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Stable Isotope Geochemistry of the Creede, Colorado, Hydrothermal System

by

Robert O. Rye[1]
Geoffrey S. Plumlee[1]
Philip M. Bethke[2]
Paul B. Barton[2]

U. S. Geological Survey

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[1] Denver, CO
[2] Reston, Va

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 (Rye 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 Foley et al., (1982), Hayba et al. (1985), and to published abstracts for the other symposium talks (Bethke, 1987; Foley et al., 1987; Hayba, 1987; Plumlee 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. Printing in italics was added for the clarification of this report, and was not included in the original talk as presented.

INTRODUCTION

Our study of the stable isotope geochemistry of the Creede district now includes nearly 1000 measurements. Most of this effort during the last fifteen years has been on very well-documented samples from the southern part of the district. However, initial work in the Northern Exploration Area[1] in just the last few months has greatly increased our understanding of the stable isotope geochemistry of the system. I will first discuss the hydrogen and oxygen isotope systematics of the hydrothermal system, move on to a discussion of the isotope geochemistry of vein and travertine carbonate minerals, and then conclude with a discussion of the systems sulfur isotope geochemistry.

SLIDE LEFT - *Schematic hydrology of the Creede hydrothermal system.*

You have already seen in a previous talk today by Phil Bethke (Bethke, 1987) the basic hydrology of the Creede hydrothermal system. I will leave this summary schematic slide on the left-hand screen for reference during much of my presentation.

SLIDE 1 -*Summary of the isotopic composition and source of the Creede Fluids*

We have recognized four end member fluids that appeared at various times and places in the hydrothermal system. The isotopic compositions of these fluids and their point of recharge are summarized on the right-hand hydrogen-oxygen isotope plot. Three of these fluids are indicated on the system hydrology slide on the left. Saline fluids recharged from Creede Formation sediments south of the district dominated main stage mineralization in the southern veins and coarse sphalerite mineralization in the NEA. There is some evidence that dilute ^{18}O *exchanged northern recharged meteoric fluids played a role in the NEA mineralization but the extent of their contribution to mineralization is currently unclear. The entire system was overlain by dilute unexchanged ground water which flooded the veins when the main system collapsed. These dilute meteoric derived fluids interfaced and mixed with the saline fluids throughout the life of the system, the details of which are still being studied. Finally, isotopically heavy fluids from Creede Formation sediments were present in the southern parts of the district during pre-main-stage carbonate deposition.* The next series of slides on the right-hand screen will document the isotopic evidence for these fluids.

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[1] *The term "northern exploration area" (abbreviated 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. The "southern" vein systems and mineralized areas referred to in the talk include the southern Bulldog Mountain and Amethyst vein systems, the OH and P veins, and disseminated mineralization in Creede Formation caldera moat sediments. See SLIDE 9 for a district map.*

SLIDE 2 - *H-O isotopic compositions of Creede inclusion fluids.*

This slide on the right summarizes the hydrogen and oxygen isotopic composition of water in the inclusion fluids of some major generations of minerals from the southern vein systems, and of inclusion fluids in one sphalerite sample from the NEA. The tie-lines connect coexisting (but usually not truly contemporaneous) samples. Most of the data fall on a linear trend extending off of the meteoric water line. This indicates that most measured fluid compositions were mixtures of two fluids. When fluid inclusion data are considered (Hayba, 1987) one of these was a saline hydrothermal fluid with a δD of about -50‰ that was dominant during main-stage sphalerite, galena, and fluorite mineralization. The other was a dilute, unexchanged meteoric water with a δD of -100 to -110‰ with which the hydrothermal brines mixed during main stage mineralization. The meteoric water component predominated only during late-stage pyrite mineralization. There is also some indication of a third dilute fluid that appears as an ^{18}O-shifted meteoric water component in some of the sphalerites (especially the one sample with the near-vertical tie-line). These data represent direct analyses of fluids in the Creede system, and will appear faded for reference purposes in the next series of slides. The major uncertainty with this type of data is how well they represent the actual compositions of primary fluids in the host minerals as opposed to being mixtures of isotopically distinct generations of inclusion fluids. For example, you may have noticed that the main-stage barite and chalcopyrite fluids shown by the solid triangles plot on the meteoric water line, and not with the rest of the main-stage fluid samples. This is because most barite and probably most chalcopyrite fluid inclusions were flushed when the system was flooded by meteoric water after the collapse of the main-stage system.

SLIDE 3 - *H-O isotopic compositions of main stage vein chlorites.*

Here we have added data on the isotopic compositions of main-stage vein chlorites from the NEA and OH vein. These data reflect only the temperature and isotopic composition of the hydrothermal fluids, and do not have any uncertainty, as do the fluid inclusion data, created by the possible presence of multiple generations of fluid inclusions. The significant point here is that the range of values for the chlorites is narrow, and is identical for the northern and southern district. The range of ^{18}O values is about 4 ‰, while the range of deuterium values is only 10 ‰. This means that the chlorites were deposited over a rather narrow temperature range from fluids that were isotopically uniform throughout the district. Although there is some uncertainty in the fractionation factors, the average δD-$\delta^{18}O$ composition for the chlorite fluids at 250°C was similar to that of the unmixed saline fluids that produced main stage minerals. These data are compelling evidence that during all stages in the south and course sulfide-chlorite stages in the NEA hydrothermal fluids entering the veins throughout the district from depth were saline and had a uniform isotopic composition with δD of about -50 ‰ and $\delta^{18}O$ of about -3 to -4 ‰.

SLIDE 4 - *H-O isotopic compositions of main-stage quartz*

In the lower right corner of this slide, we have included a histogram of the ^{18}O values of quartz from the OH vein and the NEA. The ranges of ^{18}O values in quartz from both suites are similar, and are nearly twice the range of the contemporaneous chlorites seen in the last slide. This reflects the larger range in temperature and ^{18}O content of the quartz-precipitating fluids, and indicates that the deposition of quartz involved substantial fluid mixing. In this δD-$\delta^{18}O$ diagram, the δD values of inclusion fluids from select whole quartz crystals are plotted against the $\delta^{18}O$ values of the fluids calculated from the ^{18}O mineral data shown in the histogram. The long horizontal dimension of the symbols reflects the range of temperatures used in the calculations. The compositions for quartz fluids determined in this manner plot in a different part of the diagram than the other main stage fluids. However, the δD analyses were made on fluids extracted from bulk crystals that contained both primary and pseudosecondary inclusions. Primary and pseudosecondary inclusions from an OH vein bulk sample were carefully separated by Nora Foley (Foley, et al., 1982) of the U.S.G.S., and the respective fluids analyzed separately for δD. As indicated by the tie lines, the primary inclusion fluids in OH vein quartz are isotopically more like those of the other main-stage fluids, while the pseudosecondary fluid compositions are more like those of meteoric water. It is impossible to physically separate completely the two types of fluid inclusions, so these data are not exact end member compositions. The important point about the data is, however, that they indicate that quartz mineralization on the OH and other southern vein systems occurred near the interface between the saline main stage fluids and overlying meteoric water and they support mixing as the cause of quartz deposition. Note that the NEA bulk samples have δD values similar to that of meteoric water. We can make a strong case therefore that some NEA mineralization was deposited by fluids with a dominant component of meteroic water that had been shifted to heavier ^{18}O values by interactions with wallrocks at depth in the sustem.

SLIDE 5 - *H-O isotopic compositions of main-stage alteration illites*

This slide summarizes the H-O isotope data on illites from alteration zones in the NEA, and on the OH and southern Amethyst veins. The δD and δ^{18}O values of these illites define a nice linear trend, with increasing ^{18}O and decreasing deuterium values toward the southern parts of the district. This is a remarkably systematic data set, and it indicates that all of the clay alteration in the district was related to the evolution of a single hydrothermal system. The nature of the illite-water isotope fractionations is such that this trend must reflect in part a decrease in the alteration temperature from north to south in the district. This temperature decrease is supported by an increase in the expandable layer content of the illites from north to south in the district.

SLIDE 6 -*H-O isotopic composition of main stage alteration fluids*

This shows the calculated composition of the fluids in equilibrium with some of these illites as indicated by the tie lines. The temperature of formation for the NEA illites is assumed to be 200 °C. The temperature of formation for the southern Amethyst illites is assumed to be 150 °C, which is probably close to the minimum required to form illites with less than 10 % expandable layers. The important point is that, regardless of the temperatures we choose, the composition of the alteration water shifted to lower deuterium and higher ^{18}O content in the southern part of the district. The ^{18}O increase in the fluids must reflect exchange with the wall rocks and the fact that the alteration system became more rock dominated to the south. The decrease in the deuterium content of the fluids must reflect increased mixing of overlying meteoric water in the southern part of the district. Again, the fluid composition for the NEA clays indicate a component of exchanged meteoric water in the northern part of the system.

SLIDE 7 - *H-O isotopic compositions of pre-ore rhodochrosite fluids*

On this slide, we have added data for the pre-ore rhodochrosite fluids from the Bulldog Mountain vein system in the southern part of the district. These compositions are based on the measured δD of inclusion fluids and δ^{18}O values calculated from temperature and ^{18}O mineral data. The large horizontal bars reflect the uncertainty in the temperatures used in the calculations. The rhodochrosite fluids show a considerable range of isotopic compositions from north to south in the vein system. This suggests that fluids isotopically similar to main-stage saline fluids in the northern Bulldog Mountain system mixed with high-^{18}O fluids in the southern part of the system. These high-^{18}O fluids evidently disappeared from the system before main-stage mineralization.

SLIDE LEFT 2 - *Schematic summary of fluid sources in Creede system*
SLIDE 8 - *H-O isotopic composition summary of Creede fluids*

The stable isotope evidence points to the presence of four isotopically distinctive fluids in the Creede hydrothermal system. All of these fluids were ultimately derived from meteoric water that fell on highlands in the northern parts of the district. No evidence for magmatic fluid input into the system is recognized in the stable isotope data, although a contribution of 10 % would probably escape detection. The isotopic composition of the southern main-stage and NEA sphalerite fluids is extraordinary for a hydrothermal system in a Tertiary volcanic environment. The composition of these fluids virtually demands that they evolved from meteoric water by extensive evaporation of lake waters and diagenesis in sediments. The isotopically light waters that were drawn into the far northern part of the hydrothermal system underwent oxygen isotopic exchange with wallrocks. *These northern- and southern-recharged waters apparently underwent some mixing across the system's upwelling plume.* The shallow northern meteoric ground waters that flowed along the top of the system were largely unexchanged. These overlying waters also appear to have dominated the latest stage of mineralization in the veins. The origin of the pre-ore high-^{18}O carbonate waters is less certain. The most likely possibility is that they were derived from the dehydration of zeolites or buried evaporite minerals in the Creede formation moat sediments. The attractive feature of this scenario is that these minerals would dehydrate upon heating in the early stages of the hydrothermal system, and, once dehydrated, would not contribute to the system again. Until the Creede Formation is drilled, however, we can only speculate about the origin of these waters.

SLIDE 9 - *$\delta^{13}C$ - $\delta^{18}O$ isotopic compositions of Bulldog Mountain rhodochrosites*

Now let's move on to a discussion of the carbonate isotope geochemistry at Creede. This plot summarizes the carbon and oxygen isotope compositions of rhodochrosites for the Bulldog Mountain vein system. The carbon and oxygen values show a relatively good correlation: although the variations are not entirely systematic spatially along the vein system, the heaviest carbonates occur in the south, and the lightest tend to occur in the north. Calculated fluid compositions indicate that the carbon isotope values of the fluids were lower in the northern part of the Bulldog Mountain vein system than in the southern part of the system. We suspect that this decrease was related to the breakdown of isotopically light organic matter in fluids that were derived from the Creede Formation.

SLIDE 10 - *Creede district map, showing distribution of Creede Fm. travertines*

A proper interpretation of the vein carbonates requires that we consider the isotope geochemistry of travertines in the Creede Formation moat sediments. These travertines formed some one million years earlier than the vein carbonates, and are volumetrically many orders of magnitude more abundant than the vein carbonates. This Creede district map shows the distribution of travertines, and the locations of travertine occurrences which we've studied.

SLIDE 11 - *$\delta^{13}C$ - $\delta^{18}O$ isotopic compositions of Creede Formation travertines*

This slide shows the carbon and oxygen isotope data on the travertines. The tie-lines connect analyses of samples from individual travertine mound localities. Notice that the tie-lines have positive slopes. These slopes are typical of data arrays that are observed in presently forming and fossil travertine deposits throughout the world. They reflect the isotopic evolution of travertines as they precipitated at successively lower temperatures away from the orifice of individual springs.

SLIDE 12 - *$\delta^{13}C$ - $\delta^{18}O$ isotopic evolution of travertines*

This slide demonstrates the general principles governing the isotopic evolution of travertines. Travertine deposition occurs because of the loss of CO_2 as hydrothermal solutions vent at the surface. The maximum depositional temperature for travertines at the orifice of individual springs is approximately 70°C. Higher-temperature solutions lose their CO_2 at depth, and do not form travertines at the surface. Near the orifice, travertines usually precipitate in isotopic equilibrium with the solutions. Subsequent isotopic evolution, however, depends on the rate of travertine deposition. When the deposition rate is slow, the compositions of successively-precipitated travertines tend to follow an equilibrium trend with declining temperature. When the rate of deposition is fast, the isotopic compositions can evolve along non-equilibrium trends with slopes as steep as one. Fluids of a single isotopic composition will therefore deposit travertines of highly variable compositions.

SLIDE 13 - *$\delta^{13}C$ - $\delta^{18}O$ isotopic evolution of Creede travertines*

If we apply this model to the Creede travertines, we see that most of the mineral compositions can be accounted for by kinetic deposition from fluids with average $\delta^{13}C$ values of -8 ‰ and $\delta^{18}O$ values between -2 and +8 ‰.

SLIDE 14 - *$\delta^{13}C$ - $\delta^{18}O$ isotopic compositions of travertine and vein carbonate fluids*

This shows the carbon and oxygen isotope data for the travertines and vein carbonates, along with the calculated compositions of their fluids. The interesting thing here is that the compositions of the two fluids are very similar. There is currently a lot of uncertainty in the modeling, but it seems very likely that the vein carbonates and travertines got their water and carbon from the same sources in the Creede Formation, even though the vein carbonates formed some one million years later than the travertines, in totally different hydrothermal events.

It has been demonstrated that high-pH volcanic lake waters can contain high concentrations of atmospheric CO_2. It is most likely that this atmospheric CO_2 was the major source of carbon in both the travertines and vein carbonates. The fact that fluid compositions are slightly lighter than the -7 ‰ value typical of atmospheric CO_2 indicates that some of the carbon was probably also derived from the breakdown of organic matter that was (and still is) very abundant in the Creede Formation. Contrary to what has been reported in the literature (Steven and Friedman, 1967; Bethke and Rye, 1979), there is no indication of a Mesozoic sedimentary limestone source for the travertine carbon, and there is no indication of a magmatic source for the rhodochrosite fluids.

SLIDE 15 - *Sulfur isotopic compositions of main-stage Creede sulfides and barite*

I would now like to talk about sulfur isotope systematics at Creede.

This figure summarizes the sulfur isotope data on main-stage sulfides and barite for the entire district. The sulfides have a rather narrow range of $\delta^{34}S$ values that average close to 0 ‰. Most sphalerites, for example, have $\delta^{34}S$ values between -2 and +1 ‰. These data are typical of those that have been observed repeatedly for sulfides in hydrothermal ore deposits that occur in volcanic terrains.These data indicate that the main-stage sulfide sulfur for the entire district was isotopically buffered near to 0 ‰, and was therefore probably derived from an igneous source either: directly as H_2S from a magma, or; indirectly from the leaching of igneous sulfide minerals.

The coexisting barites, on the other hand, show a tremendous range of sulfur isotope values, from about +1 to +44 ‰, with the lowest values occurring in the NEA. As far as we are aware, these barite data are unprecedented for an epithermal deposit. This fact alone indicates that there was some element present in the Creede system which is seldom observed in other epithermal systems. As we demonstrated nearly 15 years ago, the narrow range of isotope values for sulfides and the wide range for contemporaneous barites clearly shows that hydrothermal sulfide and sulfate were not in sulfur isotopic equilibrium. These species thus had independent sources, and did not exchange sulfur in the hydrothermal system.

SLIDE 16 - *Sulfur isotopic composition of fluids versus temperature of deposition*

When plotted on a histogram the sulfur isotope data appear uninteresting. However, the very detailed stratigraphy for the OH vein sphalerite enables us to investigate time-space variations on a very detailed scale. We have observed no systematic time-space trends in the sulfur isotope values of the OH sphalerites. However, when we plot the $\delta^{34}S$ values of sphalerite versus the filling temperature of fluid inclusions of an individual growth zone that can be traced throughout the OH vein (Hayba, 1985) we consistently observe a good correlation such as you see here. The progressive decrease of $\delta^{34}S$ values with progressive mixing can not be the result of isotopic reservoir effects that resulted from the prior precipitation of sulfides. They are also probably not a result of progressive exchange with sulfate. Since fluid inclusion studies indicate that the temperature decrease is due to mixing with overlying dilute waters that interfaced with the main stage saline fluids, the data strongly suggest that some isotopically light sulfide was present in the overlying water. These data also indicate that the sulfur isotopic composition of the deep H_2S was about -1 per mil while that of H_2S.in the overlying fluid was significantly lighter. This correlation and data we will present on late stage sulfides and the gas chemistry data presented by Gary Landis (Landis and Rye, 1987) indicate a sediment source for sulfur in the northern part of the system.

