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Environment of Ore Deposition in the Creede Mining District, San Juan Mountains, Colorado: Part IV. Sources of Fluids from Oxygen, Hydrogen and Carbon Isotopic Studies

by

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ABSTRACT

The hydrogen isotopic composition of fluids responsible for formation of the near-surface silver-base metal vein deposits at Creede was measured by direct analysis of inclusion fluids in sphalerite, quartz, and rhodochrosite and was estimated from analyses of illite and chlorite. The oxygen isotopic composiiton was determined directly on inclusion fluids in sphalerite and was estimated from analyses of quartz, illite, rhodochrosite, siderite, and adularia. The carbon isotopic composition was estimated from analyses of rhodochrosite and siderite. The ranges in isotopic composition for water and CO₂ in <u>the fluids</u> associated with the formation of each of the minerals is given below (number of determinations given in parentheses):

Mineral	۶D _{H20} 0/00	\$ ¹⁸ 0 _{H2} 0/00	5 ¹³ C _{C02} °/00			
Sphalerite	-81 to -54 (4)	-10.1 to -4.5 (4)	-			
Quartz	-97 to -86 (4)	- 5.9 to 1.8 (18)	-			
Illite	-62 to -50 (8)	- 1.6 to 1.2 (7)	-			
Chlorite	-64 to -55 (10)	- 2.2 to 0.8 (10)	-			
Adularia	-	4.2 (1)	-			
Rhodochrosite	-82 to -78 (2)	4.2 to 9.4 (9)	-5.7 to -4.2 (9)			
Siderite	-	4.9 to 9.9 (6)	-6.9 to -2.7 (6)			

The $\S D_{H_20}$ and $\S^{180}_{H_20}$ values of fluids associated with the formation of sphalerite, quartz, illite/chlorite, and carbonate minerals differ substantially from one another, and these differences appear to have been maintained throughout the depositional history, regardless of the positions of the minerals in the paragenetic sequence.

The data suggest that waters from three coexisting reservoirs fed the vein system alternately and episodically during vein formation, and apparently there was little mixing of the fluids from the different reservoirs. The hydrogen, oxygen and carbon isotope data suggest that the carbonáte waters were deep-seated, probably dominantly magmatic, in origin. The sphalerite and illite/ chlorite waters must have been dominantly meteoric in origin and substantially "oxygen shifted" by exchange with the volcanic country rocks. The quartz waters were also "oxygen shifted" meteoric waters but were 40 to 50% oo lower in deuterium content than the sphalerite and illite/chlorite waters.

We propose that the quartz fluids entered the vein system from reservoirs beneath the mountainous areas to the north in the vicinity of the present Continental Divide and that the sphalerite and illite/chlorite fluids, on the other hand, entered the vein system from a topographically low area to the south along the structural moat of the Creede caldera. The difference in ⁶D between the two meteoric waters may reflect differences in altitude of the recharge areas for the two reservoirs, or may be due to isotopic evolution of the closedbasin lake and interstitial waters in the moat surrounding the Creede caldera.

INTRODUCTION

This paper is the fourth in a series in which the geologic, hydrologic, and chemical environments of deposition of the middle Tertiary silver-base metal ores of the Creede mining district are examined. We present here the results of the initial phase of our investigations of the carbon, oxygen, and hydrogen isotopic composition of the ore fluids. This study was begun in an effort to establish the sources of the ore fluids and to gain an understanding of their thermal history. Although these objectives have been met in a broad sense, it is clear that the Creede district has had a much more complex hydrologic history than originally anticipated. Specifically, the data suggest that the ore fluids were dominated by meteoric waters from at least two distinct sources throughout most of the vein-filling history. Each had a different isotopic signature, - entered the hydrothermal system from a different recharge area, and was associated with deposition of a specific mineral assemblage recurrently throughout the period of mineral deposition. A magmatic component has not been unequivocally detected, but neither can it be excluded, either as a contributor of the oreforming fluids themselves or of some critical components of those fluids.

Geological and Mineralogic Background

The ore deposits of the Creede district are near-surface silver-base metal veins that fill faults and fractures in welded tuff of quartz latitic to rhyolitic composition (figures 1 and 2). Nearly all the production of the district has come from veins filling the Amethyst, OH, P-vein, and Bulldog Mountain faults or fault systems. In the first paper in this series, Steven and Eaton (1975) summarized the geologic history of the district, based primarily the work of Steven and his coworkers (Steven and Ratte, 1965; Ratte and Steven 1967; Steven and others, 1967; and Lipman and others, 1970) and on the early work of Emmons and Larsen (1913 and 1923). The recent publication on the calderas of the San Juan Mountains by Steven and Lipman (1976) is an excellent description of the history of the volcanic activity and of the nature of the volcanic country rocks that enclose and underlie the mineralized veins of the Creede district. Bethke and others (1976) have shown that mineralization followed the last dated volcanism in the Creede district by 1-2 million years.

The mineralogy and paragenesis of the Creede ores have been described in several recent reports, (Bethke and Barton, 1971; Barton and others, 1977; Wetlaufer, 1977; Hull, 1970; Steven and Ratté, 1965). In spite of much effort, the study of the detailed time-space relations is not yet complete, although these relations are probably better known for Creede than for any other district. For the purposes of the present study, the paragenetic sequence is described in terms of five stages of mineral deposition as outlined in Table 1. The relationships between stable isotopic composition and mineralogy and paragenesis is an important part of this study and some aspects of Table 1 deserve emphasis. Quartz is a major component at stages A through D, whereas sphalerite is present in significant quantities only in stages B and D, the two ore stages. Carbonate minerals are present only in A-stage (rhodochrosite) and C-stage (sideritemanganosiderite), and the C-stage occurrence is volumetrically very minor. Chlorite appears to be present in stages A, B, and D, but its main period of deposition was in B-stage. Illite occurs as a product of wallrock alteration in the upper portions of the vein systems and although the alteration zone may have developed over a longer period, the material we have analyzed appears to represent D-stage.

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PROCED URE S

The hydrogen, oxygen, and carbon isotopic compositions of the hydrothermal fluids responsible for the deposition of the Creede ores were determined directly from analyses of the fluids in fluid inclusions or were estimated from calculations based on analyses of the isotopic compositions of minerals presumed to have been in equilibrium with the hydrothermal fluids. The amount of CO₂ obtained when fluid inclusions were opened for analysis by crushing in vacuo was too little either for analysis or to affect the oxygen isotopic composition of the water. Further, in the moderately oxidizing fluids which existed at Creede (Barton and others, 1977), isotope effects due to the presence of reduced species (CO, CH4, H2) can be ignored (Ohmoto, 1972; Ohmoto and Shettel, 1974).

Materials Analyzed

We have measured the δ D values of the hydrothermal fluids directly from analyses of water in fluid inclusions in carbonate minerals and quartz, and both the δ ¹⁸0 and δ D values directly from analysis of water in fluid inclusions in sphalerite. We have estimated the hydrogen and/or oxygen isotopic composition of the ore fluids from analytical data on illites ¹) formed by wallrock alteration

1) In previous reports (Bethke et al., 1976; Barton et al., 1977), the intensely altered rocks found along the upper parts of all vein systems in the Creede district were described as "sericitic". X-ray diffraction studies indicate that the material is actually an illite with from 10 to 20 percent interlayered smectite (P.H. Wetlaufer and P.M. Bethke, unpub. data, 1978).

and on vein-filling chlorite, quartz, adularia, and carbonate minerals. The samples were chosen to provide a geographic distribution and to represent the entire history of vein filling as indicated in Table 1. Because we know much more about the details of the sequence of deposition of the ores filling the OH vein, it provided most of our samples. A few samples from the Bulldog Mountain vein system and Amethyst vein were also included as were several from minor hanging wall fractures to the Amethyst vein and one sample of illite from the P vein. The locations of samples on or near the Amethyst and OH veins are shown on figure 3A, and of those on or near the Bulldog Mountain vein system on figure

3B.

Sample preparation

Illite and chlorite were purified for analysis by sedimentation techniques. The samples were dispersed in 500 ml of distilled water to which a few drops of a 1 percent solution of calgon had been added. After 1 hour, the material remaining in suspension was decanted, centrifuged, and washed twice in both distilled water and acetone. Adularia was separated by standard heavy-liquid techniques. Quartz was chipped or drilled from small hand specimens, slabs, or doubly polished thick sections. Sphalerite, quartz, and calcite that contained fluid inclusion samples were broken from uncut hand specimens, single crystals, or thick slabs. The samples were selected to have a very high probability of containing predominantly primary fluid inclusions (Rye, 1966).

Analytical Techniques

The techniques for stable-isotope analyses used in this investigation have been standard for several years, and pertinent references have been summarized by Rye and Sawkins (1974).

