# Variations in $\delta^{18}$ O values, water/rock ratios, and water flux in the Rico paleothermal anomaly, Colorado

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Abstract—The Rico paleothermal anomaly, southwestern Colorado, records the effects of a large. ore-forming, hydrothermal system which was active at 4 Ma. A porphyry molybdenum deposit lies 1.5 km deep in the center of the system and marks the location of the system's heat source. Effects of the hydrothermal system vary symmetrically around the heat source, including mineral alteration patterns, paleotemperatures, and the degree of partial annealing of fission tracks. Whole-rock oxygen isotope ratios of altered rocks also follow this pattern:  $\delta^{18}$ O values of the widespread, 65 Ma hornblende latite porphyry range from -4.0 to 9.9 per mil. The values decrease smoothly from nearly unaltered values of about +9 in distal areas of the hydrothermal system, to values as low as -4.0 in the deeper central part of the system. The <sup>18</sup>O-depleted values suggest that meteoric groundwater was the dominant reservoir for the hydrothermal fluid which altered the latite. Open-system water/rock ratios are highest (0.54 to 1.10) in the central part of the system overlying the porphyry deposit, where the high ratios mark the location of a convecting hydrothermal plume that was 3 km wide. The water/rock ratios are lower (<0.01 to 0.41) in distal parts of the system. The water/rock ratios can be used to calculate the mass of water which has interacted with the latite: 20 to 45 mol H<sub>2</sub>O per Representative Equivalent Volume (REV = 10 cm-diameter sphere) have exchanged oxygen with the latite in the plume, whereas  $<10 \text{ mol } H_2O/REV$  have exchanged with the distal latite. Water flux through the latite ranged from  $0.5 \times 10^{-9}$  to  $5.3 \times 10^{-9}$  mol/cm<sup>2</sup> · sec for hydrothermal durations of 100,000 to 500,000 years. Hydrothermal changes in the mass of major elements in the latite can be balanced with the mass of fluid to determine maximum changes in fluid concentrations due to water-rock interaction. Na+ is added to the fluid by the latite throughout the hydrothermal system, whereas the latite nearly always removes Mg++ and K+ from the fluid. Ca++ is added to the fluid unless the fugacity of carbon dioxide is high enough to produce calcite.

## **INTRODUCTION**

OXYGEN ISOTOPE RATIOS of hydrothermally altered rocks are very useful measures of the mass of water which has interacted with the rocks (e.g., TAYLOR, 1971, 1979; GREGORY and TAYLOR, 1981; CRISS and TAYLOR, 1983; LARSON and TAYLOR, 1986). Mass balance of oxygen between a hydrothermal fluid and an altered rock can be used to calculate water/rock ratios if the temperature of interaction, the initial  $\delta^{18}$ O value of the rock, and the initial  $\delta^{18}$ O value of the fluid are known (TAYLOR, 1979). These techniques have been applied to continental hydrothermal systems, where they have revealed that  $\delta^{18}$ O values of altered igneous rocks are lowered, vary regularly around thermal centers, and can be contoured (TAYLOR, 1971; CRISS and TAYLOR, 1983; LARSON and TAYLOR, 1986). The depleted  $\delta^{18}$ O values of the altered rocks reflect the effects of high-temperature interaction between the rocks and meteoric-hydrothermal fluids integrated over the life of the hydrothermal system.

A young, 4 Ma, ore-forming hydrothermal system has altered rocks in a broad area in the Rico dome, Colorado (NAESER *et al.*, 1980; LARSON, 1987; LARSON *et al.*, 1991b). The system's thermal effects include partial annealing of fission tracks in older, 65 Ma intermediate intrusive rocks: fission

tracks in zircon and apatite exhibit greater degrees of partial annealing nearer the center of the system (NAESER *et al.*, 1980). These data show that temperatures near the center were higher for longer periods of time than in peripheral regions. Therefore, the Rico paleothermal anomaly (PTA) (CUN-NINGHAM *et al.*, 1987) is an ideal location in which to apply oxygen isotope analyses to measure the magnitude of water/rock interaction, and to use these data to monitor the changes in fluid composition which result from this interaction.

