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REFERENCES USED IN COMPILATION OF THERMAL SPRING  
DATA FOR THE WESTERN UNITED STATES

June 1977

National Geophysical and Solar-Terrestrial Data Center

EDS/NOAA

(GEORGE BERRY)

Boulder, Colorado 80302

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WASHINGTON

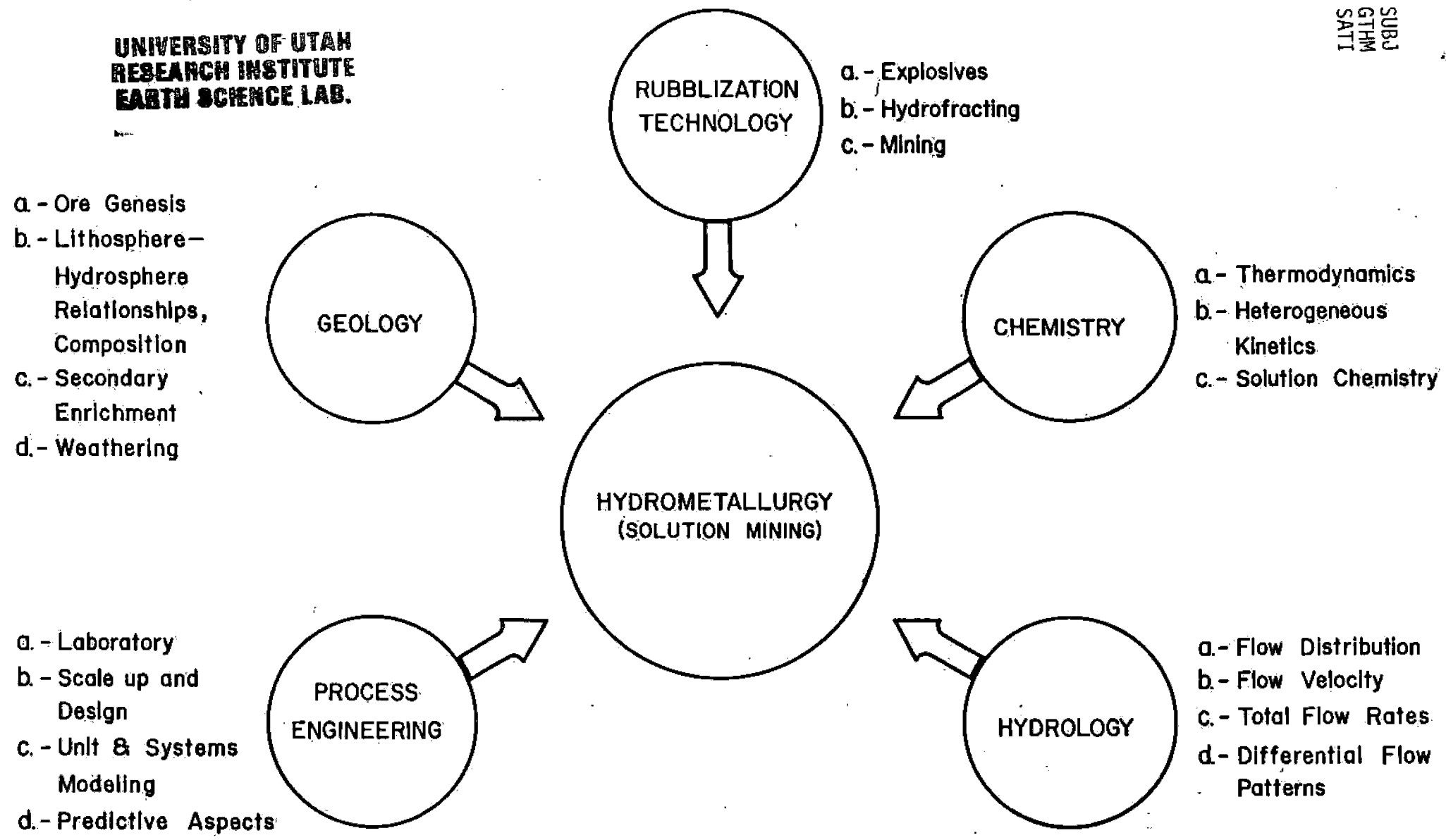
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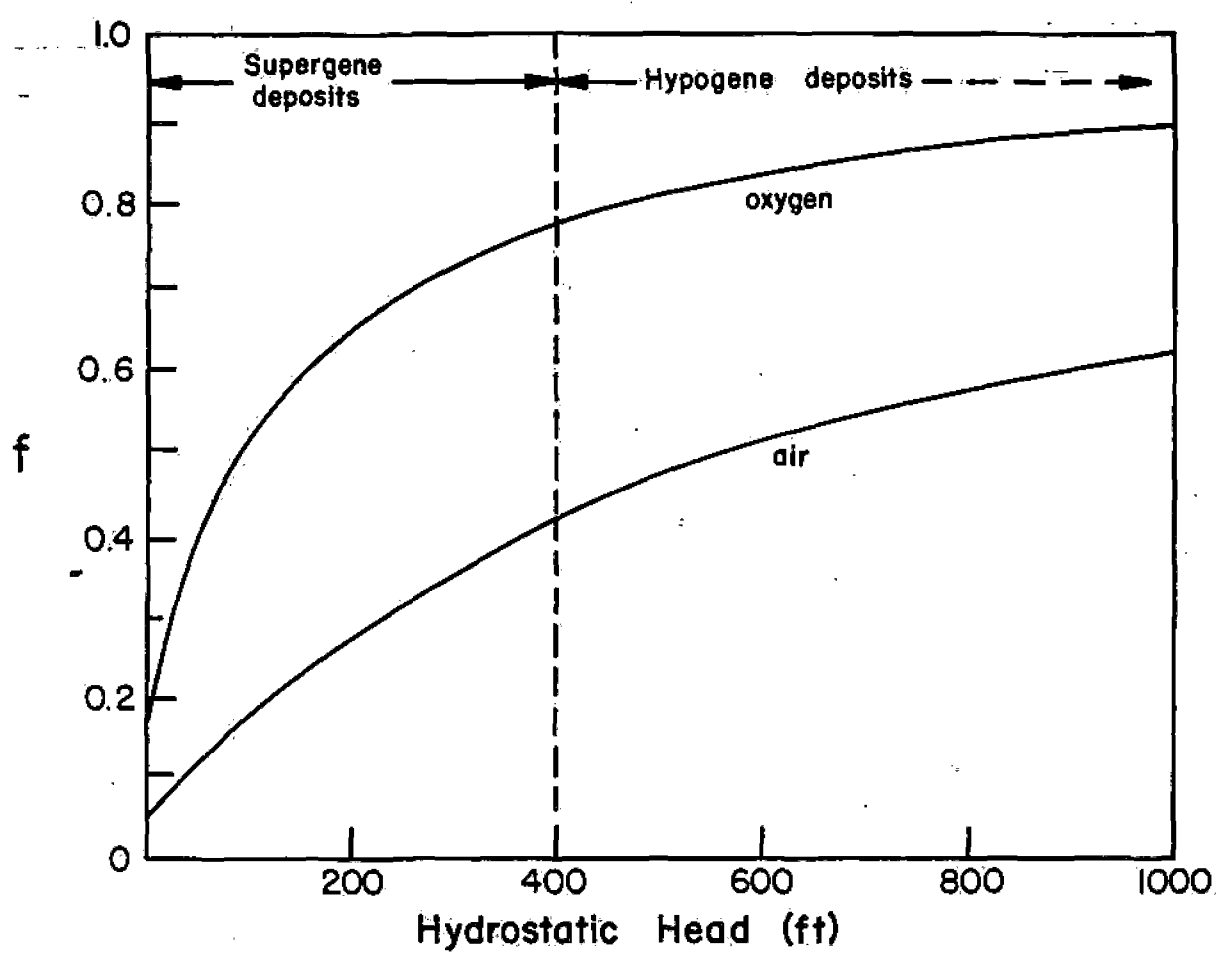
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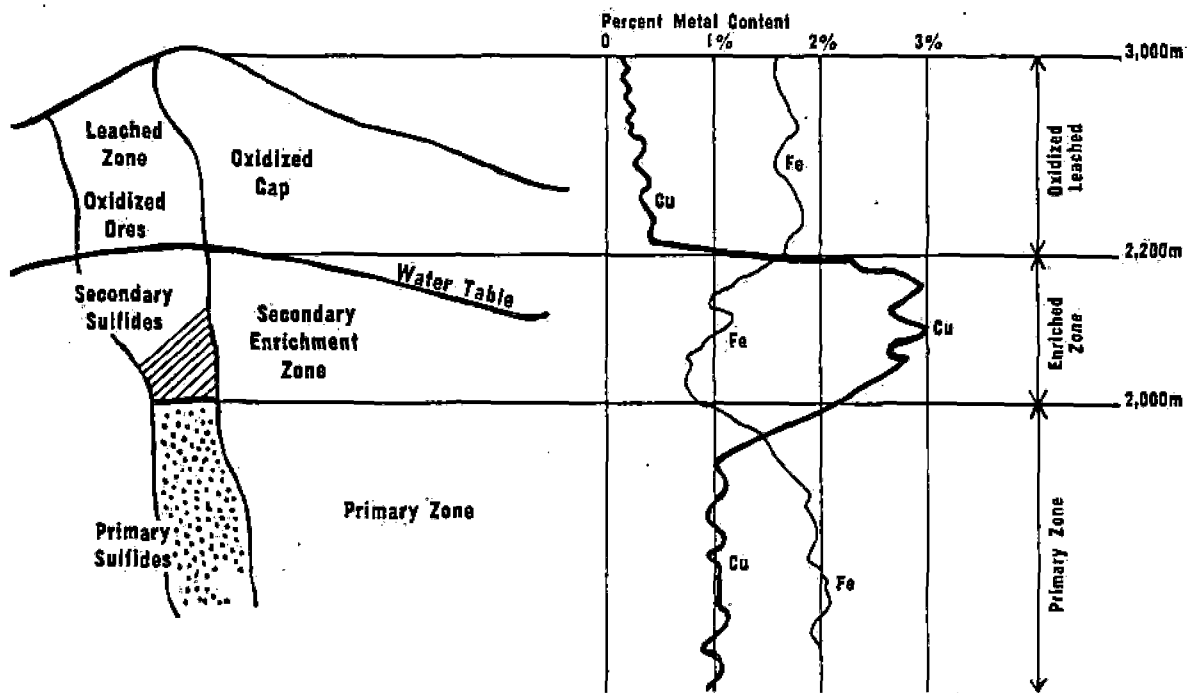
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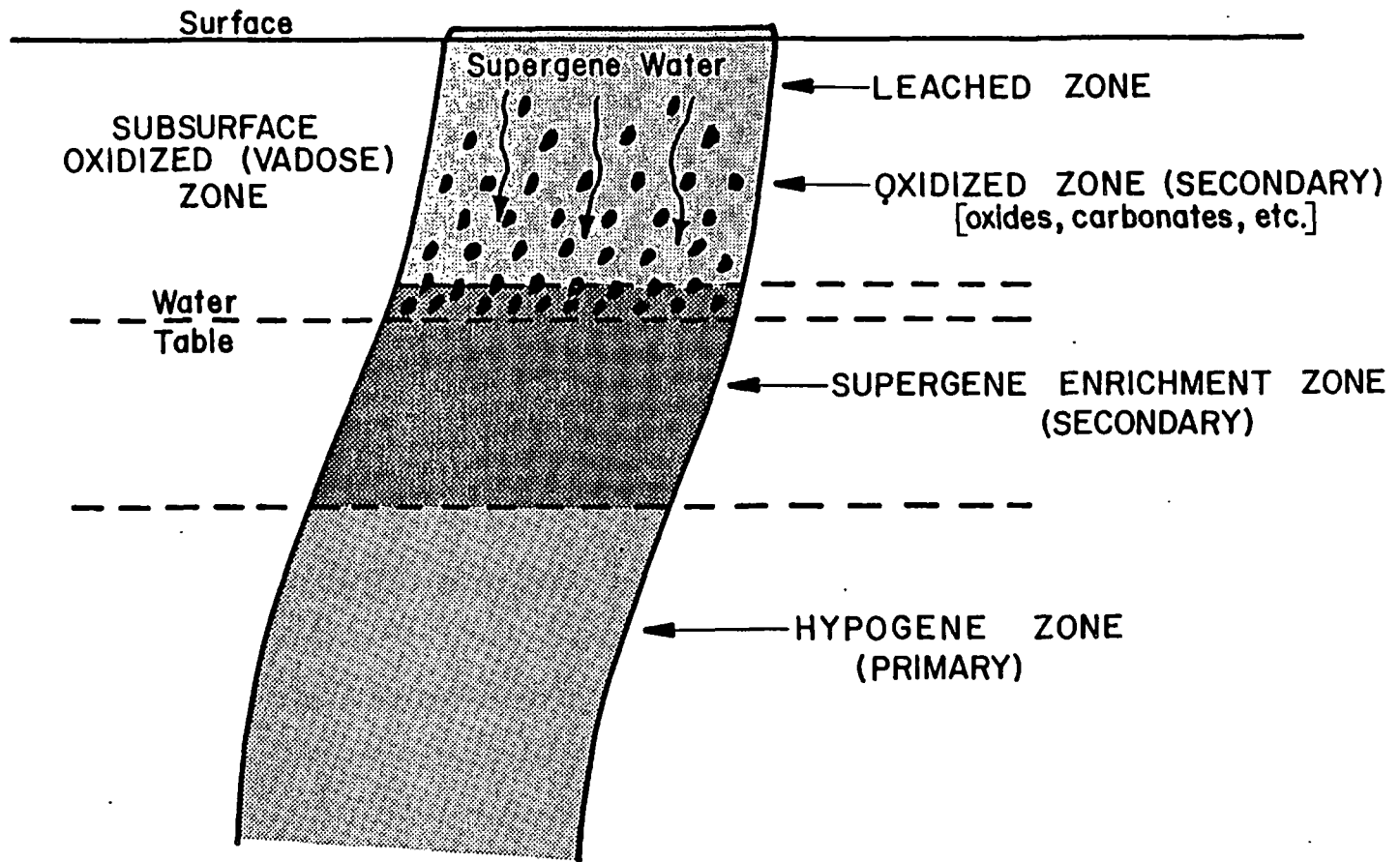
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SCIENCE AND TECHNOLOGY INTERFACES  
IN HYDROMETALLURGY





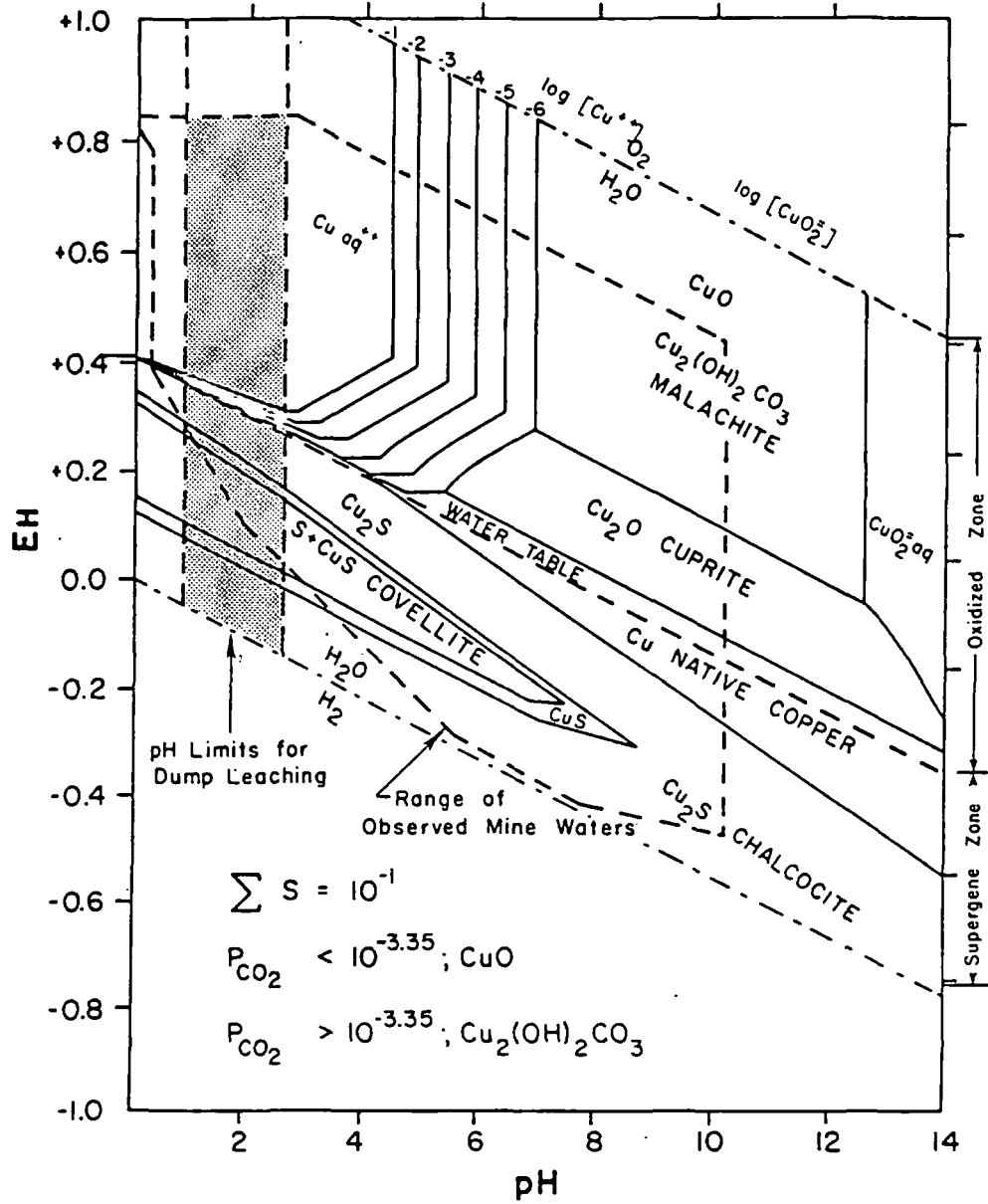


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## COPPER MINERALS

<p>OXIDIZED ZONE (SECONDARY)</p>	<p>Native Copper Malachite★ Brochantite★ Antlerite★ Atacamite★ Azurite★ Chrysocolla★ Cuprite★ Tenorite★</p>
<p>SUPERGENE ENRICHMENT ZONE (SECONDARY)</p>	<p>Chalcocite★ Covellite Native Copper</p>
<p>HYPOGENE ZONE (PRIMARY)</p>	<p>Chalcopyrite Bornite Enargite★ Tetrahedrite★ Tennantite★ Covellite</p>

★always in position indicated (Forrester)

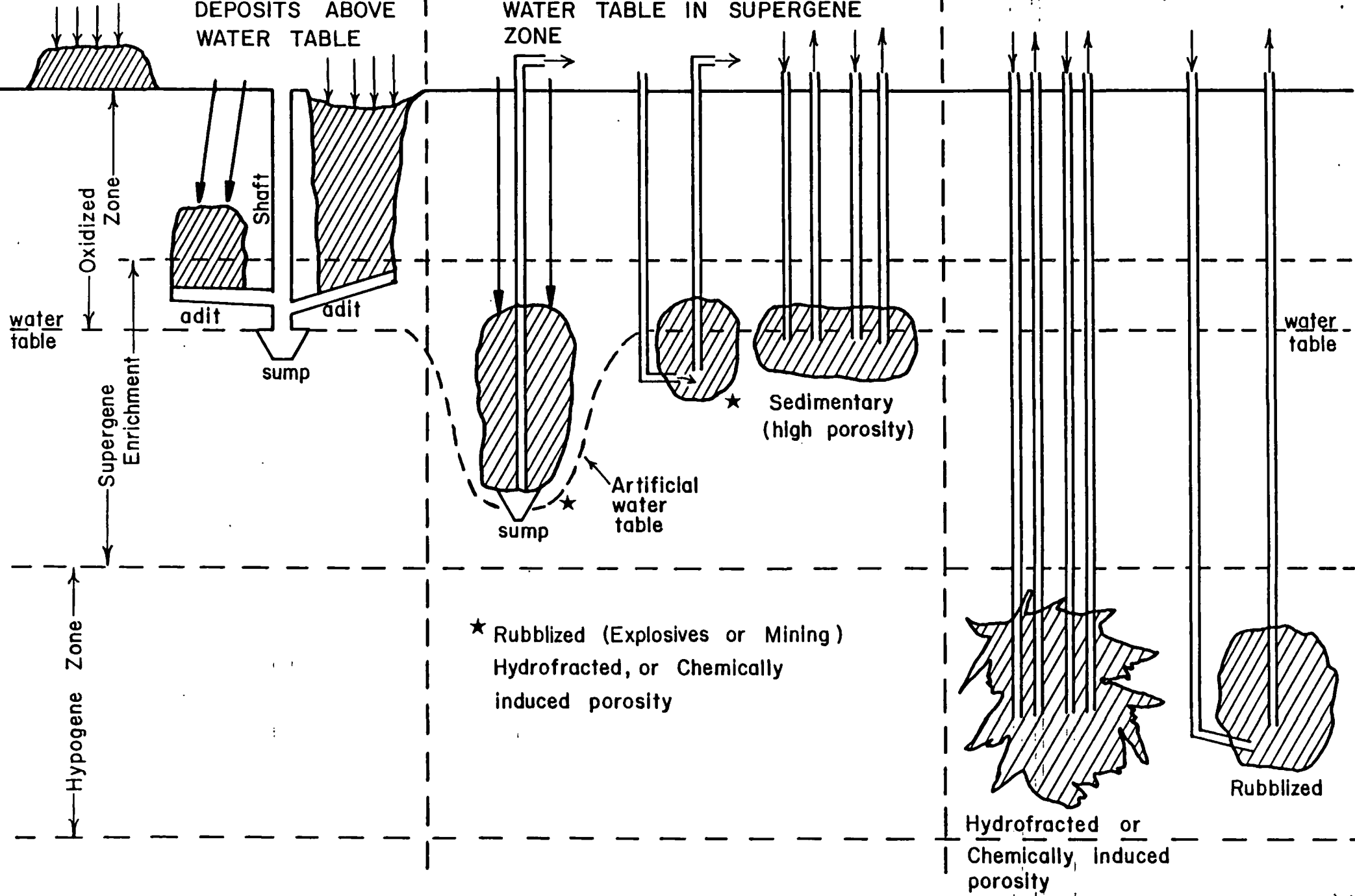


# SOLUTION MINING SYSTEMS

I- DUMPS AND DEPOSITS ABOVE WATER TABLE

II- DEPOSITS EXTENDING UNDER WATER TABLE IN SUPERGENE ZONE

III- DEEP HYPOGENE DEPOSITS





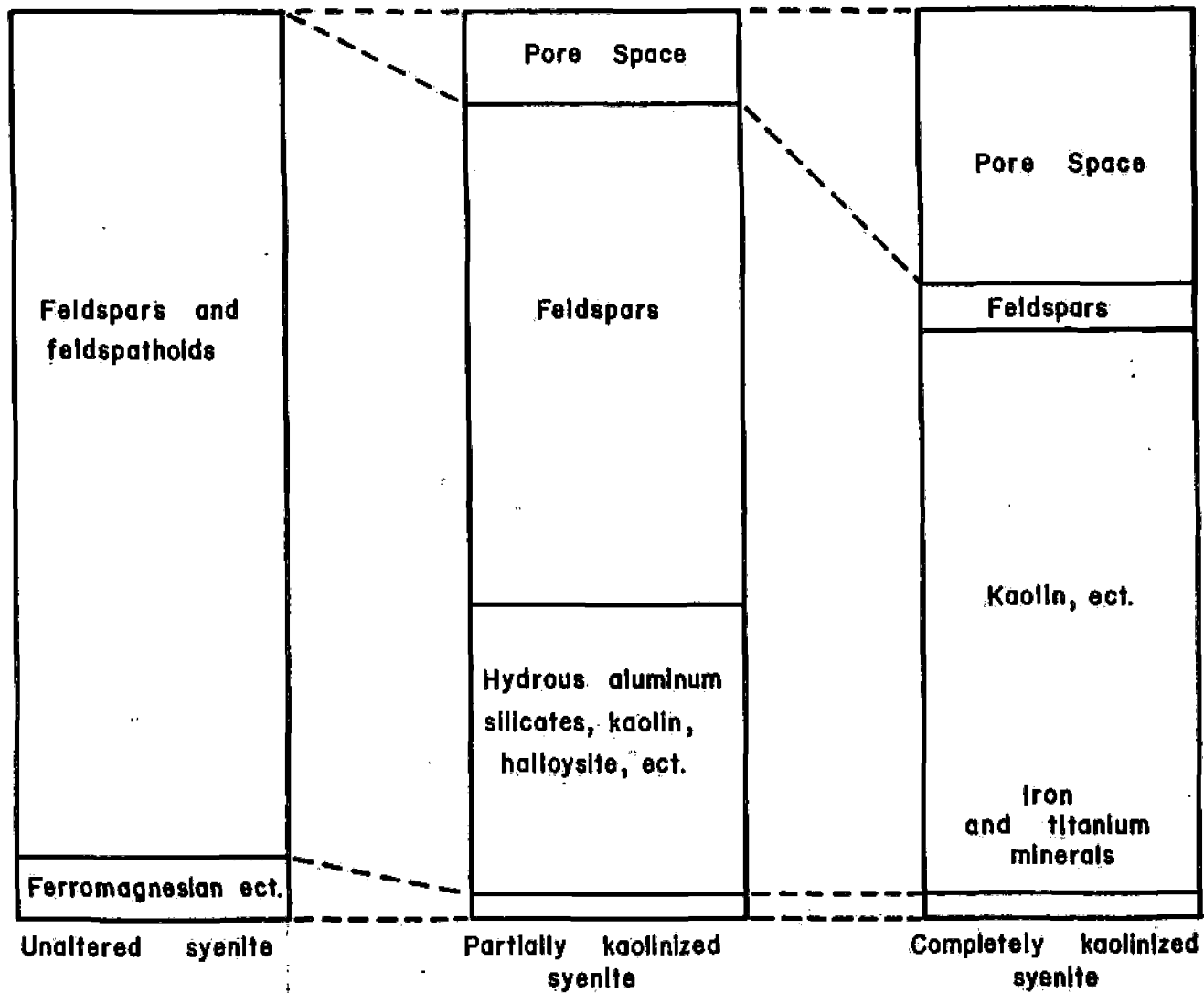
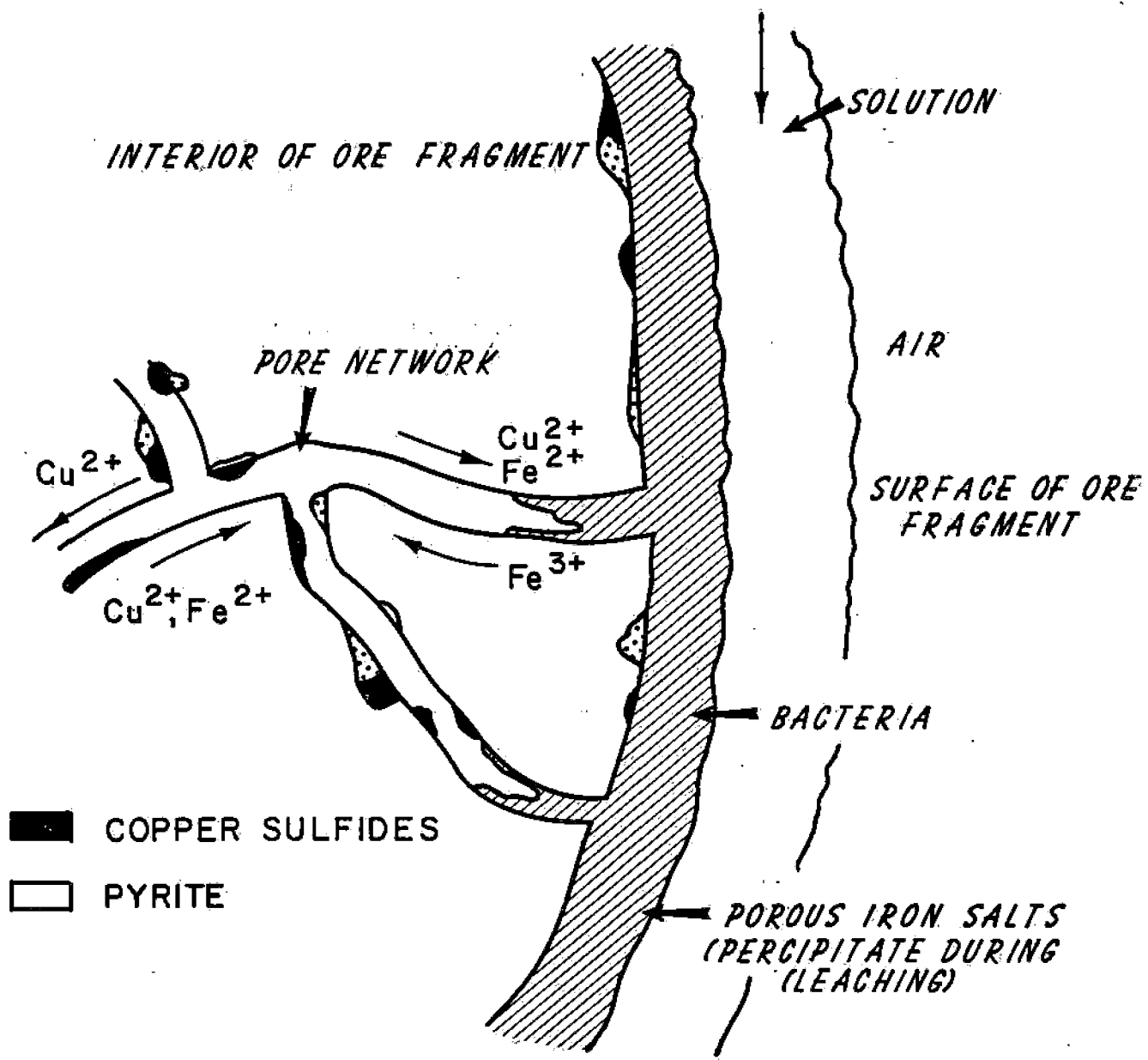
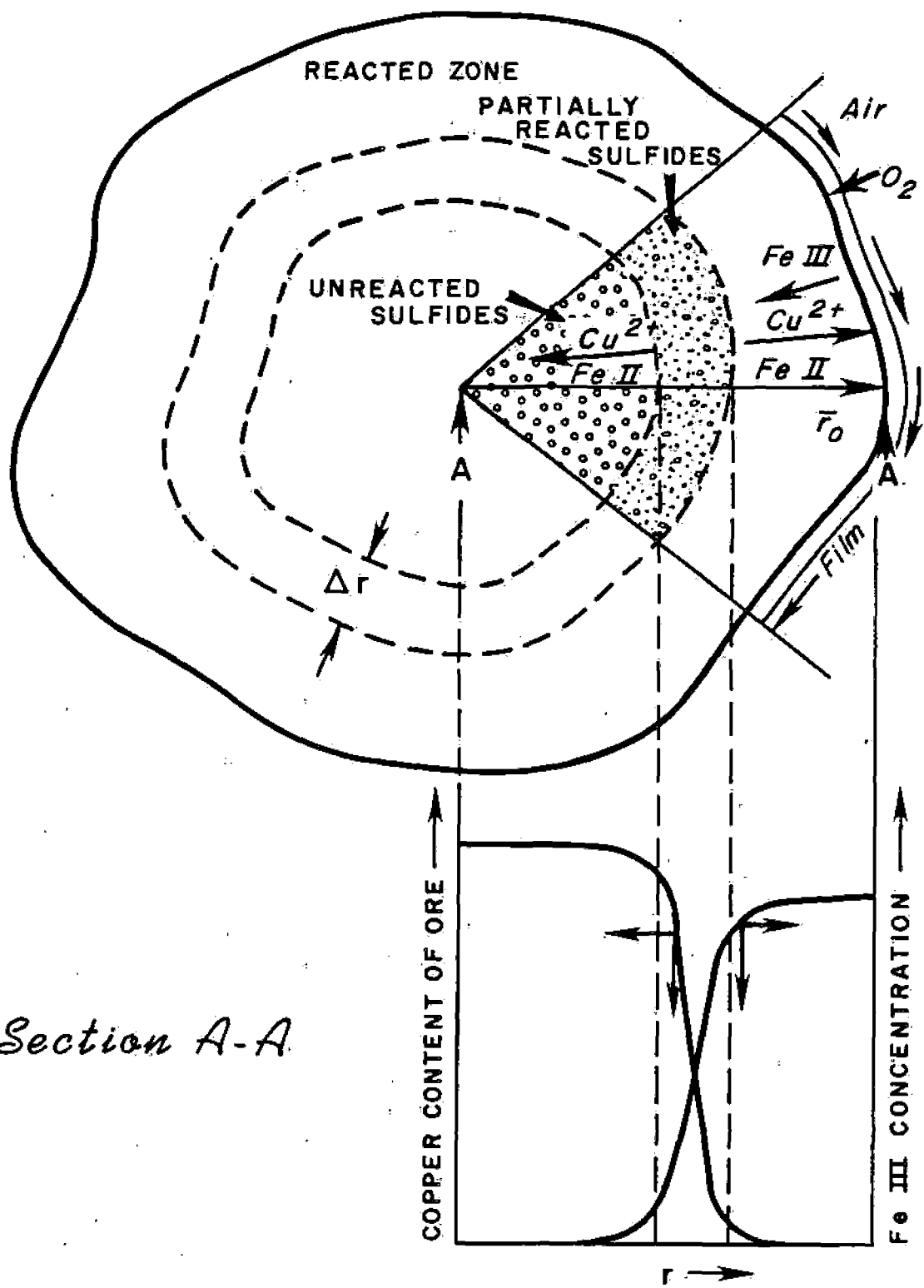
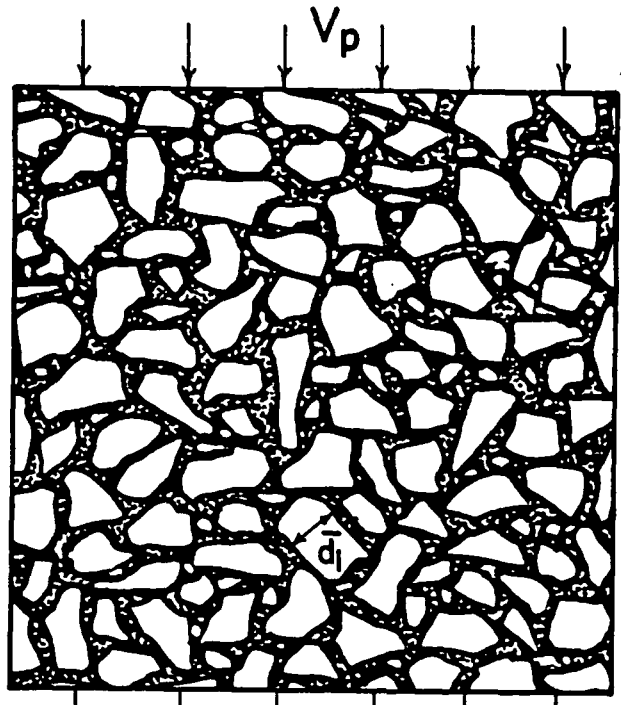


Diagram showing changes of volume and of minerals in the weathering of syenite. (W.J. Mead, Econ. Geol.)