All carbon and oxygen, and most hydrogen isotope analyses were made on a modified Nuclide Corporation 2 RMS-60, 6-inch, 60° sector mass spectrometer.

2) Any trade names in this publication are used for descriptive purposes only and do not constitute endorsement by the U.S. Geological Survey.

Most of the hydrogen isotope measurements on waters in fluid inclusions were made on a mass spectrometer constructed from a Nuclide Corporation RMS-60, 3-inch, 60° sector analyzer tube. The carbon, and the hydrogen and oxygen isotope data are presented in the familiar notation & relative to PDB and SMOW respectively. Routine analytical precision (+ 0.1 %) of or carbon and oxygen, and +1%) of or hydrogen) was maintained for all analytical procedures. For interlaboratory comparisons, our average value for NBS-28 is 9.5%/00.

Estimation of Fluid Composition from Mineral Data

There are currently serious practical limits on the precision with which one can estimate the 6 ${}^{18}O_{H_2O}$, 6 D_{H_2O} , and 6 ${}^{13}C_{CO_2}$ of hydrothermal fluids from the analytical data on minerals. For most minerals, fractionation factors relating the isotopic composition of the minerals to that of the fluid from which they formed are significantly temperature dependent. Therefore, uncertainties in the estimation of the temperature of last equilibration lead to uncertainties in the calculated isotopic composition of the fluid. The temperature of deposition of the Creede ores ranged from 190°C to 270°C and had a median value of about 250°C according to fluid-inclusion homogenization measurements reported by Roedder (1965). It is known that many of the analyzed samples grew over substantial temperature ranges, but all fluid calculations have been made assuming isotopic equilibrium at 250° C. Also, the isotopic composition of the ore fluids probably changed with time. Therefore, calculated isotopic compositions reported here represent average values integrated over a finite interval of mineral deposition. An additional uncertainty, compounding those due to temperature and paragenetic effects, arises from the inexactness of our knowledge of the mineral-water fractionation factors. (See discussion by Taylor, 1974a, and Bottinga and Javoy, 1973). There are uncertainties in the experimental and theoretical curves and their extrapolation to lower temperatures, and uncertainties caused by variations in the compositions of some minerals. For this study we have used the quartz-water curve based on the partial equilibrium data of

Clayton et al. (1972) as suggested by Taylor (1974a) and the muscovite-water, chlorite-water, and alkali feldspar-water curves summarized by Taylor (1974a, figs. 2 and 4). We have assumed that the isotopic compositions of fluids in equilibrium with the Mn-Fe carbonate minerals at Creede can be approximated by the calcite-water and calcite-CO₂ curves of 0'Neil and others (1969) and Bottinga (1968). Finally, the δ ¹⁸0_{H₂0} values estimated from the mineral analyses have not been corrected for activity effects due to the salinity of the Creede ore fluids (Truesdell, 1974). For the salinity range of 4 to 12 weight percent NaCl reported by Roedder (1965), the reported values for δ ¹⁸0 of the fluids may need to be corrected by as much as -2°/oo. As these various uncertainties are gradually eliminated, our calculated values will obviously need revision. The revisions, however, should not be large and should not alter our principal conclusions.

ISOTOPIC COMPOSITIONS OF THE FLUIDS

The results of the isotopic analyses of minerals are listed in Table 2. The isotopic compositions of fluids, either calculated from the mineral data or measured directly on inclusion fluids, are also listed. The table is arranged to group the samples by vein system. Within each vein system, the samples are listed in order of increasing depth. Coexisting minerals known to have been in contact with one another are indicated by brackets, but in no sample does compelling textural evidence suggest that the paired minerals equilibrated with the same fluid.

In figure 4, the hydrogen and oxygen isotopic compositions of the fluids are shown as functions of both mineralogy and paragenetic sequence. A distinct grouping of isotopic values by mineral is evident in figure 4 and Table 2, and we shall discuss the data in terms of the isotopic compositions of fluids from which each of the minerals is presumed to have grown.

Sphalerite Fluids

Samples of inclusion fluids in four sphalerite specimens were analyzed for δD_{H_20} and $\delta^{18}O_{H_20}$. The fluids analyzed were from samples that represent all three major substages of the typically coarse grained D-stage (see Table 1), and which were collected from both the OH and Bulldog vein systems. The δD_{H_20} and $\delta^{18}O_{H_20}$ values in all but the latest substage (sample MB-S-188) fall in a fairly narrow range ($\delta D_{H_20} = -54$ to $-70^{\circ}/00$ and $\delta^{18}O_{H_20} = -5.8$ to $-4.5^{\circ}/00$). These initial data suggest that the δD_{H_20} and $\delta^{18}O_{H_20}$ values of the ore fluids during all but the time of deposition of the very latest coarse sphalerite were fairly uniform in both time and space on the OH and Bulldog veins; thus, the data are consistent with the conclusions of Steven and Eaton (1975) and Barton et al. (1977) that the major veins in the Creede district were filled penecontemporaneously during the same hydrologic event.

The δD_{H_20} and $\delta^{18}O_{H_20}$ values of the fluids in the very late sphalerite (MB-S-188) are about -80 and -10°/00, respectively, and are distinctly lighter than those of the earlier D-stage sphalerite fluids. Fluid-inclusion data reported by Roedder (1965) show that filling temperatures of this very late substage average about 210°/00 ± 20°C, significantly lower than the 250° ± 30°C reported for the earlier D-stage sphalerite. Both the isotope and filling temperature data strongly suggest that a fundamental change took place in the hydrothermal system during the final stages of sphalerite deposition, but much more detailed fluid inclusion heating and freezing studies coupled with isotopic determinations are necessary to document and to evaluate the nature and significance of such a change.

Quartz Fluids

6¹⁸O values were measured on 17 samples of quartz from 14 localities on the OH, Amethyst, and Bulldog Mountain vein systems and cn one sample from a small hanging wall structure about 300 meters west of the Amethyst vein. The samples were chosen to span the depositional sequence, but we cannot clearly document any quartz belonging to stage B. At this time it is very difficult to correlate growth zones between quartz and sphalerite samples within stages. It is important to point out that most, if not all, of the quartz samples studied probably grew over significant time and temperature intervals.

Four quartz samples, all from the OH vein, were chosen for measurement of the δD of the waters trapped as fluid inclusions. Two of these samples are clearly intergrown with D-stage sphalerite. One sample was an unusually coarse (1 x 2.5 cm) and clear vug-filling, A-stage quartz crystal. The fourth sample was a 1 cm milky quartz zone which grew on C-stage fluorite and was in turn overgrown by early D-stage sphalerite.

The values of $\delta^{18}O_{H_2O}$ calculated from the mineral data (assuming a temperature of equilibration of 250°C) range from -6.9 to 0.8°/oo (Table 2). This range is much larger than that determined directly on the sphalerite inclusion fluids (excluding sample MS-S-188). If the range in temperature from fluid inclusion studies is taken into account in the calculation of fluid compositions, the range is even larger. On the other hand, it is also possible that the observed variation in $\delta^{18}O$ qtz is actually <u>due to</u> differences in temperature of deposition; the entire range in $\delta^{18}O_{H_2O}$ over the temperature range of 190° to 270°C suggested by the fluid inclusion studies of Roedder (1965). These uncertainties can be removed only by careful selection and analysis of individual growth zones known, from fluid inclusion studies, to have grown over a narrow temperature interval.

The deuterium content of the quartz fluids is particularly interesting. Regardless of whether the quartz appears to have before, contemporaneously with, or after the D-stage sphalerite, the δD_{H_20} values of fluids from inclusions on the quartz range from -86 to -96°/00; substantially more negative than those for the sphalerite inclusion fluids which range from -54 to -70°/00 (neglecting the very late sphalerite of MB-S-188).

Carbonate Fluids

Fifteen carbonate samples were analyzed for $\delta^{18}O_{H_2O}$ and $\delta^{13}C_{CQ}$ and the inclusion fluids of two samples were analyzed for δD_{H_2O} . The samples represent both the early rhodochrosite of A-stage and the later siderite-manganosiderite of C-stage and were taken from the Bulldog, OH, and Amethyst structures. One sample was collected from a small hanging-wall vein 300 meters west of the Amethyst vein. Wetlaufer (1977) has described the textural, compositional, and paragenetic relations of both carbonate generations.

