Mixed-layer illite/smectite as a paleotemperature indicator in the Amethyst vein system, Creede district, Colorado, USA

Duane G. Horton¹

University of Illinois, Urbana, Illinois, USA

Abstract. Ordered illite/smectite is the most abundant and widespread product of argillic alteration associated with the Oligocene, epithermal, Ag-Pb-Zn-Cu-Au Amethyst vein system, southwest Colorado. Hydrothermal illite/smectites exhibit all Reichweite from 1 to \geq 3 and span the composition range from about $25%$ to about $3%$ illite. - The composition and Reichweite of illite/smectite vary smoothly with distance from the Amethyst vein. With increasing distance from the vein, percent illite and the Reichweite decrease. When composition-temperature relationships of illite/smectite from modern geothermal systems are applied to the fossil Amethyst system, isotherms describing the thermal regime at the time of argillization can be estimated. Temperatures near 240° C appear to have existed near the Amethyst vein; these temperatures agree with homogenization temperatures obtained from fluid inclusions in vein minerals. The most distal illite/smectites, sampled about 260 m from the vein, indicate temperatures near 110° C. Estimated thermal gradients are on the order of 0.4 to 1° C per meter. Although illite/smectite composition and structure vary systematically with distance from the Amethyst vein, there are no systematic trends associated with the numerous, smaller veins and veinlets in the hanging wall of the system. This indicates that temperatures of both wallrock and the fluids in all but the major Amethyst vein were nearly the same during clay formation. Apparently, the hydrothermal system had reached a fairly steady, mature, thermal state at the time of argillization.

Introduction

Mixed-layer illite/smectite forms as an alteration product or as a newly precipitated phase under a variety of relatively low temperature (100° -300°C) petrologic conditions. Illite/ smectites in modern geothermal systems exhibit systematic variations in composition (i.e. percent illite) and structure (i.e. order expressed in terms of Reichweite) with respect to depth (Steiner 1968; Sumi 1969; Eslinger and Savin 1973; McDowell and Elders 1980). Certain types of ore deposits are interpreted to be fossil geothermal systems (Wetlaufer et al. 1979; Henley and Ellis 1983) and mixedlayer illite/smectite is present in some of these. Although variations in illite/smectite (I/S) composition and Reichweite are fairly well documented in a few modern geothermal systems, they are not as well studied in ore deposits. A few studies have, however, either reported compositional and structural variations or published X-ray diffraction patterns from which variations can be interpreted to exist with respect to ore horizons in Kuroko-type deposits (Shirozu 1974) and with respect to distance from major veins (Tooker 1963; Harvey and Vitaliano 1964; Inoue and Utada 1983).

This report concerns argillic alteration associated with an epithermal vein deposit in the Creede mining district, southwestern Colorado. Evidence is presented to show that the composition and the structure of I/S vary systematically with respect to distance from a major vein in the district. The interpretation of the systematic distribution of I/S composition and structure at Creede is based on studies of the occurrence of these clay minerals as an alteration product in modern, active geothermal areas and as a diagenetic mineral in sedimentary rocks.

The Oligocene, Ag-Pb-Zn-Cu-Au Amethyst vein system was chosen for study because there the I/S is known to be a product of hydrothermal alteration (Bethke et al. 1976) and the ore deposits in the Creede district have been well studied. The structural setting (Steven and Ratté 1965; Steyen and Eaton 1975), the hydrologic setting (Steven and Eaton 1975; Barton et al. 1977), the petrology of unaltered country rock (Ratté and Steven 1967), the physical and chemical environment of ore deposition (Roedder 1962, 1963, 1974; Barton et al. 1977; Wetlaufer 1977), age relations among host rock, mineralization and alteration (Bethke et al. 1976), and the origin of the hydrothermal waters (Bethke and Rye 1979; Wetlaufer 1977; Foley et al. 1982) are all well documented. This wealth of information makes Creede an ideal site for a detailed study of wall-rock alteration. Finally, the vast labyrinth of underground workings and abundant diamond drill core allow detailed sampling throughout much of the vein system.

Geologic framework

The Creede mining district lies in the center of the Bachelor caldera, central San Juan Mountains (Fig. 1). Several major NNW striking, normal faults are located within the district (Fig. 2). These faults, which contain most of the ore, are radial to the Creede caldera and cut the Bachelor Mountain Member of the 26.7 to 27.8 m.y. old Carpenter Ridge Tuff (Lipman et al. 1970). The Bachelor Mountain Member con-

^{} Present address:* Rockwell Hanford Operations, P.O. Box 800, Richland, Washington 99352

Fig. 1. Generalized map of the San Juan volcanic field (modified from Steven and Eaton 1975). The Creede mining district is in the center of the Bachelor caldera (B). The calderas are (from oldest to youngest): *BZ,* Bonanza; P, Platoro; *SM,* Summitville; U, Ute Creek; L Lost Lake; *UN,* Uncompahgre; *S J,* San Juan; *MH,* Mount Hope; *LG,* La Garita; S, Silverton; B, Bachelor; M Mammoth Mountain (postulated); *SL,* San Luis; *CP,* Cochetopa Park; C, Creede, *LC,* Lake City

Fig. 2. Simplified geology map of the Creede mining district (modified from Bethke and Rye 1979). The box near the center of the district marks the study area

sists of rhyolitic tufts which fill the Bachelor caldera. The Bachelor caldera predates the Creede caldera and is unrelated to the ore-forming system.

