UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Diverse Chemical Processes in a Complex Epithermal System: A Progress Report from Creede, Colorado

by

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This report is preliminary and has not been edited or reviewed for conformity with U. S. Geological Survey editorial standards and stratigraphic nomenclature.

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This report includes the transcript and figures of a talk presented at the San Juan Volcanic Field symposium, Rocky Mountain GSA, in Boulder, Colorado, May, 1987 (Plumlee et al., 1987). Because the talk was presented as one of a series on epithermal mineralization at Creede, some references in this report to other talks in the series or to district geological features may be unfamiliar to the reader. For background, the reader is referrred to Hayba et al. (1985), and to published abstracts for the other symposium talks (Bethke, 1987; Foley et al., 1987; Hayba, 1987; Rye et al., 1987; Landis and Rye, 1987; Barton, 1987).

Slides presented in the talk are reproduced here in black and white, and labeled as "SLIDE LEFT", "SLIDE 1", etc., at the appropriate points in the text. Two slides labeled "SLIDE LEFT 1" and "SLIDE LEFT 2" were shown on a left-hand side screen, while all other slides were shown on a right-hand side screen. "SLIDE LEFT 1" remained on the left-hand screen for reference during most of the talk.

Printing in italics was added for the clarification of this report, and was not included in the original talk as presented.

SLIDE LEFT 1 - *Schematic representation of the Creede system hydrology, showing where different types of chemical processes occurred in the hydrothermal system.*
SLIDE 1 - *Chemical processes in the Creede mineralizing system.*

The epithermal mineralization at Creede was deposited by a complex hydrothermal system whose chemistry varied extensively in time and space. Becuse of the detailed geological and geochemical framework developed by many people for the Creede system, we can begin to understand some of the processes which influenced chemistries of the fluids in recharge areas, at depth in the system, in the plume, and in the shallow ore zones *(see SLIDE LEFT for these locations).* Changes in these processes also occurred over the life of the system, but will not be discussed today.

Because the ores themselves are available for direct examination and study, our understanding of the system's chemistry is best-developed in the shallow ore zones. Our understanding of the deeper and recharge parts of the system is much more speculative and incomplete, however, and is based largely on inferences made through studies of minerals deposited in the ore zones.

SLIDE 2 - *Chemical processes in recharge areas of the system.*

The Creede hydrothermal system was dominated by waters of meteoric origin that were recharged from highlands in the northern parts of the district and from the Creede caldera moat to the south. Major chemical differences between these two recharge waters strongly affected the nature of mineralization that they each deposited.

The southern recharged waters evolved chemically and isotopically in an evaporative playa-lake in the Creede caldera moat. Evaporation, reactions with volcanic glasses, mineral precipitation, bacteriogenic sulfate reduction, and other processes in the lake and moat sediments transformed the fresh waters into brines rich in NaCl, bicarbonate, sulfate and organic constituents. The brines contained isotopically heavy hydrogen, oxygen and sulfur. These istopically and chemically distinctive southern recharge waters were not your typical epithermal mineralizing fluids.

In contrast to the southern brines, the northern recharge fluids were fresh, unevolved meteoric waters with isotopically light hydrogen, oxygen and sulfur. These recharge waters were more typical of mineralizing fluids generally seen in epithermal ore deposits.

SLIDE 3 - *Internal[1] chemical reactions of fluids at depth*

Once drawn into the hydrothermal system, the recharged waters evolved chemically through internal reactions and reactions with wallrocks.

Some of the possible internal chemical reactions the fluids underwent at depth are summarized in this slide. As temperatures rose above 100°C, organics carried by the southern brines probably became more reactive, and started to thermochemically reduce aqueous sulfate, and decompose thermally. The precipitation of minerals with retrograde solubilities may also have modified fluid compositions.

SLIDE 4 - *Fluid-rock chemical reactions at depth*

Among the chemical reactions possible between the recharged waters and wallrock at depth were the sodium and carbonate metasomatism of wallrocks by the southern brines, reaction of sulfate with reduced iron in deep andesites, and the oxidation of organics and the fluids as a whole by hematite and magnetite in ash flow tuffs.

Most significantly, reactions with deep wallrocks likely served as a major source for metals, carbon, and reduced sulfur in the hydrothermal fluids.

SLIDE 5 - *Chemical reactions of meteoric water with magmatic fluids at depth*

It is possible that the recharged fluids may have interacted at depth with a magmatic vapor plume, and picked up some metals, salts, H_2S and other magmatic gases. We have seen no evidence of such interactions in the mineralization stable isotope systematics, although a small magmatic component could go unnoticed.

SLIDE 6 - *Approach to equilibrium at depth*

The degree to which the fluids attained chemical equilibrium at depth in the system depended upon the temperatures they reached and the duration of their stay at high temperatures.

SLIDE 7 - *Approach to equilibrium at depth, cont.*

In the hottest mineralization stages, most constituents of the fluids apparently approached equilibrium both internally and with the surrounding wallrocks. Stable isotope data *(Rye et al., 1987)* and recent gas analyses by Gary Landis *(Landis and Rye, 1987)* show that, even during the hottest stages, equilibrium was not reached between aqueous sulfate and sulfide species, sulfate and water, and organic species in solution. During the lower temperature waxing and waning stages of the system, few constituents of the fluids reached chemical equilibrium, and the fluids apparently did not interact significantly with the wallrocks at depth.

SLIDE 8 - *Chemical reactions in the main-stage plume*

Even though our understanding of the actual processes modifying fluid chemistries at depth is still very limited, we can quantify chemical controls on the main stage ore fluids as they flowed into the shallow ore zones from the upwelling plume.

In their studies of the OH vein, Paul Barton and Phil Bethke proposed that the redox and sulfur chemistries of the hydrothermal fluids were buffered by the vein assemblage chlorite, pyrite and hematite, and that fluid pH's were buffered by wallrock Kspar and Kmica. These buffers are summarized by the chemical reaction shown in this slide. Daphnite is used here to approximate the Creede iron-rich chlorite.

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[1] *"Internal" refers to chemical reactions that occurred within the fluid phase, and reactions that triggered mineral precipitation from the fluid. The term is not meant to include reactions between the fluids and external mineral phases such as wallrock minerals.*

Pyrite, chlorite and hematite are also common in the northern exploration area[1], both as vein and alteration minerals. It thus appears that fluids in the hottest parts of the plume throughout the district were driven toward the relatively oxidizing, low total reduced sulfur chemistries of the pyrite-chlorite-hematite buffer. It is not yet clear why the fluid chemistries were driven toward this buffer, although it may reflect reactions at depth of the fluids with both reducing andesites and oxidizing ash flow tuffs.

By assuming that the fluid chemistries in the plume approached equilibrium with these buffers, we can calculate the pH, redox state, and concentrations of sulfur, metals and other species in solution as a function of temperature and salinity. Fluid inclusion temperature and salinity variations across the district thus show how fluid chemistries varied across the plume.

SLIDE 9 - *Summary of district fluid inclusion data*

Fluid inclusion data trends from the district's vein sytems presented by Dan Hayba *(Hayba, 1987)* are summarized in this temperature-salinity plot. The data trends for the NEA are based on unpublished data from Kosro Bazrafshan and Dave Norman. The fluids entering the vein systems from the plume most likely had temperatures and salinities falling at the hottest portion of each trend, areas outlined by dashed lines. The progressive increase in salinities from the northern exploration area to the southern vein systems marks the change in dominance from northern recharged fluids to southern recharged fluids.

Variations in fluid chemistries across the plume depended strongly upon variations in temperature and salinity, and can therefore best be illustrated by contouring concentrations of various fluid constituents on temperature-salinity plots.

SLIDE 10 - *Calculated pH variations across the Creede plume*

The salinity variations across the plume strongly influenced the wallrock-buffered pH of the ore forming fluids. For a constant sodium to potassium ratio across the plume, the high salinity fluids entering the southern veins clearly had the lowest pH values, as low as 5.2. The higher the potassium content of the fluids, the lower the pH. The dilute northern recharged fluids entering the northern vein systems probably had considerably higher pH values, as high as 6.4 to 6.6.

