

## Precious and Base Metal Deposition in an Active Hydrothermal System, Sulphur Springs Area, Valles Caldera, New Mexico

John A. Musgrave, INC-7, Los Alamos National Laboratory, Los Alamos, New Mexico 87545 and David I. Norman, Department of Geosciences, New Mexico Institute of Mining and Technology, Socorro, New Mexico, 87801

Development of the Valles caldera complex began as early as 1.75 Ma, when felsic ash flow tuffs of limited extent began erupting near the crest of the Jemez volcanic field. At 1.45 Ma, catastrophic eruption of at least 300 km<sup>3</sup> of felsic ignimbrite resulted in the Toledo caldera and emplacement of the Otowi Member of the Bandelier Tuff. A second major felsic pyroclastic eruption of similar volume at 1.12 Ma produced the Tshirege Member of the Bandelier Tuff and formed the now-exposed Valles caldera.

Sulphur Springs is the most active surface expression of hydrothermal activity in the Valles caldera with numerous hot springs, mud pots, and fumaroles, and is the site of Continental Scientific Drilling Program coreholes VC-2A and VC-2B. They were drilled in part to investigate ore deposition in an active hydrothermal system; a system which has been operating for the past 1.0 Ma. Corehole VC-2A (528 m TD) intercepted subore grade molybdenite (0.5 wt % MoS<sub>2</sub>) mineralization. Corehole VC-2B (1762 m TD) drilled 600 m to the northeast of VC-2A penetrated none of the unusual molybdenite mineralization.

Geothermal drilling and geologic mapping at Sulphur Springs has shown that the Sulphur Springs system is overlain by a vapor cap of several hundred meters thickness. Below this cap is a dilute, neutral-chloride, liquid dominated hydrothermal system, circulating primarily in the caldera-fill ignimbrites. The vapor-dominated cap has evolved from a liquid-dominated precursor.

Host rocks to the mineralization in the Sulphur Springs area include Precambrian quartz monzonite, Pennsylvanian siliciclastic and carbonate units, Permian redbeds composed of sandstone and shale, Tertiary sandstone, and Pleistocene ignimbrite sequences. Rocks cored at Sulphur Springs are readily correlated with those exposed within and near the Valles caldera or penetrated by previous geothermal and scientific drill holes. The entire stratigraphic sequence has undergone varying degrees of fracturing of both tectonic and hydrothermal origin. The intensity of fracturing is strongly dependent on rock type and elevation in the Sulphur Springs system. Much of the ignimbrite sequence is strongly fractured and the Precambrian quartz monzonite is similarly though moderately fractured; however, the intervening Paleozoic sequence is only weakly fractured.

## HYDROTHERMAL ALTERATION

Hydrothermal alteration at Sulphur Springs reflects the intensity and distribution of fracturing and brecciation and host lithology. Accordingly, the ignimbrites and the Precambrian quartz monzonite are extensively altered, whereas the intervening Paleozoic section, with few exceptions, is unaltered. Presumably the shales and the marbleized limestone of the Paleozoic rocks act as an aquitard to the hot hydrothermal fluids.

At the top of the system, the alteration is characterized by a surficial advanced argillic assemblage of illite, montmorillonite, quartz, kaolinite, alunite, sulfur and lesser amounts of gypsum, alunogen ( $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ ), halotrichite ( $\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ ), rozenite ( $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ ), and szomolnokite ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ). 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 is moderately to strongly chlorite-sericitized. The propylitic assemblage in the Pennsylvanian section contains varying amounts of illite, chlorite, epidote, wairakite, kaolinite, calcite and rectorite.

#### VEIN MINERALIZATION AND PARAGENESIS

Twenty-six gangue and ore minerals have been identified by optical microscopy, X-ray diffraction, and SEM/EDS scans. 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 (tetradymite?). Most vein minerals form fine- to coarse-grained intergrowths of subhedral to euhedral grains. Small (0.5 to 1 mm) epitaxial cappings of euhedral sulfides are present on the terminations of quartz and calcite. Vein fillings can be complete with the entire fracture filled to partially filled with abundant open spaces to fractured rock with sparse secondary mineralization.

Two stages of mineralization are recognized in VC-2A: Stage I 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. Sphalerite color ranges from colorless to honey yellow, and it displays no color zonation. Stage II is characterized by euhedral to subhedral quartz and calcite, sphalerite, pyrite, galena, chalcopyrite, and late fluorite and rhodochrosite.

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.

GENERALIZED PARAGENETIC DIAGRAM, VC-2A

	EARLY	STAGE I	STAGE II	LATE
QUARTZ	-----		-----	
CALCITE		- - - - -	- - - - -	-
CHLORITE		- - - - -		
ILLITE/PHENGITE	- -	- - - - -	- - - - -	
ADULARIA	-----	----		
ALBITE	-----			
FLUORITE			- - - -	-----
RHODOCHROSITE	----			- - - - -
PYRITE	- - - - -	- - - - -	- - - - -	- - - - -
SPHALERITE	- - -			- - - -
MOLYBDENITE		-----		
GALENA				---
CHALCOPYRITE				--