The Amethyst vein system consists of the Amethyst vein and many related hanging wall veins (Fig. 2 and 3). The Amethyst vein closely follows a thick zone of silicified, tectonic breccia that marks an earlier fault formed during resurgence in the core of the Bachelor caldera. Within this breccia zone the Amethyst vein has a variable character. In places, it is as thin as two meters and is a single, well defined vein. In other places, it widens to as much as 40 m and is represented by a zone of silicified fault breccia which can be indistinguishable from the earlier tectonic breccia. Numerous hanging wall veins splay off the main Amethyst vein (Fig. 3). These veins thin and bifurcate upward making the upper portions of the system much more shattered and structurally complicated than the deeper portions. Hanging wall veins vary in width from a few millimeters to about 2 meters and they pinch, swell, branch and converge along strike.

The hanging wall of the Amethyst vein is dominantly Campbell Mountain tuff, the middle bed of the Bachelor Mountain Member of the Carpenter Ridge Tuff. It is the host rock for most of the ore and the parent rock for most hydrothermal alteration in the system. Campbell Mountain tuff is a rhyolitic, welded, ash flow tuff containing 5-10% phenocrysts and 1-10% lithic fragments in a matrix of volcanic ash, shards and pumice which are devitrified to quartz

Fig. 3. Generalized cross section through the Amethyst vein system and along the 19,800 crosscut. The cross section shows the relations among veins, argillic alteration *(stippled),* rock units and sample locations in drill holes CDS-20, CH-28, and the 19,800 crosscut *(open triangles). Tbw,* Willow Creek tuff; *Tbc,* Campbell Mountain tuff; *Tbs,* Bachelor sediments; *Tw,* Wason Park Tuff; dashed lines indicate approximate geologic contacts

and orthoclase. Sanidine and plagioclase are the dominant phenocrysts. Biotite, clinopyroxene, and magnetite are present in some samples but generally make up less than one percent of the rock (Ratte and Steven 1967).

Most Campbell Mountain tuff in the study area experienced extensive potassium metasomatism prior to 26.7 m.y. ago, probably during resurgence of the Bachelor caldera. Potassium metasomatism increased the K_2O content of the tuff from approximately 5% to as much as 11%. Most of the K_2O resides in groundmass K-feldspar and K-feldspar that replaces plagioclase. Metasomatism also decreased the $Na₂O$ content from around 4% to less than 1% and significantly decreased the MgO, CaO and total iron concentrations (Ratté and Steven 1967). Potassium metasomatized Campbell Mountain tuff is the parent rock onto which silicification and argillization were superimposed.

In addition to Campbell Mountain tuff, local volcaniclastic sediments, informally called the Bachelor sediments, are hydrothermally altered. Little is known about these sediments because they have been found in only six diamond drill cores and in all of these occurrences they are hydrothermally altered. The Bachelor sediments are dominantly fine-grained mudstone and sandstone with a few matrixsupported conglomerates. Fragments of Campbell Mountain tuff are common but not abundant in the coarsergrained units. The mineralogy of the sediments is variable, but quartz and clay minerals are ubiquitous and K-feldspar is common. Hematite, calcite and chlorite are locally abundant.

Ore at Creede is dominantly in veins and shows textures typical of open space filling. The major ore minerals are sphalerite, chalcopyrite, galena, pyrite, tetrahedrite-tennantite, silver sulfides and some native silver. Associated gangue minerals consist of quartz, hematite, Fe-Mn carbonates, chlorite, fluorite and barite. Mineral assemblages in the veins at Creede appear to be zoned on a district scale and indicate that hot fluids ascended in the north, then flowed southward precipitating ore and gangue, and descended to be reheated and recharged with metals (Steven and Eaton 1975; Barton et al. 1977). Stable isotope studies of hydrothermal minerals and fluids in fluid inclusions have shown that the ore solutions were dominantly heated meteoric water but that some magmatic water may have been involved during carbonate gangue deposition (Bethke and Rye 1979; Bethke et al. 1973; Wetlaufer 1977).