This paper presents the results of whole-rock oxygen isotope measurements of the 65 Ma hornblende latite porphyry, an intrusive igneous rock that occurs as dikes and thick sills throughout the Rico dome (PRATT et al., 1969; MCKNIGHT, 1974; PRATT, 1976). The results define a typical concentric pattern of depleted <sup>18</sup>O/<sup>16</sup>O ratios which center on the deep, 4 Ma Silver Creek porphyry molybdenum deposit. Intrusive rocks associated with this deposit were the heat source which drove convective meteoric-hydrothermal circulation in the PTA. Other hydrothermal effects have been measured in the latite, and their variations are also distributed zonally about this heat source, including mineral alteration assemblages, alteration mineral structures and compositions, bulk rock density changes, and major element exchange between the latite and the

hydrothermal fluid (LARSON *et al.*, 1991a,b). Here, we use the oxygen isotope ratios in the altered latite to calculate water/rock ratios, from which we constrain the minimum mass of fluid that has interacted with each of the samples. These data are combined with fluid/rock element exchange to calculate the change in the fluid concentrations of major dissolved cations during the alteration event. Both the fluid flux and change in fluid composition vary gradationally with respect to the central heat source in patterns that are similar to those of the other hydrothermal alteration effects.

## **GEOLOGIC SETTING**

The 12 by 12 km Rico dome (Fig. 1) comprises a thick sequence of Paleozoic and Mesozoic sedimentary rocks that have been uplifted more than 1 km (PRATT *et al.*, 1969; MCKNIGHT, 1974; PRATT, 1976). The dome has been eroded to a group of high peaks just off the western

edge of the San Juan Volcanic Province, Colorado. The Dolores River flows from north to south and dissects the central part of the dome. This erosion provides more than a kilometer of vertical relief and access to deep structural levels. Deep diamond drill core from the central part of the dome provides an additional 1.5 km of vertical exposure. East-west and northwest-southeast trending fault zones are prevalent and intersect in the east-central part of the dome. These structures bound a central horst of Precambrian greenstone and quartzite.

Igneous rocks have been emplaced during two episodes. (1) Two contemporaneous and cogenetic intrusive rocks, the hornblende latite porphyry and an augite monzonite, were intruded about 65 Ma (MCKNIGHT, 1974; NAESER *et al.*, 1980). The latite is found as dikes and thick sills throughout the district, whereas the monzonite forms a circular 2.5 km-diameter stock in the west central part of the dome. (2) A series of basalts, andesites, rhyolites, and lamprophyres is found as dikes throughout the district. One small rhyolitic stock is exposed at Calico Peak near the western end of the dome. Radiometric dating of several of these rocks yields ages between 3.4 and 4.5 Ma, contemporaneous with hydro-thermal activity in the district (NAESER *et al.*, 1980).

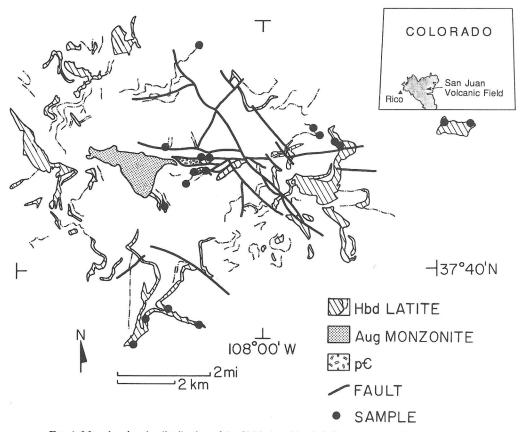


FIG. 1. Map showing the distribution of the 65 Ma hornblende latite porphyry and augite monzonite in the Rico dome, Colorado (modified from PRATT *et al.*, 1969 and PRATT, 1976). The horst of Precambrian greenstone and quartzite is also shown. The annular distributions of thick exposures of latite represent sills dipping outward and away from the center of the dome. The Silver Creek porphyry molybdenum deposit lies 1.5 km below the prominent zone of intersecting faults in the east-central part of the dome. Locations of samples used in this study are shown by heavy dots. Detailed sample locations are given in LARSON *et al.* (1991b).

Hydrothermal mineralization occurs in a diverse array of deposits (RANSOME, 1901; MCKNIGHT, 1974; BARRETT et al., 1985; LARSON, 1987). A 1.5 km-deep porphyry molybdenum deposite has been recently discovered in the central part of the dome (Fig. 1), and radiometric dating of alteration minerals has shown that intrusive activity associated with the molybdenum deposit is contemporaneous with alteration and mineralization throughout the district (NAESER et al., 1980). Shallower replacement deposits in calcareous sedimentary rocks and vein mineralization were exposed at the surface and were the source of historic metal production in the district (more than 80,000 tons each of Pb and Zn, more than 5000 tons of Cu, 14,513,288 ounces of Ag, and 83,045 ounces of Au from 1879 through 1968; MCKNIGHT, 1974).