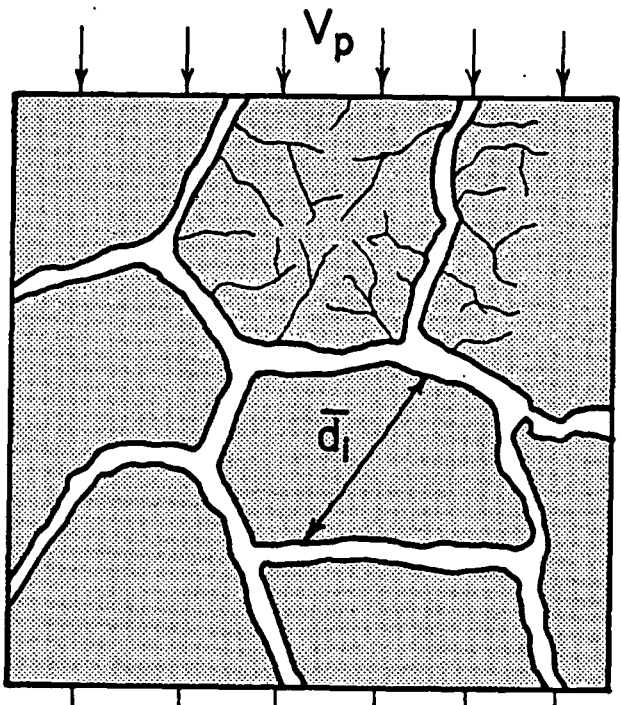
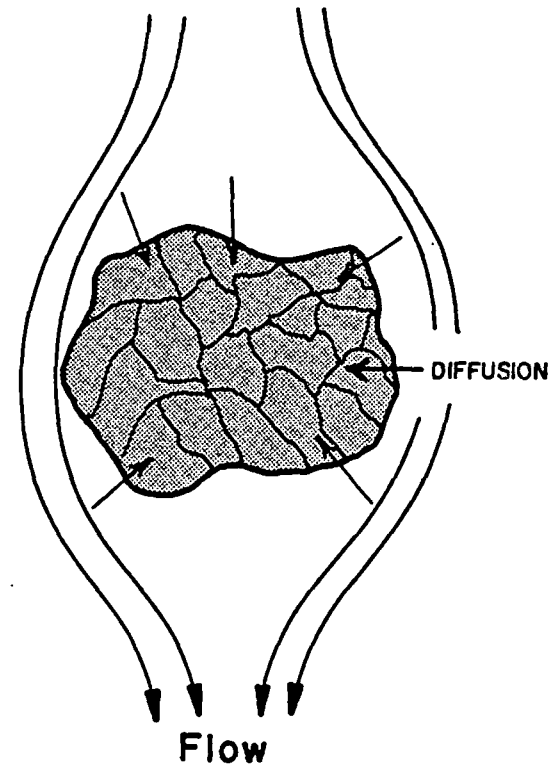




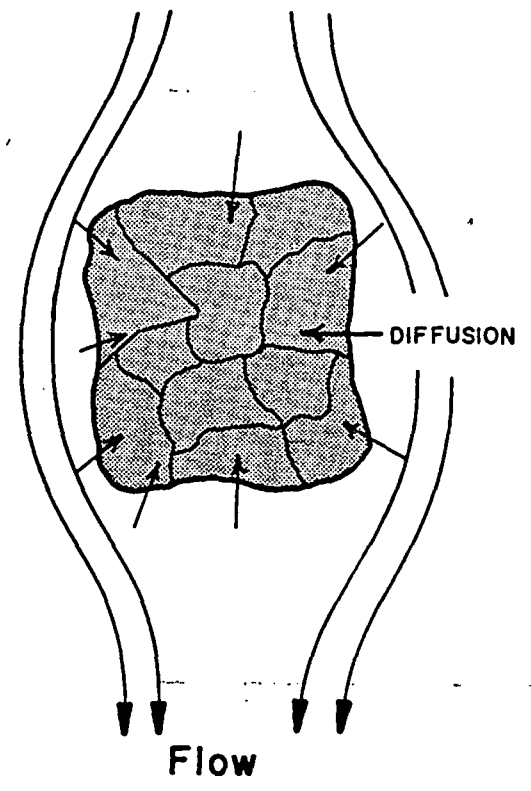
Section A-A



RUBBLIZED



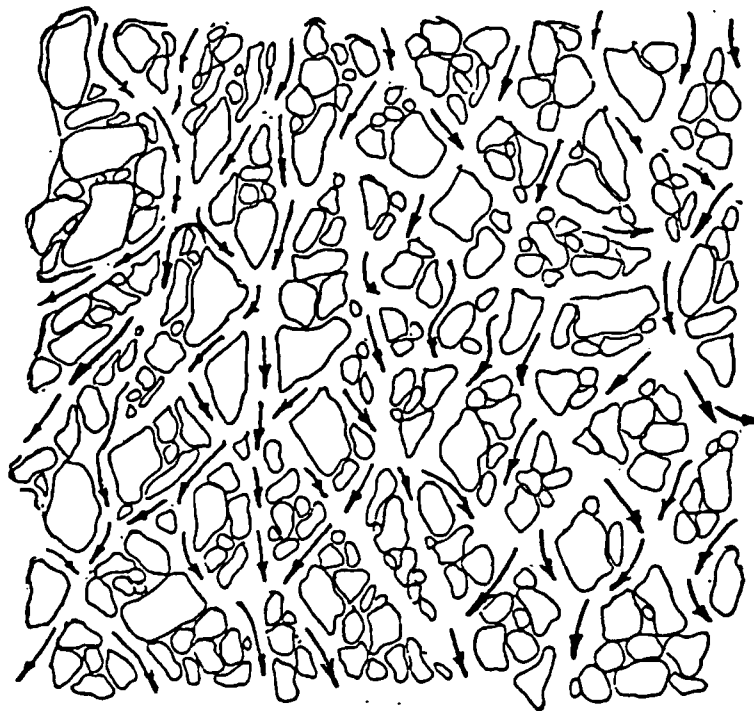
HYDROFRACTURED



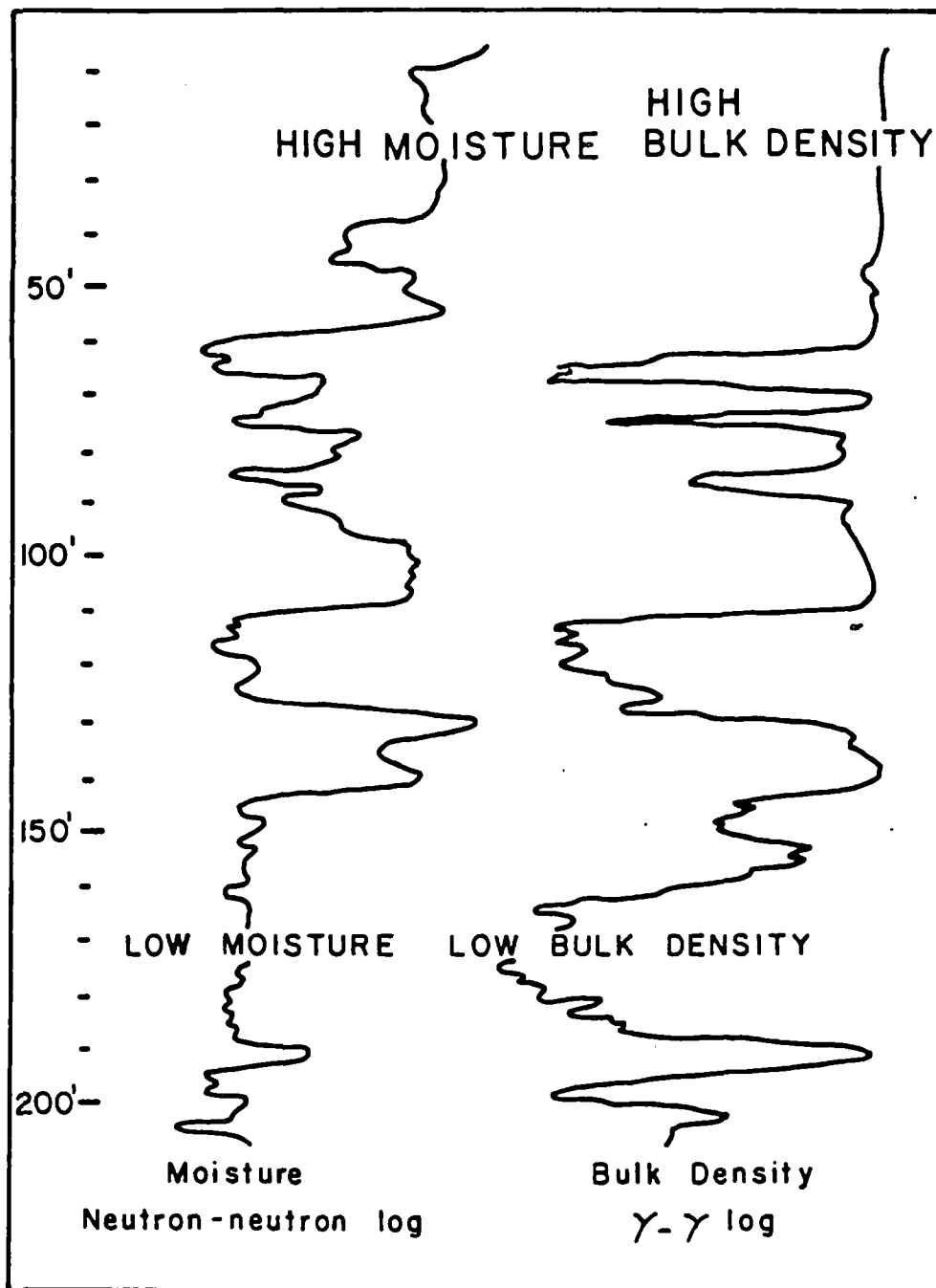
FLUSH REACTION: RAPID RELEASE  
PARTICLE DIFFUSION: ATTENUATED RELEASE

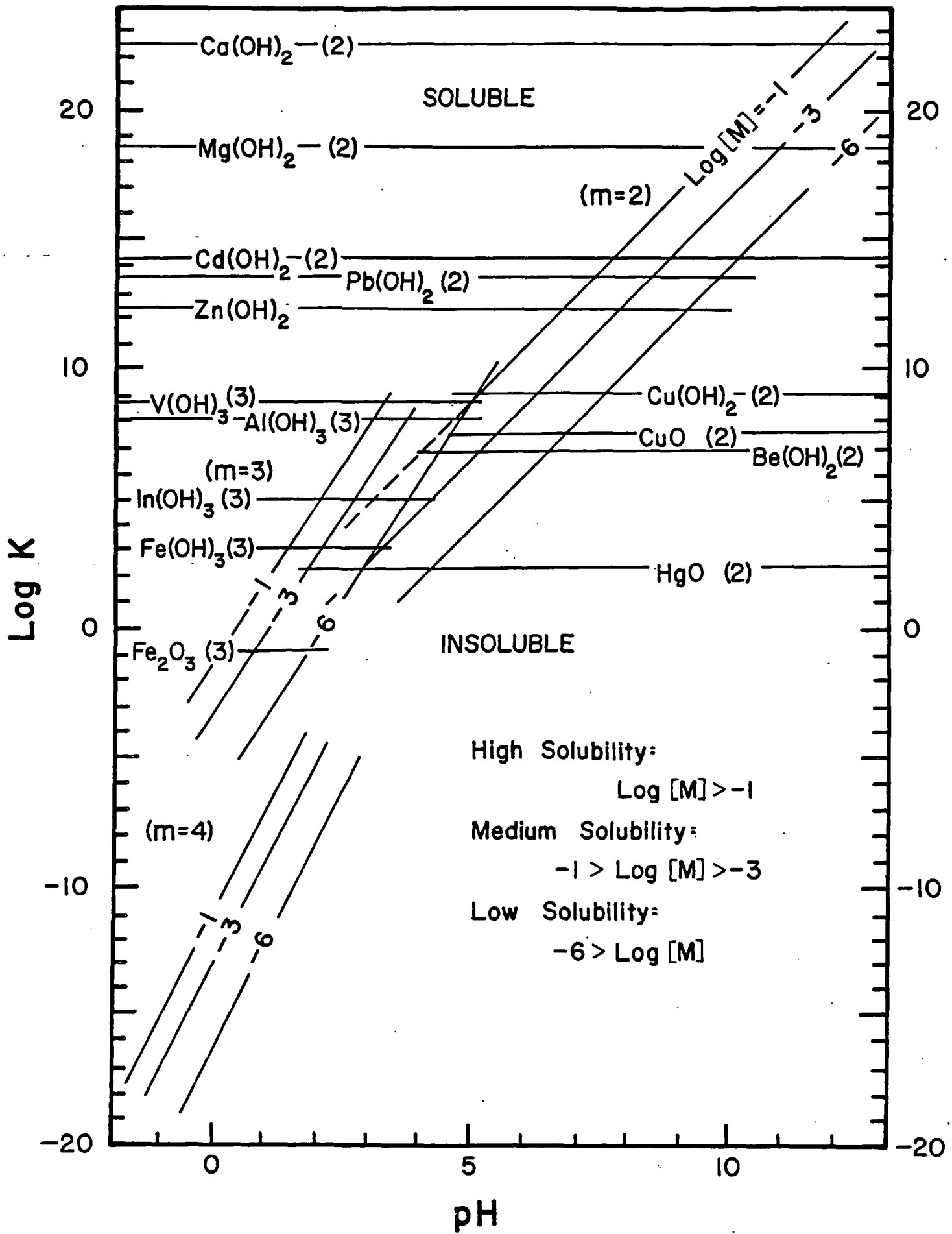


**Low bulk density**



**High bulk density**





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*Geothermal Res. of Neb.*

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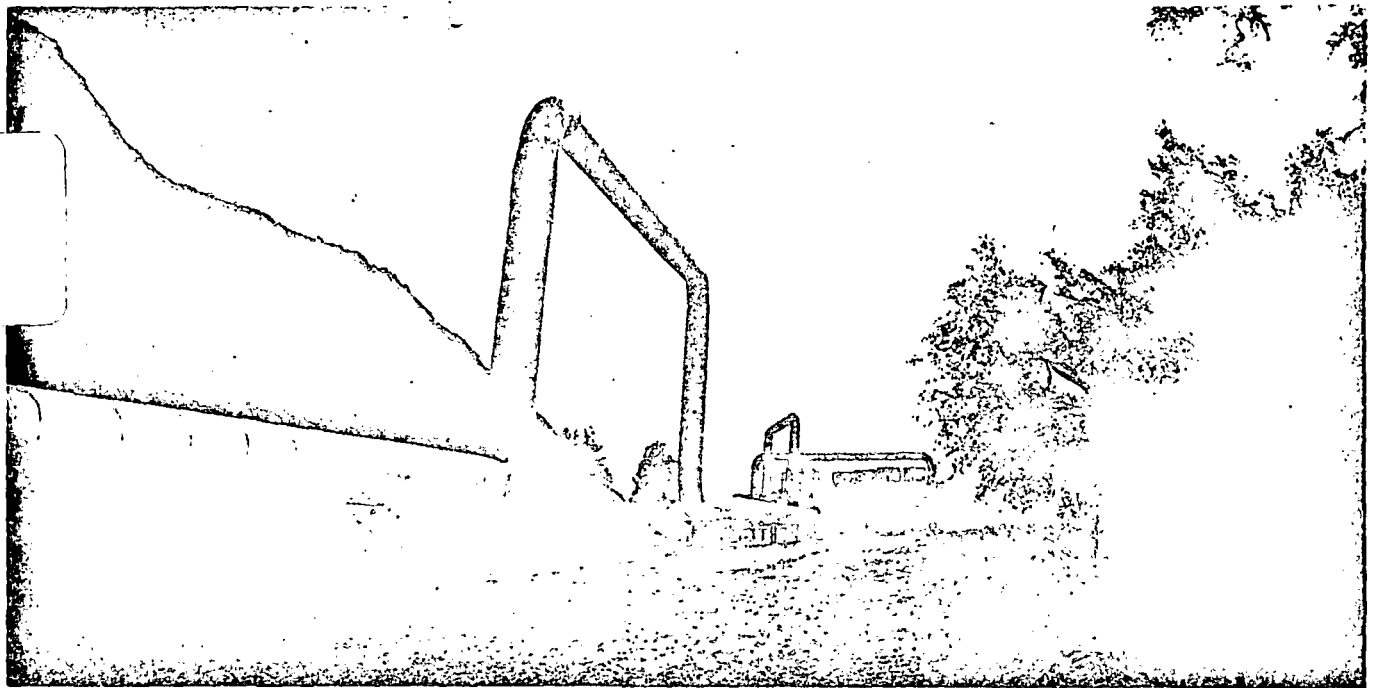
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These expansion loops carry geothermal steam from wells drilled to a depth of more than 1.5 mi. to Pacific Gas and Electric's plant at The Geysers, Sonoma County, California.

## Salt Domes As A Source of Geothermal Energy

by Charles H. Jacoby

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International Salt Co.

UNIVERSITY OF UTAH  
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The economic importance of salt domes has been recognized throughout the world, primarily because of oil and gas accumulations on their flanks, and to a lesser degree, for the value of their salt and potash. Recently they have become of value as hosts for cavities used to store hydrocarbons. In the near future we believe that their main value will be a source of geothermal energy.

Although tremendous effort has been expended on the understanding of the geology and physical characteristics of the strata intruded by salt domes, relatively little energy has been exerted in the comprehension of the salt dome itself. Salt domes have long been recognized as a geological heat anomaly. With respect to other sedimentary rocks, salt is a good conductor of heat. Expressing values in  $10^{-3}$  cgs units, sedimentary rocks vary from 1.0 to 8.0; metamorphic rocks from 5.2 to 8.4 and igneous rocks from 3.1 to 9.8. Rock salt in its pure form has a thermal conductivity of 17. Thus a salt dome can be expected to act as a conduit bringing heat vertically from deep within the earth's crust.

This was in part substantiated in 1958 when a horizontal core hole was drilled from within the Avery Island Mine at the 500 ft level. The horizontal hole was started where the ambient temperature of the salt was 74°F. and drilled toward the center of the dome. At the end of the 2000 ft hole the temperature was 90°F, indicating a horizontal temperature gradient of 7°F./1000 feet. Because this core hole penetrated a shear zone containing connate water that appeared as a "cold spot" on the temperature gradient, the foregoing data can only be regarded as indicative.

The source rock of our southern salt domes is the Louann formation. Depending on the location of the dome, the Louann has been estimated to have been buried at a depth of 40,000 to perhaps as deep as 60,000 ft. Balk has estimated that salt domes at a depth of 25,000 feet experience a temperature of 570°F. Gussow<sup>37</sup> states that salt becomes completely plastic in all axial directions at 662°F. Hiroy<sup>35</sup> reports, at a depth of 14,552 ft the temperature of a salt dome was recorded to be 460°F.

Several postulations have been made with respect to salt domes. One of these is that the younger the dome the hotter the dome. The reason suggested for this has been given as a loss of heat in the older domes to the surrounding rocks. It should also be taken into consideration that the older domes in the Gulf Coast region have their "mother" bed at a depth considerably below that of the younger domes. Another factor which should be given consideration is the heat generated as the halite moved along its dodecahedral glide plane, which in the case of the younger domes, would have had less time to dissipate. It has also been suggested that the salt in the base of the dome is of a lower temperature than the surrounding rocks. We agree with this theory since the thermal conductivity of the salt would allow for the heat's transfer up the stock of the dome.

Due to the deep-seated origin, high thermal conductivity of salt, and the enormous size of the dome, it presents a unique geologic structure for the extraction of geothermal energy.

We know thermal conductivity  $K =$

$$K = \frac{\text{Heat flow}}{\text{Temperature gradient}} = \frac{\text{calories (or Btu's)}}{\text{time} \times \text{distance} \times \text{temperature change}}$$

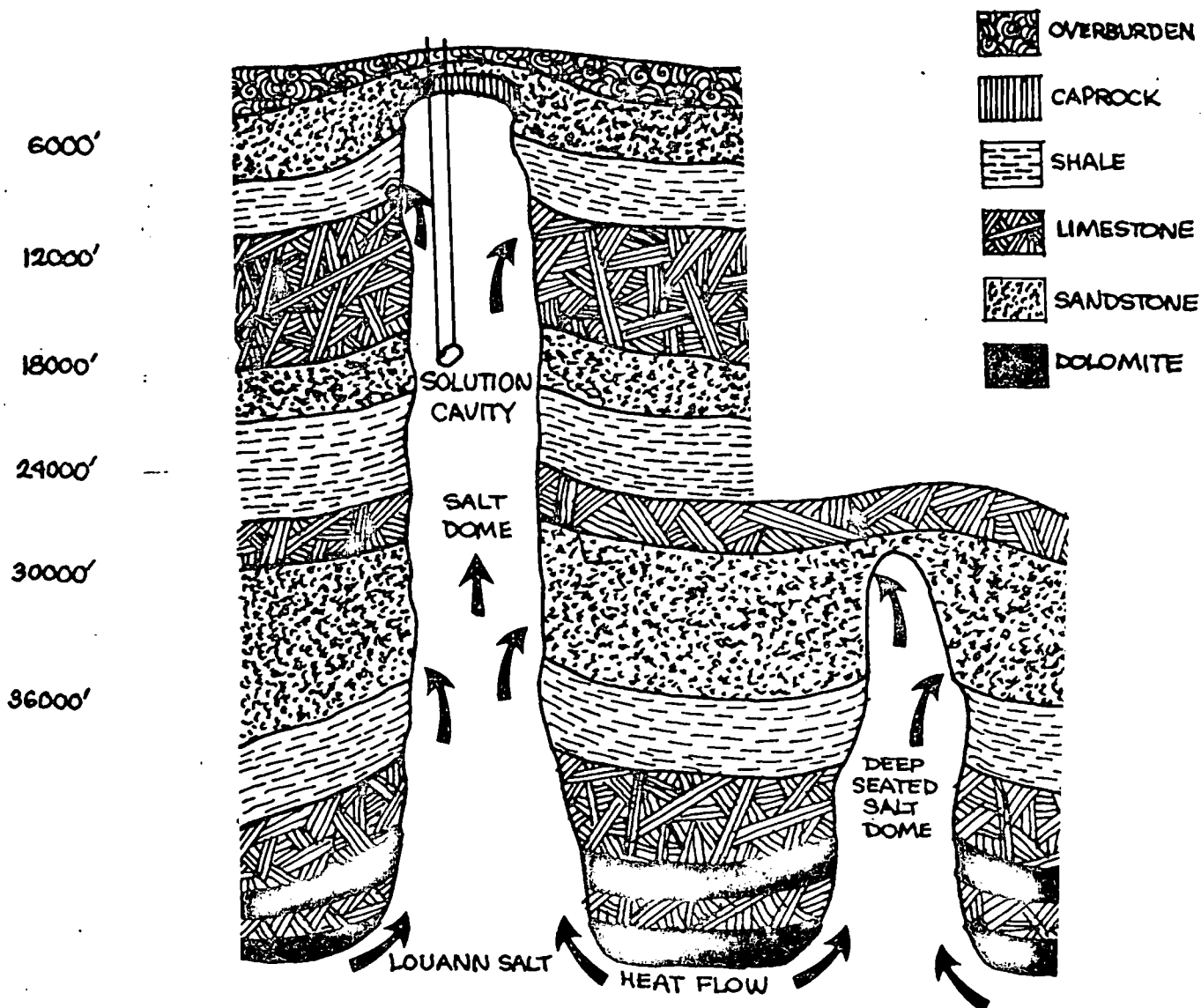
The thermal conductivity of rock salt varies from

$$8 \times 10^{-3} \text{ cal/cm}^2\text{-sec.-c}^\circ\text{-cm}$$

$$\text{to } 17 \times 10^{-3} \text{ cal/cm}^2\text{-sec.-c}^\circ\text{-cm}$$

$$(1.93 \text{ Btu/hr/ft}^2/\text{c}^\circ\text{F/ft} \text{ to } 4.16 \text{ Btu/hr/ft}^2/\text{c}^\circ\text{F/ft})$$

Typical salt dome as shown below could act as a conduit, bringing heat vertically from deep within the earth's crust. Source of the salt is the Louann formation, buried at 40-60,000 ft.





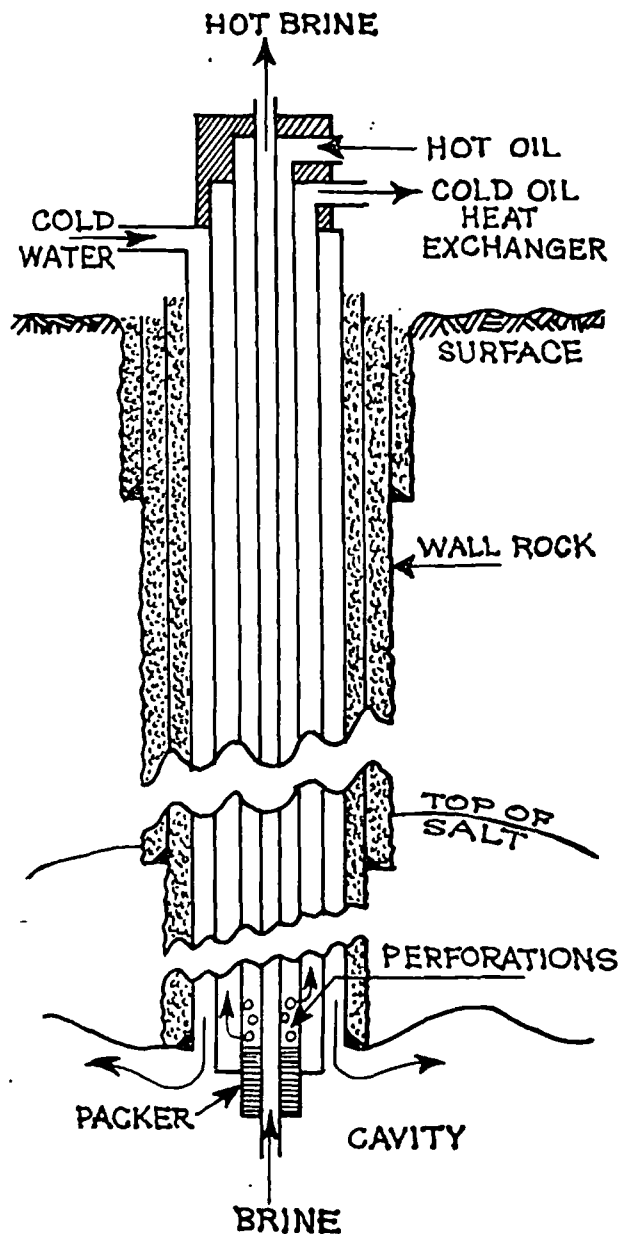


Diagram of a single-well system shows the piping configuration required to produce hot brine. Hot oil is used to prevent crystallization during the ascent.

The value of thermal conductivity varies with temperature. This value is two to five times that of most sedimentary rocks associated with salt domes. Heat flow is accomplished by conduction, radiation and convection mechanism along certain temperature gradients. The heat flow in salt domes should depend upon a complex combination of the heat flow by the agencies of all mechanisms.

The average heat flow in the Gulf Coast area is  $1.2 \times 10^{-6}$  cal/cm<sup>2</sup>-sec. whereas the geothermal flow rate in salt domes has been found to be between  $6.2 \times 10^{-6}$  cal/cm<sup>2</sup>-sec. to  $10.1 \times 10^{-6}$  cal/cm<sup>2</sup>-sec. The heat flow, which is a product of temperature gradient and thermal conductivity, is five to eight times larger than in the average area.

The geothermal gradient also varies by a wide margin. Temperatures of 330°F. at 10,000 ft, 455°F. at 15,000 ft, 580°F. at 20,000 ft are typical in salt domes. The typical geothermal gradient will vary from 2.2° to 2.6°F./100 ft. The geothermal gradient will also vary according to the location of the probe in the dome itself.

There are a number of ways the geothermal heat of the salt domes can be utilized. Some of the typical concepts are outlined below.

### Geothermal Saturator

In this concept a salt dome is drilled to a predetermined depth of between 12,000 and 15,000 ft, depending on the characteristics of the dome and the location on that dome. A single-well system or a two-well system is created. In a single-well system the water is injected into the outer annulus and pumped into the cavity with the resultant brine being forced up the central tubing. Numerous piping configurations can be used. Hot oil is used to keep this central tubing warm to prevent crystallization during the hot brine's 2½ mi flow to the surface. It is probable that two additional strings of pipe would be required; one for an oil or pneumatic pad while the other might be a "sand string" depending on the quantities of anhydrite sand that were produced.

A more preferred system embodies the construction of two wells drilled to the desired depth. One would be deflected from its vertical trajectory over the course of its last few thousand feet. The lower portion would be underreamed after installation of the main casing.

After a bore hole survey had located the precise position, a second well, which subsequently would become the production well, would be drilled to intersect the underreamed portion of the first well. It would be cased in such a manner as to insulate and/or protect the brine tubing from heat losses which might cause the premature crystallization of salt in the production tubing.

The nether ends of the wells, if not connected by intersection, can be connected by using one of several other devices that are available. With the connection of the two wells, water is circulated down the injection well and produced through the adjoining well. In the case of the geothermal saturator, the main purpose is to produce a brine sufficiently hot so that it flashes to produce salt and steam. Thus, any domal temperature sufficiently in excess of the 220°F. boiling point of brine will be satisfactory to meet the needs of the process.

Before the selection of a temperature depth for the location of the cavity's construction within the dome, certain basic parameters must be established such as the total volume of salt the facility is expected to produce, the temperature required for the brine at the wellhead, and the average rate at

which the well is expected to produce. During the early youth of the cavity, an undersaturated brine will be produced. As the cavity grows, the retention time in the cavity grows with an increase in the salinity and the temperature of the brine produced. As the cavity matures the support of the casing in the deviated hole or injection well will be removed, causing the casing to seek a plumb position. Eventually it will be necessary to carry an oil or pneumatic pad around the injection well to limit the vertical growth of the cavity.