The δ^{180} values of all carbonate samples range from 11.0 to 16.7°/00, and all but three samples are within the range 13.6 to 16.7°/00. The corresponding δ^{13} C values range from -4.0 to -8.2 °/00 (Table 2). No correlation appears to exist between the δ^{180} or δ^{13} C values and chemical composition or position of the carbonate samples in time or space in the ore deposit. The fairly narrow range in δ^{180} and δ^{13} C of the minerals indicates that the temperatures and $\delta^{13}C_{CO_2}$ and $\delta^{18}O_{H_{O_2}}$ values of the hydrothermal fluids were fairly uniform in the district from one period of carbonate deposition to another, even though the periods were separated by one of the two main stages of carbonate-free sulfide deposition. The calculated $\delta^{18}O_{H_{20}}$ values of the fluids in equilibrium with the carbonates at 250°C range from 4.2 to 9.9°/00. For the same reasons discussed for the quartz fluids, the actual range in $\delta^{18}O_{H_{20}}$ may have been substantially larger or smaller. Although considerable uncertainty exists regarding these calculated fluid compositions it is clear that the $\xi^{18}_{0H_20}$ values of the carbonate fluids were much higher than those of the fluids in equilibrium with any other mineral investigated.

Assuming a pH less than 7.1 (Barton and others, 1977, indicated a pH of 5.4 for B- and D-stage sphalerite deposition), CO₂ would be dominant carbonate species in the fluid at 250°C. The calculated ξ^{13} C values of CO₂ in the fluids are very close to those of the minerals and have an approximate range of -2.7 to -6.9 °/oo.

The waters in inclusion fluids in two A-stage rhodochrosites from the Bulldog mine were analyzed for D_{H_20} . The waters have values of -82 and -78 % of and are distinctly different from the quartz fluids and from all but the latest sphalerite fluids. Although the rhodochrosite samples analyzed were selected to have a high probability of containing an overwhelming proportion of primary fluid inclusions, we cannot be certain that this was the case in the absence of systematic heating and freezing studies. We are less confident, therefore, the δD_{H_20} values of the carbonate fluids than those of either the quartz or sphalerite fluids.

Illite Fluids

Seven samples of illite were analyzed for D and f^{180} , and one for D alone. Of these, five were collected along the OH vein at the base of the zone of intense wall-rock alteration (see Barton and others, 1977) and one from the same zone on the P-vein some 700 meters east of the OH vein. One sample (PMB KP) was taken from a hydrothermally altered boulder in a coarse clastic tongue of the Creede Formation, which fills the paleo-stream channel incised into the wall of the Creede caldera and truncated by the Amethyst fault, and one sample was taken from the 9550 level of the Bulldog Mountain mine.

The structure and composition of the illites have not yet been fully characterized, but from X-ray diffraction profiles, all appear to have IM structures, with as much as 20% smectite interlayering. Most samples are very fine grained; the materials analyzed were taken from a <10 micron size cut. Three of the samples (PMB-BA, PMB-BC, and PMB-KP) were used for K/Ar dating as reported by Bethke and others (1976).

The six samples from the base of the altered zone have tightly clustered $\S D$ values of -93 to -880/oo: and $\18 0 values of +1.8 to +3.90/oo, suggesting that the isotopic compositions of the fluids with which they last equilibrated were nearly constant. Several lines of evidence suggest that the development of at least the base of the altered zone overlapped in time with deposition of the D-stage sphalerite, but at this time, the paragenetic position of these samples cannot be fixed any more precisely. The calculated $\$ D_{H_20}$ and $\$^{180}_{H_20}$ values for the fluids in equilibrium with with these six illites at 250°C range from -50 to -62°/oo and from +1.2 to -1.7°/oo, respectively. The calculated range in $\$ D_{H_20}$ values virtually coincides with that for all but the latest D-stage sphalerite fluids but the $\$^{18}_{0H_20}$ values are several permil larger. Sample PMB-KP is somewhat enriched in ¹⁸⁰ and depleted in D relative to the other samples, which probably reflects a lower temperature of the altering fluids in the paleo-stream channel of the Creede Formation.

Chlorite Fluids

Chlorite occurs throughout the paragenetic sequence, but in most samples, the bulk of the chlorite appears largely to be related to B-stage mineralization. It is nearly impossible to fix the position of the material analyzed within these stages, however, and although we note all of our analyzed samples as Bstage, it is not improbable that some may have formed during A-stage or even Dstage precipitation. It must also be remembered that the chlorite was in contact with, and may have exchanged with, later fluids. With the exception of sample PMB-JJ, all chlorites were taken from the OH vein. PMB-JJ was collected on the Commodore 4 level from a small hanging wall fracture about 230 meters west of the main Amethyst vein in the southern part of the workings (figure 3). Optical, microprobe, and X-ray diffraction studies indicate that the chlorites are of a high-iron (probably thuringite) variety, consistent with the chemical analysis of one sample of chlorite from the Amethyst vein as reported by Emmons and Larsen (1923). The optical and X-ray studies also suggest that there is a significant but undefined range in chlorite composition in the OH vein. The large uncertainty in the fractionation factors between chlorite and water makes our lack of detailed compositional information immaterial for the purposes of this study. As judged from the settling rates during mineral separation, the materials used for analysis were less than 5 microns in diameter.

Calculated values of $\delta^{18}_{P_20}$ and $\delta_{D_{H_20}}$ for the chlorite fluids show about the same range as those of the illite fluids (0.8 to -2.2°/oo and -55 to -65°/oo). In view of the uncertainty in our knowledge of the D and ¹⁸0 fractionation factors between chlorite and water (particularly high-iron chlorite), the actual ranges in $\delta_{D_{H_20}}$ and $\delta^{18}_{P_20}$ should not be considered well established.

Adularia Fluids

The single sample of adularia analysed for ¹⁸0 was a split of the material used for K/Ar age determination (Bethke et al., 1976). Its paragenetic position is fixed as early in the depositional history (A-stage). The vein quartz with which it is intergrown was also analyzed. The textural relations are too complex to establish the co-deposition of the pair, but the calculated $\delta^{18}_{\rm H_20}$ of the fluid in equilibrium with the adularia at 250°C is -4.2°/oo

(Table 2), essentially the same as the value of $-4.3^{\circ}/_{\circ\circ}$ calculated for the quartz, suggesting that isotopic equilibrium was achieved between the mineral pair.

Summary of Isotopic Compositions of Fluids

The oxygen and hydrogen isotope data for the various fluids are summarized on the now-standard SD vs. $S^{180}_{\rm H_2O}$ plot in figure 5. Most analyzed modern meteoric waters (except those that have undergone excessive evaporation) lie within a few permil of the meteoric water line, and presumably all paleometeoric waters, at least those as recent as the middle Tertiary, would also fall along this line (Craig 1961, Taylor 1974a). The isotopic compositions of almost all primary magmatic waters are inferred to lie within the box labeled "Deep-Seated Water" (Rye, 1966; Taylor, 1974a, and 1977), and presumably waters derived from the crystallization of shallow magmas at Creede would also have isotopic compositions within this range. The isotopic compositions of Creede fluids, as reported in Table 2, are plotted on the diagram. The solid symbols represent samples wherein both δD_{H_20} and $\delta^{18} O_{H_20}$ have been determined. The open symbols represent quartz and carbonate samples whose oxygen isotopic composition alone was measured; these are plotted on the diagram at the average δDH_{20} value of quartz or carbonate fluid inclusions. Three modern surface waters (two from springs and one from mine drainage) are plotted on the meteoric water line at their measured hydrogen isotopic compositions.

Three important observations can be made regarding the data plotted in figure 5.

(1) The fluids associated with the deposition of each of the different mineral groups (sphalerite, quartz, carbonates, and hydrous minerals) had substantially different isotopic compositions. (2) Only the carbonate fluids plot close to the field for deep-seated waters; the other fluids plot at positions considerably displaced toward the meteoric water line, suggesting a considerable involvement of meteoric waters. (3) These other waters (with the exception of the fluid inclusions in the very late sphalerite) fall into two distinct $\&D_{H_20}$ groupings, one including sphalerite and phyllosilicte fluids at $-58 \pm 10^{\circ}/oo$, the other representing quartz fluids at $-91 + 6^{\circ}/oo$.

The significances and implications of these observations are discussed in the following sections.