The latite initially contained about 35 volume percent plagioclase phenocrysts and 5 to 10 volume percent hornblende phenocrysts set in a fine grained matrix of orthoclase, quartz, and plagioclase. Apatite and zircon are ubiguitous accessories. Now, all exposures of the latite exhibit some effects of interaction with a hydrothermal fluid. Hydrothermal alteration in the latite comprises a distal propylitic facies and a proximal facies which contains a quartzillite-calcite assemblage and a chlorite-epidote assemblage. Detailed descriptions of the latite and its alteration products are given in LARSON et al. (1991b). The propylitic assemblage is defined by two reactions: (1) reaction of primary plagioclase phenocrysts (An<sub>30-40</sub>) to illite and nearly pure albite  $(An_{<2})$ , and (2) reaction of hornblende to chlorite and hematite with or without calcite, illite, and epidote. The quartz-illite-calcite assemblage also exhibits the first propylitic reaction, but the hornblende has reacted to quartz and illite. The chlorite-epidote assemblage consists of pervasive replacement of primary phases by chlorite, epidote, and quartz.

#### **METHODS**

Oxygen was extracted from latite whole-rock samples and converted to  $CO_2$  at Washington State University using standard fluorination techniques (CLAYTON and MAYEDA, 1963; BORTHWICK and HARMON, 1982). The samples used for the extractions were aliquots of 7 to 10 grams of finely powdered and chemically untreated sample. CIF<sub>3</sub> was used as an oxidizing agent. Precision in the laboratory is better than 0.2 per mil, and NBS-28 has a  $\delta^{18}$ O value of +9.6 on the laboratory's scale.

Major-element chemical gains and losses in the latite samples were calculated using whole-rock X-ray fluorescence measurements of major-element concentrations and assuming immobility of TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> during the alteration process. Petrographic examination of the samples and major-element trends from unaltered to highly altered samples validate this assumption. Sample locations, the methods of calculating gains and losses, and the majorelement data are presented in LARSON *et al.* (1991b). It is convenient to present the chemical concentrations normalized to a representative equivalent volume (REV) of rock (NORTON, 1984), which is chosen to be a 10 cmdiameter sphere (523.60 cm<sup>3</sup>). Bulk density measurements of the samples used for this normalization are tabulated in LARSON *et al.* (1991b).

### $\delta^{18}$ O VARIATIONS IN THE RICO PALEOTHERMAL ANOMALY

## $\delta^{18}O$ variations and water/rock ratios

Whole-rock oxygen isotope ratios of the hornblende latite prophyry range from -4.0 to 9.9 per

Table 1. Oxygen isotope ratios, water/rock ratios, and the mass of fluid which has exchanged oxygen per Representative Equivalent Volume (REV) of rock

Sample	δ <sup>18</sup> Ο	(W/R) <sub>OPEN</sub>	М	
RI-40	-0.7	0.66	26.59	
<b>RI-41</b>	9.9	_		
RI-42	9.8			
<b>RI-43</b>	-3.6	1.10	43.97	
<b>RI-45</b>	-1.8	0.87	34.78	
<b>RI-46</b>	2.6	0.41	16.35	
RI-51	0.8	0.54	21.80	
RI-52	-0.2	0.63	25.12	
RI-53	-4.0	1.09	43.64	
RI-54	8.9	0.01	0.41	
RI-55	-1.7	0.85	34.22	
RI-56	-0.6	0.72	28.75	
<b>RI-60</b>	8.7	0.02	0.70	
RI-61	9.0	0.00	0.05	
RI-62	8.9	0.01	0.27	
HP-1	4.0	0.39	15.68	
HP-2	9.6		_	
HP-6	7.0	0.13	5.39	
HP-7	6.1	0.20	8.07	
HP-8	6.3	0.17	7.01	
HP-9	6.9	0.24	9.53	
HP-10	7.6	0.13	5.34	

Isotope ratios are per mil relative to S.M.O.W. Water/rock ratios are from Eq. (1). *M* is the moles of water/REV.

