and eclogite are also found. A large part of the assemblage is a chaotic mixture of heterogeneous rock fragments with dimensions of a few centimeters to tens of kilometers and enclosed in a pervasively sheared matrix of shale, sandstone, or graywacke. Further details of the Franciscan assemblage are described elsewhere in this report.

There is, unfortunately, little or no publicly available information at present concerning hydrothermal alteration in cuttings or cores from the Franciscan reservoir rock at The Geysers. Several examples of hydrothermal alteration are present locally, however, in the near surface cap rocks, and these have been described in relation to the paragenesis of mercury deposits in north-central California (White and Robertson, 1962; Barnes, et al. 1973b; Sorg, et al. 1978). The mercury deposits are found in association with silica-carbonate alteration assemblages developed within the serpentinite sheets of the upper Mesozoic rocks of the Franciscan assemblage in the vicinity of the Geysers (Sorg, et al. 1978). Frequent fault movement is thought to have provided fracture zones in bedrock that enabled thermal meteoric waters, heated by a magma-hydrothermal system at depth, to move into shallow rocks beneath The Geysers/Clear Lake area where they reacted with serpentinite and formed silica-carbonate alteration assemblages and deposited mercury. Up to six distinct periods of fracturing and brecciation have occurred, followed by complete or partial healing by various forms of quartz

during formation of the silica-carbonate alteration assemblages on the southeastern and southwestern peripheries of the Geysers (Sorg, et al. 1978). The early quartz is predominantly chalcedony, trending toward crystalline, vuggy, euhedral quartz in successively younger periods of fracturing. Deposition of cinnabar was confined to a single post-fracturing episode late in the paragenetic sequence. The available evidence indicates that temperatures during cinnabar deposition did not exceed 120°C.

Thermal waters saturated in amorphous silica, containing high chloride, and associated with free CO₂ emerge from basement complex rocks in the vicinity of The Geysers and are thought to be responsible for altering serpentinite to silica-carbonate assemblages (Barnes, et al. 1973b). The silica carbonate assemblages consist of cryptocrystalline to macrocrystalline quartz, magnesite, ankerite, and dolomite replacing serpentine minerals. Barnes, et al. (1973b) used water analyses from springs in the area together with thermochemical data to show that the thermal waters are commonly supersaturated with silica, magnesite, dolomite, and ankerite while undersaturated with serpentine, brucite, and talc. They presented thermodynamic explanations for the relative abundances of silica and carbonate minerals as functions of the availability of CO₂ and serpentine.

Most of the CO₂ rich waters differ markedly in both oxygen-18 and deuterium contents from locally derived meteoric water. These high CO₂ fluids enriched in deuterium and oxygen-18 are classified with the metamorphic waters described by Barnes (1970). Estimates of the possible temperature range of formation of the carbonate minerals in the altered wall-rock indicate values less than 100°C. The isotopic data permit any mixture of metamorphic

and meteoric waters from oxygen-18 enriched metamorphic waters reacting at higher temperatures to locally derived meteoric waters containing metamorphic CO₂ reacting at mean annual temperature. The latter interpretation is favored by Barnes (1970).

O'Neil and Barnes (1971) have shown that the oxygen-18 and carbon-13 contents of fresh water carbonates associated with ultramafic rocks and serpentinites in the Coast Ranges are of near surface, low-temperature origin. These carbonates included travertines derived from Ca⁺²-OH⁻ type water (as well as travertines produced by dispersion of Mg⁺²-OH⁻ type) into Ca⁺²-rich water. The isotopic data indicate the two modes of origin for the travertine may be clearly delineated by their isotopic contents. The Ca⁺²-OH⁻-type waters produce a travertine which is significantly lighter in both oxygen-18 and carbon-13.

At The Geysers geothermal field radon (²²²Rn) has been used by Kruger et al. (1977) to determine several characteristics of the reservoir. Using simple linear and radial flow models they were able to make estimates of permeability and thickness of the reservoir. They also observed that in steam condensate water, radon and ammonia gas correlated linearly (r = 0.97), indicating that both components have a similar region of origin in the reservoir and are both conservative in transport.

II. LONG VALLEY

The Long Valley caldera is in southern Mono County in east-central California. The caldera floor is elliptical in plan, 17 by 30 km, with its long axis aligned east-west. The caldera margin is formed by a prominent ridge from Bald Mountain to Glass Mountain in the north and by a dissected volcanic tableland to the east. The Long Valley caldera lies nearly astride a major

fault system that separates the tectonically active Basin and Range province to the east from the relatively stable Sierra Nevada tectonic province to the west.

Cenozoic volcanism began about 3.2 m.y. ago and has continued intermittently until present. The major event that resulted in the formation of the caldera took place 0.7 m.y. ago with the eruption of the rhyolitic, Bishop Tuff. Heat flow data indicate that a resurgent dome overlies a residual magma chamber. Seismic and teleseismic studies also indicate that an anomalously hot or partially molten mass persists below 6-8 km under the western part of the caldera. It has been assumed that the Bishop Tuff provides the principal hot water reservoir that feed numerous hot springs in the area.

II.A. Geochemistry of Primary Volcanic Rocks

II.A.1 Petrology and geochemistry

The chronology of various Quaternary volcanics has been determined using ^{14}C (Wood, 1977), thermoluminescence (May 1976), K-Ar (Bailey et al., 1973), and uranium-series disequilibrium techniques (Baranowski et al., 1978). Volcanism in the vicinity of Long Valley began about 3.2 m.y. ago with eruption of basalt, andesite, and rhyodacite from widely scattered centers. Volcanism specifically associated with Long Valley began 1.9 m.y. ago with the rhyolite of Glass Mountain (Bailey et al. 1976). This rhyolite is an aphanitic to sparsely porphyritic, peraluminous subalkaline rhyolite. These lavas contain 2-3 ppm Sr and <20 ppm Ba (Noble et al. 1972).

The Bishop Tuff, erupted during the collapse of Long Valley Caldera, represents a sample of a single, large, silicic pluton, which was quickly emplaced, erupted, and quenched. It is a crystal-rich, high-silica rhyolite tuff containing

up to 30 percent phenocrysts. Phases present in the tuff are quartz, sanidine, oligoclase, biotite, titanomagnetite, ilmenite, zircon, and apatite; allanite, augite, hypersthene, and pyrrhotite are sparsely present. Mineral species tend to be very uniform in composition and change progressively with temperature. Fe-Ti oxide temperatures increase systematically from 720°C at the bottom of the sheet (top of magma chamber) to 790°C at the top of the sheet (bottom of chamber) (Hildreth 1970).

Whole-rock major element analyses of the Bishop Tuff (Table III-1) show a small but significant variation from the bottom (sample 1) to the top (sample 2) of the tuff sheet (Bailey et al. 1976; Hildreth, 1979). With progressive tapping of the chamber, silica content dropped from >77 to about 75 percent, and K₂O, CaO, MgO, TiO₂, P₂O₅ and total Fe increased. MnO and Na₂O were most abundant at the top of the chamber and decreased as eruption proceeded.

Detailed geochemical studies of the Bishop Tuff by Hildreth (1979) show that in contrast to the relatively modest major element concentration gradients, trace element gradients are very steep. For example, Ba, Sr, Eu, Ti, Fe, Co, Mg, Zr, and LREE (light rare earth elements) were depleted near the top of the magma chamber, whereas Rb, Cs, Y, Nb, Mo, Sb, Ta, W, U, Th, Mn, Sc, and HREE were enriched at the top.

Following eruption of the Bishop Tuff and attendant caldera collapse, eruption within the caldera of "early rhyolite" tuffs, flows, and domes occurred. These rocks consist of less than 3 percent of phenocrysts of quartz, plagioclase, biotite, hypersthene, and Fe-Ti oxides, and rare phenocrysts of fayalite and augite. These rhyolites contain about 75 percent SiO₂ (e.g. Rinehart and Ross, 1964) and do not vary significantly in chemical composition.

TABLE III-1
 ANALYSES OF BISHOP TUFF
 (in wt. percent)
 [From Bateman, 1965]

	1	2
SiO ₂	75.6	76.7
Al ₂ O ₃	13.1	13.0
Fe ₂ O ₃	.8	.5
FeO	.13	.26
MgO	.18	.13
CaO	.56	.52
Na ₂ O	3.8	3.7
K ₂ O	4.8	4.5
TiO ₂	.11	.06
P ₂ O ₅	.01	.00
MnO	.04	.03
H ₂ O	.35	.34
CO ₂	.16	.08
	99.64	99.82

Following resurgence of the "early rhyolites", eruption of the "moat rhyolites" occurred. These are pumiceous, coarsely porphyritic hornblende-biotite rhyolite, with up to 20 percent phenocrysts of hornblende, biotite, quartz, sanidine, and plagioclase. A chemical analysis by Rinehart and Ross (1964) shows this rhyolite to have above 72 percent SiO₂.

Later extrusive rocks have progressively lower silica contents. The

"rim rhyodacites" are crystal-rich hornblende-biotite rhyodacites, with silica contents ranging from 74-59 percent. The main phenocrysts are hornblende, biotite, augite, and hypersthene, with minor olivine, plagioclase, sanidine, and quartz. Considerable mineralogical and chemical heterogeneity exists within individual eruptive centers (Bailey et al., 1976).