SLIDE 11 - *Calculated total reduced sulfur variations across the Creede plume*

Here, contours of total reduced sulfur in equilibrium with the chlorite-pyrite hematite buffer are shown. The lowest total reduced sulfur occurs at the highest salinities and lowest pH values.

SLIDE 12 - *Calculated total zinc variations across the Creede plume*

The pH, total reduced sulfur, and total chloride in solution strongly influenced the amounts and types of metals that were transported by the fluids entering the ore zone from the plume.

Solubilities of metals such as zinc that form strong chloride complexes are promoted by high chloride concentrations, low pH, and low reduced sulfur in solution. Here, contours of the log of total zinc molality in sphalerite-saturated solutions show that the southern chloride-rich brines had the capacity to transport some eight orders of magnitude more zinc than the northern dilute fluids. Lead and copper have contours similar to those of zinc.

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[1] *The term "northern exploration area" (abbreviated subsequently as "NEA") describes the northern parts of the district that are currently targeted for exploration by several mining companies, and encompasses the northern Amethyst and Bulldog Mountain fault systems, and the Equity fault. See SLIDE 19 for a district map.*

SLIDE 13 - *Calculated total silver variations across the Creede plume*

Silver forms strong chloride and weaker bisulfide complexes. Its solubilites are thus not quite as salinity-dependent as those for zinc and lead, but still have the same general appearance. Thus the silver-transport capacity of fluids across the plume was not quite as variable as for zinc, lead, and copper.

SLIDE 14 - *Calculated total gold variations across the Creede plume*

Metals such as gold, antimony, and arsenic form strong bisulfide or hydroxy complexes instead of chloride complexes, and so have a very different solubility behavior from that of base metals. The solubilities of bisulfide complexed metals are enchanced by higher total reduced sulfur in solution and higher pH values. Here contours of total gold in solution show that the dilute northern fluids had the capacity to transport one to two orders of magnitude more gold than the southern brines.

SLIDE 15 - *Comparison of calculated total gold and total zinc variations across the Creede plume*

Just for comparison, gold and zinc solubility contours are plotted on the same diagram. The high salinities of southern recharged brines, and their resulting low pH and low total reduced sulfur contents, promoted transport of major quantities of base metals in solution as chloride complexes. The dilute northern recharge fluids had much lower salinities, with correspondingly higher pH and reduced sulfur values, and so had the capacity to transport greater quantities of gold, arsenic and antimony, and much smaller quantities of base metals.

One could also conclude from this plot that mixing of the dilute northern-recharged and saline southern-recharged fluids in the plume may have led to significant deposition of gold and base metal sulfides at depth before the fluids even entered the shallow ore zones.

SLIDE 16 - *Shallow main-stage processes*

After flowing up the plume from depth, the hydrothermal fluids were subjected to shallow level hydrologic processes such as mixing and boiling. Here, the fluid chemistries evoloved rapidly in respose to these processes, and began to deposit their metals in the district's ore zones.

Possible fluid chemistry evolution paths and ore deposition mechanisms associated with mixing and boiling are currently being evaluated using computer driven chemical modeling. I will now show a brief example of how such modeling can be used to help interpret mineral zoning patterns along the southern vein systems at Creede.

SLIDE 17 - *OH, Amethyst vein mineral zoning and fluid inclusion data*

Before discussing the chemical modeling, I must first present some mineral zoning and fluid inclusion information as background.

The B stage of mineralization in the southern Creede vein systems is strongly zoned. B stage mineralization along the OH vein is sphalerite- and galena-rich, with chlorite, pyrite and hematite gangue. In contrast, mineralization from the same stage farther south along the southern Bulldog Mountain and southern Amethyst vein systems is more silver-rich, with sphalerite, galena, sulfosalts, acanthite, native silver, and abundant barite gangue.

Previous talks today have demonstrated the importance of mixing between the deep brines and shallow dilute groundwaters as an ore deposition mechanism along the southern vein systems. Fluid inclusion data for the OH and Southern Amethyst B stage mineralization, shown graphically on this slide, document a trend of decreasing temperatures and salinities up and to the south along the vein systems. This would suggest that the B stage mineral zoning patterns reflect progressive fluid mixing, a hypothesis that can be tested by chemical modeling.

SLIDE 18 - *Calculated mineral precipitation during fluid mixing.*

Shown in this slide are the calculated amounts of various minerals that would precipitate during the progressive mixing of a deep brine at 250°C with a dilute groundwater at 100°C. The inital chemistry of the deep brine was calculated assuming equilibrium with the chlorite-pyrite-hematite-Kspar-quartz buffer assemblage discussed earlier. The cool fluid was assumed here to be pure ground water with no dissolved constituents. The calculated mixing begins at 250°C, shown on the right of the slide, and proceeds to lower temperatures on the left. Note that ore mineral assemblages deposited during the earliest stages of mixing are sphalerite- and galena-rich, in agreement with observed zoning patterns. At the lowest temperatures and highest degrees of mixing, the ore mineral assemblages precipitated are rich in acanthite and native silver, also in accordance with observed zoning patterns. Barite, hematite, chlorite and pyrite are not precipitated, however, along this particular mixing path. Calculations currently in progress indicate that boiling of the deep brines prior to mixing may have triggered deposition of the chlorite, pyrite and hematite. The calculations also suggest that the waters with which the brines subsequently mixed must have carried significant quantities of sulfate in order to precipitate barite. Mixing with overlying sulfate-bearing steam heated waters likely produced some barite deposition, but the bulk of the barite may have been deposited in response to mixing of the hydrothermal brines with sulfate-rich Creede formation pore fluids in the southernmost vein systems.

SLIDE LEFT 2 - *Main-stage mineral zoning patterns at Creede (map)*
SLIDE 19 - *Main-stage mineral zoning patterns at Creede (text)*

Although much more extensive chemical modeling of ore deposition is currently underway, the detailed fluid inclusion and mineralogical data available for the Creede mineralization and chemical modeling completed to date allow us to say much about the chemical processes responsible for the district-wide mineral zoning patterns depicted on this map.

The large-scale variations of gold to base metal ratios across the district, as discussed earlier, probably reflect the dominance of the northern versus southern recharged fluids.

Boiling of the dilute northern fluids deposited carbonate - adularia - quartz - precious metal - base metal sulfide assemblages with higher gold to base metal ratios, as seen in the NEA assemblage.

The southern brines deposited base metal and silver-rich ores. Initial boiling of the southern brines likely triggered deposition of chlorite, pyrite, hematite, adularia, quartz, fluorite and abundant base metal sulfides. Subsequent mixing of the brines with dilute groundwaters likely triggered deposition of sphalerite and galena rich ores, with increasing acanthite, sulfosalt, native silver, and barite contents to the south. Deposition of the extreme barite-rich mineralization in the southern vein systems likely reflects the mixing of the hydrothermal brines with pore fluids from the Creede moat sediments.

SUMMARY

In summary, the strongly zoned, mineralogically complex main-stage epithermal mineralization at Creede resulted from the complex temporal and spatial interactions of diverse chemical processes. Our understanding of these processes continues to grow, especially with the recent explosion of information generated by exploration activities in the northern district, and by drilling program research. We can only hope for deep drill holes to generate a similar explosion of information about deep and recharge processes in the system.