As the deep-seated cavity is under high pressure and temperature, plastic closure of the salt cavity is expected. Extensive studies in rock mechanics

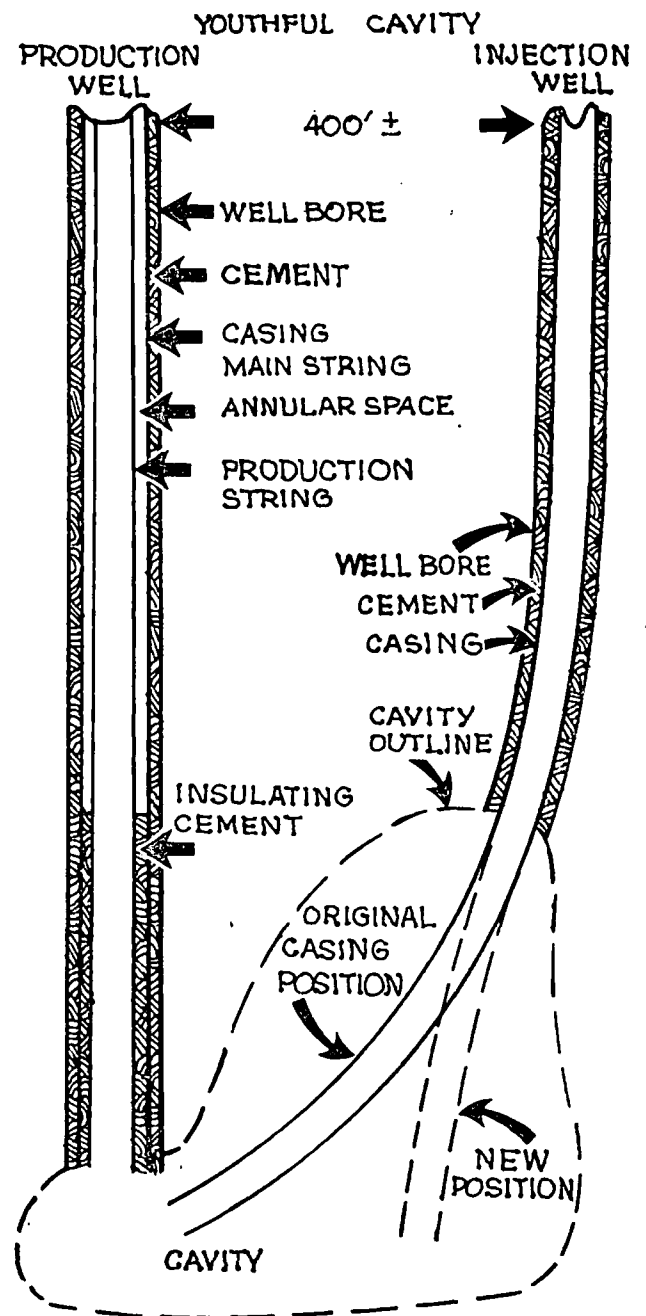
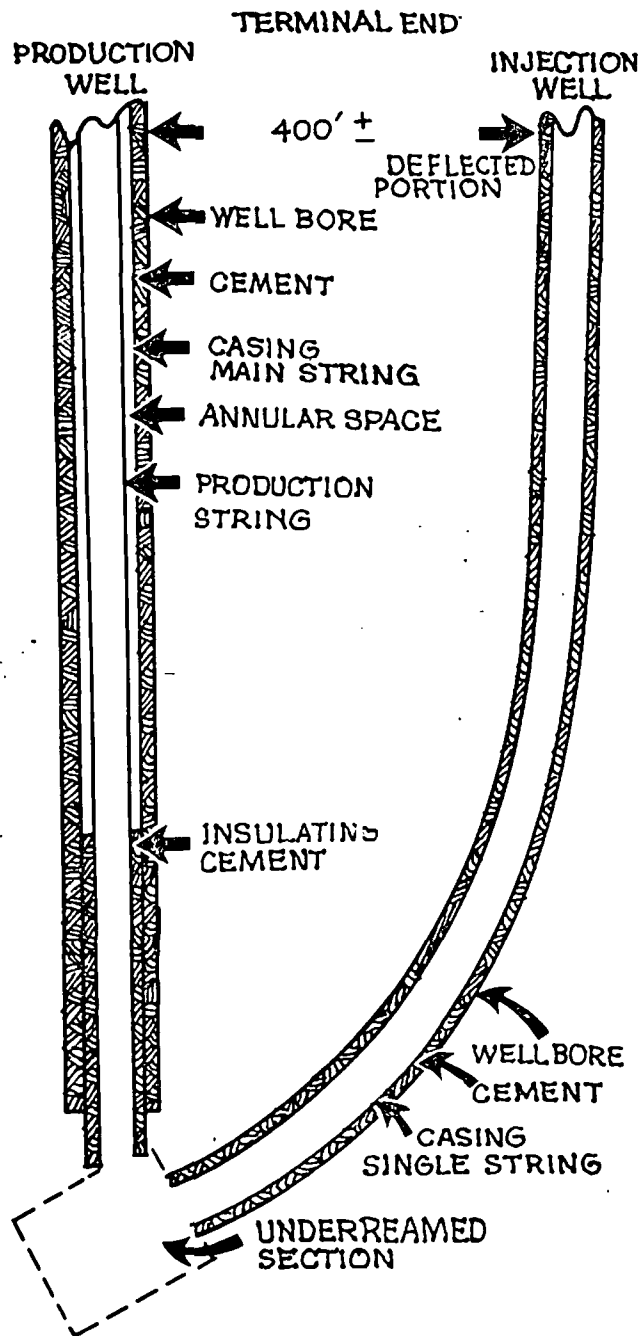
have verified that a desired shape and size of the cavity can be maintained and controlled closures can be achieved. The plastic movement will prevent any sudden roof fall or other forms of unexpected rock failures.

The high rate of geothermal heat flow will continually replenish the extracted heat and thereby assure the continuous operation of the process. In every case the rate of heat flow, plastic closures, and the rate of extraction of hot brine have to be properly balanced to ensure optimum recovery.

The advances in drilling technology, especially in the oil industry, have shown that problems associated with high pressure and temperature in deep

Two-well system, showing the under-reamed section after the installation of the main casing.

Water circulated down the injection well will produce a youthful cavity (shaded area).



drilling can be overcome. For the continuous success of the process, proper heat control must be maintained in the injection well, in the cavity, and in the production well. The success of the process will depend primarily upon successful heat insulation in the production well.

### Peak Shaving of Power by Compressed Air Storage

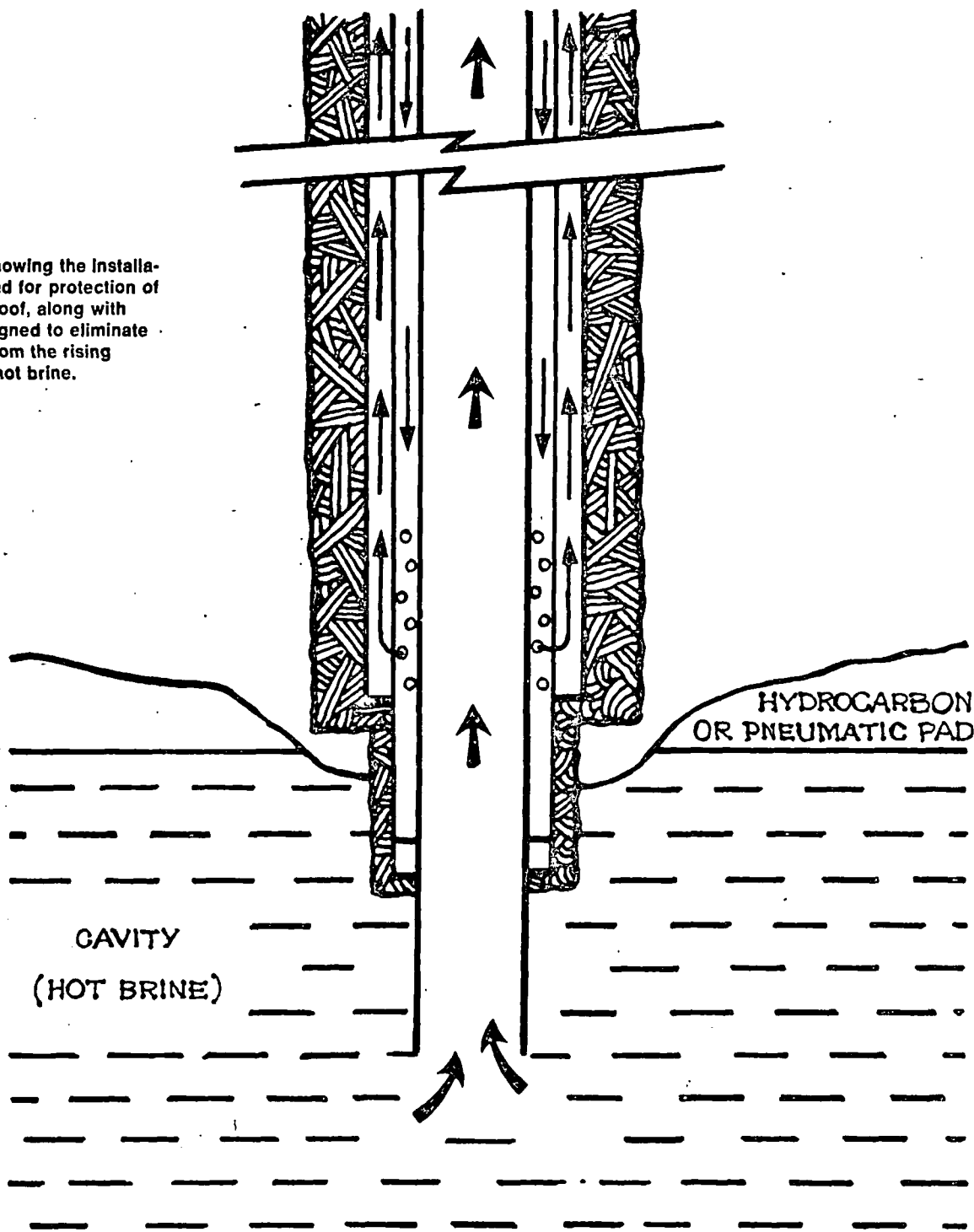
This concept involves the evacuation of a deep-seated cavity to dryness. Compressed air would then be stored in the cavity during off-peak periods of electrical consumption. The compression would be augmented by the ambient temperature of the

cavity with a resultant increase in the pressure of the stored air due to the increase in temperature. The exit well is capped until a peak power period when the heated high-pressure air is returned to drive a generator and produce extra power. This concept can have a number of variations with multiple cavities.

### Geothermal Heat Exchanger

After a cavity has been excavated in a salt dome by either a single- or multi-well system, the brine can be displaced or replaced by a salt-insoluble heat exchanger fluid. This fluid in a relatively cool state would be injected into the cavity through an

Diagram showing the installation of a pad for protection of the cavity roof, along with piping designed to eliminate heat loss from the rising column of hot brine.



injection well and extracted from an insulated recovery well. The hot fluid would be passed through a heat exchanger on the surface and then returned to the cavity. The recovery of this energy would entail no air, water or thermal pollution of any type. From time to time, as plastic flows tend to close the cavity, it will be necessary to dissolve additional quantities of salt. This would be required so that the retention time in the cavity will give the volume of fluid flowing through the system adequate time to heat.

### Steam Generation

A calculated volume of water could be injected into a deep-seated hot cavity which had been emptied of fluids. The water would travel down a long injection pipe, through increasing geothermal temperature, and would be in a pre-heated condition as it entered the cavity. Based on heat flow into the cavity and the surface area of salt exposed in the cavity, the calculated volumes of water introduced would produce calculated volumes of steam which then pass through an insulated recovery well and enter a steam turbine to produce electrical energy. The shape and size of the cavity could be made to recover maximum quantity of steam per unit volume of the cavity.

### Geothermal Chemical Retort

Various endothermic reactions can be caused by the introduction of specific chemicals into a hot, dry cavity. By equipping the well with concentric strings of tubing, multiple reactants in calculated volumes can be introduced into the geothermal chemical retort. Although salt is inert to many chemicals, some care would be necessary in the selection of reactants and the resultant products. Catalytic agents could be installed in the cavity.

Geothermal cavities in salt would be impervious to most chemicals, with little or no chance of fluid losses in the cavity itself.

### Geothermal Water Purification

This concept envisions the introduction of a brackish or polluted water into a hot deep-seated cavity which had previously been evacuated to dryness. A recovery well could carry steam which would produce power and recover potable water.

These concepts will demonstrate how this underutilized energy source may be used for economic purposes. Of course, as in all other new concepts, there would be some trial and error. Nonetheless, this vast geothermal energy resource in the salt domes will find various uses. For the formation of wells, cavity, and the utilization of energy, salt will be a much easier product to handle. Dome salt has purity that approaches 99 percent in many cases and the impurity is mainly calcium sulphate. In some instances the effluent will be a marketable commodity, thus completely avoiding all pollution prob-

lems. Other geothermal brine contains numerous basic and acid radicals which create pollution and operational problems in the handling of the effluent.

Because of the deep-seated origin of the salt domes, sometimes reaching 10 to 12 mi underground, the energy will continue to be replenished in almost inexhaustible quantities. The rate of supply and demand must be balanced.

### Conclusions:

In view of America's future energy needs, it appears that we will eventually turn to the salt domes of Louisiana, Texas, Mississippi and Alabama for a sizeable portion of our needs. Here, unlike exhaustible reserves of oil and gas, is a vast reserve of almost inexhaustible energy. To properly and fully develop this "pipeline" of power will require creativity, innovation, capital, and time. Many known problems and even more numerous unknown problems will be encountered where answers will be needed.

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## Sulfur dioxide in geothermal waters and gases

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(Received 19 March 1976; accepted in revised form 18 June 1976)

**Abstract**—Methods were developed for stabilizing  $\text{SO}_2$  in water and gas samples. The pararosaniline colorimetric method and a gas chromatographic method using a flame photometric detector specific for sulfur gases were used to assay  $\text{SO}_2$ . Assays were also performed for sulfide, elemental sulfur and sulfate.

A large number of acidic, neutral, and alkaline springs in Yellowstone National Park were sampled:  $\text{SO}_2$  was found in small amounts in most of them. The highest concentration detected in water was 0.5–0.6  $\mu\text{g}/\text{ml}$  (expressed as sulfur). Sulfur dioxide was never detected in gases emanating from hot springs, or in fumaroles, although  $\text{H}_2\text{S}$  was readily detected. Because of the high solubility of  $\text{SO}_2$  in water, and its low  $pK$ , it is unlikely that environmentally significant quantities are volatilized from geothermal systems of the low-temperature type characteristic of Yellowstone Park. Laboratory studies suggest that in acid waters, ferric iron is the primary oxidant, as  $\text{H}_2\text{S}$  is not oxidized by  $\text{O}_2$  at low pH. At neutral or alkaline pH,  $\text{O}_2$  is the likely oxidant, because sulfide is oxidized by  $\text{O}_2$  at these pH values, and neutral and alkaline hot springs are always low in iron. Although bacteria capable of oxidizing sulfide and elemental sulfur are present in most of the springs sampled, it is concluded that the oxidation of reduced sulfur compounds to sulfur dioxide is primarily a chemical process, because of the rapidity with which it occurs and the lack of any evidence that bacteria produce sulfur dioxide.

### INTRODUCTION

ALTHOUGH sulfur dioxide is a common constituent of volcanic gases (WHITE and WARING, 1963), it is usually considered to be absent from geothermal systems with temperatures under  $100^\circ\text{C}$  (ALLEN and DAY, 1936; GUNTER and MUSGRAVE, 1966). As stated by ALLEN and DAY (1936): "To say that... sulphur dioxide never occur(s) in magmatic emanations is to go beyond the range of available evidence, but in the hot-spring stage of volcanism all observations point to hydrogen sulphide as the primary sulphur gas". It is difficult to make any general conclusions, however, because sampling and analytical problems have been quite considerable for this most reactive of sulfur compounds (FINLAYSON, 1970), so that only where large amounts of  $\text{SO}_2$  are present has it been possible to demonstrate it unequivocally. Indeed, in the extensive series of geochemical papers presented at the United Nations Symposium on the Development and Utilization of Geothermal Resources in Pisa (1970), no papers were found which present assays for either  $\text{SO}_2$  or sulfite, either in geothermal gases or waters.

From a geochemical point of view, traces of  $\text{SO}_2$  or sulfite in geothermal systems would probably not be significant, but from an environmental viewpoint the situation may be different. Sulfur dioxide has a greater toxicity than hydrogen sulfide (STEERE, 1971) and has been of considerable concern in air pollution research (FERRY *et al.*, 1973). This has led to the development of methods for stabilizing sulfur dioxide and sulfite so that they can be kept from reacting before analysis (WEST and GAEKE, 1956). It has also led to the development of the specific and highly sensitive

flame photometric detector for gas chromatography, which permits assaying concentrations of sulfur dioxide far lower than previously approachable (STEVENS *et al.*, 1971). Because of the increasing interest in geothermal power (ARMSTEAD, 1973; KRUGER and OTTE, 1973), it seemed of interest to carry out assays for sulfur dioxide and sulfite in geothermal waters and gases using these sensitive and specific techniques.

Our studies have been carried out in Yellowstone National Park. This area has been extensively studied geochemically (ALLEN and DAY, 1936; GUNTER and MUSGRAVE, 1966; FOURNIER and TRUESDELL, 1970) and considerable previous work on the sulfur cycle in Yellowstone geothermal systems has been carried out in this laboratory (BROCK and MOSSER, 1975; MOSSER *et al.*, 1973; FLIERMANS and BROCK, 1972). The availability of a field laboratory at W. Yellowstone, Montana, where a gas chromatograph could be set up, made it possible for us to develop and test methods for sulfur dioxide and sulfite, and to perform chemical assays soon after samples were taken. Our data indicate that sulfur dioxide and its ionization products are widespread in geothermal waters at a variety of pH values, although the concentrations are low. Sulfur dioxide was detected only rarely in gases emanating from hot springs, but because of the  $pK$  of the sulfur dioxide–water system, it is almost certain that sulfur dioxide is being volatilized continuously, albeit at low concentrations, from many acid hot springs. Thus, attention to the possible environmental consequences of sulfur dioxide air pollution in natural and man-made geothermal systems is warranted.

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For background in interpreting the results of this paper, the relative proportions of the various ionization products of sulfurous acid at various pH values are given here:

pH	Sulfite SO <sub>3</sub> <sup>2-</sup>	Bisulfite HSO <sub>3</sub> <sup>-</sup>	Sulfur dioxide* SO <sub>2</sub>
8	99.99%	0.01%	0
7	96	4	0
6	85	15	0
5	37.5	62.5	0
4	7	92	1
3	1	90	9
2	0	65	35
1	0	15	85
0	0	4	96

From SAUNDERS and WOOD (1973).

\* The nonionized form in aqueous solutions is almost entirely uncombined SO<sub>2</sub>, rather than sulfurous acid (SCHROETER, 1966).

The solubility of sulfur dioxide in water is very high. For comparison, the weights in grams of several geothermal gases dissolved in 100 g of water at a total pressure of 760 mm at 40°C are: sulfur dioxide, 5.41; hydrogen sulfide, 0.2361; carbon dioxide, 0.0973; methane, 0.001586; and hydrogen, 0.0001384 (DEAN, 1973).

## METHODS

### Stabilization

Because of its high instability, and the necessity of returning samples to West Yellowstone, Montana for analysis, a suitable method for trapping and stabilizing sulfur dioxide was needed. Dry ice-acetone traps did not trap sulfur dioxide quantitatively. The method finally used was that of WEST and GAEKE (1956), in which sulfur dioxide is trapped using sodium tetrachloromercurate (STCM). This reagent, commonly used in air pollution studies, has the advantage that it traps sulfur dioxide reversibly so that it may be assayed colorimetrically or liberated into the head space by strong acid for gas chromatographic analysis. Hydrogen sulfide is trapped irreversibly as mercuric sulfide, and thus does not interfere with either assay. Hydrogen sulfide was trapped and stabilized with zinc acetate as previously described (BROCK and MOSSER, 1975).

### Field procedure

Both gas and water samples were assayed. To assay gas samples, a large plastic funnel was fastened to the end of a long pole and held under the water in regions of active bubbling. A plastic tube led from the funnel to the edge of the spring. After a few minutes, the pressure of the gas in the bubbles forced all of the air out of the tubing and steam and gas issued at a reasonable rate from the end of the tubing. A sample of gas was then taken using a 50 ml plastic gas-tight syringe, adapted so that it snugly fitted into the end of the tubing. The syringe was then fitted with a needle, and the gas was slowly bubbled through 2 ml STCM solution in a 5 ml vial. Some air contamination almost certainly occurred, but water displacement or any of the other methods described by FINLAYSON (1970) were not satisfactory for this soluble and unstable gas. For hydrogen sulfide assays, the gas was bubbled through 2 ml of zinc acetate solution.

When fumaroles rather than springs were being sampled, the procedure was similar except that the funnel was placed directly into the gas vent. Fumaroles with appro-

appropriate openings for the funnel were selected. Most fumaroles in Yellowstone National Park have sufficient gas pressure so that the air was readily displaced from the system.

When sampling geothermal waters for sulfur dioxide and its ionization products, it was found essential that the water from acid springs first be neutralized if trapping of sulfur dioxide was to be complete. On site at each spring, a 16 ml sample of water was first taken and the amount of either 0.1 N NaOH (spring pH > 2) or 1.0 N NaOH (spring pH < 2) necessary to neutralize it was determined by titration using 0.1% congo red as indicator. For the actual sample, 16 × 125 mm test tubes (18 ml) with Teflon-lined screw caps were used. The determined amount of NaOH was first added to the tube containing 2 ml STCM, and the test tube was filled to the top with spring water, capped, and rapidly shaken to mix the contents. Hydrogen sulfide in these waters was stabilized in a similar fashion except 2 ml acidified zinc acetate solution was substituted for STCM.

When each spring or fumarole was sampled, its temperature was determined with a Yellow Springs Instrument Co. (Yellow Springs, Ohio) thermistor and bridge. A water sample was taken in a 60 ml plastic bottle for laboratory determination of pH, elemental sulfur, and sulfate.

### Chemical methods

Sulfur dioxide was determined by the pararosaniline method (WEST and GAEKE, 1956). Samples were filtered to remove particulate debris and mercuric sulfide, which gave a positive interference. Since it was possible that some factor in the spring water other than sulfur dioxide could cause color development, we considered it essential to confirm the results of this assay using a gas chromatographic method.

A Packard 419 gas chromatograph fitted with a Tracor flame photometric detector (FPD) was used. The FPD will detect nanogram quantities of sulfur compounds in the presence of 10,000-fold excesses of carbon compounds (BANWART and BREMNER, 1974). The column used was that developed for air pollution research by STEVENS *et al.* (1971), operated isothermally at 100°C, at which temperature sulfur dioxide has a retention time distinct from twelve other low molecular weight sulfur compounds (BANWART and BREMNER, 1974).

Six millilitres of the preserved sample in STCM was added to a 15 ml serum stoppered vial. To this, 3 ml of concentrated phosphoric acid was added rapidly using a syringe and needle. The vial was shaken 2 sec and a 5 ml sample of the head space was taken with a gas-tight syringe and immediately injected into the gas chromatograph. This method is as sensitive as the pararosaniline method, and is highly specific for sulfur dioxide, but cannot be considered quantitative because of the rapid loss of sulfur dioxide after acidification due to oxidation and absorption onto the serum stopper; however, it is useful as a means to corroborate the results of the colorimetric method. The quantitative data given in this paper were obtained using the pararosaniline method, but there was qualitative agreement between the colorimetric and gas chromatographic methods.

Hydrogen sulfide was determined by the methylene blue method of Pachmayr as described by BROCK *et al.* (1971), modified in the following way to separate the methylene blue from particulate matter in the spring waters. After color development was complete, 0.1 ml 0.1% sodium lauryl sulfate was added to each 10 ml sample, followed by 5 ml of chloroform, and the two phases were shaken vigorously for 10 sec. The detergent caused the methylene blue to be extracted into the chloroform layer (AMERICAN PUBLIC HEALTH ASSOCIATION, 1971), leaving the particulate matter in the aqueous phase. The optical density of the chloroform phase was determined at 652 nm with a Beckman DB-G spectrophotometer. This method was satisfac-

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tory for all waters except those containing very large amounts of clays, in which case distillation must be used (BROCK and MOSSER, 1975).

Elemental sulfur was assayed by extraction of the sample into trichloroethylene and determining the optical density at 276 nm (FLIERMANS and BROCK, 1973).

Sulfate was measured by the gelatin-barium chloride method of TABATABAI (1974).

#### Oxidation of sulfide in acid waters

Experiments on the oxidation of hydrogen sulfide in acid waters were done in sealed tubes to obviate the problem of H<sub>2</sub>S volatility. Test tubes with Teflon-lined screw caps were used for most experiments. When oxygen was used as oxidant, pH 1.8 sulfuric or hydrochloric acid was oxygenated by bubbling at room temperature with pure O<sub>2</sub> for 30 min. The oxygenated acid was quickly transferred to the screw-capped tubes which were filled to the top, sealed, and equilibrated to temperature (usually 70°C). This resulted in a solution with an oxygen concentration of about 14 µg/ml (as measured by Winkler assay), supersaturated at 70°C. If ferric chloride was used, the solution was not oxygenated (sometimes it was rendered anaerobic with N<sub>2</sub>, but this had no significant effect), and the solution of ferric chloride at the same pH was added to the tube before temperature equilibration. To initiate the reaction, a solution of Na<sub>2</sub>S·9H<sub>2</sub>O was added using a syringe equipped with a long needle of large diameter, which permitted injecting the sulfide solution rapidly into the middle of the tube. Usually a volume of 1.5 ml sulfide solution was added. To effect this addition without losing either oxygen or sulfide, the tube was opened, the syringe needle quickly inserted to the middle of the tube, the volume injected while allowing liquid to flow out of the top, and the cap quickly returned. To permit mixing, several small glass beads were placed in each tube. With practice, it was possible to add the sulfide solution without losing any significant amount of H<sub>2</sub>S. When low concentrations of sulfide were used, the addition of sulfide had no effect on the pH, but when higher concentrations were used, to

avoid a rise in pH the pH of the acid solution was lowered by a determined amount so that the final pH after addition of sulfide was still pH 1.8.

After incubation, tubes were removed from the water bath and sampled for the various assays. Samples were removed quickly with a syringe and placed in stabilization solutions and assayed as described above. A sample was first removed and placed in trichloroethylene for the elemental sulfur assay. The sample for sulfide was placed in acidified zinc acetate containing sufficient sodium hydroxide to raise the pH to around 7. The sample for sulfite was placed in sodium tetrachloromercurate containing sufficient sodium hydroxide to raise the pH to around 7. The remaining sample was filtered through a 0.45 µm membrane filter using a Swinnex attachment on the syringe, and the filtrate bubbled with N<sub>2</sub> for 5 min to drive off remaining H<sub>2</sub>S; this solution was then used for the sulfate assay following TABATABAI (1974).

## RESULTS

### Survey of springs

The results of our survey of springs is shown in Table 1. This table presents not only sulfur dioxide assays, but also assays for other sulfur compounds. In certain cases, assays were also performed on gases emanating from these springs. As seen, water from virtually every spring had detectable amounts of sulfur dioxide, although marked variation in concentration occurred from spring to spring. In most cases, the presence of sulfur dioxide was confirmed by sampling again on a later date. Usually, both samples were positive, although the actual concentration may have been different. Considerable experience in chemical assays on Yellowstone springs has shown that temporal variations in a variety of constituents are not uncommon, especially in the acid springs.

Table 1. Sulfur compounds in geothermal waters and gases from geothermal waters

Site	T(°C)	pH	Sulfide*	Water (µg/ml)†		Sulfate	Gas (µg/50 ml)	
				Sulfur	Sulfite		H <sub>2</sub> S	SO <sub>2</sub>
Norris Geyser Basin								
Congress Pool	81.5	3.6	0.03	0.08	0.23	103		
	79	2.4			0.06			
Black Pool <sup>1</sup>	85	3.3	1.83	2.00	0.05	36.2	900	0.0
		3.5			0.06			
28-7 <sup>2</sup>	65	2.2	0.23	4.8	0.00	258		
	65	2.1			0.04			
Cinder Pool	86	4.5	0.0	16.9	0.12	41.3	310	0.0
	87	4.0						
Verma Spring	51	3.0	0.12	8.7	0.02	50.0		
	51	3.1			0.04			
Horseshoe Spring	86	3.5	1.22	7.8	0.0	58.6		
	86	2.9			0.0			
Emerald Pool	92	3.4	0.05	—	0.02	—	1.5	0.0
Cistern Pool	92	7.5	0.38	0.78	0.18	27.6		
	91.5	6.5			0.10			
30-9 <sup>3</sup>	80.5	3.2	0.70	—	0.0	—		
Black Hermit	88	2.9	0.03	7.38	0.0	121		
	88	2.9			0.05			
Green Dragon	90	3.5	0.17	11.28	0.1	43.1	25.0	0.0
	89	3.3			0.04			
Yellow Funnel	80	3.7	0.75	6.60	0.05	37.9		
	90	3.1			0.04			
Monarch Geyser	90	6.0	0.94	0.74	0.03	48.2		
	91	5.0			0.0			
26-5 <sup>4</sup>	88	2.1	—	—	0.0	—		

Table 1. (Continued)

Site	T(°C)	pH	Sulfide*	Water (µg/ml)†		Sulfate	Gas (µg/50 ml)	
				Sulfur	Sulfite		H <sub>2</sub> S	SO <sub>2</sub>
Sylvan Springs Area								
Treetops <sup>5</sup>	86	6.0	0.33	1.1	0.03	53.4		
	85	5.8	0.17		0.04			
56-3 <sup>4</sup>	63	1.9	0.03	5.0	0.0	397		
	55	1.9	0.06		0.0			
58-1 <sup>6</sup>	78	6.7	0.26	3.1	0.0	70.7		
	79	6.5	0.23		0.02			
56-2 <sup>7</sup> inlet	84	5.3	0.12	—	0.08	104		
	87							
56-2 outlet	88	3.3	0.10	1.3	0.04	—		
			0.04		0.04			
59-1 <sup>4</sup>	79	1.9	0.15	27.3	0.0	484		
	76	1.8	0.17		0.05			
			5.7*					
Evening Primrose	45	1.1	0.03	651	0.6	1928		
	41	1.1	0.12		0.0			
55-4 <sup>8</sup>	81	2.3	0.04	412	0.5	276		
	81	2.2	0.17		0.25			
54-5 <sup>4</sup>	78	2.0	0.07	—	0.0			
59-2 <sup>4</sup>	70	1.4	0.03	0.30	0.24	1172		
Geyser Hill Area								
Brierley No. 3 <sup>9</sup>	76	2.5	0.02	56.2	0.03	120		
33-4 <sup>10</sup>	92	6.8	0.58	0.6	0.12	41.4		
34-1 <sup>10</sup>	92	6.8	0.58	0.6	0.12	41.4		
34-4 <sup>10</sup>	89	3.5	0.02	39.7	0.02	103		
34-8 <sup>10</sup>	91	2.5	0.01	0.9	0.0	86		
Mud Volcano Area								
Moose Pool <sup>4</sup>	65	1.6	0.02	291	0.10	1104	38	0.0
		1.6	0.00		0.0			
Sour Lake <sup>11</sup>	26	1.9	0.02	0.43	0.0	776		
		1.8	0.00		0.0			
Mud Geyser <sup>12</sup>	63	1.7	0.01	230	0.03	689	60	0.0
		1.7	0.23		0.02			
Sulfur Caldron <sup>4</sup>	64	1.5	0.02	1950	0.03	1928	24	0.0
	64	1.5	0		0.05			
Old Sulfur <sup>13</sup>	59	—	0.01	520	0.0	310	2	0.0
Caldron	59		0.0		0.0			
Alkaline Springs								
Ojo Caliente	94.5	7.8	1.3	0.04	0.0	8.9		
57-4 <sup>14</sup>	92	8.9	2.7	0.0	0.0	8.9		
58-1 <sup>14</sup>	92	9.0	1.9	0.02	0.04	9.3		
Boulder Spring	92	9.3	2.4	0.0	0.03	7.6		
Pool A <sup>15</sup>	84	8.6	0.013	0.0	0.08	6.5		
Sulfide Spring <sup>16</sup>	72	6.8	2.3	0.12	0.16	14.4		

\* Sulfide values in many of the acid springs are low compared to assays run by distillation by BROCK and MOSSER (1975). Present assays reflect primarily readily soluble sulfide, probably H<sub>2</sub>S alone.

† All assays are expressed as sulfur equivalents.

<sup>1</sup> Black, pyrite-containing pool on Porcelain Terrace, north side.

<sup>2</sup> Opalescent silica-depositing pool at west end of Porcelain Terrace.

<sup>3</sup> Spring near Echinus Geyser and Arch Steam Vent.

<sup>4</sup> See BROCK and MOSSER (1975) for more data on this spring.

<sup>5</sup> Unofficial name of a large, silica-depositing spring on the southwest part (upper slope) of the Sylvan Springs complex.

<sup>6</sup> Small turbid spring near effluent channel of upper terrace at Sylvan Springs.

<sup>7</sup> Large bluish pool with pinkish silica deposit, main source of water for upper Sylvan Terrace effluent.

<sup>8</sup> Large yellow pool on same terrace with Evening Primrose.

<sup>9</sup> BRIERLEY (1966) station No. 3.

<sup>10</sup> Small springs in Geyser Hill area near BRIERLEY (1966) station No. 3.

<sup>11</sup> Large cold lake near Black Dragon's Caldron.

<sup>12</sup> Samples from south side of this large spring complex.

<sup>13</sup> See WHITE *et al.* (1971) for a map locating this spring.

<sup>14</sup> Small sulfide-rich springs in the River Group, east of Ojo Caliente.