RELATIONSHIP BETWEEN ISOTOPIC COMPOSITON OF FLUIDS AND MINERALOGY

The isotopic composition of the fluids responsible for the depositin of each of the various minerals occupies a relatively small field on the {D vs. δ^{180} plot. Futhermore, only the illite and chlorite fields overlap; the fields for other minerals are widely separated. This association of different minerals with hydrothermal fluids of different isotopic compositions has been observed in at least two other deposits but the situation at Creede is more definitive. At the Pasto Bueno wolframite-sulfide deposit in northern Peru, two periods of wolframite deposition were related to relatively low §D waters that were presumably meteoric in origin (Landis and Rye, 1974). At the Panasqueira, Portugal, tin-tungsten deposit, quartz and wolframite were associatd with fluids having an average $\delta D_{\rm H_2O}$ of -55% oo, whereas other minerals such as cassiterite, apatite, and arsenopyrite were deposited from fluids that had distinctly more negative $\int DH_{20}$ values (Kelly and Rye, in press). At both of these deposits, but especially at Panasqueira, the origin of the fluids was difficult to interpret because the $\delta^{18}O_{H_{2}O}$ values of the fluids were very high and rather uniform, indicating that regardless of their origin, the fluids

had undergone a high degree of oxygen isotope exchange with the country rocks. At Creede, however, the δ ¹⁸0 values for the hydrothermal waters show nearly a complete range between those typical of virtually unexchanged meteoric waters to those typical of magmatic water.

In addition to the abovementioned considerations, it is particularly important to reiterate that for those minerals that we have sampled at various positions in the depositional sequence, this specificity of isotopic composition of the fluid associated with a particular mineral <u>is maintained regardless of</u> <u>the mineral within the depositional sequence</u>. The carbonate and quartz data in particular illustrate this point. As illustrated in figure 4, the oxygen isotopic composition of the A-stage rhodochrosite waters covers essentially the same range as does that of the C-stage siderite-manganosiderite fluids. Both are much more enriched in ¹⁸0 than the fluids representing any other mineral. Quartz is an important mineral throughout the depositional sequence, and throughout that sequence the isotopic composition of the quartz-depositing fluids appears to have been substantially different from those associated with the deposition of any other mineral.

There are several important implications of the above discussion. First, the oxygen and hydrogen isotope data require that the various minerals were deposited from fluids having different isotopic compositions and, therefore, different origins and/or histories of rock-water interaction.

Second, the paragenetic and isotope data suggest that these different fluids occupied the vein system (at least in the vicinity of the present ore bodies) episodically and repetitively throughout the history of vein filling, and there is little evidence of large-scale mixing of the different fluids.

Third, although many of the minerals are intergrown (even as coarse crystals lining vugs, a typical relation for D-stage sphalerite and quartz), they must have grown alternately from the different fluids. The most striking examples are the intimately intergrown quartz and rhodochrosite of samples PMB-KA, PBB-145, and PBB-147 (Table 2). In these samples, the quartz is finely intergrown as a minor phase in massive rhodochrosite. These samples were specifically selected for sampling as mineral pairs. In PBB-147, textural evidence suggest that at least some of the quartz actually veins the rhodochrosite, but in the other two samples, no textural evidence suggests anything but mutual growth. The \int^{18} 0 values of these quartz fluids are the highest we have found for quartz, but the calculated oxygen isotopic composition of the quartz and rhodochrosite fluids still differ by 4 to 60/00 and must therefore represent two distinct fluids. This is true whether the two fluids mixed and coprecipitated the guartz and rhodochrosite, the difference in $\int 180$ being due to kinetic factors, or whether the differences in S^{180} represent equilibrium fractionation during alternate deposition of the two minerals.

Fourth, the evidence that different minerals, although intergrown in the same hand specimen, were deposited from fluids of different origins and/or histories of rock-water interactions has very important implications regarding the assumption of chemical equilibrium between minerals. It may be assumed, until proven otherwise, that fluids from different sources or with different histories of rock-water interactions will differ in chemical composition, and therefore minerals deposited from different fluids will not be in total chemical equilibrum. This is particularly important for minerals whose chemical composition is used in equilibrium arguments, but may be somewhat less critical where the presence or absence of one or more minerals is the equilibrium requirement (see discussion by Barton and others, 1963). The chemical arguments of Barton and others (1977) for the OH vein were based on the observed presence of quartz, sericite (illite), potassium feldspar, chlorite, pyrite, hematite and chalcopyrite; the lack of observed bornite, covellite, magnetite and pyrrhotite; and the FeS content of sphalerite. These evidences still seem valid, but the multiple fluid model developed here may explain the recurrent hydrothermal leaching of sphalerite and certain other post-depositional changes in sphalerite and other sulfide minerals, described by those authors.

The complexity of the hydrologic regime implied by the above considerations is one of the most surprising and intriguing results of this study. The strong contrasts among the isotopic compositons of the fluids responsible for the depositon of the various minerals together with the regularities in the covariation of temperature and salinity determinations of fluid inclusions with paragenetic position found by Roedder (1976) provide a great deal of leverage in our continuing attempts to unravel the complexities.

ORIGINS OF THE HYDROTHERMAL FLUIDS

The $\&D_{H_20}$ and $\&^{18}O_{H_20}$ of hydrothermal fluids are, in a general sense, the products of the original isotopic compositons of the source fluids modified by the degree of isotopic exchange between the fluids and the rocks which they traversed. The isotopic signature of the water may be further modified by mixing of fluids, by boiling, or by introducing or producing of significant amounts of reduced species such as CO, H₂O, or CH₄. Boiling has been demonstrated for the Creede fluids (Barton and others, 1977), but at 250° the fractionation of both ^{18}O and D between liquid and vapor is too small for boiling to affect the isotopic composition of the fluid significantly unless the salinities of the fluids were increased strongly due to boiling as in a vapor-dominated system. None of the fluid inclusion observations have shown the presence of such high salinities at Creede, nor have they suggested large differences in salinities between fluid inclusions in quartz and sphalerite (Roedder, 1965; J.T. Nash, written communication, 1968). (See discussion by Truesdell and others, 1977, on the affects of boiling on the isotopic compositions of fluids in the Yellowstone geothermal system.) Further, the chemical environment, as outlined by Barton and others (1977), precludes the existence of significant amounts of reduced species in the Creede fluids. Therefore, we must look to original differences to explain the variations in isotopic composition of the fluids.

The geologic history of the Creede district and the close time relation of ore deposition to volcanism suggests that the only sources that need be considered as contributors to the ore fluids are meteoric and magmatic waters. We may now consider what contribution each of these sources may have made to the constitution of the various isotopically distinct waters.

Carbonate Fluids

The range of calculated δ^{180} values (4.2 to 9.90/00) is essentially the same for both the rhodochrosite and siderite fluids. These ¹⁸⁰ contents are much higher than those known for any other mineral in the Creede veins and fall within or very near the "normal" isotopic range for magmatic water. The direct determinations of δD on fluid inclusions from two rhodochrosite samples (-78 and -82°/00) fall near the lighter end of the "normal" δD range for magmatic waters. These oxygen and hydrogen isotope data suggest that either the carbonate fluids contained a very substantial magmatic component, or that they were meteoric waters that underwent extensive oxygen isotope exchange with deep-seated country rocks.

The carbon isotope data are consistent with the above conclusion. The range of δ^{13} C values of the vein carbonates (-8.2 to -4°/00) lies within that of deep seated carbon as indicated by analyses of carbonatites and carbonates in igneous rocks (Ohmoto and Rye, 1979). These values are also typical of numerous hydrothermal carbonates associated with felsic intrusives in various parts of the world throughout geologic time. δ^{13} C values of -8 to -5°/00 have been observed in hydrothermal and carbonate minerals that occur in all types of country rocks and irrespective of whether or not carbonate rocks are known, or inferred, to be in the area. The convergence of the carbon, hydrogen and oxygen isotope data on values typical of magmatic environments strongly suggests a magmatic source for the carbonate fluids.

On the other hand, under certain extreme conditions the observed isotopic compositions of the vein carbonates conceivably could be produced by a deeply circulating meteoric water interacting, at moderate temperature, with a buried marine carbonate unit. In figure 6 we have plotted the \int^{180} and $\int^{13}C$ data for the carbonate minerals. Also plotted, for comparison, are the data of Steven and Friedman (1968) on Creede Formation travertines. The Creede Formation is a clastic unit composed of volcanic ash and debris deposited in a shallow lake which occupied the moat of the resurgent Creede caldera. The travertines were deposited while the volcaniclastic sediments of the Creede Formation accumulated, and they predate the vein carbonates by as much as 2 million years and are volumetrically much more important (Steven, 1969; Bethke et al., 1976). Steven and Friedman (1968) concluded that the travertines were deposited by meteoric water at low temperatures and that they derived their carbon from dissolution or decarbonation of thin wedge of Mesozoic sedimentary rocks containing marine carbonate beds they presumed to underlie the volcanic rocks of the central San Juan Mountains.

If the vein carbonates formed from circulating meteoric waters that interacted with such deep marine carbonates a pH of 9 or greater must have obtained (assuming at temperature of interaction of approximately 300°C) and total carbon, but only partial oxygen isotope exchange between the fluids and the carbonate would be required. In our opinion such required conditions are excessive. We suggest that the convergence of the \S^{13} C, \S^{18} O and \S D values of the carbonate fluids on values typical of deep-seated or magmatic fluids <u>favor</u> a magmatic origin for both the CO₂ and H₂O components, and <u>require</u>, at least, a deep, high temperature history for the carbonate fluids.