GENERALIZED PARAGENETIC DIAGRAM, VC-2B

EARLY

LATE

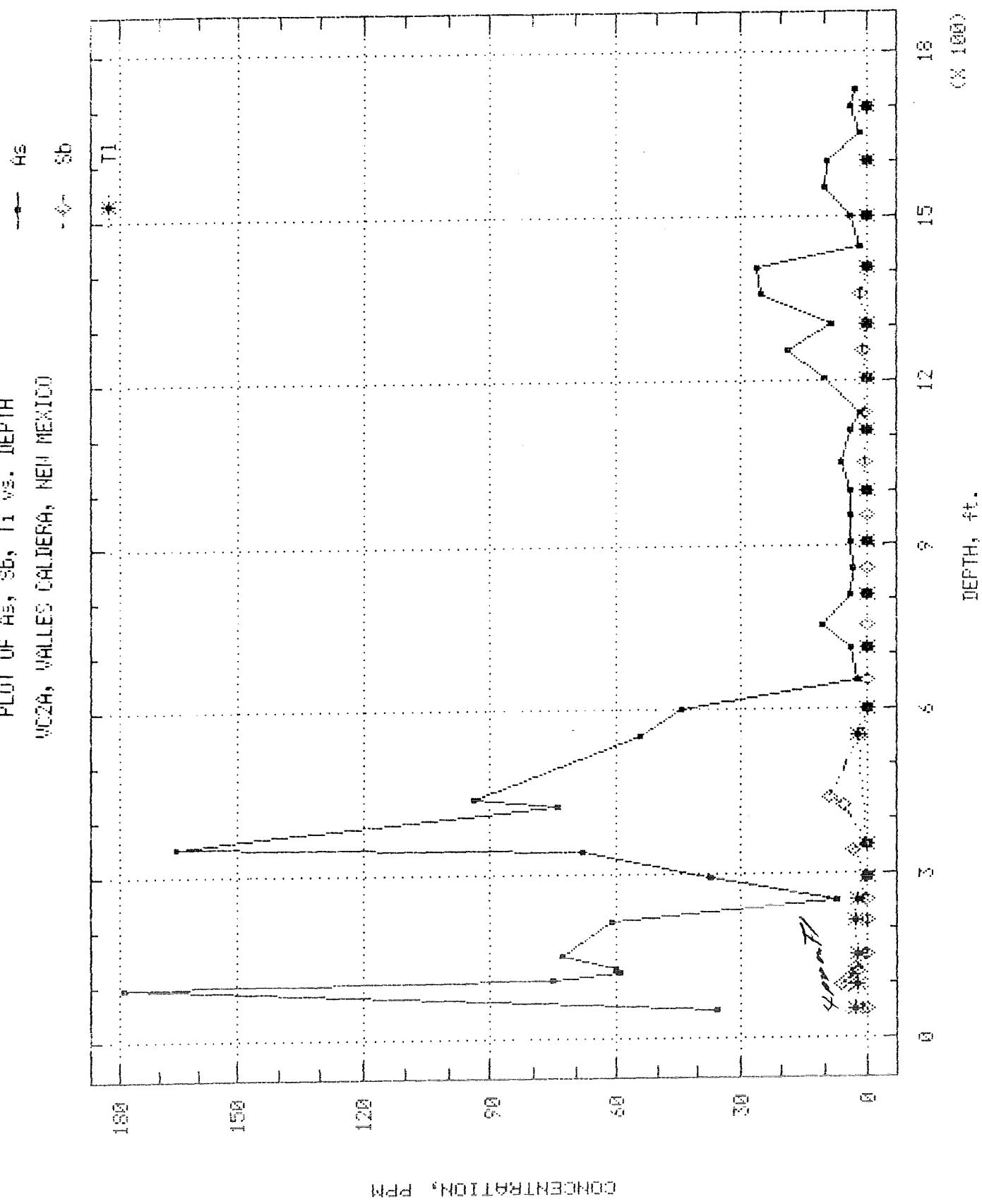
QUARTZ	-----	-----
CALCITE	----	-----
FE-DOLOMITE		----
CHLORITE	- - - -	
ILLITE-SMECTITE		-----
ILLITE	-- ---	-----
KAOLINITE		-----
WAIRAKITE	-----	
FLUORITE		-----
RHODOCHROSITE		-----
ANHYDRITE		-----
BARITE		-----
HEMATITE	-- - - -	?
ADULARIA (?)	- - -	-----
ALBITE (?)	- - -	
EPIDOTE	-----	
PYRITE	----- - - - -	
PYRARGARITE		---
SPHALERITE		----
CHALCOCITE		---
CHALCOPYRITE		---
STIBNITE (?)		---

#### TRACE ELEMENT STUDIES

Trace element studies were conducted in order to see if the Valles hydrothermal system followed the same elemental zonation observed in other active geothermal and some fossil hydrothermal systems. Thirty-four whole rock samples from VC-2A and 20 whole rock samples from VC-2B, and thirteen vein and wall rock sections from VC-2A were examined for their trace element content using the Los Alamos nuclear microprobe facility (PIXE). The whole rock and the PIXE analyses covered the entire drilled interval in VC-2A, from 30 m to 515 m. In general, the trace element chemistry follows the trends noted in other systems with the volatile elements and gold enriched in the highest elevations of the system along with gold and base metals show a crude increase with depth. Molybdenum is confined mostly to the upper 165 m.