<sup>15</sup> See BROCK and BROCK (1971).

<sup>16</sup> Sulfide-rich spring near Hot Lake in the Lower Geyser Basin.

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Our samples of gas emanating from springs never contained detectable amounts of sulfur dioxide, although all contained H<sub>2</sub>S. The dominance of H<sub>2</sub>S in the gas reflects the lower solubility of this gas in water than SO<sub>2</sub>, and the higher pK for the H<sub>2</sub>S-HS<sup>-</sup> couple (6.88 for H<sub>2</sub>S as compared to 1.9 for SO<sub>2</sub>). At pH values of 1-3, all of the sulfide is in the undissociated H<sub>2</sub>S form, whereas at pH 2 only 35% of the SO<sub>2</sub> is undissociated and at pH 3 only 9% (see introduction to this paper). There is no obvious correlation between sulfur dioxide concentration and pH.

The highest concentrations of sulfur dioxide found in spring waters were around 0.6 µg/ml of sulfur dioxide sulfur (1.2 µg/ml SO<sub>2</sub>). These concentrations were found in two acid springs in the Sylvan Springs area. Several springs had concentrations around 0.2-0.4 µg/ml: Congress Pool (pH 3.6) had 0.23 µg/ml at one sampling time and Cistern Pool (pH 7.5) had 0.18 µg/ml. There seemed to be no correlation between sulfur dioxide concentration and concentration of sulfide or elemental sulfur, two sulfur species which are probably the source of sulfur dioxide. Thus, Evening Primrose had the highest sulfur dioxide concentration and a fairly high elemental sulfur concentration, but Sulfur Caldron had an even higher elemental sulfur concentration and a similar pH, but a quite low concentration of sulfur dioxide.

#### Fumaroles

Gases emanating from three fumaroles were studied. Two were at Roaring Mountain and one on the Porcelain Basin of Norris. Temperatures of all three fumaroles were at the boiling point (92.5°C). No SO<sub>2</sub> was found in any of the fumaroles and H<sub>2</sub>S was the only sulfur gas present. Concentrations of H<sub>2</sub>S were 55 and 290 µg/50 ml gas at the two Roaring Mountain fumaroles and 500 µg/50 ml at the Porcelain Basin site.

#### Source of sulfur dioxide

The presence of sulfite in sulfide springs of neutral or alkaline pH is consistent with the data of CHEN and MORRIS (1970) showing that small amounts of sulfite are formed during the chemical oxidation of sulfide. Under these conditions, the oxidant is probably O<sub>2</sub>, as ferric iron is highly insoluble and is virtually absent from the waters.

Under acid conditions, sulfide is oxidized by molecular O<sub>2</sub> very slowly. CHEN and MORRIS (1970) found undetectable rates at a pH value of 6.0. We have extended these studies to pH 1.8-2.0, the pH of many of the acid springs, using both sulfuric acid and hydrochloric acid systems. Even after 24 hr at 70°C, at levels of sulfide around 1-2 µg/ml, essentially none of the added sulfide was oxidized. On the other hand, if ferric ions were present, the oxidation proceeded so rapidly that the rate could not be measured, even at room temperature. Most of the acid springs studied have significant amounts of ferric ions, concentrations varying from around 1 µg/ml to 200 µg/ml (BROCK *et*

*al.*, 1976). Thus it is reasonable to conclude that oxidation of hydrogen sulfide in these springs is brought about by ferric ions [see also SCHOEN and RYE (1970)].

It was of interest to determine whether sulfur dioxide was formed during the oxidation of sulfide by ferric ions. When the concentration of sulfide was low, around 1-2 µg/ml, neither elemental sulfur nor sulfur dioxide was detected, the oxidation apparently proceeding all the way to sulfate (this experiment was done in sulfuric acid so that sulfate assays could not be run). When a much higher concentration of sulfide was used, 60-80 µg/ml, and the ferric ion concentration was raised proportionately, small amounts of sulfur dioxide were detected, 0.02-0.09 µg/ml, and the main product was elemental sulfur, with only traces of sulfate being formed. However, none of the springs have total sulfide levels this high, although some have concentrations of 10-15 µg/ml (BROCK and MOSSER, 1975). Since the major reduced sulfur compound in most of the springs is elemental sulfur, experiments were set up to see whether ferric iron would oxidize elemental sulfur with the production of sulfite. To increase the reaction rate, colloidal sulfur was used. It was found that elemental sulfur was quite stable to oxidation by ferric ions, and that neither sulfur dioxide nor sulfate were formed in significant quantities.

#### DISCUSSION

Our results show that sulfur dioxide is formed in small amounts in most geothermal waters sampled in Yellowstone National Park. Our methods of detection are considerably more sensitive than any used previously, so that it is not surprising that sulfur dioxide has not been reported before in geothermal systems. We cannot conclude that the majority of springs contain sulfur dioxide, since we sampled primarily springs with high amounts of reduced sulfur compounds. Presumably, the large number of springs of neutral to alkaline pH in Yellowstone which have close to zero levels of reduced sulfur compounds would not contain sulfur dioxide. Indeed, even some springs with relatively high levels of sulfide (e.g. Boulder Spring and Spring 57-4 in Table 1) were devoid of detectable sulfur dioxide.

However, the actual concentration of sulfur dioxide, as measured in our chemical assay, does not give any direct indication of the rate at which this component might be formed. The concentration measured is presumably the steady-state concentration, and its level would be influenced by the rates of formation, decomposition, volatilization, and the rate of mass water movement into the spring through the underground circulation system. As we showed for a number of acid springs (BROCK and MOSSER, 1975), even in springs where there was no surface flow, underground water flow was often rapid, as measured experimentally by a chloride-dilution technique. Constituents such as sulfur dioxide are presumably being

diluted at the same rate as chloride, and hence are being lost to the subsurface flow.

Sulfur dioxide is almost certainly oxidized in the surface waters of the springs. Oxidants present are  $O_2$  and (in acid springs)  $Fe^{3+}$ . The latter is a highly reactive oxidant and probably is responsible for most of the oxidation of reduced sulfur species in acid springs. As shown in our other work (BROCK *et al.*, 1976), most acid springs contain significant amounts of  $Fe^{3+}$ , and often this ionic form predominates over  $Fe^{2+}$ . As we also showed in the other work, bacteria of the species *Sulfolobus acidocaldarius*, present in most hot, acid waters, are able to rapidly oxidize  $Fe^{2+}$  back to  $Fe^{3+}$ , using  $O_2$  as oxidant, so that  $Fe^{2+}$  formed as a result of the reduction of  $Fe^{3+}$  by reduced sulfur compounds will be reoxidized, thus maintaining a significant concentration of  $Fe^{3+}$  oxidant. Thus, even though  $H_2S$  is stable in the presence of  $O_2$ , it will be oxidized as a result of the combined processes of  $Fe^{3+}$  reduction (by  $H_2S$ ) and  $Fe^{2+}$  oxidation (by  $O_2$ ).

There is no evidence that the bacteria produce sulfur dioxide as an oxidized product. It is well established that *S. acidocaldarius* will oxidize elemental sulfur to sulfuric acid (SHIVERS and BROCK, 1973; MOSSER *et al.*, 1973). In some unpublished work, we found that *S. acidocaldarius* would also oxidize sulfide, using  $O_2$  as electron acceptor (experiments done in the absence of  $Fe^{3+}$ ; in the presence of  $Fe^{3+}$  the spontaneous oxidation of sulfide is so fast that a bacterially-catalyzed reaction cannot be measured). However, when *S. acidocaldarius* oxidized sulfide, no sulfur dioxide was formed, the sole product being elemental sulfur (a small amount of sulfate was probably also formed, but since the experiments were done in pH 1.6 sulfuric acid, this sulfate could not be measured). Since it can be shown in the laboratory that sulfur dioxide is formed, albeit in small amounts, during the chemical oxidation of sulfide by  $Fe^{3+}$ , we conclude that the sulfur dioxide found in the geothermal waters is formed as a result of spontaneous chemical reactions. Not all of the oxidation in the natural waters may be due to reaction with  $Fe^{3+}$ , since heavy metals, clays, and natroalunite present in some spring sediments (BROCK *et al.*, 1976) may catalyze the oxidation of sulfide by  $O_2$ .

The environmental significance of the sulfur dioxide formed in these geothermal waters is unclear. Almost certainly little or none of this gas escapes into the atmosphere, because of the high solubility of sulfur dioxide and its low pK. Since the water leaves many of the springs by underground seepage (BROCK and MOSSER, 1975), it is conceivable that the inability of plants to grow in the acid soils of these habitats (FLIERMANS and BROCK, 1972) is due not only to acidity but to sulfur dioxide toxicity. However, it would be the atmospheric effect which would be of most significance in the environmental impact of a geothermal power plant. As our assays show, only  $H_2S$  was present in the gases leaving springs and fumaroles.

Large amounts of  $H_2S$  are volatilized from many of these springs, and since  $H_2S$  will oxidize to  $SO_2$  in the atmosphere (KELLOGG *et al.*, 1972), some  $SO_2$  is almost certainly present in the atmosphere. Methods for trapping this  $SO_2$  were not available to us when we did this work, hence we do not have any data on actual concentrations present. Because many plants (including lichens) grow apparently without difficulty near sources of geothermal  $H_2S$ , it would be of interest to measure  $SO_2$  concentrations and assess the tolerance or susceptibility of these plants to this natural source of air pollution.

*Acknowledgements*—Supported by the College of Agricultural and Life Sciences and ERDA Contract COO-2161-30. The laboratory experiments were done by JOHN GUSTAFSON.

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STATUS OF ECONOMICS AND FINANCING  
GEOTHERMAL ENERGY POWER PRODUCTION

by

B. Greider

Chevron Oil Co. report

May 29, 1975

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Introduction

There developed in the last decade a strong movement by people concerned with the environmental effect of coal and nuclear fueled electric generating plants to find alternative sources of energy that would abate the spectre of a nuclear disaster or a sulfur and ash drenched landscape. This was supposed to be a compelling argument to find and develop geothermal and solar energy. Several nontechnical articles had indicated that except for the minor investment in a few holes, geothermal energy was abundant and free for the person with imagination and modest funds. People with little experience in resource development or exploration pronounced that geothermal energy was attended by no risk, infinite production, and only minor environmental concerns. Economic calculations were usually simple arithmetic guesses at assumed costs. The full impact of taxes and indirect costs on geothermal development was not described in the literature until recently. By contrast economic papers by Armstead, Banwell, Kaufman, Bradbury and Facca-Ten Dam which appeared basic to an understanding of profitability of geothermal development by governmental agencies briefly described the risk of failure, recovery of costs and how to calculate the effect of these on profitability.

Five years ago in the United States Pisa symposium actual histories of development from every geothermal project in the world were reported. From

Aug 76 Note: WELL COSTS HAVE INCREASED 45% SINCE THIS WAS GIUDY  
CONSTRUCTION COSTS 25%, OPERATING COSTS 20%

that background of information and new field operations in the last five years the technical world has discovered that dry steam geothermal fields are strong competitors as a source of energy used to generate base load electricity.

Successful flashed steam developments located in New Zealand, Japan and Mexico are producing electricity at costs less than fuel prices for oil or coal delivered to the generating plant. There are no economically successful low enthalpy heat exchange plants running today though two heat exchange plants ran for several years in the Lardarello-Castlenuovo areas using the initial fluid at 401°F and fresh water for the secondary fluid. These had 79 MW capacity. The Paratunka pilot plant in Russia has been running since 1967, and is the first actual binary plant using a low boiling point fluid to drive the turbine.

### Market for Electricity

The increasing use of energy has created an awareness that the major question facing the energy user will not be which alternate fuel is used but what fuel can be used. Electricity is becoming an important segment of world energy because it can be transported cheaply long distances by ultra high voltage D.C. lines (.3 to .4 mill/KWH/<sup>100</sup>~~1,000~~ miles) and can be used for space heating, lighting and electro mechanical devices. Remote energy supply areas now become accessible for population centers' energy.

To determine the growth of the geothermal industry we must examine the electrical industry. The electric power industry in the U.S.A. is a mix of public and investor owned utilities. Federal owned facilities generate 10% of the U.S.

electricity and investor-owned utilities provide 75% of the total. The balance is produced by municipalities, state and local cooperatives. A fairly complex system of Federal and State regulations has evolved to control the location, size and type of electrical generating systems used by the investor-owned utilities. This has resulted in the flexibility of utility planning being reduced and plant lead times increased by 100% in the last five years.

Electricity generation in the United States has doubled every 10 years during the last 40 years. During the last year the annual 7% increase energy produced dropped to 0.6% due to the oil embargo, electricity rate increase and reduced business activity. Fossil fuel steam plants now produce 80% of the total power generated. Nuclear now produces about 9% and is expected to increase to 35% of the United States' annual requirements sometime between 1985 and 1990. 70,000 MW of nuclear power is generated in the world. Coal has supplied about 50% to 54% of the electrical generation fuel required since 1971.

#### Fuels for Electrical Generation

In the past electric utility management has had reasonable selection of fuels available at a low cost for electric power production. This selection of fuels from a large number of vendors has allowed the utilities to use that fuel most familiar to them. For many years, the fuel industry supplied the basic research and development that enhanced the competition between energy sources. Recent changes in the bountiful supply of available fuels and environmental and regulatory procedures have required utilities to become more involved in the

economics and utilization of fuels.

The strong demand for fuel supplies will cause a competition for investment funds and technical manpower between ventures offering a low risk normal rate of return and an increased risk venture with a higher rate of return. As an example, the exploration for coal and uranium and the development of these fuels uses well know techniques. Though the risks are high for a successful project, the costs are predictable. Sale of these products is assured and the demand has caused a favorable price. There is a delay of three to five years after finding before a producing facility (mine) can be built.

Let us review one of these energy commodities and compare its economics with those of geothermal energy. This will set the framework for examining the competitiveness of geothermal power. The development of each of these is capital intensive and funds to participate in the business must come from those expected to be available for energy investments.

The growth in total energy use will most likely be held to about 2.5 to 3.5% per year for the next decade. Figure 1 depicts the position that generation of electricity is expected to grow between 5.5% and 6.5% per year as it's use will be increasing at a greater rate than total energy use because present uses of oil and gas for space heating and cooling will be transferred to electricity. Within the next ten years the use of oil and gas for any boiler fuel may not be allowed. The share now planned for nuclear power generation is shown below the "total" curve. The amount represented between "nuclear" and "total" will use the other available fuels. There is ample opportunity for geothermal to participate in this growth.

## Nuclear Competition and Effect On Geothermal Exploration

The use of nuclear reactors to generate electricity has been favored by utility planning groups as they can operate at near base load capacity and have had a very low fuel cost. Present nuclear fuel costs of 2.1 Mills/KWH can only be matched by hydropower. It is expected this fuel cost will be increased by 50% within the next five years.

Prediction of uranium reserves necessary to meet the needs of reactors scheduled for completion this decade is straightforward. Late in 1974 it became apparent the reserves of uranium were not as extensive as suggested in 1969-1973. The rate of discovery for this fuel has been falling short of that needed. As inflation's effect on mining and processing costs continued, the amount of reserves that can be mined for an \$8.00/pound mining cost shrunk by about 25%. The high cost of building reprocessing plants and the uncertainty of their functioning has caused the cancellation or deferral of such systems so that the amount of uranium found must be increased to fuel plants now being built. The generating plants now operating in the world use 30,000 tons of  $U_3O_8$  per year. Figure 2 shows this demand will, in 1990, increase to 225,100 tons per year. The rest of the world will need almost twice the amount required in the U.S.A.

Figure 3 from the U.S. Energy Research and Development Agency shows that the capability of the present industry to produce and mill uranium ore will be exceeded by requirements about 1978. Ore deposits identified will meet the requirements to 1980 if the mines and mills are constructed. This



situation has created a strong upward move in price for  $U_3O_8$  and has now made some deposits of less than .10% attractive. Figure 4 from John Klemenk's work illustrates that rates of return above 25% can be expected at today's prices and costs of mining.

The need to schedule power facilities is a requirement for the electric utility industry. Figure 5 shows the lead time (commitment to operation) for electric plants is eight to ten years for nuclear plants and around five years for coal, oil and geothermal plants. With the increased regulatory overview on energy sources these lead times are increasing. This must be considered when estimating cost of energy from a project as the cost of capital invested during construction must be added to the fuel cost. Mines have lead times off three to seven years. The lead time delay in constructing coal mines is due to a four to five year backlog on mining machines. When the federal government's moratorium on coal leasing is lifted, equipment delays will be compounded as the necessity for mining equipment is increasing while the production facilities are not.

So this gives an investor interested in exploration ventures a choice. Figure 6 compares the exploration and acquisition investment with the supply facility cost following a successful project. To find and acquire a 100,000,000 ton coal prospect will cost twice what a geothermal 200 MW field should cost or a 3,650 tons of  $U_3O_8$  project cost.

The coal mine, to produce 5,000,000 tons a year for 20 years, would provide fuel for 28,000 MW years. The rate of return would approximate

15% (Project Independence 74). The uranium mine would produce 7,300 pounds of  $U_3O_8$  per year for 10 years and provide fuel for 17,500 MW years. The rate of return would be 21-26% (Klemenic 74). The geothermal prospect would provide 200 MW capacity for thirty years and may have a rate of return of 15% (Bloomster 74). To be competitive for dollars and manpower better returns will be required for geothermal projects.

### U.S.A. Geothermal Industry

The geothermal industry in the United States will probably develop with an energy finder supplier and an electric utility as a converter and distributor. The finder will be an expert in using geology and geophysics to locate and evaluate reservoirs with commercial base temperatures.

The mining and energy supply companies have the organization and technical experience in using these sciences. Energy supply companies have operational experience in handling large fluid producing and injection complexes in many areas of the world. The financial resources of these two groups enables them to invest in exploration and production facilities with long lead time before income is obtained. The exploration for geothermal energy by the mining and energy supply companies makes economic sense as their experience with high risk ventures spans the local geographic areas within which the utility companies operate.

The utility industry is experienced in assessing the most economical method for electrical generation, transmission and marketing. The price

the energy supplier charges by geothermal energy will be the competitive cost the utility is willing to pay and to generate electricity for sale at regulated rates. There are no posted prices for geothermal energy. The pricing is similar to that used for coal sales. A negotiated price between the user and producer requires each to know or to be able to predict future costs of operation and future need for his product.

The finding and development of geothermal energy is expensive and capital intensive. The usefulness and price of this energy will be dependent on its quality. The utility planners must have confidence in geothermal reservoir capacity providing for long delivery of uniform quality fuel and recognize an economic advantage in this energy source. The energy supplier must be technically capable and financially able.

#### Profitability Factors

Recent reports on the scope of geothermal resources have not been successful in expressing a consensus on the size of generating capacity that can be expected in the next 10 years. This illustrates the uncertainty that exists in determining the size and types of reserves. The rate of growth is dependent on economic vitality and size of reserves being found. To establish the profitability of geothermal investment we must know:

- I. Exploration and evaluation costs.
- II. The volume and temperature of the carrier of the energy.

III. The development schedule.

IV. Power plant design.

V. Government regulation and taxes.

VI. The market price of electricity.

#### Exploration Costs

In 1973 the author presented a detailed breakdown of prices of services, costs of exploration and development with expected rates of return. (Greider 73).

These costs were then presented in budget form to establish the order of magnitude of money required to find a successful hot water-flash steam field. A statistical risk was used in determining the net profit the energy supplier could expect and the rate of return that would result. In the last two years significant increases in cost have taken place in exploration, field development and generating plant equipment. Figure 7 consolidates 1974-1975 exploration costs by function. The significant 1975 cost increases result in these new expenditures listed by the monthly charges:

Geophysics groundnoise and micro seismic	\$20,000-\$40,000
Resistivity surveys	\$15,000-\$20,000

Temperature holes

\$40,000-\$50,000

Land acquisition costs have increased to an average, including acquisition, of \$7.00/acre. A maximum of over \$3,000/acre has been paid for acreage near production. Prices are reasonable in higher risk areas with non surface indications.

Drilling costs have increased such that an exploratory well evaluating a 5,000 foot sedimentary section will require between \$365,000 and \$550,000. Geothermal wells are more expensive than onshore oil or gas wells due to the heat, abrasive sections and low hydrostatic pressures. A typical budget of expenditures is shown in figure 8. Geological and geophysical work will cost \$85,000 to \$90,000. In this instance the exploratory hole cost \$410,000. Three stepout wells were used to evaluate the reservoir performance. \$540,000 is listed for combinations of testing procedures to establish that production has commercial potential. A development program would follow the \$2,183,000 exploratory program.

Figure 9 presents the logic of exploration risk and the effect on money needed. It is estimated that to find a geothermal field having a capacity of 200 MW sixty-four prospects will be evaluated with geological and geophysical work.

Half of these will require additional geophysics to select twenty-four that justify temperature hole programs. From that work sixteen will be attractive enough to spend the money required for drilling. If the work and anomalies selected are better than the industry average one of the sixteen exploratory

64  
24  
16  
1

wells will find the objective 200 MW field. Additional testing and confirmation drilling will complete the project to the point that a development program would be justified. Though any given project might be explored for a little over \$2,000,000 the odds are the successful venture will have evolved from a total of \$13,500,000.

## FINANCING GEOTHERMAL PROJECTS

### Non U.S.A. Development

The financing of geothermal projects in the world outside of the U.S.A. has followed a straightforward system. Government geological surveys have usually established broad areas of interest. These surveys have been paid from local funds and involved either government agency personnel or private-public companies working on a contract. If initial work indicates an assessment should be made of the areas of interest a second phase will require additional government funds being budgeted. These may be matched by a grant from a foreign government or by the United Nations. At times a private company has been invited to conduct this phase of work. Union Oil's participation in the Tiwi Area of the Philippines has followed this pattern. When the assessment has been completed and a power project is justified the plant may be constructed and financed by the electrical operating entity. This may be federal, state agency, or a private electrical taxpaying company. Cerro Prieto in Mexico was developed with Mexican federal funds using national scientific personnel. Ahuachapan, El Salvador is an example of sharing the risk in early phases by using United Nation's dollars and technical personnel as well as El Savadoran funds and scientists.

Cerro Prieto is the first successful geothermal project in Latin America and was developed with Mexican funds by the Comision Federal de Electricidad. The geological and engineering work has outlined an area that may have a 500 MW potential. 75 MW has now been developed and work is underway on the next 75 MW. As of October 1973 \$19,824,000 U.S. had been spent. Figure 10 summarizes the expenditures made that resulted in a capital cost of \$264/KW for this hot water steam flash field.

In 1965 the Republic of El Salvador signed an agreement with the United Nations to determine the potential of geothermal areas located by early geologic reconnaissance by government agencies. The program consisted of two phases with funds provided by the United Nations Development Program Fund and by the El Salvador Government. The initial phase cost \$1,748,048 U.S. and was shared 59% UN and 41% El Salvador. The second phase concentrated on the drilling evaluation of and plant design for Ahuachapan. This cost \$1,191,500 U.S. and was shared 45% UN and 55% El Salvador. The project total cost of \$3,906,043 U.S. was shared 51% UN and 49% by the Republic of El Salvador. A project with a possible 166 MW size is now having the first 33 MW plant completed. The capital cost for this project appears to be \$347/KW and will produce electricity for a price between 7.76 mills and 8.93 mills per KWH if an 80% load factor can be maintained. Figures 11 and 12.

#### U.S.A. Development

In the United States geothermal work is financed by government agencies using tax funds and by companies using investor funds. If the private inventor

projects are successful and make a profit, 50% of that profit will be paid into federal tax funds. The Federal and State agencies finance research and regional assessments of natural resources occurrences. The funding results in agency grants to universities and private-public companies for conducting these studies. Funding of regulatory agencies at three levels of government provides a bit of direction to and control of geothermal development. The geothermal energy can be owned by individuals, county, state and federal governments, and by corporations. This mixture of ownership provides an opportunity for forty-four governmental agencies to be involved with geothermal exploration and development. If there is a deliberate restriction applied to geothermal growth in the U.S.A. the effort is probably resident in some of those forty-four entities. Private funds are used for research and prospecting and developing projects.

The diverse ownership of geothermal rights requires a land leasing activity that is unique to the United States exploration effort. The fact that areas must not only be identified but must be acquired if work is to be continued into a development phase adds costs of landmen and skilled negotiators. Using these talents, areas of land leased by different companies or individuals over an attractive prospect can be assembled into a unit of sufficient size for evaluation.

Power plants are usually built by utility companies and they operate the transmission and distribution systems associated with the plants. Utility companies share in the costs of building the larger, more efficient nuclear and fossil fuel plants. At this time the utilities have indicated a willingness to joint venture more expensive geothermal plants in areas near their service regions.



### Producing Projects - Steam

At this time in the U.S.A. only Pacific Gas and Electric Company (P G & E) has built successful geothermal generating plants. These are located in The Geysers in Northern California about 80 miles north of San Francisco. This field is an example of a successful electrical generating geothermal project developed and operated by non-government funds. This month the productive capacity has become 502 net MW. The efficiency of this operation is possible as the well drilling and steam production facilities are operated by an oil company to make a profit by selling the steam to an investor-owned utility that must provide service at a regulated customer price. The steam price is calculated from a base price which is adjusted by the cost of other fuels used by the utility in their other thermal plants. Presently the steam supplier is paid 6.9 mills for each kilowatt hour generated. The supplier reinjects the excess condensed steam from the power cycle and charges a service fee of .5 mill.

The actual investment in the steam supply system at this field has not been published. I have estimated that wells and surface facilities to supply the first eleven plants cost about \$93/KW or \$46,700<sup>000</sup> and for units 12 through 15 \$105/KW or \$42,600,000. This is a total of \$89,300,000. Table 1.

Eleven generating units, with a net output of 502 MW have been built for a cost of \$63,300,000 for \$126/KW average. Union Oil Company of California, the operator of the steam supply system, has drilled and developed steam for almost twice the present generating capacity. An additional 406 MW of capacity is planned by P G & E and is awaiting State of California governmental

approval. These four plants are estimated (Worthington, 74) to cost \$63,600,000 or \$156.6/KW. Upon completion of these the P G & E 's 908 MW will represent an investment of \$126,900,000 and the average cost per KW capacity will be \$139.7. Electricity from unit #15 at 80% plant factor<sup>for</sup> will have an estimated busbar price of 12.8 mils. Unit 13, a 135,000 KW unit, at 80% plant factor is expected to produce electricity at 10.6 mils/KWH. This difference in production costs is due to construction costs for these plants. The development of The Geysers to 2,000 MW by 1985 seemed to be a reasonable objective in 1972. The state's delay in certifying plants has now extended the time such that it will probably be 1990 before this can be achieved. Cost for manpower and machinery have risen to such levels that the high risk initial development wells could not be drilled for \$40,000 to \$150,000 each as the pioneers were able to do so. Present value of money is now around 8% per annum on these projects. The time value of money will increase the actual investments reported here as time lengthens for a project to be completed. So the excellent economics of The Geysers should not be used as a model for what could be achieved today unless a better performing dry steam field could be located at a lesser depth and easier drilling area.

#### Producing Projects Hot Water Dominated

We shall now examine the economics of low enthalpy systems. Exploration scientists and engineers have found that there are many more geothermal areas with fluids in the 320°F to 400°F range than above. There are no operating systems to use effectively this large resource of heat. There are also areas of high heat and high salinity in environmentally sensitive areas.

These might be favorable for development if a closed system could be used to convert their heat to electrical energy. Research underwritten by Governmental and private funds is directed to systems that can produce electricity economically. The efficiencies of these systems are such that high volumes of geothermal water must be used. The systems below 400° become very expensive. The lower heat content requires more than twice as many wells to supply a plant at 310° F as required for 410°F. Heat exchanger and turbine size must be increased accordingly.

B. Holt has published (Holt, 1974) studies on the requirements of binary systems. In these systems the heat energy from the geothermal well vaporizes a low boiling point fluid which drives the turbine. The vapor is condensed and recycled. His studies used an ambient temperature at 60°F. Figure 13 has a curve added to this cost chart to reflect increase of exchanger and well capacity required by Imperial Valley ambient well bulb temperature of about 80°F causes increased construction costs of about 50%.

Figure 14 shows that a 55 MW plant using 400°F fluid requires about 20 mill per KWH to pay for the hot water energy supply system and cover the normal fixed charges and operating maintenance charges of the power production plant. The assumed 15% fixed charge is very low for a complex experimental binary plant.

Let us compare costs expected to be associated with steam, hot water flash and those expected for a binary system. Each will have 200 MW capacity. Figure 15 forecasts cost for projects commenced in 1975. The energy supply

section is treated separately but is the size required for each of the generating systems. Costs are shown for 20 miles of electric transmission and are the same for each. The investor for a steam field exploration and development program should expect a cost of about \$29.6 million and a lot of skill and luck (\$148/KW). The generating plant investor will need around \$74.6 million and the capital cost for energy supply and generation of electricity is \$373/KW).

A review of hot water (500°F) flash systems shows \$31.3 million will be needed for the energy supply system (\$157/KW). This is due to increased number of wells, larger injection volume of cooled fluid, and evaluation testing. The plant is more complex due to the lower quality of steam and physically greater amount of liquid to handle. The cost of this becomes \$78.4 million. (\$392/KW). The supply, generation and transmission systems total \$112.7 million. (\$564/KW).

I have used the same field development costs for binary as for flash. The best published costs for binary systems in the 400°F range are based on 1972-1973 costs. Severe escalation in construction and material costs have pushed the generating systems price to near that for the basic coal fired plants, without sulfur scrubbers. The total binary supply and plant should be brought in for about \$655/KW. This is competitive with the capital cost for pressurized boiling water nuclear reactors. Operation of the fuel supply and injection systems will need to be low enough to compete with the 3 to 3.5 mill fuel cost for the nuclear systems or the 10 mill cost for coal fuel.

#### Comparison of Generating Systems

Whether a central government agency decides which system of electrical

generation is used, or whether this is determined by private investors the criteria are pretty much the same. Figure 16 displays the major factors of unit size, reserve availability, plant siting requirements, capital requirements, and expected busbar price of electricity for coal, nuclear, diesel and geothermal plants. Geothermal plants will be constructed in small modules and several modules may be located together in one plant. As the ultimate capital requirements per KW is not much different, the small size of the geothermal plant allows it a distinct advantage in areas that cannot finance the large investment required for 1,000 megawatt installations. However, the geothermal electric plants must be located near the energy source just as any other direct use of the geothermal heat such as space heating and cooling, agriculture, industrial processing.

After its environmental problems are recognized as being at most comparable to other power sources, the busbar price for geothermal electric energy will be critical to its wide spread use. In areas where a valuable exportable fuel can be displaced by geothermal for local energy production, another economic advantage develops. The dollar exchange value on the export market of the transportable fuel then must be considered as an added value to the geothermal fuel savings forecast.

#### NON ECONOMIC SYSTEMS "75"

##### Geopressure

The potential economics for developing the geopressured reservoirs can now be estimated with a good deal more clarity than was available at the time of the

Hickel NSF Report. Exploration for oil and gas along the Gulf Coast region of Texas and Louisiana has defined an area several hundred miles long and about 100 miles wide that contains sands with entrapped water at 300°F to 400°F, and at formation pressures about twice normal. Figure 17 is adapted from work by P. Jones of the U.S.G.S. This shows the major geopressured section is found between 10,000 and 15,000 feet. The waters are in Tertiary sandstone reservoirs isolated from normal pressured sections by a thick shale wedge. The waters in this zone may contain methane in solution. Oil or gas production has not been sustained from these extensive and erratic sandstones. While geologists and engineers familiar with the details of these potential reservoirs are not agreed that water production in economic rates can be maintained for the required twenty years production per power plant, there may be areas where such production can be expected.

Dow Chemical Company has conducted a detailed analysis of the investment and costs of a system to produce electricity from this potential resource. Evaluation of this geopressured system, required using the kinetic and thermal energy of the water and recovering the dissolved methane for sale at \$2.00 a million BTU. Single stage and two-stage low-pressure flash turbine systems as well as binary systems were considered. Two models were developed. The first used average reservoir characteristics of all deep wells in Hidalgo County, Texas. The second used average values for the Lower Rio Grande Embayment of south Texas. These compared with the actual well used in the Eugene Herrin Air Force Project in 1972 (Herrin, 1972). At 1974 prices, a two-stage flash steam plant with 25,000 KW capacity would require \$10,500,000 for the 6 well supply system, and about \$16,500,000 for the surface equipment.

Using a 5% per year escalation to obtain project cost in 1980 the investment becomes \$34,000,000. A 66 megawatt plant would require 15 wells costing \$25,000,000 for equipment. The total project in 1974 costs would be \$61,000,000 and the 1980 cost would be \$78,000,000. Electricity costs using a \$2.00 MCF credit for the contained methane gas would be around 26 mills/KWH for the larger installation and about 38 mills/KWH for the smaller Hidalgo County plant. It is possible to believe that with design improvement, and careful research on well costs, the generated power may be produced for 20 to 25 mills. A comparison of size of unit and type of generation scheme is shown in figure 18. A summary of the data used in deriving these costs is presented in Table 2 from the Dow-State of Texas Report (Kaufman, 1974).