Following this intermediate extrusive activity, eruption of basaltic flows and cinder cones occurred within Long Valley. This activity is not specifically related to the Long Valley magma chamber, but rather is part of a much more extensive chain of mafic volcanism extending from southwest of Mammoth Mountain to 45 km northward into Mono basin. These rocks are chemically and mineralogically similar to late Cenozoic basalts occurring throughout the Basin and Range province.

The last extrusive activity at Long Valley resulted in the Inyo domes. Three of these are fluidic mixtures of two distinctly different rock types, a coarsely porphyritic hornblende-biotite rhyodacite, and a sparsely porphyritic rhyolite obsidian. The rhyodacite is mineralogically similar to the rhyodacites of Long Valley caldera, whereas the rhyolite obsidian is similar to that of the Mono craters. The mineralogical and volume relations suggest that the Inyo domes represent mixing along north-south fractures of magmas from the Long Valley caldera with magmas from beneath the Mono craters ring fracture zone (e.g., Bailey et al., 1976).

By using ^{14}C to age date well preserved conifer logs stratigraphically associated with the tephra, Wood (1977) deduced an age of 720 ± 60 y. before present.

II.A.2 Petrogenesis of volcanic rocks

A model for the evolution of magmas associated with the Long Valley caldera was presented by Bailey et al. (1976). They postulate that the concentric zonation of post-caldera volcanic rocks resulted from progressive downward crystallization of a magma chamber which was zoned from rhyolite in its upper part to rhyodacite in its lower part. The continuous decrease in SiO_2 from 75% in the early rhyolites to 64% in the rim rhyodacites reflects intermittent tapping of the magma chamber at progressively greater depths along ring fractures.

The upper part of the chamber was erupted as the rhyolite of Glass Mountain. Noble et al. (1972) have indirectly inferred the origin of the magmas which produced the rhyolites of Glass Mountain. Nearby Quarternary rhyolite and rhyolite obsidian were found to have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.706 and 0.707. These values are nearly identical to those of the upper Cenozoic basalt and are lower than would be expected if the rocks had been generated by partial melting of Mesozoic or older basement rocks to the area. They propose the Glass Mountain rhyolites were formed by fractional crystallization of fairly alumina-rich subalkaline mafic magma also rich in strontium and in radiogenic strontium. During the eruption of the Bishop Tuff and consequent caldera collapse the chamber was drained of the zone of magma containing 75-77 percent SiO_2 . Hildreth (1979) concludes that the compositional and thermal gradients measured in the Bishop Tuff existed in the liquid prior to phenocryst precipitation. The very modest gradients in major-element concentrations and the uniformity of mineral grains, however, rule out

fractional crystallization as a major cause of the observed compositional zonation. Instead, this zonation is established through the combined effects of convective circulation, internal diffusion, complexing, and wall-rock exchange controlled by the thermal and gravitational fields of the magma chamber itself.

Following eruption of the Bishop Tuff, successive tapping of deeper levels of the chamber at later times brought progressively more crystallized and less silicic magma to the surface (Bailey et al., 1976).

From the chemistry of the Glass Mountain lavas, Noble et al. (1972) suggest that these lavas were derived from a "parent" silicic lava by crystallization of alkali feldspar and perhaps biotite. The parent magma may have been derived by fractional crystallization of a fairly alumina-rich subalkaline mafic magma with Sr content of 1000 ppm and $^{87}\text{Sr}/^{86}\text{Sr}$ rate of 0.706 - 0.707.

II.B Fluid chemistry

Sorey et al. (1978) classified the groundwater system in the Long Valley caldera into two parts: (1) a shallow subsystem in which temperatures are not much higher than ambient land surface temperatures, groundwater flow paths are relatively short, and the dissolved solids are relatively low and (2) a deep subsystem in which temperatures are high, groundwater flow paths are long and circuitous, and concentrations of dissolved solids are high. In general the shallow subsystem is contained in the fill above the densely-welded Bishop Tuff. The deep subsystem consists of Bishop Tuff with subordinate amounts of pre-Bishop Tuff volcanics and metasedimentary rocks. In large part, the variations in chemical character reflect sharp differences between the deep hot water system and the shallow cold water system and they also indicate local

proportions of these two contrasting types (California Dept. of Water Resources, 1967). The chemical characteristics of the two types are as follows.

II.B.1 Shallow Groundwater

These waters are generally of a non-saline sodium bicarbonate type (Table 1, no.6). The cold water contains proportionally more calcium and magnesium and less chloride than the thermal spring waters. In general the proportion of sodium chloride decreases as the total dissolved solids decrease. As suggested by Lewis (1974), such a trend indicates that the shallow aquifer has been contaminated by mixing with thermal fluids.

II.B.2 Thermal system

Saline sodium bicarbonate-chloride waters are discharged by the thermal springs (Table 1, sample 5). A marked decrease occurs in the proportion of divalent to monovalent cations, sodium and potassium (Mariner and Willey 1976). Waters from Hot Creek suggest a loss of CO_2 and a precipitation of carbonate at depth. Also springs having high Cl/Ca and Cl/Mg ratios generally have lower Ca/Mg ratios perhaps indicating precipitation of magnesian calcite. Cl/Rb, Na/Rb and Na/Li ratios are smallest for hot springs along Hot Creek, increasing as spring temperatures decrease (Mariner and Willey, 1976). The slight increase in Cl/Li and Cl/F as the spring temperatures decrease may indicate loss of these minor elements into alteration minerals.

Smith (1976) and Sorey et al. (1978) compared the present rates of discharge of characteristic hot spring elements such as B, Li, Cl and As from the Long Valley hydrothermal system with amounts contained in the evaporite deposits in Searles Lake, the closed discharge point in the surface water system. Approximately 70% of the B would have been deposited, assuming a

constant flow, equivalent to present flow rates, over the 32,000 year period of evaporite formation based on dating of interbedded mud layers.

Applications of mixing models to estimate mixing ratio and temperatures of the hot water component at depth have been made by Marine and Willey (1976). Reservoir temperatures, estimated from the silica geothermometer of Fournier and Truesdell and a silica chloride mixing model, ranged from 200°C to 225°C. These models suggested that a single reservoir underlies or at least feeds all the major hot springs in the caldera. A more recent analysis of the geothermometer and isotope data of Fournier et al., using chloride enthalpy relations, suggest a more complicated system including a deep aquifer with water at 282°C.

The isotopic data for deuterium and oxygen from fresh waters and hot springs in Long Valley have been summarized by Fournier et al. (1976). They suggest that fresh water typical of the recharge for the geothermal system has $\delta^{18}\text{O} = -15$ and $\delta\text{-deuterium} = -112$ per mil. The meteoric water percolates underground and reacts with the reservoir rock to form an end member geothermal component with $\delta^{18}\text{O} = -13$ and $\delta\text{-deuterium} = -112$ per mil. This hot end-member then migrates toward the surface where it mixes with a cold, meteoric water having $\delta^{18}\text{O} = -17$ and $\delta\text{-deuterium} = -130$ per mil to produce the mixing trend observed for the thermal springs in the area. The isotopic shift in $\delta^{18}\text{O}$ for thermal springs in Long Valley is less than for most other major thermal areas and suggests the hot spring system is moderately old and has isotopically well flushed conduits. The isotopic data has also been used to demonstrate that for several samples the thermal end-member must have boiled while ascending before mixing with the cold, meteoric end-member.

The dissolved sulfate-water isotope geothermometer has been applied to Long Valley waters by McKenzie and Truesdell (1975). The average $\delta^{18}\text{O}$ (SO_4) value is -7.5 per mil and the calculated $\delta^{18}\text{O}$ (H_2O) value is -13.2 per mil. Using empirically derived relations for the temperature dependence of the fractionation between dissolved sulfate and water indicates an equilibration at 268°C, which is reasonably consistent with the silica-derived aquifer temperature.

II.C Hydrothermal alteration

Hydrothermal and fumarolic activity at Long Valley is controlled by caldera ring fractures and young faults within the caldera. Surface manifestations of hydrothermal alteration of caldera fill have been reviewed by Bailey, et al. (1976). Tuffaceous lacustrine sediments on the east and southeast flank of the resurgent dome are being argillized by acid waters associated with fumarolic activity. Oxidation of fumarolic H_2S has produced acid sulfate waters that have resulted in intense opalization of sediments locally. The alteration sequence with increasing depth and temperature in the surface caldera fill deposits is silicification, argillization, and zeolitization. Traces of alunite and montmorillonite are also present.

III. RIO GRANDE RIFT

The Rio Grande rift is a major continental rift consisting of a series of interconnected north-south trending grabens and associated flanking uplifts that stretch from central Colorado across New Mexico to the vicinity of Chihuahua, Mexico and west Texas. In central and southern Colorado and northern New Mexico, the rift lies between two salients of the Southern Rocky Mountain physiographic province. From central New Mexico southward the rift merges with the Basin and Range province. The present phase of rifting began

approximately 25 m.y. ago. There is abundant evidence of hydrothermal activity based both on heat flow measurements and hot spring activity.

The Jemez Mountains-Valles Caldera is a dominant tectonic feature at the intersection of the Rio Grande Rift and the Jemez lineament in north central New Mexico and has been the focus of intense volcanism throughout much of the Pliocene and Quaternary. Caldera collapse associated with the last major lava flow (1.1 million years B.P.) was followed by reinjection of magma that caused resurgence of the caldera floor and formation of rhyolite domes along the caldera margin. Within the caldera, a major high-temperature hot-water geothermal system is capped by a small vapor-dominated system; reservoir temperatures exceed 290°C. The recency of volcanism and the presence of high temperature hydrothermal convection suggest that still-molten magma underlies the Valles Caldera. Published geophysical surveys are incomplete and the depth of magma is uncertain, but 5-8 km is a reasonable range.