Sphalerite Fluids

The $\{D \text{ values of the fluid inclusions in sphalerite (figure 5) are well within the range of values for "normal" magmatic waters, and are much heavier than the values of present-day surface water. The <math>\{S^{180} \text{ content of the fluid inclusions, however, is much lower than that of "normal" magmatic waters and lies close to the meteoric water line. The sphalerite fluids must have been either: 1) meteoric waters whose deuterium content was significantly higher than present surface waters and whose ¹⁸⁰ content was shifted to higher values by reaction with the volcanic rocks enclosing the vein system; 2) magmatic waters whose ¹⁸⁰ content shifted to much lower values by low-temperature exchange with the wall rocks; or 3) mixtures of the two.$

For years it has been recognized that meteoric waters can obtain large $\int ^{180}$ values, even as high as those typical of magmatic fluids, as a result of exchange with high-temperature country rocks (Craig, 1963). The $\int ^{180}$ values of magmatic waters, normally near 6 to $8^{\circ}/00$ (Rye, 1966; Taylor, 1974a, 1977), can decrease as a result of low-temperature exchange with country rocks that host the ore deposit. The actual decrease in $\int ^{180}$ values of magmatic water

depends on the degree of exchange, the water/rock ratio, the temperature of equilibration and the original S^{180} of the rocks. The lowest ξ^{180} values of exchanged magmatic fluids will be produced when water/rock ratio, temperature and δ^{180} of the country rocks are all as low as possible.

The rocks immediately enclosing the productive parts of the veins at Creede (the Bachelor Mountain Member of the Carpenter Ridge Tuff) underwent extensive potassium metasomatism during an earlier hydrothermal event several million years prior to ore deposition (Ratte and Steven, 1967). This introduction of potassium affected a large volume of rock in the Creede district and produced rocks having greater than 8 weight percent K20 and having K20/Na20 weight ratios as high as 18. We have measured the oxygen isotopic and chemical composition of a large number of these potassium metasomatized wallrocks (R.O. Rye and P.M. Bethke, Unpubl. data, 1977). The potassium metasomatism has been found to be accompanied by an ξ^{180} shift in the rocks to lower values, and a good correlation exists between ξ^{18} 0 and K₂0/Na₂0 ratio. The lowest ξ^{18} 0 observed thus far in the country rocks is about 4.30/00. If the ore fluids exchanged with rocks that had such low S^{180} values at temperatures as low as 200°C under conditions of very low water/rock ratios, the S^{180} of the fluid could have reached values as low as -40/00. For several reasons, however, this is an unreasonable lower limit.

First, to achieve such a low value would require both complete water-rock oxygen isotope exchange and a small water/rock ratio, an exceedingly unlikely combination in an open fissure system such as existed during mineralization. Second, significant exchange is unlikley to have occurred at a temperature as low as even 250°C. In most open hydrothermal systems, the fluids are not in equilibrium with the host rock at the site of ore deposition, but, rather, with higher temperature rocks much deeper in the system (Rye, 1966; Rye and Sawkins, 1974). Third, host rocks having δ^{180} values as low as 4.30/00 constitute a small volume of the total host rock in the Bachelor Mountain unit. Such low values have not been observed in the overlying and underlying units near the vein systems. Unless the volcanic and Precambrian rocks deep within the hydrothermal plumbing system were somehow depleted in ¹⁸⁰ prior to ore deposition, most of the host rock with which the fluids could have exchanged probably had δ^{180} values considerably larger than 4.30/00. A more realistic lower limit for δ^{180} values of exchanged magmatic waters in the Creede system would probably be <u>2 to 30/00</u>.

Thus, on the basis of ξ^{180} data alone, the sphalerite fluids <u>must</u> have had a major meteoric component. Although in no way do the data rule out the possible contribution of a magmatic component, the sphalerite fluids must have been <u>dominated</u> by waters of meteoric origin.

Illite and Chlorite Fluids

If the isotopic compositions of the fluids calculated from those determined on the minerals are correct, the δD_{H_20} range of the illite and chlorite fluids was essentially identical to that of all but the latest sphalerite fluids, but the $\delta^{180}_{H_20}$ values of the fluids were several permil larger. In spite of the previously discussed uncertainties in the values of the mineral-water fractionation factors used to calculate the fluid composition, we feel that this difference in $\delta^{180}_{H_20}$ is probably real and that the δD_{H_20} correspondence is reasonable. The larger $\delta^{180}_{H_20}$ values may indicate a larger magmatic contribution to the fluid, a higher degree of isotopic exchange with the country rocks, or a lower effective water/rock ratio during the <u>formation</u> of the illite and chlorite. The available evidence provides no basis for choosing among these possibilities. The same arguments presented for the source of the sphalerite fluids apply to the illite and chlorite fluids, and even if a larger magmatic contribution was the cause of the $\delta^{18}_{H_20}$ difference, the fluids must still have been dominated by meteoric waters.

Quartz Fluids

The oxygen isotopic compositions of the guartz fluids calculated from the mineral compositions cover a broad range and oovrlap both the sphalerite and illite-chlorite fluid compositions. Most of the S^{180} values were obtained early in the study; the hydrogen determinations were made later. In the absence of data on the hydrogen isotopic composition of the quartz fluids, their SD was initially assumed to be also about -60% oo, and the quartz fluids seemed to bridge the gap between the sphalerite and illite-chlorite fluids (Bethke et al., 1973). When the hydrogen isotopic compositions of inclusion fluids in four samples of quartz were determined, it became apparent that this assumption was wrong and that the quartz was deposited from a fluid having an isotopic composition strongly contrasting with that associated with the deposition of any The low values of D_{H_2O} , as well as all the arguments other mineral. concerning oxygen isotopic shift through exchange with country rock, virtually require that the quartz fluids also originated primarily as meteoric waters, but of lower deuterium content than the meteoric waters responsible for sphalerite, illite, and chlorite formation.

The abovementioned considerations on the origin of the fluids appear to require that at least three distinct waters occupied the Creede vein system recurrently during the depositional history. One of these fluids, the one responsible for depositing both carbonate stages, must have been of deep-seated, probably magmatic origin. The other two waters were dominantly meteoric in origin but differed greatly in their hydrogen isotopic composition. Creede is not unique in having waters from different sources involved during vein formation. We have pointed out previously that the wolframite-sulfide deposits at Pasto Bueno in northern Peru and the tin-tungsten deposit at Panasqueira, Portugal appear to have been formed by fluids from more than one source. In addition, the studies of Kamilli and Ohmoto (1977) at Colqui and of Sawkins and Rye, (1974 and unpub. data, 1977) at Caudalosa show that these two Peruvian vein deposits also show evidence of waters from diverse sources. What does appear unique about Creede (and perhaps Panasqueira) is the paragenetic evidence that requires that the three waters coexisted in separate reservoirs that fed the Creede vein system episodically throughout the period of vein filling.

SPECULATIONS ON RECHARGE AREAS AND & D VARIATIONS OF METEORIC WATERS

The discovery that two meteoric waters whose § D values differed by as much as $40^{\circ}/\circ \circ$ were involved in mineral deposition in the Creede vein system, apparently alternately throughout most of the life of the system, is one of the most significant, if perplexing, results of this study. Such a situation could arise in two general ways. Either: 1) the two meteoric waters were <u>originally</u> <u>different in hydrogen isotopic composition</u>, or, 2) the hydrogen isotopic composition of the surface waters over the entire area was uniform, but waters in different reservoirs <u>underwent substantially different isotopic evolution</u> prior to entering the vein system.

The first alternative has at least two possible variations. Either: a) the two waters were generated at different times and entered the system from a single recharge area, or b) waters of substantially different isotopic composition entered the system during the same interval, but at two or more separate recharge areas feeding different reservoirs. Sparse data from both eastern (Taylor, 1974a,b) and western (Forester and Taylor, 1972; Taylor, 1974a; Casadevall and Ohmoto, 1977) San Juan Mountains show that the $\int D$ values of surface waters that have existed in the San Juan Mountains during the past 30 million years have varied by at least 70°/oo. This variation must be the result of several factors related to the geologic history of the San Juan Mountains and of the Western United States. These factors include high relief, regional uplift, and changes in the relative influence (perhaps in both time and space) of Pacific and Gulf of Mexico air masses. Although it appears to be generally true that the distribuiton of $\int D$ values of meteoric water in the Western United States during much of Tertiary time was nearly the same as that of the present day, it is clear that one must be very careful in applying such an assumption to specific deposits in the San Juan Mountains, or in many other areas of presently high relief.