Considerable research must be completed before large sums of money should be invested by privately funded organizations. Title to this resource needs to be established as it is clouded by having kinetic energy, heat energy and dissolved methane, each transported by usually low-salinity water. By establishing ownership, a form of appropriate leasing can be developed and perhaps reach agreement as to which of the regulatory agencies will administer the development. Ownership may well establish the logical source of funds to be used in directed research on the technical aspects of this type of geothermal system. Work can now be directed toward site selection, test well design, and production facilities to make optimum use of the three types of energy expected and assessment of the environmental impact. The applicability of the 1966 Shell Oil Company patents must be established (hotlman, 1966).

This source of energy does not appear to be economic at this time. Since these reservoir conditions exist in most Tertiary sand and shale marine basins around

the world the potential importance of this type of geothermal prospect is very large. Research and development emphasis is justified and must be undertaken by initiating field projects.

### Hot Dry Rock

The hot dry rock geothermal system concept has had two excellent locations selected as the best in the United States and worked by federal government sponsored groups. These very experienced teams failed to find the dry rock part of the concept. The "hot" part was not there either. To provide high heat storage in a local spot, a collector for that heat must exist. Usually the high sensible heat of water, coupled with its mobility, provides this function. The "dry" part of the concept must be considered a large part of the risk of success. There are not enough data derived from the present projects to make a prediction as to when success will be proclaimed, or what will be the cost of electricity.

### Growth of Geothermal Power by 1985

If the economic outlook for energy projects continues to improve during the next five years, we should witness a several fold increase in geothermal power projects. To understand how rapidly geothermal projects can mature in the United States, a look at what is required has been made by many diverse groups. In determining what can be developed within the next ten years, it is paramount that the forecaster make a clear distinction between reserves and resources. Reserves can be developed with technology now available and are located where they can be legally produced at an agreed price.



Resources that are thought to be present may be recoverable in the future with improved technology and higher costs. Dr. Carol Otte, working as chairman on the Project Independence Industry Liaison Committee, reported that it was geologically possible to have 20,000 MW of geothermal electricity capacity by 1985. I would like to discuss why I think it is actually possible to have about 6,000 MW developed.

The world's best geothermal field is The Geysers. The last plant constructed required about twenty-one months to complete and put on line after certification. There are presently 406 MW represented by four plants waiting California Public Utility Commission certification for construction. It has taken fifteen years to add 502 MW of capacity. As this rate of increase may decrease even more, it seems very unlikely that The Geysers project will exceed 1,500 MW by 1985.

To find 4,500 MW successful exploration drilling must commence now. Fields that will add to productive total by 1985 must be found and have established their commercial worth by 1980. This results from the five-year lead time required between discovery of the resource and electrons flowing. If the average well produces 4 MW, 1,125 wells must be located, drilled, completed, and tested. This would require \$506 million if their cost averages \$450,000 during the next seven years — a more likely figure is \$642 million if costs escalate 5% per year for five years. Injection facilities will cost \$321 million.

It is most likely that successful fields making up this 4,500 MW will be high temperature flash, and the plants will cost \$392/KW. If this is escalated

5% per year for five years the capital cost will be \$498/KW. The plant cost will be \$2.24 billion for these fields.

\$75 million for minimal transmission facilities brings the production facilities cost to \$3.26 billion.

Twenty-three 200 MW fields will have to be discovered in the next five years. This will require about 23 x \$13,000,000, or \$299 million to be spent by industry or government exploration. So it appears that about \$60 million will be needed for the exploration program each year.

The total sum of \$3.5 billion is less than a 1% portion of the \$420 billion that will probably be used for capital investments in the energy portion (23%) of U.S.A. business investments forecast for 1975-1985 (Project Independence). The electrical industry forecasts an investment of between \$217 to \$271 billion for generating plants and transmission lines. Nuclear fuel alone will cost \$8.9 billion to fuel the forecast nuclear plant requirements. The coal investors will use about \$7.8 billion for new coal mines. In this context, there is ample money to meet the 6,000 MW geothermal goal. To reach the 20,000 MW goal, the approximately \$14 billion worth of work would create strong competition for men, materials, prospects and money.

### Summary

Geothermal steam used in electrical generation should provide the most economic and beneficial use of earth energy. Flash steam fields will be competitive with fossil fuels when reservoir temperatures are above 500°F.

If technology can lower binary costs these generation units may be competitive with fossil and nuclear plants and have extensive use.

Key issues that must be resolved before geothermal development can significantly penetrate the electrical generation industry are:

1. Power conversion system technology must be developed to withstand the hostile geothermal resources.
2. Competition from conventional fuel sources for capital, material and technical manpower.
3. Field exploration expenditures must be designed for cost effectiveness.
4. The politics of environmental capriceousness must be resolved, thus reducing the soaring costs created by redundant studies and reviews the public is required to pay.
5. Economic planners must learn the difference between an unlimited resource base and finite reserves.

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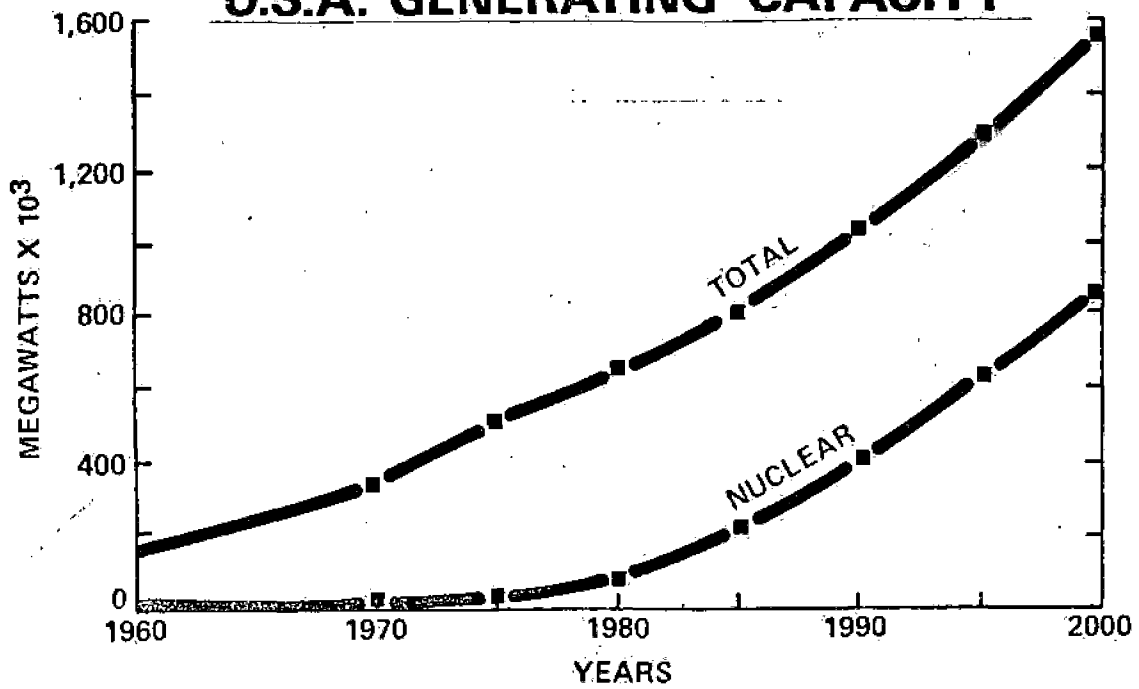
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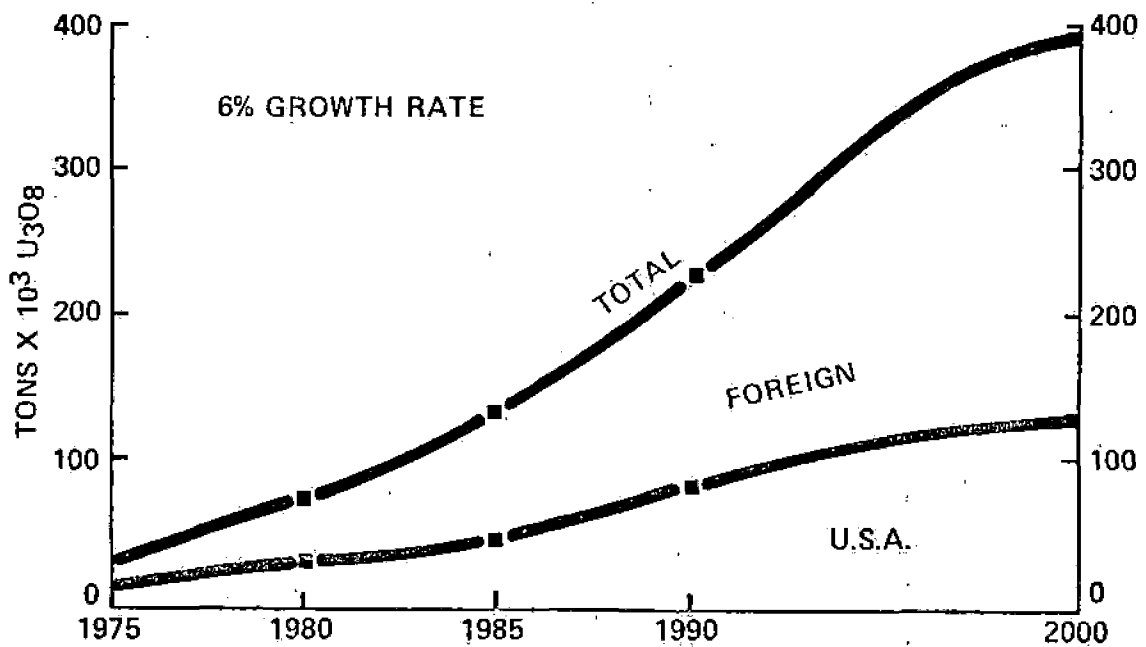
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# U.S.A. GENERATING CAPACITY



WASH 1139 - 1974

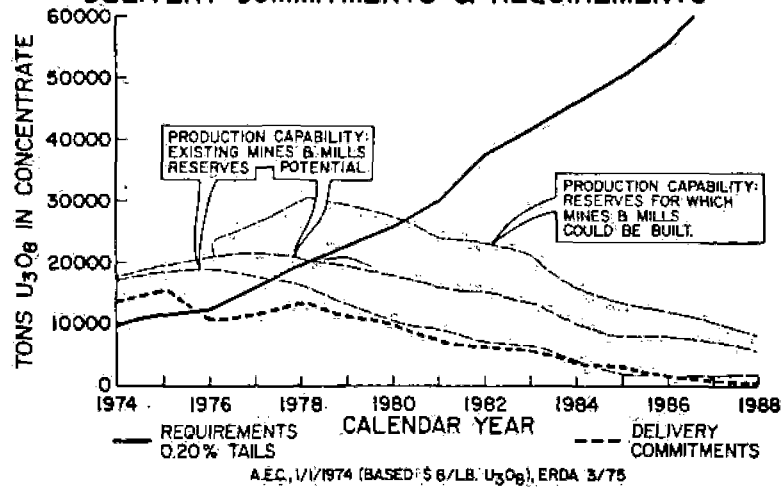
FIGURE 1



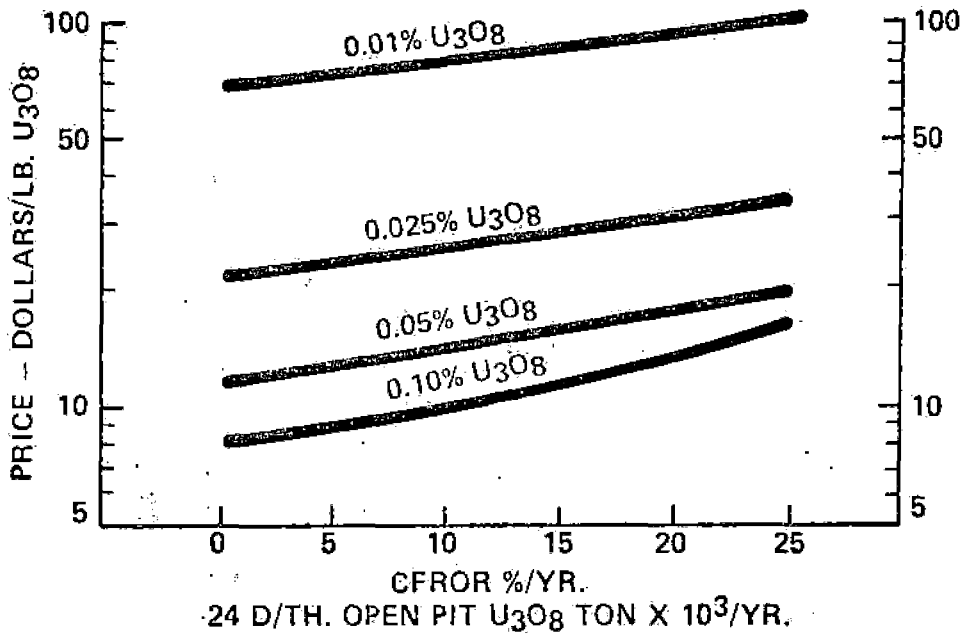
WASH 1139 - 1974

FIGURE 2

**DOMESTIC PRODUCTION CAPABILITY,  
DELIVERY COMMITMENTS & REQUIREMENTS**



**FIGURE 3**



**PRICE vs GRADE**

KLEMENIC AEC 1974.

**FIGURE 4**



# ENERGY FACILITY ESTIMATED LEAD TIME\*

<u>TYPE</u>	<u>YEARS LEAD TIME</u>
<u>ELECTRIC PLANTS</u>	
NUCLEAR	8-10
COAL	5
OIL	5
GEOTHERMAL STEAM	4-5
GEOTHERMAL BINARY	5
HYDROELECTRIC	20
<u>ENERGY SOURCES</u>	
<u>MINES</u>	
URANIUM	3-5
COAL	5-7
<u>FIELDS</u>	
GEOTHERMAL	3-10
OIL ONSHORE	1-3
OIL OFFSHORE	2-4

**FACTORS CAUSING LONG LEAD TIME:**

1. FORTY FEDERAL GROUPS HAVE ROLE.
2. STATE & COUNTY AGENCIES EVALUATE PROPOSED WORK AND SITES.
3. NO NATIONAL REQUIREMENT TO COORDINATE ENERGY, ENVIRONMENT AND SOCIAL NEEDS.

\*PROJECT INDEPENDENCE FINAL REPORT 1974

FIGURE 5

## INVESTORS CHOICE

	COAL	URANIUM	GEOTHERMAL
OBJECTIVE	100,000,000 TONS	3,650 TONS	200 MW
INVESTMENT	\$ 7,500,000	\$ 3,500,000	\$ 2,900,000
SUPPLY FACILITY (EXPLORATION & ACQUISITION)	\$ 60,000,000	\$ 30,000,000	\$ 32,000,000
RATE OF RETURN	15%	21%	15%
MEGAWATTS FUELED	28,000 MW YRS.	17,500 MW YRS.	6000 MW YRS.

FIGURE 6

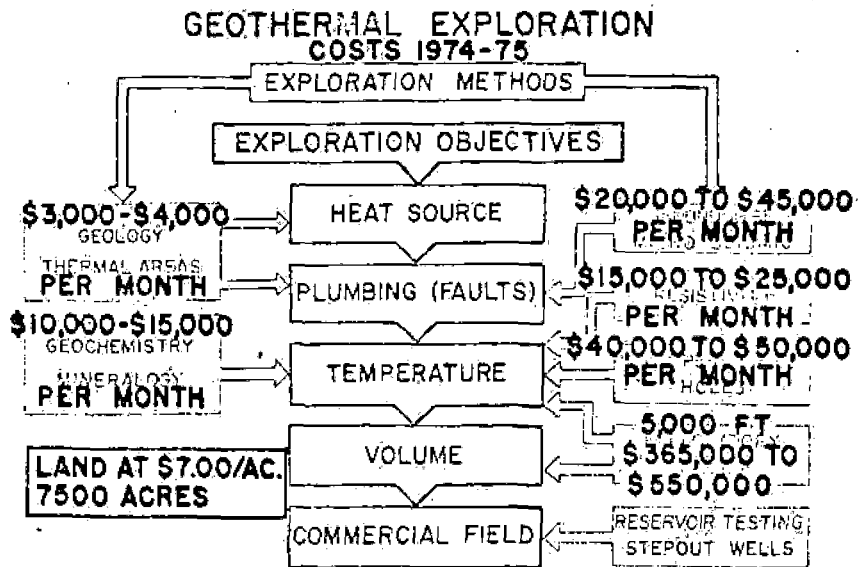


FIGURE 7

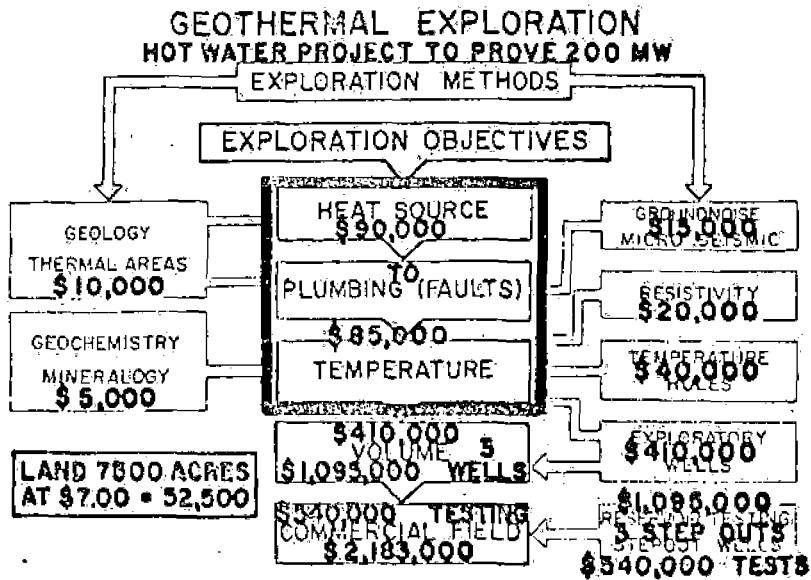


FIGURE 8

64x

**STATISTICAL INVESTMENT**  
**EXPLORATION OBJECTIVE: 200 MW FIELD**  
 OPTIMISTICALLY, FOUR AREAS STUDIED LOCATES ONE FOR DRILLING.  
 A 200 MW FIELD LOCATED FROM SIXTEEN DRILLED PROSPECTS.

	\$ COST	(TOTAL \$ 000)
GEOLOGY & GEOPHYSICS 64 AREAS (\$40,000) <sup>50</sup>	2,560,000	
ADDITIONAL GEOPH. 32 AREAS (\$15,000)	480,000	
TEMPERATURE HOLES 24 AREAS (\$40,000)	960,000	
	<u>4,000,000</u>	4,000
LAND ACQUISITION: 7500 ACRES X 32 AREAS (\$7.00/ACRE)	1,680,000	5,680
DRILLING & TESTING 5000' DEPTH X 3 <sup>70</sup>		
12 FAILURES (\$365,000)	4,380,000	
3 FAILURES W/CASING RUN (\$450,000) <sup>750,000</sup>	1,350,000	
1 DISCOVERY PLUS 3 CONFIRMATION \$750,000 <sup>750,000</sup>	1,505,000	
	<u>7,235,000</u>	12,915
TESTING TO ESTABLISH	540,000	<u>13,455</u>

50

29  
3

FAULT PATTERN DEF'N.  
 H.R. SEISMIC }  
 ISOTOPE. }  
 MODELING }  
 ENVIRONMENTAL

\$ 500,000<sup>00</sup>

\$ 300,000<sup>00</sup>

FIGURE 9

40 x 0.75M  
10M.

### CERRO PRIETO, MEXICO

HOT WATER FLASH 75 MW (x 2.666) =

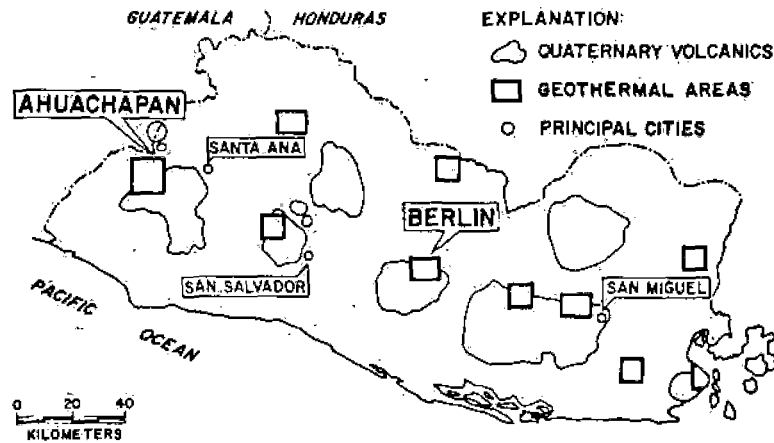
	CAPITAL INVESTMENT (\$000)	
<u>STEAM PRODUCTION</u>		
WELLS (19), SURFACE GATHERING, COLLECTORS, SEPARATORS, TESTING	50 x 0.75	\$ 5,072
<u>GENERATING PLANT</u>		
TURBINES, CONDENSORS, EJECTORS, BUILDINGS, WATER TREATMENT	120 m	6,272
<u>SUBSTATIONS AND TRANSMISSION LINES</u>	10 m	1,872
<u>TOTAL DIRECT INVESTMENT</u>		\$13,216
<u>INDIRECT COSTS</u>		-6,608
<u>TOTAL COSTS</u>		\$19,824
CAPITAL COST \$264 /KW		
GENERATION COST \$0.008/KWH		

15% Cont  
 of Working  
 Cap. Costs

\*SR. S. PARADES 10-73

FIGURE 10

\$ 400 - 700<sup>a</sup> /KW



**GEOHERMAL AREAS  
 REPUBLIC OF EL SALVADOR**

**FIGURE 11**

**EL SALVADOR PROJECT**

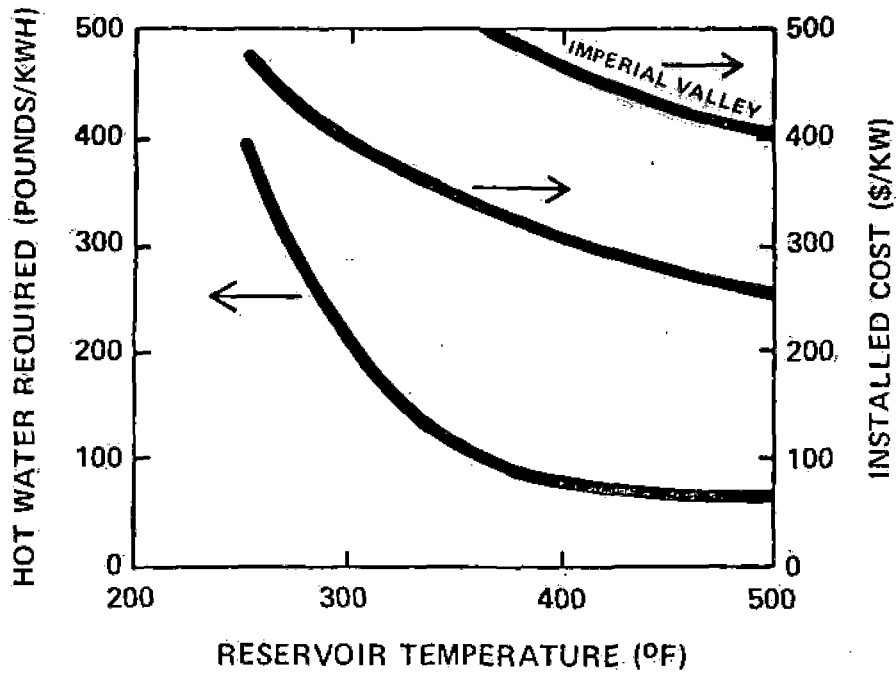
**AHUACHAPAN AREA**

CAPITAL INVESTMENT	COST MILS/KWH* CAPITAL CHARGE RATE 10%–12%		
STEAM SUPPLY AND DISPOSAL	\$ 3,145,000	1.67	1.93
POWER SWITCH AND TRANSMISSION	5,198,000	2.75	3.19
ENGINEERING, INTEREST CONTINGENCIES	<u>3,117,000</u>	<u>1.89</u>	<u>2.36</u>
TOTAL	\$11,460,000	6.31	7.48
	OPERATING COST	<u>1.45</u>	<u>1.45</u>
CAPITAL COST \$347/KW	TOTAL COST MILS/KWH	7.76	8.93

\*80% LOAD FACTOR

**FIGURE 12**

**50 Mwe PLANT  
COST vs WATER TEMPERATURE AND VOLUME**



HOLT SEPT. 1974

**FIGURE 13**

**THEORETICAL BINARY SYSTEM**

PLANT: 55 MW    COST: \$ 26,675,000    \$ 485/KW

FIXED COST (15%)                      10.4 MIL/KWH

OPERATION & MAINTENANCE (2%)    1.4 MIL

TOTAL PLANT CHARGES    11.8 MIL

VALUE OF 400°F WATER FOR 20 MIL BUSBAR

$$20 \text{ MIL} - (10.4 + 1.4) = 8.2 \text{ MIL}$$

**FIGURE 14**

**TYPICAL GEOTHERMAL FIELD DEVELOPMENT & POWER GENERATION  
INVESTMENT COST SUMMARY (\$ MILLIONS)**

<b>INVESTMENT <sup>(1)</sup></b>			
<b>Field Development</b>	<b>400° Hot Water</b>	<b>500°+ Flash</b>	<b>Steam</b>
Exploration & Field Evaluation	2.8	2.9	3.1
Producing Wells & Facilities	15.1	14.0	18.0
Injection Wells & Facilities	5.6	6.0	1.6
Pipe Lines	4.2	4.7	4.0
Contingencies & Overhead	<u>3.8</u>	<u>3.5</u>	<u>2.9</u>
<b>Total Field Investment/200 MW</b>	<b><u>31.5</u></b>	<b><u>31.3</u></b>	<b><u>29.6</u></b>
<b>Generation Plant</b>			
2-110 MW Turbo-Gen. Plants	95.0	77.0	40.6
Sub Stations	<u>1.4</u>	<u>1.4</u>	<u>1.4</u>
<b>Total Generation Plants (200 MW)</b>	<b><u>96.4</u></b>	<b><u>78.4</u></b>	<b><u>42.0</u></b>
<b>Transmission</b>			
500 KV - 20 Miles	<u>3.0</u>	<u>3.0</u>	<u>3.0</u>
<b>Total Investment - 200 MW (Net)</b>	<b><u>130.9</u></b>	<b><u>112.7</u></b>	<b><u>74.6</u></b>

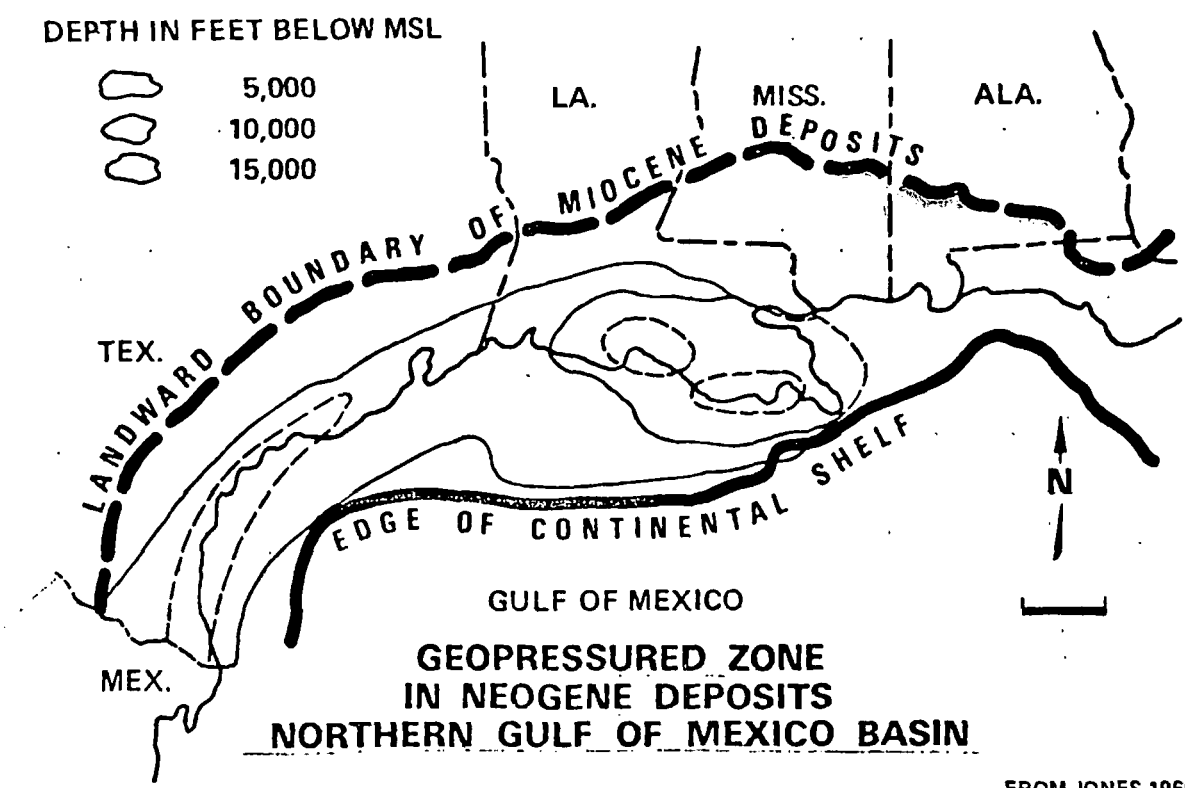
(1) Order of magnitude cost estimates. 1975 U.S. West Coast basis. No escalation.

**FIGURE 15**

**COMPARISON OF ENERGY SOURCES**

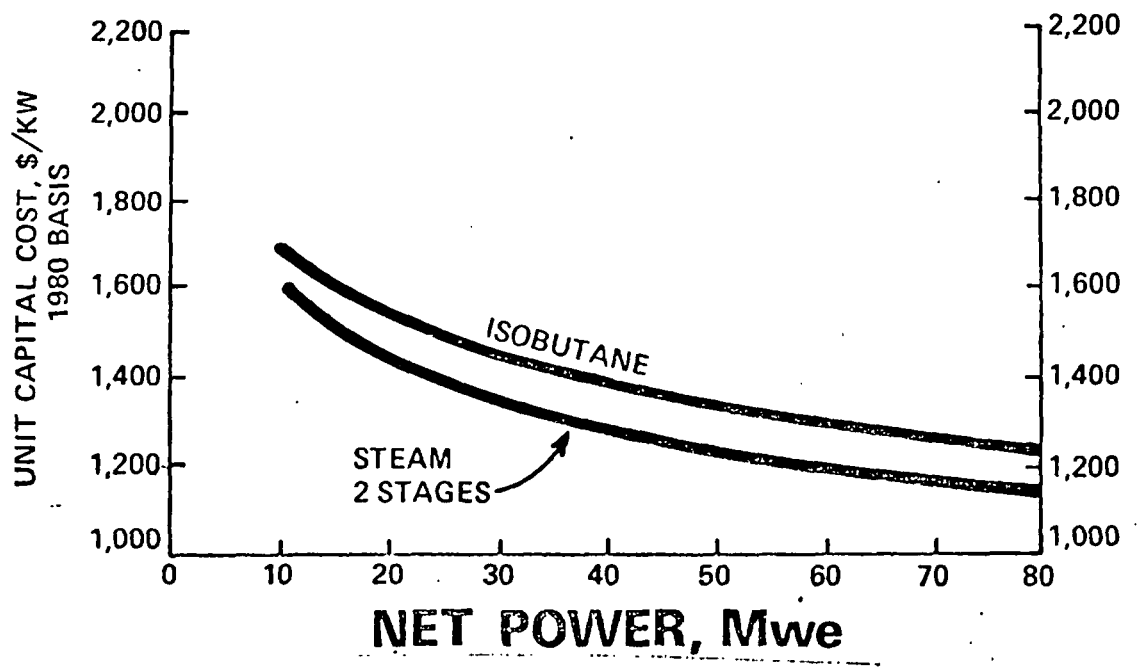
	<b>GEOTHERMAL</b>	<b>COAL</b>	<b>NUCLEAR</b>	<b>OIL-DIESEL</b>
<b>UNIT SIZE (MW)</b>	55-110	750-1200	365-1200	75-1200
<b>FUEL RESERVE</b>	NOT IDENTIFIED	VERY LARGE	MODERATE	LIMITED
<b>PLANT SITING</b>	AT SOURCE (3-5 ACRES)	FLEXIBLE (260 ACRES)	RESTRICTED (550 ACRES)	FLEXIBLE (70 ACRES)
<b>CAPITAL COST (PLANT INST. \$/KW)</b>	DRY STEAM 200 FLASH STEAM 390 BINARY SYSTEM 400-500	500-600	600-720	400-500
<b>BUSBAR PRICE (MIL/KWH)</b>	DRY STEAM 10-13 FLASH STEAM 10-18 BINARY SYSTEM 16-20	20-23	19-20	28-30
		COAL AT \$ 0.90/BBTU	U <sub>3</sub> O <sub>8</sub> AT \$ 20.00/LB.	OIL AT \$ 12.00/BSL. DIESEL AT \$ 13.80/BSL.

