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Abstract

Fluorine-rich hydrothermal mineral assemblages developed at Henderson, Colorado, as 12 rhyolitic stocks of Oligocene age were emplaced, crystallized, and cooled inside a much larger and slightly older, rhyolitic intrusion, forming a Climax-type molybdenum deposit. The stocks are grouped into three intrusive centers, and the mineral assemblages, including ore minerals, are grouped according to their temperatures of formation as either high-, moderately high, moderate-, or low-temperature assemblages. The latter three groups are termed lower temperature assemblages, which are subdivided into two suites on the basis of position: above intrusive centers and on the flanks of the Seriate center. Integration of the mineralogy, sequence, and spatial positions of mineral assemblages defines the geochemical evolution of hydrothermal fluids, places qualitative constraints on mass transfer, and provides insight into the development of the geochemical halos that are used in exploration for porphyry orebodies.

A reconnaissance fluid inclusion study targeted the lower temperature assemblages, and a geologic assessment of results indicates that we were unable to identify fluid inclusions from several assemblages. After pooling meaningful results, the ranges of temperatures of formation for each group of lower temperature assemblages are moderately high, 600° to 460°C; moderate, 530° to 510°C; and low, 390° to 200°C, with significant differences in salinity between the two suites of assemblages. The suite formed above intrusive centers was deposited by more saline fluids (salinity commonly 28–65 wt % NaCl ± KCl equiv) than the suite formed on the flanks of the Seriate center (mostly <29 wt % NaCl + KCl equiv). The lower temperature assemblages described here do not overlap in space with higher level propylitic alteration, but fluid inclusions in one sample of propylitized rock indicate temperatures of 320° to 310°C and salinity <29 wt percent NaCl + KCl equiv.

Phase equilibria suggest that, at comparable temperatures, the suite of assemblages that formed above intrusive centers formed at higher $f_{\text{H}_2}\text{O}$, $f_{\text{CO}_2}$, and $a_{\text{K}+/a_{\text{H}+}}$ and slightly lower $a_{\text{K}+/a_{\text{H}+}}$ than the suite of assemblages that formed on the flanks of the Seriate center. From inception of potassic alteration (~600°C) to termination of sericitic alteration (~300°C), values of $\log a_{\text{K}+/a_{\text{H}+}}$ of fluids remained essentially constant (~3), but the $a_{\text{K}+/a_{\text{H}+}}$ of fluids increased. Fluids were undersaturated with respect to topaz during high-temperature silicic and intense potassic alteration, but topaz precipitated in both suites of assemblages after further fluid evolution. Topaz formed in certain less intense potassic, transitional potassic-sodic, and sericitic assemblages as the $a_{\text{K}+/a_{\text{H}+}}$ of fluids increased with decline in temperature and probably pressure, before the fluid again became undersaturated with respect to topaz. Because fluids associated with sericite-pyrite alteration at Henderson were unusually saline (mostly 29–36 wt % NaCl equiv), coiling of evolved, magmatic fluids (rather than dilution by meteoric water) likely drove sericitic alteration by cooling through the K-feldspar-sericite buffer at nearly constant $a_{\text{K}+/a_{\text{H}+}}$. Indeed, halite-bearing fluid inclusions persist into intermediate argillic assemblages that precipitated sphalerite and F-bearing, Mn-rich garnet.

Fluorine was continuously added to wall rocks by hydrothermal fluids along the entire evolutionary paths of both suites of assemblages. The alkalis underwent a complex history of mass transfer, with the behavior of potassium fluctuating between periods of strong leaching and strong addition to the rock. Iron was leached at high to moderately high temperatures and then fixed in the rock at lower temperatures, first mainly as magnetite and then as pyrite and minor pyrrhotite and specular hematite. Molybdenum and tungsten show no evidence of any period of significant leaching or recycling.

