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TITLE: STATE OF THE SULPHUR SPRINGS HYDROTHERMAL SYSTEM, VALLES CALDERA,  
NEW MEXICO: FROM FLUID INCLUSION EVIDENCE

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SUBMITTED TO: GEOCHIMICA ET COSMOCHIMICA ACTA  
Special Issue on Fluid Inclusion Research

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## ABSTRACT

Core holes VC-2A and VC-2B were drilled as part of the Continental Scientific Drilling Program at Sulphur Springs, Valles caldera, New Mexico. Mineralization consists of quartz, calcite, fluorite, and minor molybdenite and sphalerite, and trace amounts of chalcopyrite, galena, and pyrrhgarite dated at 0.83 to 0.6 Ma. Associated alteration includes propylitization and sericitization. Host rocks include Quaternary caldera-fill ignimbrite and volcanoclastic rocks; Tertiary sandstone; Paleozoic sandstone, shale, and limestone; and Precambrian quartz monzonite. Valles caldera is host to an active hydrothermal system with bottom hole temperatures as high as 340°C and an average salinity of 0.5 equiv. wt.% NaCl. Fluid inclusion studies were conducted on primary, pseudosecondary, and secondary inclusions in quartz, calcite, fluorite, sphalerite, and epidote. The data indicate past temperatures in the volcanic rocks averaged 230°C and salinity averaged 0.9 equiv. wt.% NaCl. Past temperatures in the Paleozoic-Precambrian rocks averaged 290°C and salinities averaged 2.4 equiv. wt.% NaCl. Molybdenite deposition occurred at temperatures between 220-230°C and base metal deposition was at temperatures of about 235°C. Preliminary bulk fluid inclusion gas analyses indicate that the fluid in the past may have had higher concentration of H<sub>2</sub>S than the present fluid, but molar ratios of the other gaseous species are similar to present day Valles thermal waters. Some of the measured salinities may be apparent salinities due to concentrations of CO<sub>2</sub> that may be as high as 1.8 mole per cent. Boiling is indicated in the paleogeothermal system to depths of at least 1000m below the present land surface. Geologic evidence and the fluid inclusion data indicate a caldera lake, possibly as deep as 200 m, was present in the Sulphur Springs area. The data indicate that the paleo-hydrothermal system was stacked with a cooler, 200-230°C, dilute fluid circulating in the volcanic rocks and a hot, 275-305°C, saline, up to 2.4 equiv. wt.% NaCl, fluid circulating in the Pennsylvanian-Precambrian rocks. The system has cooled 30°C at shallower depths and 10°C at depths of 1750 m. In great part this temperature decrease is postulated to have resulted from breaching of the southwestern caldera wall and draining of

a caldera lake that overlay the Sulphur Springs hydrothermal system with a water depth that may have been as deep as 200 m. Ore minerals appear to have been deposited by hybrid fluids resulting from mixing of deeper, higher temperature and high TDS fluids with dilute waters in the shallow system.

## INTRODUCTION

Valles caldera in north-central New Mexico has been the target of geothermal exploration for the last 20 years because of its Quaternary volcanic features and abundant hot springs (Fig. 1). As a result, very few active hydrothermal systems have been so thoroughly and deeply explored (Hulen and Nielson, 1986). Bottom hole temperatures as high as 340°C have been encountered in the Valles system. Valles caldera possesses a diverse suite of thermal waters that are typical of those existing at many geothermal areas around the world (Henley and Ellis, 1983; Goff and Grigsby, 1982). Drilling and geochemical studies in the Valles caldera have revealed two reservoirs or subsystems: the Redondo Creek reservoir and the Sulphur Springs reservoir (Goff et al., 1988); therefore, the Valles geothermal system provides an excellent laboratory in which to study geothermal processes because of the extensive data base and complex geothermal system.

Numerous studies of active geothermal systems have concentrated on the fluid chemistry and mineralogy of alteration and vein fillings. Fluid inclusion investigations, although few in number, have proven valuable, and have shown that these systems evolve thermally and chemically (e.g. Hedenquist, 1983; McKibben et al., 1988; Moore and Adams, 1988; Bargar and Fournier, 1988). This report uses fluid inclusions from vein filling minerals to examine the evolution of the Sulphur Springs subsystem. In addition, study of the Valles hydrothermal system reveals how ore deposits are formed.

The analogy of active geothermal systems to hydrothermal ore deposits was first proposed by White (1955) and has been further advocated by Henley and Ellis (1983) and Henley (1985). Hulen and Nielson (1986) have found numerous parallels between the Valles geothermal system and fossil systems, namely the Adularia-Sericite type epithermal silver/base metal vein deposit (Hayba et al., 1985). Hulen and Nielson (1986) point out similarities between Valles and Creede caldera, Colorado in tectonic setting, host rock type, alteration mineralogy and zoning, and

water origin. Salinities are generally higher at Creede (Barton et al., 1977), but the salinities measured in the Valles are not unlike those for other volcanic-hosted epithermal deposits, e.g. Sunnyside and Lake City, Colorado (Casadevall and Ohmoto, 1977; Slack, 1980). Trace element geochemistry in Valles core samples show zoning similar to that described from fossil epithermal systems (Musgrave and Norman, 1990b; Rogers et al., 1990; Silberman and Berger, 1985; Berger and Silberman, 1985).

## GENERAL GEOLOGY

The Jemez Mountains volcanic field contains a suite of basaltic through rhyolitic rocks that were erupted from >13 to 0.13 Ma, although the field is best known for the Valles caldera and the Bandelier Tuffs (Smith and Bailey, 1968; Bailey et al., 1969; Smith et al., 1970; Gardner et al., 1986). The Valles caldera complex developed as early as 1.78 Ma (Spell et al., 1989) when felsic ash-flow tuffs of limited extent began erupting near the crest of the Jemez volcanic field. At 1.50 Ma (Spell et al., 1989), a major felsic pyroclastic eruption resulted in the development of the Toledo caldera and the emplacement of the Otowi Member of the Bandelier Tuff. A second major eruption of felsic ignimbrite at 1.13 Ma (Spell et al., 1989) produced the Tshirege Member of the Bandelier Tuff and formed the presently exposed Valles caldera. Shortly following caldera collapse, the caldera underwent resurgent doming and emplacement of a series of domes and flows above the ring fracture system that have age dates which span 1.06 to 0.13 Ma (Doell et al., 1968).

## SULPHUR SPRINGS HYDROTHERMAL SYSTEM

The hydrothermal fluid produced at Sulphur Springs is distinct from the fluid produced from the Redondo Creek area of the Valles geothermal system. Based on isotopic, chemical, and noble gas studies, two fluids have been identified in the Redondo Creek reservoir (Truesdell and Janik, 1986; Smith and Kennedy, 1985). Redondo Creek fluids could be termed "typical" Valles geothermal fluids having Cl = 1900-2500 ppm and TDS = 0.5 equiv. wt.% NaCl. The

Sulphur Springs fluid may represent yet a third type being higher in Cl (2949 ppm) and TDS (0.7 equiv wt.% NaCl) and isotopically heavier ( $\delta^{18}O = -7.1, \delta D = -74$ ) than Redondo Creek fluids (Meeker and Goff, 1988). Over 40 deep wells have been drilled inside and outside the Valles caldera. Most recently, three core holes, VC-1, VC-2A and VC-2B drilled as part of the Continental Scientific Drilling Program, have been completed in the western half of the caldera (Fig. 2a and 2b). A primary objective of core hole VC-1, drilled in the southwest ring-fracture zone, was to test the model of hydrothermal outflow from the Valles caldera (Goff and Nielson, 1986; Goff et al., 1988). Sulphur Springs was chosen as a drilling site of holes VC-2A and VC-2B because answers to questions regarding the nature of the interface between vapor-dominated and liquid-dominated systems and deposition of ore minerals in an active geothermal system could be addressed (Goff and Nielson, 1986). The Sulphur Springs hydrothermal system is the hottest, most active surface expression located in the Valles caldera having numerous hot springs, fumaroles, and mud pots (Fig. 2b). Sulphur Springs fluids are typical of an acid-sulfate, vapor-dominated system (White et al., 1971). The water in the springs consists of condensed steam and acid sulfur gases oxidizing to sulfuric acid and mixing with near-surface groundwater (Charles et al., 1986). Deep reservoir fluids were encountered by drilling at Sulphur Springs beneath the acid sulfate/vapor-dominated zone capping the liquid dominated part of the hydrothermal system. They are neutral-chloride waters, typical of those found in other volcanic geothermal systems such as Yellowstone and Broadlands, New Zealand, with anomalous concentrations of As, B, Br, Cs, Li, and Rb (Goff et al., 1989). Stable isotopic studies of spring and deep reservoir waters indicate they originate from meteoric precipitation and slow infiltration of cool groundwater to depth. Recharge of these waters appears to be occurring in basins of the northern and eastern caldera moat and in the resurgent dome of the caldera (Goff et al., 1985; Vuataz and Goff, 1986). Sulfur isotopic analyses by ion microprobe on pyrite from 57.3 m in VC-2A indicate values centered on 0 per mil, and show as much as 22 per mil variation in  $\delta^{34}S$  within a single crystal (McKibben and Eldridge, 1990).

## OTHER FLUID INCLUSION STUDIES

Previous fluid inclusion studies in the Valles caldera include the work of Gonzales (1988), Hulen et al. (1987), Musgrave and Norman (1988, 1989, 1990a and 1990b), Sasada (1987, 1988 and 1989a and 1989b), and Wronkiewicz et al. (1984). Wronkiewicz et al. (1984) demonstrated in their fluid inclusion investigation of the Cochiti mining district that the veins formed at temperatures of 195-375°C and salinities of 0-4 equiv. wt.% NaCl. Sasada (1989b) has indicated that there has been a recent increase in the thermal profile at the Fenton Hill Hot Dry Rock geothermal test site just west of the caldera margin. The investigations by Gonzales (1988), Hulen et al. (1987), and Sasada (1987 and 1989a) suggest that mineralization at Sulphur Springs took place as a result of deposition from dilute fluids at temperatures around 200°C. Sasada (1988) showed that for corehole VC-1, the deep paleofluid had salinities of up to 5 equiv wt.% NaCl., a maximum temperature of 275°C, a possible CaCl<sub>2</sub> component, and at least 0.35 wt.% CO<sub>2</sub>. A younger, shallow fluid (above 723 m) in VC-1 had a maximum Th of 220°C and maximum salinities of 2 equiv. wt.% NaCl. Hulen and Nielson (1988) in their investigation of hydrothermal breccias in VC-1 also suggested the two fluid model.

## CORE HOLES VC-2A AND VC-2B

Core holes VC-2A and VC-2B were drilled at Sulphur Springs, located in the western ring fracture zone of the caldera (Fig. 2a and 2b). VC-2A was completed to a depth of 528 m in September of 1986 and VC-2B was completed to a depth of 1762 m in October of 1988. Core recovery for both core holes was better than 95%. Bottom hole temperatures for VC-2A and VC-2B are 212°C and 295°C, respectively. These bottom holes temperatures are typical of those found elsewhere in the Valles hydrothermal system. Fluids from VC- 2A and VC-2B have average salinities of 0.7 and 0.9 equiv. wt.% NaCl, respectively.

The stratigraphy of the Sulphur Springs area as revealed by VC- 2A and VC-2B consists of caldera-fill ignimbrite and volcaniclastic units, Tertiary Santa Fe Group sandstones, Permian

Yeso Formation (sandstones), Permian Abo Formation (mudstones), Pennsylvanian Madera Limestone, Pennsylvanian Sandia Formation (sandstones), and biotite quartz monzonite of Precambrian age (Fig. 3). The entire stratigraphic sequence penetrated by the core holes has undergone varying degrees of fracturing of both tectonic and hydrothermal origin for which the intensity of fracturing is strongly dependent on rock type and depth in the Sulphur Springs system (Hulen et al., 1989).

Hydrothermal alteration in VC-2A and VC-2B reflects the intensity and distribution of fracturing, brecciation, and host lithology. Accordingly, the ignimbrites and the Precambrian quartz monzonite are extensively altered, whereas the intervening Paleozoic section, with few exceptions, is relatively unaltered (Hulen et al., 1989).

The upper most part of the Sulphur Springs system is characterized by surficial advanced argillic alteration composed of kaolinite and other clays, alunite, native sulfur, quartz, and hydrated sulfates containing Fe, Ca and Al (Charles et al., 1986). Below this surficial alteration, quartz-sericite-pyrite is the predominant alteration assemblage. This assemblage extends to about 165 m in VC-2A and 300 m in VC-2B. Sericite-chlorite alteration is dominant in the remainder of the ignimbrite section. Deep in the Sulphur Springs system the alteration is predominantly propylitic (chlorite-calcite-epidote-sericite-pyrite), but in intensely fractured regions of the Precambrian, the quartz monzonite displays moderate to strong chlorite-sericite alteration (Hulen et al., 1989). The propylitic alteration in the Pennsylvanian section contains varying amounts of illite, chlorite, epidote, wairakite, kaolinite, pyrite, calcite and rectorite.

## **VEIN MINERALOGY AND PARAGENESIS**

Twenty-four gangue and ore minerals have been identified by optical microscopy, X-ray diffraction, and SEM/EDS scans (Fig. 4). In order of approximate decreasing volumetric abundance within a particular vein, these minerals are quartz (5-100%), calcite (2- 100%),



fluorite (1-100%), illite/illite-smectite (<1-80%), chlorite (1-30%), epidote (1-30%), molybdenite, (1-25%), anhydrite (<1-20%), hematite (<1-10%), sphalerite (<1-10%), pyrite (<1-5%), rhodochrosite (<1-5%), and trace amounts of chalcopyrite, galena, pyrargyrite, stibnite, chalcocite, adularia, albite, kaolinite, wairakite, Fe-dolomite, barite, and a bismuth telluride (tellurobismuth?) (Musgrave and Hulen, 1989). Most vein minerals form fine- to coarse-grained intergrowths of subhedral to euhedral grains. Calcite exhibits massive and bladed or "snowflake" textures. Small (0.5 to 1 mm) epitaxial cappings of euhedral sulfides are present on the terminations of quartz and calcite. Vein fillings range from complete, to partial fillings with abundant open spaces, to fractured rock with sparse secondary mineralization.