SLIDE 17 - *Sulfur and oxygen isotopic compositions of Creede barites*
This figure summarizes the sulfur and oxygen isotopic data on Creede district barites. Almost all of the data lie within a triangle that must reflect some kind of three-component mixing scenario. Within this triangle, different vein systems show different data distributions which I will comment on later. First, I would like to discuss the origin of the different sulfates that formed the end members of this triangular data distribution.

SLIDE LEFT 3 - *Schematic summary of sulfate sources in Creede system*
SLIDE 18 - *S-O isotopic composition Creede sulfate sources*
The slide on the right *(SLIDE 16)* shows the barite data set with the addition of three sulfate composition fields which we propose for end members of this mixture. The slide on the left shows where these sulfate sources occur in the system.

The next series of slides will clarify the origin of these three end member sulfates.

SLIDE 19 - *Sulfur and oxygen isotopic compositions of Creede Fm. sulfate*
The only way we can get large positive values for both sulfur and oxygen in sulfate is through a cycle of bacteriogenic reduction in a sedimentary environment. This means that the sulfate for the right-hand apex of the triangle must have evolved within the Creede Formation moat sediments prior to ore deposition. The Creede caldera moat was a large catch basin that probably received sulfate from several sources during sedimentation. Possible sources include: sulfate from the oxidative weathering of sulfides in the rocks, or; the oxidation of H_2S in fumaroles that may have been associated with the volcanic or hydrothermal activity. Other possible sources are the sulfate which adsorbed onto volcanic glass, and sulfate from spent solutions that produced earlier porphyry-type mineralization. Finally, there is a faint possibility that evaporite minerals from deeply-buried sediments may have been added to the moat by deeply-circulating fluids that were responsible for travertine deposition. This possibility is considered remote, however, as recent strontium isotope studies on the travertines show no evidence of a sedimentary signature (R.O. Rye and K. Futa, unpublished data).

The isotopic enrichment of residual sulfate during bacteriogenic reduction usually follows a 4:1 or 2:1 isotopic enrichment on this type of diagram. You can see that 2:1 isotopic enrichment of sulfate from a number of the postulated sources could account for the isotopic composition of sulfate near the right-hand apex of the triangle. Another possibility is that the isotopic enrichment may have occurred along a steeper slope if the sulfate exchanged with ^{18}O-enriched chemical sediments. The important point here is that, regardless of how its composition evolved, one of the sulfate sources for the hydrothermal fluids was most likely the pore solutions of the Creede Formation moat sediments.

SLIDE 20 - *Sulfur and oxygen isotopic compositions of heavy $\delta^{34}S$ sulfate*
The sulfate near the uppermost apex of the data triangle has very heavy sulfur and intermediate oxygen isotope compositions. The moat sediment pore fluid sulfate was probably initially far out of oxygen isotopic equilibrium with the -3 to -4 ‰ pore fluids. As soon as the moat sediment pore fluid sulfate was heated, its oxygen would start to equilibrate isotopically with the water in the fluids. The vertical lines on this slide indicate the oxygen isotope values of sulfate in equilibrium with -4 ‰ $\delta^{18}O$ fluids at various temperatures. When the temperature of the fluids reached about 100°C, the sulfate would also start to be reduced by thermochemical reaction with organic matter. If only partial reduction occurred, the residual sulfate would have become enriched in ^{34}S. If both oxygen isotope exchange and reduction of sulfate occurred, it is reasonable that the moat sediment pore fluid sulfate would obtain a composition similar to the sulfate in the upper apex of the triangle. This reduction and exchange could have occurred in two places where moat sediment pore fluid was heated in the presence of organic matter. One was underneath the district after the moat sediment pore fluids were recharged into the deeper parts of the hydrothermal system. The other place was where the Creede Formation pore fluids interfaced with the hydrothermal fluids in the southern vein.

SLIDE 21 - *Sulfur and oxygen isotopic compositions of light $\delta^{34}S$ sulfate*
The only way that we can get near 0 ‰ $\delta^{34}S$ sulfate characteristic of the lowermost apex is through the kinetic oxidation of H_2S. There were two places in the hydrothermal system where H_2S could have been oxidized. One was in the upwelling plume as a result of reaction with the oxidizing ash-flow tuffs. The other was in the very shallow parts of the system by reaction with dissolved oxygen. The lower part of this slide shows the sulfur and oxygen isotopic composition of these fluids and of sulfate derived from the oxidation of sulfate in these fluids. In this case, only sulfate derived from the hydrothermal oxidation of H_2S has a composition that lines up with the lowermost apex of our triangle. There is no evidence that any of the barite sulfate in the system was related to the surficial oxidation of H_2S. If the aqueous sulfate had also reached sulfur isotopic equilibrium with the large reservoir of 0 ‰ H_2S in the system, it would have had compositions falling somewhere (depending on the temperature of equilibration) within the parallelogram on the diagram. The fact that no barites occur in this compositional region demonstrates that the residence time of sulfate in the system was not long enough for it to reach equilibrium with the H_2S. The important point of this discussion is that sulfate was derived basically from two sources: from the Creede formation pore solutions, and by oxidation of H_2S within the hydrothermal system. A third sulfate composition was created wherever the pore fluid sulfate was heated in the presence of organic matter, either during recharge at depth in the system, or during mixing with the hydrothermal fluids in the southern ore zones.

SLIDE 22 - *Sulfur and oxygen isotopic compositions of Creede channel and Holy Moses barites*
If we go back and look at the data, the trends for the different vein systems and disseminated mineralization can be explained by different mixing scenarios involving the three end member compositions. The linear trend for the Holy Moses mineralization and the disseminated mineralization in the Creede Formation channel, for example, is most easily explained by mixing of hydrothermal sulfate derived from the oxidation of H_2S with partially reduced moat sediment pore fluid sulfate. This most likely occurred along the top of the system where shallow pore fluids within the overlying Creede Formation interfaced directly with the laterally flowing hydrothermal fluids.

SLIDE 23 - *Sulfur and oxygen isotopic compositions of Bulldog Mountain and Amethyst barites*
The triangular Bulldog Mountain and Amethyst data distributions can be explained by the mixing of sulfate from hydrothermal oxidation of H_2S, partially reduced moat sediment

sulfate, and an additional component of moat sediment sulfate that did not receive enough heat to undergo reduction and isotopic exchange at the far southern end of the district. We have not observed obvious systematic isotopic variations in barite within the Bulldog or Amethyst vein systems or across individual crystals. This indicates that mixing during barite deposition in the southern vein systems occurred along an interface which repeatedly fluctuated back and forth along the vein system and wiped out any systematic spatial variations in barite isotopic compositions.

SLIDE 24 - *Sulfur and oxygen isotopic compositions of NEA and Midwest barites*
The NEA and Midwest trends reflect the mixing of sulfate from hydrothermal oxidation and partially reduced sulfate from the Creede Formation moat sediments. The trend for the ^{18}O values for the NEA barites indicates that the Creede moat sediment sulfate that was recharged into the system did not reach oxygen isotopic equilibrium with the hydrothermal fluids at high temperatures.

SLIDE 25 - *Sulfur isotopic equilibration rates*
The lack of isotopic equilibrium in the barites can be used to give us a handle on the residence times of hydrothermal fluids in various parts of the system. For example, this figure shows the sulfate-sulfide sulfur isotopic equilibrium curve and the time in years required to obtain 90% equilibration between sulfate and sulfide for Creede-type solutions. Sulfate will reach equilibrium with sulfide in 70 hours at 400°C, 17 days at 350°C and only 4.4 years at 250°C. The temperature of the hottest part of the Creede hydrothermal system is not known, but it probably was at least 350°C. The kinetics of sulfur isotope exchange in sulfate are such that the sulfate could not have resided in the hottest parts of the hydrothermal system for more than a few days without undergoing substantial isotopic exchange with sulfide. The oxygen isotope exchange rates for sulfate are less well-quantified, but are generally faster than those shown here for sulfur. This implies that the moat sediment sulfate traveled nearly 10 km laterally at depth in the system without being heated substantially until it reached the system's hottest parts in the northern parts of the district. Once the fluids were heated, they had to have moved up the plume very rapidly to escape sulfur and oxygen isotopic equilibration.

Once deep drill hole information is available, we should be able to use the lack of isotopic equilibrium in sulfate to quantify not only the residence times, but also the flow rates of the hydrothermal fluids in different parts of the system.

SLIDE 26 - *Sulfur isotopic compositions of late-stage sulfides*
Finally, this figure summarizes the sulfur isotope data for late-stage botryoidal pyrite, marcasite and other sulfides from Creede. Here, we have measured a tremendous range of δ^{34}S values, from -44 to +50 ‰! This spans nearly the entire range of values observed for all naturally occurring sulfides. Some of this isotopic variation can perhaps be explained as a result of disproportionation of intermediate-valency aqueous sulfur species; however, the magnitude of the range requires that some sulfide sulfur was derived from intra-caldera moat sediment sources, either by breakdown of sulfur-bearing organic matter or by reduction of isotopically distinctive sulfate. Geoff Plumlee presented evidence at the San Antonio GSA *(Plumlee and Rye, 1986)* that the light sulfur was derived from buried moat sediments in the northern parts of the district, while the heavy sulfur was derived from the Creede Formation. Our studies have indicated that these sources contributed isotopically distinctive sulfur to the fringes of the system during main-stage mineralization, but not until the main-stage saline system collapsed did their contribution become obvious in the deeper veins.

SUMMARY

In summary, the complex stable isotope systematics which we've documented in the Creede hydrothermal system resulted from the mixing of different fluids and components from multiple sources in different parts of the system. We have long known that such mixing is a characteristic feature of epithermal ore deposits. What makes the stable isotope geochemistry of the Creede system unique is the contribution of isotopically evolved water, sulfate, sulfide and organic matter from intra-caldera moat sediments. It has provided us with powerful tracers for identifying constituent sources and defining the system's hydrology to an extent normally not possible in other epithermal systems.

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Rye, R. O., Plumlee, G. S., Bethke, P. M., and Barton, P. B., Jr., 1987, Stable isotope geochemistry of the Creede, Colorado, hydrothermal system [abs]: Geol. Soc. America Abstracts with Programs, v. 19, no. 5, p. 330-331.

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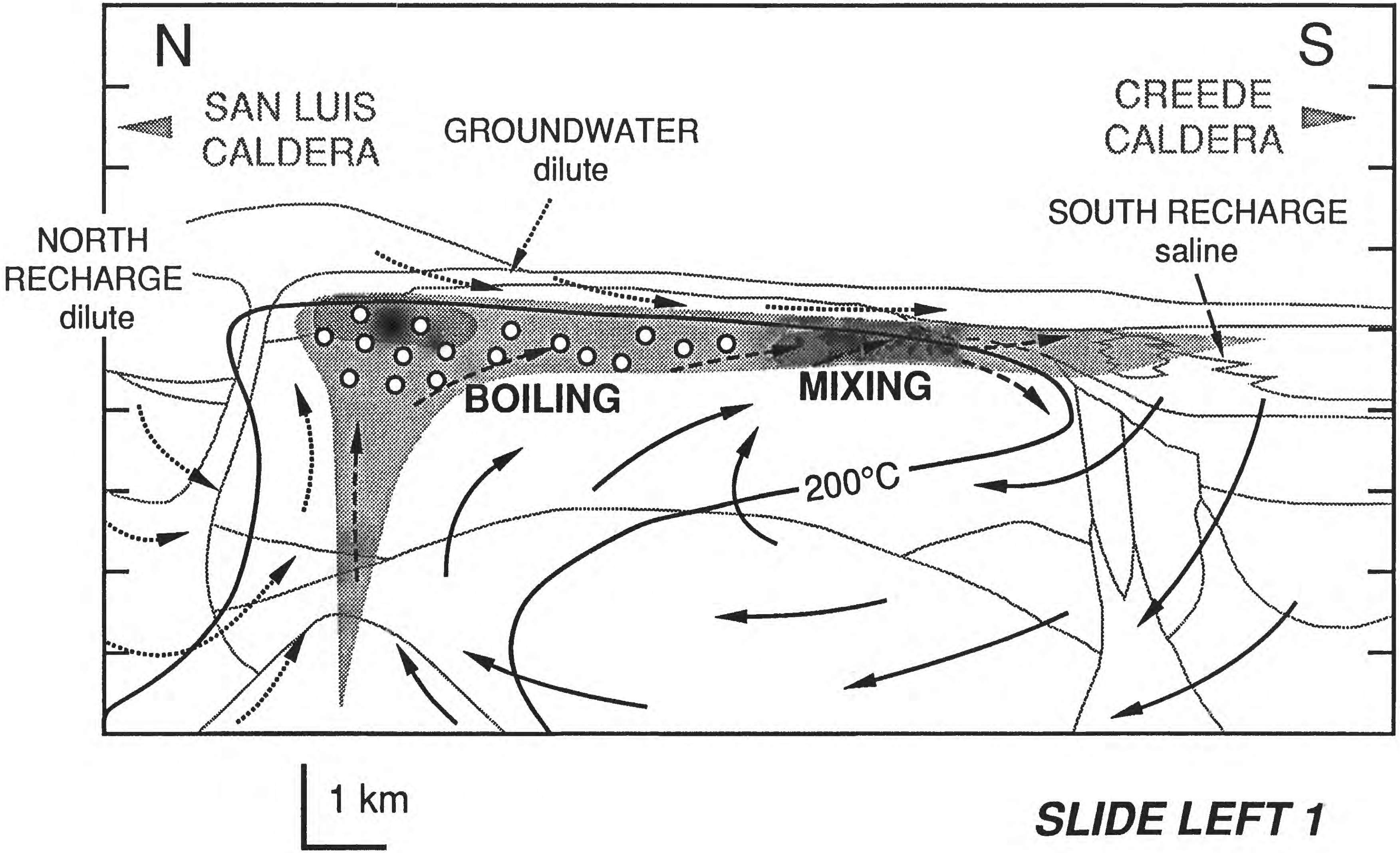
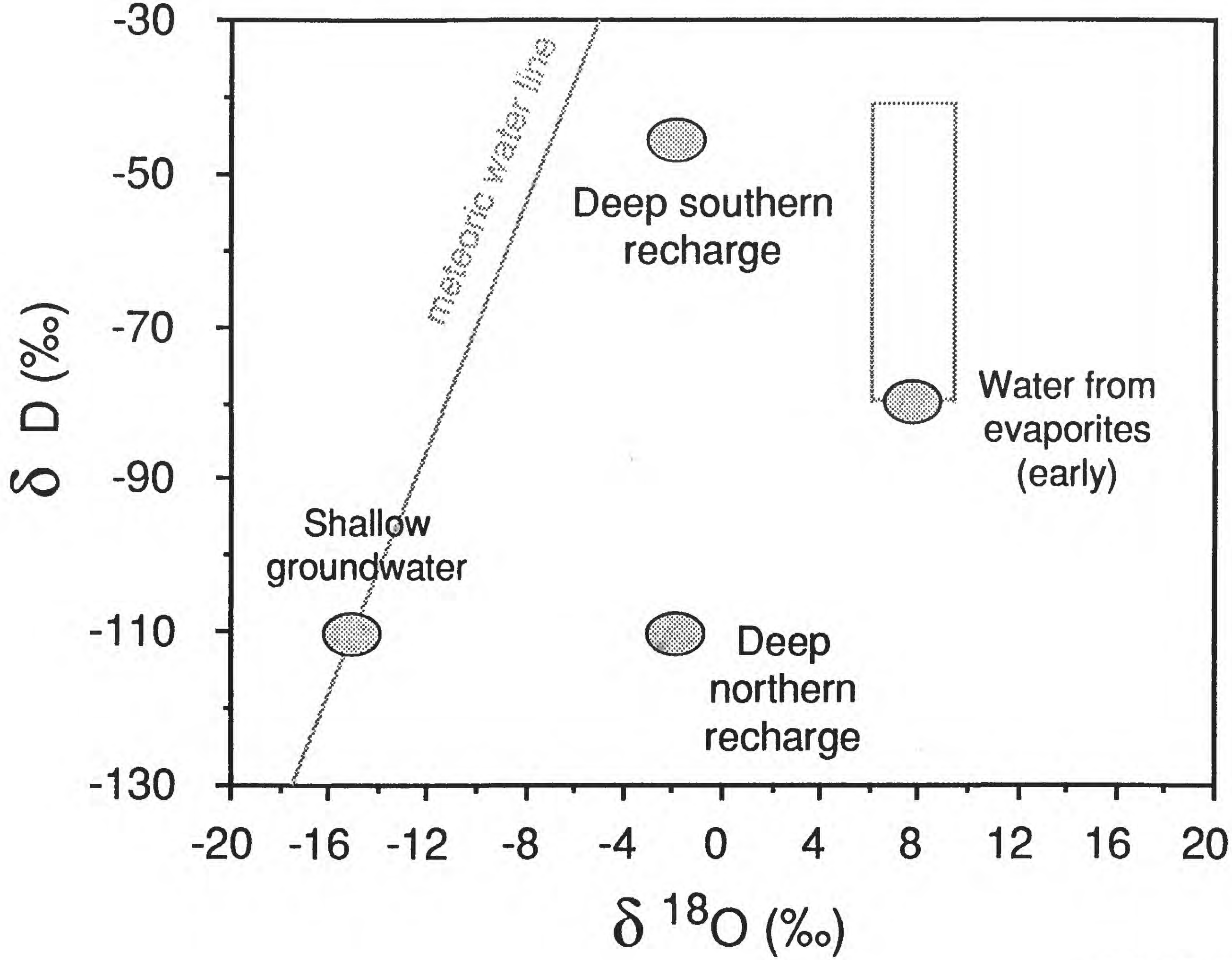
MAIN STAGE CREEDE SYSTEM HYDROLOGY