REV = 523.60 cubic centimeters.

mil (Table 1). The  $\delta^{18}$ O values vary gradationally both vertically and horizontally, with lower values deeper and closer to the system's center (Fig. 2). It is difficult to determine the initial value for the latite because the phenocryst assemblage typically does not contain quartz, which could be measured to

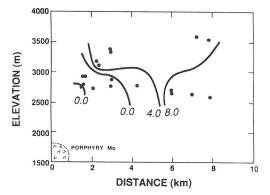


FIG. 2. Radial cross section of contours of latite oxygen isotope ratios in the Rico dome. The sample locations are plotted as a function of elevation and distance from a vertical pole through the center of the porphyry molybdenum deposit, which marks the location of the heat source for the Rico hydrothermal system. The latite grades to lower  $\delta^{18}$ O values deeper and closer to the center of the system.

estimate the initial  $\delta^{18}$ O value (CRISS and TAYLOR, 1983), and all of the samples exhibit some effects of interaction with the hydrothermal fluid. The least altered samples yield  $\delta^{18}$ O values near +9.0 and this is probably near the igneous value. The depleted  $\delta^{18}$ O values suggest that meteoric water was the dominant reservoir for the hydrothermal fluids which altered the latite. Note, however, that a magmatic water component has been identified in the fluid which produced the deep, central prophyry molybdenum deposit (LARSON, 1987). This component was not detected in the fluids from which quartz precipitated in the shallower veins, even though some of these veins are 1.5 km directly above the porphyry deposit (LARSON, 1987).

Water/rock ratios also vary gradationally and were highest in the central part of the dome (Fig. 3). Open-system material-balance water/rock ratios  $(W/R_{OPEN})$  have been calculated on the basis of molar oxygen for the latite using the equation of TAYLOR (1979):

$$W/R_{OPEN} = \ln \left[ ({}^{i} \delta^{18} O_{W} + \Delta + {}^{i} \delta^{18} O_{R}) / ({}^{i} \delta^{18} O_{W} - ({}^{f} \delta^{18} O_{R} - \Delta)) \right]$$
(1)

where the superscripts i and f refer to the initial and final isotope ratios, respectively, of the water (subscript W) and rock (subscript R), and  $\Delta$  is the waterrock oxygen isotope fractionation. W/R<sub>OPEN</sub> curves have been calculated for the latite for temperatures of 100, 200, 300, and 400°C using an initial rock  $\delta^{18}$ O value of +9.0 and an initial meteoric water value of -16.0 (Fig. 4). Fluids from which quartz precipitated in the Rico epithermal veins define a typical <sup>18</sup>O-shifted trajectory (LARSON, 1987) which is characteristic of meteoric-hydrothermal fluids

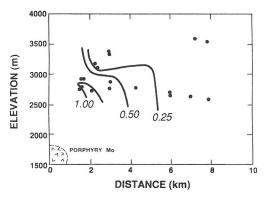


FIG. 3. Open-system water/rock ratio contours for the latite in the Rico dome. See caption for Fig. 2 for explanation of the composite cross section. The high values of W/R above the location of the system's heat source, the porphyry molybdenum deposit, mark the location of a convective hydrothermal plume.

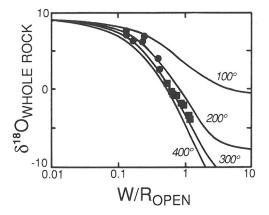


FIG. 4. Open-system water/rock ratio curves (log scale) for the hornblende latite porphyry.  $\delta^{18}$ O values are per mil relative to S.M.O.W. Open-system water-rock behavior is demonstrated by the ability of the fluid to transport a significant mass of components into and out of the latite. The initial water  $\delta^{18}$ O value was -16.0. The feldspar (An<sub>30</sub>) water fractionation of O'NEIL and TAYLOR (1967) was used to approximate the rock-water fractionation. The positions of the latite samples are also shown. These data are coded as distal (circles) or proximal (squares) to the porphyry molybdenum deposit, and this designation is based on the sample's alteration assemblage and position within the paleothermal anomaly (see LARSON *et al.*, 1991b).

(CRAIG, 1963). The water-rock isotope fractionation is assumed to be approximately equal to that of plagioclase (An<sub>30</sub>)-water. This assumption is valid because the latite contained about 40 volume percent oligoclase-andesine prior to alteration (LARSON *et al.*, 1991b). The feldspar-water fractionation factors of O'NEIL and TAYLOR (1967) were used in these calculations.