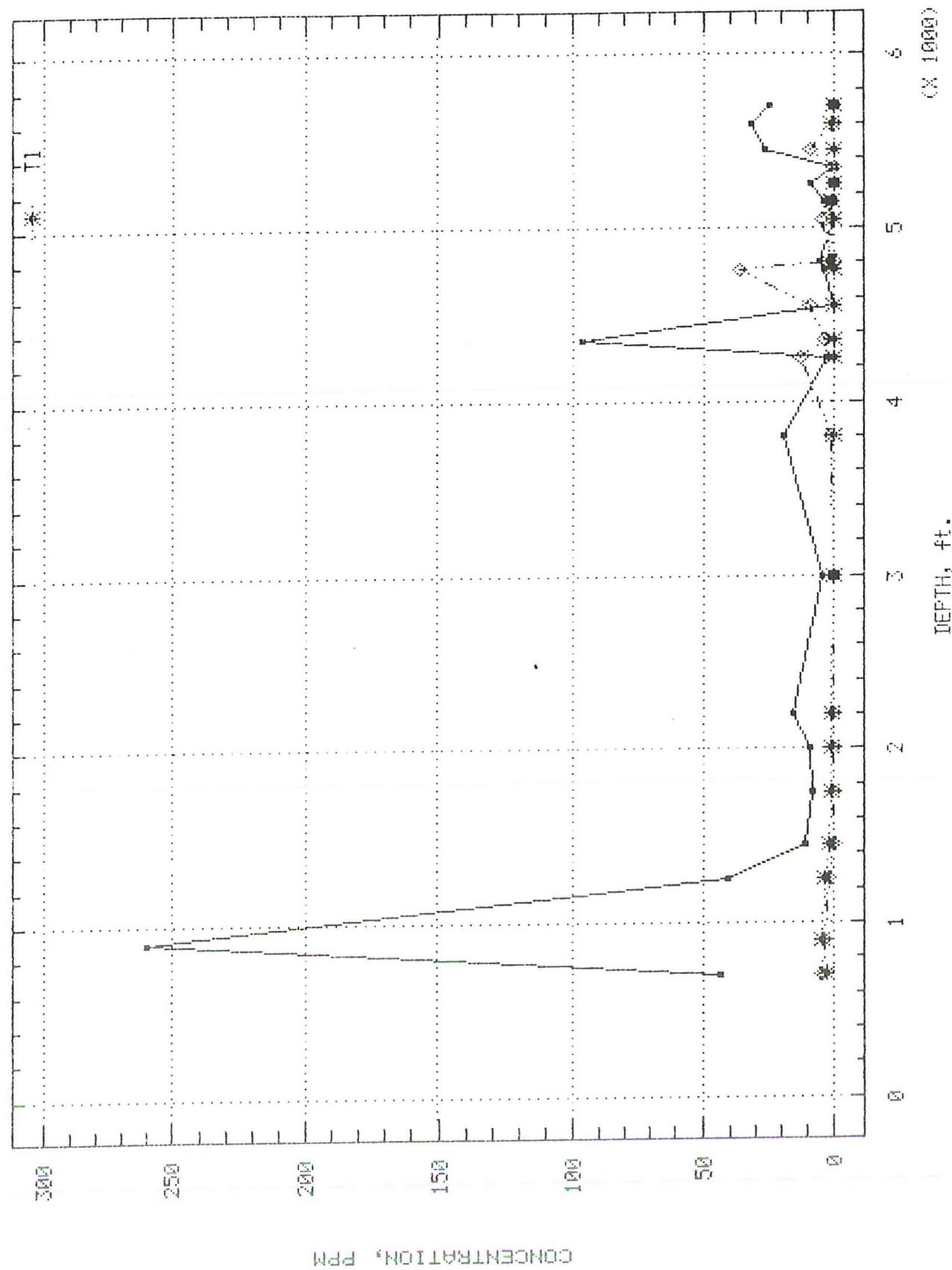
Paragenetic studies of the vein fillings in VC-2A indicates that Mo was deposited early. Analyses of vein and wall rock pyrites show that pyrite in the wall rock is more enriched in Mo than the vein pyrite. This data also suggests that the Mo was early paragenetically, and later vein filling stages were not as enriched in Mo as the early stages.

PLOT OF As, Sb, Ti vs. DEPTH  
HC2A, VALLES CALDERA, NEW MEXICO



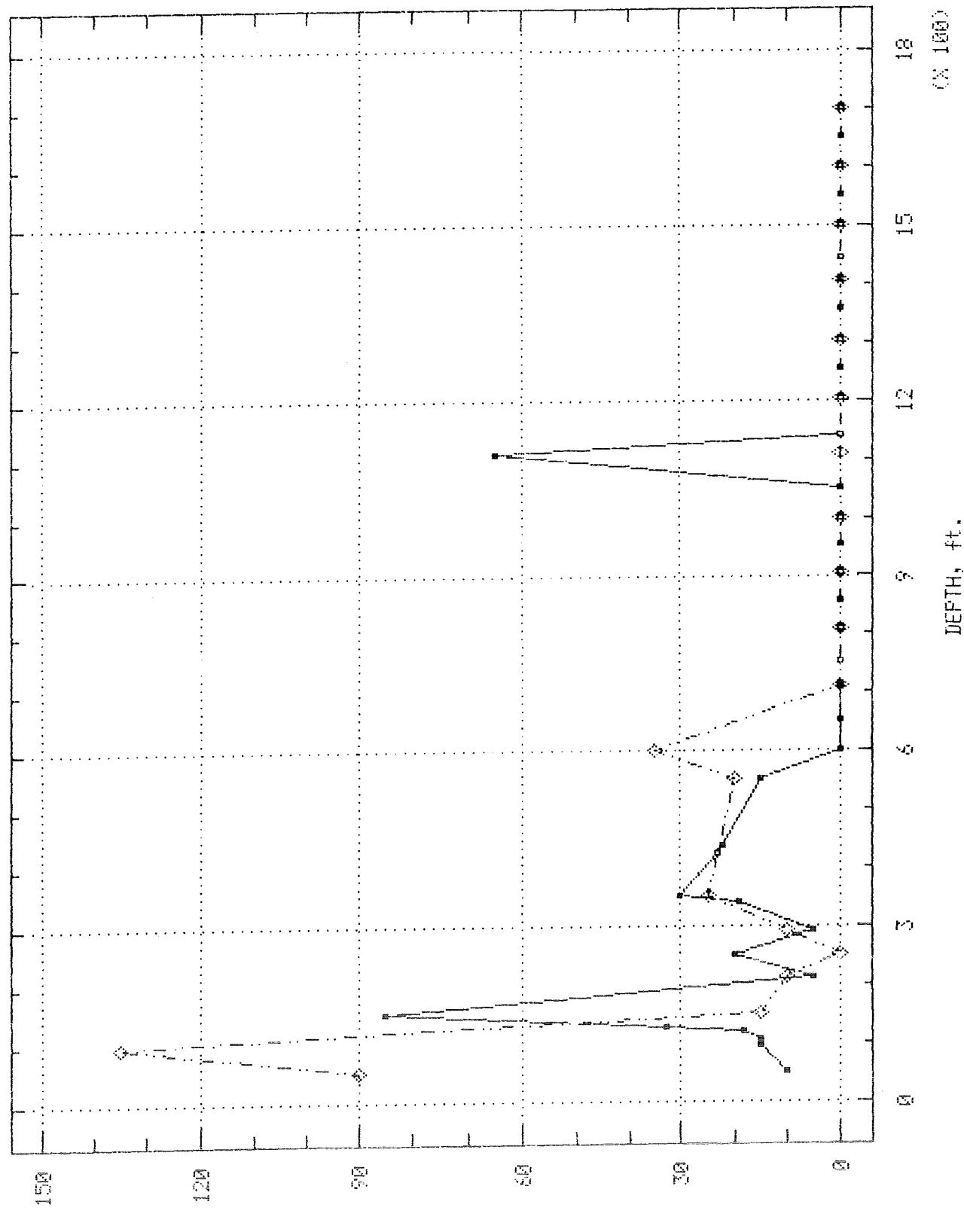
PLOT OF As, Sb, Tl vs DEPTH  
MC2B, VALLES CALDEERA, NEW MEXICO