III.A Geochemistry of primary volcanic rocks

III.A.1 Petrology and primary mineralogy

III.A.1.a Jemez Mountains

The volcanic field consists of 4 sequences (Bailey et al., 1969; Smith et al., 1978):

- | | |
|-------------|--------------------------------------|
| Tewa Group | 4. Bandelier sequence 0.1 - 1.5 m.y. |
| | 3. Tschicana Fm. 2 - 7.4 m.y. |
| Keres Group | 2. Palize Canyon Fm. 7 - 9 m.y. |
| | 1. Borrego sequence 9.5 - 10.4 m.y. |

Sequence 1 is a bimodal basalt-rhyolite sequence. Sequences 2 and 3 are basalt-

andesite-dacite-rhyolite sequences. In sequence 2 andesite is volumetrically dominant, whereas in sequence 3 rhyodacite is the dominant rock type.

Sequence 4 consists of rhyolitic tuffs associated with two cycles of caldera formation.

Chemically, the rocks of the Jemez volcanic field are on the alkaline side of calc-alkaline and range to alkali-calcic (Bailey et al., 1969). The Bandelier tuff approaches peralkaline compositions. Silica content of these rocks ranges from 47-77 percent, with a gap between 58 and 60 percent. This gap is compatible with preliminary Pb and Sr isotopic data suggesting that the mafic rocks have a mantle source and the silicic rocks a crustal source (Smith et al., 1978).

Smith (1979) presented detailed data on Nb concentrations of the Bandelier sequence. Silica has only a very narrow range of variation between 68 and 77 percent. However, Nb varies from a "baseline" level (thought to be close to the immediate Bandelier parent composition) of approximately 14 ppm to about 200 ppm, with most of the variation (50 - 200 ppm) occurring in magmas with >76 percent SiO₂. Fluctuations in Nb do not correlate with silica content. Such alternating enrichments and depletions with successive eruptions probably reflect gradients in temperature and volatile concentration between the roof of the magma chamber and a convecting system that underwent periodic eruption, rather than processes of fractional crystallization. In addition, other elements such as Ta, U, Th, Cs, Rb, Li, Sn, Be, B, W, Mo, F, Cl, Pb, Zr, Sm, and HREE are concentrated near the top of the magma chamber, whereas Ba, Sr, Eu, Ti, Cr, Co, Se, Au, and Cu concentrate downward.

III.A.1b Basaltic rocks of the Rio Grande Rift

Volcanic fields of dominantly basaltic rocks include the lavas of the Taos Plateau in the southern San Luis Basin; the Cerros del Rio field of the Espanola basin; several small lava fields of the Albuquerque-Belen basin; and the Elephant Butte, Jornada del Muerto, Carrizozo, and West Potrillo Mountains fields of the southern rift. See for example Luedke and Smith (1978). All fields are less than about 5 m.y. in age.

The Taos Plateau lavas consists of a relatively thick pile of low-alkali, aluminous olivine tholeiite (Aoki, 1967; Lipman, 1969; Lipman and Mehnert, 1975). At least 35 small central volcanoes, forming an imperfect concentric pattern, occur on the surface of this pile. Tholeiitic shield volcanoes occur in the center of the field, andesitic volcanoes occupy an intermediate position, and rhyodacite volcanoes occur farthest out. Two small silicic domes occur in the center of the field (Lipman and Mehnert, 1979). A preliminary model suggested by Lipman and Mehnert (1979) to explain the composition and distribution of the Taos volcanic field involves generation of the tholeiitic lavas by large degrees of partial melting at relatively shallow depths within an upward bulge of the mantle beneath the rift. The andesitic and rhyodacitic lavas represent smaller amounts of partial melting in the mantle or mafic lower crust adjacent to the main thermal anomaly. Low pressure fractional crystallization appears significant only for the volumetrically minor rhyolite and quartz latite.

Lavas from the Cerros del Rio volcanic field in the Espanola basin include both alkalic and tholeiite basalts, and range to latite-andesites (Baldrige, 1979; Aubele, 1979) on the east margin of the Jemez Mountains. At least four parental basaltic compositions are present: high-alkali

olivine tholeiite, basaltic andesite, alkali olivine basalt, and basanite, all erupted approximately penecontemporaneously. Latite-andesite was derived from basaltic andesite by subtraction of olivine, pyroxene, and plagioclase, and by addition of quartz and sodic plagioclase which occur as xenocrysts in the lavas (Baldrige, 1979). Baldrige (1979) suggested that these lavas were derived at depths of from greater than 50 km to as shallow as 35 km along a major lithospheric fracture zone (Jemez Lineament) that intersects the rift in the Jemez Mountains.

Smaller volcanic fields of the Albuquerque - Belen basin include the Santa Ana Mesa field, the Albuquerque Volcanoes, Wind Mesa and Isleta volcanoes, the Cat Hills field, Cerro de Los Lunas, and Cerro Tome (Kelley and Kudo, 1978; Baldrige, 1979). Kelley and Kudo (1976) point out that in contrast to dominantly tholeiitic volcanism in the northern rift (e.g., Taos volcanic field) and alkalic volcanism in the southern rift, volcanism in the central rift consists of both alkalic and tholeiitic basalts. The Albuquerque Volcanoes consist of low-alkali olivine tholeiite (Kelley and Kudo, 1978; Aoki and Kudo, 1976; Baldrige, 1979), similar to those of the Taos Plateau. Lavas from the Santa Ana Mesa and Cat Hills fields are higher-alkali olivine tholeiite, whereas those from the Wind Mesa and Isleta volcanoes consist of both tholeiitic and alkalic basalts. Cerro Tome and Cerro de Los Lunas are dominantly andesitic in composition. Zimmerman and Kudo (1979) suggest that these lavas originate by partial melting of hornblende-bearing upper mantle material with superimposed fractional crystallization and crustal contamination.

Most basaltic rocks from the southern Rio Grande rift are alkalic in composition - e.g., the Elephant Butte, Jornada del Muerto, and West Potrillo Mountains fields (Aoki and Kudo, 1976; Renault, 1970). The Carrizozo field is exceptional in that it is olivine tholeiite (Renault, 1970).

Late Cenozoic volcanic rocks from the Jemez lineament (generally considered to belong to the Rio Grande rift, broadly defined) include nephelinites, alkali olivine basalts, mugearites, trachytes, olivine tholeiites, and basaltic andesites (e.g., Stormer, 1972a, b; Lipman and Mehnert, 1972; Crumpler, 1980) generally, however, volcanic rocks lying along this lineament are petrologically and chemically not well characterized.

In summary, a single petrogenetic model for the origin of basaltic lavas in the Rio Grande rift does not exist. Most of the lavas were clearly derived from the mantle. Since none have truly primitive compositions, all have undergone at least some modification in the crust. Lavas such as the more silicic basaltic andesites and latite-andesites of the Cerros del Rio probably have substantial residence times in the crust where fractional crystallization and assimilation of xenocrytic material occur.

III.A.2 Geochemistry

Geochemical data (non-isotopic) on basaltic rocks from the Rio Grande rift are sparse. Lipman and Mehnert (1979) present rare earth element (REE) data from rocks from the Taos Plateau. They show (1) that all are light REE enriched, and (2) that total REE concentrations generally increase from basaltic to andesitic compositions, then decrease with further increases in silica content from andesite to rhyolite. They conclude that tholeiitic magmas of the Taos Plateau were generated from material in which heavy-REE-retaining phases (garnet or hornblende) were absent in the residuum. Other mafic lavas, with larger ratios of light to heavy REE, resulted from smaller proportions of melting where garnet or hornblende were stable residual phases.

Limited trace element (including REE) data for silicic rocks from the Taos Plateau, Cerros del Rio, and Cerro Tome were presented by Zimmerman and Kudo (1979). All rocks are LREE enriched, suggesting that these magmas were generated from a source with residual garnet or, more probably, hornblende. Both Eu depletion (for a Taos Plateau rhyolite) and enrichment (Cerros del Rio and Tome andesite) indicate the important superimposed effect of plagioclase.

Using Sr isotope abundance Kudo et al. (1972) have offered an explanation for the diverse origins of the nepheline-normative alkali basalt and the olivine tholeiite. They observed that the nepheline normative basalts have a very restricted range in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, being similar to oceanic basalt (0.703-0.704), but the hypersthene-normative basalts have ratios that range from 0.703 to as high as 0.708. Furthermore, an inverse hyperbolic relationship exists between Sr content and Sr isotopic ratio, which is a sensitive indicator of crustal contamination. Because of its high Sr content, the nepheline normative basalt originating deep in the mantle cannot be the parent magma which becomes contaminated to form the hypersthene normative basalt; rather a basalt lower in Sr than the hypersthene-normative basalt must be its parent. Such a magma could fractionate directly from the mantle at a shallower depth. It is possible that the low Sr basalt which gave rise to the hypersthene-normative basalt could be contaminated in the shallow magma chambers within the Precambrian granitic crust.

De Paolo et al. (1976) have used variations in the isotopic ratio $^{143}\text{Nd}/^{144}\text{Nd}$ in volcanics to make inferences about their magma source and the mantle structure. They observed that, based strictly on the Nd isotopic results, the

continental flood basalts and other young volcanics could be distinguished from oceanic basalts. The results imply the existence of at least two distinct ancient magma sources to supply oceanic and continental basalts.