Each mineralizing intrusion introduced juvenile magmatic hydrothermal fluids containing metals and other components, but the deposition of metals and other components was staggered over time and a wide temperature range. The order of deposition was Mo to W to Pb-Zn to Mn. The spatial zoning of metals from proximal to distal around any intrusive center generally—but not always—corresponds to the temporal sequence early to late. Moreover, the metals that were deposited relatively late tended to be deposited at about the same time throughout the system, so that Pb-Zn and Mn introduced with the earliest intrusions were not deposited until much later, after other intrusions and hydrothermal fluids were introduced. Hence, there was progressively greater decoupling between the times of introduction and deposition of metals in the order Mo to W to Pb-Zn to Mn, and this time delay lengthened for any given component introduced by an earlier intrusion compared to the same component introduced by a later intrusion. The degree of decoupling of introduction and

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deposition of components may reconcile discrepancies between differing interpretations of when the majority of Cu is deposited in porphyry copper deposits.

Hydrothermal mineral assemblages that formed above intrusive centers at Henderson resemble assemblages in other Climax-type porphyry molybdenum deposits associated with high-silica rhyolites. In contrast, the suite of assemblages that formed on the flanks of the Seriatic center is similar to alteration-mineralization products formed in porphyry molybdenum deposits related to alkali syenites and in porphyry tungsten-molybdenum deposits associated with rhyolites and granites. Hydrothermal assemblages in granite-related molybdenum deposits of the differentiated monzogranite suite and granite-related molybdenum-copper deposits have little in common with either suite of assemblages at Henderson.

Introduction

Geochemical investigations provide insight into the geologic and geochemical processes that form orebodies and their distal expressions, but space-time relationships of metasomatic systems must be resolved in the field and laboratory in advance of meaningful geochemical modeling (Barton et al., 1991a, b). If geochemical investigations are firmly grounded geologically, the resulting model is of greater predictive value than a purely empirical model because the geochemical insights aid interpolation between and extrapolation beyond preexisting empirical data points. Sound geochemical models commonly generate new questions, catalyzing new rounds of field, analytical, and theoretical investigation.

Diversity among deposits, as embodied in the variations on a theme concept of Gustafson and Hunt (1975), is widely appreciated for porphyry-related deposits. Nonetheless, the geochemical evolution of hydrothermal fluids as a function of space, time, temperature, and composition is well documented for few porphyry-related hydrothermal systems (as is apparent from Gustafson, 1978; Einaudi, 1982; Clark, 1993; Lang et al., 1995), because comprehensive, detailed, field-based studies, which are themselves uncommon, must be coordinated with subsequent geochemical and petrologic investigations to deduce geochemical paths. Although a few igneous-related hydrothermal systems have been successfully modeled (e.g., Heinrich and Ryan, 1992), the documentation of geochemical evolutionary paths has progressed only modestly since the definition of a main line ore-forming environment by Barton (1970); consequently, the causes of zonation within a deposit and sources of diversity between deposits are incompletely understood. Although some causes of zonation and sources of diversity have been confirmed and others are predicted by experimental data and theoretical models (Meyer and Hemley, 1967; Barnes, 1975; Gustafson, 1978; Hemley et al., 1980; Barton et al., 1991a; Candela, 1992; Hemley and Hunt, 1992; Cline, 1995; Dilles et al., 2000a), significant operative processes may remain unidentified. Moreover, variable geochemical paths within single hydrothermal systems (e.g., Einaudi, 1977) have rarely been recognized and sources of such variability have hardly been examined.

The Henderson porphyry molybdenum deposit is ideally suited to a study of wall-rock alteration and metal deposition because it has been studied over a protracted period of time (Meyer and Hemley, 1967, p. 166–167); indeed, it stands as one of the best-documented porphyry deposits in the world. Wallace et al. (1978), White et al. (1981), and Geraghty et al. (1988) established the geologic setting, and Carter et al. (1988a, b) described the development of silicic and intense potassic alteration at high temperatures (generally above 500°C). This paper is part of a study examining the evolutionary paths of lower temperature fluids (mostly 530°–200°C), which includes the transitions from potassic to sericitic and from sericitic to intermediate argillic alteration. The first paper (Seedorff and Einaudi, 2004) established the space-time relationships of lower temperature mineral assemblages by documenting the sequence and abundance of hydrothermal mineral assemblages and compositions of hydrothermal minerals and by identifying the flow paths of progressively evolving fluids, based on careful study of veinlets, their crosscutting relationships, and the crosscutting contacts of multiple intrusions.