—●— As  
—♦— Sb  
—◊— Tl



PLOT OF  $\text{Hg}$  and  $\text{Hg}_2$  vs. DEPTH  
MC2A, VALLES CALDERA, NEW MEXICO

$\text{Hg}$   
 $\text{Hg}_2$



CONCENTRATION, PPB

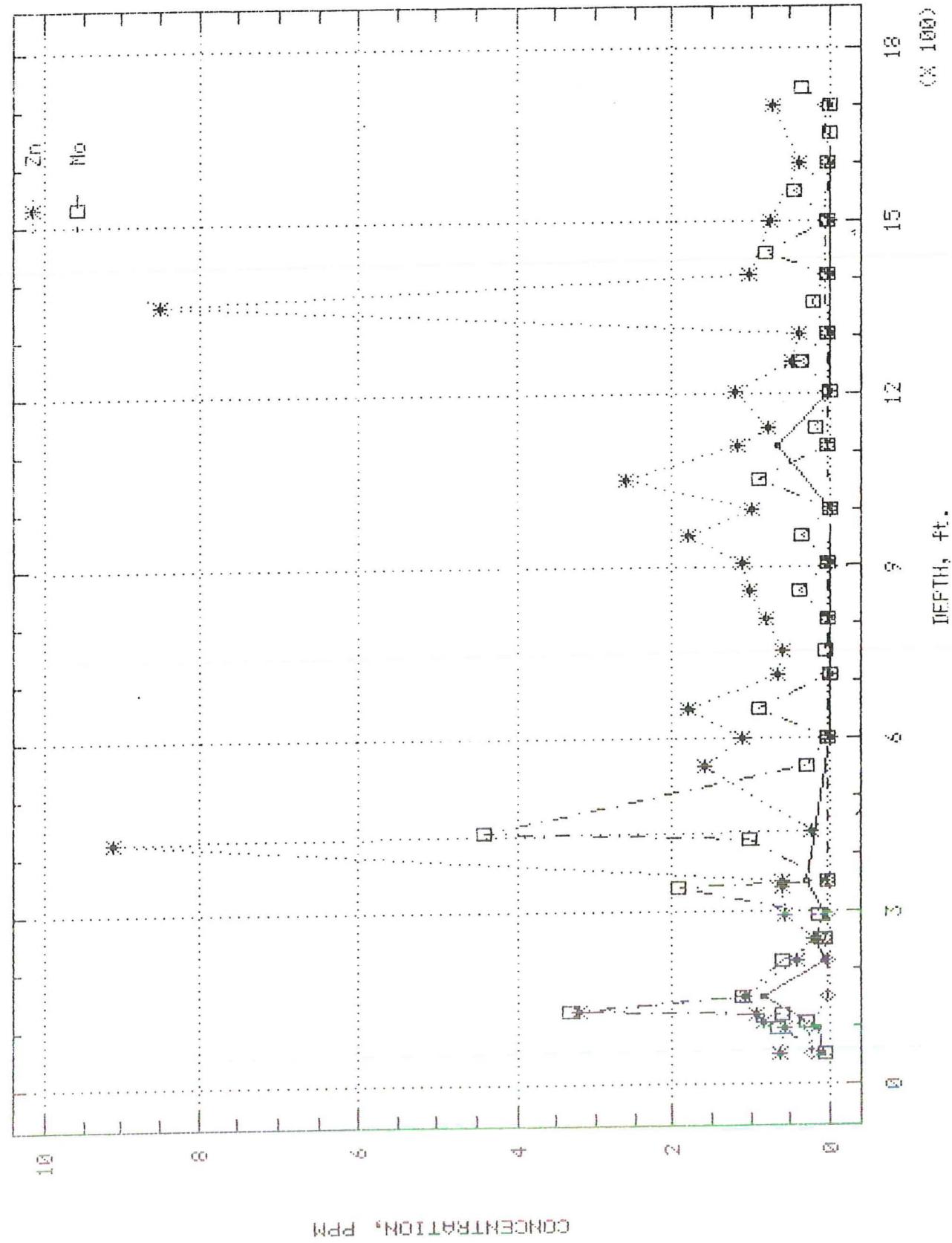
( $\times 1000$ )

DEPTH, ft.