The fluids responsible for mineralization and alteration were relatively hot, alkali chloride brines (Barton et al. 1977). Temperatures, as determined from fluid inclusions in quartz and sphalerite from the OH vein, ranged from 198 \degree C to 269 \degree C with a mean of 250 \degree C (Barton et al. 1977). Salinity ranged from 4 to 12 $wt\%$ (NaCl equivalent), chloride content from 0.92 to 1.86 molal and Na/K molal ratio from 7.4 to 9.9 (Barton et al. 1977). Using measured potassium concentrations in fluid inclusions and assuming quartz saturation and muscovite-K-feldspar equilibrium, Barton et al. (1977) calculated a pH of 5.4 for the ore fluids. This pH is near neutral at 250° C. Fluid inclusions from the OH vein indicate that the ore fluids boiled at times (Roedder 1965). Boiling at depth would release acid volatiles which would condense and concentrate in the shallower portions of the deposit forming an acidic solution which Barton et al. (1977) feel is responsible for much of the argillization in the Amethyst system. Both mineralization and argillization have been dated by K-Ar methods to be 24.6 ± 0.3 m.y. old (Bethke et al. 1976). This places the main period of mineralization and alteration about 2 m.y. later than the youngest volcanism in the district.

Definitions

The structure, or range of order, in mixed-layer crystallites is described by the term "Reichweite" (Reynolds 1980). The Reichweite (R) signifies the most distant layer in a crystal influenced by any given layer. For example, $R = 1$ designates nearest neighbor influences. $R = 3$ describes a structure in which a given layer influences all neighboring layers up to and including those which are three layers away from the given layer. Thus, an $R=3$ ordered, illite/ smectite means that, given a smectite layer, the next three layers must be illite layers. A much more thorough discussion of ordered, mixed-layer structures is given by Reynolds (1980).

The composition of mixed-layer I/S is the proportions of illite and smectite expressed in terms of either percent illite or percent smectite layers. Thus, composition, as used in this report, refers to mineralogic composition and not chemical composition.

Methods

Rock samples used for this study include drill core and hand specimens collected underground and on the surface. Sample locations are shown on Figs. 3 and 4. The cross section in Fig. 3 is along the 19,800 crosscut (Fig. 4). Note that drill holes CDS-20 and CH-28 are superimposed onto the cross section. Their locations relative to the 19,800 crosscut is shown in Fig. 4.

Whole rock powders were prepared for XRD analysis by grinding approximately 20 g of material in a tungsten carbide container in a ball-mill. Samples were ground for 10 min then sieved to minus 150 mesh. This procedure was repeated until all material passed 150 mesh. The powder was side packed into an aluminum sample holder for analysis. Semi-quantitative XRD modes were

Fig. 4. Simplified map showing locations of samples *(open circles)* from drill holes CH-26, CH-29, and the 19,800 crosscut. The two solid circles mark the locations at which drill holes CDS-20 and CH-28 penetrate the plane of the map. Tbc, Campbell Mountain tuff; Tbs, Bachelor sediment

174

made using a method described by Hoffman (1976). The method involves the comparison of the intensity of a single characteristic peak for each mineral in the unknown with the intensity of the same peak in a monomineralic external standard. Multiple determinations on several samples indicate that the precision of the method is about \pm 5% of the determined amount (Horton 1983). The accuracy has not been evaluated but similar methods are accurate to within $+10\%$ for phases present in amounts greater than about 15% (Schultz 1964).

X-ray characterization of clay minerals was made from a second portion of the hand specimen. Twenty to 30 g of rock were gently crushed with a mortar and pestle and dispersed in distilled water using a Waring blender. Then the suspension of the ≤ 1 or \leq 2 µm size fraction was obtained by centrifugation. Preliminary analyses indicated that I/S composition and structure do not vary with particle size (Horton 1983). Oriented clay aggregates were prepared for XRD by suction onto porous, ceramic tiles. Diffractograms of both air-dried and ethylene glycol-solvated specimens were used for identification of clay species. Solvation was accomplished by applying glycol directly to the specimen with an eyedropper. For mixed-layer clays, determination of the composition and ordering characteristics were made by comparing experimentally obtained XRD patterns from glycol-solvated samples with computer calculated diffraction profiles. The estimated error for I/S compositions determined in this manner is about 2% illite in iUite/ smectite. A modified version of the computer program described by Reynolds (1980) was used.

X-ray diffraction (XRD) data were obtained with a Phillips diffractometer using Ni-filtered Cu radiation, a scintillation counter, a 1° divergence slit, 0.006 inch receiving slit, and a 1° beam slit. Samples were scanned at 1° 2 θ /min and data were recorded by a strip chart recorder at 1° 2 θ /0.5 inch.

Argillic alteration

Figure 3 shows the distribution of argillized rock along one generalized cross section through the Amethyst vein system. Deep in the system, argillically altered rock occurs as pods and envelopes around major veins. Higher in the system, argillization is more pervasive and often cannot be related directly to any specific vein. This pervasive alteration forms a clay cap across much of the ore deposit. Few veins penetrate the clay cap.