III.B Fluid geochemistry

Although the Rio Grande Rift has been shown by heat flow measurements to be a site of a pronounced geothermal anomaly, only a few of the associated thermal springs have been investigated in detail. Swanberg (1976, 1979) has shown that for the entire rift system, there is a linear relationship between temperature based on silica content of groundwater and the regional heat flow measurements. The Rio Grande Rift as a whole is characterized by a ribbon of high silica geotemperatures. In general, springs occur near the margins of the rift at relatively high altitudes. Sources of thermal waters may be considerable distances from the springs.

III.B.1 Valles Caldera - Jemez Mountains

The most detailed work on the aqueous geochemistry has been associated with the Valles Caldera-Jemez Mountains regions at the western margin of the Rio Grande Rift. These waters have generally be classified as follows.

III.B.1a Vapor dominated systems

. Trainier (1974) describes a small number of springs within the Valles Caldera which are low in pH and chloride, high in sulfate, and release H₂S and CO₂. Springs such as Sulphur Springs (72°C) are indicative of a local vapor dominated reservoir of the type described by White and others (1971). However, the reservoir appears to be of limited potential and extent.

III.B.1b Hot Water Systems

Trainer (1975) classified these waters as sodium chloride types which originate in the hydrothermal reservoir in the Valles Caldera and have drained laterally outward along faults and fractures. These waters contain significant concentrations of lithium, bromide and boron. Deep thermal waters from the Valles Caldera yield calculated Na-K-Ca temperatures of 280°C, close to known reservoir temperatures of about 266°C.

In addition to these deep reservoir waters, Trainer (1974) described several warm springs in rhyolite within the ring-fracture zone of the caldera. These waters are of a much more dilute sodium chloride composition suggesting that they have not circulated to great depth and have not mixed with water in or from the main geothermal reservoir beneath the caldera.

III.B.1c Carbonate groundwater

Calcium carbonate waters are associated with the Pennsylvanian and Permian Magdalena carbonate rocks. Smith and others (1978) suggest the presence of limestone beneath the volcanic rocks in the sunken block of the caldera. If limestone is present it may play a significant role in the development of porosity because of its susceptibility to attack by hot CO₂-rich volcanic water (Trainer, 1974). Additional calcium carbonate is apparently dissolved as the reservoir waters move outside the confines of the caldera through San Diego Canyon. Travertine deposition at or near Soda Dam coupled with high bicarbonate concentrations are indicative of extensive dissolution of limestone up-gradient in the flow path.

III.B.1d Groundwater in volcanic rocks

Cold, dilute, sodium-calcium bicarbonate waters are associated with perched groundwaters in the Tertiary volcanics.

In general, the large warm springs located in the southern Jemez mountains and studied by Trainer (1974, 1975), Trainer and Lyford (1979), and Goff et al. (1980), represent mixtures of the hydrothermal and meteoric waters. The B/Cl ratios of these mixed waters resemble those calculated from deep thermal waters. The moderate SO_4 concentrations of the mixed waters probably originate from three sources: H_2S oxidization, oxidization of pyrite, and reaction of thermal waters with organic sulfur contained in carbonate and shale units. Trainer (1975) estimated, based on trace element dilution, that the extent of mixing varied between 1 and 12 parts cold meteoric water to 1 part thermal water. Estimated temperatures of the water in the reservoir based on a mixing model using the silica geothermometer was $169^{\circ}C$.

III.B.2 Other areas in the Rio Grande Rift

Trainer and Lyford (1979) made a reconnaissance study of the northern Rio Grande Rift southward from the San Luis Basin. They found that groundwater flow in the near-surface parts of both valley fill and volcanic rocks is toward the regional drainage provided by the Rio Grande. Mixing models indicated that very large proportions of cold water were mixed with thermal waters. B/Cl and Br/Cl plots suggested that the thermal water was similar in composition to the water in the Jemez mountains.

Trainer and Lyford (1979) and others have distinguished two groundwater types in the Lucero Uplift southeast of Albuquerque. One is a mineralized water containing predominant concentrations of Na, Cl and SO_4 which are discharged by numerous springs at the eastern margin of the uplift. It is

suggested that this water comes from the west, principally through the Madera Limestone (Pennsylvanian). In addition a component of this water may be hydrothermal, based on higher-than-ambient temperatures of the springs. The less mineralized water occurs in valleys west and north of the eastern edge of the uplift and is suggested to have originated largely from local precipitation.

In the southern Rio Grande Rift near Las Cruces, New Mexico, Swanberg (1975) found that a prominent north-northwest trend of thermal springs paralleled the path of a major fault sequence. Based on the Na-K-Ca geothermometer, the maximum reservoir temperature was in excess of 200°C. Temperatures estimated by the silica geothermometer were generally lower, suggesting dilution by meteoric groundwater (Swanberg, 1975). High concentrations of fluoride and boron generally reinforced the pattern of distribution of geothermal waters based on the geothermometers.

III.C. Hydrothermal alteration

There is evidence of hydrothermal activity, commonly as hot springs, at several locations along the Rio Grande Rift including Taos, Ojo Caliente, San Ysidro, Valles Caldera, Lucero Uplift, Socorro, Truth or Consequences, Radium Springs, and the Gila Wilderness. With the exception of the Valles Caldera, there is virtually no information available on subsurface hydrothermal alteration at these sites.

Information about mineral alteration within the hydrothermal reservoir at Valles Caldera is restricted, due to proprietary reasons. At the present time, the most complete set of data on subsurface hydrothermal alteration at the Valles Caldera is that provided by Lambert and Epstein (1980) in their stable isotope investigations of Union Oil Company drill hole cuttings from the

geothermal system. Samples were studied from the wells Baca No. 4 and Baca No. 7. A continuous sequence of rock types encountered in Valles Caldera is typically represented in Baca No. 7, an almost completely sampled well that reached a depth of 1687 m. All but five samples analyzed by Lambert and Epstein (1980) came from Baca No. 7. Petrographic thin sections and x-ray diffraction were used to identify minerals and textures in unaltered and altered samples. No major element analyses for whole-rock samples or reactant and product phases were presented.

There is little evidence of hydrothermal alteration - texturally, mineralogically, or isotopically - in the upper 600 m of Baca No. 7. the shallowest depth of hydrothermal alteration is between 500 and 700 m (100°C). Epidote was first encountered at 600 m, occurring as pale-green prismatic crystals altering calcic feldspars and ferromagnesian minerals in caldera fill of igneous-derived material. The Bandelier Tuff (700 m to 930 m, 150°C to 180°C) shows pervasive hydrothermal alteration of the originally glassy groundmass to quartz and kaolinite with traces of sericite and calcite. The alteration of the Bandelier Tuff produced similar products but was more intense in Baca No. 4 located nearer the center of the caldera. The Santa Fe Formation (930 m to 1160 m, 180°C to 200°C), stratigraphically below the Bandelier Tuff, consists of volcanically-derived tuffaceous and arkosic sandstones. The Santa Fe and Bandelier units are similar mineralogically and have experienced similar degrees of hydrothermal alteration. Both units have undergone more intense alteration than the overlying volcanic rocks and caldera fill at Baca No. 7. Pyrite is first observed at 1130 m in Santa Fe Formation in Baca No. 7. Wairakite is found below 1420 m (~ 220°C) near the top of a silicified limestone unit where it occurs in a matrix between quartz crystals.

IV ROOSEVELT HOT SPRINGS

Roosevelt Hot Springs is a newly discovered geothermal area located in Utah on the western margin of the Mineral Mountains and the eastern boundary of the Basin and Range Province. The Mineral Mountains consist dominantly of a Tertiary granite pluton with young (.5-.8 M.Y.B.P.) rhyolite volcanism. Faults bounding the Milford Valley apparently control the flow of hydrothermal water upward from a heat source presumed to lie under the Mineral Mountains. Shut-in bottom hole temperatures in the geothermal field have been measured at 260°C.

IV.A. Geochemistry of primary volcanic rocks

IV.A.1 Petrology, primary mineralogy and geochemistry

Cenozoic volcanism in the Roosevelt Hot Springs area began 20 m.y. ago with eruption of calc-alkalic lavas. Eruption of rhyolitic lavas occurred 9.7, 8.0, and 2.3 m.y. ago. Basalt, dated as 7.6 m.y. old, was extruded on the southern flank of the Mineral Mountains, and Quaternary basalt was erupted on the northeast flank of the Mineral Mountains. The youngest episode of volcanism began 0.8 m.y. ago with extrusion of two rhyolite flows. These are overlain by bedded pumice falls and nonwelded ash flows. The youngest activity, 0.6 and 0.5 m.y. ago, produced at least ten rhyolite domes and small flows of rhyolite distributed along the crest and western flank of the Mineral Mountains (Ward et al., 1978).

The two rhyolite flows extruded at 0.8 m.y. ago are crystal-poor, containing less than 0.5 percent total phenocrysts consisting mainly of alkali feldspar with trace amounts of oligoclase, biotite, titanomagnetite, and ilmenite. The two flows are virtually identical in composition. They are typical high-SiO₂ rhyolites, with 76.5 percent SiO₂, >9 percent total

alkalies, and 0.16 percent F. Eruption temperatures determined from compositions of Fe-Ti oxides and coexisting plagioclase and alkali feldspar range up to about 785°C (Lipman et al., 1978; Ward et al., 1978).