W/ROPEN ratios have been calculated for the individual samples (Table 1) and are plotted in Fig. 4. The ratios are calculated for the samples using Eqn. (1), where initial rock and water  $\delta^{18}$ O values are identical to those used to construct the theoretical curves, final rock  $\delta^{18}$ O values are the measured values tabulated in Table 1, and water-rock oxygen isotope fractionation is again assumed to be approximately that of plagioclase  $(An_{30})$ -water. The temperature of interaction for each sample was calculated using the empirical chlorite tetrahedral Al (Al<sup>IV,CHL</sup>) geothermometer developed by CATH-ELINEAU (1988) (chlorite compositions and structural formulae are presented in LARSON et al., 1991b). Al<sup>IV,CHL</sup> has been found to be a useful parameter at Rico because it varies gradationally with respect to vertical and horizontal distance from the PTA's heat source, and chlorite is nearly ubiquitous in the samples (LARSON et al., 1991b). The water/ rock data show that water-rock oxygen isotope interaction in the latite can be satisfactorily estimated by open-system exchange between a meteoric-hydrothermal fluid and the latite at about 300°C for proximal alteration samples and at 100 to 300°C for the distal alteration samples. Proximal samples also exhibit higher water/rock ratios (0.54 to 1.10) than the distal samples (<0.01 to 0.41).

Thus, the latite oxygen isotope data from Rico exhibit characteristics that are similar to other meteoric-hydrothermal systems. The latite becomes progressively depleted in <sup>18</sup>O both vertically and horizontally closer to the PTA's heat source (e.g., similar depletion patterns have been found in the Miocene Lake City caldera, Colorado, hydrothermal system; LARSON and TAYLOR, 1986). Water/ rock ratios at Rico are variable and range up to between 1 and 2. These data represent water-rock isotope exchange integrated over the life of the hydrothermal system. The highest ratios are found in the central part of the PTA, where temperatures were also higher. Water/rock ratios of this magnitude appear to be typical of other meteoric-hydrothermal systems (TAYLOR, 1979).

## Water flux

The water/rock ratios calculated from the oxygen isotope data provide a minimum estimate of the mass of fluid which has flowed through and interacted with the rocks. It is therefore convenient to normalize the latite samples' water/rock ratios to the mass of water that has exchanged oxygen with an REV of rock. Oxygen isotope water/rock ratios (W/R<sub>OPEN</sub>) calculated using Eqn. (1) are molar ratios of oxygen in the water to that in the rock. These are converted to moles of water which have exchanged oxygen with an REV (M, in units of mole H<sub>2</sub>O/REV) by multiplying W/R<sub>OPEN</sub> by the inverse of the number of moles of water oxygen per mole of H<sub>2</sub>O ( $m_{O,WATER}$ ), and by the moles of rock oxygen per REV ( $m_{O,ROCK}$ ). Thus,

$$M = (W/R_{OPEN})(m_{O,WATER})^{-1}(m_{O,ROCK})$$
(2)

where  $m_{O,WATER}$  is 1 and  $m_{O,ROCK}$  is calculated by summing the contribution of oxygen from each major oxide in the least-altered latite samples. The average  $m_{O,ROCK}$  for the six freshest latite samples is 39.77 moles per REV, and this was used for all the calculations of mole H<sub>2</sub>O/REV (Table 1).

Water/rock ratios in units of moles of  $H_2O$  which have exchanged oxygen with an REV of rock vary from 0 to 44.0. The highest ratio of the volume of water to the volume of rock is 1.5, assuming that the fluid had a density of 1 gram per cubic centimeter. Distal propylitized latite has interacted with relatively low masses of fluid, usually less than 10 moles of H<sub>2</sub>O per REV. W/R<sub>OPEN</sub> values for these samples are also low and are generally less than 0.2. In contrast, proximal altered latite has exchanged oxygen with large masses of water, typically more than 20 moles of  $H_2O$  per REV, and  $W/R_{OPEN}$  values for these samples are all greater than 0.4. The area of proximal alteration in the Rico dome lies directly over the PTA's heat source, the porphyry molybdenum deposit, and exhibits water/rock ratios which are an order of magnitude greater than in the distal areas. Thus, these data support the conclusion of LARSON et al. (1991b) that the proximal area marks the location of an upwelling convectively driven hydrothermal plume which was 3 km wide and whose path is now exposed for over 2 km vertically.