The §D values of meteoric water at a specific recharge area for a hydrothermal system can change considerably with daily, seasonal, and yearly climatic variations, but probably not by as much as $40^{\circ}/\circ\circ$ even in areas of high relief and where mixing of different air masses occur. In any event, because the residence time of meteoric waters in hydrothermal systems is much longer than annual weather cycles, short term variations in the §D of meteoric water at a single recharge area would probably be homogenized within the hydrothermal reservoir. We consider it unlikely that the observed differences in §D were generated by such short term fluctuations.

The & D values of meteoric waters at specific locality may also change over long periods of time. For example, & D values of meteoric waters can become more negative during general uplift of an area or as a result of a decrease in the annual mean temperature of precipitation. The & D values of the ore fluids at Climax, Colorado became progressively depleted in deuterium with time, and one interpretation was that ore deposition was going on during uplift (Hall et al., 1974). At Creede, however, the quartz fluids are much depleted in deuterium relative to the sphalerite (and illite and chlorite) fluids even though the quartz was deposited throughout the paragenetic sequence. This requires that two fluids must have coexisted during the period of vein filling. It is conceivable that, as a result of general uplift, a single, isotopically zoned reservoir having an early, heavy water at depth and a light, younger water on top might have been produced. In the absence of convective overturn, such a reservoir might have persisted for a significant length of time. However, the range of homogenization temperatures of fluid inclusions in quartz is about the same as that for those in sphalerite (Roedder, 1965), and it is difficult to imagine how such vertically zoned reservoir could have escaped convective mixing if both the lower and upper parts were heated to approximately the same temperature by any source of heat at depth. It seems much more likely that the two waters, whatever the origin of their differences in D, coexisted in two separate reservoirs.

The geology and paleotopography of the Creede area as described by Steven and Eaton (1975), Steven and Lipman (1976), Steven (1968), and Steven and Ratte (1965) are compatible with the presence of two distinct recharge areas, differing significantly in altitude. The ore occurs along fractures that make up the NNW trending Creede graben structure (fig. 1). To the north, the fractures can be traced into the ring fracture system of the San Luis Peak caldera near the present Continental Divide. To the south, along the present position of the headwaters of the Rio Grande, the fractures transect the ring fracture zone of the Creede caldera and cut the volcaniclastic sediments of the Creede Formation, which partially fill the moat of the caldera. It is probable that the vein system was fed by waters from both of these areas and that they supplied waters differing in &D by as much as 40 to 50°/00, but both heavier than the present-day surface waters whose &D is $-112^{\circ}/00$. Accepting the proposition that the quartz waters entered the vein system from one recharge area, and the sphalerite and illite/chlorite fluids from another we may inquire as to the causes of the differences in the hydrogen isotopic differences of the meteoric wastes in the two areas.

The &D value of meteoric water is largely a function of annual mean temperature of precipitation which is related to both altitude and latitude. The presence of an <u>unevolved</u> meteoric water having a &D of -550/oo at the time of ore deposition in the Creede district would require that 24 million years ago the Creede district was much lower than at present and that few significant mountain ranges existed between Creede and the Pacific Ocean and/or the Gulf of Mexico. These conditions are reasonable in the light of available geologic evidence.

Reconstruction of the Western United States during the Eocene indicates that prior to basin and range faulting the distance from Creede to the Pacific Ocean may have been 300 km less than today (Hamilton and Myers, 1966). Also, altitudes in the Western United States were considerably less. Most significantly, however, the Creede area was about a kilometer lower than its present altitude (Steven and Eaton, 1975) and was part of a large poorly drained volcanic plateau surmounted by a few isolated hills (Steven, 1968, and oral commun. 1976). The Sangre de Cristo Range did not exist (Taylor, 1975). In the absence of the Sangre de Cristos, no major mountain barrier existed between the Gulf of Mexico and the Creede district; thus, the δ D values of rain falling on the caldera wall and supplying recharge for the ring structure of the caldera could have been about $-55^{\circ}/\circ\circ$.

On the other hand, a §D value of about -950/00 or less would not have been unreasonable for precipitation falling near the present Continental Divide north of Creede because the high plateau and surmounting hills surrounding the Creede caldera were as much as 1200 meters higher than the lake level in the caldera moat (Steven and Lipman, 1976), and because the divide region could have received substantial precipitation from Pacific air masses. In areas of abrupt altitude changes, such as the east side of the present Andes, the isotopic composition of meteoric water can change quite abruptly over short distances.

A second possible cause of the differences in ΔD between the two recharge areas is particularly appealing; such a difference might be due to a difference in isotopic evolution within the reservoirs. The clastic Creede Formation is a potential reservoir where meteoric waters could evolve isotopically to heavier values of $\int D$ and $\int \frac{18}{0}$. According to Steven and Ratté (1965), the Creede Formation accumulated in an accurate closed basin formed by the subsidence and later resurgent doming of the Creede caldera. The bulk of the material filling the moatlike basin consists of thin-bedded silty shales and sandstones and some tuff beds, all of which accumulated in a shallow lake or playa environment. Along the margins, these beds intertongue with stream sediments, primarily sandstones and conglomerates, and with fanglomerates and talus-regolith deposits. Large masses of travertine, deposited from mineral springs concurrently with sedimentation, are widespread throughout the Creede Formation. Much of the clastic material which makes up the Creede Formation was deposited as air-fall and ash-flow tuffs from the Fisher Quartz Lattite volcanoes which erupted along the ring fracture of the Creede caldera at the time the Creede Formation was

accumulating. Much of this material, along with material derived from the weathering of the surrounding ash-flow tuff sheets was reworked by stream and wave action. In short, the moat of the Creede cladera was the site of a shallow closed-basin lake, or playa, in which silicic volcanic ash, the bulk of it glassy when deposited, and the weathering products of silicic volcanic rocks, accumulated to a thickness of about 1 km or more (Steven and Lipman, 1976).

The climate during Creede time was similar to that at present (Steven and Eaton, 1975). It would be expected that under such conditions a shallow closed-basin lake would evolve chemically toward an alkaline saline lake through the combined processes evaporation and diagenesis. Many similar closed-basin lakes exist in the western United States at present (Jones, 1966; Eugster and Hardie, 1979). Neither the degree nor trend of the chemical evolution of Lake Creede can yet be evaluated because little is known of the mineralogy of the lacustrine facies of the Creede formation. No evaporite facies have been reported, but Steven and Van Loenen (1971) have shown that some of the tuff beds have been converted to clinoptilolite or clinoptilolite-smectite mixtures, and according to Steven and Ratté (1965), calcite was precipitated in thin limestone beds, as cement between clasts, and as travertine around spring orifices. What little is known of the mineralogy of the Creede Formation supports the evolution of a shallow, moderately alkaline, saline lake and groundwater reservoir during the deposition of the Creede Formation.

The processes of evaporation and diagenesis (particularly the hydration reactions of glass to clay) both lead to isotopic, as well as chemical evolution, of the lake waters. The fractionation of hydrogen and oxygen isotopes during evaporation from standing bodies of water was first investigated experimentally by Craig and others (1963) and most recently by Sofer and Gat (1975). As evaporation takes place, the residual water is enriched in both deuterium and ¹⁸0. The relationship between the enrichment trends is such that $\&D = 5 \times \sqrt{180}$, consistent with the trends observed in many of natural evaporite systems.

In contrast to the effects of evaporation on the isotopic compositions of the lake and interstitital waters, the effects of diagenetic reactions, such as hydration of glass to smectite or zeolite, or the precipitation of calcite, cannot be estimated without a much better knowledge of the quantitative mineralogy of the Creede Formation. However, by analogy with the isotopic evolution of waters in closed basins (cf Taylor, 1974a), we would expect that the result of such evolution, like that caused by evaporation, would be to increase both the deuterium and 180 contents of the waters.

Assuming an average thickness of the lake beds in the Creede Formation of 750 m, an outer diameter of 20 km, an inner diameter of 8 km for the moat, and an arc of deposition of 270° (figs. 1 and 2), the total original volume of Creede lake sediments would have been nearly 100 km³. If these sediments had an average effective porosity as low as 0.1, the Creede Formation would have been an enormous reservoir containing 10 km³ of meteoric water, whose isotopic composition probably was substantially evolved toward larger values of D and

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180.$ Thus, whether or not there was a significant difference in isotopic composition of meteoric waters falling on different parts of the central San Juan Mountains 25 million years ago, subsequent evolution of the waters in different reservoirs could account for the contrasting isotopic compositions of the quartz waters and of those responsible for sphalerite (and illite/chlorite) formation. Waters entering the system from the mountain areas to the north would have exchanged oxygen with the volcanic rocks as they became heated but would have remained almost constant in deuterium content. These waters would

have been responsible for the bulk of the quartz deposition. Waters entering the vein system from the low moat area to the south would have evolved isotopically through evaporation and diagenesis to larger values of &D (and &¹⁸0) and would have been responsible for sphalerite deposition and for illite and chlorite formation.