The purpose of the present paper is to characterize the physical and chemical environment of fluid evolution at Henderson, encompassing the introduction and deposition of metals and other components and the resultant zoning patterns. The environment is constrained by coexisting minerals and their compositions, characteristics of veins, phase equilibria, and results of fluid inclusion study. Pressure and depth information arises from geologic constraints, which are tested against phase equilibria. We deduce the evolution of hydrothermal fluids and the role of topaz by integrating field relationships with the geochemical environments of assemblages. We illustrate fluid evolution by geochemical paths in phase diagrams, which reveal sources of diversity of hydrothermal mineral assemblages. The mineralogy, sequence, and distribution of assemblages provide qualitative constraints on mass transfer. The spatially extensive time lines available at Henderson (Seedorff and Einaudi, 2004) permit us to evaluate (1) the sources of chemical components, (2) the degree of recycling of ore components, and (3) the relative importance of changes over time in compositions of juvenile magmatic hydrothermal fluids that were injected into the hydrothermal system versus temporal evolution of migrating hydrothermal fluids. Synthesis of the data constrains the origin of sericitic and intermediate argillic fluids at Henderson and provides a context for comparing alteration-mineralization products in porphyry deposits.

This study builds on previous contributions to the understanding of alteration-mineralization at Henderson (MacKenzie, 1970; White and MacKenzie, 1973; Ranta et al., 1976; Wallace et al., 1978; Gunow et al., 1980; White et al., 1981; Carter et al., 1988a, b), especially on the work of MacKenzie, White, and Carter. The fluid inclusion portion builds on earlier work by Kamill (1978) and White et al. (1981) and complements past and ongoing studies directed at the high-temperature mineral assemblages (Carter, 1987; Carter et al., 1988c).

Geologic Setting and Intrusive History

Henderson and Urad constitute a stacked pair of Climax-type porphyry molybdenum orebodies associated with Oligocene...
intrusions of biotite-high-silica rhyolite at Red Mountain, Clear Creek County, Colorado (Wallace et al., 1978; White et al., 1981; Geraghty et al., 1988; Carten et al., 1993; Wallace, 1995). The older, shallower, and much smaller Urad deposit (Fig. 1) is hosted by stocks of rhyolite porphyry and by the Silver Plume Granite, a Proterozoic biotite-muscovite granite. The Urad orebody is cut off by a cylindrical intrusion, the Red Mountain porphyry, which flares out into a larger body, the urad porphyry, at depth (Wallace et al., 1978).

The Henderson deposit is associated with a dozen or more, small, texturally and compositionally zoned stocks (Carten et al., 1988a, b) that intruded the Urad porphyry (Fig. 1). The stocks are grouped into three closely spaced intrusive centers, Henderson, Seriate, and Vasquez. The Henderson orebody consists of three overlapping ore zones, each of which is associated with one of the intrusive centers. The three ore zones are themselves composite, because each individual stock developed its own ore shell. The Henderson intrusive center is composed of five stocks, several prominent dikes, and a breccia body. The focus of intrusion subsequently shifted to the east-northeast, where the four stocks of the Seriate center intruded, and finally shifted to deeper levels, where three stocks of the Vasquez center were emplaced (for further information, see Carten et al., 1988b; Seedorff and Einaudi, 2004).

Assemblages herein are grouped by their temperatures of formation: high, moderately high, moderate, and low based on geologic relationships and mineralogy prior to study of associated fluid inclusions. In the text, each complete assemblage is represented by an abbreviation in capital letters (Fig. 2). The reader is referred to the companion paper (Seedorff and Einaudi, 2004) regarding the nomenclature and use of notation in citing mineral assemblages.