**FIGURE 16**



FROM JONES 1969

**FIGURE 17**



DOW CHEM. 1974

# GEYSERS U.S.A.

DRY STEAM 502 MW\*

	CAPITAL	COST/KW
STEAM SUPPLY AND DISPOSAL**		
THROUGH PLANT* UNIT 11	\$ 46,700,000	\$ 93
PLANTS 12-15	<u>42,600,000</u>	<u>105</u>
TOTAL	\$ 89,300,000	\$ 98 AVG.
<hr/>		
GENERATION PLANT		
THROUGH UNIT 11	\$ 63,300,000	\$126.0
PLANTS 12-15, 406 MW	<u>63,600,000</u>	<u>156.6</u>
TOTAL GENERATING INV.	\$126,900,000	\$139.7 AVG.
908 MW FIELD AND PLANT	\$216,200,000	\$238/KW
<hr/>		
FUEL SUPPLIED TO PLANT	6.9 MIL/KWH	
EFFLUENT DISPOSED	<u>.5 MIL/KWH</u>	
TOTAL	7.4 MIL/KWH	

\*PLANT 11 COMPL. APR. 1975

\*\*STEAM SUPPLY SYSTEM ESTIMATED

TABLE I

## GEOTHERMAL FACILITY SUMMARY (GEOPRESSURE)

<u>POWER CYCLE</u>	<u>WATER BBL/DAY</u>	<u>WELLS</u>	<u>NATURAL GAS SCF/DAY X 10<sup>6</sup></u>	<u>NET MWE</u>	<u>CAPITAL COST \$/KW (1980)</u>	<u>COST MILS/KW (1980)</u>
<u>MODEL ONE</u>						
HIDALDO CO., TEX.	262,600	6	7.8			
ISOBUTANE				25.28	1485	43.4
STEAM - 2 STAGE				24.50	1393	37.6
<u>MODEL TWO</u>						
RIO GRANDE EMBAY.	713,100	15	21.4			
ISOBUTANE				68.66	1276	33.3
STEAM - 2 STAGE				66.50	1169	26.8

**CONDITIONS FOR CALCULATIONS:**

WELL DEPTH - 15,000 FEET  
 WATER TEMPERATURE - 385°F  
 METHANE CONTENT - 30 SCF/BBL  
 METHANE VALUE - \$2.00/1000 SCF  
 RETURN ON INVESTMENT - 20%

TABLE I



# EXPLAIN CURVES

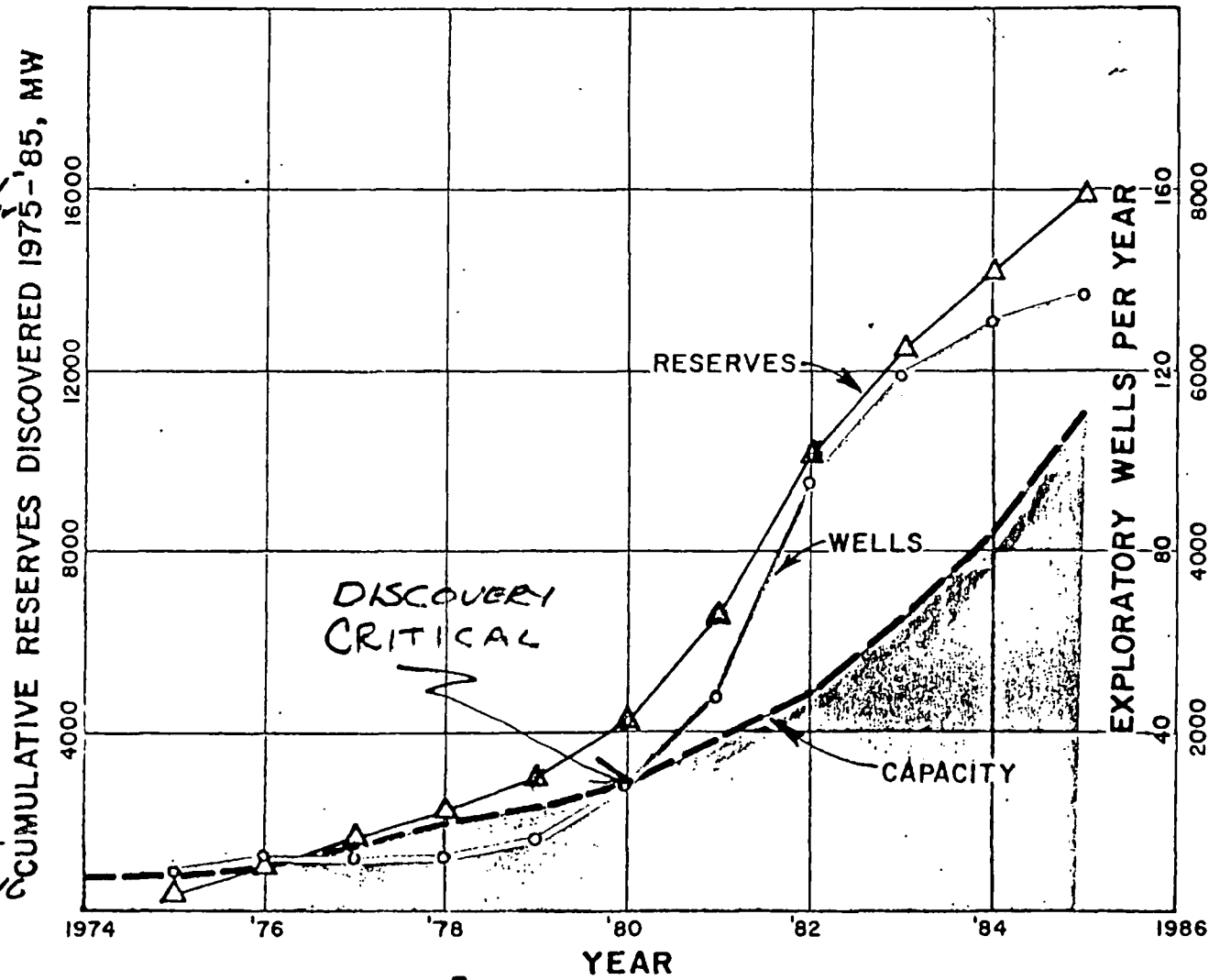
① FORECAST BY 1985 U.S.A. WILL HAVE DEVELOPED 6,000 MW

② GEYSERS ADDED 318 MW IN SEVEN YEARS - 1500 MW 1985

1,000 MW Frees  
15-40M bbls Oil/yr

1975-85  
17-21.1 M<sup>3</sup> for  
NEW GENERATING  
PLANTS

7.8 M<sup>3</sup> FOR NEW COAL MINES 8.9 M<sup>3</sup> = U<sub>2</sub>O<sub>8</sub> mine



③ REQUIRE 23  
200 MW FIELDS  
\$300M EXPL COST

④ MUST BE  
DISCOVERED BY  
1980

⑤ ASSUME  
IMPROVED DISC  
RATIO TO 16%  
from 6%

⑥ 1100 DEU WE  
\$506M @ \$450M  
642M ESCAL

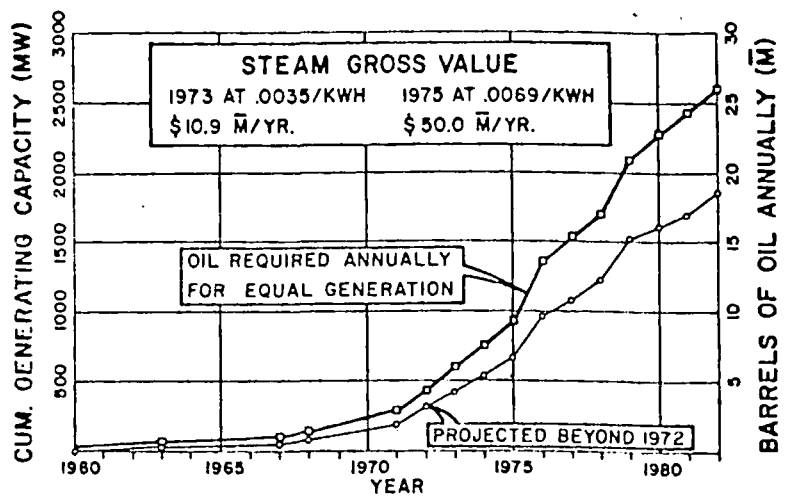
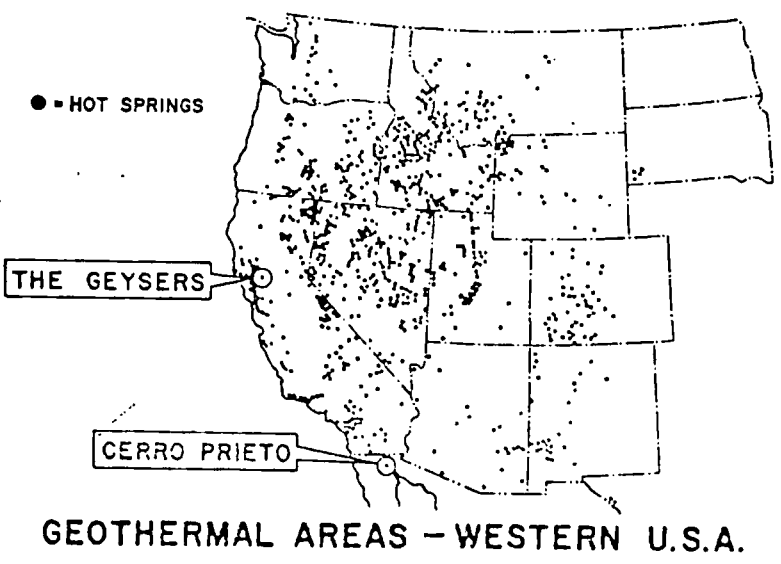
⑦ \$321M INJEC  
FACILITIES

⑧ 4,500 MW PLAN  
\$2.24M<sup>3</sup>

⑨ \$18M TRANSMISSION

## U.S. GEOTHERMAL INDUSTRY FORECAST, 1975-'85

\$60M/yr EXPL, \$960M DEV & INJ FACILITIES, \$2.24 Billion Plants 18M TRA  
\$3.5 BILLION TOTAL < 1% of \$420M<sup>3</sup> FOR ENERGY FACILITIES 1975-'85

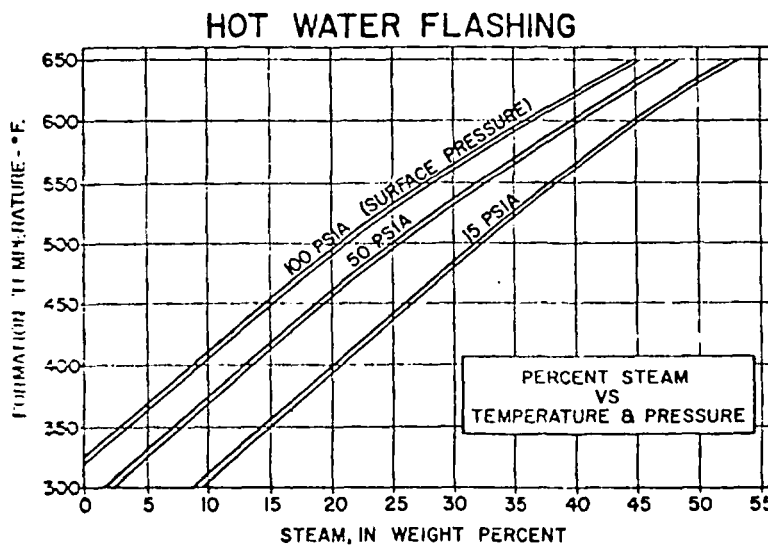


**THE GEYSERS GEOTHERMAL FIELD**  
 MAGMA ANNUAL REPORT, 1972

## UTILITY ACCEPTANCE OF GEOTHERMAL ENERGY

WILL REQUIRE:

1. RELIABLE & ENVIRONMENTALLY ACCEPTABLE EQUIPMENT.
2. CONFIDENCE IN RESERVOIR CAPACITY.
3. PREDICTABLE GOVERNMENTAL APPROVAL.
4. ECONOMIC ADVANTAGE.
5. ENERGY SUPPLIER - FINANCIALLY & TECHNICALLY CAPABLE.



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GEOHERMAL SYSTEMS

- HOT WATER  
CERRO PRIETO \$264/kw \$.008/kwh
- HOT WATER WITH DRY STEAM RESERVOIR  
\* GEYSERS NO.15, \$205/kw \$.0135/kwh  
at 70%
- GEOPRESSURED  
MODEL STUDY \$920/kw \$.0205/kwh
- DRY HOT ROCK
- NORMAL GRADIENT

\*PLANT, TRANSMISSION-EX SUPPLY

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\*PLANT, TRANSMISSION-EX SUPPLY

## SODIUM/LITHIUM RATIO IN WATER APPLIED TO GEOTHERMOMETRY OF GEOTHERMAL RESERVOIRS

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*Laboratoire de Géochimie des Eaux, Groupe du L.A. 196 Université Paris 7, 75221 Paris Cédex 05, France*

**Abstract**—We propose here a new geothermometer for natural waters. Analyses from many explored geothermal fields allow us to define two empirical thermometric relationships.

One is for waters of low to moderate salinity ( $Cl^- < 0.3 \text{ M}$ )

$$\log Na/Li = 1000/T - 0.38, \quad (a)$$

and one for marine waters and brines ( $Cl^- > 0.3 \text{ M}$ )

$$\log Na/Li = 1195/T + 0.13. \quad (b)$$

These relationships, which at present are not well understood, result mainly from the increase of Li concentrations in waters with temperature.

Equation (a) proved to be adequate for spring waters from mostly known geologic origin; this is an important feature in geochemical surveys for geothermal prospecting.

Furthermore, when comparison between springs and drillhole chemistry of a given geothermal field is possible, the Na/Li geothermometer gives more reliable temperature estimates from the spring compositions than do classical geothermometers.

### INTRODUCTION

Natural hydrothermal systems are an important means of studying water – rock interactions. Determination of the equilibrium temperature existing at depth in a field has always been a major goal and in the past 15 years the evolution of geothermal power utilization has enhanced still further the interest in temperature estimation. Several workers have proposed relationships between the chemical composition of geothermal solutions and deep temperatures.

### CHEMICAL GEOTHERMOMETERS

Two thermometers are sustained by the evidence of chemical equilibria between deep solutions and mineral phases, respectively quartz (Fournier and Rowe, 1966), and alkali feldspars (White, 1965; Ellis, 1970). The quartz solubility relationship can lead to precise temperature determinations for waters tapped by drillholes (Mahon, 1966). However, it is difficult to use the silica geothermometer when working on natural springs, as in high temperature areas the silica content of geothermal fluid is so high that sinter deposition can occur even with large-flow boiling springs. The direct use of quartz solubility gives underestimated temperature values. In low temperature areas ( $t < 150^\circ\text{C}$ ) the knowledge of which solid phase controls dissolved silica concentration is critical (see for example Arnorsson, 1970, 1975 and Boulègue *et al.*, 1977). The quartz geothermometer seems then to be restricted in the temperature range  $150 - 230^\circ\text{C}$  (Truesdell and Fournier, 1976). In low temperature areas, with small discharge springs, dissolved silica can achieve re-equilibration with amorphous silica, the water becoming cool by conductive heat loss (Tonani, 1970; Fournier *et al.*, 1974). Numerous examples of this situation are to be found in the French Massif Central (Fouillac *et al.*, 1976a).

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Additional difficulties occur because of the mixing of rising hot solutions with cold superficial waters. In this case, application of the mixing models approach proposed by Fournier and Truesdell (1974) and Truesdell and Fournier (1976) is sometimes biased by surprisingly high silica contents of the colder water fraction (see for example Giggenbach, 1978; Fouillac *et al.*, 1976b).

Compared to the silica geothermometer, the sodium/potassium ratio is less affected by chemical re-equilibration occurring during the ascent of solutions; but, it may be slightly disturbed by mixing with cold dilute superficial waters. The deposition of aluminium-rich minerals, like kaolinite, has been invoked by Michard *et al.*, (1979) to explain the freezing of deep Na/K ratios. However, Na/K ratios can be modified by exchange reactions with clay minerals as shown by Weissberg and Wilson (1977), or by addition of potassium from sedimentary rocks in subsurface reservoirs (Michard *et al.*, 1976). The application of the Na/K geothermometer to superficial waters very often leads to high estimated temperatures, and this is obviously troublesome for geothermal surveys.

Fournier and Truesdell (1973) have proposed an improved Na/K/Ca empirical geothermometer. The true meaning of their formulae is not clear, but reflects an equilibrium between alkali feldspars, calcium-bearing silicate (or calcite) and deep solutions (Shikazono, 1976; Michard and Fouillac, 1976). Fournier and Truesdell's formulae are not applicable to cold concentrated solutions (cf. sea-water). Also, for CO<sub>2</sub>-rich springs, as pointed out by Paçes (1975) and Paçes and Cermak (1976), Fouillac and Michard (1977), the Na/K/Ca relationship is not reliable. An attempt to correct the Na/K/Ca geothermometer for CO<sub>2</sub>-rich waters (Paçes, 1975) was not entirely satisfactory.

In summary, chemical geothermometers provide good temperature estimates for high temperature tapped by drillholes but their use is more difficult when working on surface hydrothermal manifestations.

#### SODIUM AND LITHIUM IN WATERS

The occurrence of lithium as a common element of most hot waters is well known and was discussed by White (1957). A few years later, Ellis and Wilson (1960) in a careful chemical study of Wairakei (N.Z.) drillhole discharges pointed out that a low Na/Li ratio seemed to be related to the hottest zones of the field. This was also shown by Koga (1970) for Otake and Hatchobaru (Japan) geothermal wells.

A geochemical survey of French hot springs has been undertaken since 1975 in the Massif Central (Fouillac *et al.*, 1976a) and in the Eastern Pyrenees and Corsica (Boulègue *et al.*, 1977). The latter two regions include fields with estimated deep temperatures down to 60°C. This enlarges the temperature range of hydrothermal systems available to test geothermometers. When looking for possible thermometric relationships, sodium and lithium appeared to be promising elements. A wide search for lithium data in geothermal waters was thus undertaken. Four groups of water systems were used to build up a thermometric relation.

1. *Explored geothermal systems*: with measured deep temperatures.
2. *Natural hot springs*: temperature is obtained by Na/K and silica geothermometers. For French thermal waters only the systems showing concordant estimates are selected. For samples from other countries, we have taken into consideration the estimates given by authors in the literature.
3. *Analyses of surface waters*: here, measured temperatures are available. For very dilute samples, we have only considered flameless A.A.S. lithium determinations. Some studies showed lithium values only twice the announced detection limit and accordingly these samples were not considered further.

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4. *Water-rock interaction experiments of Ellis and Mahon (1967)*: for each rock type we have selected runs at lower temperatures in order to approach natural conditions as closely as possible.

A first progress report of this work has been published as a short note (Fouillac and Michard, 1979).

### SODIUM/LITHIUM GEOTHERMOMETER

Selected data covering the entire range of geothermal systems are presented. They include sodium chloride, sodium bicarbonate and acid sulphate hot water types. Surface waters of widely different geologic environments are also considered.

More for clarity and convenience than for theoretical reasons, we have computed for each sample the decimal logarithm of sodium, lithium and Na/Li ratio (all in molal units) and the inverse of absolute temperature. For geothermal systems, the results along with work references and locations are listed in Table 1. The chloride content of waters is also reported. As far as possible, individual temperature measurement and chemical compositions are considered for drillholes. This was not possible at Reykjanes (Iceland), where the lithium value pertains to a natural spring (Bjornsson *et al.*, 1972) and the temperature is only a rough mean value for the thermal field.

Table 1. Sodium and lithium in geothermal waters

Locality		1/T	-log Li	-log Na	log Na/Li	Cl <sup>-</sup> ppm	References
<b>Chile</b>							
<i>El Taio</i>							
Well T1	m	2.07	2.63	0.84	1.63	5840	Giggenbach (1978)
Well T2	m	2.00	2.39	0.82	1.56	6020	
Well T3	m	1.90	2.51	0.93	1.56	4490	
Well T4	m	2.03	2.54	0.82	1.71	5650	
Well T5	m	2.06	2.33	0.78	1.55	6690	
Well T6	m	2.20			1.53	2219	
Well T10	m	1.96			1.52	6544	Cusicanqui <i>et al.</i> (1976)
Well T7	m	1.87			1.51	6402	
Well T11	m	2.00			1.52	6348	
Well T12	m	1.92			1.51	6154	
El Taio Brine	m	2.16	3.14	-0.67	3.80	185,000	
<b>France</b>							
<i>Massif Central</i>							
La Bourboule	e	2.44	3.18	1.23	1.95	1757	Fouillac (unpub.)
Croizat	e	2.41	2.71	0.95	1.77	3106	
Félix	e	2.36	3.07	1.21	1.85	1590	
Gabriel	e	2.41	3.14	1.21	1.92	1505	
St. Nectaire	e	2.07	2.69	1.07	1.61	1710	
Royat	e	2.02	3.00	1.41	1.59	873	
Petitjean	e	2.11	2.89	1.19	1.70	1349	
St. Laurent	e	2.66	4.03	2.09	1.94	16.3	
Bagnols	e	2.40	3.67	2.10	1.57	23.7	
La Chaldette	e	2.73	4.3	2.03	2.26	15.6	
Vichy	e	2.45	3.10	1.09	2.00	326	Michard <i>et al.</i> (1976)
<i>Pyrénées</i>							
Les Aigues	e	2.74	4.88	2.54	2.34	11.2	Laboratoire de Géochimie des Eaux (1978a)
Amélie	e	2.61	4.56	2.36	2.20	22	
Az les Thermes	e	2.49	4.88	2.67	2.21	12	
Canavilles	e	2.60	4.88	2.55	2.33	7.1	
Carcantières	e	2.64	4.86	2.64	2.22	4.5	
Dorres	e	2.82	5.15	2.73	2.42	5.3	
Escouloubre	e	2.68	4.85	2.63	2.21	4.4	
Ponchaude	e	2.77	5.40	2.87	2.53	3.6	
La Preste	e	3.06	5.52	2.77	2.75	1.8	
Llo	e	2.72	4.88	2.50	2.38	5.0	
Naussa	e	2.81	5.00	2.50	2.50	14.2	
St. Thomas	e	2.77	4.92	2.57	2.34	7.8	
Thucs	e	2.58	4.92	2.55	2.37	7.1	
Usson	e	2.77	5.01	2.72	2.28	4.5	
Vernet	e	2.71	5.00	2.60	2.39	7.8	
<i>Corsica</i>							
Baracci	e	2.83	5.01	2.40	2.61	71	Laboratoire de Géochimie des Eaux (1978b)
Caldane	e	3.12	5.64	2.60	3.04	33	
Caldanella	e	2.48	4.51	2.27	2.24	49	
Caldanaccia	e	2.61	4.49	2.16	2.32	100	
Guagno	e	2.59	4.79	2.48	2.31	25.7	
Guitera	e	2.94	5.15	2.63	2.52	14.2	
Pietrapola	e	2.45	4.75	2.52	2.23	28	
Urbalacone	e	3.02	5.22	2.55	2.67	35	



Table 1. (continued)

Locality		1/T	-log Li	-log Na	log Na/Li	Cl <sup>-</sup> ppm	References
<i>West Indies</i>							
<i>Bouillante</i>							
Well BO2	m	1.94	3.20	0.63	2.58	13,350	Fouillac and Ourounian (1977)
Well BO3	m	1.94	3.20	0.61	2.59	12,530	
<i>Paris Basin</i>							
<i>Melun</i>							
Well PM2A	m	2.83	3.69	0.74	2.94	7170	Boulègue (1978)
Well PM2B	m	2.83	3.69	0.76	2.92	7171	
Well PM2C	m	2.83	3.69	0.74	2.94	7170	
<i>Chailly</i>							
Well CH1	m	2.89	3.74	0.87	2.87	4790	Boulègue (1978)
Well CH26	m	2.87	3.74	0.83	2.91	5540	
Well CH28	m	2.87	3.74	0.83	2.91	5570	
Well CH101	m	2.89	3.74	0.87	2.87	4790	
<i>Iceland</i>							
<i>Geysir area</i>							
A Geysir	m	1.89	4.53	2.04	2.49	129	Bjornsson <i>et al.</i> (1972)
Reykjanes	e	1.87	2.97	0.20	2.77	19,500	
<i>Hveragerdi</i>							
Well G3	m	1.90	4.36	2.03	2.32	260	Ellis (1970)
<i>India</i>							
<i>Puga</i>							
Well GW2	e	1.84	3.02	1.51	1.50	475	Shanker <i>et al.</i> (1976)
Well GW5	e	1.84	3.09	1.65	1.44	445	
Well GW7	e	1.84	3.09	1.60	1.49	464	
Well GW8	e	1.96	3.06	1.60	1.46	411	
Well GW10	e	1.96	3.02	1.60	1.42	448	
Well GW11	e	1.96	3.03	1.61	1.42	443	
<i>Indonesia</i>							
<i>Kawah Kamojang</i>							
Well 6	e	2.01	3.97	2.36	1.60	2.0	Kariokusumo <i>et al.</i> (1976)
<i>Italy</i>							
<i>Cesano</i>							
Well 1	m	1.91	1.25	-0.53	1.79	42,850	Calamai <i>et al.</i> (1976)
<i>Phlegraean Fields</i>							
Spring 5	m	2.26	3.36	0.40	2.90	14,620	Baldi <i>et al.</i> (1976)
<i>Japan</i>							
<i>Otake</i>							
Well 7	e	2.14	3.18	1.43	1.75	1219	Koga (1970)
Well 8	e	2.07	3.20	1.45	1.75	1243	
Well 9	e	2.05	3.13	1.39	1.74	1474	
Well 10	e	2.11	3.08	1.32	1.76	1753	
<i>Haichobaru</i>							
Well H1	e	1.84	2.79	1.21	1.58	2327	Hayashi and Yamasaki (1974)
Well H2	e	1.89	2.99	1.28	1.71	2300	
<i>Hakone</i>							
Well II	m	3.02	5.00	2.41	2.59	20	Oki and Hirano (1970)
Well III	m	2.74	3.45	1.18	2.27	2570	
Well IVa	m	2.95	4.40	1.71	2.70	617	
<i>Naruyo area</i>							
Tosenro	m	2.68	4.13	1.55	2.57	600	Noguchi and Miyazawa (1974)
Farmer's h.	m	2.85	4.49	1.65	2.84	125	
Higashitaya	m	2.68	4.07	1.60	2.46	630	
<i>Mexico</i>							
<i>Cerro Prieto</i>							
Well 5	m	1.63	2.56	0.56	1.96	10,420	Ellis (1970)
Well M31	m	1.71	1.95	-0.12	2.07	14,170	Mercado (1976)
<i>New Zealand</i>							
<i>Brooklands</i>							
Well 1	m	1.81	2.80	1.33	1.48	1700	Mahon and Finlayson (1975)
Well 2	m	1.78	2.77	1.33	1.44	1740	
Well 3	m	1.80	2.75	1.34	1.42	1800	
Well 4	m	1.83	2.76	1.33	1.43	1850	
Well 5	m	1.93	3.14	1.21	1.93	1140	
Well 6	m	2.40	3.75	1.72	2.04	28	
Well 7	m	1.81	2.66	1.25	1.42	1823	
Well 8	m	1.83	2.78	1.37	1.41	1858	
Well 9	m	1.76	2.73	1.39	1.34	1709	
Well 10	m	1.81	2.86	1.40	1.46	1245	
Well 11	m	1.82	2.75	1.35	1.40	1795	
Well 12	m	1.82	2.83	1.18	1.65	1546	
Well 13	m	1.82	2.81	1.37	1.44	1670	
Well 14	m	1.75	2.81	1.42	1.40	1480	
Well 15	m	1.75	2.78	1.33	1.44	1750	
Well 16	m	1.82	3.04	1.60	1.44	528	
Well 17	m	1.77	2.82	1.36	1.47	1780	
Well 18	m	1.78	2.79	1.32	1.47	1985	
Well 19	m	1.83	2.77	1.38	1.39	1720	
<i>Kawerau</i>							
Well 7A	m	1.85	3.11	1.49	1.62	1400	Ellis and Mahon (1964)
Well 8	m	1.85	3.10	1.49	1.61	1310	
Well 4	m	2.11	3.29	1.75	1.54	585	
Well 10	m	1.91	3.17	1.55	1.62	1098	
Well 12	m	1.84	3.09	1.56	1.52	1003	
Well 14	m	1.82	3.04	1.48	1.56	1136	Mahon (1962)

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Table 1. (continued)

Locality		1/T	-log Li	-log Na	log Na/Li	Cl ppm	References
Ngawha							
Well 1	m	1.98	2.82	1.43	1.40	1658	Ellis (1970)
Orakeikorako							
Well 2	m	1.88	3.34	1.62	1.72	546	Ellis (1966)
RotoKaua							
Well 1	m	2.02	2.63	1.18	1.65		Ellis (1970)
Waiatiapu							
Well 6	m	1.85	3.02	1.42	1.59	1450	
Wairakei							
Well 471	m	2.02	2.74	1.25	1.49	2140	Ellis and Mahon (1964)
Well 20	m	1.95	2.70	1.25	1.45	2215	
Well 44	m	1.89	2.69	1.24	1.44	2260	
Well 24	m	1.91	2.71	1.26	1.45	2230	Ellis (1970)
Well 48	c	1.88	2.72	1.28	1.43	2156	Koga (1970)
Well 5	c	2.26	3.77	2.00	1.76	546	Shanker et al. (1976)
U.S.A.							
Arizona							
Casagrande							
Expt. Well	m	2.68	3.68	1.49	2.19	1250	Dellechiaie (1976)
California							
Salton Sea							
Well 2D	m	1.63	1.51	-0.36	1.88	150,000	Helgeson (1967)
Well 1 State	m	1.70	1.57	-0.31	1.89	127,000	
Long Valley							
3S 28E13ES3	c	2.36	3.40	1.74	1.63	200	Mariner and Wiley (1976)
3S 28E32E9	c	2.36	3.40	1.77	1.61	280	
3S 28E21PS1	c	2.33	3.68	1.87	1.79	150	
3S 29E28HS1	c	2.11	3.62	1.76	1.85	170	
3S 29E34KS1	c	2.14	3.64	1.85	1.92	150	
3S 2E23AS4	c	2.23	3.48	1.76	1.69	225	
Kettleman North Dome							
Tb (1)	m	2.68	3.68	0.24	3.44	19,500	Merino (1975b)
Tb II(8)	m	2.68	3.57	0.31	3.24	18,200	
Tb III(8)	m	2.68	3.67	0.45	3.22	16,000	
Tb IV(1)	m	2.68	3.73	0.47	3.26	12,600	
Tb V(1)	m	2.68	3.79	0.52	3.28	16,600	
UM (5)	m	2.68	3.60	1.01	2.59	3380	
LM (4)	m	2.68	3.38	0.80	2.57	4720	
Moniano							
Alhambra	c	2.58	4.26	2.03	2.23	8.5	Robertson et al. (1976)
Boulder	c	2.43	4.42	2.27	2.15	24	
Broadwater	c	2.45	4.09	2.03	2.06	27.5	
Gregson	c	2.50	4.00	2.10	1.89	10	
Norris	c	2.49	4.85	2.02	2.79	27	
Silver star	c	2.42	4.26	2.12	2.14	15	
Müsstüpf							
Homer Currie	m	2.48	2.42	0.45	-2.82	165,000	Carpenter et al. (1974)
U.S.S.R.							
Cheleken Brine							
Well P152	m	2.83	2.85	-0.46	3.31	143,500	Lebedev (1973)
Well U1	m	2.83	2.95	-0.49	3.44	158,000	
Red Sea							
Discovery							
Station 717 1-2	m	3.38	4.43	0.24	4.19	155,000	
Station 728 1	m	3.14	3.83	-0.08	3.91	155,000	
Station 728 3-13	m	3.29	3.95	-0.05	4.00	155,000	
Station 729 20	m	3.39	4.5	0.33	4.17	42,000	
Station 729 23	m	3.30	4.02	-0.08	4.10	42,000	
Atlantis							
Station 726 9	m	3.37	4.42	0.24	4.18	80,000	Brooks et al. (1969)
Station 727 9	m	3.38	4.48	0.26	4.22	80,000	
Station 727 23	m	3.03	3.21	-0.69	3.90	80,000	
Station 726 23	m	3.03	3.17	-0.68	3.85	80,000	
Station 722 19	m	3.32	4.27	0.18	4.09	80,000	
Station 722 2(10-5)	m	3.38	4.45	0.23	4.22	80,000	
Station 722 2.23	m	3.15	3.65	-0.33	3.98	80,000	
Station 715 10	m	3.38	4.52	0.15	4.37	80,000	
Station 715 13	m	3.29	3.58	-0.36	3.94	80,000	
Station 715 23	m	3.03	3.16	-0.71	3.87	80,000	
Station 718 14	m	3.39	4.49	0.24	4.25	80,000	
Station 718 1	m	3.15	3.58	-0.34	3.92	80,000	

c = Estimated deep temperature.  
m = Measured temperature.