Stage I mineralization in VC-2A is characterized by euhedral quartz, molybdenite, illite, pyrite, and fluorite. The chlorite and early rhodochrosite of this stage are found deeper in the corehole, below the molybdenite zone. The molybdenite ranges from a well crystallized form to a poorly crystalline form. Stage II is characterized by euhedral to subhedral quartz and calcite, sphalerite, pyrite, galena, chalcopyrite, and late fluorite and rhodochrosite. Sphalerite color ranges from colorless to honey yellow, and it displays no color zonation. Potassium-argon dates on hydrothermal illites from the molybdenite zone indicate a minimum age of formation of about 0.66 Ma for the molybdenite mineralization (WoldeGabriel and Goff, 1989).

Although drilled only 600 m from VC-2A, VC-2B penetrated none of the unusual molybdenite mineralization found in the shallower corehole. In VC-2B, however, the ore minerals (although in trace amounts) show a distinct vertical zonation; stibnite and pyrargyrite occur at higher elevations with base metal sulfides confined to deeper levels. The paragenesis of the gangue minerals is similar to VC-2A, but the ore minerals appear to be a late stage event (Fig. 4).

## FLUID INCLUSIONS

Approximately 90 samples as thick sections and numerous cleavage chips were prepared for fluid inclusion observation and analysis. Measurements were made on over 800 inclusions in quartz, calcite, sphalerite, fluorite, and epidote, with all freezing runs conducted prior to heating runs (Table 1). Sizes of inclusions measured range from 3 to 70  $\mu\text{m}$ , with most between 8 and 15  $\mu\text{m}$ . An SGE adapted USGS gas flow heating-freezing stage was used. The stage was calibrated by Los Alamos National Laboratory's standards and calibration group and by melting points of a series of organic and inorganic standards.

Inclusions were classified as primary if they had spatial relationship to growth zones or occurred as random 3-D arrays. Criteria for distinguishing pseudosecondary and secondary inclusions follows those outlined by Roedder (1984). Fluid inclusions in calcite and fluorite are predominantly of secondary origin. Many of the inclusions in quartz and calcite had "tails" suggesting necking-down had occurred. Examples of inclusions are shown in Fig 5.

Fluid inclusions in the Sulphur Springs samples can be grouped into four types based on room temperature liquid-vapor ratios. Type 1 consists of liquid-rich inclusions which possess liquid >70% of the inclusion volume. This type includes all primary inclusions in sphalerite, most primary and secondary inclusions in fluorite and most primary inclusions in quartz and calcite. Type 2 are vapor-rich; vapor is >40% of the inclusion. Inclusions with 40-90% vapor are rare; inclusions with vapor >90% and comprise the majority of the vapor-rich inclusions. These vapor-rich inclusions commonly occur with liquid-rich inclusions in the same growth zone; however, the volume of vapor precluded measurement of Th. The third type is a single phase liquid inclusion, and the fourth type is a two phase liquid-rich inclusion with a small, apparently isotropic mineral, which appears to be an accidental crystal of fluorite. Type 3 and 4 inclusions were observed only in fluorite.

## MICROTHERMOMETRY

Primary fluid inclusion Th (homogenization temperatures) associated with minerals from the upper levels of the Sulphur Springs system range from 185 to 290°C with an average of 230°C, whereas the range for the Paleozoic-Precambrian section is 250 to 334°C with an average of 290°C (Fig. 6 and Table 1). Th values for primary inclusions from late stage fluorite of the upper levels of the system range from 175 to 219°C with an average of 190°C. Homogenization temperatures in fluorite from the Precambrian section of VC-2B range from 287 to 319°C with an average of 305°C. Depth versus temperature for the inclusion data and the present day temperature logs from VC-2A and VC-2B are plotted in Figures 7a-d.

Equivalent salinities were calculated using the computer program FLINCOR (Brown, 1988). Salinities for VC-2A show a wide range from 0 to 5.5 equiv. wt% NaCl (Fig. 6a), whereas salinity data from high stratigraphic levels in VC2B are tightly clustered at 0 to 0.7 equiv. wt% NaCl. The data from the Paleozoic-Precambrian section show a greater range in salinity from 1.3 to 5.2 equiv. wt.% NaCl. Late stage fluorite salinities from both core holes, on the average, range from 0 to 1 equiv wt.% NaCl. The largest grouping of salinity data for all periods of mineralization from Sulphur Springs is around 0.90 equiv. wt.% NaCl.

The fluid inclusion data for VC-2B clearly falls into two groups one having Th values about 300°C and salinities about 2.4 equiv. wt.% NaCl and the other having Th values of about 230°C and salinities about 0.7 equiv. wt.% NaCl (Fig. 6b). The higher temperature measurements are from deeper parts of the core hole, and the fluid inclusion data from the shallow VC-2B core appear to be all of the lower temperature type fluid.

A vein sample from VC-2A (452 m) allows evaluation of temperature and compositional changes through the paragenetic sequence (Fig. 8). From textural evidence, it was determined that quartz is the first phase deposited followed by sphalerite and finally calcite. Quartz was deposited from a fluid at about 245°C and 0.8 equiv. wt.% NaCl. The sphalerite stage

shows about a 10°C cooling to 235°C but the salinity remains constant. The calcite stage was deposited at 206°C and 0.64 wt.% NaCl.

The fluid inclusion data show, in general, a similar temporal variation to that illustrated by the single vein sample and also exhibit spatial variation (Table 2). Primary inclusions in early quartz and sphalerite from VC-2A and early quartz and calcite from VC-2B for the volcanic section (0-666 m) have Th on average 30°C higher than primary inclusions in late stage fluorite. Fluid inclusions in early quartz, calcite and epidote in VC-2B from the Paleozoic-Precambrian section (920-1726 m) have Th 10°C higher than late stage fluorite for this depth. Salinities from the early minerals of the volcanic section (0-666 m) average 0.3 equiv. wt.% NaCl higher than the late stage fluorite. The salinity data for the early minerals in the Paleozoic-Precambrian rocks (920-1726) average 1.3 equiv. wt.% NaCl higher than the late stage fluorite.

### ANALYSIS OF FLUID INCLUSION GASES

Bulk analyses of inclusion volatiles were measured by mass spectrometry (Norman and Sawkins, 1987) (Table 3). Sample size averaged 0.1 grams, and inclusions were opened by thermal decrepitation. The four samples (all from VC-2A) are early quartz from 3 depths and a sample of late (Stage II) calcite from 522 m.

Principal gaseous species are CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>S (Table 3). The relatively high amounts of H<sub>2</sub>, and the variable amounts of CO are an artifact of thermal decrepitation at temperatures above the trapping temperature (Tt). CH<sub>4</sub> will react with H<sub>2</sub>O yielding H<sub>2</sub> and CO<sub>2</sub> at temperatures above Tt (Norman, 1991). The analyses have been corrected for the spurious H<sub>2</sub> as described in Norman (1991). This was done for a temperature of 260°C, which is the upper limit of Th values, and it would seem logical that vapor inclusions have been trapped at times of maximum temperature.

The amounts of CO<sub>2</sub> in the analyses is unrealistically high. Similar analyses of inclusions with excess gas species have been interpreted as being mixtures of volatiles from inclusions of

trapped liquid and inclusions of trapped vapor in which high gas/water ratios would be expected (Norman and Sawkins, 1987). This explanation is appropriate for the analyses presented here because the samples have inclusions of vapor presumably trapped during times of fluid boiling.

It is not clear, because of the lack of Th values from vapor-rich inclusions, and the wide spread in Th values, if the gases in vapor-rich inclusions are in equilibrium with the liquid-rich inclusions. Giggenbach (1980) addressed the problem of excess gas in analyses of geothermal waters and developed a function,  $Kc''$ , with which to test if an analysis of thermal water contained excess gas, or the fluid had been partially depleted in gases by boiling. The corrected analyses plot in the area of fluids with excess vapor (Fig. 2 in Giggenbach, 1980), and appear to be equilibrium concentrations of the gaseous species. The steam fraction,  $y$ , indicated by plotting the analyses on this figure are in Table 4.

Assuming the inclusions measured were mixtures of trapped vapor and trapped liquid, the concentration of each gaseous species may be related to the concentrations in liquid and vapor by mass balance equation

$$c_{li}(1 - y) + c_{vi}y = c_{mi}(1)$$

where  $c_{li}$ ,  $c_{vi}$ , and  $c_{mi}$  are, respectively, the concentrations of gases specie  $i$  in liquid, vapor, and as measured by th analysis. Dividing the above equation by  $c_{li}$ , substituting the distribution coefficient  $B_i$  that equals  $c_{vi}/c_{li}$ , and rearranging yields:

$$c_{li} = \frac{c_{mi}}{1 + y(B_i - 1)}(2)$$

The concentration of gaseous species in aqueous inclusions was calculated (Table 4) using this equation for the principal gases for which distribution coefficients are available at elevated temperatures (Giggenbach, 1980; Naumov et al., 1971). The calculated  $c_{li}$  maybe in some

error because of errors in determining  $y$ , because to precisely calculate  $y$  the trapping temperature should be well constrained. However, the purpose of the calculation is to compare the gases in aqueous fluid inclusions to analysis of gases in present Valles thermal waters and this can be done even though the calculated values may depart from true values in view of the great sample to sample variation in analyses of Valles waters. There is considerable uncertainty if analyses of well waters truly represent those in reservoir fluids. Analyses may have included vapor or be of fluids that have lost considerable gases from boiling. Overall, Table 2 indicates that volatiles in aqueous inclusions are similar to Valles thermal waters but that  $\text{CO}_2$  may have been somewhat higher than present fluids, and definitely sulfur-bearing gases are in higher concentrations in some of the inclusions.

Molar ratios of  $\text{CO}_2/\text{H}_2\text{S}$  are about 1:2 to 100:1; these values are similar to ratios noted in other active geothermal systems (Giggenbach, 1980), and the high  $\text{CO}_2$  generally is associated with high  $\text{H}_2\text{S}$  (Henley, 1985). Inclusions in quartz have higher concentrations of sulfur-bearing gases than are indicated in analyses of Valles thermal waters. On the other hand, the concentration of  $\text{H}_2\text{S}$  in inclusions in late calcite, and for that matter concentrations of all other common gas species, is similar to present Valles waters and gases emanating from Sulfur Spring (Table 4).

$\text{NH}_3$  has been reported in analysis of some Valles waters (Truesdell and Janik, 1986). This gas is difficult to measure in trace amounts by mass spectrometry because  $\text{NH}_3$  mass peaks maybe obscured by  $\text{CO}_2$  and background  $\text{H}_2\text{O}$  mass peaks; small amounts may have gone undetected.  $\text{CO}$  is considered to be spurious. It is measured commonly among inclusion volatiles released by thermal decrepitation and is associated with organic compounds (Norman and Sawkins 1987).  $\text{C}_2$  and above hydrocarbon compounds have not been reported in Valles waters, but similar species have been measured in thermal waters.

## DISCUSSION

### *Evidence for Boiling*

Many lines of evidence indicate that boiling of deep reservoir fluids has taken place at Sulphur Springs in the past, including coexisting liquid-rich and vapor-rich inclusions and high gas to water ratios (Musgrave and Norman, 1988; Sasada and Goff, 1989), mineralogic (bladed or "snowflake" calcite and adularia), structural (hydrothermal breccias) (Hulen and Gardner, 1988), and sulfur isotopic data. Bodnar et al. 1985 have shown that fluid inclusion evidence for boiling must include more evidence than simply having liquid-rich and vapor-rich, but that the inclusions coexist in the same growth zone as observed in Valles inclusions. Subsurface boiling zones have been identified on the basis of mineral assemblages, quartz, K-feldspar(adularia), and bladed calcite, and texture (Browne and Ellis, 1970; Keith et al., 1978; Tulloch, 1982). Hydrothermal breccias themselves are not evidence for boiling, but the hydraulic fracturing attending breccia development result in fluid decompression which in turn may lead to boiling (Sillitoe, 1985). Boiling at times may have been violent during events when large volumes of water flashed to steam (Sillitoe, 1985). The large variation in sulfur isotopes observed by McKibben and Eldridge (1990) may be explained by boiling. Changes in fluid pH,  $f_{O_2}$ , and ionic strength can bring about sulfur isotopic variation (Ohmoto, 1972), and boiling is an effective means to cause changes in fluid chemistry (Drummond and Ohmoto, 1985; Spycher and Reed, 1989).

We estimate the paleo-boiling horizon occurred as deep as 1000 m relative to the present ground surface, and this is based solely on the existence of coexisting liquid- and vapor-rich inclusions. Boiling may have taken place intermittently at deeper levels in the system. The fluid inclusion gas data indicate the fluid contains higher gas concentrations, which would in turn depress the boiling point curve. Adding in the effect of 1 wt.%  $CO_2$  to the 300°C fluid at 1760 m, the boiling point horizon would occur at about 2000 m, not an unreasonable depth considering at Broadlands drilling to over 2500 m has not penetrated beneath the boiling zone (Henley, 1984).

### *Dilution*

The data suggest that mixing-dilution has been an important process in the evolution of the hydrothermal fluid. The deep fluid apparently flows up fractures and mixes with the shallow fluid. Trends similar to this have been observed in other studies of convectively- driven hydrothermal fluid (Shepherd et al., 1985). Projection of the dilution trend suggests mixing with steam-heated water as opposed to mixing with cold ground water.