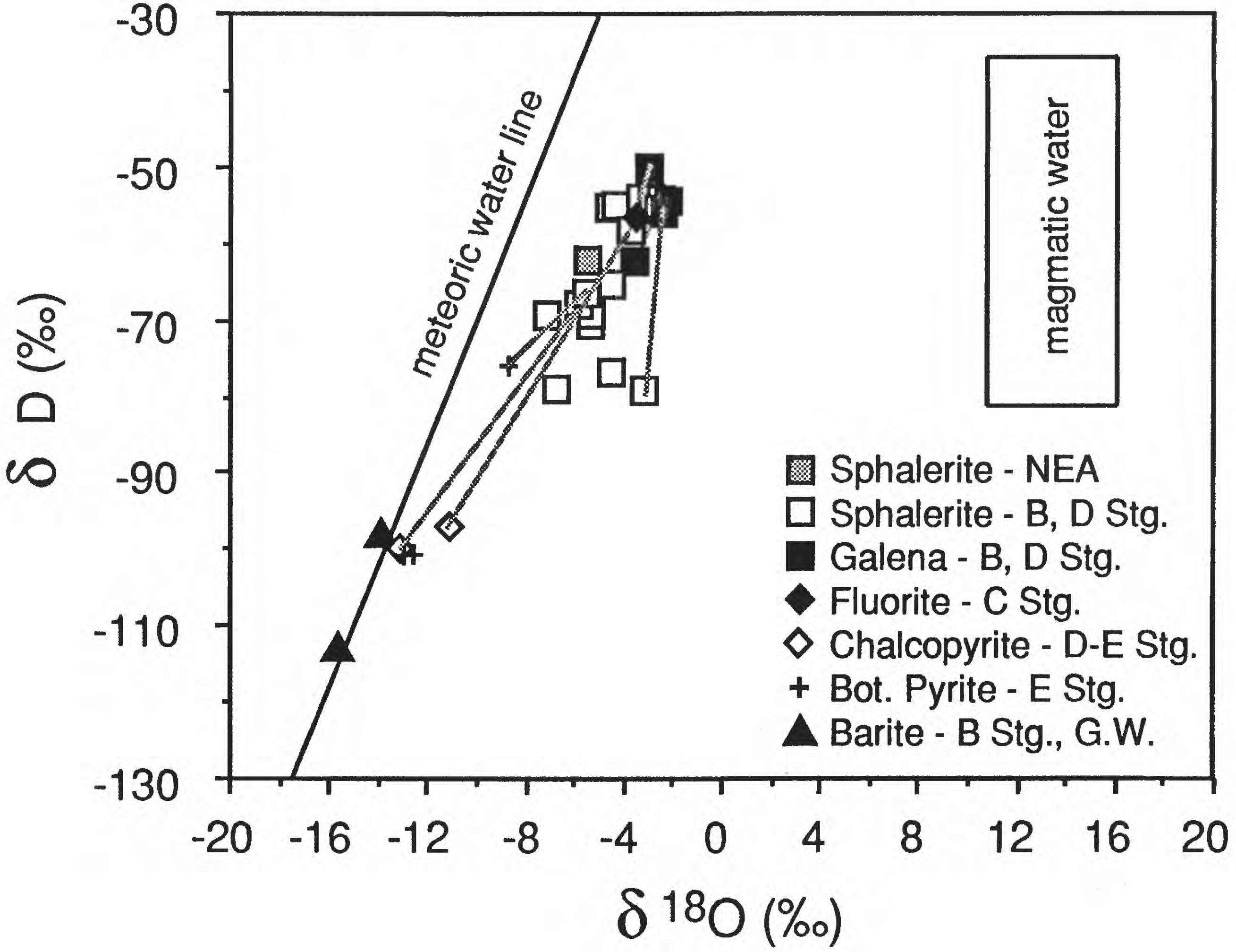
SLIDE LEFT 1

ISOTOPIC COMPOSITIONS OF WATERS IN CREEDE HYDROTHERMAL SYSTEM



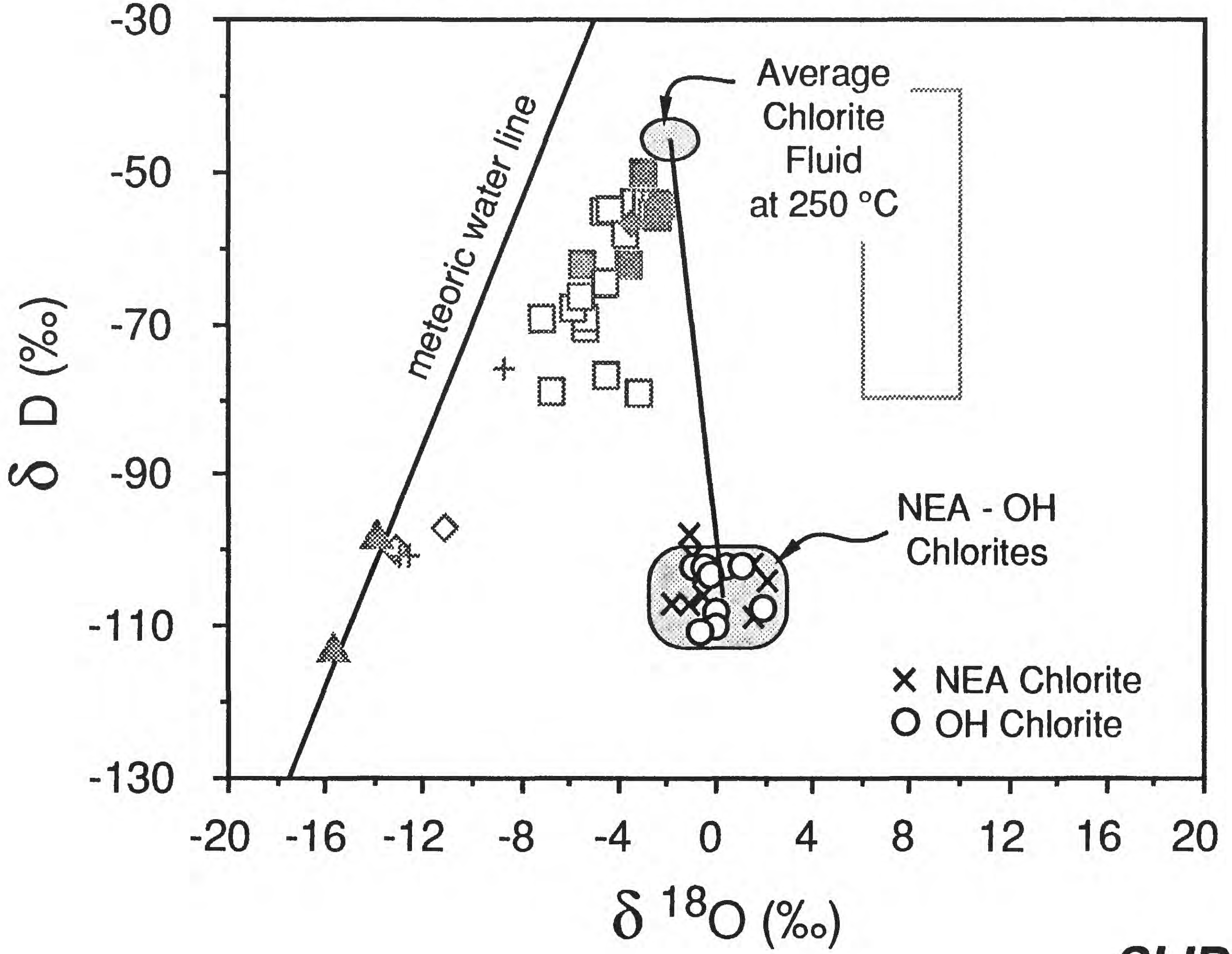
SLIDE 1

H - O ISOTOPIC COMPOSITION OF MAIN & LATE STAGE INCLUSION FLUIDS



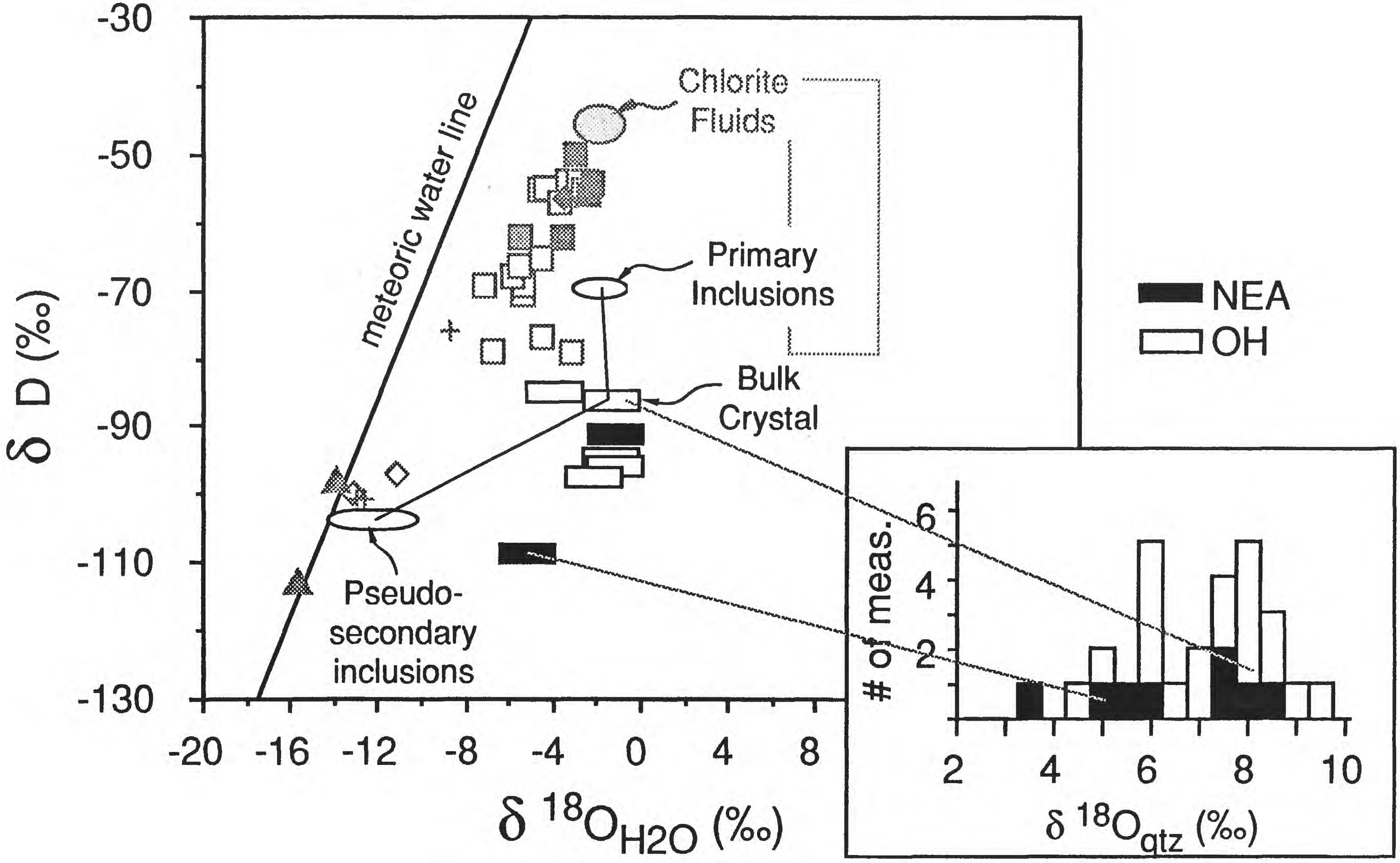
SLIDE 2

H-O ISOTOPIC COMPOSITION OF CHLORITES AND CHLORITE FLUIDS



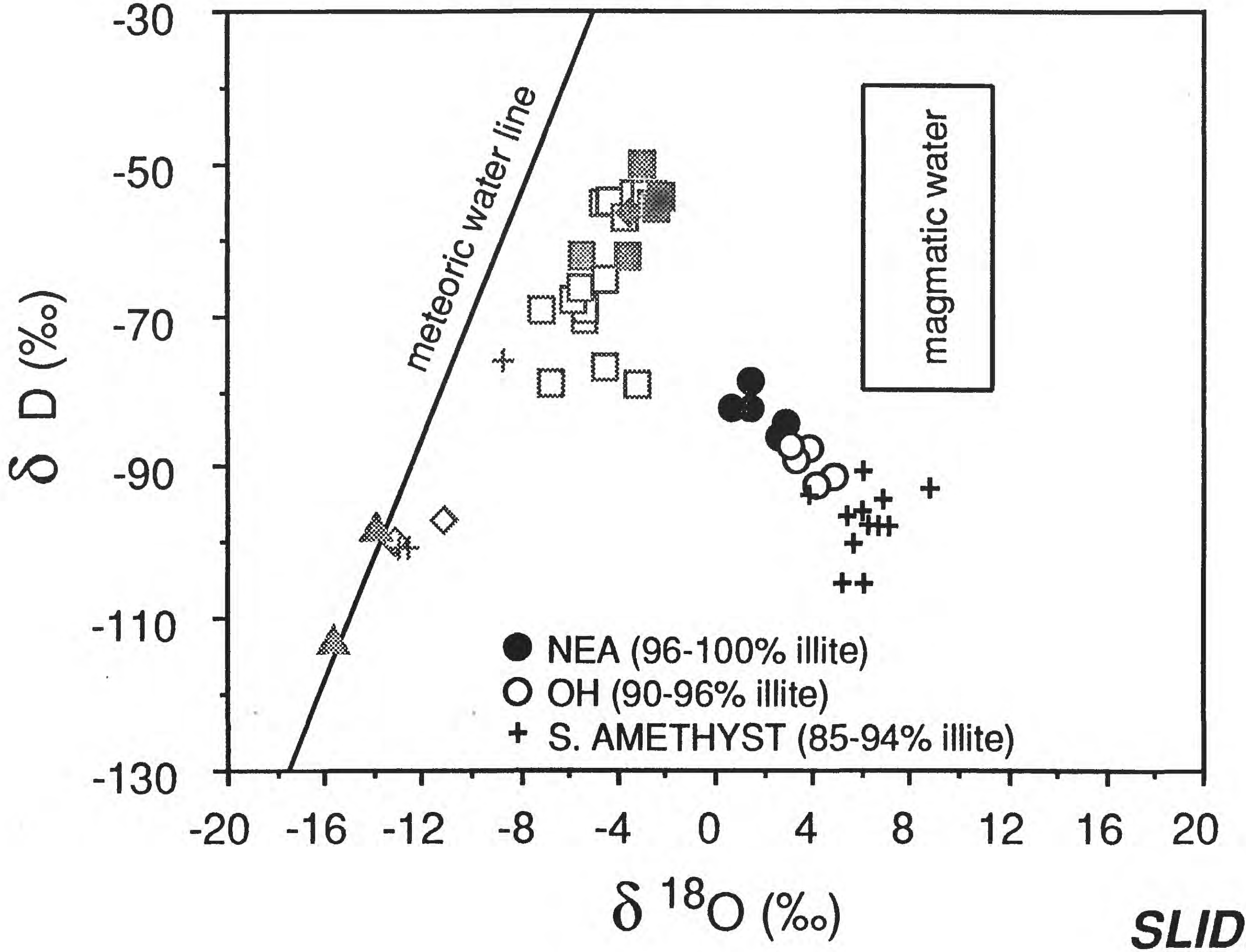
SLIDE 3

H-O ISOTOPIC COMPOSITION OF PRIMARY AND PSEUDOSECONDARY INCLUSION FLUIDS IN OH-VEIN QUARTZ



SLIDE 4

H-O ISOTOPIC COMPOSITION OF ALTERATION ILLITES



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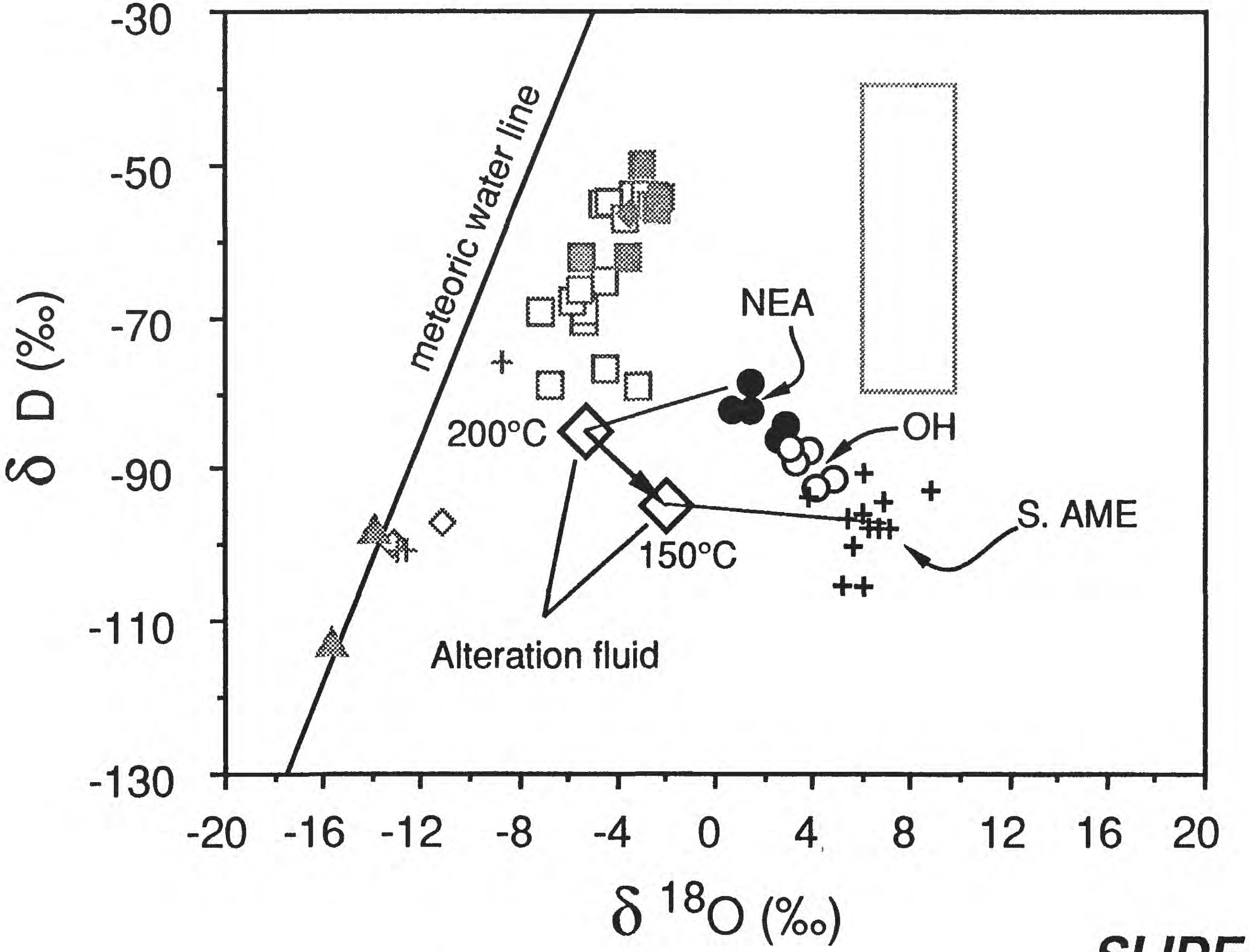
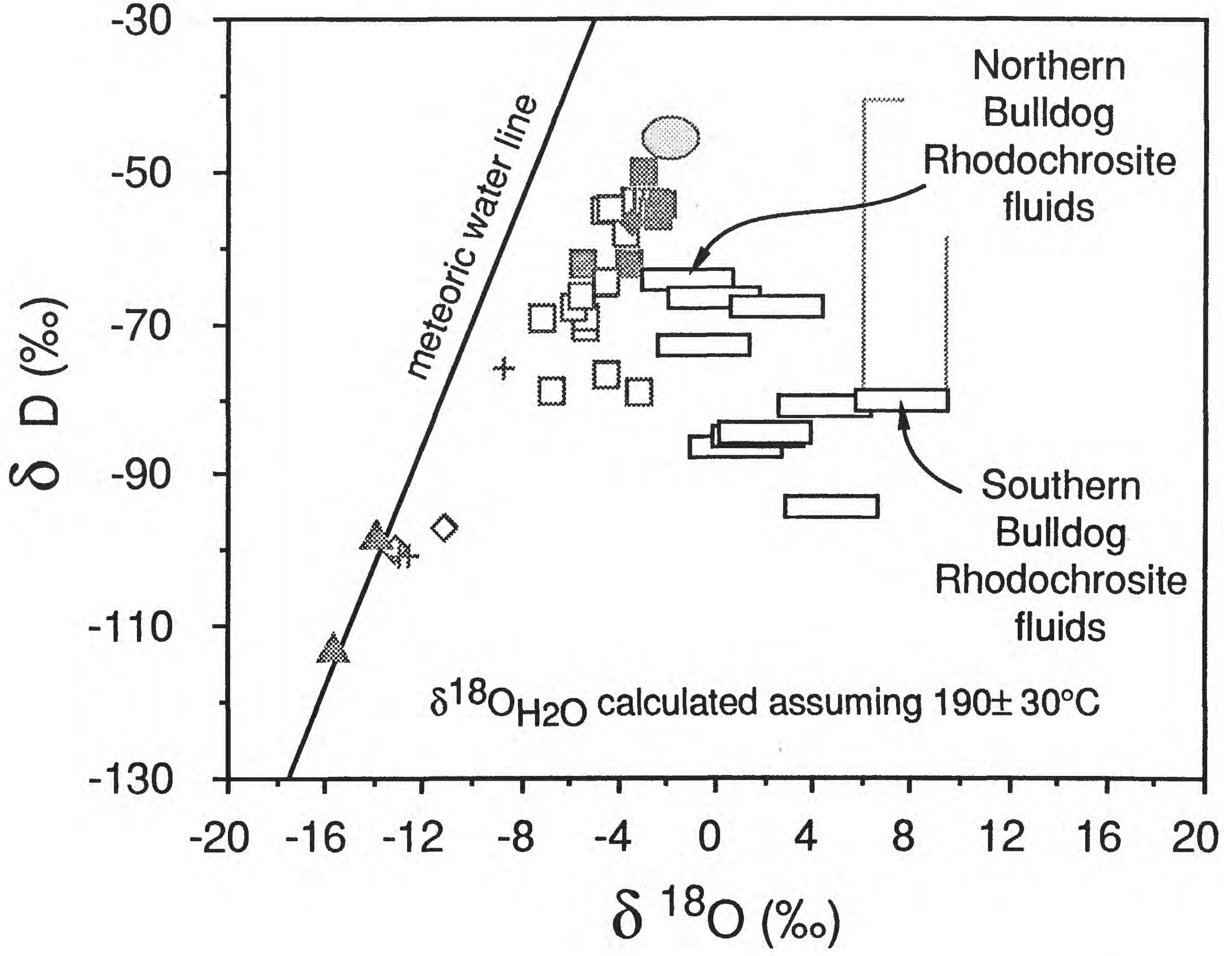
H-O ISOTOPIC COMPOSITION OF ALTERATION ILLITES