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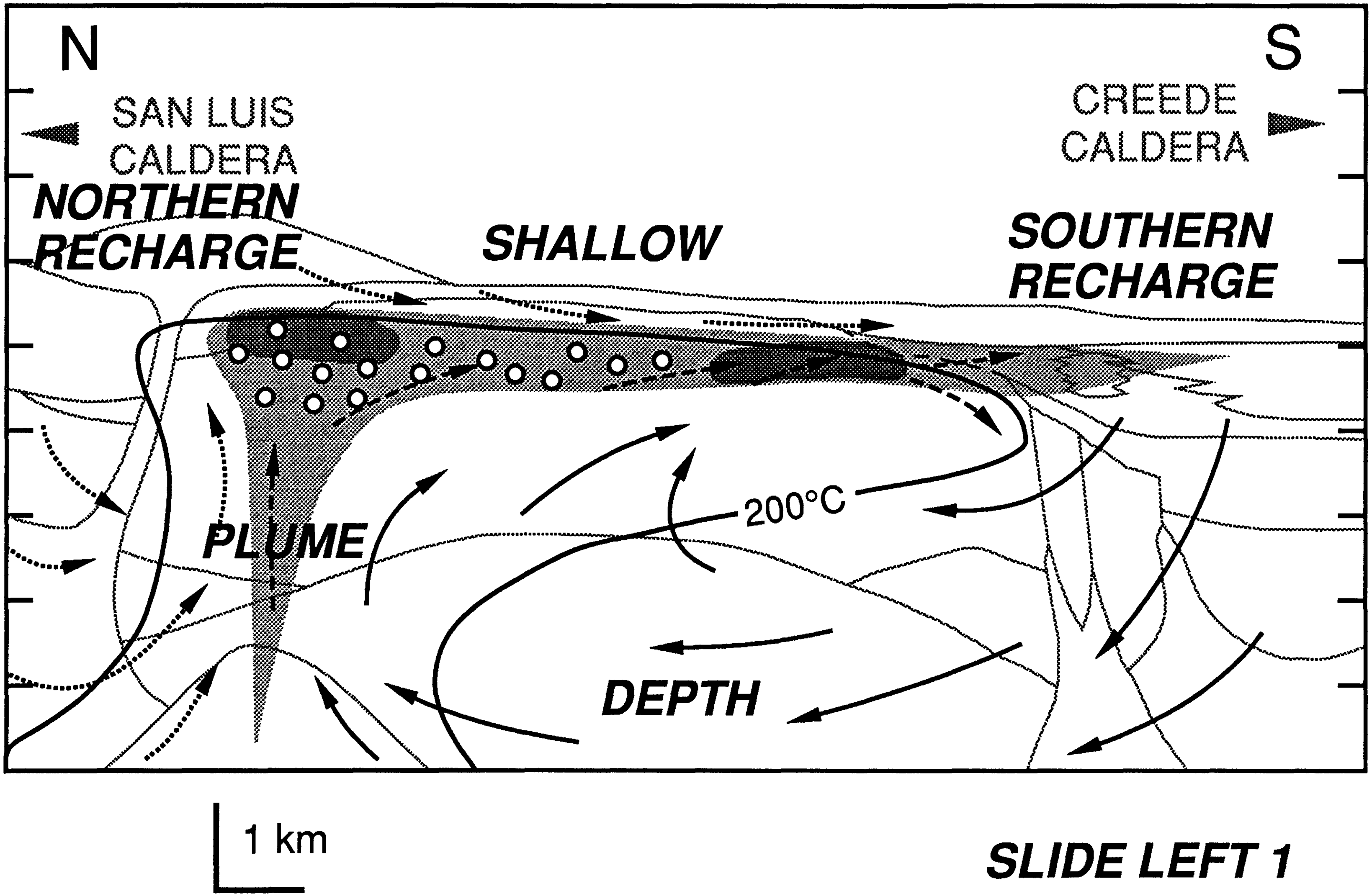
CHEMICAL PROCESSES IN THE CREEDE HYDROTHERMAL SYSTEM



SLIDE LEFT 1

SLIDE 1

CHEMICAL PROCESSES IN THE CREEDE MINERALIZING SYSTEM

A. Processes influencing chemistry of recharge fluids.

B. Fluid chemistry evolution at depth in system.

C. Chemical controls on fluids in plume prior to entering ore zones.

D. Chemical effects of shallow hydrologic processes (boiling, mixing); the chemistry of ore deposition.

E. Changes in chemical processes throughout system over time.
- early-stage
- late-stage

SLIDE 2

RECHARGE

I. SOUTHERN RECHARGE:

A. Evolved meteoric water from Creede caldera moat sediments

- formed in evaporative, playa-lake environment
- rich in Na^+, Cl^-, HCO_3^-, $SO_4^=$, organic compounds
- isotopically evolved heavy H, O, S

II. NORTHERN RECHARGE:

A. Fresh meteoric waters

- unevolved chemically
- isotopically light H, O, S

SLIDE 3

DEPTH

I. Fluid chemistry evolution at depth

A. Internal fluid chemical reactions (adjustments to increasing T, P)

1. Thermochemical sulfate reduction by organics.
2. Increased organic solubilities in water.
3. Thermal decomposition of organic constituents
   - decarboxylation: $CH_3COOH \Rightarrow CO_2 + CH_4$
4. Precipitation of minerals with retrograde solubilities.
   - calcite, anhydrite (?)

SLIDE 4

DEPTH

I. Fluid chemistry evolution, cont.

B. Fluid-rock interactions

1. Na - metasomatism (Kspar ⇒ albite)
2. Carbonate metasomatism (plag ⇒ calcite)
3. Thermochemical reduction of sulfates by reduced minerals in wallrocks.
4. Thermochemical oxidation of organic constituents.
5. Leaching of metals, sulfur, and other constituents from wallrocks.
6. Reaction of fluids with organic-rich sediments at depth.
7. Isotopic exchange with wallrocks.

SLIDE 5

DEPTH

II. Interactions of meteoric waters with magmatic fluids?

A. Input of various salts, gases, metals, salinity.

SLIDE 6

DEPTH

III. Approach to equilibrium

A. Extent and types of chemical reactions occurring at depth depended upon:

1) Temperatures which fluids attained.
2) Residence time of fluids at high temperatures.
3) Rock types with which fluids reacted.

SLIDE 7

DEPTH

III. Approach to equilibrium, cont.

B. Main stages (T = 200 - 300°C)

1) Most constituents of fluids approached internal chemical equilibrium, and equilibrium with surrounding wallrocks.

2) Aqueous $SO_4^=$-S°-H_2S, H_2O-$SO_4^=$, and fluid-hydrocarbon reactions did not attain equilibrium, even in hottest stages.

C. Early and late stages (T< 200°C)

1) Relatively few constituents of fluids equilibrated, chemically or isotopically.

SLIDE 8

PLUME (MAIN-STAGE)