### *Depth Estimate of the Caldera Lake*

Fluid inclusion data for the upper 129 m of VC-2A plotted for depth versus temperature lie off the pure water boiling point curve (Fig. 7a). Data from inclusions within 39 m of the present ground surface have a range in Th of 200-210°C. The minimum depth at trapping, assuming hydrostatic conditions, is 160 to 200 m. This would imply that a minimum of 160 to 200 m has been removed by erosion, but this is unlikely at the location of the core holes within the Valles caldera. Mapping in the Sulphur Springs area revealed that a caldera lake was present (Goff and Gardner, 1980); therefore, the caldera lake most probably supplied the necessary hydrostatic head. Taking dissolved gases into account would tend to make this estimate greater, but at shallow depths the paleofluid must have been mostly degassed from boiling. If the boiling point curve (Fig. 7a) is raised 180 m, the data better fall on the curve. Hence we conclude that the draining of the lake result in a loss of up to 180 m of hydrostatic head and decrease in fluid temperatures. Breaching of the southwestern caldera wall at about 0.5 Ma (Goff and Shevenell, 1987) resulted in draining of the lake and lowering of the watertable and development of the vapor- dominated system that now overlies the Sulphur Springs system. Some of the data points that lie off the curve may be due to overpressuring of the system prior to hydraulic fracturing and hydrothermal breccia development. Erosion may have been accelerated in the Sulphur Springs area due to the breaching of the caldera wall and



uplift associated with the formation of the resurgent dome. Therefore, it is not certain if the caldera lake was as deep as 180 m.

*System Temperatures and Fluid Composition: From Fluid Inclusion Data*

Fluid inclusion data suggests there has been a decrease in fluid temperatures in the shallower part of the system but less so in the deep part. Fluid inclusion data from veins in the volcanic rocks beneath Sulphur Springs indicate that the average temperature of vein formation was around 230°C (Fig. 9). Base metal deposition, at 452 m in VC-2A was slightly higher than this average, with Th values near 235°C, molybdenite deposition was at 220-230°C, and late stage fluorite deposition was in the temperature range of 190-200°C. Data from the veins in the Paleozoic rocks indicate the average Th is 270°C, whereas data from the Precambrian rocks indicate the average Th is 305°C. Late stage fluorite from the Precambrian veins also average around 305°C.

Salinity data for Sulphur Springs is highly variable, only sphalerite shows a fairly narrow range (Fig. 9). The largest grouping of salinity data is  $\leq 1$  equiv. wt.% NaCl. This group probably best represents the actual salinity for the veins in the volcanic rocks. For systems where gas (mainly CO<sub>2</sub>) dominates over dissolved salts, a near vertical trend results on salinity versus Th plots (Hedenquist and Henley, 1985). Four weight percent (about 1.8 mole %) CO<sub>2</sub> in solution would depress the freezing point of the fluid equivalent to 2.8 wt.% NaCl (Henley, 1985). A large grouping of zero salinity values occurs at 190-225°C. These inclusions most likely represent trapped steam condensate (Fig. 9). Low salinity fluids trapped in this manner are extremely common in geothermal systems (Moore et al., 1990), and these fluids typically have temperatures below the 234°C maximum enthalpy of steam. Salinity data for the Paleozoic-Precambrian rocks (Th 240- 330°C) average 2.4 equiv wt.% NaCl; this also may represent a high gas fluid, but the fact that there are salinities as high as 5.0 equiv. wt.% NaCl suggest that the fluid inclusion ice melting temperatures are not solely the result of dissolved

CO<sub>2</sub>; the deep fluid is higher in salinity than the shallow fluid. Both the fluid inclusion gas analyses and the present day gas data show highly variable gas contents; therefore, it is difficult to precisely quantify the contribution of dissolved gas to the salinity measurements.

*Sulphur Springs - Past and Present*

Fluid inclusion data indicate that the upper portions of the system have cooled from about 240°C to 205-210°C at 452 m. Fluid composition has not changed radically in last 0.83 to 0.66 Ma. Present day fluid salinities from the volcanic rocks are around 0.7 equiv. wt. % NaCl compared to about 0.8 to 0.9 equiv. wt.% NaCl based on fluid inclusion data. However, the gas content of the fluid appear to be higher in the past. Fluid inclusion evidence suggests the deep levels of the hydrothermal system have not cooled as dramatically as the upper portions. At 1726 m in VC-2B, cooling appears to be only 10°C, from 305°C to 295°C. Fluid composition has changed quite significantly from about 2.4 equiv. wt.% NaCl to 0.94 equiv. wt.% NaCl.

Salinity data from veins in the Paleozoic-Precambrian rocks present somewhat of a problem. The data suggest that when these veins formed the salinity may have been about 2.4 equiv. wt.% NaCl. The present day salinity is around 0.9 equiv. wt.% NaCl. This represents is a significant decrease in the salinity for the deep portion of the system. If the data represent apparent salinities due to high gas contents, the true salinity salinity may be closer to the present day value; late stage fluorite salinity is similar to the present day value, 1.1 equiv. wt.% NaCl. Alternatively, the salinity data could represent true salinities. The dramatic change in fluid composition may be due to encroachment of dilute waters as a result of cooling of the system. A process similar to this has been suggested during thermal collapse of porphyry systems, and the formation of lower temperature veins (Gustafson and Hunt, 1975).

Fluid inclusion data suggest the Sulphur Springs hydrothermal system was a stacked system in the past, with a relatively cool, dilute fluid circulating in the upper levels and a hot, apparently saline fluid circulating in the deep portions. Minor communication occurred between the upper

and lower cells along the Sulphur Creek and its subsidiary faults (Fig. 10), with mixing-dilution between the deep and shallow fluids. The stacked system model would work for either interpretation of the deep fluid salinity. Separation of the shallow and deep cells is accomplished by the intervening Permian shales and sandstones which act as an aquitard or pressure seal in order to keep the high gas content of the fluid. The present day fluid produced at the bottom of VC-2B may be the same fluid but degassed.

The data presented in this study indicate that a fluid of an average temperature of 230°C and a salinity of about 0.8 to 0.9 equiv. wt.% NaCl circulated in the volcanic rocks of Sulphur Springs prior to the loss of the caldera lake and concomitant drop in the maximum elevation of the hydrothermal fluid. The resultant effects of the loss of the caldera lake are the development of the vapor cap overlying the liquid-dominated reservoir and the cooling of the upper portions of the system.

Boiling is an effective mechanism for degassing a fluid. The deep fluid may have migrated up the numerous faults and fractures, boiled, and produced, at least in part, the fluid inclusion data observed at Sulphur Springs (Fig. 9). Mixing-dilution processes contributed to some of the trends in the fluid inclusion data (Fig. 9).

Ore minerals are being deposited in the Valles hydrothermal system. However, our data show that the bulk of the ore mineralization at Sulphur Springs occurred prior to 0.5 Ma and the draining of the caldera lake. Fluids of composition not radically different from those today were responsible for the mineralization, but the fluid inclusion gas analyses indicate the past fluids were richer in the sulfur species. Boiling and fluid mixing are indicated to be the mechanisms causing the deposition of the ore minerals.

The ore mineralization is largely confined to the upper 500 m of the Sulphur Springs hydrothermal system, with associated quartz-sericite-pyrite alteration. The upper part of the system is indicated to be a zone of mixing between the dilute, shallow fluid and the more

saline deep fluid, and boiling was probably more vigorous here as indicated by the higher fluid inclusion gas contents and hydrothermal breccias.

## CONCLUSIONS

Fluid inclusion data presented in this study suggest that the paleo-hydrothermal system was stacked with a cooler, 200-230°C, dilute fluid circulating in the volcanic rocks and a hot, 275-305°C, apparently saline, up to 2.4 equiv. wt.% NaCl, fluid circulating in the Pennsylvanian-Precambrian rocks. Communication between the two cells occurred, presumably along the numerous faults in the Sulphur Springs area, and this resulted in dilution and mixing of the fluids. Veins in portions of the volcanic rocks formed at least 0.6 Ma prior to draining of the caldera lake. Boiling of the fluid has taken place in the past and continues today. The caldera lake present in the Sulphur Springs area had a maximum depth of 180 m, and when it emptied about 0.5 Ma there resulted a lowering of the maximum level of the hydrothermal system and cooling of the upper portions of the system. The system since then has cooled between 10 and 100°C from the present ground surface to a depth of 1750 m, and this may mostly be the result of loss of head when the caldera lake drained.

## ACKNOWLEDGEMENTS

The authors wish to thank F. Goff, P Dixon, D. Janecky and J. Moore for stimulating discussions and critical reviews of earlier versions of this paper. W. Zaelke and K. Beebe drafted the figures. This work was supported under the auspices of the United States Department of Energy/Office of Basic Energy Sciences. We are especially grateful to E.T.C Spooner and C. Bray for their hospitality during the PACROFI III meeting in Toronto and for organizing a well run conference.

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Table 1. Summary of all inclusion measurements, Sulphur Springs hydrothermal system.  
P=Primary, PS=Pseudosecondary, S=Secondary, QTZ=Quartz, CC=Calcite,  
EPI=Epidote, FLR=Fluorite, SL=Sphalerite

Sample	Mineral	Type	Number of Measurements	Th, degrees C	T <sub>mICE</sub> , degrees C	Salinity, equiv. wt.% NaCl
VC2A 96	FLR	P	39	154.9-196.8	-0.15- -2.40	0.26-4.08
VC2A 107	QTZ	P	37	198.4-278.0	-1.30- -3.40	2.30-5.50
VC2A 173	QTZ	P	28	197.1-286.4	-1.10- -2.20	1.90-3.70
VC2A 192	QTZ	P	32	201.2-258.9	-1.30- -2.20	2.30-2.37
VC2A 277	QTZ	P	26	183.9-277.0	-0.02- -0.10	0.08-0.35
VC2A 313	QTZ	P	20	198.4-294.6	0.00- -0.20	0.00-0.40
VC2A 425	SL	P	1	217.6		
VC2A 425	QTZ	P	38	192.7-276.5	-0.15- -2.35	0.26-3.90
VC2A 555	FLR	P	12	155.9-202.3	0.00- -0.05	0.00-0.08
VC2A 645	FLR	P	6	194.4-197.5	-0.50- -0.55	0.87-0.98
VC2A 1108	FLR	P	27	180.5-210.6	0.00- -0.45	0.00-0.78
VC2A 1137	CC	P	16	213.9-314.8	0.00- -0.60	0.00-1.05
VC2A 1485	CC	P	8	199.2-228.3	-0.30- -0.45	0.52-0.78
VC2A 1485	SL	P	9	224.6-319.4	-0.20- -0.90	0.35-1.56
VC2A 1485	QTZ	P	16	209.0-294.7	-0.20- -1.00	0.35-1.73
VC2A 96	FLR	S	3	133.5-143.7		
VC2A 277	QTZ	S	2	175.1-165.4	-0.10- -0.15	0.17-0.26
VC2A 555	FLR	S	21	157.1-182.4	0.00- -1.08	0.00-1.80
VC2A 645	FLR	S	5	161.3-180.2	-0.20- -0.50	0.35-0.87
VC2A 1108	FLR	S	19	150.6-182.9		
VC2B 656	CC	P	8	213.9-218.7	-0.10- -0.20	0.17-0.35
VC2B 757	QTZ	P	38	198.0-269.6	0.00- -0.25	0.00-0.44
VC2B 932	QTZ	P	33	209.9-262.8	0.00- -0.05	0.00-0.04
VC2B 1246	FLR	P	11	188.2-212.0	-0.20- -0.40	0.35-0.7
VC2B 1322	FLR	P	1	219.0		
VC2B 2183	CC	P	21	215.5-236.2	-0.20- -0.30	0.35-0.53
VC2B 2183	FLR	P	14	184.4-193.8	-0.40	0.70
VC2B 3017	CC	P	31	216.8-226.4	0.00- -0.25	0.00-0.44
VC2B 4565	CC	P	36	258.6-313.0	-1.70- -3.10	2.88-5.10
VC2B 4755	QTZ	P	37	266.7-329.6	-1.00- -2.00	1.89-3.37
VC2B 5237	EPI	P	1	292.4		
VC2B 5237	QTZ	P, PS	24	269.5-334.4	-1.00- -2.50	1.89-4.07
VC2B 5533	QTZ	P	40	238.1-302.0	-0.35- -1.50	0.58-2.5
VC2B 5661	FLR	P, PS	1	232.4-319.0	-0.55- -1.03	0.91-1.70
VC2B 1246	FLR	S	59	148.6-181.4	-0.10- -0.20	0.17-0.35
VC2B 1322	FLR	S	21	155.9-187.1	-0.10- -0.20	0.17-0.35
VC2B 2183	FLR	S	14	174.2-179.9	-0.40- -0.50	0.70-0.87

Table II. Average fluid inclusion Th and salinities that illustrate temporal and spatial variation in trapped fluids.

Depth/Host Rock	Early Minerals	Late Minerals	Ave. Th, degrees C	Salinity, equiv. wt.% NaCl
VC-2A				
0-130 m, Tuffs	Quartz		220	2.2
346-452 m, Tuffs	Quartz		235	0.74
347 m, Tuffs	Calcite		274*	0.51
425 m, Tuffs	Sphalerite		235	0.90
452 m, Tuffs	Calcite		206	0.64
0-338 m, Tuffs		Fluorite	190	0.90
VC-2B				
0-666 m, Tuffs	Quartz, Calcite		220	0.19+
920-1762 m, Sandstone, Limestone, Quartz Monzonite	Quartz, Calcite		290	2.40
0-666 m, Tuffs		Fluorite	190	0.52
1726 m, Quartz Monzonite		Fluorite	305	1.13

\* Boiling indicated, but large number of stretched inclusions.

+ Numerous steam condensate inclusions.

Table III. Analysis of Inclusion Volatiles.