Campbell Mountain tuff, the parent rock for most argillic alteration in the Amethyst system, displays a complete gradation from non-argillized to completely argillized tuff. As the intensity of argillization increases, various rock components are altered to I/S one after another. Incipient or minor argillization results in pumice fragments altered to I/S but the matrix generally remains unaffected. As the intensity of argillization increases, lithic fragments then matrix are, in turn, altered to I/S. Finally, with very intense

Fig. 5A-E. X-ray diffraction patterns *(left)* and corresponding calculated X-ray profiles *(right)* for several I/S from the Amethyst vein system.

- A $R = 1$ ordered, 75% illite;
- B R = 2 ordered, 80% illite;
- $C R = 3$ ordered, 85% illite;
- **D** R \geq 3 ordered, 90% illite;
- E R \geq 3 ordered, 97% illite.

All experimentally obtained XRD patterns were made from oriented, glycol-solvated, ≤ 1 µm or ≤ 2 µm size fraction of Bachelor sediment (A, B and C) or Campbell Mountain tuff (D and E). Calculated profiles A, C and D were made using the random powder Lorentz factor and \bm{B} and \bm{E} were made using the single crystal Lorentz factor. Braces denote low-angle reflections discussed in the text. *CH,* chlorite; S, discrete smectite; all other reflections are I/S ; CuK_a radiation

Fig. 6. Histogram of illite/smectite composition in samples from the Amethyst vein system. Numbers indicate the Reichweite; crosshatch indicates $R \ge 3$

alteration, sanidine phenocrysts are altered to 1/S. Extremely argillized Campbell Mountain tuff shows no vestiges of its original volcanic texture and is an incompetent, massive material consisting solely of illite/smectite $+$ quartz \pm pyrite. Even quartz is altered in some extremely argillized rocks that now consist of 90-100% I/S.

Representative XRD patterns of glycol-solvated I/S from rocks of the Amethyst vein system are shown in Fig. 5 along with calculated profiles. Each experimentally obtained XRD pattern on the left hand side of Fig. 5 exhibits an irrational series of 001 reflections and relatively high intensity at low angles $($5°2\theta$). Both these features are$ indicative of mixed-layer minerals. Comparing the XRD patterns in Figure 5 with published patterns, such as those in Reynolds (1980), suggests that the mixed-layer mineral is ordered I/S. The exact range of order, or Reichweite, and the proportion of illite in I/S are obtained by calculating a series of profiles for which R and percent illite are adjusted until the calculated and experimental patterns agree.

The XRD patterns in Fig. 5 illustrate the ranges of I/S composition and Reichweite in the Amethyst system. Illite/ smectites ranging from about 75% to about 97% illite and from $R=1$ to $R \ge 3$ are found. The peak positions and intensities on the XRD patterns of I/S with $R = 1$, $R = 2$, and $R = 3$ structures closely resemble the calculated profiles (Fig. 5). The pattern labeled $R \geq 3$ ordered, 90% illite (Fig. 5D) cannot be modeled by calculation as accurately as patterns of I/S with smaller R. The two low-angle reflections (indicated by braces) are closer together on the real pattern than they are on the calculated one. The computer calculated profiles for $R = 1$, 2 and 3 structures show that the two, low-angle reflections become closer together as the Reichweite increases. Although the computer program used is not able to accurately model structures with $R > 3$, extrapolation of the convergence of the low-angle reflections suggests that the range of ordering for very low expandable I/S from Creede is greater than $R = 3$. This, however, is not known for certain and so very low expandable I/S is labeled $R \geq 3$.

Several studies have demonstrated a trend toward longer range order with increasing illite in I/S (Perry and Hower 1970; Reynolds and Hower 1970; Hoffman and

Fig. 7. I/S composition versus distance from the Amethyst vein *(top three traverses)* and distance down hole *(bottom two traverses).* Note the change in direction of the abcissa for hole CDS-20

Hower 1979; Eslinger and Savin 1973). I/S from Creede follow the same trend. Figure 6 shows a histogram of I/S composition and corresponding Reichweite. In general, I/S with more than 85% illite has $R \ge 3$ order. I/S with 82 to 85% illite has $R = 3$ or $R = 2$ with tendencies to $R = 3$ order (i.e. $P(I,I) < P(SII,I) < 1$; see Reynolds (1980) for a statistical description of partial order). The single sample with 80% illite has the only perfect $R = 2$ structure found. All I/S with less than 80% illite in I/S have $R=1$ with tendencies to $R = 2$ or perfect $R = 1$ order.

Illite/smectites from Creede show systematic variation in Reichweite and composition with respect to distance from the Amethyst vein. The composition of I/S from drill holes versus distance from the vein or distance down hole is shown in Fig. 7. I/S from each hole except CH-28 show essentially the same trend. There is an increase in the percent illite in I/S as the Amethyst vein is approached. I/S closest to the vein contains about 95% illite and is $R \ge 3$ ordered. I/S farthest from the vein contains 75% illite and is $R=1$ ordered. In contrast to all other holes I/S from hole CH-28, which is subparallel to the Amethyst vein (Fig. 3), shows almost no variation and is $R \geq 3$ with about 90% illite throughout the entire hole.