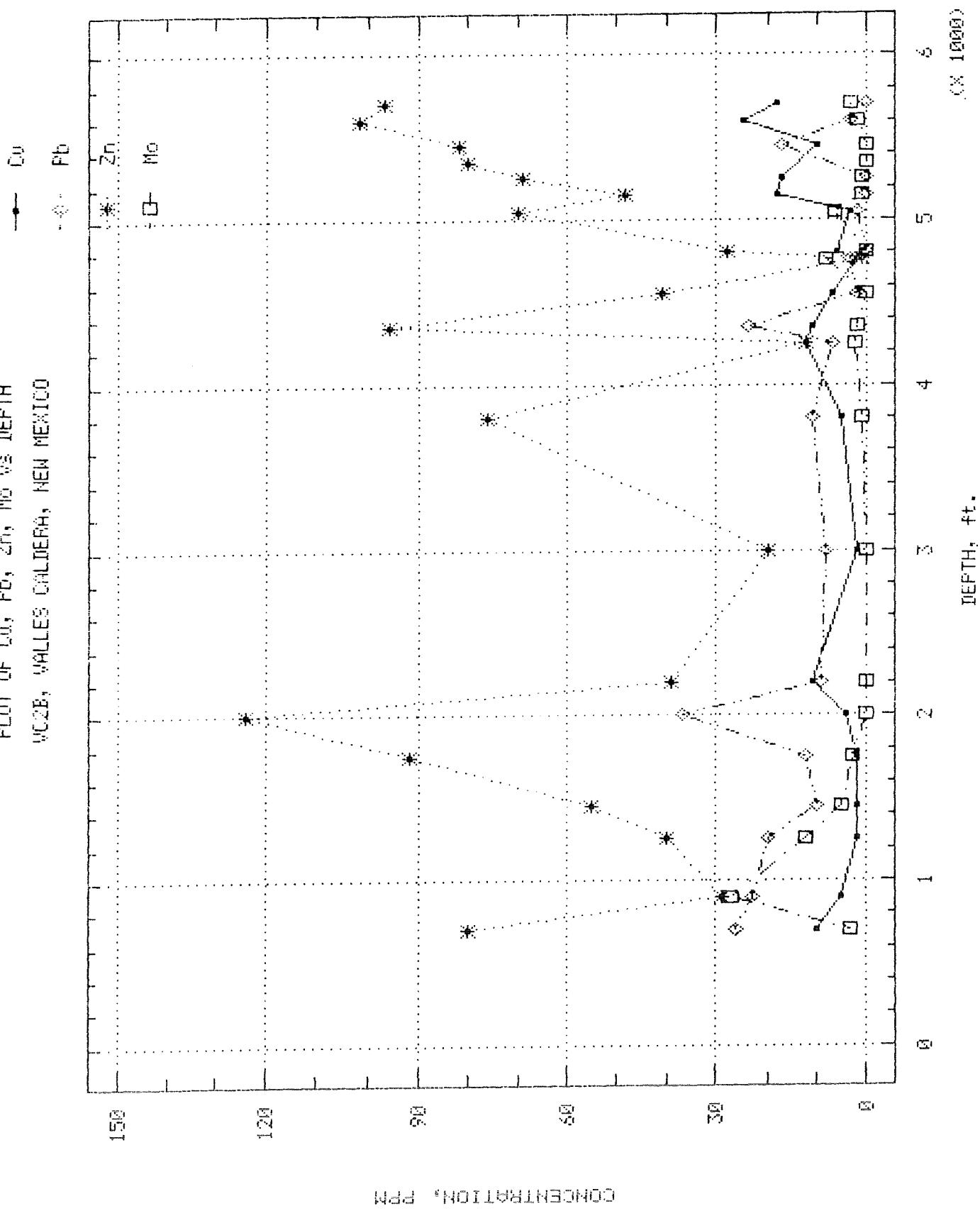
PLOT OF Cu, Pb, Zn, Mo vs. DEPTH  
MC2A, VALLES CALDERA, NEW MEXICO

Cu  
Pb

(X 100)