The upward flux of water through each REV cube (8.06 cm on a side) in the proximal part of this 2 km long plume is:

$$f_{\rm WATER} = 24,814(M)(a_{\rm REV})^{-1}(t)^{-1}$$
 (3)

where *M* is from Eqn. (2) (in mole H<sub>2</sub>O/REV),  $a_{REV}$ is the cross-sectional area of the REV (64.96 cm<sup>2</sup>), and *t* is the duration of the water/rock interaction (seconds). The duration of the Rico PTA is not known, but theoretical models of continental convective hydrothermal systems suggest that they typically endure for several hundreds of thousands of years (NORTON and KNIGHT, 1977; NORTON, 1982). Water fluxes through the REVs range from  $2.4 \times 10^{-9}$  to  $5.3 \times 10^{-9}$  mol/cm<sup>2</sup> · sec for a duration of 100,000 years, and  $0.5 \times 10^{-9}$  to  $1.1 \times 10^{-9}$ mol/cm<sup>2</sup> · sec for a duration of 500,000 years. Minimum integrated fluid fluxes within the proximal upwelling plume range from 7,600 mol/cm<sup>2</sup> to 16,700 mol/cm<sup>2</sup>.

## Changes in fluid composition

Once the mass of fluid which has interacted with the latite has been determined, the molar changes in the concentrations of major elements in the latite can be used to derive the changes in fluid concentrations. Gains and losses in the latite must be balanced by respective losses and gains in the fluid. The change in fluid composition integrated over the life of the hydrothermal system is then the change in mass of a component in the latite divided by the mass of fluid which has interacted with the latite. It is most convenient to measure these changes relative to a specific volume of rock, the REV. Table 2 shows the changes in molality of the major elements in the fluid during water/rock interaction for several of the samples. The masses of fluid used to calculate the changes in Table 2 are from Table 1, and the changes in major element

Table 2. Changes in the concentration of components in the hydrothermal fluid due to water-rock interaction with the hornblende latite porphyry

	RI-52	RI-55	HP-1	HP-10
SiO <sub>2</sub>	3.35	0.82	-0.58	-0.30
Fe <sup>++</sup>	-1.76	-0.05	0.22	-0.10
Mg <sup>++</sup>	-0.69	-0.19	-0.05	-0.22
Ca <sup>++</sup>	-4.51	-0.73	0.55	-1.00
Na <sup>+</sup>	6.02	2.75	0.59	0.33
$K^+$	1.98	-0.37	-0.15	-0.27

All data are moles per 1000 grams of water.

concentrations for each sample are from LARSON *et al.* (1991b). The data in Table 2 are maximum changes in fluid composition because the water/rock ratios derived from the isotope data are minimum values.

Several components are consistently added to or removed from the fluid during reaction with the latite. Nearly all samples release Na<sup>+</sup> to the fluid, and nearly all remove Mg<sup>++</sup> and K<sup>+</sup> from the fluid. The Na<sup>+</sup> and K<sup>+</sup> changes result from reaction of part of the plagioclase albite component and the reaction of some plagioclase and hornblende to illite, respectively. K<sup>+</sup> is also fixed in hydrothermal potassium feldspar in several of the proximal samples. These data show that the reactions tend to increase the Na<sup>+</sup>/K<sup>+</sup> ratio in the hydrothermal fluid. Mg<sup>++</sup> is typically removed from the fluid because it is concentrated in chlorite, which is a nearly ubiquitous alteration product in the latite.

 $Ca^{++}$  exhibits variable changes and is added to the fluid for some samples and removed for others.  $Ca^{++}$  is a product of both the plagioclase and hornblende reactions in the latite and is fixed in calcite, which is present in only about half of the samples. It appears, therefore, that the  $Ca^{++}$  flux is determined by the fugacity of  $CO_2$  in the hydrothermal fluid, which apparently varies, even though the major calcium-bearing minerals consistently react. The change in fluid concentration for  $SiO_2$  is variable in the proximal area, where it has been removed from the fluid by samples which contain abundant hydrothermal quartz. Distal samples all remove small amounts of silica from the fluid.