The dome-forming rhyolites (0.5 - 0.6 m.y. ago) are much more crystal-rich, containing up to about 8 percent phenocrysts of plagioclase, alkali feldspar, quartz, biotite, and Fe-Ti oxides. Trace amounts of sphene, allanite, hornblende, and zircon occur in some of the domes, and topaz occurs in the lithophysae in crystalline rhyolite. These rhyolites are also high-SiO₂ rhyolites, but compared to the earlier flows are lower in K, Ti, Fe, Ca, Ba, and Sr, and higher in Mg, Mn, Na, F, Nb, and Rb. Magmatic temperatures determined from Fe-Ti oxides and coexisting feldspars range as low as 650°C for these domes (Ward et al., 1978). Water fugacities calculated for the rhyolites in these flows and domes are 3.0 and 0.4 Kb, respectively (Nash and Evans, 1977).

Compared with the earlier, Tertiary rhyolites, these latest rhyolites are higher in SiO₂ and CaO and lower in Sr and Ba (Ward et al., 1978).

REE data of Lipman et al. (1978) show that the Pleistocene rhyolite flows and domes are LREE enriched. In addition, these chondrite-normalized data show strong Eu depletion, indicating major feldspar fractionation.

IV.A.2 Petrogenesis of volcanic rocks

Not enough petrologic or chemical data yet exist to formulate an overall petrogenetic model for the Roosevelt Springs volcanism. Lipman et al. (1978) speculate that the Pleistocene rhyolite of the Mineral Mountains may represent a late stage in the evolution of a complex magmatic system that earlier gave rise to the 10-14 m.y. old granite of the Mineral Mountains, or the rhyolite

may simply have been localized where the crust was still hot from an intrusive event. This interpretation of a shallow magmatic system is at least compatible with REE data indicating that the Pleistocene rhyolite resided in a shallow crustal environment sufficiently long to undergo major fractionation of plagioclase.

IV.B Fluid geochemistry

The thermal waters associated with Roosevelt Hot Springs are relatively dilute (ionic strength 0.1 to 0.2), sodium chloride brines (Table 1, no. 9). Sulfate concentrations vary between 48 and 120 mg/l. Parry et al (1980) demonstrate that chemical differences exist between surface and deep thermal fluids consisting principally of higher Mg, Ca and SO_4 and lower Na, K, SiO_2 in surface relative to deep water. These differences presumably reflect progressive leaching of Mg and Ca by ascending thermal fluids, oxidation of H_2S or admixture of oxidized $\text{SO}_4^{=}$ -rich surface waters, and flashing and cooling with subsequent precipitation of opal. The Roosevelt Hot Spring thermal fluids are hot-water dominated in the terminology of White (1971). Parry et al. (1980) calculated subsurface pH of 6.9 using calcite-carbon dioxide-water equilibria and a PCO_2 of $10^{-1.19}$. This pH is prior to H_2S oxidation.

Applications of the Na-K-Ca and SiO_2 thermometers to geothermal fluids indicate deep water temperatures of 241 to 280°C respectively which agree with downhole measurements. (Ward et al. 1978). Swanberg (1974) earlier estimated a temperature of 189°C based on the Na-K-Ca geothermometer. Surface studies of soil radon (Nielson, 1978); and helium (Hinkle, 1978) have been used to map faults delineating the geothermal field.

Although an extensive research program is currently being conducted, which will include data and modeling of the distribution of light, stable isotopes in geothermal fluids, the data are unavailable to the open literature at the present time (Ward et al. 1978; Parry et al. 1980)

IV.C. Hydrothermal alteration

Hydrothermal alteration at Roosevelt Hot Springs occurs within biotite-hornblende Precambrian gneiss, in Tertiary granite-granodioritic intrusions, and in alluvium derived from both. Present hydrothermal activity at the surface is occurring in association with small seeps but opal and alteration deposits attest to a more vigorous past activity.

Hydrothermal alteration at Roosevelt Hot Springs has been investigated by Bryant (1977), Dedolph (1977), and by Parry, et al. (1980). The details of alteration in the upper 70 m of the thermal area were presented by Parry, et al. (1980); studies of samples from depths greater than 2 km are in progress. The hot springs deposits consist of opaline sinter and sinter-cemented alluvium. Three shallow drill holes show that alluvium, plutonic rocks, and amphibolite facies gneiss have been altered by acid sulfate water to alunite and opal near the surface, and to alunite, kaolinite, montmorillonite, and muscovite at depths to 70 m. Marcasite, pyrite, chlorite, and calcite occur below the water table at about 30 m. Parry, et al. (1980) present several whole-rock analyses representative of samples at various depths, and they also present several weight percent modes for the altered rocks - based on mineral compositions, whole-rock analyses, and least squares mass balance calculations. The mineral compositions used in the calculations were obtained by x-ray diffraction and petrographic examination but were not reported. Calculated activities for analyzed solutions from Roosevelt Hot Springs were

plotted on mineral stability diagrams and are shown to be out of equilibrium with end-member phase compositions appropriate for the observed alteration mineral assemblages. Parry, et al. (1980) propose that a deeper brine, equilibrated with chlorite, muscovite, and calcite alteration products, rises along fractures, cools, is acidified to a sulfate brine by oxidation of H_2S , and then percolates downward to produce alunite, kaolinite, and montmorillonite from reaction with feldspar at shallow depths. Irreversible mass transfer calculations support this model.

IV.D Isotope geochemistry

The detailed studies being conducted by Ward et al. (1978) include an analysis of light, stable isotopes in well-cuttings; however, the data are not yet available.

Hinkle et al. (1978) measured the helium content in soil samples taken in traverses across the Dome fault zone of the KGRA. He observed that the measurement of helium is a good tool for exploration in known geothermal resource areas. Nielson (1978) used radon emanometry as a geothermal exploration technique in the Roosevelt Hot Springs KGRA. It was found that faults and fracture zones in the geothermal area transport anomalous amounts of radon. However, a relatively low response was detected over faults which were sealed by the precipitation of silica or clays formed during hydrothermal alteration. The highest response was interpreted as being due to a communication of the fault with the geothermal reservoir as evidenced by production wells along the trend. High radon anomalies were reasonably well correlated with resistivity anomalies.

V. SALTON TROUGH

The Salton Trough geothermal system is located principally in the Imperial Valley, southern California, where the East Pacific spreading center passes under the Colorado River delta and then is offset hundreds of kilometers to the northwest along the San Andreas fault. The Salton Trough is a region of unusually thin crust as identified by an underlying broad gravity maxima and anomalously high heat flow. The geothermal system is in Pliocene and Quaternary metamorphosed delta sediments and is associated with the young (16,000 yr old) rhyolite domes and abundant subsurface intrusive rocks of silicic and mafic composition. Several local thermal anomalies are found in the trough and each may be associated with localized igneous material intruded at or near the bottom of the sedimentary section (6-7 km in depth).

V.A. Geochemistry of primary volcanic rocks

Several geothermal fields have been recognized in the Imperial Valley of Southern California and its extension southward into the Mexicali Valley, Baja California. Most drilling thus far has taken place at the Salton Sea, Brawley, Heber, The Dunes, East Mesa, and Cerro Prieto. Because the potential sites for DOE Continental Scientific Drilling activities are restricted to the continental U. S., the discussion below is generally limited to sites occurring within the U. S. portion of the Salton Trough.

V.A.1 Petrology and primary mineralogy

Surface volcanic rocks of the Salton Sea geothermal field consist of five small rhyolite domes (the Salton Buttes). Two domes are linked by subaqueous pyroclastic deposits; the remaining domes are single extrusions with and without marginal lava flows. Petrographically, the domes consist of black to light gray obsidian, or light gray to reddish gray, micro-crystalline

rhyolite. Most lavas contain 1-2 percent of phenocrysts of anorthoclase, oligoclase, barkevikite, ferroaugite, and iron oxides, with trace amounts of quartz, fayalite, and zircon. Phenocryst compositions are presented in Robinson et al. (1976). Chemically these rhyolitic domes consist of low-calcium alkali rhyolite, intermediate in composition between peralkaline commendite and metaluminous rhyolite. No systematic variations occur between individual domes.

Basaltic rocks occur as xenoliths in the domes and as subsurface dikes, sills, and flows. The xenoliths consist of low-potassium tholeiitic basalt, with both normative hypersthene and olivine, and are similar to basalts of the East Pacific Rise. They differ from oceanic tholeiite in having slightly higher SiO_2 , Na_2O , and K_2O , and slightly lower Al_2O_3 . Subsurface basaltic rocks are mineralogically similar to the xenoliths. They differ chemically from them in being strongly enriched in K_2O , TiO_2 , and total Fe, and depleted in CaO and MgO due to extensive hydrothermal alteration (see section on secondary mineralogy and hydrothermal alteration).

Granitic xenoliths in the domes are inferred to be fragments of basement rather than intrusive equivalents of the rhyolitic magma. These xenoliths consist of sodic granite, with higher SiO_2 , CaO, and Na_2O , and lower total Fe than the enclosing rhyolite. They show various degrees of either cotectic melting along quartz-feldspar grain boundaries or disequilibrium incongruent melting of hydrous ferromagnesian minerals.