Sample No.	VC2A-129		VC2A-339		VC2A-541		VC2A-1721	
	Analysis	Corrected Analysis	Analysis	Corrected Analysis	Analysis	Corrected Analysis	Corrected Analysis	
CO <sub>2</sub>	3.66	3.42	1.07	1.03	9.63	9.61	4.65	4.61
CH <sub>4</sub>	0.24	0.54	0.1	0.15	0.031	0.074	0.197	0.25
CO	0.2	0.2	0.1	0.1	0.037	0.037	0.062	0.062
CS <sub>2</sub>			0.0006	0.0006				
Ar	0.0014	0.0014	0.002	0.002	0.0002	0.0002	0.002	0.002
H <sub>2</sub> S	1.16	1.18	0.92	0.92	0.22	0.22	0.002	0.002
SO <sub>2</sub>			0.034	0.034	0.35	0.35		
He	0.00012	0.00012	0.00001	0.00001			0.00001	0.00001
N <sub>2</sub>	0.141	0.14	0.012	0.012	0.008	0.008	0.026	0.026
H <sub>2</sub>	1.17	0.000088	0.17	0.00011	0.17	0.000015	0.196	0.00005
C <sub>2</sub> H <sub>4</sub>	0		0.044	0.044	0.6	0.6		
C <sub>4</sub> H <sub>8</sub>			0.059	0.059	0.14	0.14		
C <sub>5</sub> H <sub>12</sub>	0.0066	0.0067						
C <sub>3</sub> H <sub>8</sub>	0.0099	0.01						
H <sub>2</sub> O	93.4	94.5	97.5	97.6	88.8	89	94.9	95.1

Table IV. Calculated concentrations of gaseous species in the aqueous phase when inclusions were trapped, compared to analyse of present day Valles thermal waters. The "y" is the fraction of vapor-filled inclusions, and "t" is average inclusion trapping temperature (see text for details.)

Sample No.	VC2A-129	VC2A-339	VC2A-541	VC2A-1721	Sulfur Springs (1)	VC2A (2)	Baca 4 (3)	Baca 24 (3)
CO <sub>2</sub> (mol.%)	0.39	0.19	0.93	0.47		0.79	0.23	0.1
CH <sub>4</sub>	0.013	0.0066	0.0014	0.0055		0.0036	0.00009	0.000009
Ar	0.00004	0.0000099	0.000043	0.000016		0.00019	0.000019	0.000013
H <sub>2</sub> S	0.32	0.086	0.054	0.00005		0.00056	0.0023	0.0008
N <sub>2</sub>	0.0018	0.00018	0.000078	0.00029		0.011	0.00081	0.00069
H <sub>2</sub>	0.0000018	0.0000031	0.00000022	0.00000086		0.0056	0.00015	0.00003
H <sub>2</sub> O	99.3	99.7	99.1	99.6				
y	0.03	0.02	0.025	0.03				
t(C)	215	220	200	210				
Composition of Gaseous Species								
CO <sub>2</sub> (mol.%)	53.8	67.2	94.4	98.8	97.9	97.2	98.5	98.4
CH <sub>4</sub>	1.8	2.33	0.14	1.15	0.1	0.044	0.039	0.0085
Ar	0.0055	0.0035	0.0044	0.003	n.r.	0.023	0.0083	0.013
H <sub>2</sub> S	44.1	30.4	5.48	0.011	0.4	0.69	0.99	0.78
N <sub>2</sub>	0.25	0.064	0.0079	0.061	1	1.4	0.35	0.68
H <sub>2</sub>	0.00025	0.0011	0.0000111	0.00018	0.03	0.69	0.065	0.032

(1) ref. Norman and Bernhart, 1983

(2) unpub. analysis of VC-2A gases obtained on 5/12/87 from 490 m. (1605 ft.), by C. Janik

(3) ref. Truesdell and Janik (1986)



## FIGURE CAPTIONS

Figure 1. Location map of the Jemez Mountains, Valles caldera (closed depression), and the Rio Grande rift. Regular stipple = Tertiary- Quaternary basin fill sediments; close-spaced stipple = Tertiary- Quaternary volcanic rocks; jackstraw = Precambrian rocks.

Figure 2. a. Location map of CSDP core holes VC-1 and VC-2 in the Valles caldera. Horse shoe-shaped feature just left of center is the area of intense surface hydrothermal alteration. b. Detailed location map of CSDP core holes VC-1 and VC-2A and VC-2B.

Figure 3. Conceptualized cross section of the Sulphur Springs hydrothermal area showing the configuration of the system based on drill hole data and temperature logs. Close-spaced, large point stipple is post-caldera ring fracture rhyolites. Unpatterned area is undivided caldera-fill pyroclastic and volcanoclastic rocks (mostly Quaternary), which includes the Bandelier Tuff. Close-spaced, fine point stipple is Tertiary volcanic and sedimentary rocks, including the Santa Fe Group. Brick pattern is Permian sandstone and shales (Yeso and Abo Formations) and Pennsylvanian limestone (Madera Limestone) and sandstone (Sandia Formation). Jackstraw is Precambrian granite and gneiss. Open dot pattern is the vapor zone overlying the liquid dominated reservoir. The Precambrian and basal portion of the Paleozoic section comprise a zone of fluid-filled, poorly-connected fractures.

Figure 4. Generalized paragenetic diagrams for core holes (a.) VC-2A and (b.) VC-2B.

Figure 5. a. Primary fluid inclusions in quartz from 84 m, VC-2A. Largest inclusion is 15  $\mu\text{m}$ . b. Coexisting liquid-rich and vapor-rich inclusions from 84 m, VC-2A. Largest inclusion is 18  $\mu\text{m}$ . c. Close-up of vapor-rich inclusion in (b). Vapor is >95% of the inclusion. d. Primary fluid inclusion in sphalerite from 452 m, VC-2A. Inclusion is 8  $\mu\text{m}$ .

Figure 6. a. Temperature versus depth for VC-2A fluid inclusions. Plotted on the figure is the boiling point curve for pure water set at the present surface elevation and the boiling point

curve for pure water raised 180 m; a mid-range value for the estimated depth of the caldera lake. b. Temperature log of VC-2A, September 18, 1987. c. Temperature versus depth for VC-2B. Plotted on the figure is the boiling point curve for pure water set to the present ground surface. d. Temperature log of VC-2B, April 6, 1989.

Figure 7. a. Salinity versus homogenization temperature for primary fluid inclusions, VC-2A  
b. Salinity versus homogenization temperature for primary fluid inclusions, VC-2B.

Figure 8 Temporal variation in salinity and temperature in an individual sample from 425 m, VC-2A.

Figure 9. Salinity versus homogenization temperature for the Sulphur Springs hydrothermal system.

Figure 10. Conceptualized cross section of the Sulphur Springs hydrothermal system based on fluid inclusion evidence. Paleo-boiling horizon is based on the maximum depth where coexisting liquid- and vapor-rich inclusions were noted. Paleo-isotherms are based on the average homogenization temperature for that particular depth interval. Note the 210°C paleo-isotherm is near the present day ground surface and the slight elevation in paleo-isotherms along the Sulphur Creek fault, suggesting a region of upwelling. Rock units are the same as those in Figure 3.

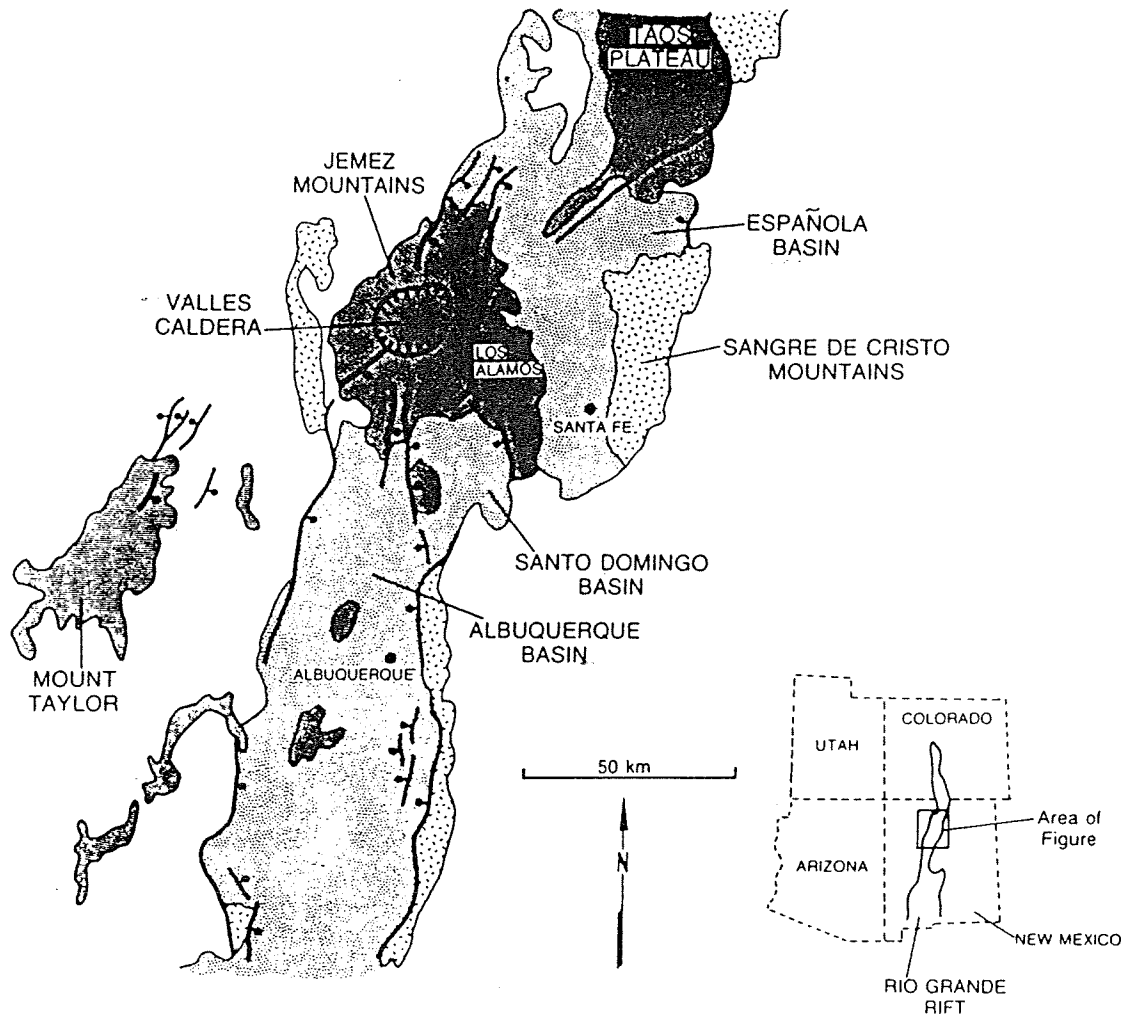
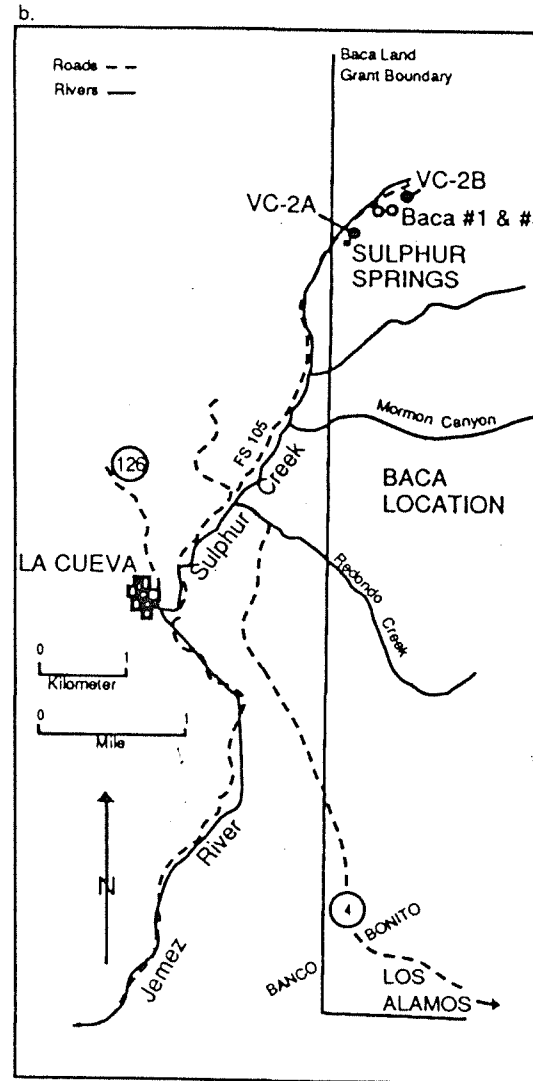
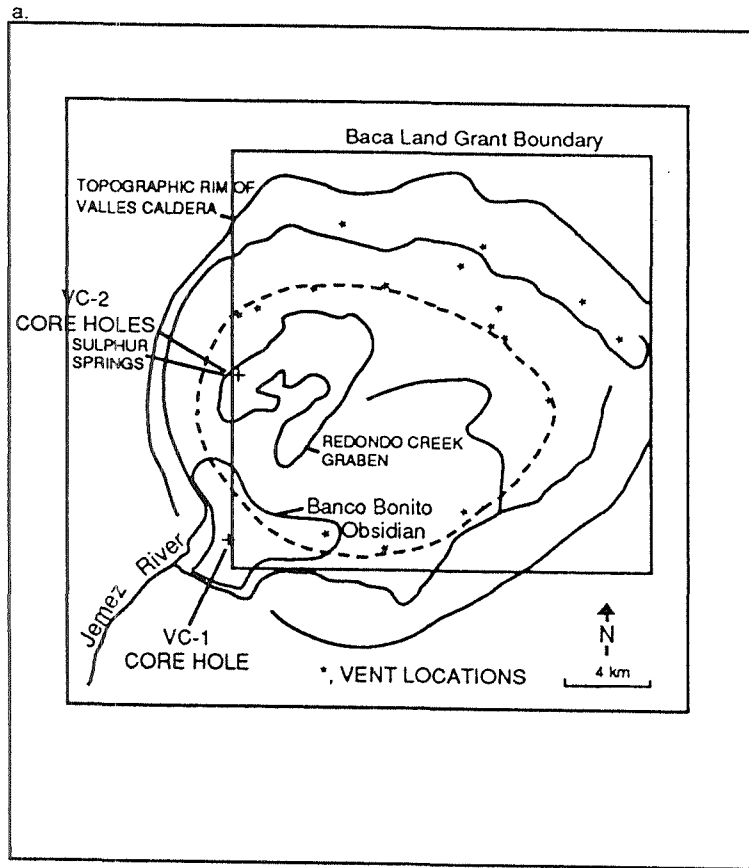