Certen et al. (1988a, b) studied high-temperature alteration-mineralization, which can be treated in terms of two simplified mineral assemblages that are related to veins filled with quartz + fluorite ± molybdenite: a silicic type, quartz + fluorite + molybdenite (molybdenite), denoted by QTZ-FL, and an intense potassic type, K-feldspar + fluorite ± quartz ± molybdenite ± (biotite), denoted by QTZ-KSP-MO (Fig. 2).

Lower temperature assemblages, which are the subject of this study, include all but the high-temperature assemblages. The lower temperature assemblages are subdivided into two suites on the basis of their spatial positions: most abundant above intrusive centers, and restricted to the flanks of the Seriate center (Figs. 2–3).

The suite of assemblages above intrusive centers includes the moderately high temperature assemblages MOTTLED KSP-QTZ and MT-KSP, the moderate-temperature assemblages TPZ-PY and SER-PY, and the low-temperature assemblages PY-CLAY, SPHAL, GAR, and RHOD (Figs. 2–3). As a group, this suite of assemblages is distinguished by the presence of K-rich hydrothermal alkali feldspar in moderately high temperature assemblages, magnetite deposited with K-feldspar but not with sericite, topaz occurring almost entirely in a single, pyritic, feldspar-destructive assemblage, and a variety of pyrite-bearing assemblages formed at low temperatures, in greatest abundance at high levels in the system.

Methods

In this paper, compositions of topaz and sericite-muscovite are used in conjunction with geologic reconstructions, crosscutting relationships, phase equilibria, and fluid inclusion results to constrain the evolving geochemical environment in terms of temperature, pressure, relative activity ratios and products, and sulfur and oxygen fugacity. Treatment of halogen fugacities (e.g., Muñoz, 1984; van Middelbaar and Keith, 1990) is beyond the scope of this contribution and is deferred to a subsequent communication. All phase diagrams were constructed using SUPCRT, an internally consistent thermodynamic database (Helgeson et al., 1978). Thermodynamic data for fluor-topaz, however, were derived from the data of Barton et al. (1982) after adjustment for consistency with the SUPCRT database (Seedorff, 1987, app. E). The model thermodynamic data for hydroxyl-topaz (Barton, 1982) were similarly adjusted, and the proton-avoidance model of Barton (1982) was adopted for topaz solid solutions. The fluid inclusion methodology is described in the Appendix.

Summary of Hydrothermal Mineral Assemblages

Assemblages herein are grouped by their temperatures of formation: high, moderately high, moderate, and low based on geologic relationships and mineralogy prior to study of associated fluid inclusions. In the text, each complete assemblage is represented by an abbreviation in capital letters (Fig. 2). The reader is referred to the companion paper (Seedorff and Einaudi, 2004) regarding the nomenclature and use of notation in citing mineral assemblages.

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The suite of assemblages on flanks of the Seriate center contains the moderately high temperature assemblages BIO-KSP and TPZ-BIO-MT, the moderate-temperature assemblages TPZ-MT, SER-MT, and GREEN BÍO, and only one low-temperature assemblage, PO, because the two suites of...
Fig. 2. Graphic definition of hydrothermal mineral assemblages in the Henderson deposit, separated by suites of lower temperature assemblages (inspired by fig. 5 of Gustafson and Quiroga G., 1995). The high-temperature assemblages (simplified from Gunow, 1983; Carten et al., 1988b) are shown next to each suite and also locally include zircon, monazite, and apatite (omitted). Assemblages are arranged across the top of the figure and minerals along the left side. Abbreviations for assemblages are based on the following mineral abbreviations: BIO = biotite, GAR = garnet; GREEN BIO = green biotite, KSP = K-feldspar, MT = magnetite, PO = pyrite, TPZ = pyrrhotite, QTZ = quartz, RHOD = rhodochrosite, SER = sericite, SPHAL = sphalerite, and TPZ = topaz. This is not a paragenetic diagram applicable to the entire deposit because of the cyclicity of the Henderson system, the differences between cycles in different intrusive centers, and the merging of suites at low temperatures (see Seedorff and Einaudi, 2004). Nonetheless, progression from high to low temperatures in each suite generally represents an evolutionary path for fluids that formed each suite of assemblages.
FIG. 3. Simplified, time-integrated view of alteration-mineralization at Henderson, showing simplified distribution and abundances of hydrothermal mineral assemblages. A. High- and moderately high temperature assemblages. B. Moderate- and low-temperature assemblages. See Figure 2 for definitions and abbreviations of assemblages.