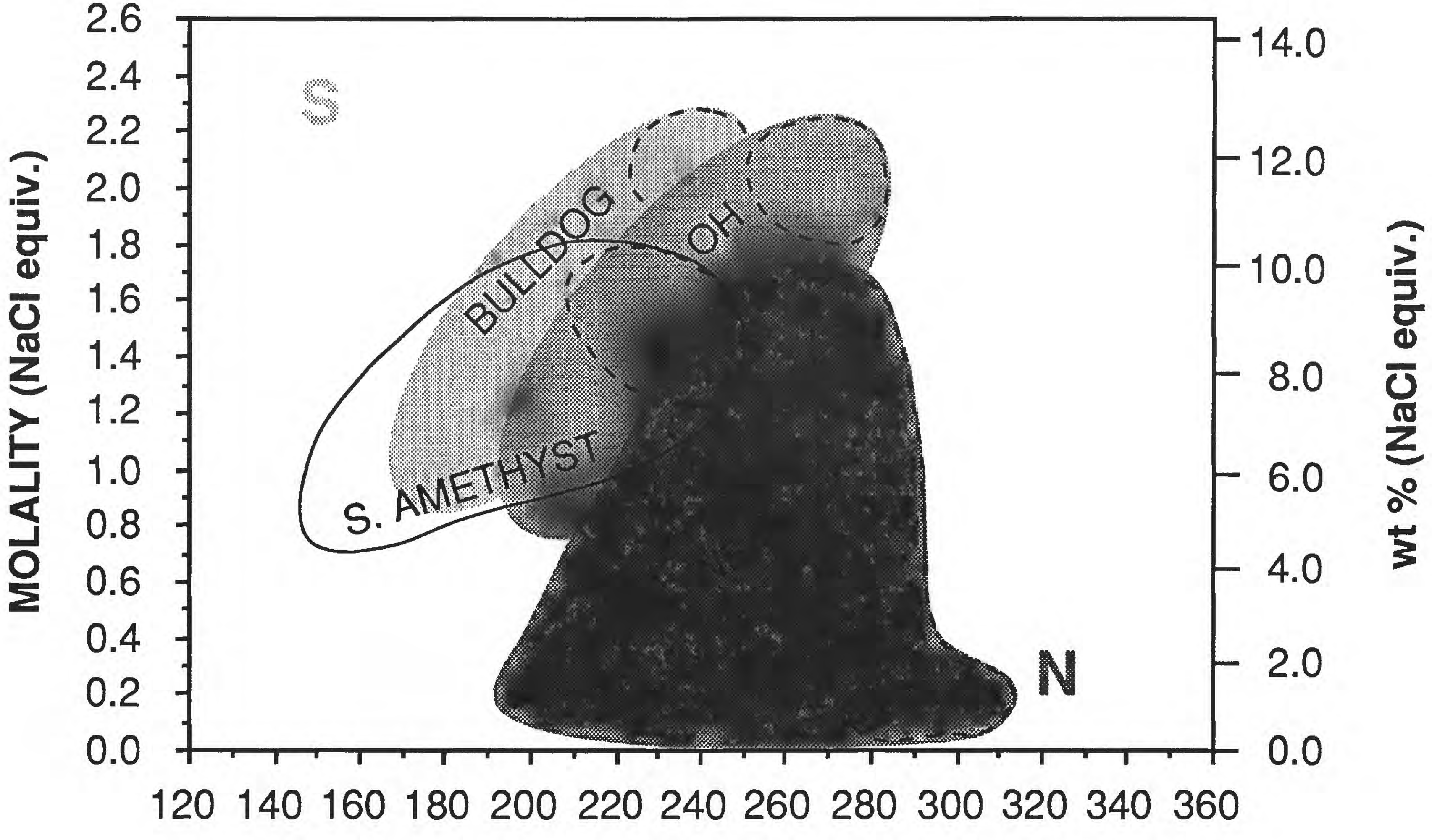
Fluids driven toward equilibrium at depth with pyrite, chlorite, hematite, and wallrock Kspar-Kmica pH buffer:

3 daphnite + 3 K-feldspar + 10 H_2S (aq) ⇔

5 hematite + 5 pyrite + 3 K-mica + 9 quartz +9 H2O + 10 H_2 (aq)

(Barton et al., 1977; Hayba et al., 1985; Plumlee & Hayba, in press.)