Fe<sup>++</sup> exhibits either gains or losses in the fluid which are usually small when compared to those for the other components. Two samples of the proximal chlorite/epidote facies (RI-51 and RI-52, Table 2), however, have removed large quantities of iron from the fluid. These samples have also added significant Al<sup>+++</sup> to the fluid (2.5 molar change per 1000 grams of water for RI-52) and removed significant manganese (-0.4 molar change per 1000 grams of water, RI-52). Aluminum and manganese changes for nearly all the other samples are small. It is interesting to note that these two samples have produced large changes in fluid concentrations for iron and manganese, which can be trivalent cations under conditions of increased oxygen fugacity, and aluminum, which is also trivalent.

Comparison of the compositional changes in the Rico fluid to typical geothermal fluids from active geothermal areas (*e.g.*, ELLIS, 1979) shows that water-rock interaction in the latite produces fluid compositions which trend toward typical geothermal fluids. However, it is not possible to use these techniques to estimate the total fluid concentrations in the Rico system because the initial, pre-interaction, fluid compositions are not known.

## SUMMARY AND CONCLUSIONS

The results of this investigation are summarized here:

- Whole-rock δ<sup>18</sup>O values of the latite range from -4.0 to +9.9. It had an initial δ<sup>18</sup>O value of about +9. The <sup>18</sup>O depletions result from water-rock interaction between the latite and a meteorichydrothermal fluid. The values decrease gradationally, both laterally and vertically, toward the center of the Rico dome. Here, the young Silver Creek porphyry molybdenum deposit, which marks the location of the hydrothermal system's heat source, lies 1.5 km beneath the surface. The gradational variation in oxygen isotope ratios is parallel to other effects of the hydrothermal system, including mineral alteration patterns and paleotemperatures, which become higher toward the center of the system.
- 2) Open-system water/rock ratios in the latite are highest in the central part of the system, where they range from 0.54 to 1.10. The ratios range from <0.01 to 0.41 in the distal parts of the system. LARSON *et al.* (1991b) have suggested that a rising, convective, hydrothermal plume was emplaced above the porphyry deposit as part of the Rico hydrothermal system. The plume is the locus of the proximal alteration facies. The water/rock ratios suggest that, indeed, the area of the plume experienced elevated fluid flow relative to the distal part of the system.
- 3) The minimum mass of water which has exchanged oxygen with the latite ranges from 0 to 44.0 mol H<sub>2</sub>O/REV. Distal samples have typically exchanged with low masses of water (<10 mol H<sub>2</sub>O/REV), whereas proximal samples from within the plume have exchanged with 20 to 45 mol H<sub>2</sub>O/REV. Water flux through the latite

ranges from  $0.5 \times 10^{-9}$  to  $5.3 \times 10^{-9}$  mol/ cm<sup>2</sup> · sec for durations of 100,000 to 500,000 years.

4) Maximum changes in the concentrations of major elements in the hydrothermal fluid can be determined using mass balance between the fluid and the latite. Na<sup>+</sup> is released to the fluid from the latite throughout the hydrothermal system, whereas Mg<sup>++</sup> and K<sup>+</sup> are nearly everywhere removed from the fluid and fixed in the latite. Ca<sup>++</sup> is typically removed from the latite by the fluid unless it can be precipitated in calcite, and calcium's mobility is therefore determined by the fugacity of carbon dioxide in the fluid. Silica and Fe<sup>++</sup> exhibit variable behavior.

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### REFERENCES

- BARRETT L. F., CAMERON D. E. and WILSON J. C. (1985) Discovery of the Silver Creek molybdenum deposit, Rico, Colorado. A.I.M.E. Preprint 85–118.
- BORTHWICK J. and HARMON R. S. (1982) A note regarding CIF<sub>3</sub> as an alternative to BrF<sub>5</sub> for oxygen isotope analyses. *Geochim. Cosmochim. Acta* **46**, 1665–1668.
- CATHELINEAU M. (1988) Cation site occupancy in chlorites and illites as a function of temperature. *Clay Minerals* 23, 471–485.
- CLAYTON R. N. and MAYEDA T. K. (1963) The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim. Cos*mochim. Acta 27, 43–52.
- CRAIG H. (1963) The isotopic geochemistry of water and carbon in geothermal areas. In *Nuclear Geology on Geothermal Areas* (ed. E. TONGIORGI), pp. 17–53. Spoleto: Pisa, Consiglio Nazionale della Richerche, Laboratorio de Geologia Nucleare.
- CRISS R. E. and TAYLOR H. P., JR. (1983) An <sup>18</sup>O/<sup>16</sup>O and D/H study of Tertiary hydrothermal systems in the southern half of the Idaho batholith. *Geol. Soc. Amer. Bull.* **94**, 640–663.
- CUNNINGHAM C. G., NAESER C. W., CAMERON D. E., BARRETT L. F., WILSON J. C. and LARSON P. B. (1987) The Pliocene paleothermal anomaly at Rico, Colorado, as related to a major molybdenum deposit. *Geol. Soc. Amer. Abstr. Prog.* **19**, 268–269.
- ELLIS A. J. (1979) Explored geothermal systems. In Geo-