fig. 1

Fig. 2



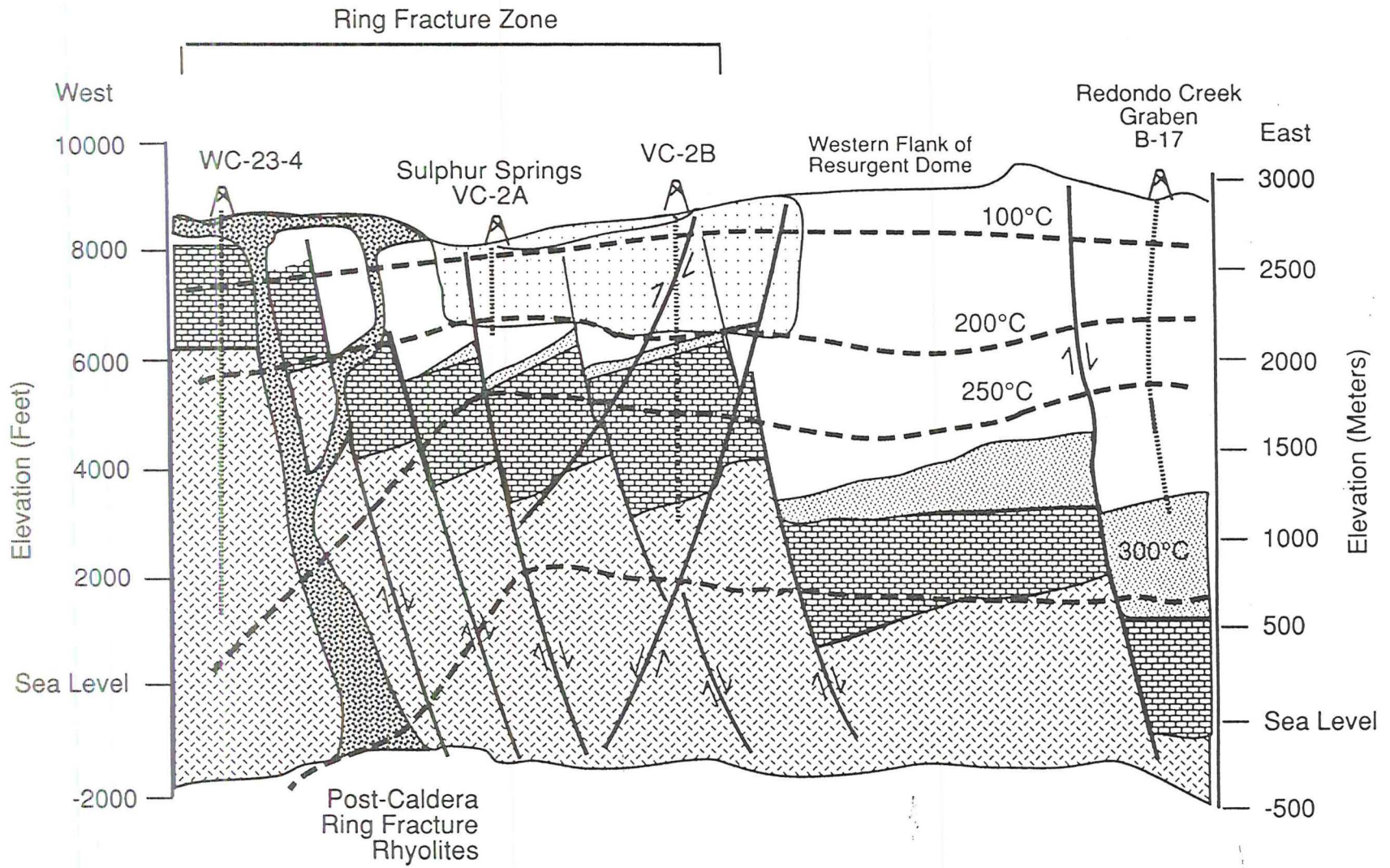


Fig. 3  
37

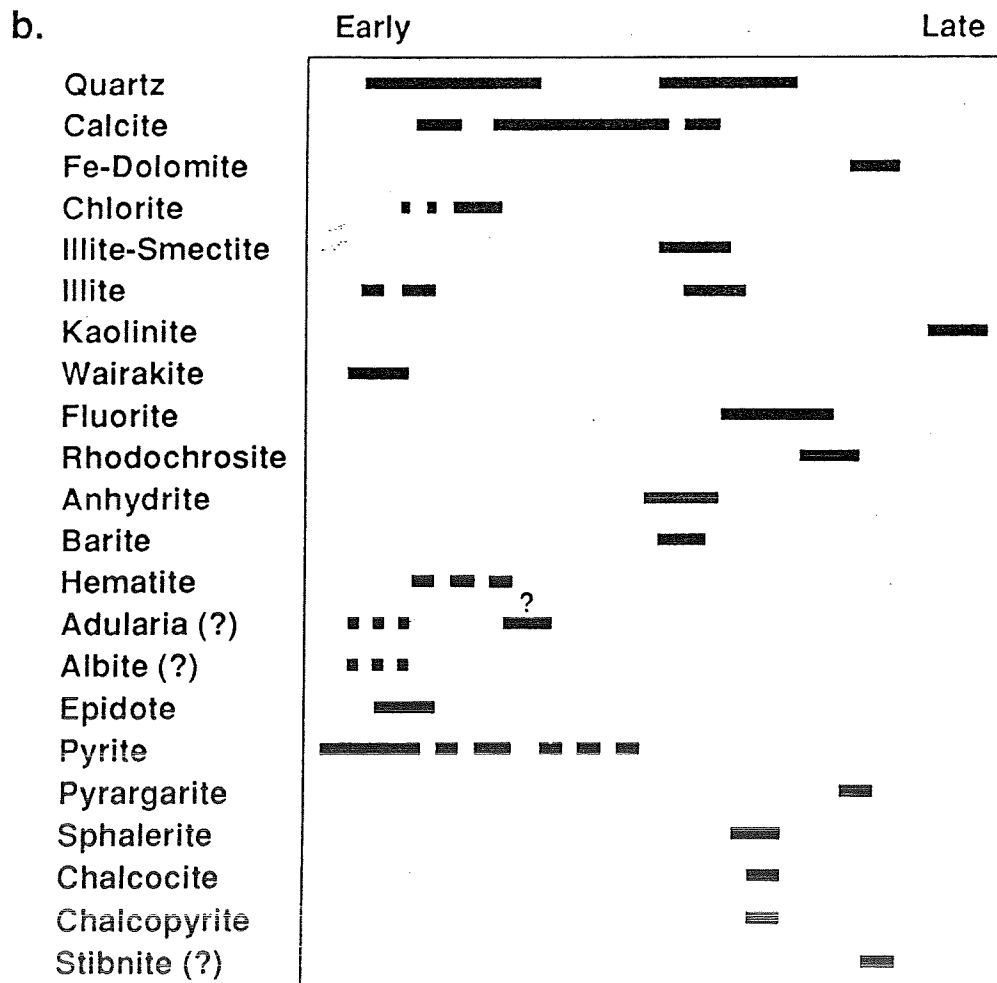
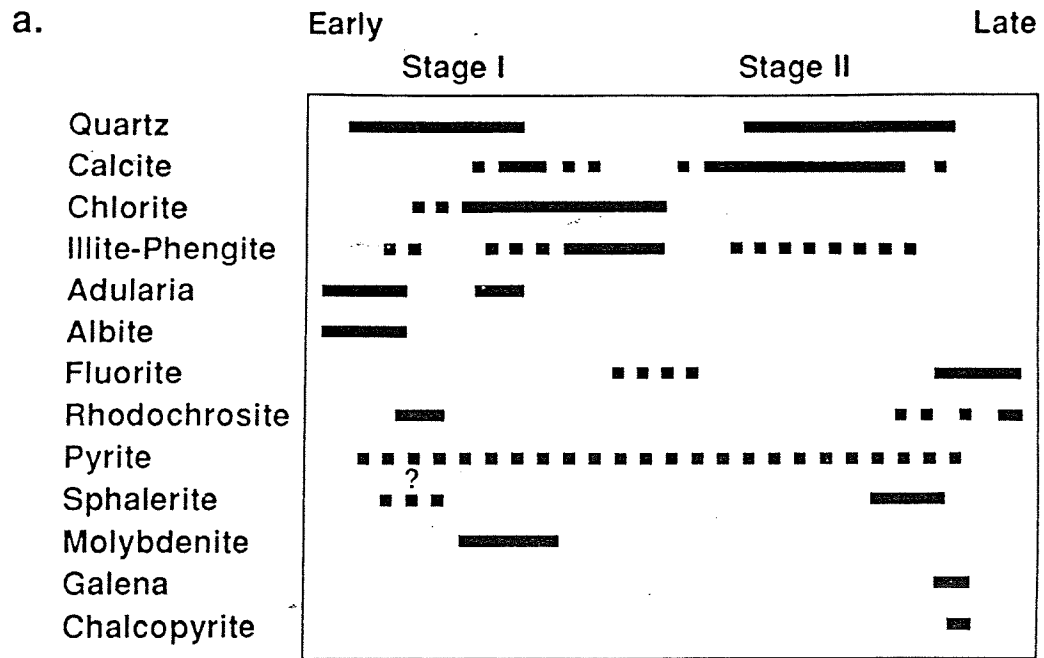