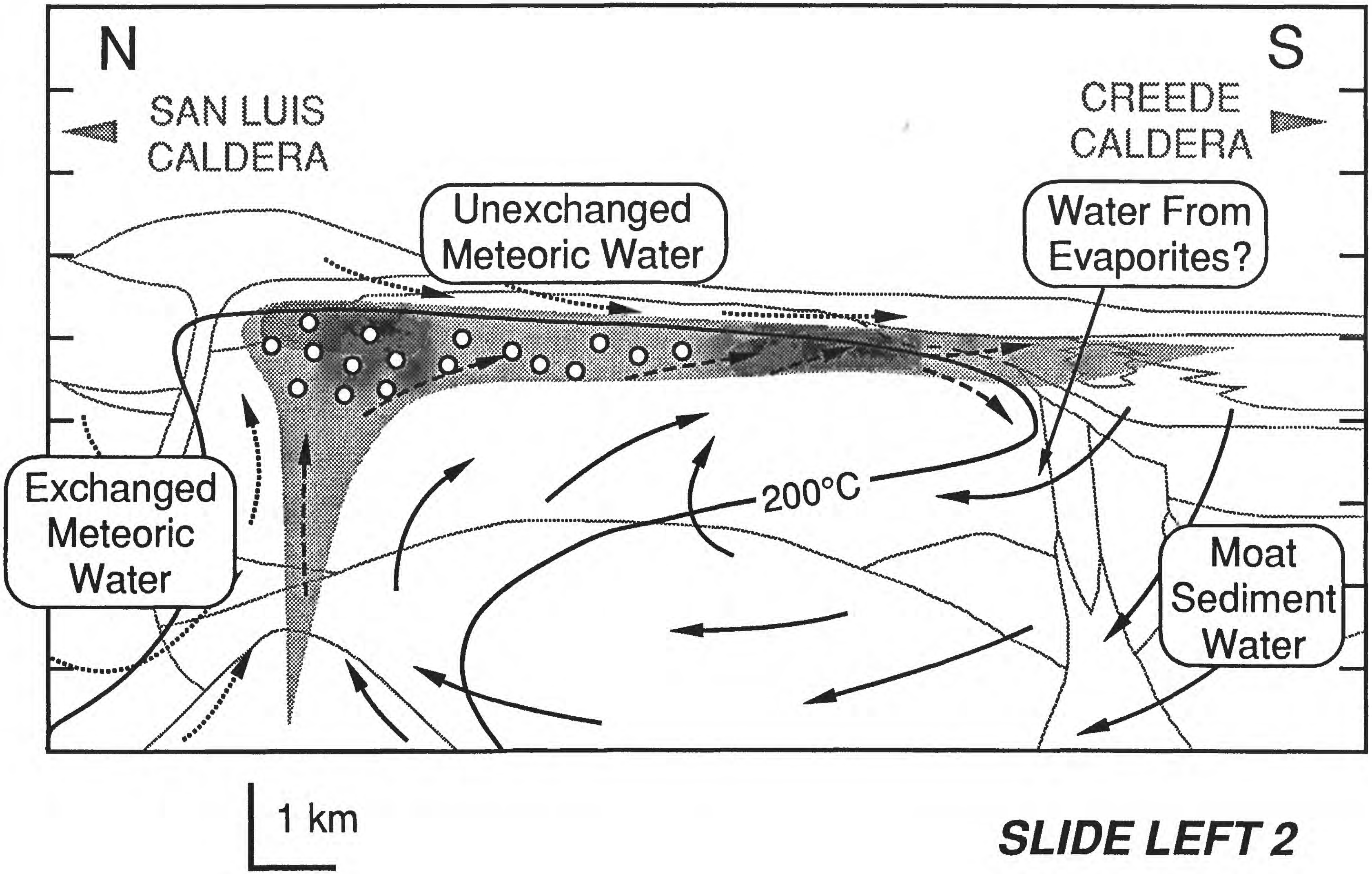
SLIDE 6

H-O ISOTOPIC COMPOSITION OF BULLDOG MTN. RHODOCHROSITE FLUIDS



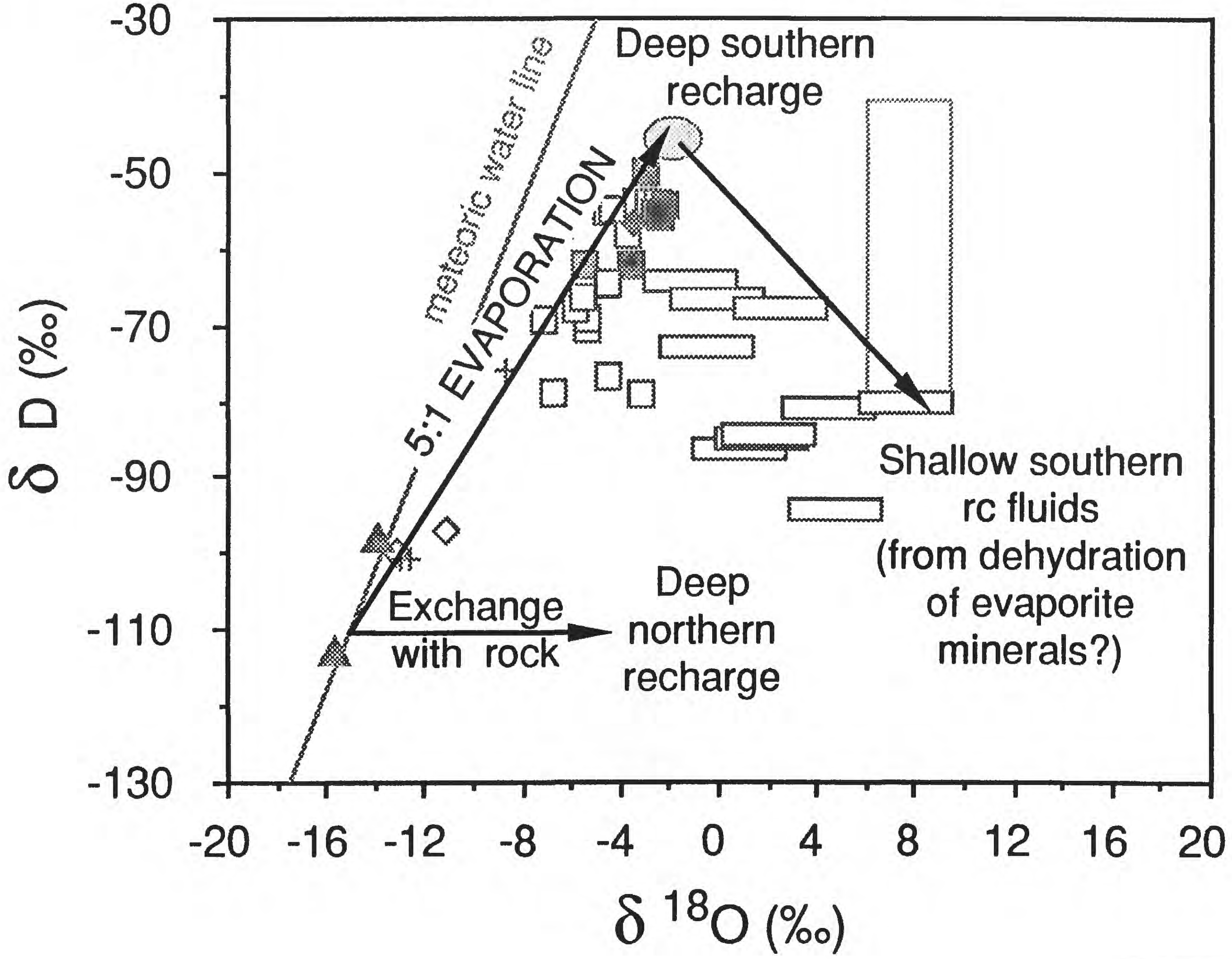
SLIDE 7

WATER SOURCES IN THE CREEDE HYDROTHERMAL SYSTEM



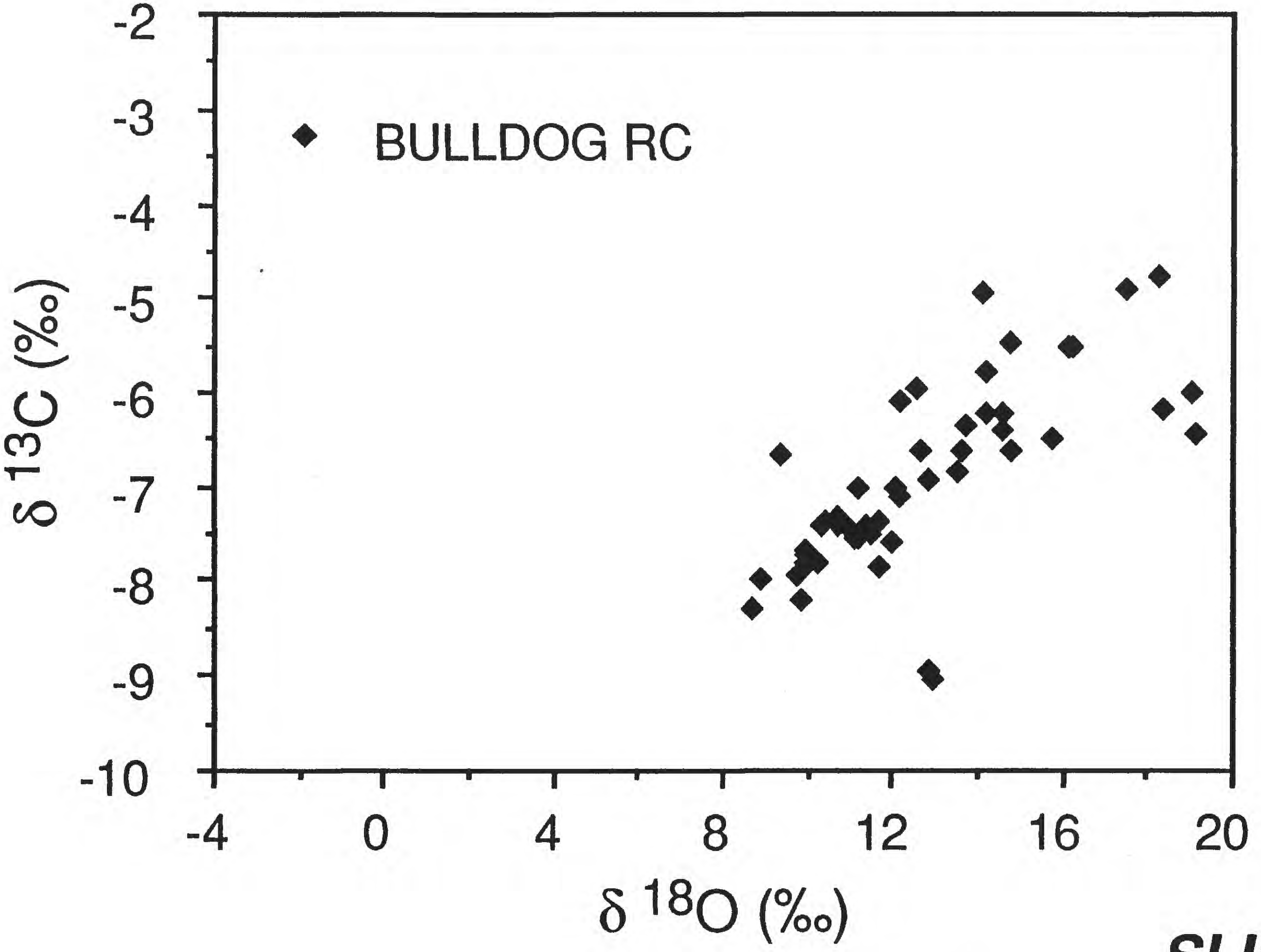
SLIDE LEFT 2

ORIGIN OF WATERS IN CREEDE HYDROTHERMAL FLUIDS



SLIDE 8

C-O ISOTOPE COMPOSITIONS OF BULLDOG MTN. RHODOCHROSITES



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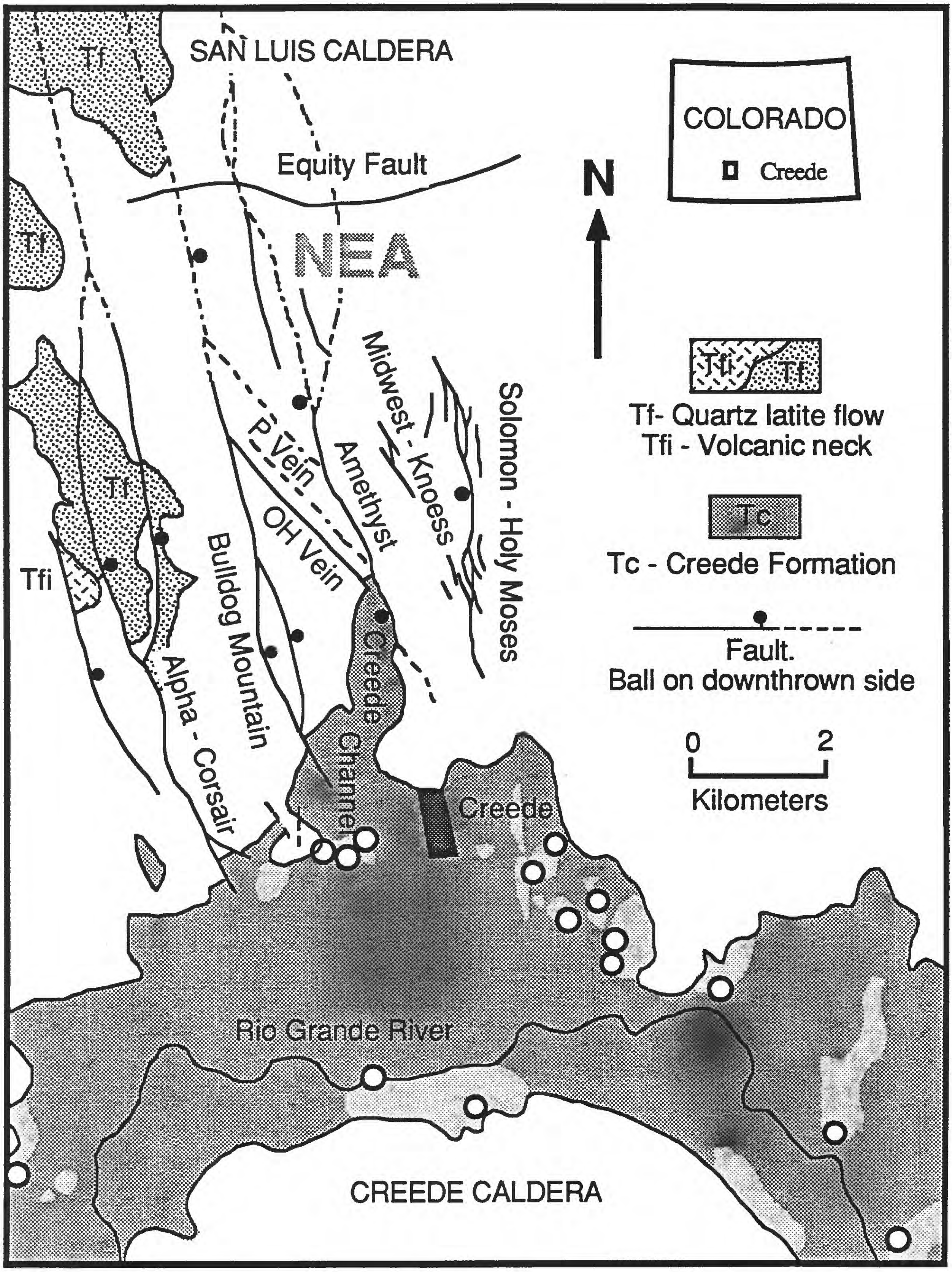
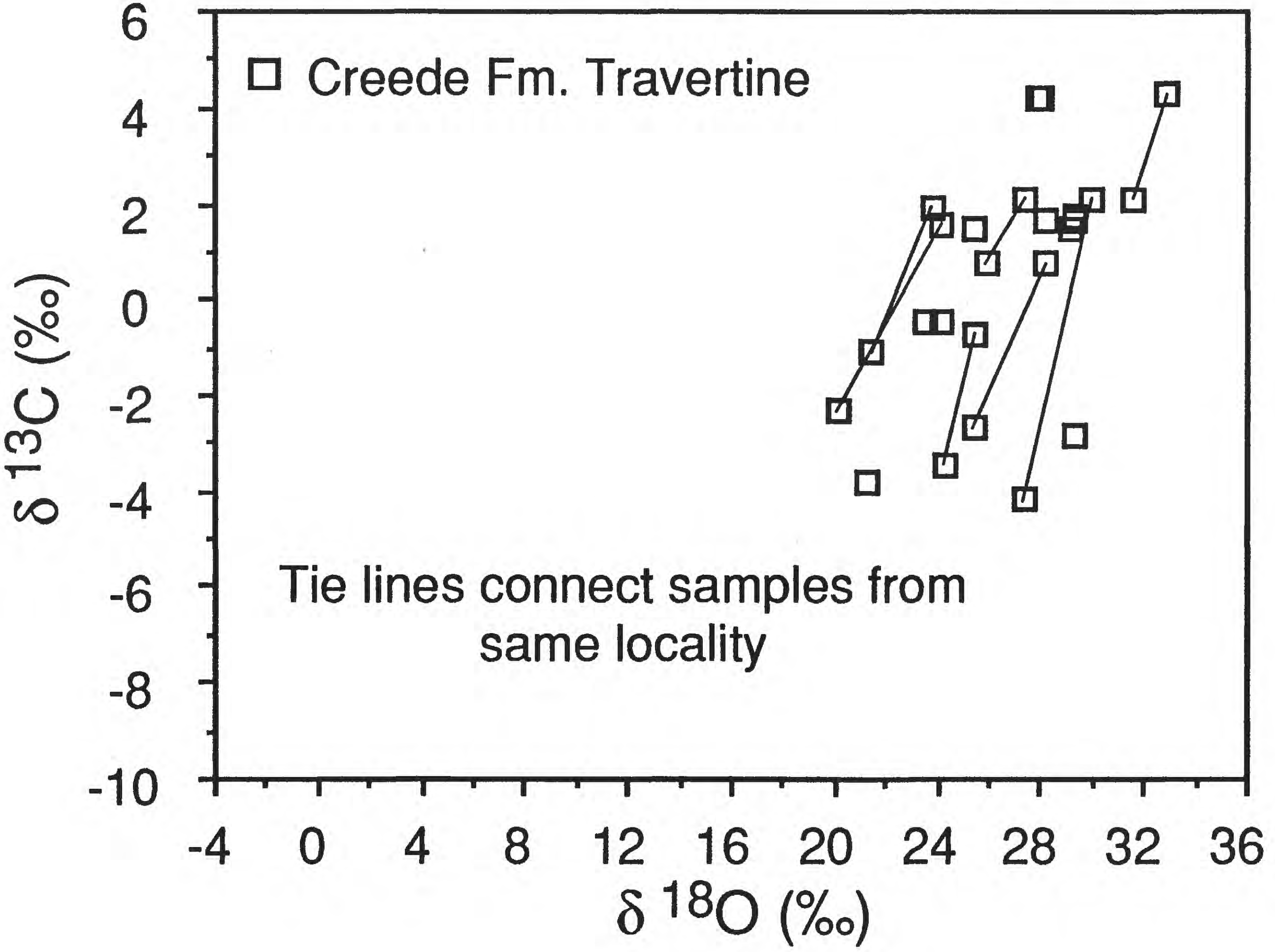