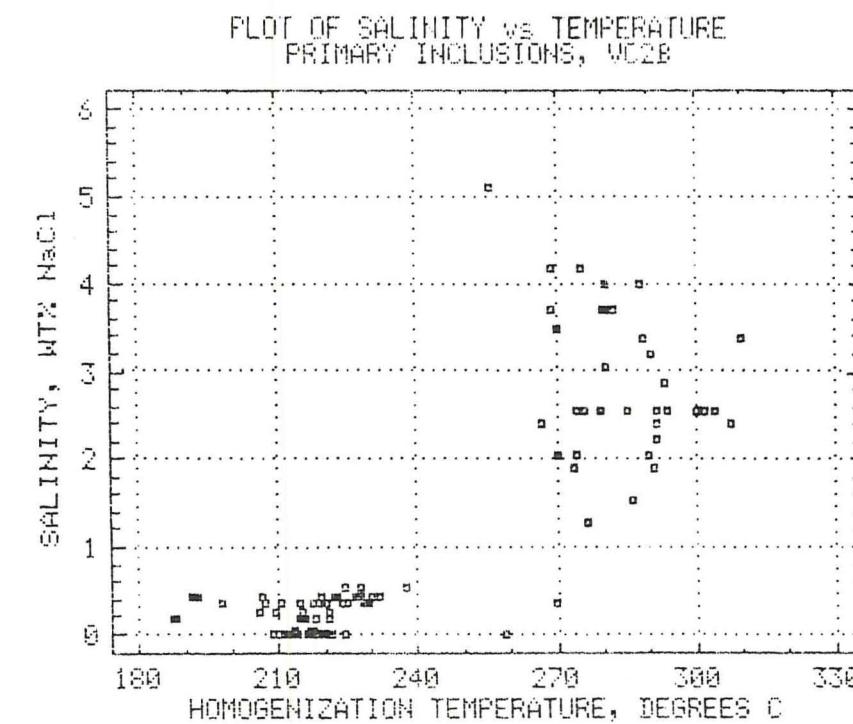
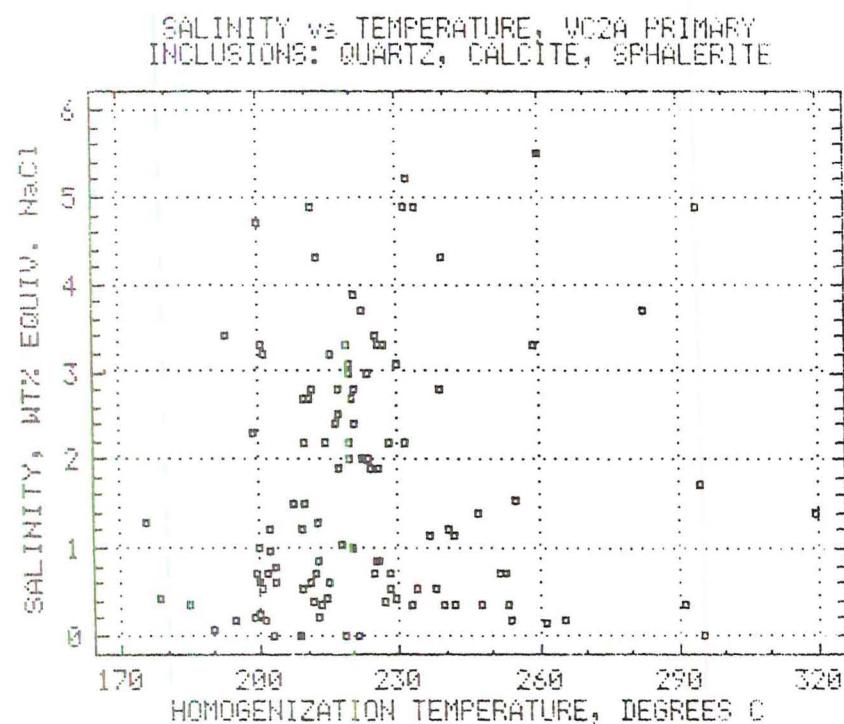
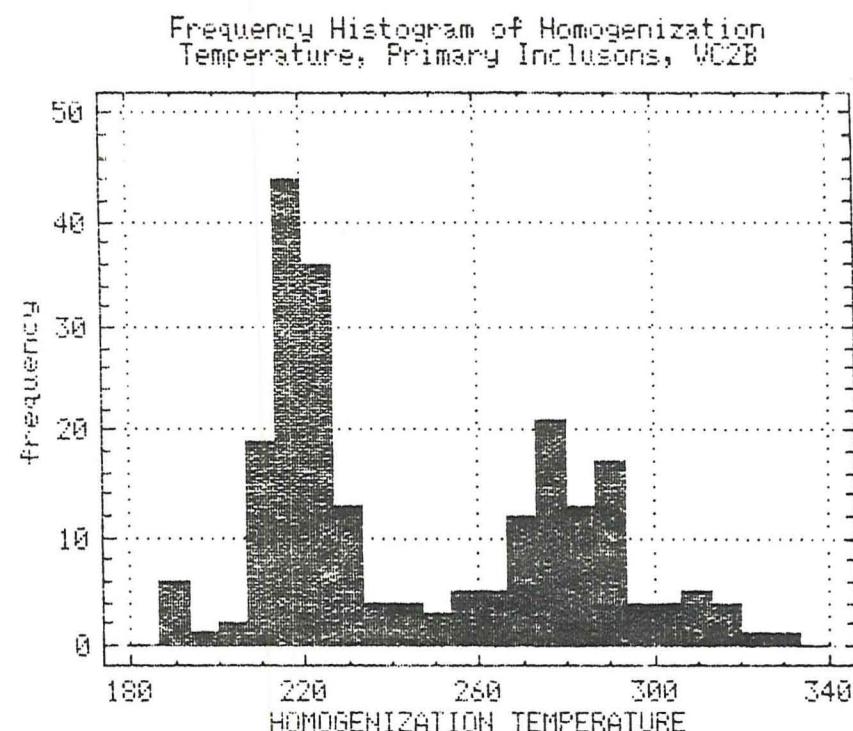
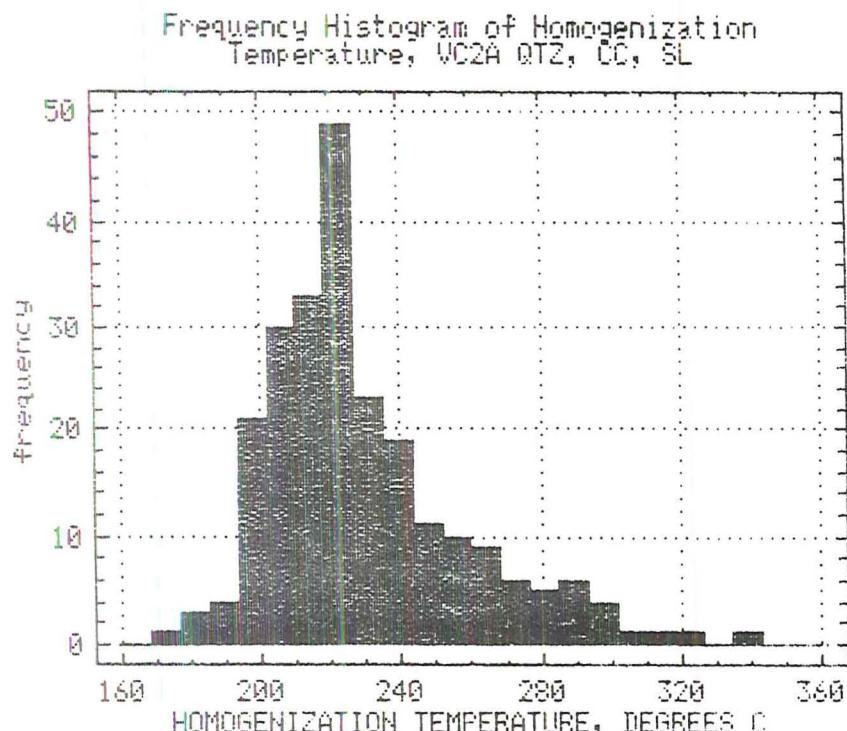