Fig. 4



Fig. 5a

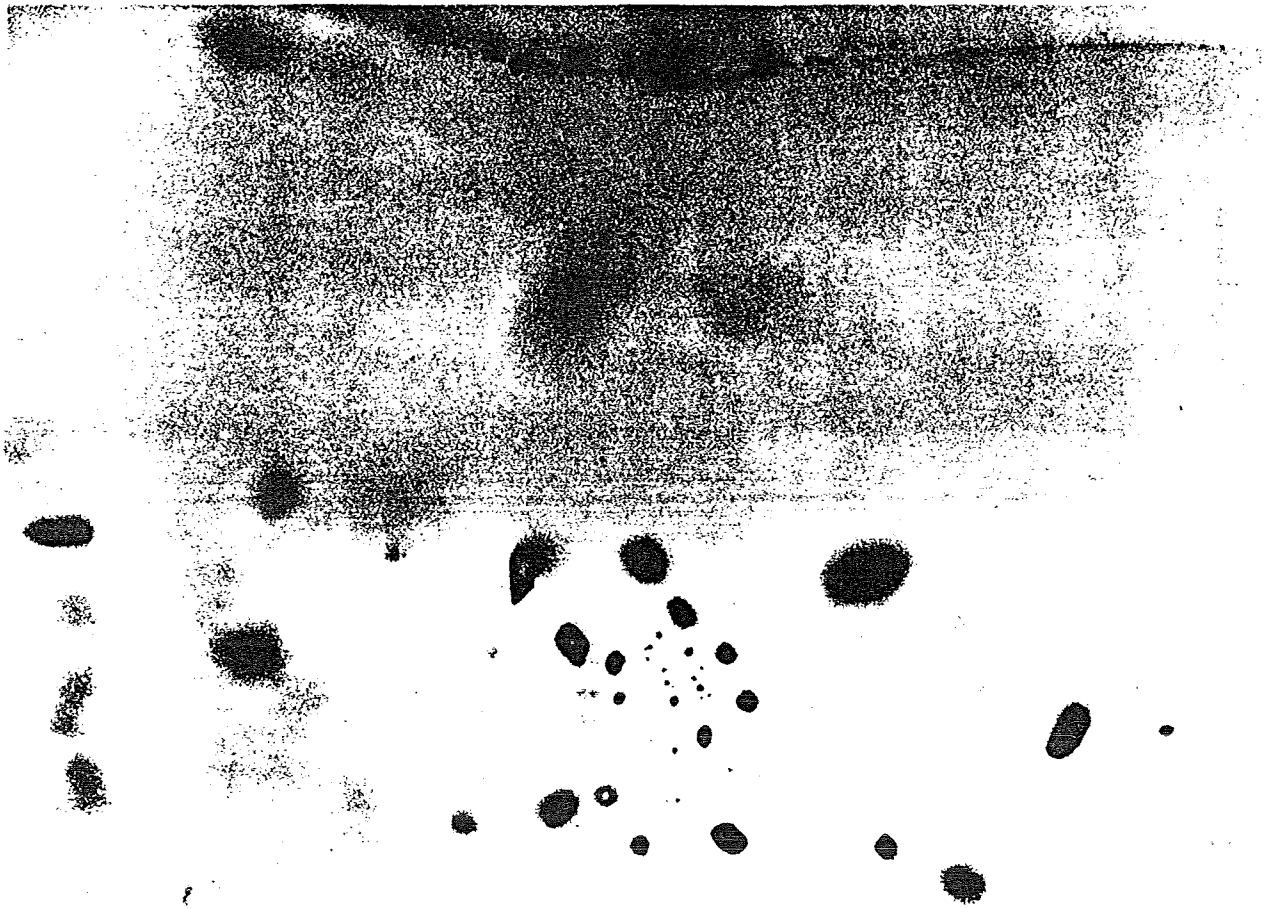


Fig. 5b



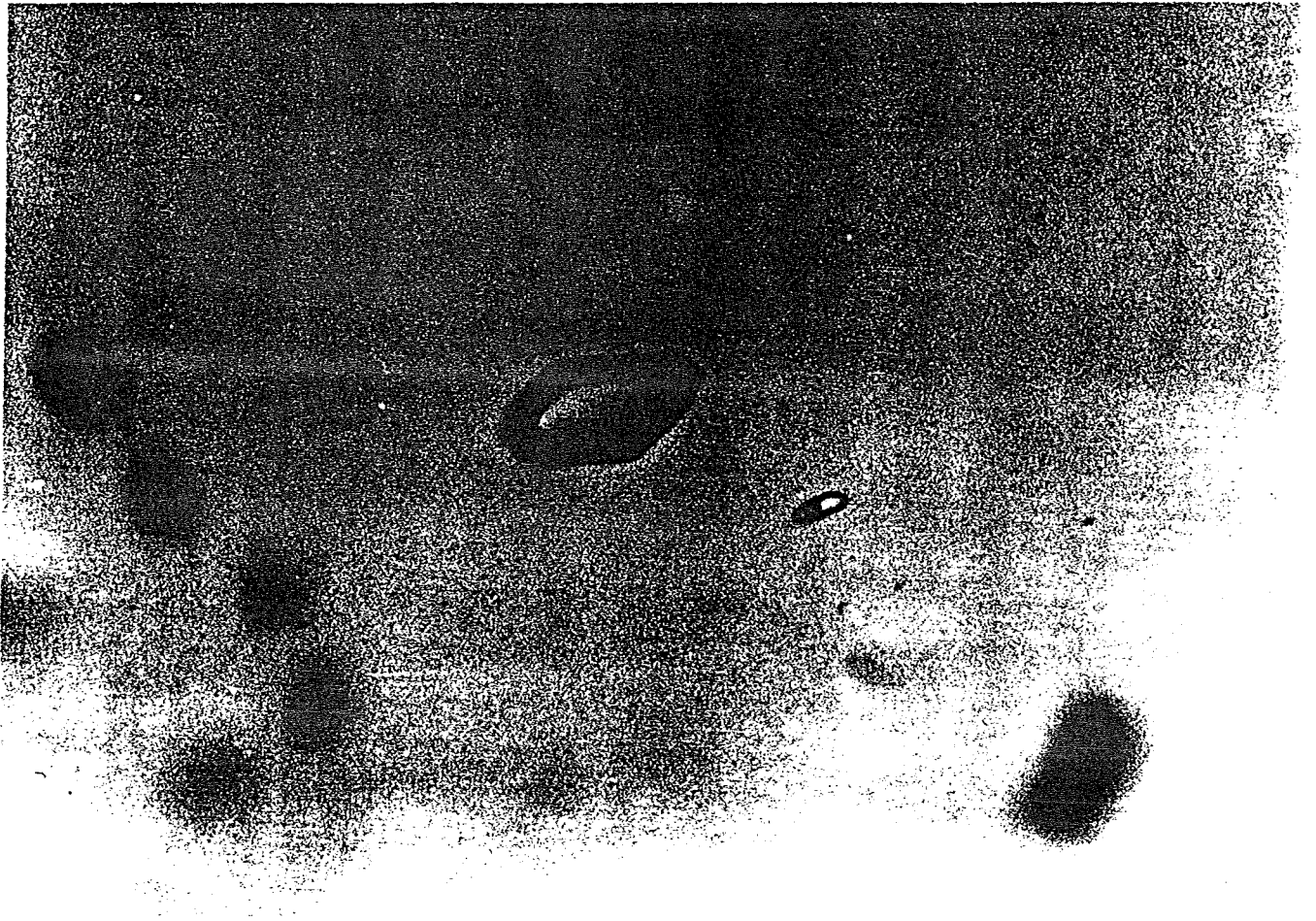


Fig. 5c

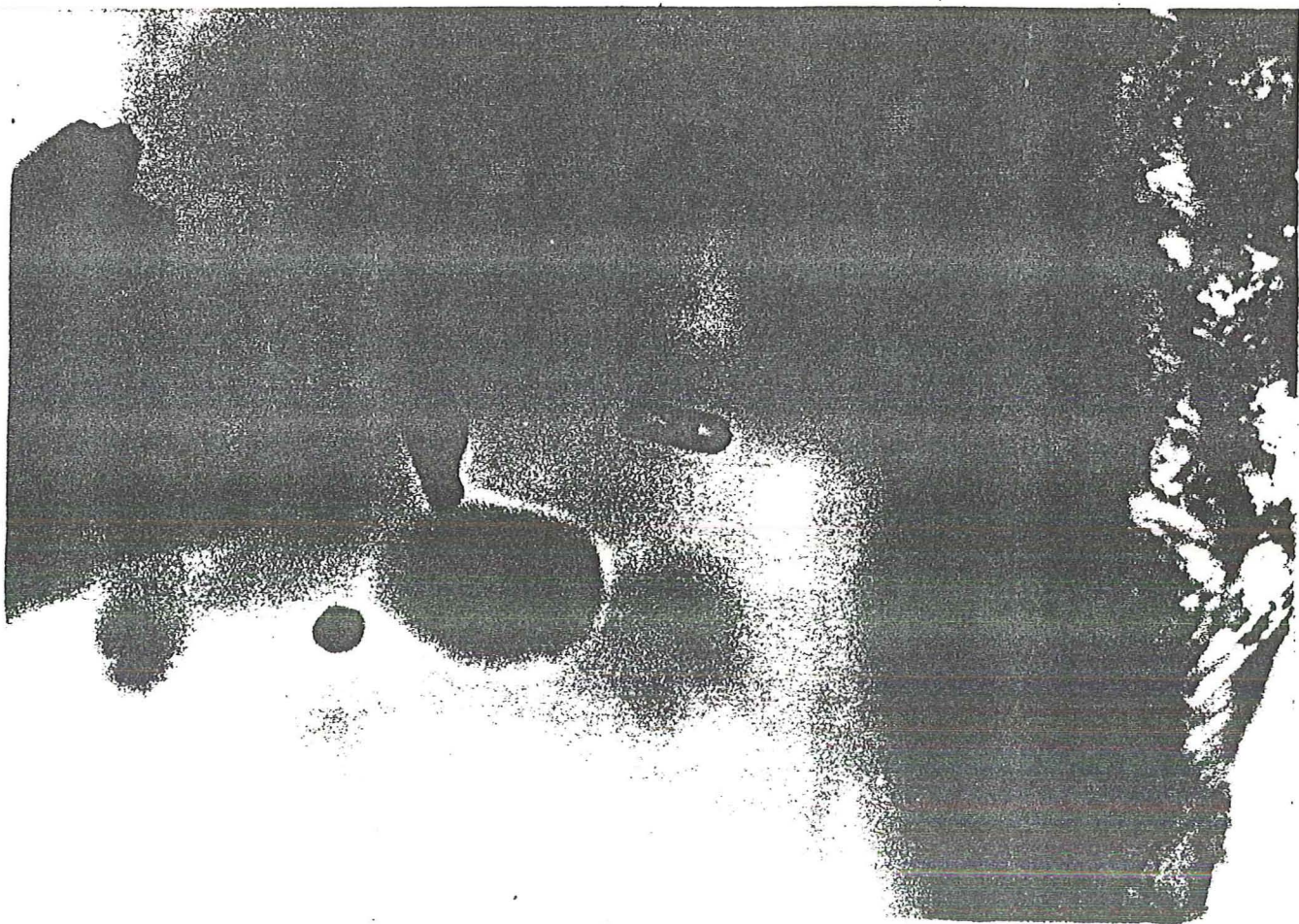


Fig. 5d

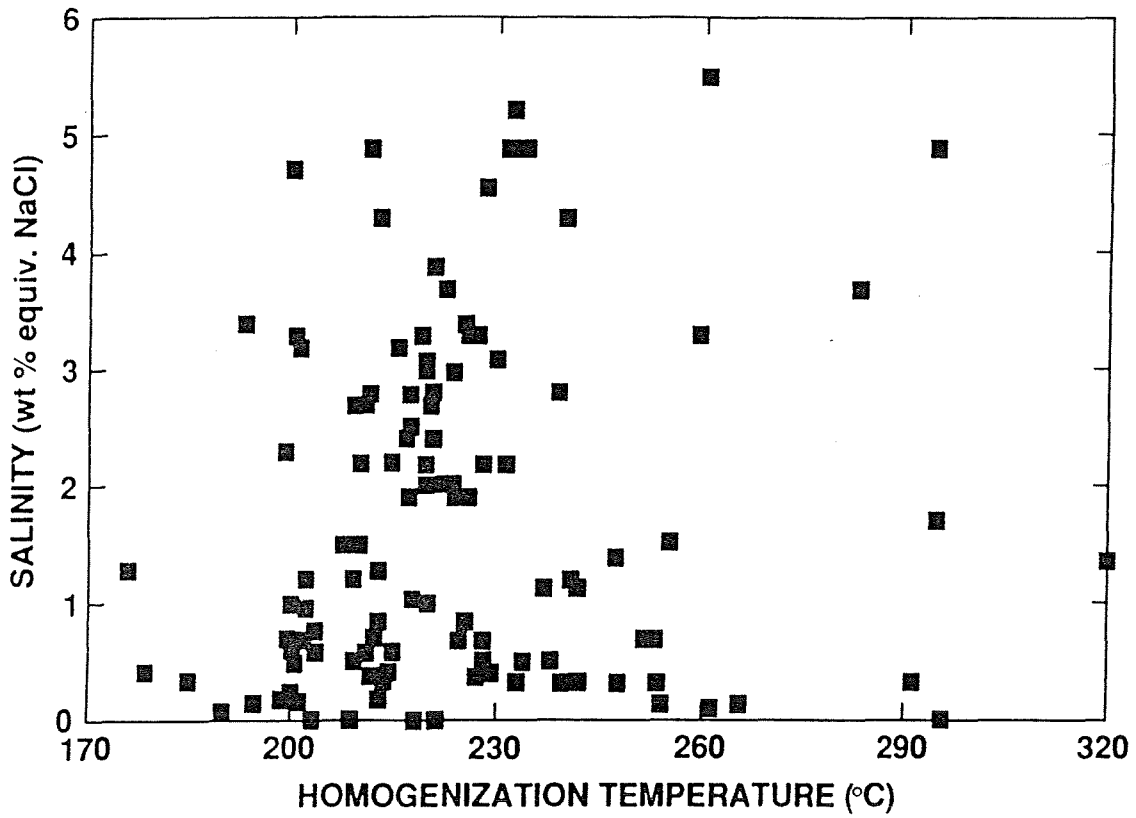
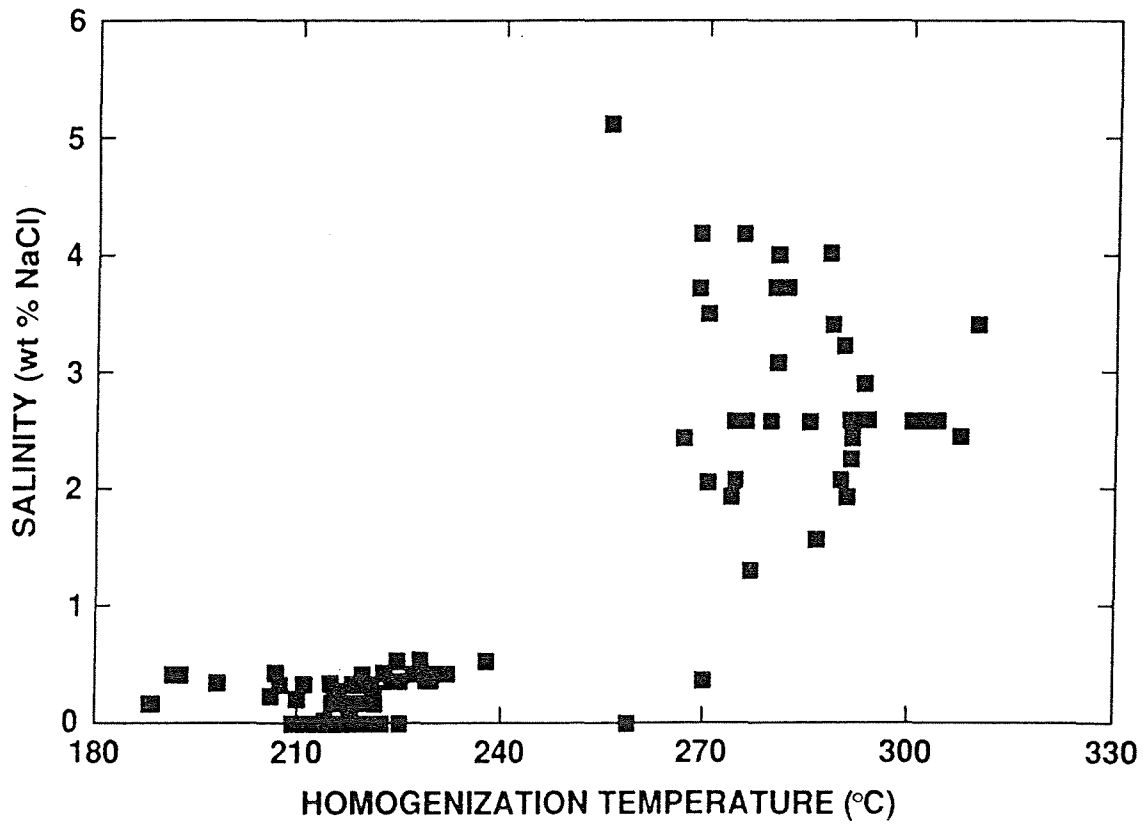