▨ CREEDE FM. TRAVERTINE

○ SAMPLE LOCATION

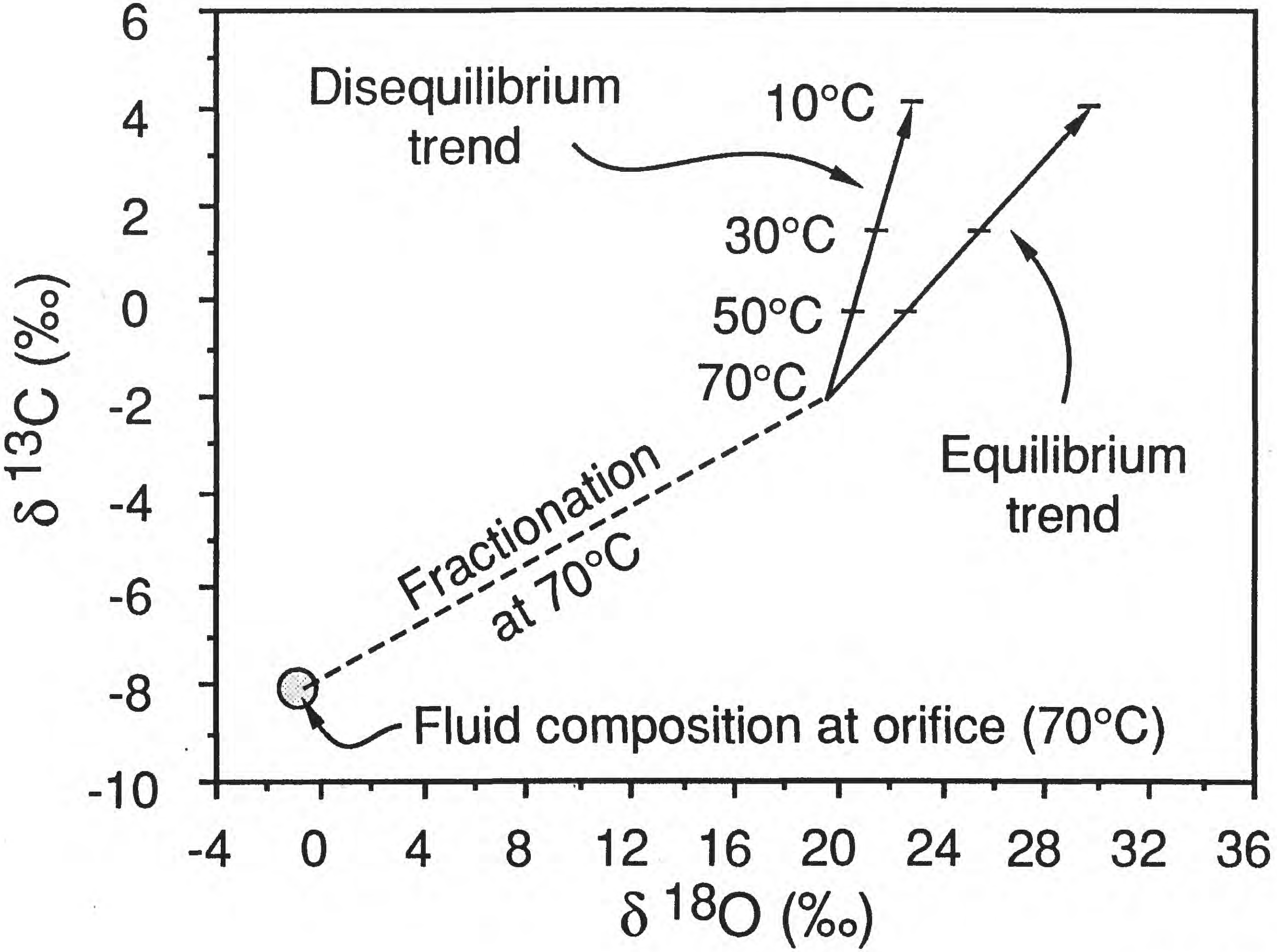
SLIDE 10

C-O ISOTOPE COMPOSITIONS OF CREEDE FORMATION TRAVERTINES



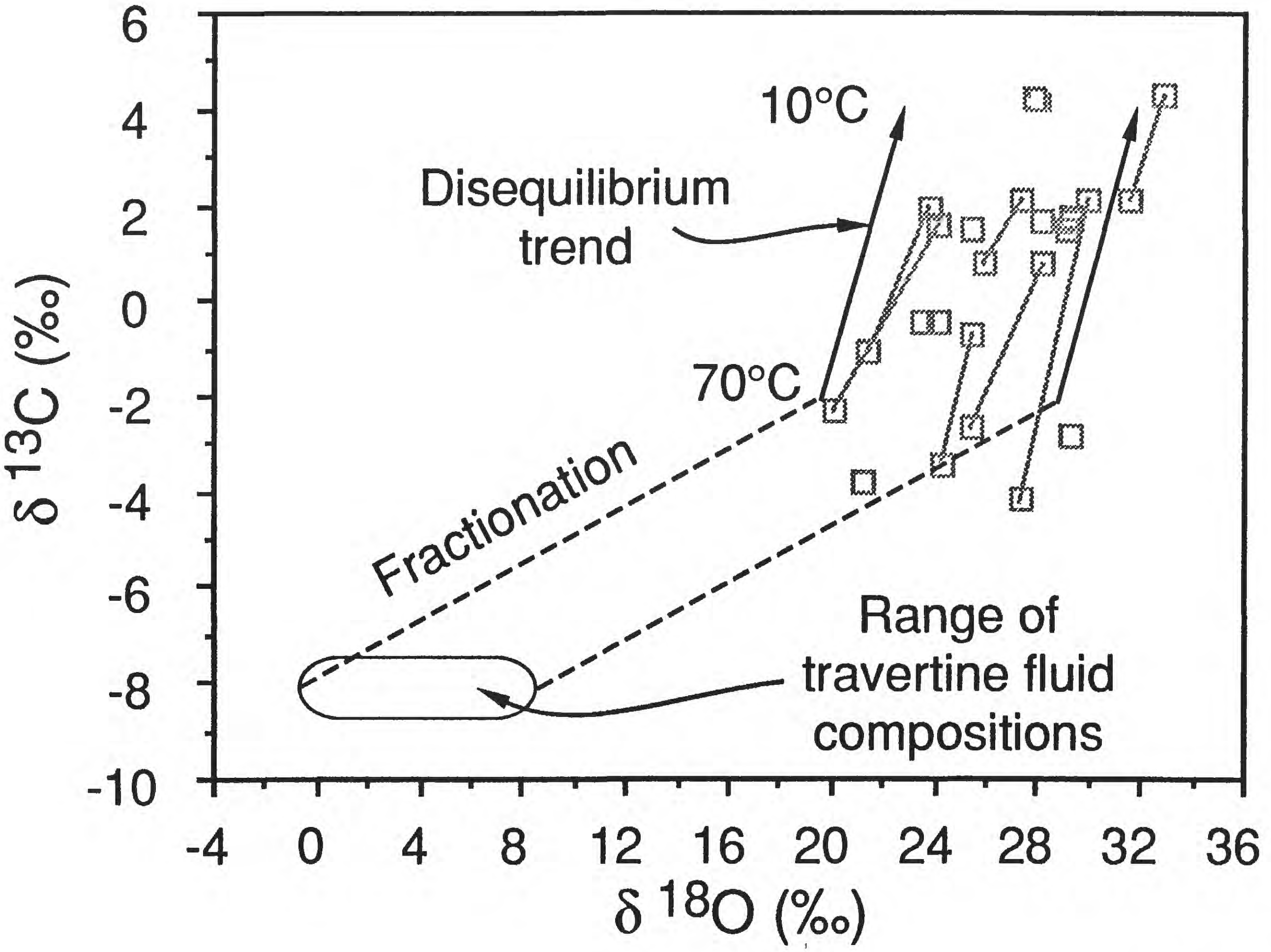
SLIDE 11

GENERAL MODEL FOR ISOTOPIC EVOLUTION OF TRAVERTINES



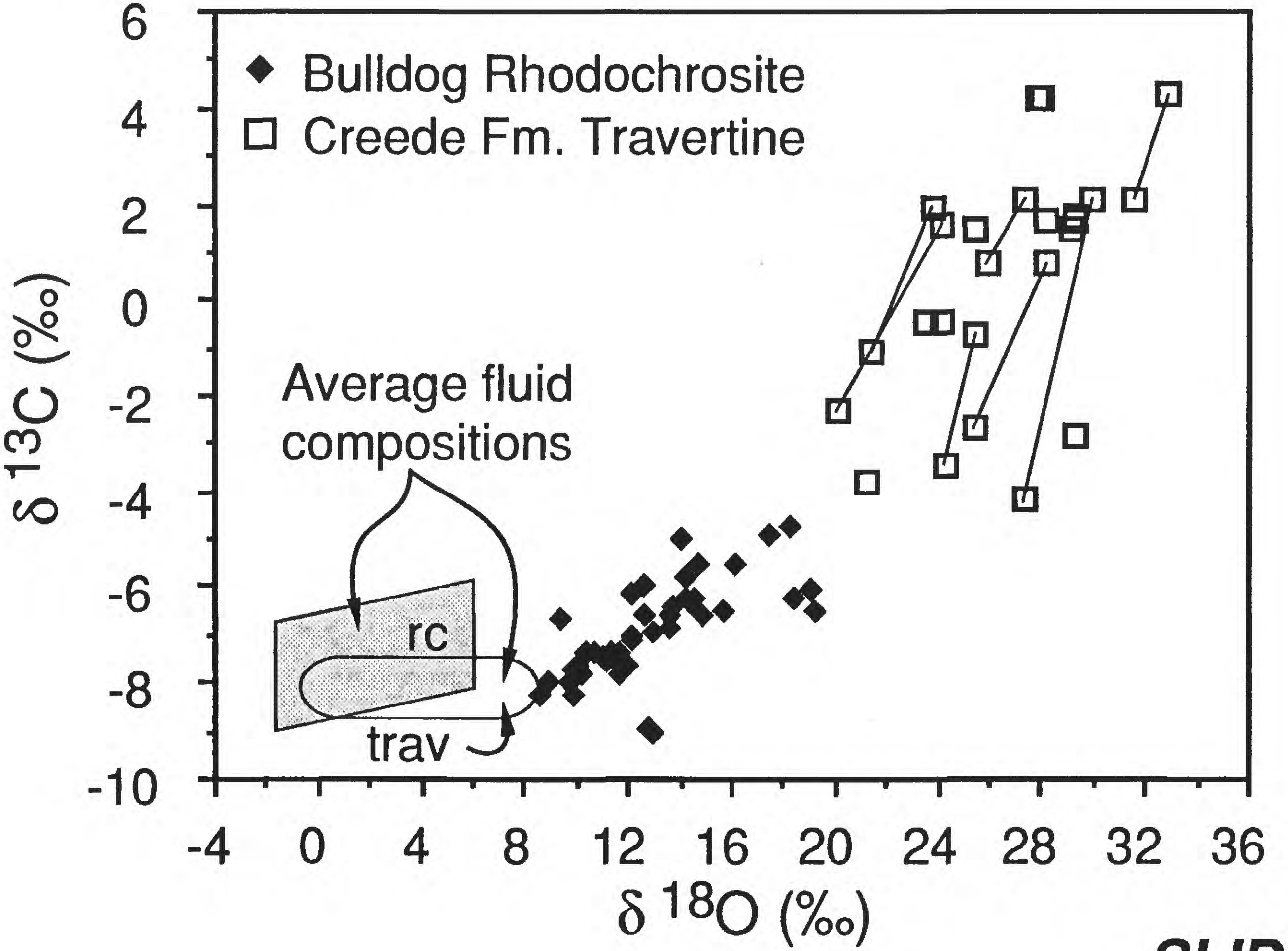
SLIDE 12

MODEL FOR TRAVERTINE FLUID COMPOSITIONS



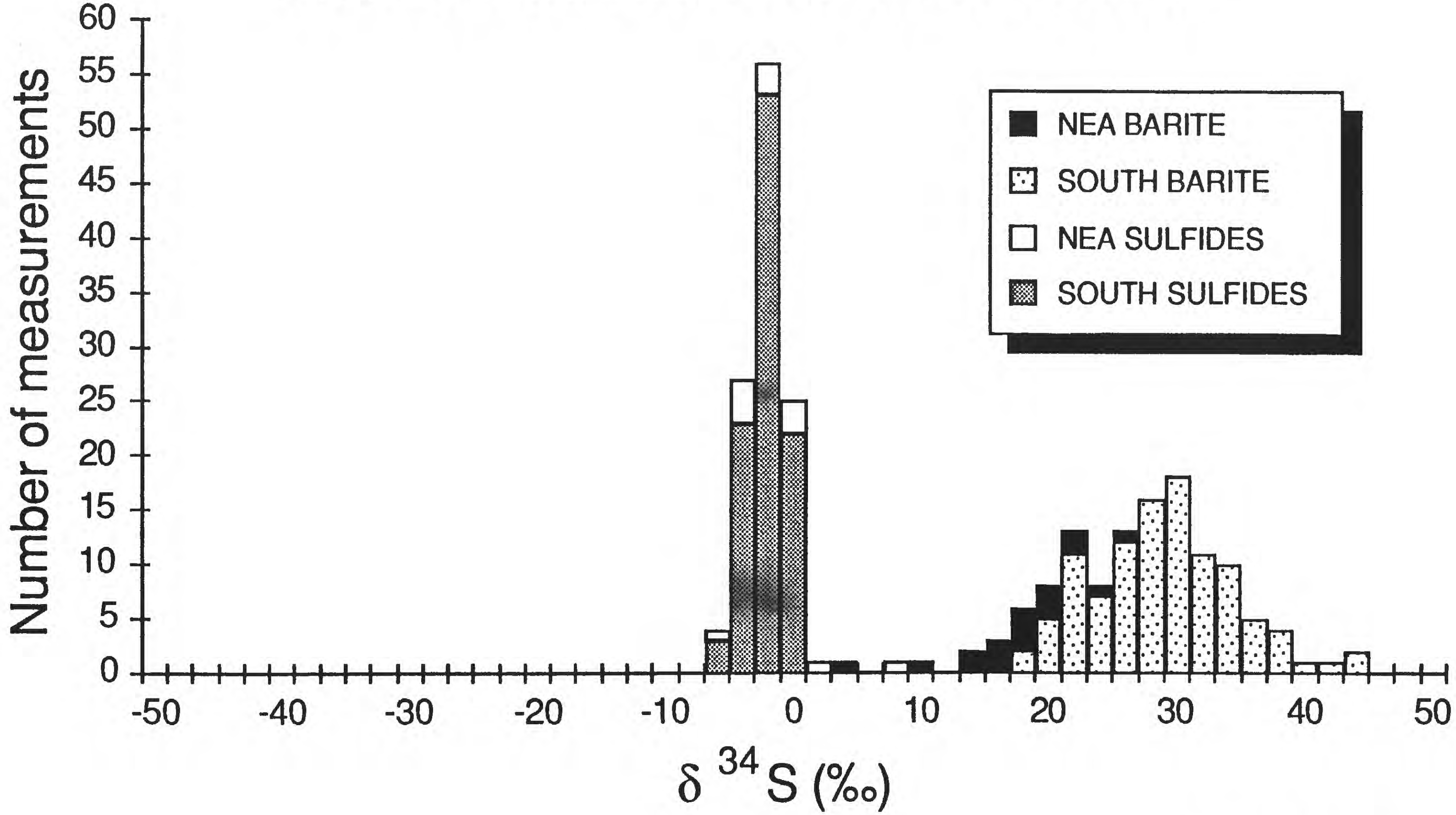
SLIDE 13

C-O ISOTOPE COMPOSITIONS OF RHODOCHROSITES, TRAVERTINES , AND FLUIDS



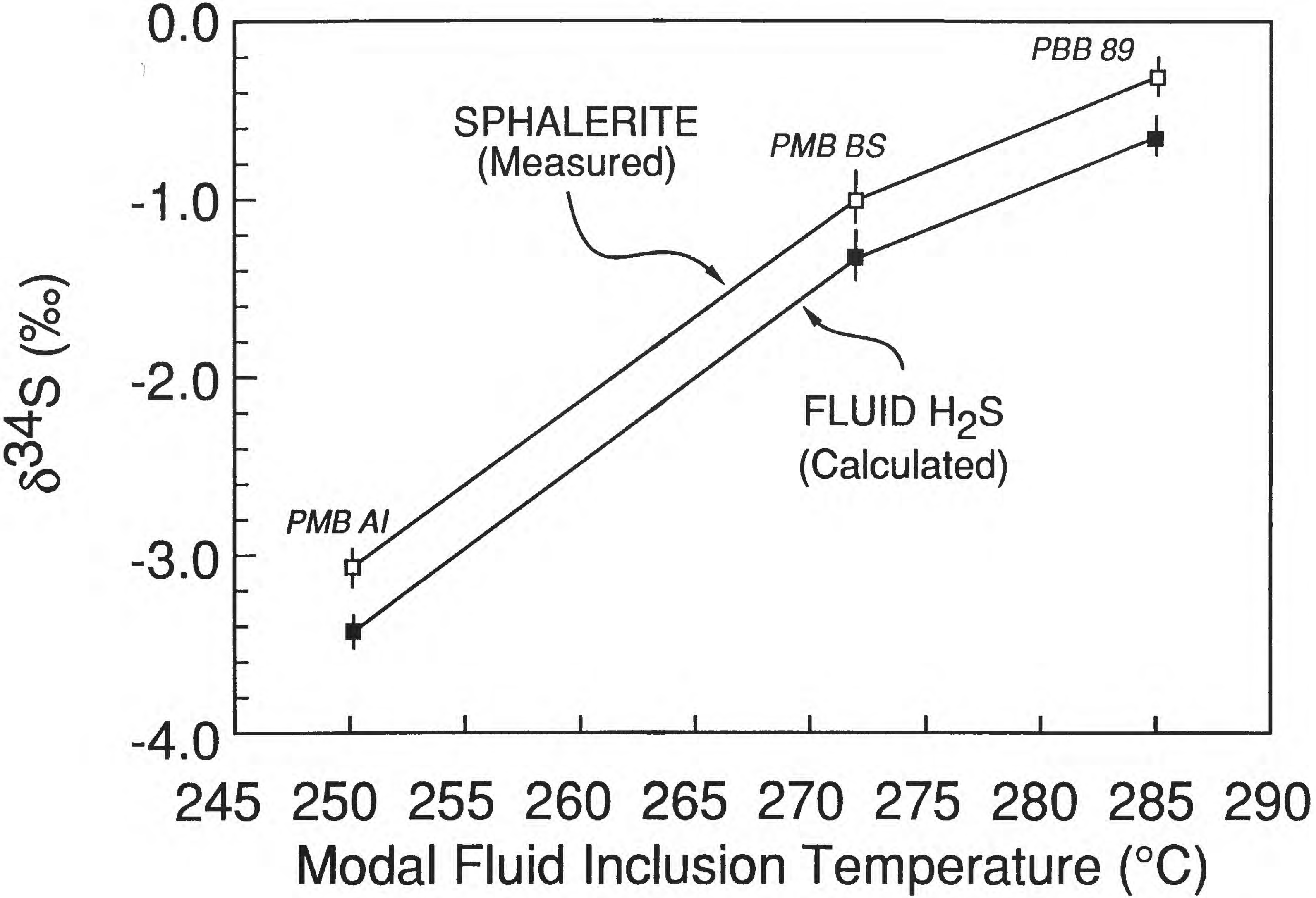
SLIDE 14