PLOT OF Cu, Pb, Zn, Mo vs. DEPTH  
MC2B, VALLES CALDERA, NEW MEXICO

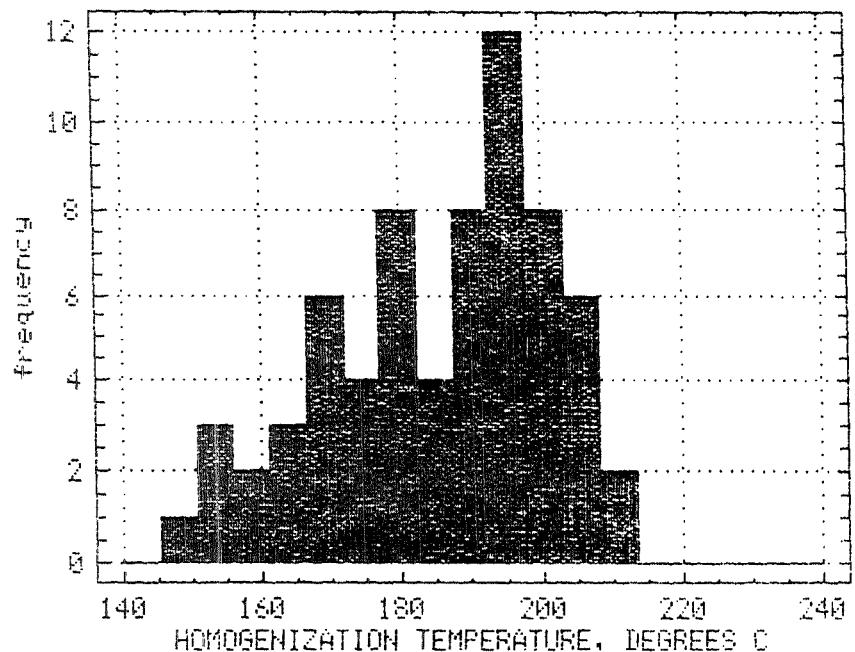


#### FLUID INCLUSION STUDIES

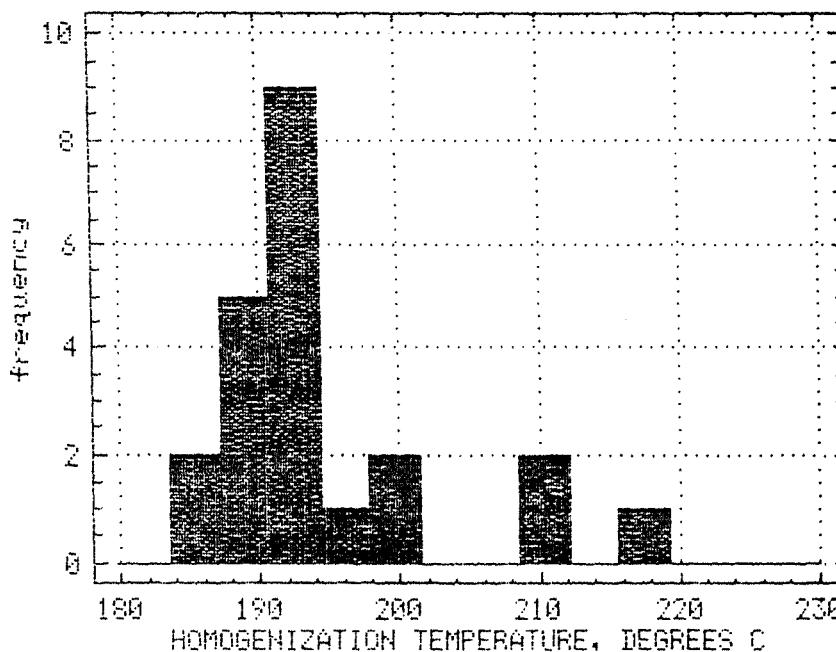
Nearly 700 fluid inclusions in quartz, calcite, fluorite, and sphalerite have been studied microthermometrically. The data from VC-2A indicate that the base metal sulfide deposition took place at temperatures of around 235-240°C from a fluid not unlike the present day composition of the hydrothermal fluid. The molybdenite mineralization was deposited from the same dilute fluid but at a slightly cooler temperature, 220-230°C. The salinity vs homogenization temperature plot shows two populations of inclusions both of which have about the same homogenization temperature but differing salinities. These inclusion samples are from the higher elevations of the system, and this difference is due to the high gas contents of these inclusions; the result of boiling. Gas analysis of inclusion fluids also indicate high gas/water ratios for these samples. Gaseous species measured by mass spectrometry in VC-2A are CO<sub>2</sub>, H<sub>2</sub>S, CH<sub>4</sub>, Ar, Ne, He, N<sub>2</sub>, and numerous organic species. The data from VC-2B also shows two populations of inclusions, but these differences are due to fluids of different compositions. Apparently the Sulphur Springs system is a stacked hydrothermal system with a cooler, dilute fluid circulating in the volcanic section and hotter, more saline fluid circulating in the Pennsylvanian and Precambrian section with the Permian redbeds acting as an aquitard.