Fig. 6a



z  
Fig. 6b

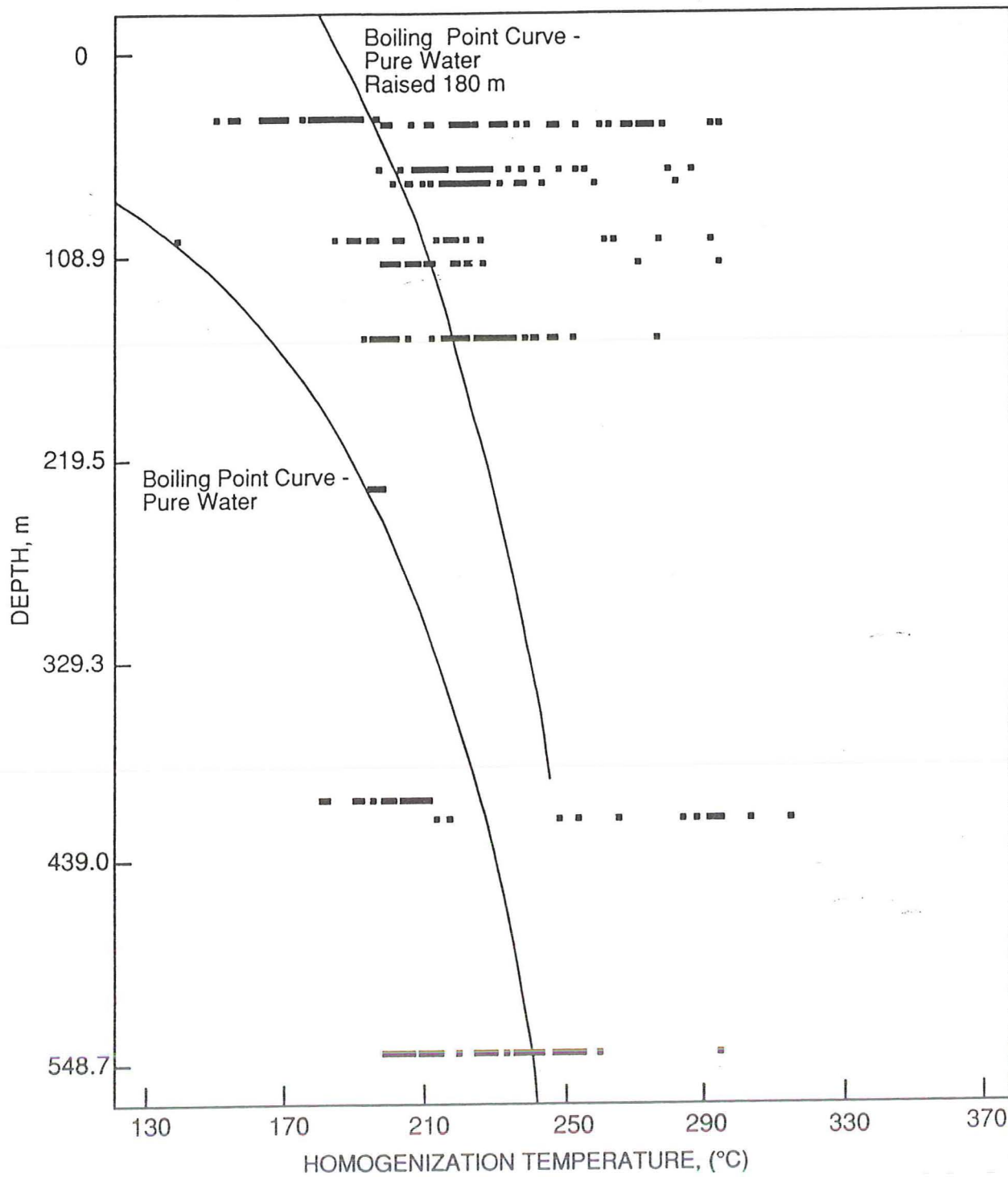


Fig. 7a

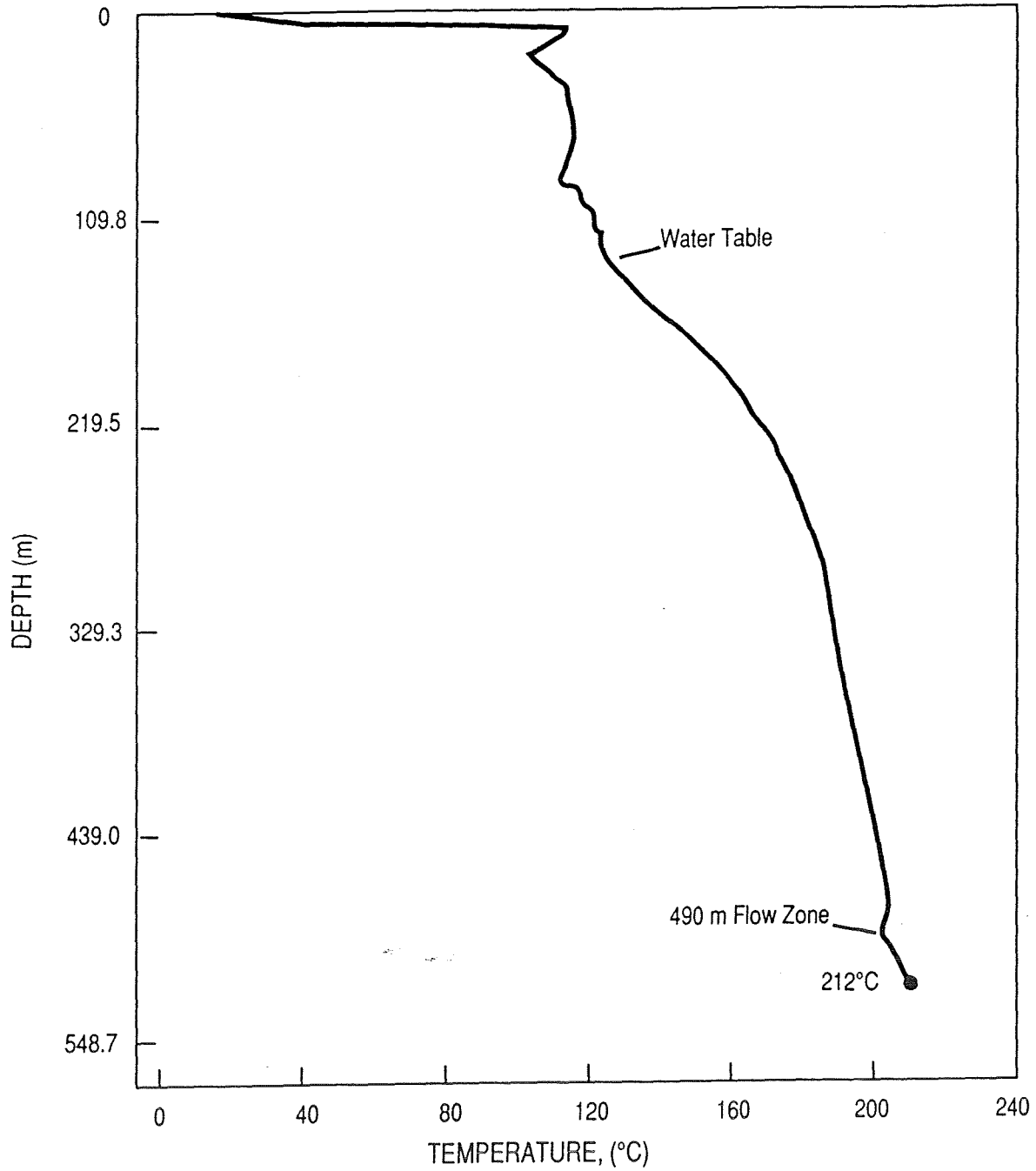


Fig. 7b

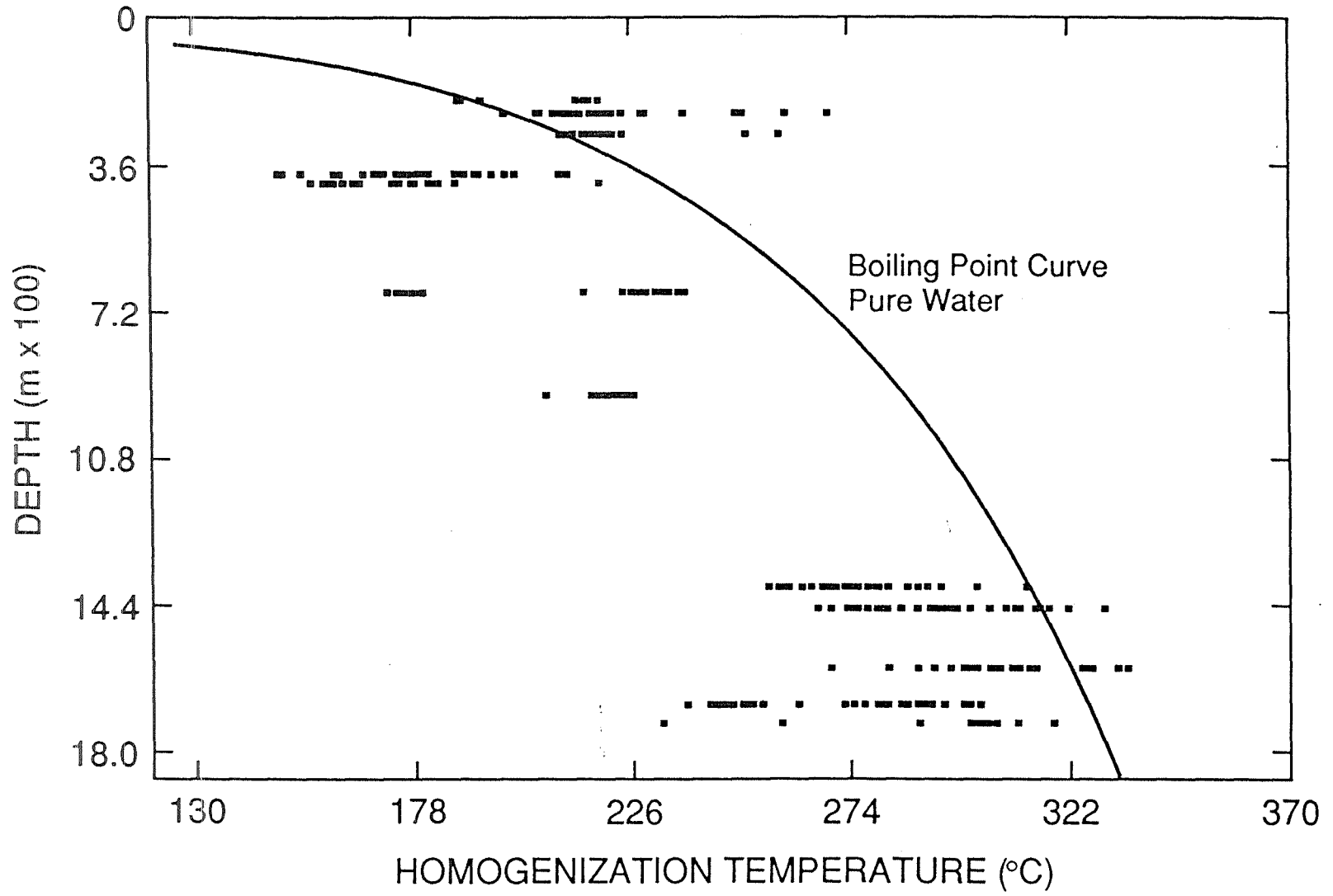


Fig. 7c  
47

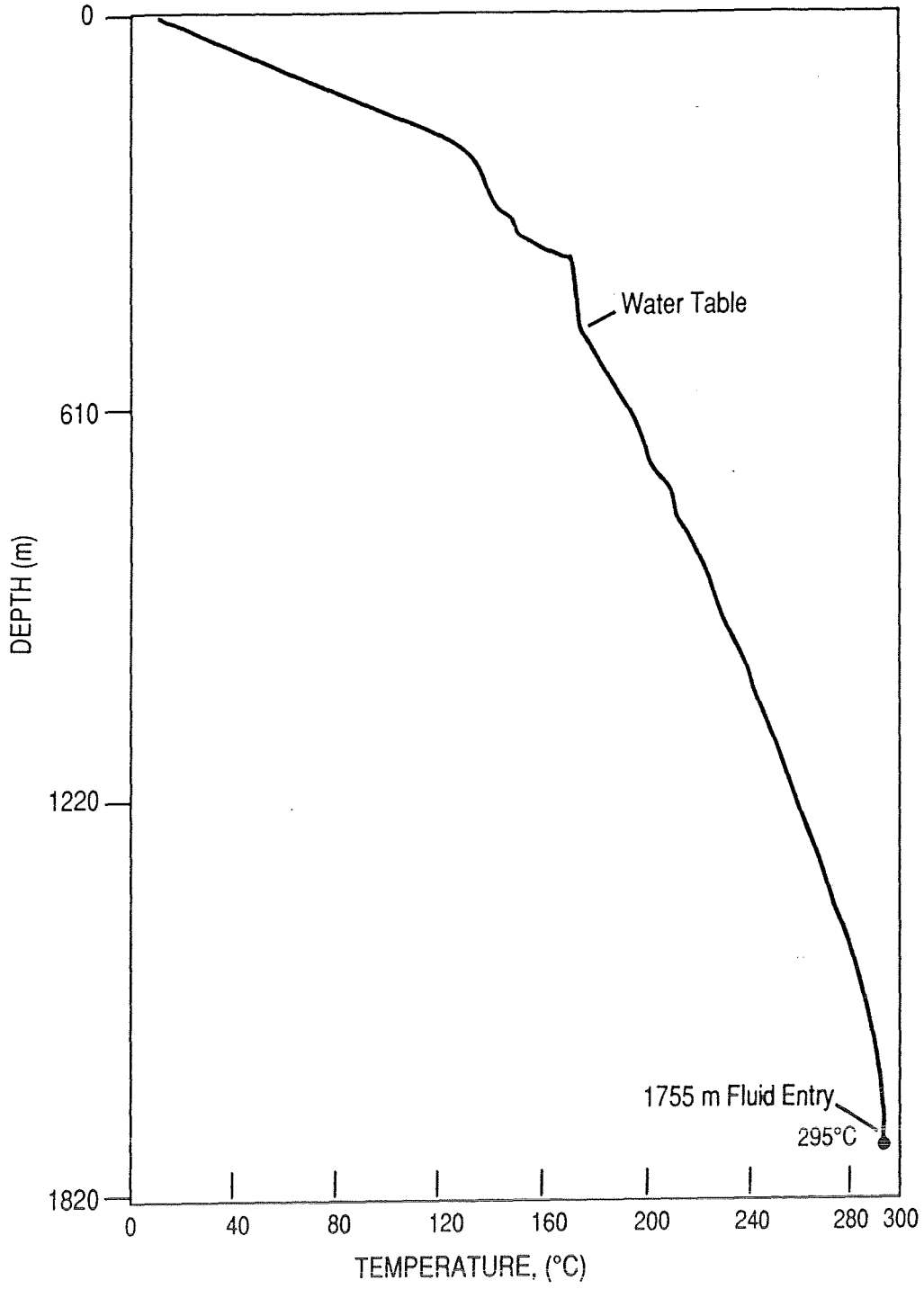