SULFUR ISOTOPE COMPOSITIONS OF MAIN-STAGE SULFIDES AND BARITES

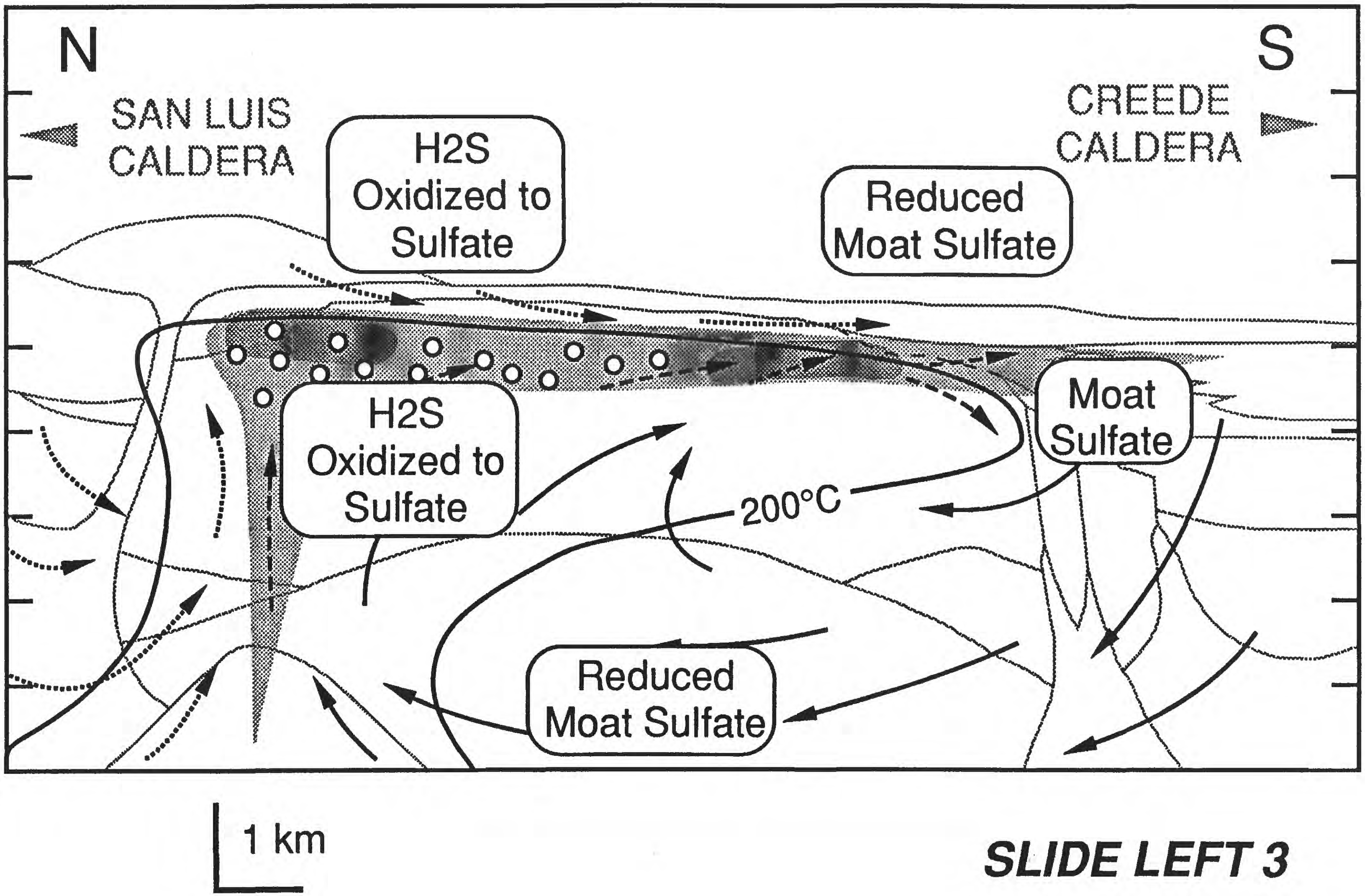


SLIDE 15

"INNER BROWN" SPHALERITE GROWTH ZONE
OH VEIN

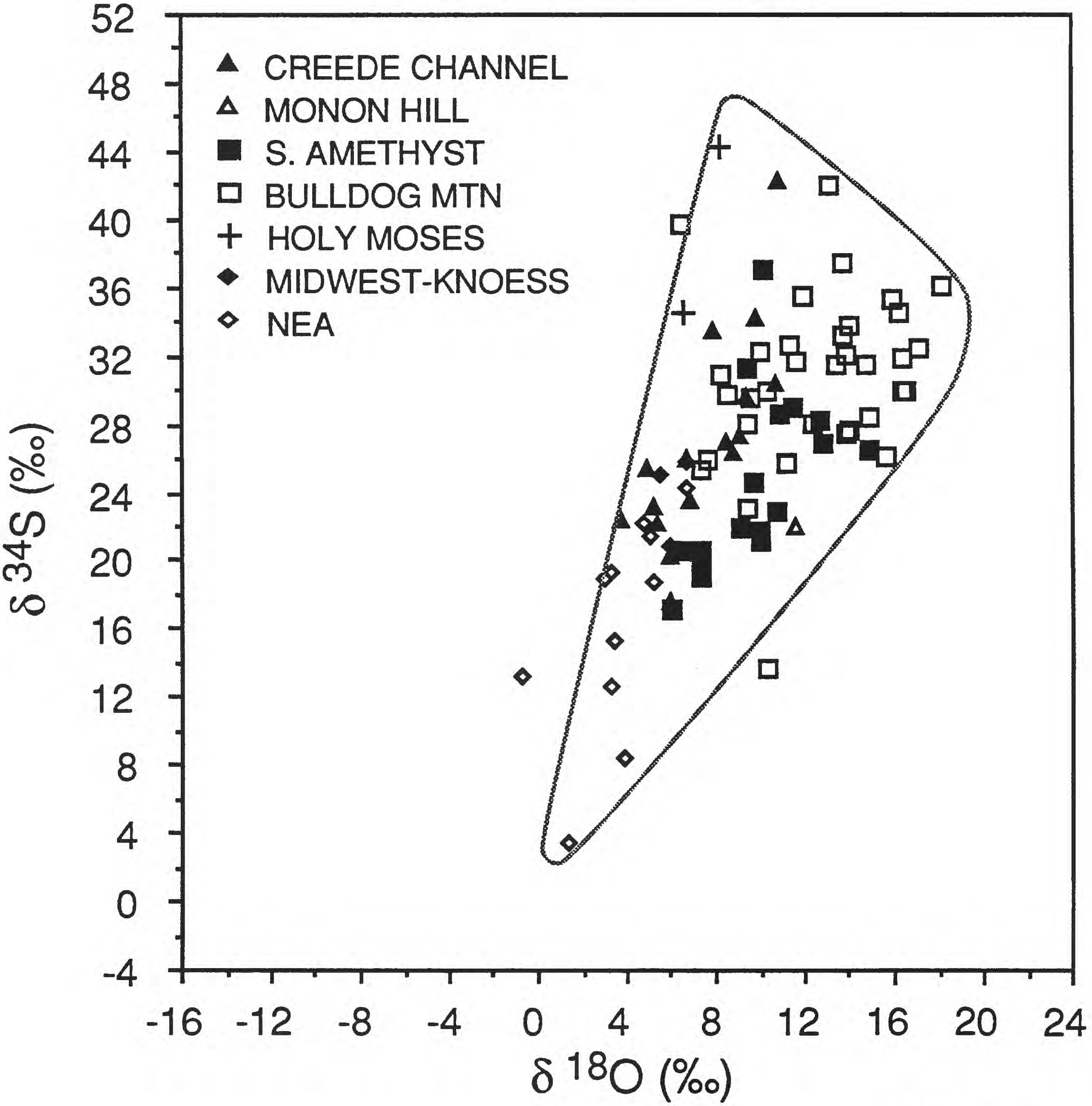


SULFATE SOURCES IN THE CREEDE HYDROTHERMAL SYSTEM



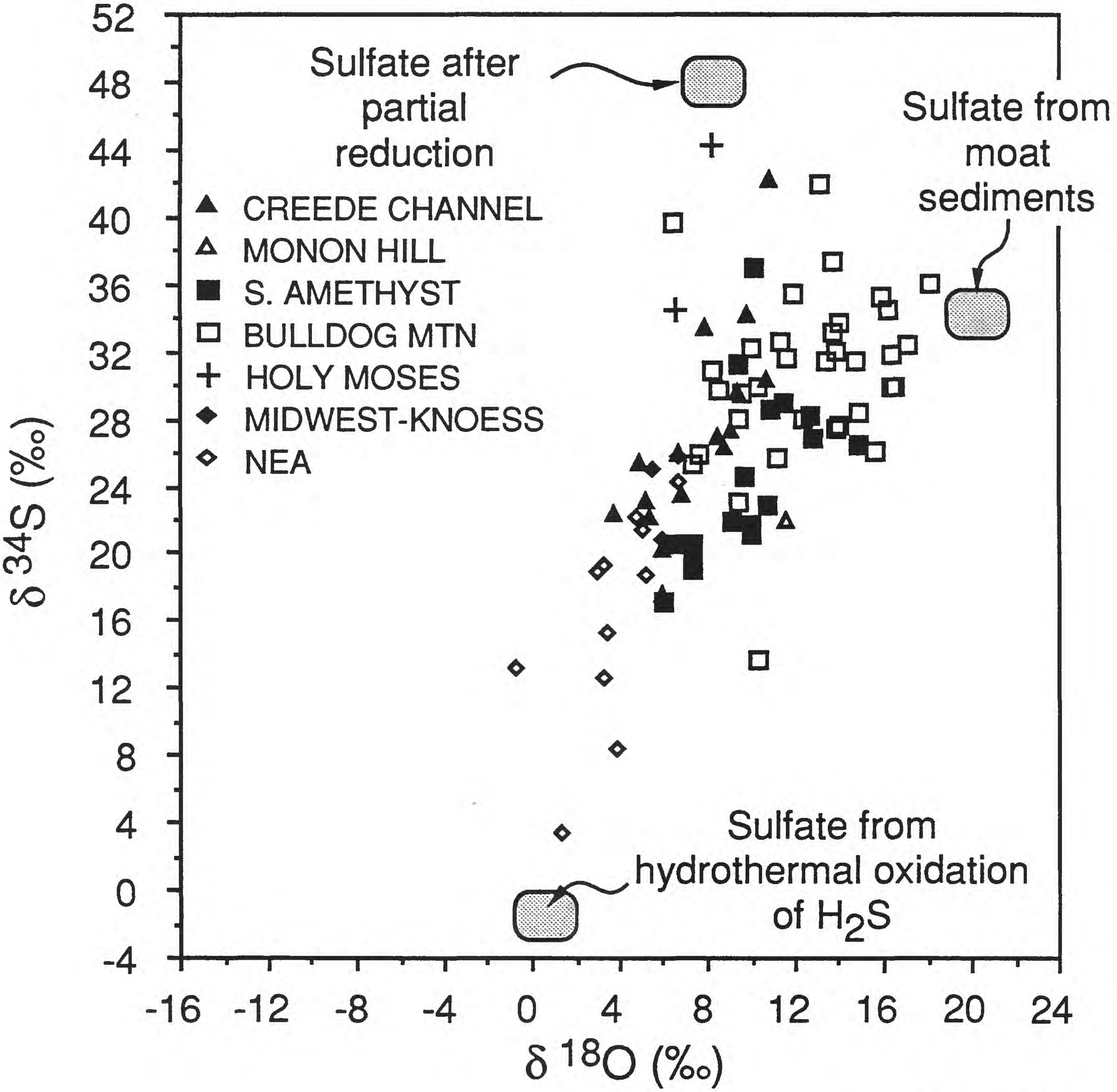
SLIDE LEFT 3

CREEDE DISTRICT BARITES
S-O ISOTOPE DATA



SLIDE 17

CREEDE DISTRICT BARITES S-O ISOTOPE DATA



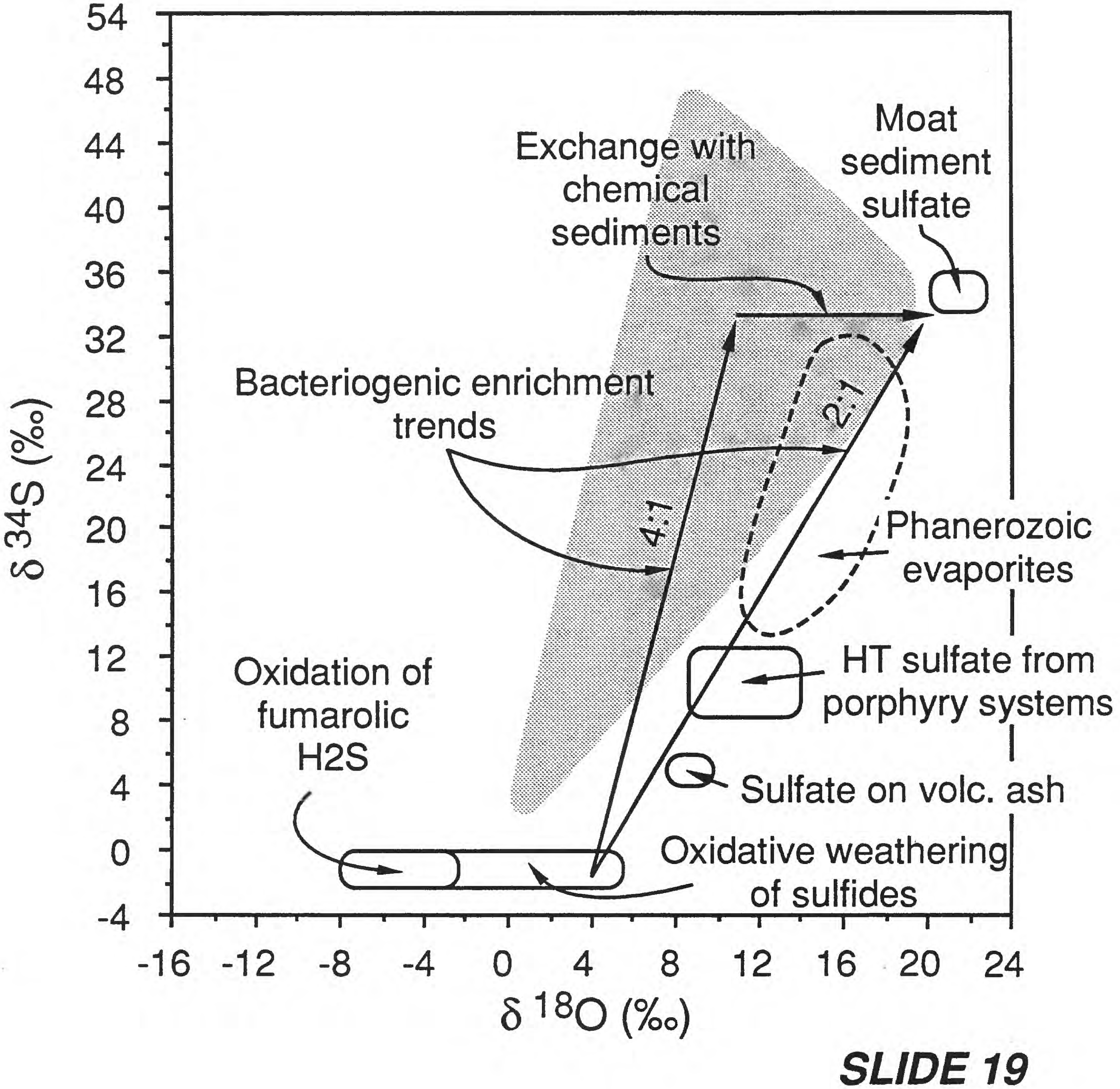
Sulfate after partial reduction

Sulfate from moat sediments

Sulfate from hydrothermal oxidation of H_2S