SUMMARY AND CONCLUSIONS

In the preceding paragraphs, we have discussed various possible alternatives whereby meteoric waters of substantially different isotopic compositions might have been generated in the Creede area and entered the vein system at various times. The paragenetic evidence requires that two isotopically different reservoirs must have coexisted and fed the vein system alternately. For that reason, we strongly favor either: 1) the alternative whereby the D of waters in the two reservoirs differed because the two widely separated recharge areas were receiving precipitation of different isotopic composition due to differences in altitute and in the relative influences of Pacific and Gulf of Mexico air masses; or 2) the alternative whereby the differences in D between the two waters resulted from the isotopic evolution of water in and above the lacustine Creede Formation sediments through evaporation modified by diagenetic changes. The difference in these two alternatives is illustrated schematically in figure 7.

Present information is not sufficient to decide between these alternatives or even to assure that either is valid. Possibly, aspects of both alternatives were important. What does seem certain, however, is that the bulk of the quartz were deposited from fluids entering the vein system from the mountainous area to the north in the vicinity of the San Luis Peak caldera, whereas the sphalerite, illite and chlorite were formed from fluids whihe entered the vein system from the moat area of the Creede caldera. The carbonate fluids must have had a deeper source, and likely represent a susbstantial magmatic contribution to the hydrothermal system. In our continuing studies, we will integrate the stable isotope data with temperature, salinity, and chemical data on fluid inclusions on a very detailed paragenetic basis. We hope this will enable us to discuss the history of the hydrothermal fluids in more detail, and, perhaps, to construct a more precise chemical, isotopic, and hydrologic model of ore deposition.

In summary, the major conclusions of our study may be listed as follows:

1. The isotope data indicate that different fluids having diferent sources and/or wall-rock exchange histories were involved in the depositon of different generations of minerals. Thus, detailed fluid-inclusion, stable-isotope, and chemical studies hold tremendous potential for developing chemical-hydrologic models for the Creede hydrothermal system.

Since fluids from different sources are likely to have different chemical parameters serious restrictions apply to the use of minerals deposited from different fluids in arguments for chemical equilibrium, particularly if these arguments require more than the presence of absence of one or more phases. The equilibrium assemblages assumed for the OH vein by Barton et al.(1977), however, appear to remain valid.

2. Direct and indirect determinations of the $\int_{20}^{18} O_{H_20}$ of the hydrothermal fluids <u>require</u> that the fluids contained a substantial meteoric component during deposition of sphalerite and quartz and probably also during formation of chlorite and illite. A substantial magmatic component <u>may</u> have been present during the deposition of carbonates. The data do not rule out some magmatic contribution to the fluids responsible for the deposition of all mineral phases.

3. The carbon isotope data as well as those for oxygen and hydrogen suggest that the carbon in the various carbonate fluids was derived from a deep-seated, probably magmatic, source.

4. Direct measurements of the $\int D$ of the hydrothermal fluids require that two meteoric waters were involved in the ore fluids, one having a $\int D$ of $-55^{\circ}/_{00}$ or larger, another having a $\int D$ of $-95^{\circ}/_{00}$ or smaller.

5. The presence of two meteoric waters of different & D values <u>requires</u> that the Creede hydrothermal plumbing system had two recharge areas. This is supported by topographic and structural reconstructions of the area during ore deposition (Steven and Eaton, 1975).

6. The differences in &D between the two meteoric waters may reflect either: 1) climatic differences in the recharge areas for the two reservoirs due to differences in altitude and related orogrpahic factors; or 2) isotopic evoluton of the waters in the moat of the Creede caldera due to evaporite and diagenetic processes, or possibly, some combination of the two.

7. The large range of & D values of meteoric waters in the Creede district as well as the San Juan Mountains as a whole indicate that considerably caution must be exercised in assuming wide uniformity of & D distribution of meteoric water in the Western United States at any time during the Tertiary.

8. The large range of δD values of meteoric waters also indicates that caution must be used in assuming that a large range of δD values in hydrothermal fluids can be considered evidence of mixing of magmatic and meteoric fluids without definite knowledge of the paleogeography, climatology, and history of rock/water interactions.

FIGURE CAPTIONS

- Figure 1. Relationship of the Creede vein system to calderas in the Central San Juan Caldera Complex. Area of figure 2 outlined by box; see Steven and Eaton (1975) for description of relationship of veins to history of caldera development. From fig. 2 of Steven and Eaton (1975).
- Figure 2. Location map for various veins referred to in text. Area of map shown in figure 1. For descritpion of geologic history, see Steven and Eaton (1975). Modified from fig. 3 of Steven and Eaton (1975).
- Figure 3. Longitudinal projections of a) the combined Southern Amethyst-OH veins, and b) the Bulldog vein system showing locations of samples used in this study. Circled symbols represent samples taken away from main structures.
- Figure 4. Relationship of δD_{H_20} and $\delta^{18}O_{H_20}$ values of fluids to mineralogy and position in depositional sequence. Degree of uncertainty in paragenetic position indicated by vertical bar. Mineral symbols offset vertically to avoid overlap.
- Figure 5. $\int D_{H_20}$ and $\int ^{18}O_{H_20}$ values of Creede ore fluids showing fields occupied by fluids responsible for the formation of different minerals. Solid symbols represent samples wherein both $\int D_{H_20}$ and $\int ^{18}O_{H_20}$ have been determined. Open symbols represent quartz and carbonate samples whose oxygen isotopic composition alone was measured; these are plotted at the average H_{20} value of quartz or carbonate fluid inclusions (see text).
- Figure 6. Relationship between \int^{13} C and \int^{18} O for carbonate minerals (mineral data, not fluid data plotted). Solid squares represent rhodochrosite samples (A-stage); solid triangles represent siderites (C-stage).

Data for travertines deposited in Creede Formation as reported by Steven and Friedman (1968) shown as circles for comparison.

Figure 7. Graphical illustration of alternative ways of producing two isotonically different meteoric waters. a) Original difference in §D due to precipitation at differing altitudes and/or from different air masses. b) Originally homogeneous meteoric water undergoing different isotopic evolution in different reservoirs; water in Lake Creede becomes heavier due to evaporation and diagenetic reactions.

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Horizontal Inclined Compaction foliation in caldera core



EXPLANATION

Older undifferentiated ash flow tuffs

11 ·Tfi

Fisher Quartz Latite Tf, Quartz latite flow Tfi, Volcanic neck



Creede Formation

Geologic contact

Fault active just before and during mineralization Dashed where uncertain or minor. Bar and ball on downthrown side

Older fault Dotted where buried. Hachures on downthrown side

1 2 KILOMETERS





F194



Fig S



Figb



Table 1. Summary of the Paragenesis of Creede Ores.

STAGE	CHARACTERISTICS	DISTRIBUTION
E-Stage (Youngest)	Fibrous pyrite with some marcasite and stibnite. Generally high in ore bodies and commonly on cross cutting fractures.	District wide
D-Stage	Relatively coarse grained sphalerite, galena, chalcopyrite and quartz, and some hematite. Silver minerals notably absent. Probably stage of illite alteration. Subdivided into three sub- stages on basis of color banding in sphalerite: inner light, middle dark and outer light.	Northern parts of OH, P and Amethyst veins. Poorly developed on Bulldog Mtn. vein sys- tem as developed thus far.
C-Stage	Volumetrically minor, sits on deep etch of earlier B-stage. Fluorite overgrowing siderite-manganosiderite and quartz. Most fluorite deeply etched commonly completely removed.	Recognized only in Northern parts of OH, P and Amethyst veins thus far.
B-Stage	On OH, P and Northern Amethyst veins, relatively fine grained sphalerite, galena, chalcopyrite, chlorite, hema- tite, pyrite, and with some tetra- hedrite-tennantite. On Southern Amethyst and on Bulldog Mtn. vein sys- tem consists of banded barite-sulfide with quartz. Sulfides mainly spha- lerite and galena with much tetrahed- rite-tennantite and other sulfo-salts. Native silver common.	District wide
A-Stage (Oldest)	Primarily quartz with minor chlorite and sulfide on OH and P veins and on Northern 2/3 of Amethyst vein. On Southern part of Amethyst vein and on the Bulldog Mtn. vein system, A stage consists mainly of both quartz and rhodochrosite.	District wide

Table 2. Relative Deuterium (D), ¹⁸O and ¹³C contents of minerals and associated fluids from the Greede mining district.