Fig. 8. Volume percent clay versus I/S composition for argillized rock in the Amethyst vein system

Although the composition and structure of I/S varies systematically with distance from the Amethyst vein, the amount of I/S does not. For example, samples from hole CH-28 have an I/S content ranging from about 15 to about 95 vol.% of the rock but the composition of the I/S remains constant at about 90% illite (Fig. 7). A plot of volume percent clay (I/S) versus percent illite in I/S for all samples is shown in Fig. 8. It is apparent that there is no strong correlation between the two variables although most rocks containing less than about 80 to 85% illite in I/S also contain more than about 45% clay. Also, most samples with less than about 80% illite are from Bachelor sediments. The amount of I/S to form in an argillized rock is a function of the extent of alteration; that is, no alteration results in no clay and extensive argillization results in abundant

clay. The extent of argiIlization is probably a function of several variables including temperature, water/rock ratio, solution chemistry, and the duration of alteration. The lack of a strong relationship between the amount and the composition of I/S indicates that whatever controlled the amount of I/S to form, some other factor determined the I/S composition.

Discussion

Figure 9 summarizes the temperature dependence of I/S composition and structure derived from results of four studies of occurrence of active I/S formation. Data are from geothermal systems at Wairakei (Steiner 1968), Broadlands (Eslinger and Savin 1973), and the Salton Sea (McDowell and Elders 1980) and from shales (Hoffman and Hower 1979). Temperatures for all three geothermal areas were measured in drill holes. Temperatures associated with I/S composition and structure for shale diagenesis were summarized by Hoffman and Hower (1979), mainly from studies of U.S. Gulf Coast Tertiary sediments. Short, dashed lines on Fig. 9 separate temperature ranges over which muscovite, illite, and I/S with different Reichweite exist in the different areas.

Generalizations concerning I/S composition-temperature relationships can be made from the data on Figure 9. At temperatures less than about 50° C, smectite is generally found. Between 50 \degree C and about 120 \degree C randomly interstratified $(R = 0)$ I/S exists and, as the temperature increases, the percent illite in I/S increases from 0 to about 65%. From 120° C to about 180° C, I/S is $R=1$ ordered and the percent illite continues to increase from about 65% to about 80 to 85% with increasing temperature. Steiner (1968) shows an XRD pattern of an $R=2$ I/S with 78 to 80% illite sampled from a depth at Wairakei corresponding to a temperature of about 190 \degree C. R = 2 I/S is not as common in nature as either $R=1$ or $R\geq 3$ I/S. Generally a transformation from R = 1 to R \geq 3 is noted near 180° C. From about 180° C to about 250° C, $R \ge 3$ I/S exists and again as the temperature increases, the percent illite in-

177

Fig. 10. I/S composition versus temperature. Graph is compiled from data given by Steiner (1968), Eslinger and Savin (1973) and McDowell and Elders (1980). Dots are median temperatures and bars are temperature ranges

Fig. 11. Generalized cross-section through the Amethyst vein system with superimposed, estimated isotherms depicting the thermal regime during argillization

creases until all expandable layers are lost at 250° C to 270° C. At the Salton Sea, illite was found below 300 $^{\circ}$ C and muscovite existed above 300° C (McDowell and Elders 1980).

The extent to which the smectite to I/S to illite to muscovite reaction sequence is controlled by kinetics is not clear. Hower et al. (1982) think that increasing percent illite layers in $R = 0$ I/S is kinetically controlled. The situation for more illitic, ordered I/S , however, may be different. The first evidence indicating that ordered I/S might be an equilibrium phase came from Perry and Hower (1970) who found that the composition of randomly interstratified $(R=0)$ I/S changes rapidly with depth (temperature) in Gulf Coast wells, but that $R = 1$ I/S with about 20% smectite persists over a broad temperature range. The persistance of $R = 1$ I/S over a temperature range of about $100-175$ ° C has since been observed by a number of other workers (Hower et al. 1976; Boles and Franks 1979). Even more compelling evidence for the stability of ordered I/S is the observation of McDowell and Elders (1980) who found $R \ge 3$ I/S pseudomorphically replacing detrital muscovite at 230°C to 250° C and recrystallization of ordered I/S to muscovite at temperatures above 300° C. Regardless of possible kinetic controls for ordered I/S, there does appear to be a correlation between temperature and I/S composition.