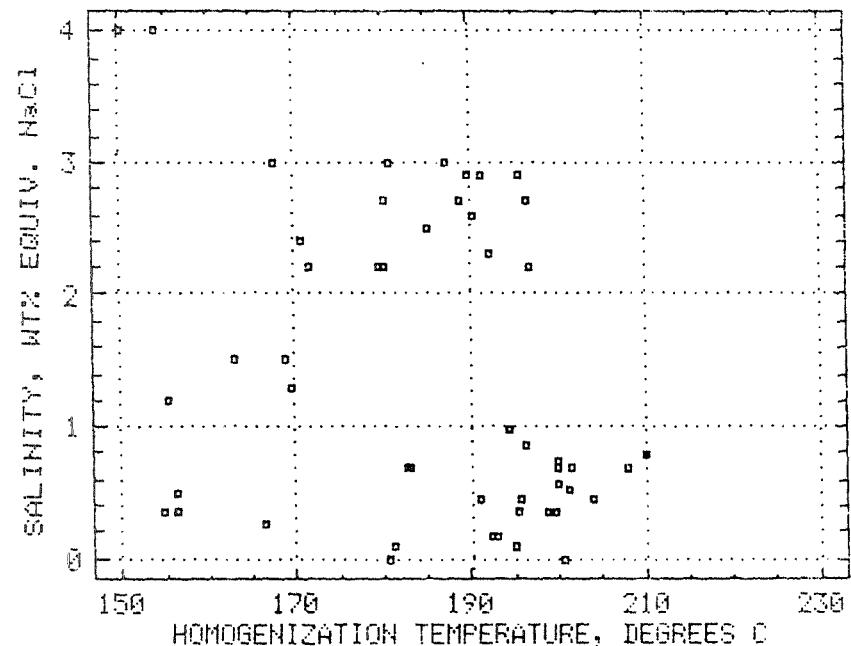
Frequency Histogram of Homogenization Temperature, Fluorite, VC2A



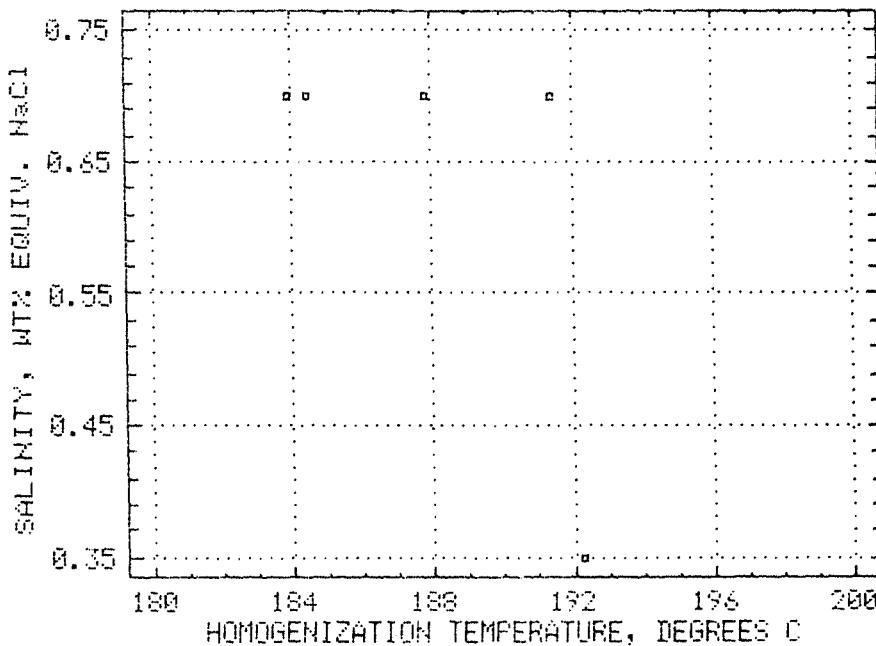
Frequency Histogram of Homogenization Temperature, Fluorite, VC2B



PLOT OF SALINITY vs TEMPERATURE  
FLUORITE, VC2A



PLOT OF SALINITY vs TEMPERATURE  
FLUORITE, VC2B



#### CONCLUSIONS

The Sulphur Springs hydrothermal system is analogous to the Adularia-Sericite type ore deposit of Hayba et al. (1985) in many respects except that no significant economic mineralization has been discovered to date.

The subore grade molybdenum mineralization in VC-2A may represent a high level expression of a deep Climax-type molybdenum deposit.

Fluid inclusion data indicate that the vapor-dominated portion of the system was once liquid-dominated with temperatures of 200-230°C. The Th and salinity data from shallow depths, however, suggest that the system must have been overpressured or the hydrostatic head was great for the fluid to remain on the boiling point-depth curve. Geologic evidence indicates that a caldera lake was present at Sulphur Springs, which would have supplied the necessary hydrostatic head for the system to remain on the curve.

The Sulphur Springs hydrothermal system appears to be a stacked system with temperatures of about 230°C and salinities generally less than 1 wt. % equiv NaCl in the volcanic section and temperatures of 275-280°C and salinities between 1-2 wt. % equiv. NaCl in the Pennsylvanian and Precambrian section. The intervening Permian redbeds acting as an aquitard.