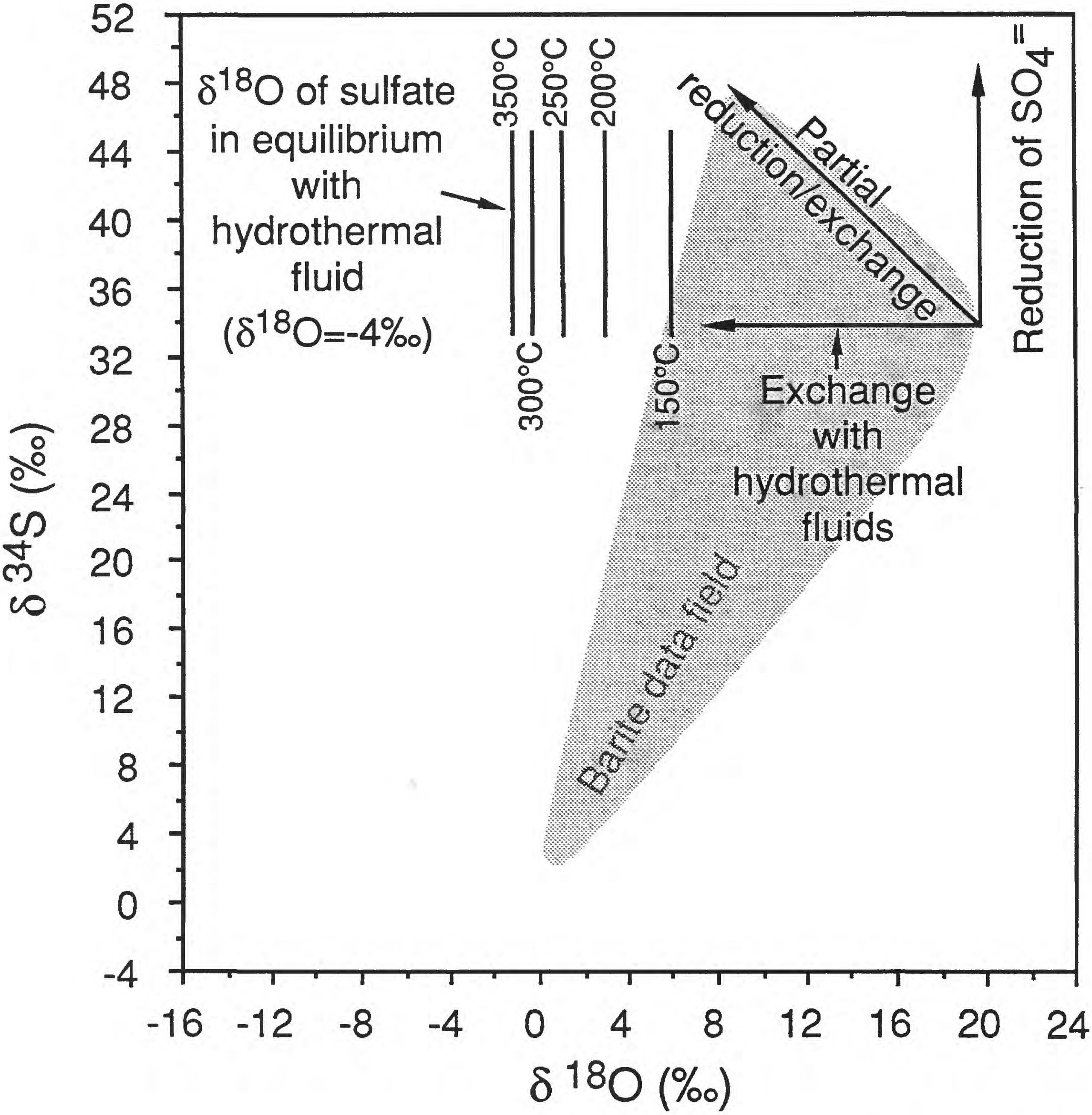
SLIDE 18

POSSIBLE ORIGINS OF HIGH-^{18}O SULFATE IN THE CREEDE CALDERA MOAT



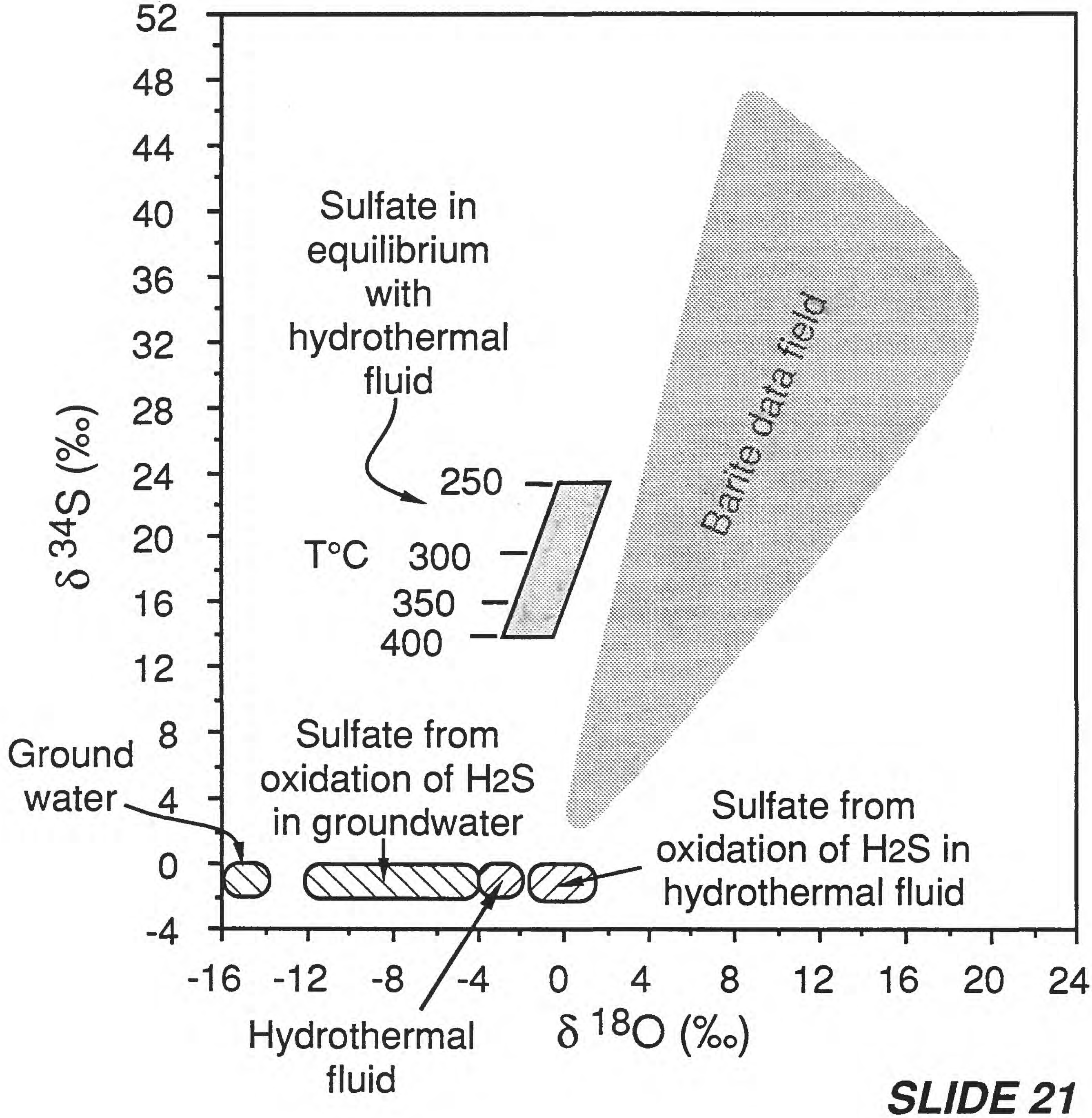
SLIDE 19

ORIGIN OF HIGH ^{34}S BARITES IN SOUTHERN DISTRICT



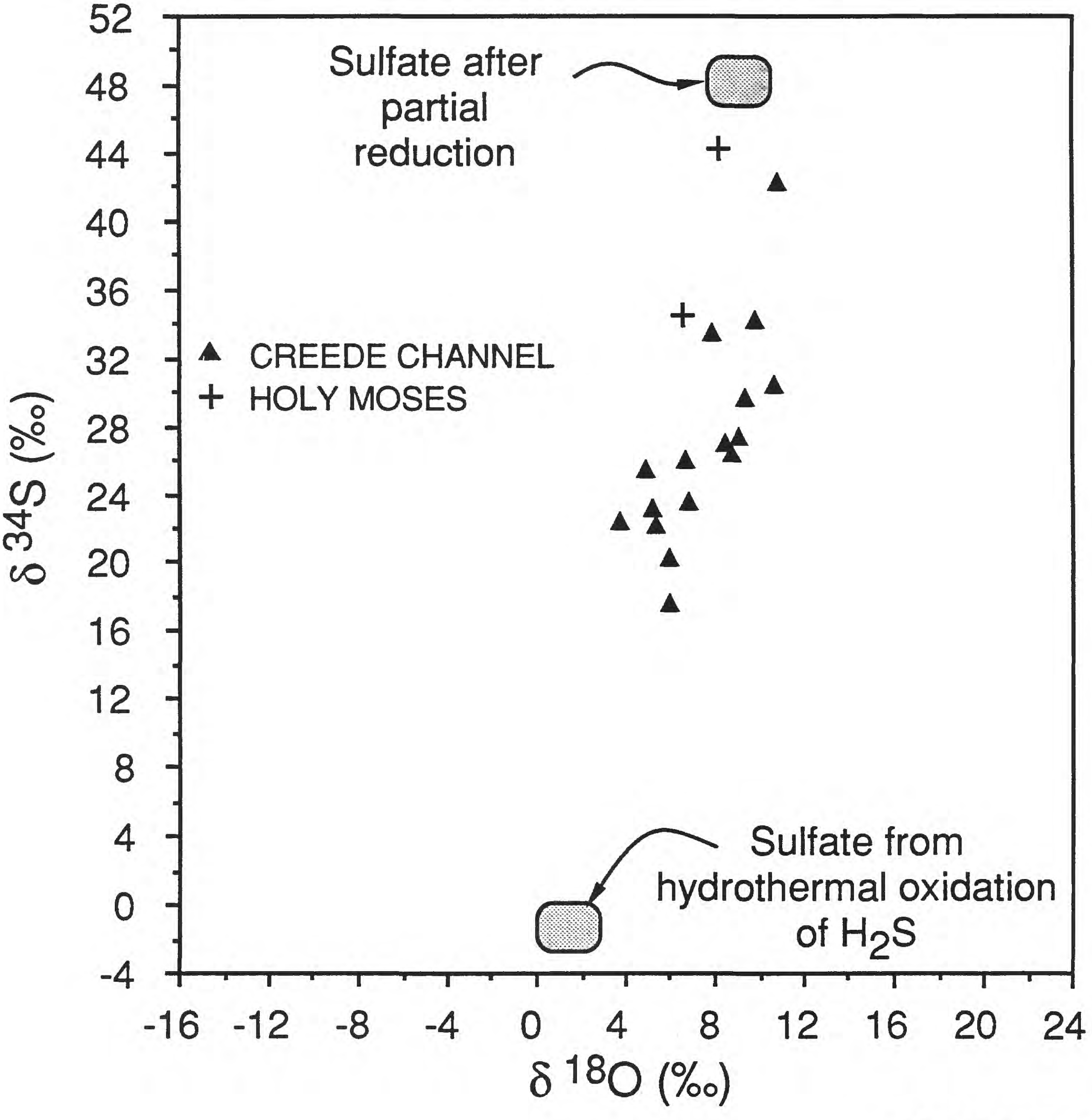
SLIDE 20

ORIGIN OF ISOTOPICALLY LIGHT BARITES IN NORTHERN DISTRICT



SLIDE 21

CREEDE DISTRICT BARITES
S-O ISOTOPE DATA

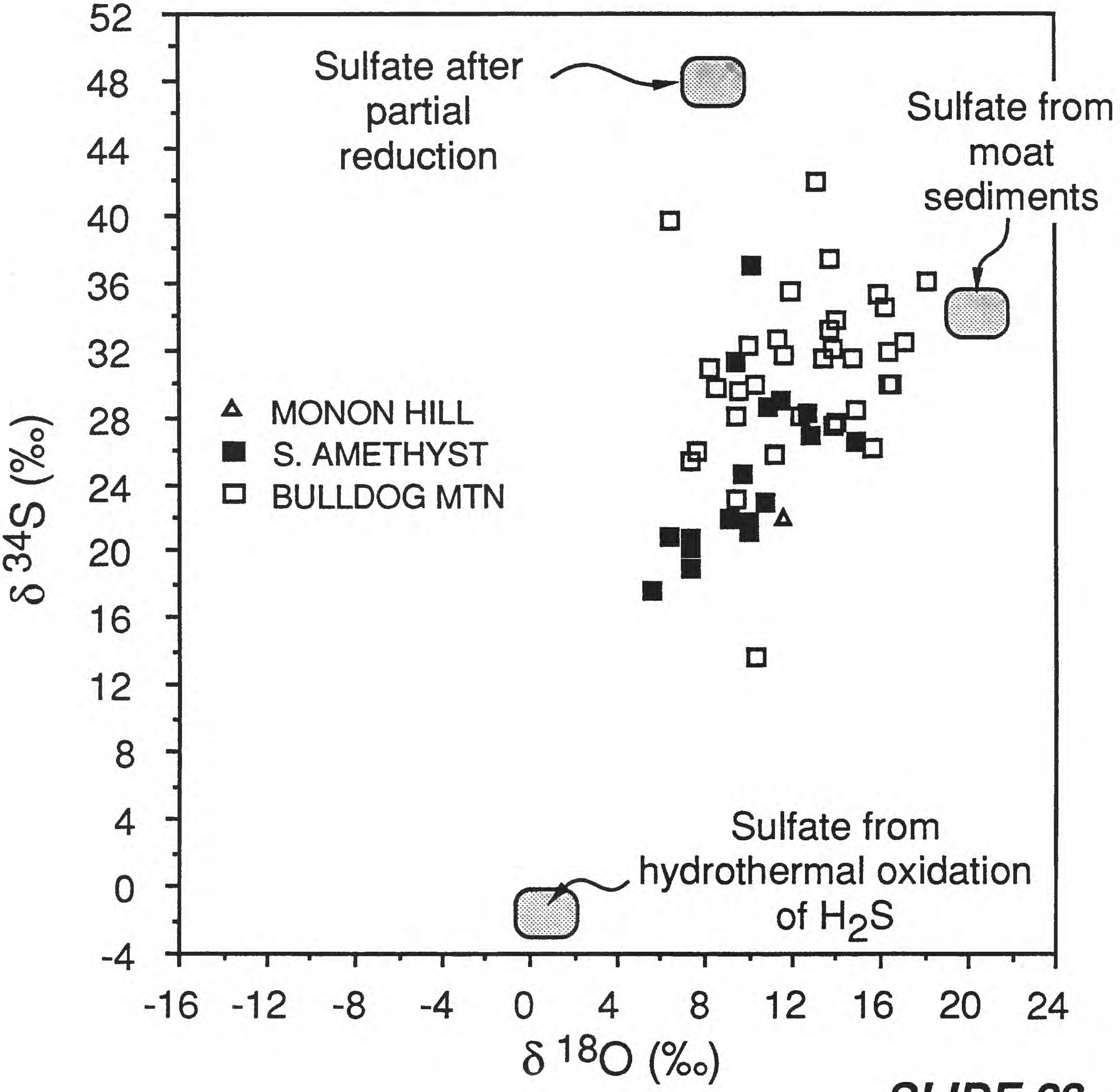


Sulfate after partial reduction

Sulfate from hydrothermal oxidation of H_2S

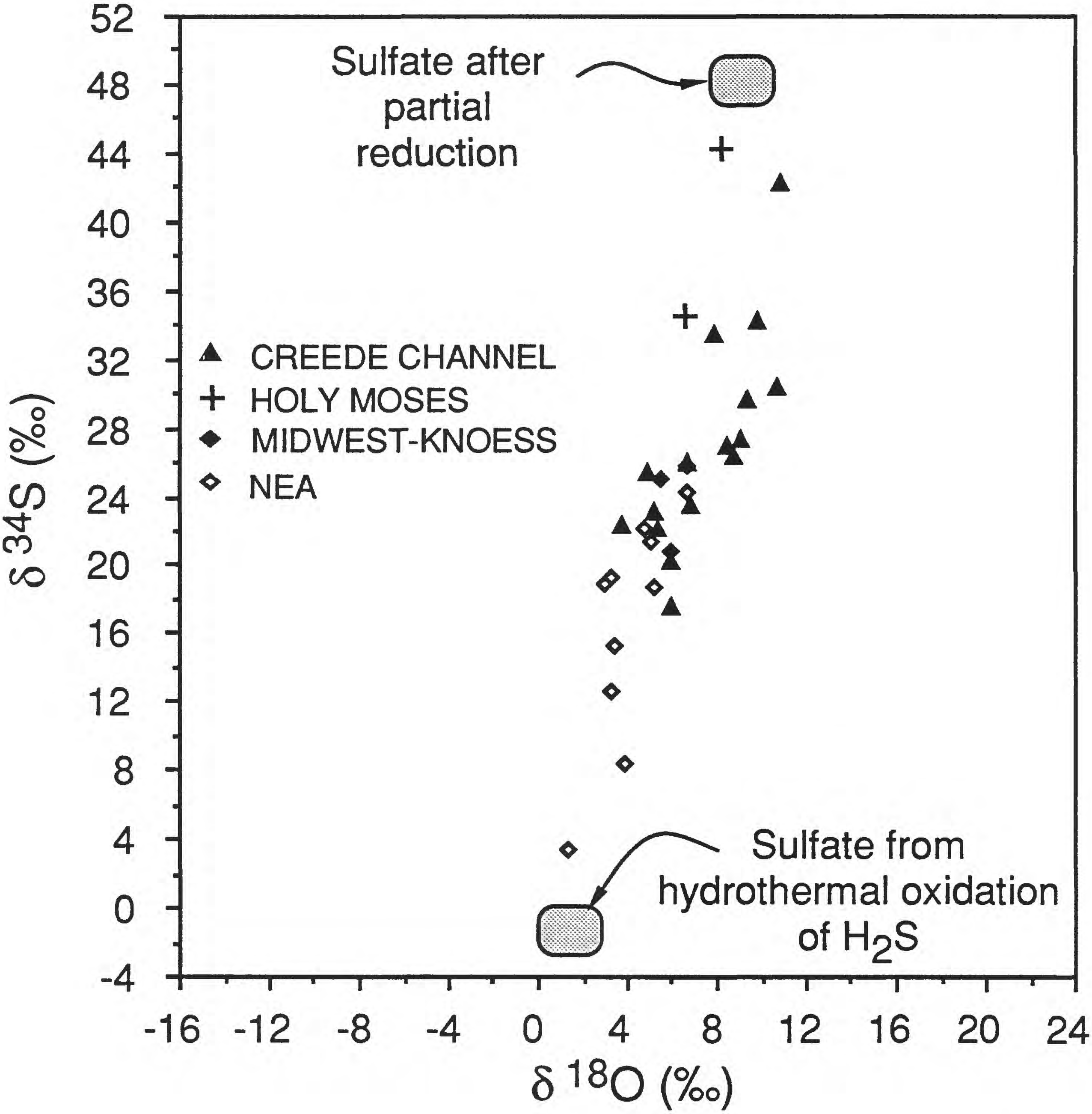