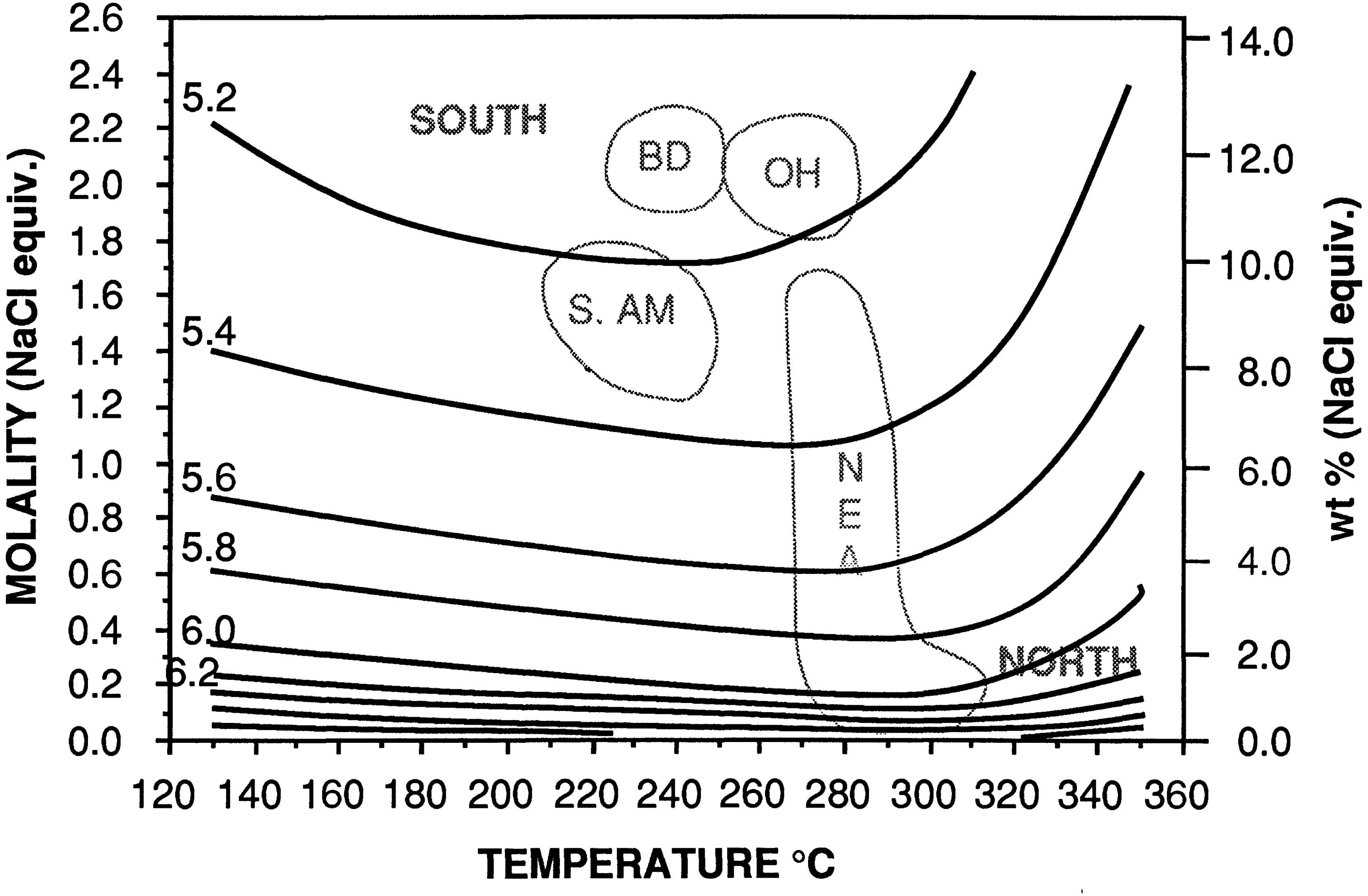
CREEDE DISTRICT
FLUID INCLUSION DATA



SLIDE 9

pH

Na:K:Ca = 9:1:1 Kspar-Kmica-Qtz Buffer

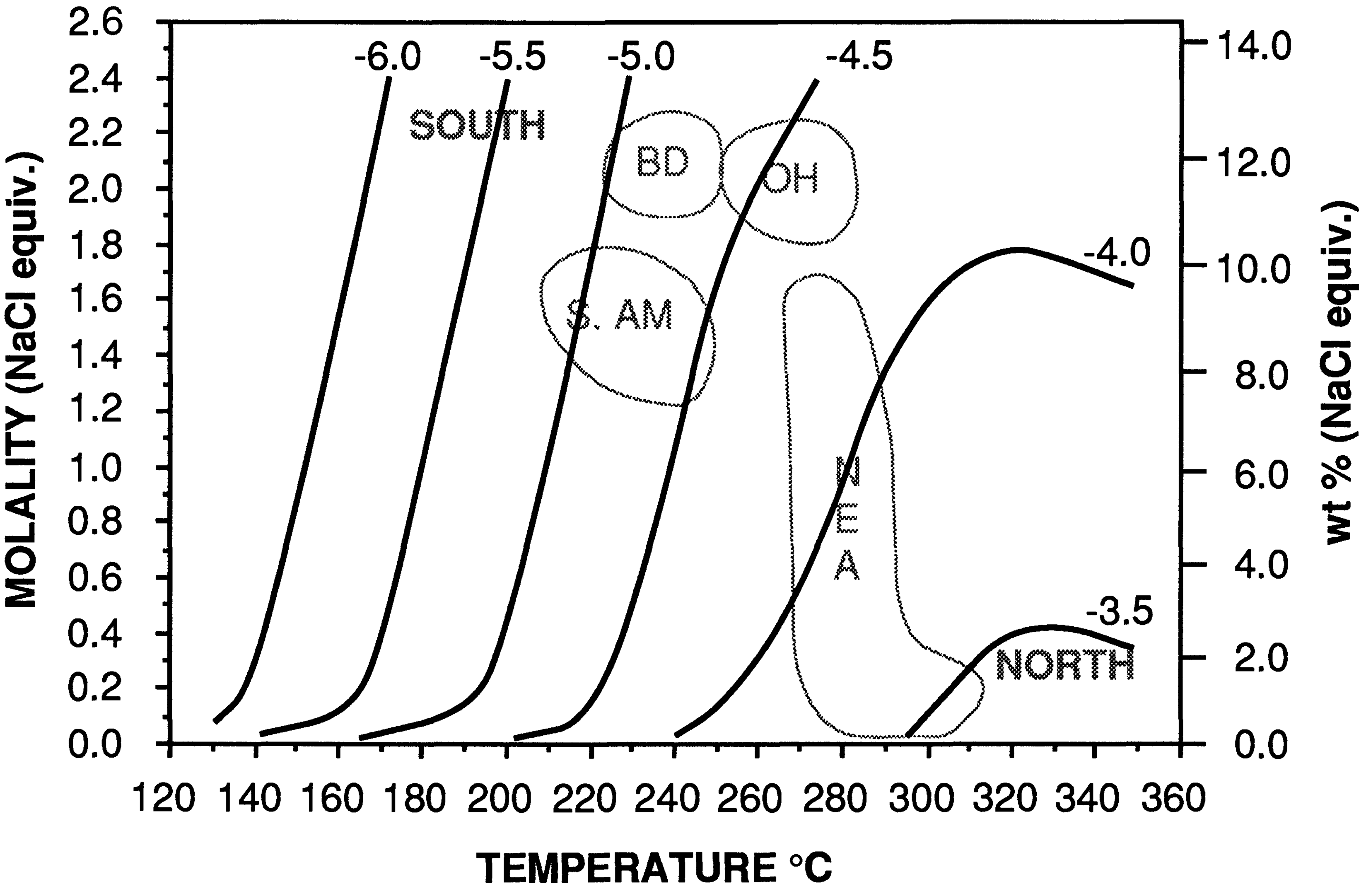


SLIDE 10

TOTAL REDUCED SULFUR

log(molality)

Na:K:Ca = 9:1:1 Py-Chlor-Hem-Kspar-Kmica-Qtz Buffer

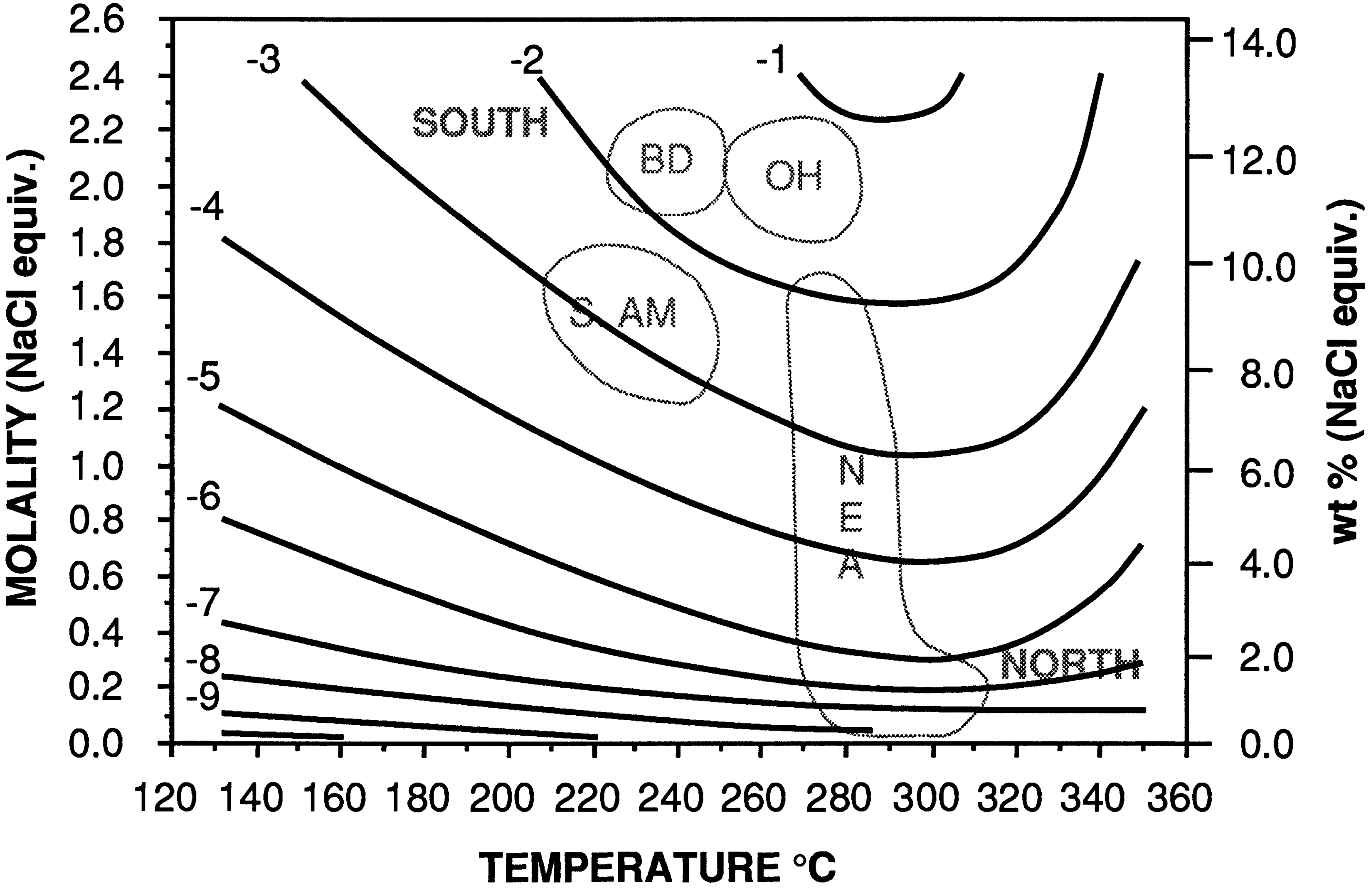


SLIDE 11

TOTAL ZINC

log(molality), sphalerite sat.