Figure 10 shows the temperature ranges and median temperatures at which specific I/S compositions exist at the three geothermal areas listed in Fig. 9. Because 75% illitic I/S was not reported from the geothermal areas cited here, the temperature of 100° C for this composition is based on the temperature of occurance of 75% illitic I/S in burial metamorphic sequences (Hower 1981). Although there is an increase in percent illite in I/S with increasing median temperature, some of the ranges overlap considerably. Some of the overlap probably is due to errors associated with reported I/S compositions. Error bars for I/S composition are not known for the data used to construct Fig. 10, but they may be as much as 5% illite based on discussions of the data in the original sources. Some of the I/S compositions given by Eslinger and Savin (1973) and by McDowell and Elders (1980), for example, are reported as composition intervals such as 90-95% illite.

Based on the median temperatures in Fig. 10, thermal gradients are estimated for each of the several drill holes from Creede. The thermal gradients are: CDS-20, 1° C/m; CH-26, 0.4° C/m; CH-29, 0.7° C/m; 19,800 crosscut, 0.5° C/m; and CH-28, 0° C/m. These gradients are for eastwest oriented holes and traverses and probably do not represent maximum gradients because changes in I/S composition suggest a north-south thermal gradient on the order of 0.1 ° C/m over a 150 meter distance (Horton 1983). Insufficient data exist, however, to evaluate fully a north-south gradient. Nevertheless, the gradients calculated for Creede are comparable to those associated with some modern geothermal systems such as Wairakei which has gradients of about 0.7 ° C/m (estimated from data in Steiner 1968) and Matsukawa, Japan with gradients between 0.4° and 0.8° C/m (estimated from data in Nakamura et al. 1970).

A cross section similar to that shown in Fig. 3 is presented in Fig. 11. Using the average temperatures from Fig. 10 and data from Creede I/S, estimated isotherms have been put on the cross section. Although the isotherms are placed on a cross section through the 19,800 crosscut, their positions are based on all data, most of which are superimposed onto the cross section. The eastward bend in the 160° C isotherm is based on the composition of one surface sample ($R \ge 384\%$ illite) collected about 50 meters upslope from the intersection of the 19,800 crosscut and the surface.

The cross section (Fig. 11) represents an east-west section through the thermal regime which is not necessarily parallel to the maximum thermal gradient. Also, the temperature values for the isotherms should be considered approximate since they are based on averages from the modern geothermal systems depicted in Figure 9. It is encouraging to note, however, that the temperature indicated by I/S near the Amethyst vein is very close to the mean temperature of 250° C from fluid inclusion studies in the Amethyst system (Barton et al. 1977).

There are some features of the inferred thermal regime at Creede that are similar to thermal regimes associated with some modern geothermal systems. Isotherms around modern systems are often compressed in the upper portion of the system (Steiner 1968; McDowell and Elders 1980). Although the differences in calculated gradients among some of the cores from Creede are not great, the thermal gradient from hole CDS-20, which penetrates the top of the Amethyst system, is the highest gradient noted. Although temperatures are high, thermal gradients are often low in the central part of many modern geothermal systems (Steiner 1968; McDowell and Elders 1980). Core CH-28, drilled near the center of the deposit and subparallel to the Amethyst vein, contains a nearly constant I/S composition indicating that all the I/S formed at or near the same temperature and that no large thermal gradient existed in this part of the system during argillization. In summary, the mineralogy of the I/S at Creede and the inferred thermal regime are similar to what is found associated with some modern geothermal systems.

Two additional points are illustrated by Figs. 3, 7 and 10. First, holes CH-26, CH-29, CDS-20 and the 19,800 crosscut all cross the Campbell Mountain tuff-Bachelor sediment contact and, except for one sample adjacent to the contact in the 19,800 crosscut, the composition and Reichweite of the I/S smoothly change across the contact. Although the original composition of the Bachelor sediment is unknown and may have been similar to that of Campbell Mountain tuff, the clays do not appear to reflect original differences, if any, in the composition and texture of the parent rock. Similar situations have been noted at Wairakei (Steiner 1968) and other places where I/S composition changes smoothly with depth regardless of lithologic changes.

The hanging wall of the Amethyst vein is highly fractured and riddled with veins and faults which are believed to have been the conduits for the hydrothermal fluids. Yet, the I/S composition and Reichweite show fairly smooth trends with distance from the Amethyst vein and these trends do not appear to be influenced by hanging wall fractures. This suggests that the temperatures of the wall rock and the fluids in the hanging wall structures were about the same. Apparently, the hydrothermal system had reached a steady-state thermal profile by the time argillic alteration occurred and that the fluids which formed the Amethyst vein were the major, local heat source.

The dissolution of K-feldspar, formation of I/S (instead of mica), the relative decrease of $SiO₂$ and most alkali and alkaline earth elements (Horton 1983), and the addition of H^+ to the rock in the form of OH⁻ in the I/S all indicate that argillization at Creede can be characterized as hydrogen metasomatism as described by Hemley and Jones (1964) . Hemley and Jones state that the driving force for $H⁺$ metasomatism is the activity and continued supply of $H⁺$ and that the hydrolysis of K-feldspar and precipitation of K-mica (or, in this case, I/S) is controlled by temperature and K^+/H^+ in solution.