Fig. 7d



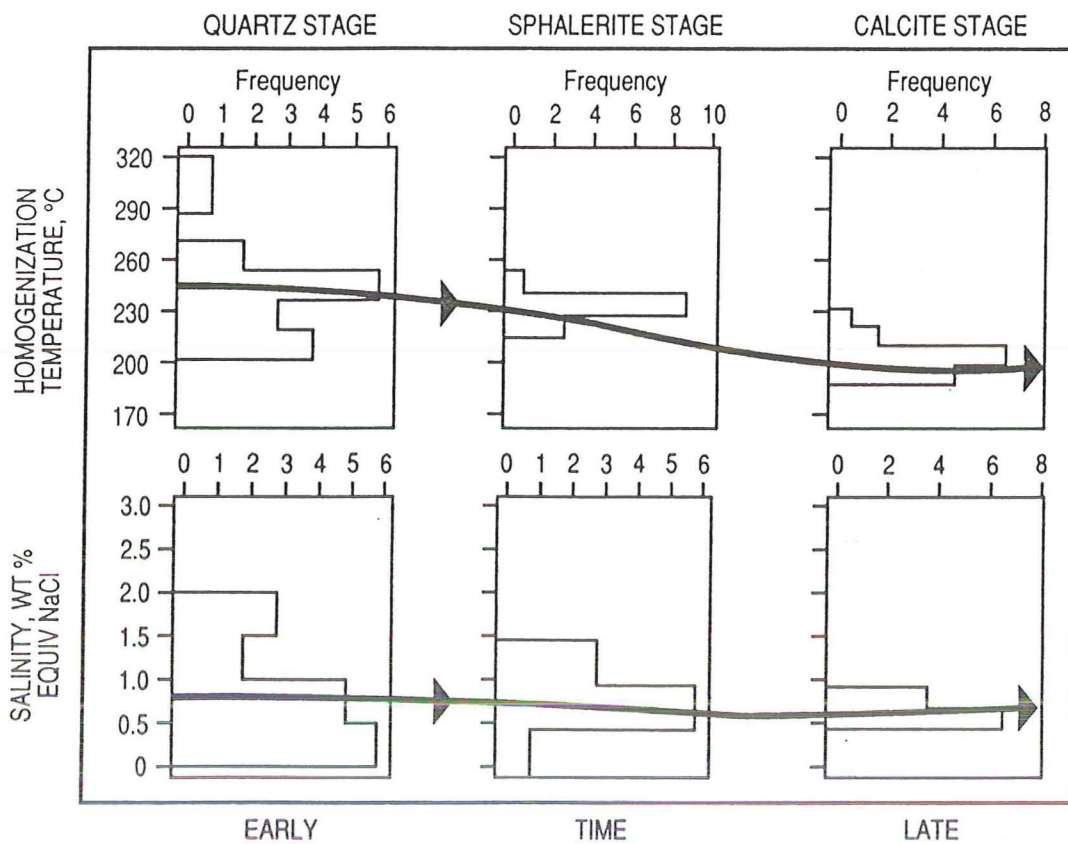
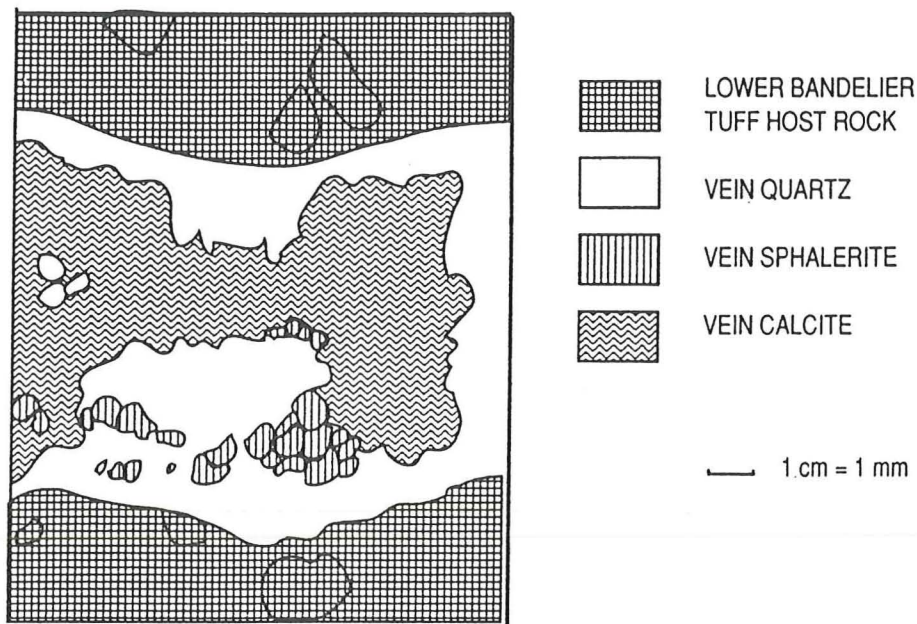


Fig. 8

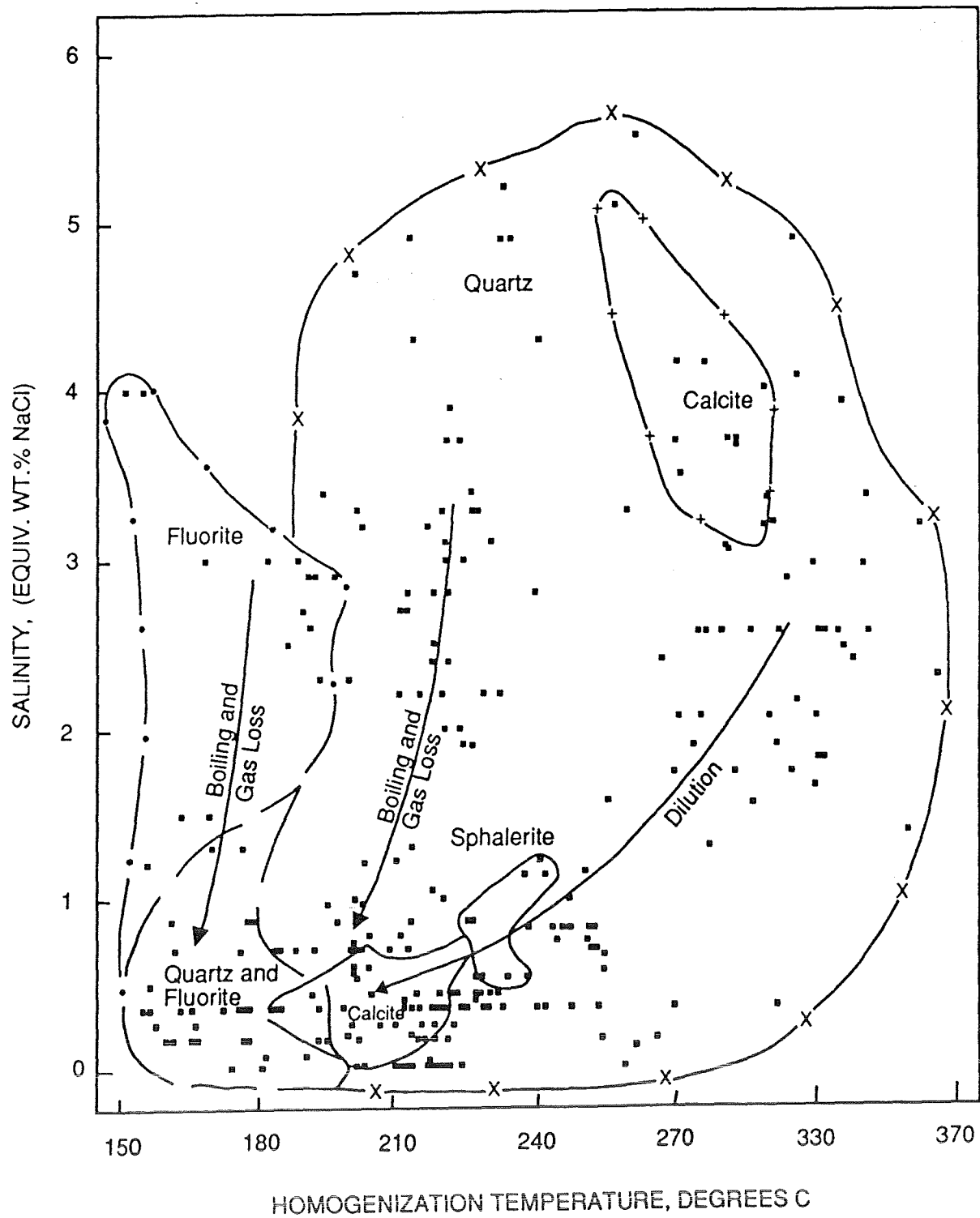


Fig. 9

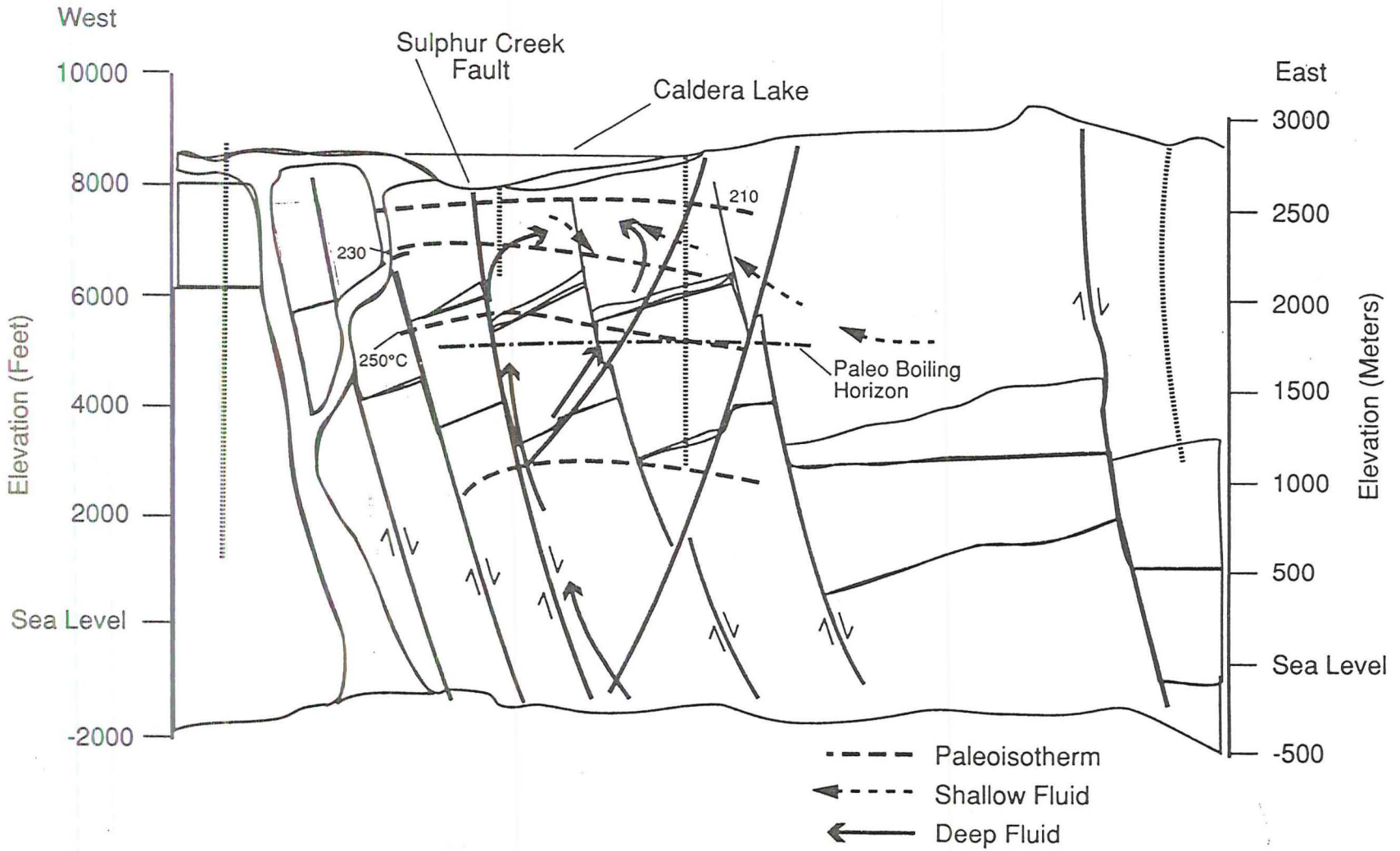


Fig. 10