Data for surface waters are given in Table 2. Values derived from the experimental work of Ellis and Mahon (1967) are in Table 3.

From Tables 1-3,  $\log m_{Na}/m_{Li}$  and  $\log m/Li$  are plotted vs  $1/T$  (Figs. 1 and 2). The Na/Li plot exhibits two linear relationships. We can see that the first line (curve a) corresponds to

Table 2. Lithium concentrations and sodium/lithium ratios in surface waters of various origins.

Description of samples	Number of sample	$1/T \times 10^3$	Average	Log Li Range	Average	Log Na/Li Range	References
<i>Waters from single rock type</i>							
Sandstones Lauraguais S.W. France	19	3.50	-6.23	-6.9 -5.8	3.18	2.52 3.48	Boulégué, J., unpublished values
Limestones S. Alps France	13	3.50	-6.33	-7 -6	3.13	2.59 3.58	Grimaud, D., et al., unpublished values
Granite Margrède Massif Central France	15	3.60	-6.85	-7 -6.7	3.0	2.99 3.02	Beaucuire, fundi 1979.
Volcanic Rocks Guadeloupe West Indies	9	3.40	-6.17	-7 -5.7	3.31	2.77 3.86	Fouillac and Ouzoulian 1977.
Granite Sangre de Cristo Range New Mexico U.S.A.	12	3.55	-6.79	-7.36 -6.36	3.08	2.3 3.78	Miller (1961)
Quartzite Sangre de Cristo Range New Mexico U.S.A.	3	3.58	-7.20	-7.23 -7.13	2.63	2.38 2.77	Miller (1961)
Sandstones Sangre de Cristo Range New Mexico U.S.A.	6	3.50	-6.78	-6.79 -6.53	2.55	2.29 2.62	Miller (1961)
<i>Waters from mixed origin</i>							
Hudson River U.S.A.	1	3.55	-6.29	2.82	2.82		Livingstone (1963)
Susquehanna River U.S.A.	1	3.55	-6.49		2.83		
Japanese Rivers	14	3.50	-5.96	-6.63 -5.38	3.01	3.47 2.34	
Major North American Water		3.55			2.66		
Sea Water	1	3.62	-5.48		4.29		

Table 3. Sodium/lithium behaviour in experimental water-rock interactions. After Ellis and Mahon (1967)

Rock type	$1/T \times 10^3$	Log Li	Log Na	Log Na/Li	Cl <sup>-</sup> (ppm)
Pumice	1.48	-3.58	-2.22	1.35	157
Obsidian	1.91	-4.18	-2.40	1.59	9
Ignimbrite	1.48	-3.79	-2.49	1.29	32
Rhyolite	1.60	-3.76	-2.49	1.27	110
Dacite	1.91	-4.02	-2.55	1.47	40
Andesite	1.91	-4.14	-2.55	1.59	52
Basalt	1.91	-4.36	-2.18	2.17	250
Greywackes	1.91	-4.14	-2.52	1.62	3

waters where chlorinity is less than 0.2 M) (about 7000 ppm); the second line corresponds to high chlorinity (> 10,000 ppm or 0.3 M) waters.

Thus, the relationships between Na/Li and temperature can be summarized by

$$(i) \log \text{Na/Li} = 1000/T - 0.38 \text{ for } \text{Cl}^- < 0.2 \text{ M,}$$

the mean square correlation coefficient is  $r = 0.965$ . This line will be called the general line in the following sections.

$$(ii) \log \text{Na/Li} = 1195/T + 0.19 \text{ for } \text{Cl}^- > 0.3 \text{ M } (r = 0.982).$$

The correlation between  $\log m_{\text{Li}}$  and  $1/T$  (Fig. 2) is clear but only fair

$$\log m_{\text{Li}} = -1503/T - 0.02 \text{ } (r = 0.75).$$

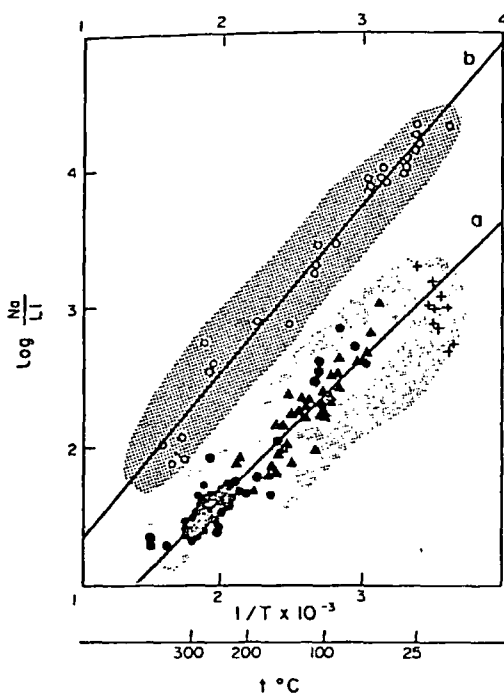


Fig. 1.

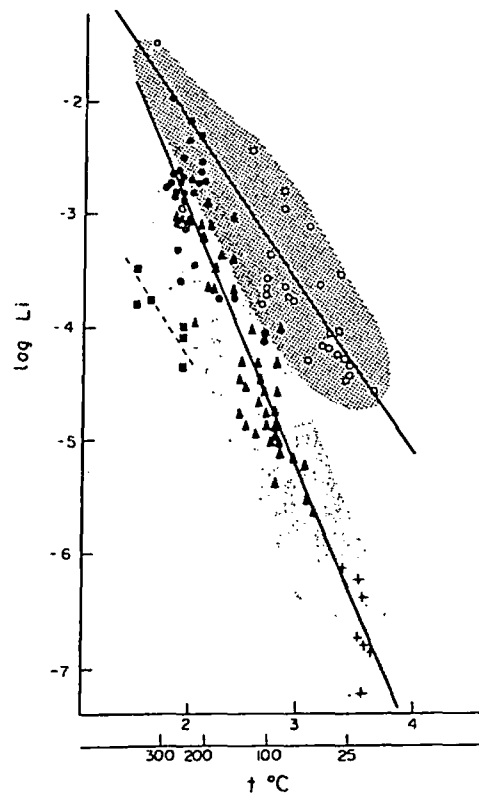


Fig. 2.

Fig. 1. Log Na/Li in waters vs the inverse of absolute temperature. Key: (a) general line, closed symbols; (b) brine line, open symbols. O, ● Measured temperatures. ▲ Estimated temperatures. + 'Surface waters. ■ Experimental water - rock interactions.

Fig. 2. Log Li in waters vs the inverse of absolute temperature. Same symbols as in Fig. 1. Darker shading is for saline waters, lighter shading for low salinity waters.

If we separate the data into the two chlorinity groups, we obtain two well-defined linear relationships:

$$\log m_{\text{Li}} = - 2258/T + 1.44 \text{ for } \text{Cl}^- < 0.2 \text{ M } (r = 0.936),$$

$$\log m_{\text{Li}} = - 1436/T + 0.61 \text{ for } \text{Cl}^- > 0.3 \text{ M } (r = 0.91).$$

The selection of data needs some comments:

For Red Sea thermal brines, we have considered temperatures and chemical analyses quoted in Brooks *et al.* (1969). More recently, several workers (Brewer *et al.*, 1971; Ross, 1972, Schoell, 1976) have reported higher brine temperatures, but detailed chemical analyses are not yet available. Neither do we consider the high temperature estimates for the input brine derived from geophysical models (Schoell, 1976). It is likely, after Shanks and Bischoff (1977) that the chemical composition of brine must reflect equilibrium at a measured temperature, due to re-equilibration during the time of water residence in low thermal layers.

All the chemical analyses of Central Mississippi brines (Carpenter *et al.*, 1974) are not considered in this compilation as their temperatures assume that all drillholes had the same temperature profile as Homer Curie No. 4 (original sample Ref. 57).

Waters from Yellowstone Park are not used in examining the thermometric relations, because of uncertainties in the aquifer temperature. The problem of this area is dealt with later.

## TENTATIVE INTERPRETATION

The different qualitative interpretation for the temperature dependence of the Na/Li ratio (and Li molality) suggested in the following pages indicate the need for further work to derive thermometric relationships.

(1) To help this discussion, the  $\log m_{\text{Na}}$  vs  $1/T$  plot is given in Fig. 3. The sodium behaviour in hydrothermal systems is generally influenced by the deposition of sodium-rich minerals (albite, sodium-rich plagioclase or analcime). Albite is a very common secondary mineral in geothermal systems (Steiner, 1953; Sigvaldason, 1962; Muffler and White, 1969; Browne and Ellis, 1970; Hayashi and Yamasaki, 1974; Oki *et al.*, 1974; Merino, 1975a). In Iceland, analcime has also been found in many drillholes in geothermal fields (Kristmannsdottir and Tomasson, 1974; Kristmannsdottir, 1976; Tomasson and Kristmannsdottir, 1972). For dilute waters, we observe an increase of Na with  $T$ , whereas the correlation between Cl and  $T$  is poor. This can be explained at high temperature, by the increase of albite solubility; and chemical composition, from one field to another, is similar enough to preserve the influence of temperature on sodium concentration. At low temperature, equilibrium is not achieved and the sodium concentration is still less than the equilibrium value.

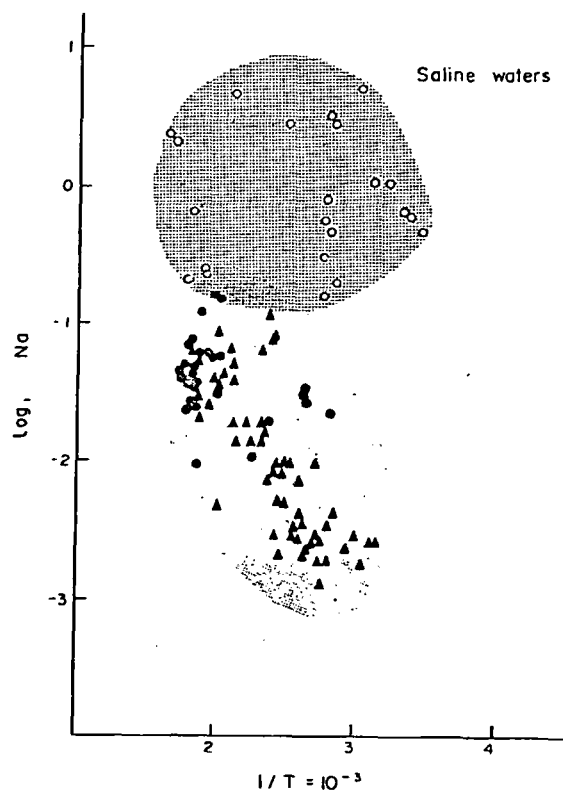


Fig. 3. Log Na in waters vs the inverse of absolute temperature. Same symbols as in Fig. 1.

The case of marine waters is different: Na is generally at least three orders of magnitude greater than silica; thus, any silicate deposition cannot rule the sodium concentration.

(2) The dependence of Li on temperature is stronger than the Na dependence: about 4 orders of magnitude between 0 and 300°C for Li instead of about 2 orders for Na.

It is unlikely that the Li temperature relationship is related to a chemical equilibrium between water and a lithium mineral. Lithium minerals seem to be very rare in hydrothermal environments. Bargar *et al.* (1973) describe a hydrothermal lepidolite at Yellowstone. This mineral is only present in the low temperature zone and it is unlikely that it controls the Li concentration at depth.

The diadochic substitution of Na by Li is difficult, with the large difference between the ionic radii of  $\text{Li}^+$  (0.78 Å) and  $\text{Na}^+$  (0.98 Å). Studies by Volfinger (1976) on the partition coefficients of the alkali ions between feldspars and aqueous solutions at high temperature ( $t > 400^\circ\text{C}$ ) did not give reliable results for Li. Thus we consider, as did Mahon (1976) that lithium behaves in hot waters as a "soluble" element, i.e. it is not co-precipitated with any secondary mineral, except perhaps near-surface clays.

The two lines of Fig. 2 should mainly reflect the increase of rock dissolution with increasing temperature. This phenomenon can be enhanced by the uptake of lithium in some weathering products (clays) at low temperature. It seems reasonable that lithium concentrations in solutions related to a given rock and with the same water-rock ratio would follow an exponential function of the temperature. It is more surprising that the influence of water-rock ratio or of the rock type seems to be unimportant. Actually, most igneous rocks (except ultramafic rocks) and sedimentary rocks (except marine shales and evaporites) have a mean lithium concentration in a restricted range (10–70 ppm, Heier and Billings, 1969). We have no precise knowledge of both mineral dissolution rates and water-rock reaction time in geothermal systems. It is not impossible that each of these two parameters have an overall variation less than an order of magnitude.

Marine sediments and especially evaporites, which have rather high solubilities and high dissolution rates, should define another group of waters. For some fields (e.g. Red Sea brines, Reykjanes) the marine origin is well acknowledged. In some other cases (e.g. Salton Sea), the most likely mechanism of formation is thought to be the leaching of marine sediments including halides (see Helgeson, 1968, pp 161–163 for discussion). The tendency for a water to follow either the general line or the brine line is not only determined by the geological environment of the aquifer. The problem is to know whether sodium and lithium of marine origin are negligible or not compared to other sodium and lithium inputs. Kettelman dome interstitial waters provide a good demonstration of this feature. For this field, sodium and lithium concentrations are not correlated. Highly saline solutions from Tremblor I to IV formations are on the brine line, whereas the dilute solutions from Mac Adam formation are very near the general line (Fig. 4). The chlorinity boundary has no theoretical justification and derives only from the observed division in two groups in the Na/Li plot.

Results of experimental work by Ellis and Mahon (1967) show, in a small temperature range, an increase of Li with temperature; lithium concentrations are smaller than for geothermal waters; this can be related to differences in the water-rock ratio and in reactions times.

(3) The two log Na/Li relationships result from the different behaviour of Na and Li in function of temperature. Furthermore, influence of some kinetic parameters is partially cancelled and the correlation coefficients are better for the (Na/Li,  $T$ ) relationships than for the (Li,  $T$ ) ones.

#### DISCUSSION OF DEPARTURE FROM EQUATIONS

There are two kinds of departure from the equations:

secondary events, namely dilution by cold waters or concentration by steam loss, can shift the representative points away from the lines; this will be marked only in the log  $m_{\text{Li}}$ ,  $1/T$  plot and will not be discussed here;

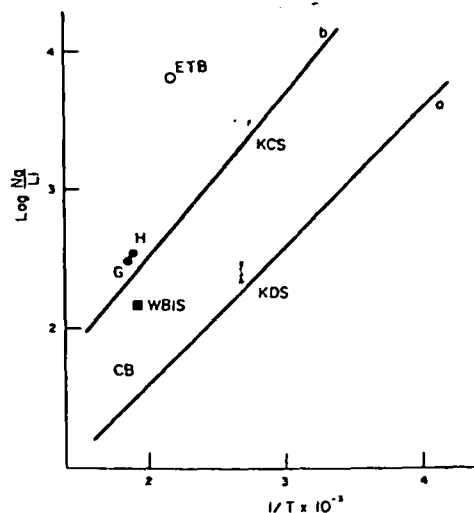


Fig. 4. Behavior of some particular hot waters. Key: KCS—Kettelman interstitial solutions; concentrated samples. KDS—Kettelman interstitial solutions, diluted samples. CB—Cesano Brine. ETB—El Tatio Brine. WBIS—Water Basalt in interaction resulting solution. HG—Hveragerdi and Geysir respectively.

other reasons originate in the deep aquifer; they are more critical and will be discussed for the Na/Li thermometer (see Fig. 4).

Three dilute waters fall far outside the general line: two of them are Icelandic waters (Hveragerdi hole G3 and a geyser); in this case the rock-type can have an effect; the third one is the run with basalt as starting material in Ellis and Mahon as experiments. As a matter of fact, the general line describes the behaviour of waters for which marine originated constituents are negligible compared to total solutes. In Iceland, the rainwater contribution to the chemistry of dilute hot waters cannot be neglected as shown by Arnason and Tomasson (1970). This input of solutes induces a shift from the general line towards the brine line. A slight shift of this kind has been observed in Corsica (Ouzounian *et al.*, 1979). In Ellis and Mahon's experiments, which are not equilibrium experiments, no development of a secondary sodium phase has been observed in the run with basalt: the increase of Na is not limited and the Na/Li ratio remains high.

Two hot brines do not follow the brine trend: Cesano and El Tatio brines. At Cesano, Calamai *et al.* (1976) have noticed that quite large amounts of sodium chloride precipitated in the well, which produces a mixture of water and solid NaCl and Na<sub>2</sub>SO<sub>4</sub>. Furthermore, thermal equilibrium in the well was not achieved when recording stopped and the temperature value was given as a lower estimate. We could presume that the analysed fluid did not represent the deep aquifer chemistry. We cannot conclude whether Cesano brine is apart from the brine line or not. The problem of El Tatio is more critical. It is possible to take this solution to be from a different origin. Note that Mahon and MacDowell (1977) after Cusicanqui *et al.* (1976) do not refuse the idea that acid, volcanic, Cl-rich emanation could have produced El Tatio brine by reaction with ignimbrite. As Giggenbach (1978) has not reported isotopic data for El Tatio brine, the problem is still unsolved.

## USE OF THE Na/Li GEOTHERMOMETER FOR GEOTHERMAL PROSPECTING

Both log Li and log Na/Li are useful for thermometric prospecting. As it is sensitive to mixing with cold water and to concentration by steam loss, the log Li thermometer is more difficult to use and needs mixing models. The Na/Li ratio, hardly modified during ascent of solution, seems to provide good estimates of deep temperatures. Some examples are given below.

*Vichy Basin (Massif Central, France)*

In this area, a great number (> 200) of mineral CO<sub>2</sub>-rich springs are flowing. A common origin for all waters is acknowledged (Armand, 1933). However, important changes in individual spring chemistry are caused by reactions with rocks in shallow aquifers (Michard *et al.*, 1976). Values listed in Table 4 show the remarkable constancy of Li concentration and the Na/Li ratio, compared with other temperature indexes. The temperature obtained with the Na/Li geothermometer (145°C) is in good agreement with the temperature previously determined (135°C) by Michard *et al.* (1976) after a detailed geochemical study of the area. The Li concentration yields too high a value (200°C).

Table 4. Evolution of thermometric indexes among selected springs from Vichy thermal area (France). After Michard *et al.* (1976)

Ref.	Spring	T°C	Na/K	Na/Ca	Na/Li	Li 10 <sup>-1</sup> (m/l)	SiO <sub>2</sub> (ppm)
F 11	Féerique	11.5	21.1	33.5	98.2	0.69	21.0
F 12	Jade	12	25.9	35.9	100.7	0.79	25.2
F 32	Mesdames	13.5	23.5	18.2	95.2	0.71	22.8
F 3	Saint Ange	17	28.2	30.5	104.2	0.76	17.4
F 28	Généreuse	24	32.9	80.2	101.5	0.79	95.0
F 26	Hopital	34	31.1	20.8	102.8	0.79	54.6
F 25	Grande Grille	40.2	33.3	31.7	101.25	0.80	70.2
F 33	Boussange	41	23.5	24.9	97.8	0.82	84.0
F 34	Dome	66	29.7	64.0	101.8	0.74	83.0

*New Zealand hydrothermal areas*

Table 5, after Mahon (1970) shows comparison between springs and drillhole chemistry for most thermal fields of New Zealand. We can see that in all systems the Na/Li geothermometer would have given good predictions for the deep temperature. Generally, Li concentration should have given a rough approximation of temperatures. However, in some places (Kawerau,

Table 5. Comparison between Na-Li geothermometer and classical geothermometers, Taupo volcanic zone — New Zealand.

Thermal areas	Molal ratios				Temperature				Obs
	Li (10 <sup>-1</sup> m/l)	Na/K	Na/Ca	Na/Li	T <sub>Na/K</sub>	T <sub>N-K-Ca (1/3)</sub>	T <sub>Na/Li</sub>	T <sub>Na/Li</sub>	
Wairakei	Hole 44	2.06	10.0	135	27.9	261	265	274	270
	Spring 97	0.98	16.6	26	29.3	199	205	268	
	Spring 190	1.45	26	83	28.5	156	193	272	
	Hole 6	0.96	9.4	150	39	269	266	234	
Waiotapu	Spring 64	1.30	13.0	60	40.6	227	236	229	260
	Spring 20	0.58	35	87	34	131	171	250	
	Hole 7A	0.77	10.3	500	41.8	257	238	226	
Kawerau	Spring 2	0.39	11.5	44	36.7	242	226	241	260
	Spring 4	0.48	12.8	53	36.2	229	223	242	
	Hole 3	0.45	10.7	440	24.5	252	254	292	
Orakeikorako	Spring 98	0.58	11.3	190	21	244	242	314	250
	Hole 1	2.0	9.7	16.0	27.7	265	269	275	
Taupo	Spring	0.67	14.7	64	26.4	217	217	282	267*
	Hole 10	1.39	10.1	737	28.2	259	281	273	
Broadlands	Spring 1	1.07	17.8	375	34	192	236	250	270
	Hole 1	1.55	19.6	53	25.2	182	205	288	
Ngawha	Jubilee								220
	Spring	1.15	22.0	185	31	171	240	261	

\*Mean value estimated between Na-K and Na-K-Ca results on hole 1.



Orakeikorako, Taupo, Broadlands) underestimates should have been caused by mixing with cold waters. Na/Ca is very different in springs and in drillholes. Na/K values in springs provide good estimates in some places (Orakeikorako, Kawerau) but not in others (Wairakei, Broadlands). Furthermore, Na/K ratios are different among springs of a given area. This can be seen in more detail in the spring chemistry of Broadlands area (Table 6, after Mahon and Finlayson, 1975). Here the Li thermometer gives too low temperatures. This is related to mixing with cold waters and the more concentrated spring gives the best value. Mixing or steam loss can therefore be pointed out by comparison of the temperatures given by the Li and Na/Li geothermometers.

Table 6. Temperature estimates from spring chemistry in Broadlands area. After Mahon and Finlayson (1975). Maximum temperature measured:  $\sim 270^{\circ}\text{C}$

Spring number	$T_{\text{Na-K}}$	$T_{\text{Na-K-Ca}}$ (1/3)	$T_{\text{Na-Li}}$	$T_{\text{SiO}_2}^*$	$T_{\text{Li}}$
1	189	223	247	219	239
3	192	197	269	204	216
4	164	182	243	203	205
5	165	185	223	183	191
6	136	178	240	196	205
7	117	167	237	191	209
A	163	177	248	185	205
B	170	188	237	189	201

\*Direct application of quartz geothermometer.

#### Yellowstone Park (U.S.A.)

The situation is more complex in this area. As far as we know, there are no definite physical temperature measurements in the deep aquifer. Only shallow drillholes (max. depth: 135 m) have been used for physical records, and in some cases the wells have not reached thermal equilibrium (White *et al.*, 1975). Besides this, numerous careful analyses of natural springs and geysers are available (Rowe *et al.*, 1973). Several geochemical studies have provided a good knowledge of possible deep temperatures in the area: Fournier *et al.* (1976), Truesdell and Fournier (1976).

From these studies the following situation can be summarized:

- (i) the existence of shallow aquifers, different from each other in temperature and chemical composition, is certain;
- (ii) a unique parent water can be expected at great depths; its temperature must be very close to  $340^{\circ}\text{C}$ ;
- (iii) individual basins in the area (Upper, Lower, Norris Basins, Mammoth area) could be distinguished as aquifers feeding springs and geysers;
- (iv) enthalpy chloride models developed in the two previously cited papers show that Norris Basin waters are quite directly related to the inferred parent water. Norris Basin is the hottest zone in Yellowstone Park and the chemistry of waters from this basin is rather homogeneous;
- (v) Upper and Lower Basins are fed by several water types. These aquifers could result from mixing of the parent water with shallower water tables. Chemical re-equilibrations can occur after mixing. Classical thermometers yield temperatures lower than in Norris Basin;
- (vi) springs of Mammoth area can be derived from Norris aquifer by mixing with dilute waters and reactions between solution and carbonate host-rock play an important role.

Using chemical analyses listed in Rowe *et al.* (1973), we compute the Li and Na/Li temperatures. Acid sulfate springs are not considered. The Li thermometer always gives underestimates of deep temperatures. This is not surprising considering the numerous mixings.

A histogram of the results given by the Na/Li geothermometer is shown on Fig. 5. This graph reinforces the theory that:

- Norris Basin waters are related to a common aquifer, the temperature of which is  $300^{\circ}\text{C}$ ;

- the Lower and Upper Basins comprise several type of waters with a quite large temperature range. Note that the Na/Li ratios seem to account for chemical re-equilibrations;
- the hot temperature obtained for Mammoth area is consistent with the assumption of a relation between Norris and Mammoth waters. In this case, the chemical changes undergone by Mammoth waters (carbonate rock dissolution) have very little effect on initial Na/Li ratios.

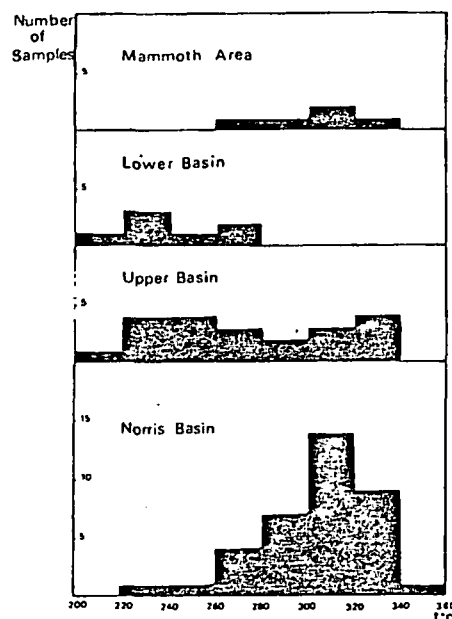


Fig. 5. Histogram of frequencies for Na - Li computed temperature of Yellowstone Park thermal manifestations.

Let us finally note that the Na/Li derived temperatures are in good agreement with those determined by Fournier *et al.* (1976) and Truesdell and Fournier (1976) using a complex model.

### CONCLUSIONS

The study of lithium concentrations and sodium lithium ratios in waters has suggested a new geothermometer. The relationships between temperature and Na/Li ratios for most of the explored geothermal fields are correctly described by two linear functions. Chloride contents of the waters provide a very simple way to choose the appropriate equation.

Obviously the Na/Li geothermometer should not be used alone, but comparison with other geothermometers and also lithium concentrations will be very useful for geochemical surveys. An interesting point is the remarkable constancy of the Na/Li ratio from aquifer to surface manifestations.

The theoretical basis for describing the Na/Li ratios by two linear relationships of the reciprocal of the temperature are not yet understood. Careful geochemical studies of well known geothermal areas and experimental work are still necessary for a better understanding of sodium and lithium behaviour under hydrothermal environments.

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THE SEARCH FOR MAGMATIC RESERVOIRS

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INTRODUCTION

The origin of magmas is still an open problem. Present trends of thought suggest that magma can be derived from the upper mantle, where it fills small pockets. When extruded from the mantle, this magma will rise to shallow depths, owing to the pressure of the overlying solid crust. An important question is whether volcanic activity is fed by vents discharging directly from the upper mantle, or from shallow reservoirs, where the magma stays for some time.

At present, it is assumed that most volcanoes have a relatively shallow magma chamber (cf. Macdonald, 1961). These chambers are, however, inaccessible to direct investigation. A convenient tool for research of this type is the usual seismic prospecting; unfortunately any magma layer will behave as a wave guide and, in this case, prospecting is unable to provide useful results. We must therefore rely upon other indirect methods which will be presently reviewed. On the whole, there is a considerable amount of evidence, but its reliability is frequently questionable.

PLUTONS, XENOLITHS AND DIFFERENTIATION

Intrusive bodies of plutonic rocks, embedded in the upper levels of the crust, are present in many areas. Some are definitely associated with volcanic rocks (Ustiyev, 1963) and may represent solidified magma chambers which fed some past volcanic activity. Very convincing evidence has been found in Scotland (see Richey, 1961), where the roots of the volcanoes were eroded by Quaternary glaciations. A detailed interpretation of the field surveys is rather difficult, but the data strongly suggest that magma chambers resulted from the sinking of conical blocks (subterranean cauldron subsidence), as shown in Fig.1. Magma seems to rise from the upper mantle through a ring dyke, and only after staying in the chamber it rises to the Earth's surface.

The form of the chamber varies widely, depending considerably on the structure of the surrounding rocks (Daly, 1933, Ch. 4); within sedimentary layers we can find laccoliths or phacoliths, whereas in an igneous

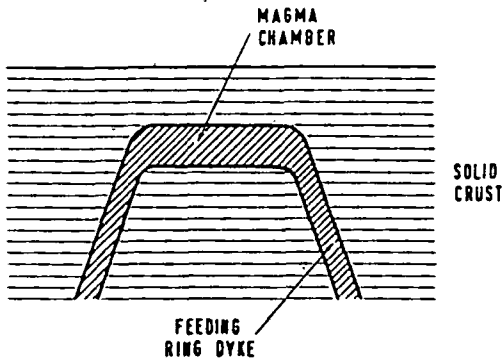


Fig.1. Scottish model of magma chamber (formed by subterranean cauldron subsidence).

environment more irregular bodies are expected. Ring structures are fairly common on continental areas; but they are also found on oceanic (or sub-oceanic) islands (Assunçao et al., 1968; Fúster et al., 1968, fig.48). Elongated structures are certainly frequent and many bodies described as sills (Daly, 1933, p.77) may probably also be considered as old magma chambers.

Gravitative differentiation is a usual feature of these intrusive bodies; they form layered intrusions, which at different levels can have compositions analogous to various volcanic lavas, and sometimes, in addition, exhibit at the bottom ultramafic cumulates formed mostly of olivine crystals (Jackson, 1967). This geological evidence suggests that actual active volcanoes can have shallow magma chambers which will eventually solidify into similar plutons. But the possibility of some volcanoes having no shallow magma chamber cannot be excluded.

The best-known case of xenoliths, giving information on a magma chamber, comes from the pyroclastic layers of Vesuvius (Rittmann, 1936, p.159). An explosive eruption, in the 12th century B.C., produced pumice layers with xenoliths of sediments down to the Triassic. The stratigraphy of the area is fairly well known and was lately confirmed by seismic studies (Imbò, 1950); the Triassic layers, which seem to form the roof of the magma chamber, lie at a depth of about 5 km. The Triassic xenoliths experienced considerable contact metamorphism, as would be expected.

Another source of indirect evidence comes from differentiated lavas. In fact, it appears that magma in the upper mantle is fairly uniform, as suggested by the similarity of the main (basic) volcanic rocks in widely distant areas of the Earth. Differentiation can, therefore, be regarded as a local phenomenon occurring in a separate chamber; the hypothesis of these shallow reservoirs has very often been invoked to account for differentiation (see, e.g., Maleev, 1964, p.218).

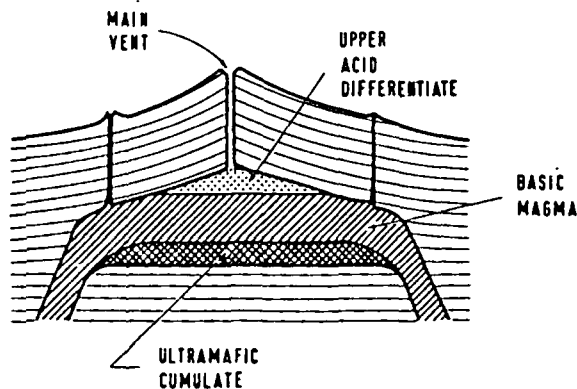


Fig.2. Idealized section of differentiated magma chamber.

Friedlaender (1929) drew attention to the fact that in many Azorean volcanoes the central vent produced acid lavas, whereas most peripheral cones are basaltic. This is what would be expected if the feeding chamber is vaulted and magma is layered by gravitative differentiation (Fig.2). During the 1563 eruption of the Agua-dePau Volcano (San Miguel, Azores), the activity started at the main vent with a Plinian explosion of trachytic pumice, but four days later basaltic lava flows came from a lower adventive vent (see Zbyszewski, 1963). Similar cases are known in a few other volcanoes.

#### SEISMOLOGICAL INVESTIGATIONS

As the usual seismic reflection or refraction methods are unsuitable for detecting magma chambers, other seismic methods have been tried for the purpose. Gorshkov (1958) found that seismic shear waves were not propagated at a depth of 50–70 km under some Kamchatka volcanoes. This was interpreted as being due to the presence of a magma layer at that depth (which corresponds to a somewhat high level of the upper mantle).

Fractional melting of a peridotitic upper mantle is indeed considered as the most probable source of volcanic magmas (Wager, 1958; Coats, 1962). Temperatures below a depth of about 50 km, derived from Gutenberg's (1959) seismic velocities, lie between the probable melting points of basalt and of forsteritic olivine (Fig.3).