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•				1	Minerals		l)2) Fluids		
SAMPLE	3) LOCATION (See fig. 3)	STAGE (See Table 1)	MI NERAL	6D	6 ¹⁸ 0	6 ¹³ C	⁸⁰ 420	^{٤¹⁸0_{H2}0}	^{د13} ر∞2
<u>OH Vein</u>									
PMB CE-251-65	130 ft sublevel at 6-1/2R.	D	Illite	-91	4.8	-	-53	0.2	-
PMB X-94-59	30 ft sublevel above Am. 5 near 19R.	D	Quarts	-	8.0	-	- <u>92</u>	-2.3	-
PMB DL-277-67	Am. 5 level near K2R.	D	Illite	-88	3.0	-	-50	-1.6	-
PMB DH-279-67	Am. 5 level between K1 and K2R.	D	Illite	-92	4.0	-	-54	-0.6	-
PMB AA-109-59	Am. 5 level near 17R.	ם	Quarts	-	6.0	-	-	-4.3	- .
PHB AA-109-59	Am. 5 level near 17R.	В	Chlorite	-108	1.8	-	-61	0.8	-
MB-S-182-59	Am. 5 level between 15 and 16R.	C/D	Quartz	-	7.5	-	- <u>97</u>	-2.8	-
XB-S-188-59	Am. 5 level between 15 and 16R.	D	Sphalerite	-	-	-	- <u>78, -81</u>	- <u>10.1</u>	-
PMB BA-200-65	7 level near KSR.	D	Illite	-89	3.2	-	-51	-1.4	-
PMB BC-206-65	7 level between K3 and K4R.	D	Illite	-88	3.9	-	-50	-0.7	-
ER-127-65	7 level between 16 and 17R.	D	Sphalerite	-		-	- <u>54,-55</u>	- <u>5.8</u>	-
PBB-33-106-59	7 level between 15 and 16R.	В	Chlorite	-111	-0.5	-	-64	-1.5	, -
PBB-40-119-59	7 level between 8 and 9R.	С	Siderite	-	16.7	-8.2	-	9.9	-6.9
ER-119-65	30 m above 9 level between 18 and 19R.	с	Siderite	-	16.4	-7.5	-	9.6	-6.2
PMB-BY-244-65	9 level between K4 and K5R.	D	Quartz	-	7.9	-	- <u>86</u>	-2.4	-
PMB-B0-227-65	9 level between K2 and K3R.	С	Siderite	-	14.9	-6.1	-	8.1	-4.8
PBB-28-90-59	9 level near 17R.	с	Siderite	-	14.6	-6.3	-	7.8	-5.0
PBB-27-86-59	9 level between 15 and 16R.	*	Quertz	-	7.4	-	-	-2.9	- ,
MB-K-93-59	9 level between 12 and 13R.	D	Sphalerite	•.			- <u>55,-65</u> , - <u>67</u>	-4.5	-
PBB 67-16-67	Above 7 level between K4 and 5R	- D	Quartz	-	9.3	-	4	-1.0	-
PrB-CA-246-65(1)	10 level near KSR.	A	Quarts	-	8.9	-	-	-1.4	-
PHB-CA-246-65(2)	10 level near KSR.	A	Quartz	-	8.1	-	-	-2.2	-
PMP-CA-246-65(3)	10 level near KSR.	· ک	Quartz	-	8.7	-	-	-1.6	-
PBB-66-15-67	10 level between 19 and KlR.	*	Quarts	-	8.3	-	- <u>96,-95</u>	-2.0	-
PrB-50-59	11 level between 10 and 11R.	С	Siderite	-	11.7	-4.0	-	-4.9	-2.7
PMB J-47A-59 PMB J-47A-59	11 level near 10R. 11 level near 10R.	A A	Quartz Adularia	-	6.0 3.0	-	-	-4.3 -4.2	-
PNB N-58-59	11 level between 8 and 9R.	B	Chlorite	-108	-0.2	-	-61	-1.2	-
PBB 13-46-59	12 level near 13R.	В	Chlorite	-102	0.5	-	-55	-0.5	-
NJP IX-59	12 level near 10R.	B	Chlorite	-102	-0.4	-	-55	-1.4	· -
PBB 25-83-59	12 level near Volunteer R.	B .	Chlorite	-110	0.0	-	-63	-1.0	-
PBB 112-36-59	15 m above CS level - Volumteer R.	c	Siderite	-	16.5	-7.0	-	9.7	-5.7
NJP IV-59	C5 sublevel between 16 and 17R.	3	Chlorite	-102	1.5	•	-55	0.5	-
PBB 8-30-59	C5 sublevel near 14R.	B	Chlorite	-103	-0.2	-	-56	-1.2	-
RJP VI-59	C5 sublevel near 14R.	B	Chlorite	-102	-1.2	-	-55	-2.2	-
		Amethyst Vein	<u>System</u>						
PBB-449-131-59(1)	Am. 5 level 30 m S of Albion x- cut.	D	Quertz	-	5.2	-	-	-5.1	-
PBB-449-131-59(2)	Am. 5 level 30 m S of Albion x- cut.	D	Quartz	-	6.7	-	-	-3.6	-
PBB-449-131-59(3)	Am. 5 level 30 m S of Albion x- cut.	D	Quartz	-	4.4	-	- '	-5.9	-
	•••••••••••••••••••••••••••••••••••••••								
	Hanging-wall St	ructures West	of Amethyst V	ein Sys	tem				
PHB FW-331-68	C4 level, 300 m West of Man. R.	٨	Rhodoch ro- site	-	11.0	-6.9) -	4.2	-5.6
PMB FX-332-68	C4 level, 300 m West of Man. R.	D	Quartz	-	7.9	-	-	-2.4	-
PHB JJ-518-71	C4 level, 230 m West of Amethys vein N end of workings.	t B	Chlorite	-102	-0.3	• •	-55	-1.3	-
PMB KP-558-71	C4 level, 400 m West of Man. R.	D	Illite	-100	5.8	-	-62	1.2	-

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Bulldog Muuntain Vein Svetem										
PMBKO-	9550 level 123 stope.	D	Illite	-96	· -	-	-58	· _	-	
PMB KA-542-71	9550 level, Al80 stope.	A	Rhodochro-)	-	13.6	-6.6	-	6.8	-5.3	
PMB KA-542-71	9550 level, Al80 stope.		Quartz	-	10.1		-	-0.2	•	
PBB 132-8-74B	9360 level, A243 x-cut.	A	Ehodochro-	-	14.2	-6.2	- <u>78</u>	7.4	-4.9	
PMB KE-547-71	9360 level, A215 x-cut.	D	Sphalerite	-	-	-	- <u>62, -70</u>	-5.4	-	
PBB 145-37-74	9360 level, 145 x-cut.	٨	Rhodochro-	-	15.2	-6.5	- ,	8.4	-5.2	
PBB 145-37-74	9360 level, A145 x-cut.	A.	Quartz)	-	12.1	-	-	1.8	-	
PMB MD-642A-74	9360 level, A145 x-cut.	▲	Rhodochro- site	-	14.6	-6.2	-	7.8	-4.9	
PBB 147-50-74	9360 level, A59 x-cut.	*	Rhodochro- }	-	14.6	-6.3	-	7.8	-5.0	
PBB 147-50-74	9360 level, A59 x-cut.		QUATE	-	8.4	-	-	1.9	-	
P19 GC-338-68	9360 level, A72 x-cut.	*	Rhodochro- site	-	16.2	-5.5	-	9.4	-4.2	
PMB LP-596-74	9200 level, P91 x-cut.	*	Rhodochro- site	-	14.8	-6.6	-	8.0	-5.3	
PMB NB-658-74	9200 level, P91 x-cut.	*	Rhodochro- site	-	11.2	-7.0	- <u>82</u>	4.4	-5.7	
• • • • • • • • • • • • • • • • • • •		<u>P-Vei</u>								
PBB 108-32D-68	4) Am. 5 level at P-vein r-	D .	Illite	-93	3.7	-	-55	-0.9	-	

1) Values determined directly from analysis of fluid inclusions in italics.

2) Calculated values assume equilibration temperatures of 250°C; see text for fractionation factors used.

3) Abbreviations used to describe location: Am. = Amethyst; C = Commodore; Man. = Manhatten; R = Reise; X-cut = Crosscut. Other abbreviations such as K as in K4R or A as in A180 stope follow company usage.

4) Locality PBB 108-32D-68 not shown on Figure 3. Locality is approximately 235 m NE (behind plane of section in Figure 3) of KlR.