V.A.2 Elemental geochemistry

A relatively comprehensive set of chemical data has been published for the rhyolitic volcanics and the subsurface silicic rocks of the Salton Sea geothermal field (Robinson, et al. 1976). The data include chemical analyses

for the residual glasses and characteristic minerals of the rhyolites as well as whole-rock analyses for the rhyolites and the altered subsurface silicic rocks. The unaltered rhyolite rocks consist of glass, anorthoclase, oligoclase, barkevite, ferroaugite, iron oxides, and traces of quartz, fayalite, and zircon. Anorthoclase consists of optically homogeneous phenocrysts with a mean composition of $Or_{19}Ab_{75}S_{n6}$. Oligoclase crystals are relatively calcium-rich ($Or_5Ab_{73}An_{22}$ to $Or_{10}Ab_{72}An_{18}$) and apparently have been derived from granite inclusions within the lavas. Barkevite compositions are intermediate between ideal barkevite and basaltic hornblende; Robinson et al. (1976) class these amphiboles as "barkevite" because of their high iron and low magnesium contents. Pyroxenes range from $(Ca_{.41}Fe_{.33})SiO_3$ to $(Ca_{.43}Fe_{.40}Mg_{.17})SiO_3$, iron-rich varieties being the most abundant. The subsurface silicic rocks are composed chiefly of alkali feldspar and quartz with micro-phenocrysts of plagioclase and clinopyroxene.

Geochemical data presented by Robinson et al. (1976) show that Sr and Ba are strongly depleted in the Salt Buttes rhyolite relative to typical silicic rock, yet are higher than values for commendite. Rb, La, Nb, Y and Zr abundances average 30, 70, 20, 100, 300 ppm, respectively.

Robinson et al. (1976) present whole-rock analyses for the low potassium tholeiitic xenoliths found in rhyolitic domes and for the subsurface basaltic dikes, sills, and flows penetrated by drill holes. Fresh basaltic xenoliths consist chiefly of zoned calcic plagioclase (An_{65-40}) and pyroxenes (augite and some hypersthene) with lesser amounts of olivine (Fo_{80}), iron oxides, and apatite. The subsurface basaltic xenoliths contain glassy and crystalline fragments.

V.A.3 Petrogenesis of volcanic rocks

The low-potassium, tholeiitic basalts of the Salton Sea geothermal field are closely related to basalts of the East Pacific Rise. Their chemical compositions suggest that they represent magma formed in the mantle at an active oceanic spreading center. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the obsidians (0.704 - 0.705) are close to the values found for oceanic basalts (0.702 - 0.704) and within the range found for continental basalt (0.703 - 0.711).

The origin of the rhyolitic magmas is somewhat problematic. Doe et al. (1966) found that the isotopic differences for lead and strontium between the volcanic glasses and nearby sedimentary rocks precluded the possibility of the volcanic rocks being derived solely by complete melting of sedimentary rocks similar to those found in the upper 1.5 km of the Salton Basin. Partial melting of the same sedimentary rocks also appears unlikely, because detrital K-feldspars and micas of any appreciable geologic age would contain strontium that is too radiogenic for the ratio observed in the volcanics. K-spars and micas are among the first melting fractions of rocks. The residues of the sedimentary rocks are also too radiogenic ($^{87}\text{Sr}/^{86}\text{Sr} > 0.713$) to yield the volcanics.

Similarly, an origin by fractional crystallization of basaltic magmas is not likely since rocks of intermediate composition are not present. Assuming a minimum value of 0.700 for $^{87}\text{Sr}/^{86}\text{Sr}$ in basaltic-gabbroic rocks and observed values of 0.713 for sediments of the Salton Trough and 0.705 for the volcanics, it appears that no more than 40% of the strontium in the volcanics could be derived by assimilation of sediments. If the lower crust or mantle are isotopically non-uniform, then it is possible that no upper crustal component was contributed to the volcanics.

Robinson et al. (1976) suggest an origin by partial melting of a quartz-normative parent, that can be represented in the system $\text{CaMgSi}_2\text{O}_6\text{-Mg}_2\text{SiO}_4\text{-SiO}_4\text{-SiO}_2$, as suggested by Yoder (1973).

Such partial fusion presumably occurs in the mantle. Experimental confirmation of such an origin does not presently exist.

V.B Fluid Chemistry

The most complete aqueous chemical data are available for the Salton Sea Geothermal area situated near the south east shore of the Salton Sea. Additional potential geothermal reservoirs underlie the East Mesa anomaly and the Dunes anomaly north of the U. S. Mexican border.

V.B.1 Surface springs Surface manifestations of thermal activity in the vicinity of the Salton Sea are currently limited to a few passive CO_2 -rich, neutral, NaCl hot springs and mud pots (Helgeson 1968a). (Table 1 col. 11). As discussed by Muffler and White (1968) these springs are aligned along northwest-trending lineaments, the northeast spring being on the projection of the San Andreas fault.

V.B.2 Geothermal brines

The geothermal brines associated with the Salton Trough are unique relative to previously described chemistries (table 1 col. 10) due to their extremely high concentrations of sodium, potassium, calcium and chloride and concentrations of ore-forming heavy elements such as silver, zinc, lead and copper. The closest chemical analog is the Red Sea brines (Craig 1969). In many cases large discrepancies exist among published analyses of the Salton Trough fluids due to difficulties in obtaining representative samples from wells producing two phase flow as well as various analytical uncertainties caused by unusual composition effects.

Sample 10 in table 1 is probably a good representative of brine composition. As discussed by Helgeson (1967), the composition of the brine in the geothermal reservoir varies with depth and radius of the geothermal system. Total dissolved solids increased from several thousand parts per million close to the surface to >250,000 ppm at depth greater than 3000m. Helgeson (1968a) also found a direct, linear relationship between temperature and salinity.

Helgeson (1968a) estimated that the fugacities of sulfur, oxygen and CO₂ also vary with temperature and therefore with depth and position in the reservoir. At 3000 m at a temperature of 300°C, they are of the order of 10⁻¹⁰, 10⁻³⁰ and 2.5 atmospheres respectively.

Geochemical and thermodynamic calculations (Helgeson 1967) suggest that reservoir fluids in the brine system are in chemical equilibrium with the mineral assemblage in the enclosing rocks comprised of K-feldspar, albite, K mica, chlorite, quartz, epidote and calcite. Chemical reaction between the original pore fluid in the rock and the sedimentary mineral assemblage has led to a relatively low pH and enrichment of K⁺, Ca⁺⁺ and Fe⁺⁺.

CO₂ accounts for over 90% by volume of the non-condensibles produced by the wells in the geothermal area, and the remainder is composed primarily of H₂S and hydrocarbon gases. A CO₂ gas field is also associated with the geothermal system and is located within the fault system in the Salton Sea geothermal area. Muffler and White (1968) attributed the CO₂ to metamorphism of Colorado River Delta sediments, principally calcite and dolomite. Tooms (1971) estimated the areal extent of the Salton Sea brine field at about 30 km² and a total volume of brine on the order of 2-1/2 to 5 km³.

Swanberg (1974) applied the Na-K-Ca geothermometer to water samples from two wells drilled into the East Mesa anomaly. In one well he found close agreement between the geothermometer and measured well temperature of 188 to 184°C but in the second, the geothermometer predicted temperatures 20-40°C higher than measured, suggesting CaCO₃ precipitation in the reservoir.

A major debate in the literature has centered around the origin of the Salton Trough brines. The most widely accepted explanation is that the brine originated as meteoric water, possibly from the Colorado River water, and has been extensively modified by reaction with the reservoir aquifer. Craig (1966) compared the concentrations of O¹⁸ and D in the brines and other waters in the same area. The various brines he sampled displayed an oxygen isotope shift, i.e., an increase in O¹⁸ with a constant D relative the local surface water value. Isotopic exchange with carbonates and silicates increases the oxygen-18 content of the local meteoric water, but the deuterium content is unaffected because of the small amount of hydrogen in rocks. More specifically, he identified the source of the brine as local precipitation ($\delta\text{-O}^{18} = -11$ per mil) entering the subsurface system along faults at the base of Chocolate Mountain, east of the Salton Sea. The relationship between chloride and oxygen-18 enrichment in these fluids also showed that the progressive increase was due to continuous interaction with sediments and not simply an increasing admixture of water from a deep reservoir where isotope exchange and solution begin suddenly to affect inflowing surface water.

Helgeson (1968a) has offered an alternative explanation in which the brines were formed by evaporation of dilute pore water through geologic time. Hot fluids would move upward to the surface through fractures or interconnected permeable sand lenses in the shale, and evaporate at the surface. The fluid

phase would become more saline and dense and would then circulate back underground. A closed system of recirculating pore fluid would be established. Craig (1969) argued against this hypothesis by showing that neither batch nor continuous evaporation processes operating on original interstitial water of present day Colorado River isotopic composition can produce the geothermal brine oxygen-18 and deuterium values observed today.

Berry (1967) has suggested that the brines achieved their high salinities as a result of hyperfiltration through semipermeable shales in the stratigraphic section. The limiting condition for the process is the establishment of a solvent pressure equilibrium between the hot concentrated brine and the cold dilute pore waters in the surrounding sediments.

A radiogenic tracer study of lead and strontium in the brines indicates that the bulk of these trace elements are acquired by leaching during metamorphism of the host sediments in the thermal environment (Doe et al., 1966). Selective concentration of many dissolved constituents of ocean water cannot produce the brines because ocean water is isotopically quite distinct from the brines in terms of both lead isotopes and strontium isotopes. Similarly, the brine lead and strontium isotopes cannot be derived from the isotopically distinct magmas which produced the rhyolite glasses in the Quaternary rhyolite domes (the Salton Buttes). A magmatic source at depth with a different strontium isotopic composition from the rhyolite glasses could be postulated, but igneous rocks with values of $^{87}\text{Sr}/^{86}\text{Sr}$ equal to 0.711 (the granite composition) are quite rare.