In addition, the rigidity of the upper mantle (as derived from the velocity of shear waves) is lower than what would be expected in a completely solid peridotitic material (Fig.4); this can give a measure of the assumed molten (basaltic) fraction. In fact, Oldroyd (1956) has shown



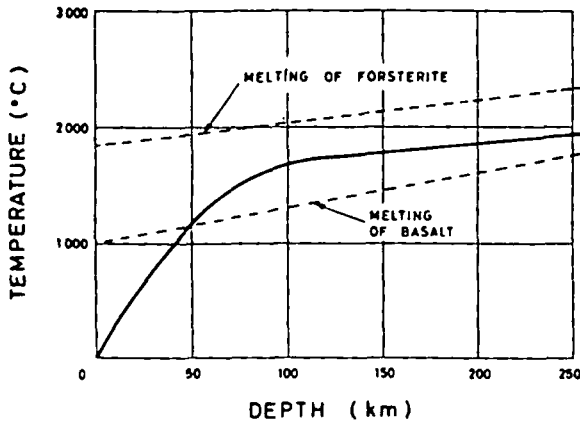


Fig.3. Probable temperatures of upper mantle (and crust) derived from Gutenberg's seismic velocities (according to Machado, 1968).

that the rigidity of a solid with small liquid inclusions can be expressed by:

$$\mu = \mu_0 \left[ 1 - \frac{15(1-\nu)}{7-5\nu} n \right] \quad (1)$$

where  $\mu_0$  is the rigidity of the solid (without inclusions),  $\nu$  its Poisson ratio, and  $n$  the volume fraction of the inclusions.

From Fig.4 we have, for a depth of 300 km,  $\mu_0 = 0.85$  Mb and  $\mu = 0.77$  Mb approximately. Then, using eq.1 with  $\nu = 0.27$ , we can estimate

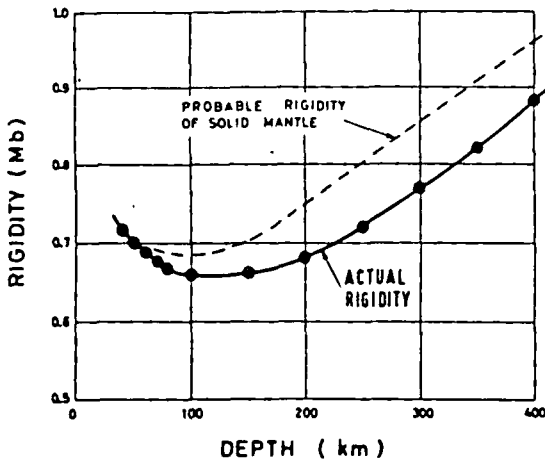


Fig.4. Rigidity of upper mantle derived from Gutenberg's seismic velocities, compared with rigidity of solid material (computed from bulk modulus with  $\nu = 0.27$ ; according to Machado, 1968).

$n = 5\%$ . On the other hand, the abundance of radioactive matter in the oceanic upper mantle (heat production:  $1.3 \cdot 10^{-13}$  cal/cm<sup>3</sup> sec; Machado, 1968) compares well with the abundance in basaltic rocks. This suggests that the material could be mostly eclogite (or some kind of metamorphosed gabbroid or basaltic material) down to some 50 km; at lower levels the temperature is probably above the melting point of this rock which would therefore melt into a basaltic magma. Ringwood (1969) assumes for the oceanic upper mantle a "pyrolitic" composition, which would have a much lower radioactive heat production.

According to these hypotheses, either by the exudation of the molten fraction available (in oceanic areas) below about 50 km, or by the remelting of the assumed eclogite layer at that same depth, a basaltic magma can be produced and would accumulate in situ. In some cases, especially in rift eruptions, this magmatic layer can directly feed a volcanic eruption (see Gorshkov, 1967, p.271), as shown in Fig.5. In most cases, however, it appears that mantle magma will rise first to some shallow levels.

Shteynberg (1965), by studying volcanic tremor, obtained ~~in~~ evidence of magmatic reservoirs at both levels. He thinks that the tremor is produced by a vertical vibration of the magmatic column, which fills the volcanic vent. The law of this vibration can be deduced very easily.

Let  $u$  be the displacement at time  $t$  of a magma particle in the vertical  $z$  direction. Neglecting body forces, the equation of motion (assumed as independent of the other space coordinates) is:

$$\frac{\partial^2 u}{\partial t^2} = -\frac{1}{\rho} \cdot \frac{\partial p}{\partial z} \quad (2)$$

$p$  being the pressure and  $\rho$  the density (see Lamb, 1945, p.479). Noting that, for small displacements:

$$p - p_0 = -\chi \frac{\partial u}{\partial z} \quad (3)$$

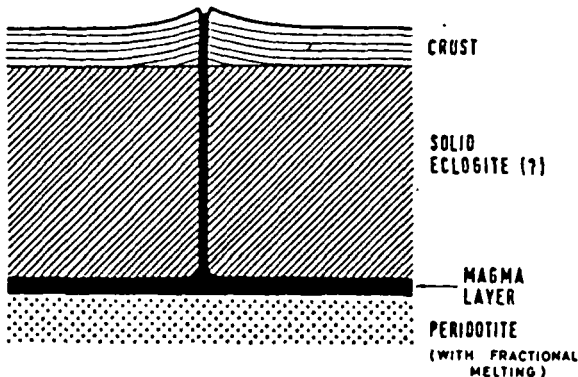


Fig.5. Idealized section of oceanic crust and upper mantle, with magma layer discharging directly to the surface.

where  $\chi$  is the bulk modulus of the magma and  $p_0$  the pressure in the undisturbed state, substituting in eq.2, we obtain:

$$\frac{\partial^2 u}{\partial t^2} = \frac{\chi}{\rho} \frac{\partial^2 u}{\partial z^2} \quad (4)$$

A solution, which satisfies the conditions  $u = 0$  for  $z = 0$  and for  $z = h$  ( $h$  being the height of the magmatic column), is:

$$u = A \left[ e^{i\omega(t+z/v)} - e^{i\omega(t-z/v)} \right] \quad (5)$$

where  $A$  is a constant,  $v = (\chi/\rho)^{1/2}$  is the velocity of compressional waves in the magma, and  $\omega$  is given by:

$$\omega = 2\pi/T = n\pi v/h \quad (6)$$

$T$  being the period of the vibration and  $n$  a whole number.

The fundamental mode of vibration ( $n = 1$ ) has therefore a period:

$$T = 2h/v \quad (7)$$

According to Shteynberg, in addition to the usual tremor with a period of 0.3–0.6 sec (cf. Minakami and Sakuma, 1953), there are components with periods of 2.5–3.5 sec and of 40–55 sec. With  $v \cong 3$  km/sec, eq. 7 would give depths of 4 or 5 km and 60–90 km. These values are exactly those one would expect for the depths of the shallow chambers, and of the deep source of magma, respectively (see Fig.6).

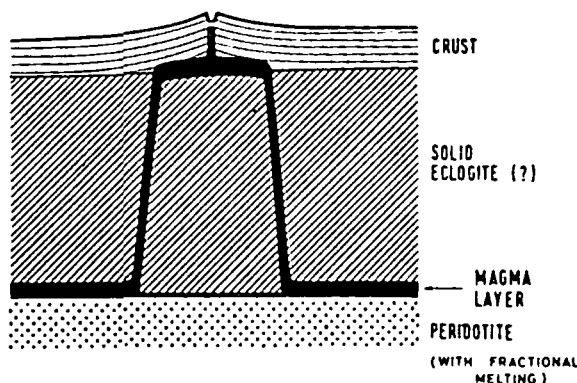


Fig.6. Idealized section of oceanic crust and upper mantle with deep magma layer and shallow magma chamber feeding a surface volcano.

Another type of investigation is based on the irregularities of the isoseismal lines in the vicinity of volcanoes (Machado, 1954; see also Howell, 1959, p. 94). In a homogeneous crust (and with a point focus) isoseismal lines would be concentric circles round the epicentre, each

radius  $\Delta$  and the corresponding maximum ground acceleration  $a$  satisfying the approximate equation:

$$a(\Delta^2 + h^2) = \text{const.} \quad (8)$$

where  $h$  is the focal depth.

Maximum acceleration of the ground vibration is related to the intensity  $I$  (Modified Mercalli Scale of 1931) by the empirical formula:

$$3 \log a = I - 1.5 \quad (9)$$

The presence of a magma chamber will absorb seismic energy, producing a decrease of the intensities; this represents an anomaly which can be defined as:

$$\delta I = I - I_0 = 3 \log (a/a_0) = 1.3 \ln (a/a_0) \quad (10)$$

the subscript zero referring to the values in the absence of the magma chamber.

This anomaly can be related theoretically to the viscosity of the magma. Let the displacement of a given point be the real part of:

$$u = A e^{i\omega t} \quad (11)$$

where  $t$  is the time (with a convenient origin) and  $A$  and  $t$ , respectively, the amplitude and period of the vibration. The maximum acceleration is:

$$a = A \omega^2 = 4\pi^2 A/T^2 \quad (12)$$

In typical near-earthquakes the maximum acceleration is always associated with compressional waves. For shear waves both  $A$  and  $t$  are greater than for compressional waves, but as they are roughly proportional to each other (e.g., both 10 times as great) the maximum acceleration is found with the smaller periods. The propagation of a compressional wave is described by the equation:

$$u = A e^{i\omega (t-x/v)} \quad (13)$$

where  $x$  is the distance travelled along the wave path, and  $v$  the velocity of propagation given by:

$$v = [(\chi + 4\mu/3)/\rho]^{1/2} \quad (14)$$

$\chi$  being the bulk modulus,  $\mu$  the rigidity modulus, and  $\rho$  the density.

For a Newtonian liquid of viscosity  $\eta$ , we substitute:

$$\mu = i\omega\eta \quad (15)$$

and obtain, if  $\omega\eta/\chi$  is small:

$$v = v_0 \left( 1 + \frac{2}{3} \frac{\omega\eta}{\rho v_0^2} i \right) \quad (16)$$

and:

$$u = A e^{-kx} e^{i\omega(t-x/v_0)} \quad (17)$$

with:

$$k = \frac{2}{3} \frac{\omega^2 \eta}{\rho v_0^3} \quad (18)$$

$v_0 = (\chi/\rho)^{1/2}$  being the velocity of compressional waves in the magma.

Maximum acceleration is now:

$$a = A\omega^2 e^{-kx} \quad (19)$$

and if damping in the solid crust is neglected:

$$a/a_0 = e^{-kL} \quad (20)$$

$L$  being the length travelled by the wave inside the magma chamber. Substitution of eq.20 into eq.9 gives finally:

$$\delta I = -1.3 kL \quad (21)$$

For the use of this method, we need an earthquake with the focus suitably situated. We have also to decide what are the theoretical intensities in the absence of any magma chambers.

The theoretical distribution of intensities can usually be chosen in such a way that the anomalies are negative in the "shadow" zones and vanish elsewhere. As the assignment of field intensities is a subjective process, the use of a dense net of accelerometers would be an improvement.

The method, notwithstanding all its limitations, has been used with some success in the Azores and Sicily (Machado, 1954, 1965). In Fig.7

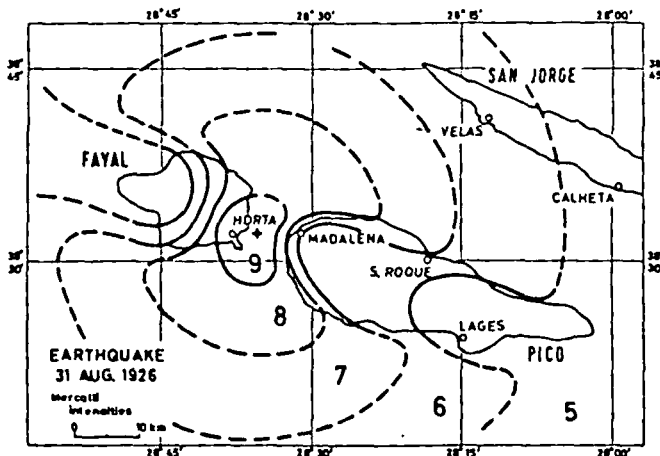


Fig.7. Isoseismal lines of the Azores earthquake of 31 August, 1926 (based on data from Agostinho, 1927).

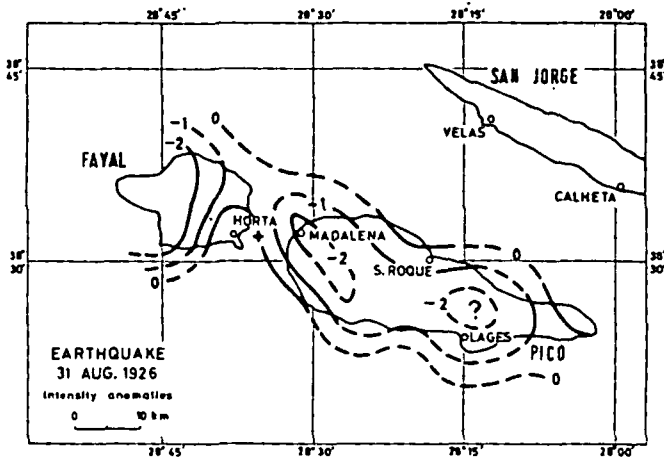


Fig.8. Intensity anomalies of the Azores earthquake of 31 August, 1926 (according to Machado, 1954).

the isoseismal lines of the Azores earthquake of 31 August, 1926 are presented (based on data from Agostinho, 1927). The assumed anomalies and a hypothetical section of the magma chambers of Fayal and Pico volcanoes are shown in Fig.8 and 9, respectively. The depth of 5 km was chosen to bring the centres of the chambers into the vertical of the main vents. The chambers of the individual volcanoes seem to be interconnected, forming a single elongated one.

A reasonable size for the magma chambers was obtained using  $k = 0.5 \text{ km}^{-1}$ . With this value and  $T = 0.2 \text{ sec}$ ,  $\rho = 3 \text{ g/cm}^3$  and  $v_0 = 3 \text{ km/sec}$ , we obtain, using eq. 18,  $\eta = 0.6 \cdot 10^9$  poises. This viscosity is surprisingly high. The mechanism of damping can be slightly more complicated (especially by reflections at the boundaries) but no big change in order of magnitude is expected. At present, only a mush of crystals with an interstitial liquid is believed to have, perhaps, such a high viscosity.

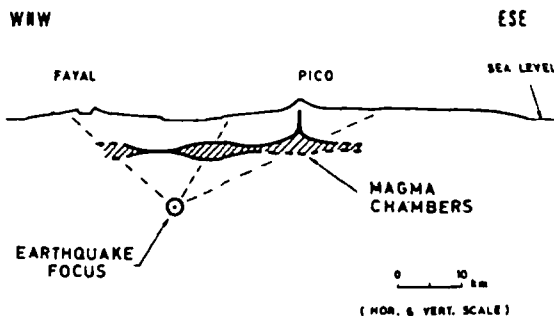


Fig.9. Longitudinal section of Fayal and Pico magma chambers, as deduced from seismic intensity anomalies (according to Machado, 1954).

## CRUSTAL DEFORMATION NEAR VOLCANOES

An important approach to the problem of magma chambers is due to Mogi (1958). The method is based on the deformation of the surface of a semi-infinite solid, produced by a change of pressure in a spherical cavity; the theoretical solution was obtained by Yamakawa (1955).

Let  $r$  and  $z$  be cylindrical coordinates with the origin at the centre of the spherical cavity (Fig.10);  $b$  is the radius of the cavity and  $h$  its mean depth. With this symmetry, the stresses are (see Timoshenko, 1934, p.309; Love, 1952, p.276):

$$\sigma_r = \frac{\partial}{\partial z} \left( \nu \nabla^2 \phi - \frac{\partial^2 \phi}{\partial r^2} \right) \quad (22)$$

$$\sigma_\theta = \frac{\partial}{\partial z} \left( \nu \nabla^2 \phi - \frac{1}{r} \frac{\partial \phi}{\partial r} \right) \quad (23)$$

$$\sigma_z = \frac{\partial}{\partial z} \left[ (2-\nu) \nabla^2 \phi - \frac{\partial^2 \phi}{\partial z^2} \right] \quad (24)$$

$$\tau_{rz} = \frac{\partial}{\partial r} \left[ (1-\nu) \nabla^2 \phi - \frac{\partial^2 \phi}{\partial z^2} \right] \quad (25)$$

where  $\nu$  is Poisson's ratio and  $\phi$  is a function of  $r$  and  $z$  satisfying the differential equation:

$$\nabla^2 \nabla^2 \phi = 0 \quad (26)$$

Here  $\nabla^2 = \partial^2 / \partial r^2 + (1/r) \partial / \partial r + \partial^2 / \partial z^2$ .

The boundary conditions are:

$$\sigma_z = 0 \quad \text{for} \quad z = h \quad (27)$$

$$\tau_{rz} = 0 \quad \text{for} \quad z = h \quad (28)$$

$$\sigma_R = -\Delta p \quad \text{for} \quad (r^2 + z^2)^{1/2} = b \quad (29)$$

where  $\Delta p$  is the change of pressure and  $\sigma_R$  is the spherical radial stress given by:

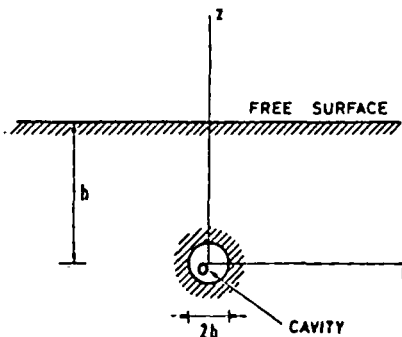


Fig.10. Theoretical model of crust with a spherical "pulsating" cavity.

$$\sigma_R = (\sigma_r r^2 + \sigma_z z^2 + 2\tau_{rz}rz)/(r^2 + z^2) \quad (30)$$

Assuming that  $\nu = 1/4$ , a solution of eq.26, satisfying conditions (27) and (28), is:

$$\phi = C [\ln(R_1 + z) + 2(z-h)/R_2] \quad (31)$$

$C$  being a constant and:

$$R_1 = (r^2 + z^2)^{1/2} \quad (32)$$

$$R_2 = [r^2 + (z-2h)^2]^{1/2} \quad (33)$$

In the vicinity of the origin, only the terms in  $R_1^{-1}$  are relevant; and we have approximately:

$$\sigma_r = -C \left( \frac{3r^2}{R_1^5} - \frac{1}{R_1^3} \right) \quad (34)$$

$$\sigma_z = -C \left( \frac{3z^2}{R_1^5} - \frac{1}{R_1^3} \right) \quad (35)$$

$$\tau_{rz} = -C \frac{3rz}{R_1^5} \quad (36)$$

and using eq.30:

$$\sigma_R = -2C/R_1^3 \quad (37)$$

Therefore, if  $b$  is much smaller than  $h$ , condition (29) is satisfied with fair approximation by making:

$$C = b^3 \Delta p / 2 \quad (38)$$

The displacements are (see Love, 1952; p.276):

$$u_r = -\frac{1}{2\mu} \frac{\delta^2 \phi}{\delta r \delta z} \quad (39)$$

$$u_z = \frac{1}{2\mu} \left[ 2(1-\nu)\nabla^2 \phi - \frac{\partial^2 \phi}{\partial z^2} \right] \quad (40)$$

where  $\mu$  is the rigidity modulus.

Using (31) and (38), these become:

$$u_r = \frac{b^3 \Delta p}{4\mu} \left[ \frac{r}{R_1^3} + \frac{2r}{R_2^3} - \frac{6r(z-h)(z-2h)}{R_2^5} \right] \quad (41)$$

$$u_z = \frac{b^3 \Delta p}{4\mu} \left[ \frac{z}{R_1^3} + \frac{2h}{R_2^3} - \frac{6(z-h)(z-2h)^2}{R_2^5} \right] \quad (42)$$

and at the free surface where  $z = h$ :

$$u_r = \frac{3b^3 \Delta p}{4\mu} \frac{r}{R^3} \quad (43)$$

$$u_z = \frac{3b^3 \Delta p}{4\mu} \frac{h}{R^3} \quad (44)$$

with  $R = (r^2 + h^2)^{1/2}$ . These are Yamakawa's (1955) results.



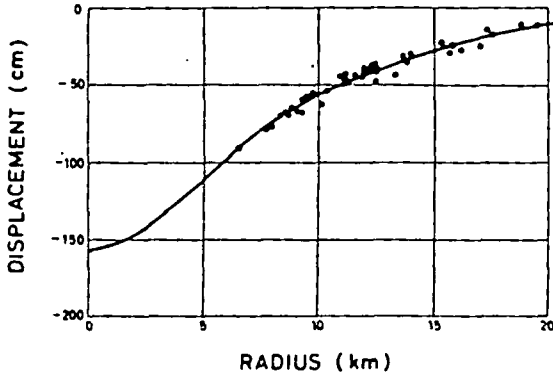


Fig.11. Vertical displacement near Sakurazima Volcano, in the years 1905–1914 (according to Mogi, 1958).

Eq.44 was used by Mogi (1958) for studying the deformation near Sakurazima Volcano (Fig.11). The fit is remarkably good if the mean depth of the magma reservoir is assumed to be about 10 km; usually the radius  $b$  cannot be obtained from eq.44 because  $\Delta p$  is unknown.

The same method was applied to Kilauea (Eaton, 1962; Decker et al., 1966; Fiske, 1968), and to Irazù (Murata et al., 1966). In both cases the depth of the “pulsating” chamber was estimated at 3 or 4 km.

A different type of deformation was observed during the eruption of Fayal (Azores) in 1958. After a violent seismic swarm (which preceded the 2nd phase of the eruption) the roof of the assumed elongated magma chamber seems to have buckled in three half waves, each about 5 km wide (Fig.12). The actual crustal strain  $\epsilon$  and the approximate radius of curvature  $R$  could be measured by geodetic surveying (Machado et al., 1962; Machado and Nascimento, 1965). Using the elementary bending theory, the thickness  $h$  of the undulated roof can be computed by the equation:

$$h = 2 \epsilon R \quad (45)$$

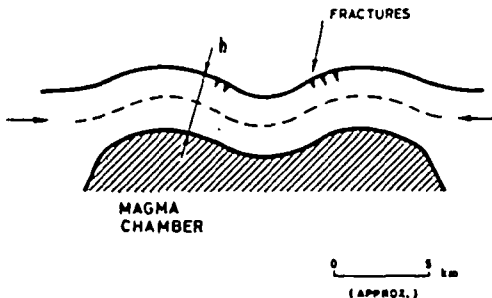


Fig.12. Buckling of the roof of Fayal magma chamber (according to Machado and Nascimento, 1965). The vertical displacement is much exaggerated.

With the measured values  $\epsilon \cong 0.5 \cdot 10^{-3}$  and  $R \cong 3000$  km (both for one of the convex belts; see Fig.12) a roof thickness  $h \cong 3$  km could be estimated. This is compatible with a mean depth of the magma chamber of some 5 km, as obtained from the seismic anomalies.

#### RATE OF EXTRUSION AND EARTH TIDE CONTROL

Very interesting information about the mechanism of eruption can be obtained from the rate of lava extrusion (Machado, 1962). The flow of lava through a cylindrical vent probably obeys Poiseuille's law:

$$Q = \frac{\pi r^4 \Delta p}{8\eta h} \quad (46)$$

where  $Q$  is the rate of flow,  $r$  the radius of the vent,  $\Delta p$  the pressure increase at the base of the vent (above hydrostatic equilibrium),  $\eta$  the viscosity of the lava, and  $h$  the length of the vent (thickness of the chamber roof).

Let  $v$  be the volume of the magma chamber and  $\chi$  the bulk modulus of the lava. A sudden decrease  $\Delta v_0$  of this volume will increase the pressure by an amount:

$$\Delta p_0 = -\chi \Delta v_0 / v \quad (47)$$

and when flow starts  $\Delta p$  will change according to the equation:

$$\Delta p \approx -\frac{\chi}{v} (\Delta v_0 + \int_0^t Q dt) \quad (48)$$

Using eq. 46, the last equation can be written as:

$$Q = Q_0 - A \int_0^t Q dt \quad (49)$$

where:

$$A = \frac{\pi r^4 \chi}{8\eta h v} \quad (50)$$

$$Q_0 = -A \Delta v_0 \quad (51)$$

Differentiating eq. 49, we obtain:

$$\frac{dQ}{dt} + AQ = 0 \quad (52)$$

whose solution, satisfying eq. 49, is:

$$Q = Q_0 e^{-At} \quad (53)$$

As a rule,  $\Delta v_0$  equals the total volume of extruded lava, so that by the end of the eruption hydrostatic equilibrium is established again.

Eq. 53 was verified approximately for several eruptions: Vesuvius in 1944, Kilauea in 1955, Fayal in 1957-1958 (see Fig.13). From the

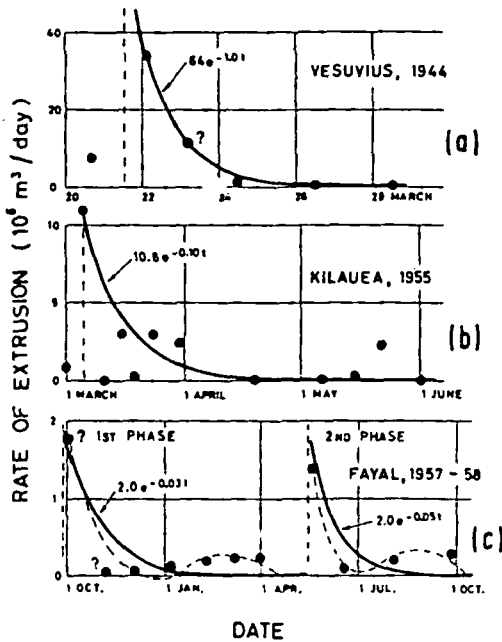


Fig.13. Rate of lava extrusion: (a) in Vesuvius, 1944 (according to Imbò and Bonasia, 1962); (b) in Kilauea, 1955 (according to Macdonald, 1959); (c) in Fayal, 1957—1958 (according to Machado, 1962).

diagrams we can obtain values for  $A$  and  $Q_0$  (and  $\Delta v_0$ ); we have also some idea of the order of magnitude of  $\chi$  and  $\eta$ . We can therefore deduce  $r^4/h\nu$ , but the separate quantities cannot be obtained.

A problem close to the last-mentioned was investigated by Imbò (1954, 1955b) who discovered during the 1944 eruption of Vesuvius a probable vertical oscillation of the lava in the upper part of the vent. We can assume that gas (or vapour) fills the vent, which is only closed by a small upper plug of liquid lava. Let  $u$  be the vertical displacement of this plug,  $m$  its mass and  $s$  the section of the vent. The motion (if frictionless) is described by the equation:

$$m \frac{d^2 u}{dt^2} = s \Delta p \quad (54)$$

where  $t$  is time and  $\Delta p$  the excess of pressure at the bottom of the plug over the pressure ( $mg/s$ ,  $g$  being gravity) due to its weight.

Assuming isothermal conditions, we have also:

$$s \Delta p / mg = -u/h \quad (55)$$

$h$  being the height filled with gas.

Using eq. 55 and introducing a friction term, eq. 54 becomes:

$$\frac{d^2 u}{dt^2} + 2\kappa \frac{du}{dt} + \frac{g}{h} u = 0 \quad (56)$$

where  $k$  is a friction coefficient. This equation is satisfied by:

$$u = A e^{-k t} \cos(\omega t + \psi) \quad (57)$$

where  $A$  and  $\psi$  are constants and:

$$\omega^2 = \frac{g}{h} - \kappa^2 \quad (58)$$

From the record of air-borne pressure waves, during a given phase of the eruption, Imbò obtained  $\omega = 0.0464 \text{ sec}^{-1}$  and  $k = 0.012 \text{ sec}^{-1}$ , and, using eq.58,  $h = 4.3 \text{ km}$ . Apparently the vent, except for a small lava plug, was filled with gas down to the magma chamber, an exceptional situation which certainly led to the following explosive activity.

The effect of semidiurnal Earth tides was recognized in several eruptions, namely in Vesuvius in 1944 (Imbò, 1955a, 1958), in San Jorge (Azores) in 1808 (Canto, 1884; Zbyszewski, 1963), and in the old Kilauea lava lake (Jaggar, 1938).

The effect of the semi-annual tide was also recognized in the Fayal eruption of 1957–1958 (Machado, 1962) and can be observed superimposed on the curve of Fig.13c. The problem is capable of theoretical treatment by including in eq.49 a term proportional to  $\sin(\omega t + \alpha)$ ,  $2\pi/\omega$  being the period of the tide and  $\alpha$  an adequate constant. We have therefore:

$$Q = Q_0 + Q_m \sin(\omega t + \alpha) - A \int_0^t Q dt \quad (59)$$

where:

$$Q_m = -A \Delta v_m \quad (60)$$

$\Delta v_m/v$  being the cubical expansion corresponding to the maximum of the tide.

Now the solution is:

$$Q = [Q_0 - Q_m \sin \psi \cos(\alpha + \psi)] e^{-A t} + Q_m \cos \psi \sin(\omega t + \alpha + \psi) \quad (61)$$

where  $\psi = \tan^{-1}(A/\omega)$ .

For the 1957–1958 eruption (2nd phase, Fig.13c) we have approximately  $Q_m = 0.5 \text{ million m}^3/\text{day}$ , and  $A = 0.05 \text{ day}^{-1}$ . This gives, by eq. 60,  $\Delta v_m = -10 \text{ million m}^3$ .

On the other hand, the tidal cubical expansion is:

$$\Delta v_m/v = fz/R \quad (62)$$

where  $f$  is a Love number,  $z$  the amplitude of the Earth tide and  $R$  the radius of the Earth. The amplitude of the solar semi-annual tide (see Bartels, 1957) is:

$$Z = 0.974 (1 - 3 \sin^2 \lambda) \quad (63)$$

where  $\lambda$  is the latitude. For Fayal Volcano ( $\lambda = 38^\circ 36'$ ), we have  $z = -0.164$  cm. Using  $f = 0.62$  (Melchior, 1966, p.300) and  $R = 6370$  km, the cubic expansion is  $\Delta v_m / v = -1.6 \cdot 10^{-10}$  and, with the previous value of  $\Delta v_m$ , the volume, on which the tide acts, seems to be  $v = 0.6 \cdot 10^8$  km<sup>3</sup>.

The volume of the magma chamber of Fayal and Pico volcanoes (Fig.9) is probably less than  $10^4$  km<sup>3</sup>. Therefore it appears that the tidal effect is exerted (in the Azores) directly on the upper-mantle magmatic layer, which must then be freely connected to the shallow magma chamber.

#### INTERPRETATION OF AVAILABLE EVIDENCE

The facts mentioned so far suggest the following mechanism for feeding volcanic eruptions.

- (1) Presence of a molten fraction in the upper mantle;
- (2) Squeezing of the molten fraction (incidentally accompanied by remelting of overlying eclogite) to form a magma layer in the upper mantle at depths of 50–60 km;
- (3) Rise of magma, through adequate fractures, usually to shallow chambers at depths of 3–10 km;
- (4) Compression of these chambers (when they exist), to feed surface eruptions.

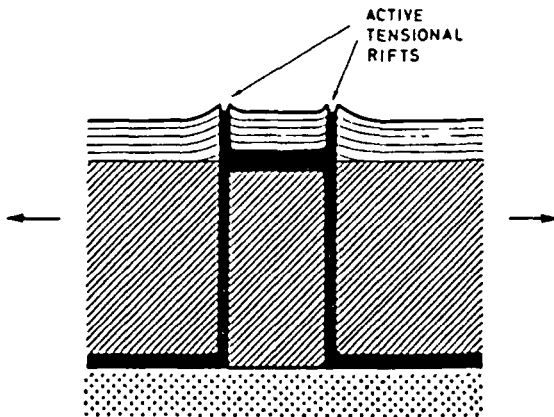


Fig. 14. Idealized section of volcanoes on tensional belt (mid-oceanic ridge).

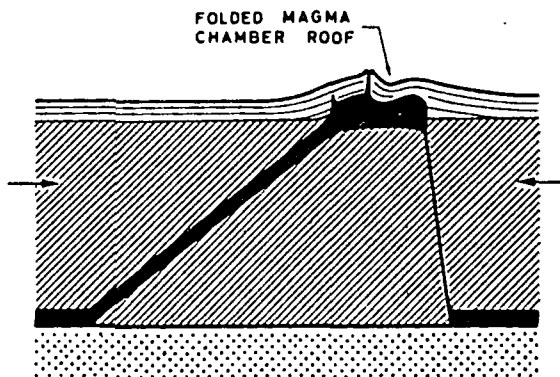


Fig. 15. Idealized section of volcano on compressive belt of orogenic type.

Volcanoes are found not only along tensional belts (mid-ocean ridges), but also in the young mountain belts and island arcs, where compression seems to be prevalent. In either case, some difference is expected in both magma type (cf. Gorshkov, 1962) and form of the conduits through which magma rises to the upper levels. In fact, tensional fractures tend to be vertical (Fig. 14), whereas in orogenic belts some of the feeding fractures probably correspond to reverse faults, dipping at angles of, say,  $30-45^\circ$  (Fig. 15). Although shallow chambers seem to be rather frequent in some cases (especially in tensional belts), magma is supposed to rise directly from the upper mantle to the surface (Gorshkov, 1967; Machado, 1969).

#### ACKNOWLEDGEMENT

The author is indebted to Dr. K.J. Murata for critical reading of the manuscript.

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