chemistry of Hydrothermal Ore Deposits (ed. H. L. BARNES), Vol. 2, pp. 632-683. John Wiley.

- GREGORY R. T. and TAYLOR H. P., JR. (1981) An oxygen isotope profile in a section of Cretaceous oceanic crust, Samail ophiolite, Oman: evidence for  $\delta^{18}$ O-buffering of the oceans by deep (>5 km) seawater-hydrothermal circulation at mid-ocean ridges. J. Geophys. Res. 86, 2737– 2755.
- LARSON P. B. (1987) Stable isotope and fluid inclusion investigations of epithermal vein and porphyry molybdenum mineralization in the Rico mining district, Colorado. *Econ. Geol.* 82, 2141–2157.
- LARSON P. B. and TAYLOR H. P., JR. (1986) <sup>18</sup>O/<sup>16</sup>O relationships in hydrothermally altered rocks from the Lake City caldera, San Juan Mountains, Colorado. J. Volcanol. Geotherm. Res. **30**, 47–82.
- LARSON P. B., ZIMMERMAN B. S., CUNNINGHAM C. G. and NAESER C. W. (1991a) Large-scale alteration effects in the Rico paelothermal anomaly, Colorado. *Geol. Soc. Amer. Abstr. Prog.* 23, 40.
- LARSON P. B., CUNNINGHAM C. G. and NAESER C. W. (1991b) Hydrothermal alteration and mass flux in the Rico paleothermal anomaly, Colorado. *Econ. Geol.* (submitted).
- MCKNIGHT E. T. (1974) Geology and ore deposits of the Rico district, Colorado. U.S. Geol. Surv. Prof. Paper 723.
- NAESER C. W., CUNNINGHAM C. G., JR., MARVIN R. F. and OBRADOVICH J. D. (1980) Pliocene intrusive rocks and mineralization near Rico, Colorado. *Econ. Geol.* 75, 122–127.
- NORTON D. L. (1982) Fluid and heat transport phenomena typical of copper-bearing pluton environments. In Advances in Geology of the Porphyry Copper Deposits, Southwestern North America (ed. S. R. TITLEY), pp. 59–72. University of Arizona Press, Tucson.
- NORTON D. L. (1984) Theory of hydrothermal systems. Ann. Rev. Earth Planet. Sci. 12, 155–177.
- NORTON D. L. and KNIGHT J. E. (1977) Transport phenomena in hydrothermal systems. Amer. J. Sci. 277, 937–981.
- O'NEIL J. R. and TAYLOR H. P., JR. (1967) The oxygen isotope and cation exchange chemistry of feldspars. *Amer. Mineral.* 52, 1414–1437.
- PRATT W. P. (1976) Preliminary geologic map of the Hermosa Peak Quadrangle, Dolores, San Juan, La Plata, and Montezuma Counties, Colorado. U.S. Geol. Surv. Open File Report 76–314.
- PRATT W. P., MCKNIGHT E. T. and DEHON R. A. (1969) Geologic map of the Rico Quadrangle, Dolores and Montezuma Counties, Colorado. U.S. Geol. Surv. Geol. Quad. Map GQ-797.
- RANSOME F. L. (1901) The ore deposits of the Rico Mountains, Colorado. U.S. Geol. Surv. Ann. Rept. 22(2), 229–398.
- TAYLOR H. P., JR. (1971) Oxygen isotope evidence for large-scale interaction between meteoric ground waters and Tertiary granodiorite intrusions, western Cascade Range, Oregon. J. Geophys. Res. 76, 7855-7874.
- TAYLOR H. P., JR. (1979) Oxygen and hydrogen isotope relationships in hydrothermal mineral deposits. In *Geochemistry of Hydrothermal Ore Deposits* (ed. H. L. BARNES), Vol. 2, pp. 236–277. John Wiley.