Coplen (1973) analyzed over 200 well and spring geothermal water samples from the Imperial Valley and concluded that most of the surface water is derived from the Colorado River.

V.C. Hydrothermal alteration

The reservoir rocks for the hydrothermal fluids of the Salton Trough consist of up to 7000 m of poorly sorted Colorado River detritus forming sandstones, shales, siltstones, and conglomerates (Muffler and Doe, 1968). The assemblages comprising these rocks, which have been described elsewhere in this report, provide the reactant phases for the major hydrothermal alteration processes occurring within the Salton Trough. Hydrothermal alteration has also been observed in small rhyolitic and basaltic intrusions penetrated during drilling at the Salton Sea (Robinson et al., 1976) and Heber (Browne and Elders, 1976; Browne, 1977). Most hydrothermal alteration studies of the Salton Trough hydrothermal system have focused on alteration of the Colorado River detritus. The results of these studies are summarized below for various areas, after which a summary of available information for the altered intrusive rocks is given.

V.C.1 Salton Sea geothermal field

The chemistry of the alteration assemblages in the Salton Sea field has been the object of several investigations over the past 15 years (Helgeson, 1967, 1968b; Skinner, et al. 1967; Muffler and White, 1968, 1969; Keith et al., 1968; Kendall, 1976; Robinson, et al., 1976; Elders et al., 1977; Elders, 1978; Tewhey, 1977; McDowell and McCurry, 1977; McDowell and Elders, 1978, 1979). These studies, based largely on cuttings from several drill holes and to a lesser extent on drill cores, represent a major contribution to the understanding of hydrothermal alteration processes in the continental crust.

Detailed subsurface mapping of hydrothermal alteration utilizing cuttings from deep drill holes has revealed a very complex metasomatic mineral zoning that can be correlated with measurable parameters such as depth, temperature, fracture density, permeability, and sedimentary textures and fabrics. Alteration

throughout the system is predominantly of the pervasive type, but some minerals (especially epidote) are also present along fractures at depth. Changes in mineralogy with depth are not in general related to original differences in the mineralogy/chemistry of the Colorado River sediments. To a first approximation, the changes in alteration mineralogy correlate primarily with temperature and secondarily with other variables (Muffler and White, 1969; Elders, 1977). In all reports to date, changes in mineralogy and mineral chemistry are progressive with increasing temperature, and the sequence of changes tends to be similar in all wells. Changes in permeability are, nevertheless, increasingly being recognized as significant determinants and products of hydrothermal alteration (Kendall, 1976; Tewhey, 1977; Elders, 1977, 1978). Dramatic changes in the density, porosity, and permeability of reservoir rocks, caused by water/rock interactions, have been documented in strata with temperatures ranging from 100°C to 365°C. More permeable reservoir rocks have been preferentially subjected to hydrothermal alteration and stable isotope exchange (Kendall, 1976), with the result that their porosity and permeability have been reduced, in some instances to the point of forming self-sealed cap rocks (Tewhey, 1977)). Hence, differences between the hydrothermal alteration products in strata at similar temperatures are often a reflection of permeability differences. In some cases, however, these differences record the effects of different thermal pulses as Elders (1977) has shown from mineral isograd and fluid inclusion data. Retrograde metamorphism could also be involved, but evidence of it is not extensive.

The original phases of the deltaic and lacustrine sediments consist of detrital quartz, calcite, K-feldspar, plagioclase, montmorillonite, illite, dolomite, kaolinite, gypsum, and anhydrite. According to Elders (1977), the progressive stages in the hydrothermal alteration of these assemblages include:

- (1) replacement of kaolinite and montmorillonite to form illite and then

sericite-phengite; (2) solution of silicates and precipitation of calcite; (3) replacement of carbonates and formation of quartz, adularia, albite, epidote, chlorite, tremolite, small amounts of talc, anhydrite, pyrite, and hematite; and (4) disappearance of anhydrite, hematite, and talc from the above assemblage, replacement of chlorite by biotite, and formation of anhydrite.

Muffler and White (1969) were able to estimate temperatures for a number of metamorphic reactions inferred from cuttings of the wells I.I.D. No. 1 and Sportsman No. 1, which are on the order of 1500 m deep and north of the thermal, gravity, and magnetic anomaly centers for the field. Detrital montmorillonite converts to illite-montmorillonite below 100°C; the latter converts to K-mica at temperatures below 210°C. Ankerite forms by conversion of calcite and/or dolomite at temperatures as low as 100°C. Dolomite, ankerite, kaolinite, and Fe^{+2} (from brine) react to produce chlorite, calcite, and CO_2 at temperatures of 180°C and possibly as low as 125°C. At temperatures greater than 290°C to 310°C, calcite, K-mica, quartz, and Fe^{+2} react to form Fe-epidote and K-feldspar with further liberation of CO_2 . Muffler and White (1968) have interpreted these reactions occurring at depth as the sources of large amounts of CO_2 at shallow levels in the now-abandoned Imperial Carbon Dioxide Gas Field, and they have suggested (Muffler and White, 1969) that the high CO_2 activity relative to H_2O activity precluded zeolite formation in the Salton Sea field. Above 300°C, the most common mineral assemblage reported by Muffler and White (1969) is quartz + Fe-epidote + chlorite + K-feldspar + albite + K-mica with sporadic pyrite and hematite. They note that Na-Ca plagioclase persists throughout the explored system.

Detailed chemical studies of alteration minerals in the Salton Sea geothermal field have been carried out by Keith et al. (1968), McDowell and McCurry (1977), and McDowell and Elders (1978).

McDowell and McCurry (1977) reported detailed mineral-chemical changes as a function of depth and temperature in mineralized sandstones from the Elmore No. 1 well. This well is located near the center of the thermal, gravitational, and magnetic anomalies that characterize the Salton Sea geothermal field. According to McDowell and McCurry (1977), there are three characteristic mineral zones in the sandstones: a chlorite + calcite zone from 600 m to 1100 m (250°C to 325°C); a biotite zone from 1100 m to 2150 m (325°C to 360°C); and a garnet zone at depths greater than 2150 m (> 360°C). All mineral zones contain albite, quartz, pyrite, and solid solutions of epidote. The sandstone is altered texturally from a porous, weakly cemented, little altered, angular detrital aggregate at depths less than 600 m (< 250°C) to a dense, tightly cemented, completely recrystallized granoblastic mozaic at depths greater than 990 m (> 315°C).

Clayton et al. (1968) have shown that the sub-surface sediments of the Salton Sea area show the expected reverse oxygen isotope shift with depletion of oxygen-18 which has enriched the circulating thermal waters.

A study was made of the petrology and stable isotope geochemistry of cuttings recovered from three wells in the Buttes area of the SSGF. Kendall, (1976) she found that extensive oxygen and carbon isotope exchange has occurred between geothermal brines and country rocks. Detrital and diagenetic carbonates have exchanged with the brines at temperatures as low as 100-150°C. Both detrital and authigenic quartz in dense, highly altered and mineralized sandstones have completely or almost completely exchanged at temperatures as

low as 290°C. Hydrothermal epidote oxygen delta-¹⁸O values are approximately 4 per mil lighter than coexisting quartz. Hydrothermal hematite is in apparent oxygen isotopic equilibrium with quartz at measured borehole temperatures (~ 300°C). Superimposed on the gross trend of lower delta values at increasing temperature is another important effect due to permeability variations in the reservoir rocks. Aquifers are characterized by low delta values, and aquitards by high values. The oxygen delta values of vein calcite are 0-1 per mil lighter than those of calcite cement in sandstones, which in turn are 1-7 per mil lighter than those of calcite in shale. Hydrothermal alteration is more extensive in zones characterized by low delta values, and differs significantly from the alteration assemblages in less permeable horizons. Aquifer permeability is predominantly secondary and lithologic variation has a strong effect on the creation of microfractures. Water circulation is largely restricted to horizontal aquifers which have been correlated between wells using delta values. Fluids within veinlets are locally derived and vertical fractures have been relatively unimportant as circulation channels.

Although the potential sites for the CSDP are restricted to the continental U.S., some recent work at Cerro Prieto, Mexico, which also lies in the Salton Trough, bears some discussion. Olson et al. (1976) found that for almost all Salton Trough geothermal fields the oxygen delta value is not just a function of temperature because of great variations in water-rock ratios, even on a very local scale. For example, the delta values for calcites at Cerro Prieto between 2000 and 220 m. depth have a range of almost 20 per mil. Vein calcite is systematically the lightest, sandstone and siltstone are intermediate, and shale has the heaviest delta values. Because of this low permeability the shales have limited interaction with geothermal fluids and so preserve

detrital diagenetic delta values. Vein calcite, however, is precipitated directly from hydrothermal fluids and is thus in equilibrium with hot water. This range in delta values represents a spectrum of increasing water/rock ratios from shale to vein calcite. Therefore, temperature estimates based on vein minerals are the most likely indicators of the reservoir conditions. Olson et al. also noted that in the SSGF wells near the center of the field showed a heavy isotope shift and a much narrower spread of delta values than wells near the margins of the field. This would indicate high temperatures and high water/rock ratios. In another part of this same study, Elders et al. (1978) documented large temporal fluctuations in temperature on the flanks of the geothermal system at Cerro Prieto.