HIGH-TEMPERATURE ASSEMBLAGES

**QTZ-FL**
- > 50 vol % Feldspars → Quartz (silicic alteration)

**QTZ-KSP-MO**
- Top of visible molybdenite
- > 5 vol % Quartz ± Fluorite ± Molybdenite veins (guide intense potassic alteration)

MODERATELY HIGH-TEMPERATURE ASSEMBLAGES

**MOTTLED KSP-QTZ**
- Absent
- Trace - 40 vol %
- Absent

**BIO-KSP**
- Present
- Absent
- Absent
- Absent
- Absent
- Absent
- Absent
- Absent
- Absent
- Absent

**MT-KSP**
- Absent
- >10 vol %
- Absent

**TPZ-BIO-MT**
- Absent
- Rare - 10 vol %
- Absent
- Absent
- Absent
- Absent
- Absent
- Absent
- Absent
- Absent

MODERATE-TEMPERATURE ASSEMBLAGES

**TPZ-PY**
- Absent
- > 3 vol %
- Absent

**TPZ-MT**
- Absent
- > 10 vol %
- Absent

**GREEN-BIO**
- Trace - 5 vol %
- Absent

LOW-TEMPERATURE ASSEMBLAGES

**PO**
- Mostly trace - 3 vol %
- Absent

**SPHAL**
- Common-abundant occurrences
- Sparse

**RHOD**
- Abundant-common occurrences
- Sparse
assemblages merge at low temperatures (Figs. 2–3). The suite of six assemblages that formed on the flanks of the Seriate center is distinguished by widespread and locally abundant hydrothermal biotite, widespread topaz, appearance of alkali feldspars of K-rich, K-Na, and Na-rich compositions, the abundance of magnetite, and local pyrrhotite.

Distribution of Metals

The only metal of economic importance at Henderson is Mo, but elements such as W, Pb, Zn, Cu, Bi, Ag, and Mn are geochemically anomalous and are of exploration interest because they are more widely dispersed than Mo (Bright, 1974; Westra and Keith, 1981).

At Henderson, practically every core interval has been analyzed for Mo (reported at Henderson in terms of MoS2). The distribution of Mo and its relationship to individual stocks are shown in Figure 4A (Carter et al., 1988b, figs. 3–4, 13–15; Seedorff and Einaudi, 2004, figs. 2–3, for greater information and detail). Note that the Mo pattern mimics the distribution and abundance of the high-temperature assemblage QTZ-KSP-MO (Fig. 3; see also fig. 5 of Seedorff and Einaudi, 2004) because this assemblage contains most of the Mo (as molybdenite) in the Henderson deposit (Fig. 2).

Although nine, long holes drilled during exploration of the deposit were analyzed for a large suite of elements (Bright, 1974), elements such as W, Zn, Cu, and Mn have not been routinely assayed. Nonetheless, the distribution of many metals can be estimated (Fig. 4) because we logged both the occurrence and relative abundance of metal-bearing minerals in the various assemblages (Fig. 2) and the distribution and abundance of assemblages (Fig. 3).