Na:K:Ca = 9:1:1   Py-Chlor-Hem-Kspar-Kmica-Qtz Buffer

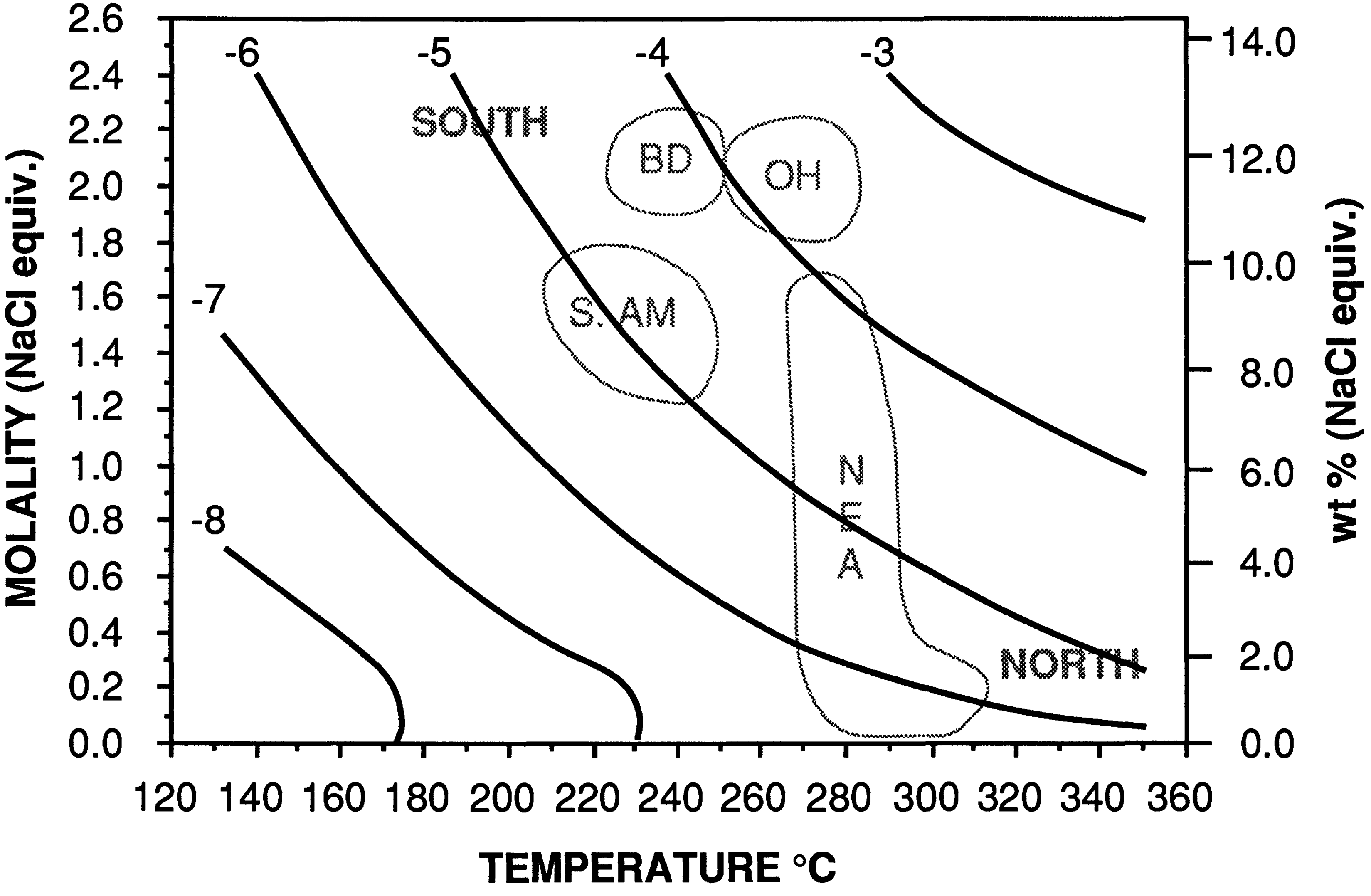


SLIDE 12

TOTAL SILVER

log(molality), Ag_2S sat.

Na:K:Ca = 9:1:1 Py-Chlor-Hem-Kspar-Kmica-Qtz Buffer

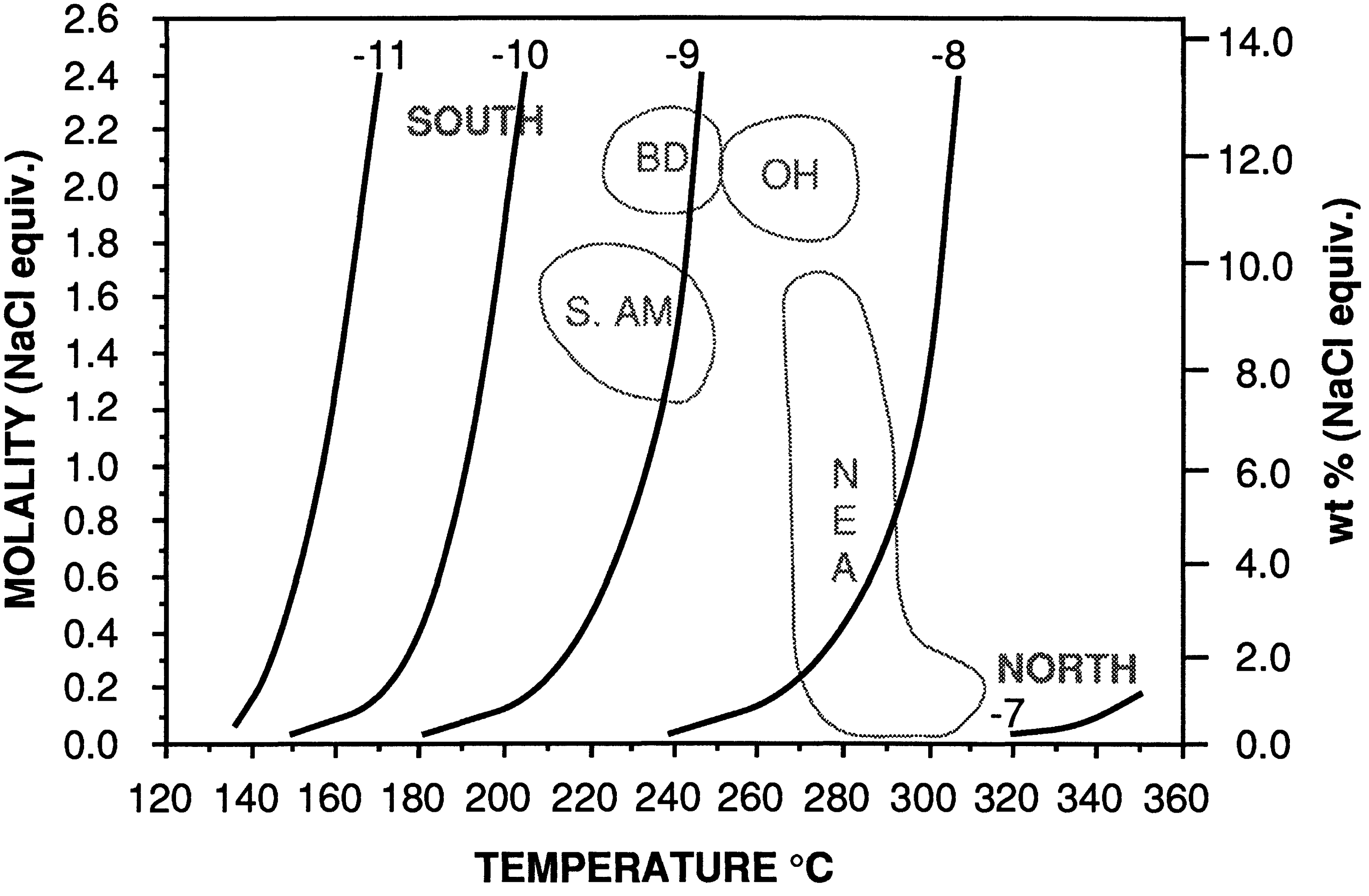


SLIDE 13

TOTAL GOLD

log(molality), native Au sat.