Figure 8 shows that there is no strong correlation at Creede between the amount of I/S in altered rock and the I/S composition. If I/S composition is a strong function of temperature, as previously discussed, another factor must be dominant in controlling the amount of clay formed. Experiments have shown that I/S composition is a function of solution chemistry (Eberl 1978; Eberl and Hower, 1971; Eberl et al. 1978). In particular, the absence of potassium retards the smectite to illite transformation. The availability of potassium, however, does not appear to be a limiting factor at Creede because many samples with less than 80% illite in I/S contain K-feldspar. It may be that the amount of clay to form in rocks at Creede depended on the length of time that the clay-forming reaction occurred, and this depended on a supply of H⁺ and the maintenance of K⁺/ H^+ and temperature values conducive to the I/S-forming reaction. The specific temperature at which the reaction took place is recorded by the I/S composition.

Summary and conclusion

Illite/smectite from the Amethyst vein system is compositionally and structurally zoned with respect to distance from the Amethyst vein. By applying an empirical temperature-I/S composition relationship derived from other geologic environments to the Creede system, inferences about the thermal regime that existed during argillization can be made. The resulting temperature gradient resembles those of modern geothermal systems.

Hydrothermal argillization is a common phenomenon associated with many types of ore deposits throughout the world and illite/smectite is known to be associated with some of these. As knowledge of recent advances in clay petrology becomes more widespread, I/S will probably be recognized and studied in many more deposits. I/S most certainly has potential as an indicator of thermal gradients and, thus, may be an important tool for mineral exploration and for the development of known deposits.

Acknowledgements. I thank the staffs of Chevron Resources Company and Minerals Engineering Company for allowing access to the property, drill cores and information concerning the deposit. Phil Bethke and Pamela Wetlaufer of the U.S.G.S. provided valuable discussion, analytical data, rock samples and laboratory facilities. This study is part of a Ph. D. dissertation done under the direction of the late Dr. John Hower, and the entire study greatly benefited from his guidence and expertise. I thank Bill Crowley for drafting the figures, Joyce Higgins for typing portions of the manuscript and Phil Bethke, Pamela Wetlaufer, David Pevear, Stephen Altaner and M.H. Reed for reviewing and improving the manuscript.

References

- Barton PB Jr, Bethke PM, Roedder E (1977) Environment of ore deposition in the Creede mining district, San Juan Mountains, Colorado: Part III. Progress toward interpretation of the chemistry of the ore-forming fluid for the OH vein. Econ Geol $72:1 - 24$
- Bethke PM, Rye RO (1979) Environment of ore deposition in the Creede mining district, San Juan Mountains, Colorado: Part IV. Source of fluids from oxygen, hydrogen, and carbon isotope studies. Econ Geol 74:1832-1851
- Bethke PM, Barton PB Jr, Lanphere MA, Steven T (1976) Environment of ore deposition in the Greede mining district, San Juan Mountains, Colorado: Part II. Age of mineralization. Econ Geol 71:106-111
- Bethke PM, Barton PB Jr, Rye RO (1973) Hydrogen, oxygen and

sulfur isotopic compositions of ore fluids in the Creede district, Mineral County, Colorado [abs]. Econ Geol 68:1205