Helium measurements and $^3\text{He}/^4\text{He}$ isotope measurements were used in the Salton Trough for surface exploration of potential geothermal fields. (Reiner, 1976; Roberts, 1975; and Welhan et al., 1978). The observed 'excess' ^3He present in the dissolved gases in the brines and in soil gases have been supplied by the mantle to the thin, extensional crust overlying it.

Muffler and Doe.(1968) used lead and strontium isotopes to determine the mean age of Colorado River detritus forming up to 7000 m of sandstones, shales, silstones, and conglomerates in the Salton Trough. Lead isotope data from the acid-insoluble fraction of Colorado River delta samples from the trough indicate that the mean age of the detritus is 1700 m.y., and Sr isotope data indicated a mean age of greater than 500 m.y. This later mean age represents the time since isotopic homogenization by igneous or metamorphic processes, and contrasts with the Cenozoic age of the delta and the Mesozoic age of the rocks of the Colorado Plateau from which the detritus

dominantly derived. A small fraction of the acid-insoluble detritus of the Colorado River delta in the Salton Trough probably was derived by direct erosion of Precambrian rocks; however, the bulk of the acid-insoluble detritus probably comprises reworked detritus of Precambrian age previously incorporated in Mesozoic and Paleozoic sediments. The isotopic data preclude any appreciable component of detritus derived from the mountains adjacent to the Salton Basin which are largely igneous and metamorphic rocks of Mesozoic (and Paleozoic?) age.

V.C.2 East Mesa geothermal field

Petrologic studies of well cuttings from borehole Mesa 6-2 penetrating 1830 m of interbedded sandstone and fine-grained sediment of the Colorado River show that the vertical extent of the hydrothermal reservoir can be defined by the distribution of hydrothermal alteration products (Hoagland, 1976a; Hoagland and Elders, 1978a and 1978b; Hoagland and Elders, 1977). A diffuse upper boundary of hydrothermal alteration underlies a thick section of clay-rich sediment and is associated with a change in thermal gradient from .13°C/m to .02°C/m, indicating the clay-rich rocks form a barrier to flow of hydrothermal fluids.

Lack of equilibrium between the present day brine (a sodium chloride and bicarbonate brine containing 2380 mg/l total dissolved solids) and the hydrothermal alteration products in the East Mesa system has been used to demonstrate that the system experienced a significant change in its hydrology (Hoagland, 1976a; Hoagland and Elders, 1978). Fluid inclusion measurements indicate an earlier regime with temperatures 15°C to 20°C above present temperature. During an earlier event, quartz, pyrite, illite, Fe-chlorite,

and adularia were deposited in the sandstones; less porous siltstones and shales altered to illite and chlorite. Montmorillonite, kaolinite, and carbonates were destroyed and feldspar was altered incipiently to K-mica and quartz. These water/rock interactions resulted in a net addition of potassium and silica to the rocks and a net loss of H^+ to the fluid. Silicification of the reservoir inhibited continued influx of the earlier fluids. Later, colder water entered the system laterally, partly dissolved silicates, and precipitated abundant calcite. Thermochemical calculations of the characteristics of the fluids based on thermodynamic data for aqueous species and the observed sequence of alteration phases indicate the earlier fluid was distinctly different from the fluid presently being discharged from the system.

V.C.3 The Dunes geothermal field

A 612 m well at the margin of the Dunes thermal area provides a good example of permeability decreases and self-sealing resulting from hydrothermal alteration and deposition (Bird and Elders, 1973, 1975; Elders and Bird 1973). The well temperature profile shows a maximum of 104°C at 285 m, and a temperature reversal below this depth. The formation fluid is a dilute NaCl solution with less than 4000 ppm total dissolved solids.

The unaltered rocks in the drill hole consist of terrigenous detritus of the Colorado River Delta, primarily medium to fine arenaceous sands and silty sands, with pebble, granule, and clay size fractions together constituting approximately 15% of the section. Four distinct sedimentary facies are present: deltaic sand, channel-fill, beach-dune, and lacustrine facies.

Stratigraphic control of hydrothermal water-rock interactions has led to the formation of seven zones of intensively silicified sands and conglomerates in the upper 318 m of drill hole section. These zones range from 5 to 35 m thick and occur primarily within the originally more permeable strata of the dune-braided stream and channel-fill facies. Shale beds of low permeability separate the silicified zones from poorly indurated sandstones cemented by varying amounts of hematite, calcite, gypsum, and montmorillonoid clays. The potassium and silica mineralization occurs as interstitial-pore cements, as later fracture fillings, and as replacement metasomatism. The degree of mineralization increases with sorting of sands, and it is usually greatest immediately below the low permeability shales.

The authigenic mineral phases deposited within the silicified zones consist of quartz, adularia, hydromuscovite, illite and pyrite. Calcite, kaolinite, ferric oxide, and montmorillonite reactant phases are absent in the silicified units. There are, however, occasional examples of retrograde alteration of authigenic pyrite to ferric oxides. The silicification of the clastic sediments is accompanied by a decrease in the porosity to as low as 3 to 4% and an increase in density to as much as 2.55 g/cc. These changes are primarily the result of quartz and adularia precipitation within pores and voids of the clastic sediments. There has been at least two episodes of fracturing within the specified zones, and many earlier fractures are completely sealed by assemblages similar to those formed interstitially in adjacent strata. The fracture mineralization consists of quartz, hematite (from oxidation of authigenic pyrite), pyrite, adularia, and calcite. Several whole-rock analyses of the silicified sediments are presented by Bird and Elders (1975).

The hydrothermally altered sands have undergone a net gain in SiO_2 and K_2O ; they have lost CaO , Na_2O , Fe_2O_3 , and MgO . The increase in SiO_2 and K_2O are the result of additions of authigenic silica, adularia, and potassium phyllosilicates. Dissolution of calcite causes depletion in CaO , and the loss of Na_2O , Fe_2O_3 , and MgO is attributed to the breakdown of smectites.

Bird and Elders (1975) characterized the hydrothermal alteration processes at the Dunes as the addition of silica and potassium by precipitation of void-filling quartz and adularia. These reactions would be favored by the decrease in silica solubility with falling temperature upon migration of hot brine into a cooler environment. The absence of montmorillonite, kaolinite, and calcite together with the replacement fabric of adularia, quartz and hydromuscovite can be interpreted as the result of metasomatic addition of potassium and loss of hydrogen.

V.C.4 Hydrothermal alteration of volcanic rocks.

Alteration minerals associated with the rhyolites exposed at the surface include secondary amphibole, secondary mica, chlorite, epidote, and pyrite. The principal reactant phase is augite altering to epidote and amphibole. Compared with the rhyolite domes, the subsurface silicic rocks have markedly higher K_2O , CaO , MgO , TiO_2 , and total iron, but lower SiO_2 and Na_2O . Ferromagnesian trace elements (Cr, Ni, V, Cu, and Mo) are significantly enriched in the subsurface rocks; Ba and Sr are strongly enriched, sympathetically with K_2O and CaO . Robinson et al. (1976) assume that the rhyolite domes and subsurface silicic rocks formed from the same lava and that the present composition differences result from intense hydrothermal

alteration of the latter. High Fe in the drill cuttings can be related to abundant pyrite, and the high K_2O to the presence of secondary mica. Secondary amphibole and epidote are probably responsible for the increased CaO. The lower SiO_2 and Na_2O are interpreted as relative reductions caused by large increases in other oxides. The composition of the subsurface silicic materials are qualitatively compatible with the Salton Sea geothermal brine (Helgeson, 1968b), which are very rich in potassium, calcium, barium, strontium, and iron -- all elements relatively enriched in the drill cutting. The glassy fragments in the basaltic xenoliths tend to be incipiently devitrified to clinopyroxene and partly replaced by K-mica. Secondary K-mica is abundant and may completely replace augite in samples. Most samples also contain carbonate, chlorite, and secondary amphibole, together with small amounts of epidote, pyrite, and K-feldspar. The extensive alteration of the subsurface basaltic rocks is reflected in their whole rock analyses which, compared with the compositions of basaltic xenoliths, are strongly enriched in K_2O , TiO_2 , and total iron while depleted in CaO and MgO. Enrichment in alkalis, especially K_2O , is sufficient to allow small quantities of normative nepheline in most of these rocks. Some cuttings of subsurface basalt are enriched in SiO_2 relative to the xenoliths, a feature probably due to alteration but possibly the result of contamination of the cuttings by sediments.

Hydrothermal alteration has also been described in a diabase dike penetrated from 1335 m to 1365 m in Holtz #1, a 1570 m well into the Heber geothermal field (Browne and Elders, 1976; Browne, 1977). Both the diabase and host rock sediments have reacted with hydrothermal fluids during cooling of the intrusion. Primary

minerals of the diabase are augite ($\text{En}_{44.5}\text{Wo}_{44.5}\text{Fs}_{11.0}$ to $\text{En}_{33.0}\text{Wo}_{38.5}\text{Fs}_{28.5}$) plagioclase (An_{15} to An_{76} , zoned), olivine, and accessory magnetite and ilmenite. Chlorite is the most abundant secondary mineral in the diabase, and it replaced olivine and plagioclase. Prehnite, with up to 6 wt.% FeO, typically replaces plagioclase and also occurs in vesicles. Calcic plagioclase is locally altered to calcite or sodic albite. Magnetite and ilmenite are partly altered to sphene or minor pyrite. Iron-rich epidote, oligoclase, albite, anhydrite, quartz (rare), and wairakite occur in veins or vugs. Potassium minerals are absent. Ground mass augite has altered to ferroaugite (up to Fs_{57}), apparently in response to hydrothermal reaction.

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