Na:K:Ca = 9:1:1 Py-Chlor-Hem-Kspar-Kmica-Qtz Buffer

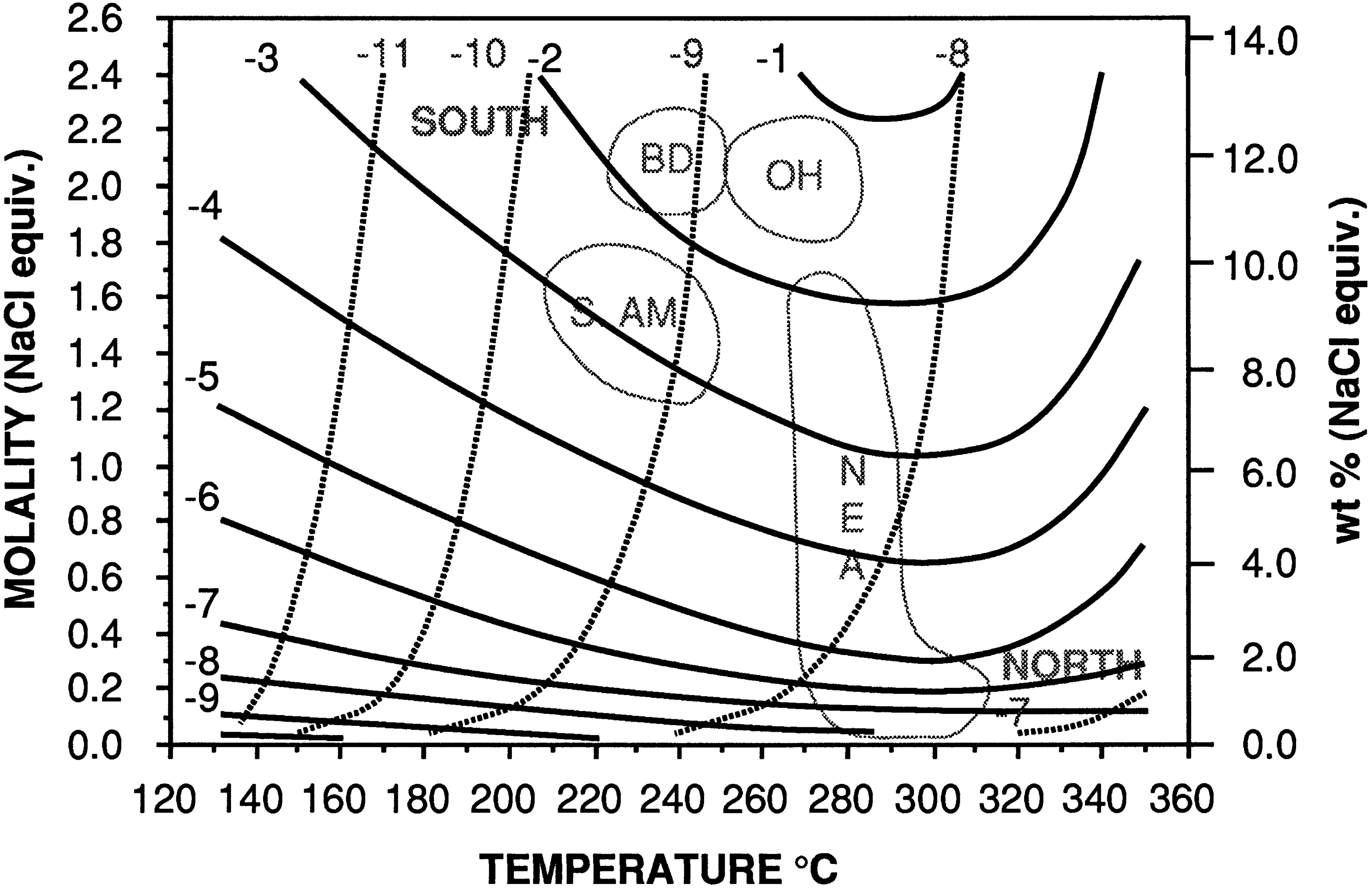


SLIDE 14

TOTAL ZINC, TOTAL GOLD

log(molality), sphalerite, native Au sat.

Na:K:Ca = 9:1:1 Py-Chlor-Hem-Kspar-Kmica-Qtz Buffer



SLIDE 15

SLIDE 16

SHALLOW MAIN-STAGE (ORE DEPOSITION)

I. Chemical evolution in ore zone in response to shallow hydrologic processes.

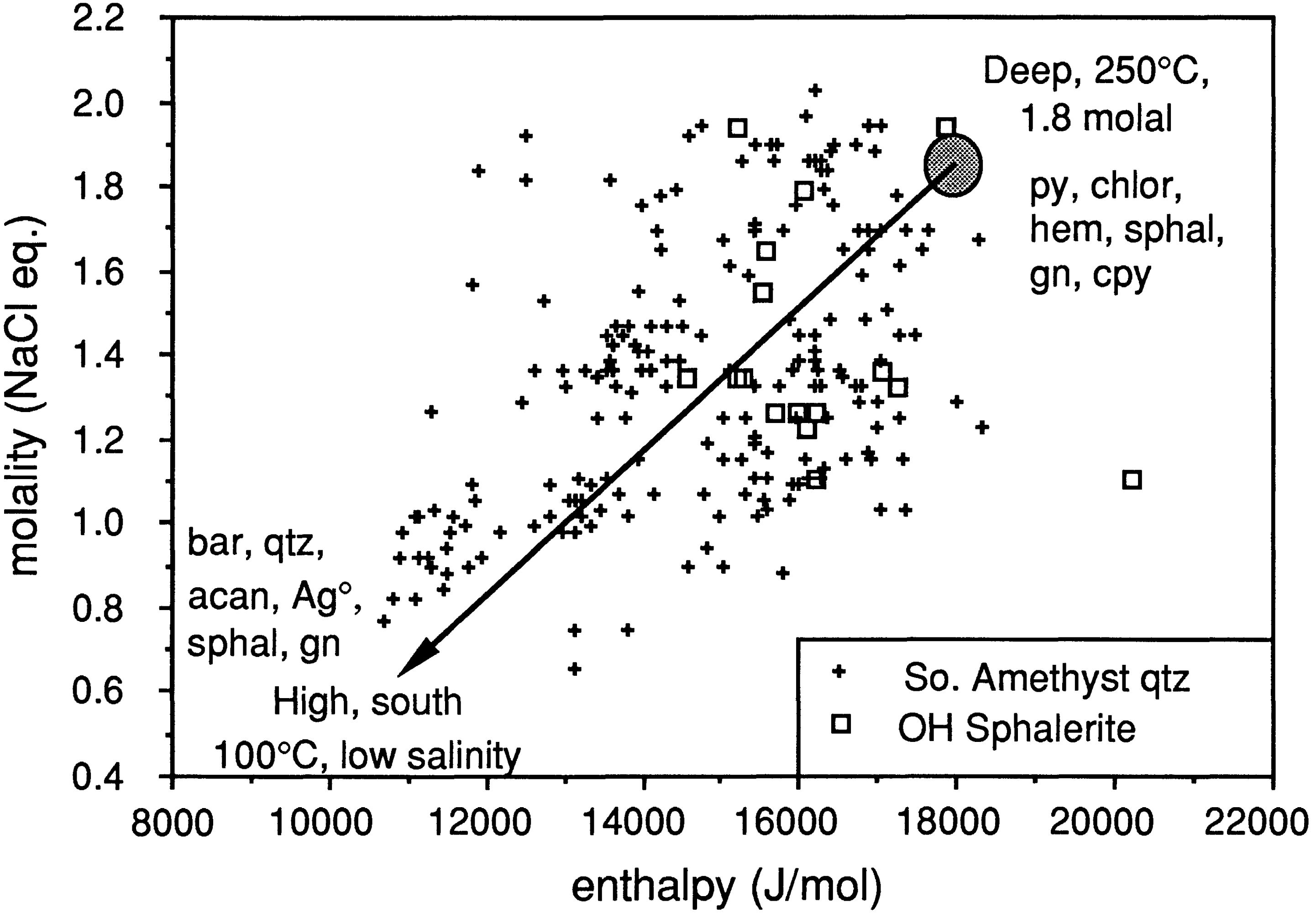
- A. Boiling
- B. Mixing

II. Quantitative chemical modeling of ore deposition

- A. Guided by detailed geological, mineralogical, fluid inclusion, stable isotope framework.
- B. Examines chemical implications of ore deposition models suggested by fluid inclusion, stable isotope studies, etc.
- C. Used as tool in conjunction with other studies.