- Boles JR, Franks SG (1979) Clay diagenesis in Wilcox sandstones of southwest Texas: Implications of smectite diagenesis on sandstone cementation. J Sed Petrol 49 : 55-70
- Eberl D (1978) Reaction of montmorillonite to mixed-layer clay: The effect of interlayer alkali and alkali earth cations. Geochim Cosmochim Acta 42:1-7
- Eberl D, Hower J (1977) The hydrothermal transformation of sodium and potassium smectite into mixed-layer clay. Clays Clay Miner 25:215-227
- Eberl D, Whitney G, Koury (1978) Hydrothermal reactivity of smectites. Am Mineral 63:401-409
- Eslinger EV, Savin S (1973) Mineralogy and oxygen isotope geochemistry of hydrothermally altered rocks of the Ohake-Broadlands, New Zealand geothermal area. Am J Sci 273:240-267
- Foley NK, Bethke PM, Rye RO (1982) A re-interpretation of δD $H₂O$ values of inclusion fluids in quartz from shallow ore bodies [abs]. Geol Soc Am Abstr with Progr 13(7):489
- Harvey RD, Vitaliano CJ (1964) Wall-rock alteration in the Goldfield district, Nevada. J Geol 72 : 564-579
- Hemley JJ, Jones WR (1964) Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism. Econ Geol 59:538-569
- Henley RW, Ellis AJ (1983) Geothermal systems ancient and modern: A geochemical review. Earth Sci Review 19:1-50
- Hoffman J (1976) Regional metamorphism and K-Ar dating of clay minerals in Cretaceous sediments of the disturbed belt of Montana. Ph D thesis, Case Western Reserve Univ, Cleveland
- Hoffman J, Hower J (1979) Clay mineral assemblages as low grade metamorphic geothermometers: Application to the thrust faulted disturbed belt of Montana, USA In: Scholle PA, Schluger PR (eds) Aspects of Diagenesis. SEPM Spec Publ $26:55 - 79$
- Horton DG (1983) Argillic alteration associated with the Amethyst vein system, Creede mining district, Colorado. Ph D thesis, Univ of Illinois, Urbana
- Hower J (1981) X-ray diffraction of mixed-layer clay minerals. In: Longstaffe FJ (ed) Clays and the Resource Geologist. Mineral Assoc Canada, Short Course Handbook 7:39-59
- Hower J, Eslinger E, Hower ME, Perry EA (1976) Mechanism of burial metamorphism of sediment; 1. Mineralogical and chemical evidence. Geol Soc Am Bull 87:725-737
- Hower J, Altaner S, Aronson JL, Whitney CG (1982) Kinetics and compositional controls of the smectite to illite reaction. Geol Soc Am, Abst with Progr $14(7)$: 519
- Inoue A, Utada M (1983) Further investigations of a conversion series of dioctahedral mica/smectites in the Shinzan hydrothermal alteration area, Northeast Japan. Clays Clay Miner 31:401-412
- Lipman PW, Steven TA, Mehnert HH (1970) Volcanic history of the San Juan Mountains, Colorado, as indicated by Potassium - Argon dating. Geol Soc Am Bull 81:2329-2352
- MeDowell SD, Elders WA (1980) Authigenic layer silicate minerals in borehole Elmore 1, Salton Sea geothermal field, California, USA. Contrib Mineral Petrol 74:293-310
- Nakamura H, Sumi K, Katagiri K, Iwata T (1970) The geological environment of Matsukawa geothermal area, Japan. Geothermics, Spec Issue 2:221-231
- Perry E, Hower J (1970) Burial diagenesis in Gulf Coast pelitic sediments. Clays Clay Miner 18:165-178
- Ratté JC, Steven TS (1967) Ash flows and related volcanic rocks associated with the Creede caldera, San Juan Mountains, Colorado. US Geol Surv Prof Pap 524-H:1-58
- Reynolds RC (1980) Interstratified clay minerals. In: Brindley GW, Brown G (eds) Crystal structures of ciay minerals and their X-ray identification. Mineral Soc of London, Monograph 5 : 249-303
- Reynolds RC, Hower J (1970) The nature of interlayering in mixedlayer illite-montmorillonite. Clays Clay Miner 18 : 25-36
- Roedder E (1962) Studies of fluid inclusions I: Low temperature application of dual-purpose freezing and heating stage. Econ Geol 57:1045-1061
- Roedder E (1963) Studies of fluid inclusions II: Freezing data and their interpretation. Econ Geol 58:167-211
- Roedder E (1965) Evidence from fluid inclusions as to the nature of the ore-forming fluids. Symposium on problems of postmagmatic ore deposition, Prague 1963, Geol Survey Czechoslovakia 2: 375-384
- Roedder E (1974) Changes in ore fluid with time, from fluid inclusion studies at Creede, Colorado. 4th IAGOD Symposium, Varna 2:179-185
- Schultz LG (1964) Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. US Geol Surv Prof Pap 391-C:CI-C31
- Shirozu H (1974) Clay minerals in altered wall rocks of the Kuroko-type deposits. Mining Geol, Spec Issue 6:303-310
- Steiner A (1968) Clay minerals in hydrothermally altered rocks at Wairakei, New Zealand. Clays Clay Miner 16:193-213
- Steven TA, Eaton GP (1975) Environment of ore deposition in the Creede mining district, San Juan Mountains, Colorado: I. Geologic, hydrologic and geophysical setting. Econ Geol 70:1023-1037
- Steven TA, Ratté JC (1965) Geology and structural control of ore deposition in the Creede district. San Juan Mountains, Colorado. US Geol Surv Prof Pap 487 : 1-90
- Sumi D (1969) Zonal distribution of clay minerals in the Matsukawa geothermal area, Japan. Proc Int Clay Conf, Japan, 501-512
- Tooker EW (1963) Altered wall rocks in the central part of the Front Range mineral belt, Gilpin and Clear Creek Counties, Colorado. US Geol Surv Prof Pap 439:1-102
- Wetlaufer PH (1977) Geochemistry and mineralogy of the carbonates of the Creede mining district, Colorado. US Geol Surv Open-File Rept 77-706 : 1-134
- Wetlaufer PW, Bethke PM, Barton PB Jr, Rye RO (1979) The Creede Ag-Pb-Zn-Cu-Au district, central San Juan Mountains, Colorado: A fossil geothermal system. Proc 5th IAGOD Symposium, Snowbird, Utah, 1978, 159-164

Received October 23, 1984/Accepted April 30, 1985