SLIDE 22

CREEDE DISTRICT BARITES S-O ISOTOPE DATA

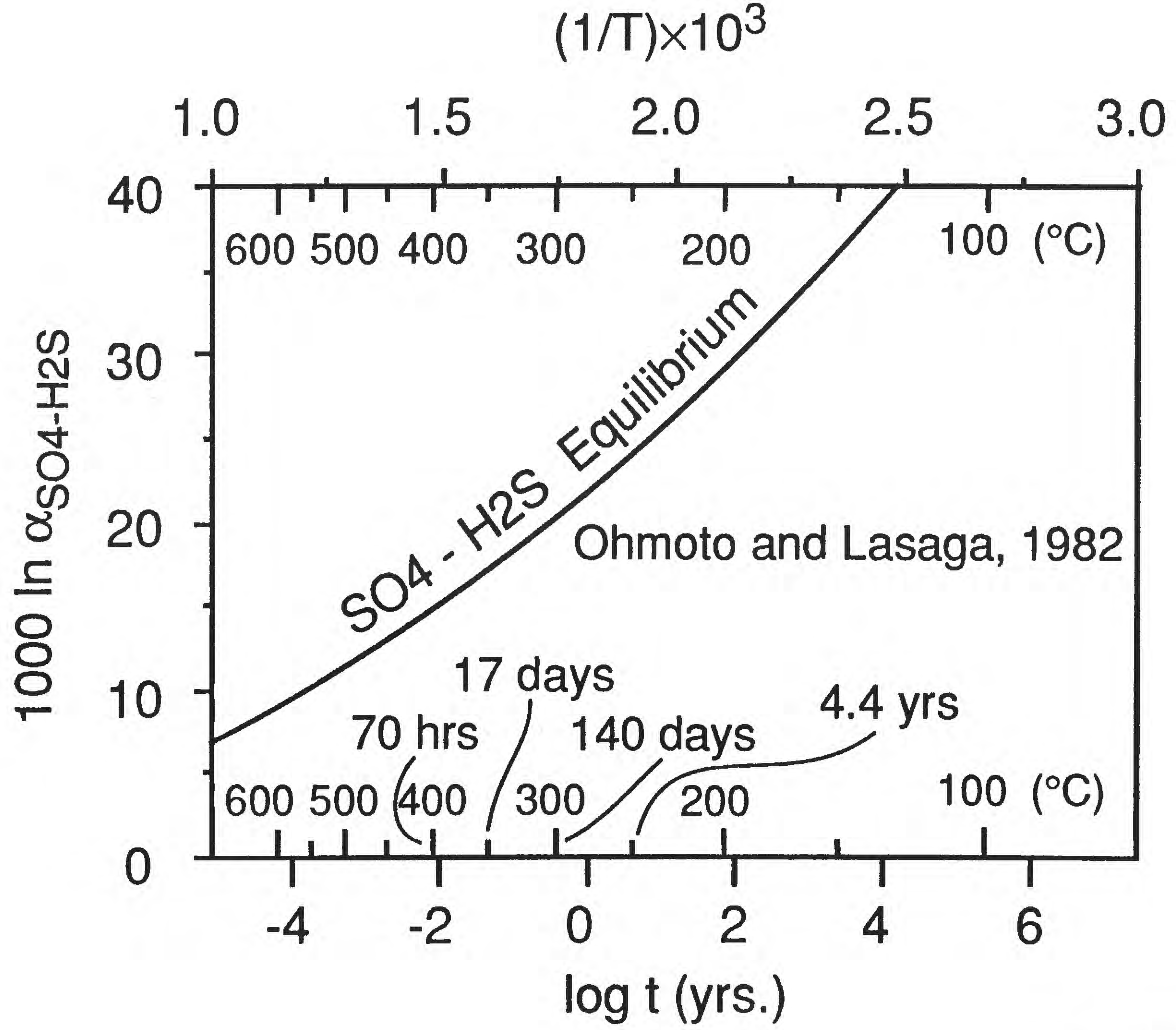


SLIDE 23

CREEDE DISTRICT BARITES
S-O ISOTOPE DATA

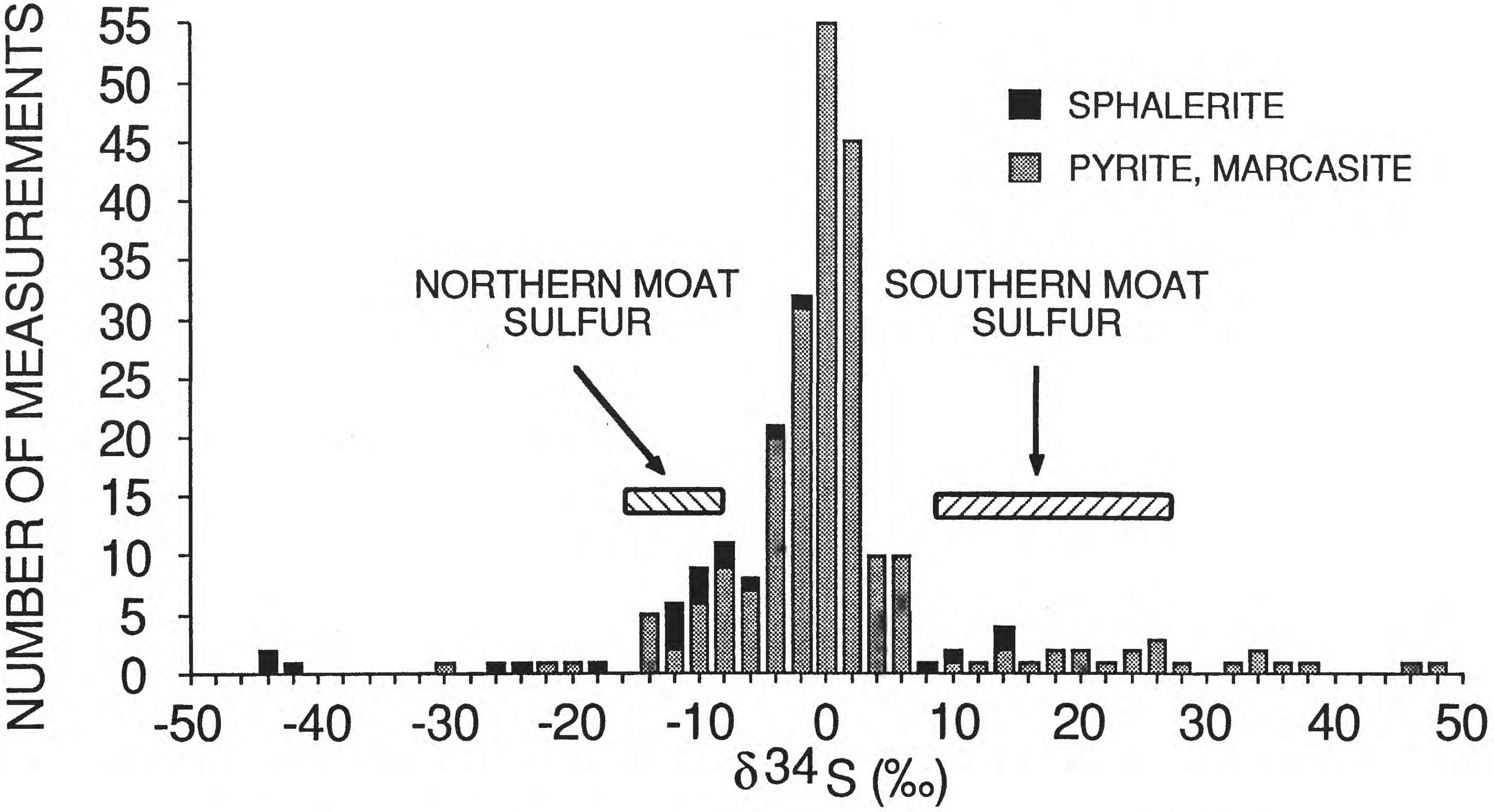


SLIDE 24

(1/T)×10^3
1.0
1.5
2.0
2.5
3.0
40
30
20
10
0
1000 ln $\alpha_{SO4-H2S}$
600 500 400 300 200 100 (°C)
SO4 - H2S Equilibrium
Ohmoto and Lasaga, 1982
17 days
70 hrs
140 days
4.4 yrs
600 500 400 300 200 100 (°C)
-4
-2
0
2
4
6
log t (yrs.)

SLIDE 25

LATE-STAGE SULFUR ISOTOPES



DATA FROM PLUMLEE AND RYE (1986, 1987)

SLIDE 26