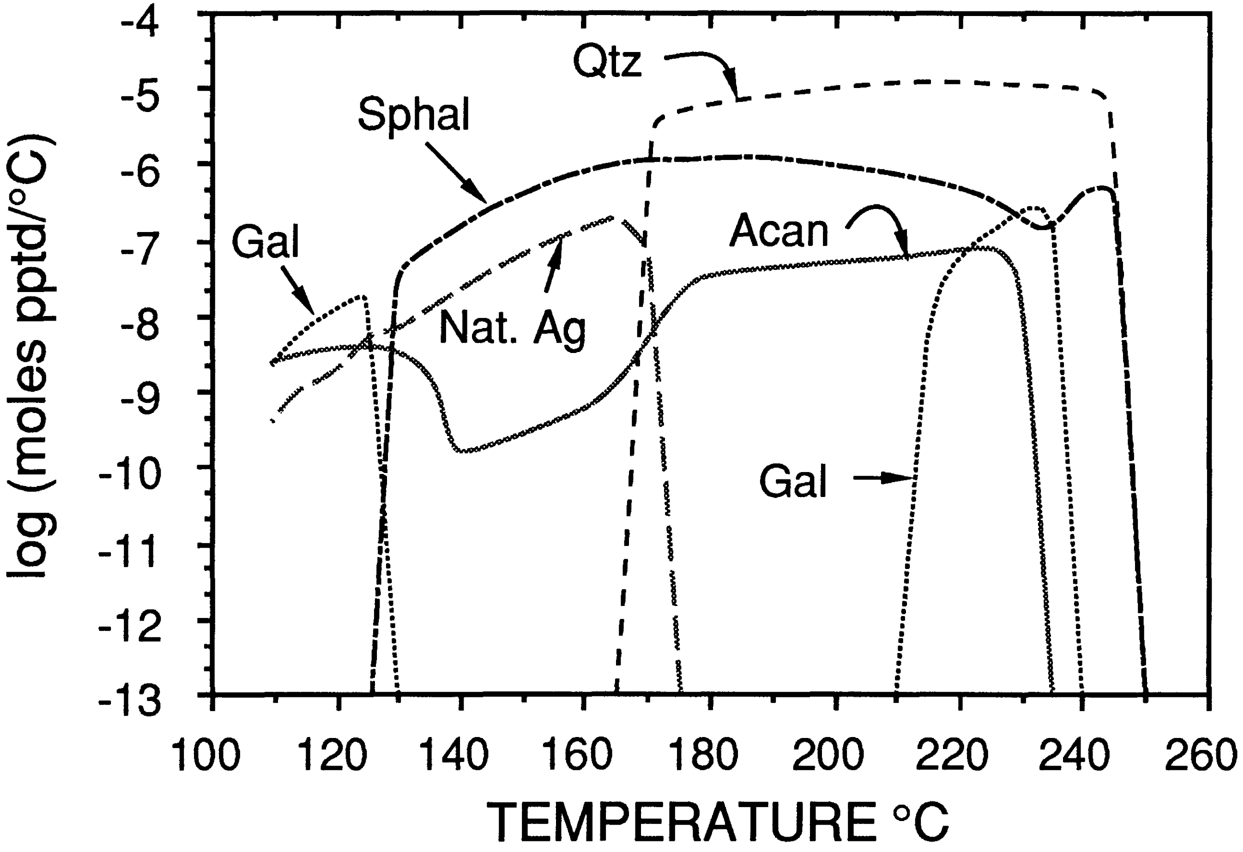
B STAGE FLUID MIXING MODEL
OH, S. AMETHYST VEINS

Fluid inclusion data from Robinson, 1981; Woods et al, 1982



MINERAL PRECIPITATION DURING MIXING

250°C, 1.8 molal brine with 100°C, 0 molal ground water



SLIDE 18

SLIDE LEFT 2

SHALLOW MAIN-STAGE

MINERAL ZONING PATTERNS -

Boiling of dilute northern fluids -

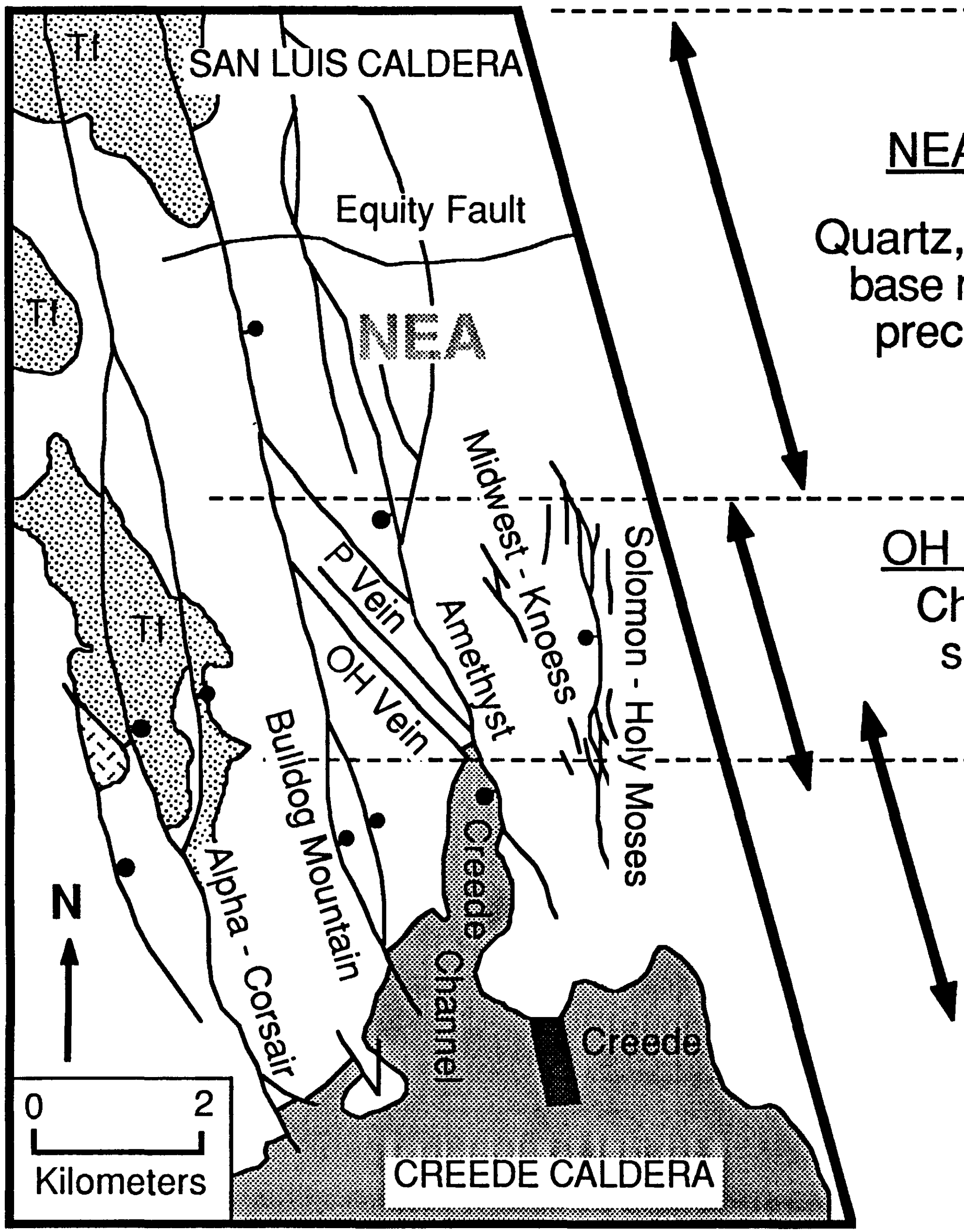
- adularia, quartz, carbonates, precious metals, lesser base metal sulfides

Boiling of southern brines -

- chlorite, pyrite, hematite, sphalerite, galena, quartz, fluorite, adularia

Mixing of southern brines (following boiling?) -

- sphalerite, galena, followed by acanthite, then native silver (?)
- major barite deposition required mixing with sulfate-rich fluid (mix with Creede Fm. pore fluids in southernmost district?)



NEA ASSEMBLAGE:

Quartz, carbonates, adularia, base metal sulfides, precious metals

OH ASSEMBLAGE

Chlorite, pyrite, hematite, sphalerite, galena, chalcopyrite, quartz, tetrahedrite

BULLDOG ASSEMBLAGE

Barite, sphalerite, galena, tetrahedrite, sulfosalts, acanthite, native silver

MAIN STAGE MINERAL ZONING

SLIDE 19