Tungsten rarely exceeds 100 ppm WO3 and thus is far less abundant at Henderson than at Climax (Wallace et al., 1978, p. 361, 364). Wolframite (~77 wt % WO3), the principal W-bearing hydrothermal mineral present at Henderson (Gunow, 1983). It occurs in many assemblages in trace abundance (Fig. 2), including several from the suite on the flanks of the Seriate center. To illustrate the point that zones of concentration of certain mineral assemblages can be used to define metal distribution, Figure 5 shows the occurrences of wolframite logged on two cross sections compared to the distribution and abundance of the assemblage TPZ-PY.

The low-temperature assemblages SPHAL and GAR contain most of the Zn as sphalerite and Pb as galena (Fig. 4C); an order-of-magnitude estimate of the metal contents corresponding to the outline of the Pb-Zn zone of Figure 4C is 500 ppm each of Pb and Zn. The trace occurrence of Cu at Henderson is virtually restricted to microscopic inclusions of chalcopyrite in sphalerite (Seedorff, 1988); thus, the distribution of Cu should follow Zn. Trace element dispersion patterns (Bright, 1974) suggest that the distribution of the SPHAL assemblage should also outline the distribution of Bi and Ag.

Temperature and Salinity Estimates— Fluid Inclusion Study

Purpose and strategy

A reconnaissance fluid inclusion study was conducted primarily to assign approximate temperatures of formation to the mineral assemblages for incorporation into a model of the geochronologic distribution of the hydrothermal system. Because porphyry systems are characterized by a multiplicity of cross-cutting, partially superimposed events (e.g., Gustafson, 1978; Tittle, 1982), samples containing a minimum number of geologic events were sought for fluid inclusion investigation (see App.). The strategy (Seedorff, 1987) is to determine the fluid characteristics of each assemblage based on relatively few microthermometric measurements from a modest number of samples. An ideal sample would contain one assemblage (the target assemblage), would not contain crosscutting or superimposed events, and would occur in a region of the deposit where other assemblages are absent. Interpretations are based on interpolation and extrapolation of data in space and time based on the best-known geologic parameters, principally the distribution and abundance of assemblages and their relative ages.

Many samples selected from Henderson contain abundant evidence of multiple events, in spite of every attempt to choose samples that are geologically simple to interpret. Although some fluid inclusions in vein-filling minerals are of obvious secondary origin, most are of ambiguous origin; similar difficulties have been acknowledged reluctantly by other students of fluid inclusions in porphyry systems (e.g., Nash and Theodore, 1971, p. 389, 398; Eastoe, 1978, p. 725; Bodnar and Beane, 1980, p. 882; White et al., 1981, p. 299; Roedder, 1984, p. 446–447; Theodore et al., 1992, p. 255–256, 269, 275; Muntean and Einaudi, 2001, p. 767). In some deposits, samples with more favorable characteristics have been found, and workers have concentrated their studies on these (e.g., Roedder, 1971; Wilson et al., 1980, p. 47–48; Cline and Bodnar, 1994, p. 1781–1782). In the case of many mineral assemblages, samples with such characteristics have not been found at Henderson.

Suitable fluid inclusions were studied in vein-filling minerals, in hydrothermal minerals in a few wall-rock alteration envelopes, and in quartz phenocrysts that are cut by a veinlet or that are in their alteration envelope. Standard petrographic observations were recorded, and heating runs were performed. Few freezing runs were attempted, because salinities could be obtained from the halite-bearing samples from heating runs, and the halite-absent inclusions generally were too small, given the optical quality of the samples (Fig. 6), to see melting phenomena. The Appendix contains information on the classification and characteristics of fluid inclusions and use of ideal geochronologic systems to model their compositions.
FIG. 4. Simplified, time-integrated view of metal distribution at Henderson, showing zones of Mo, W, Pb-Zn, and Mn enrichment on section 52N-N63E-58N. H, S, and V denote the Henderson, Seriate, and Vasquez centers, respectively. A. Quantitative distribution of Mo, which is present predominantly in the high-temperature assemblage QTZ-KSP-MO, based on assayed drill holes. For visual reference, black circles are placed in the center of the Mo ore zone related to each of the three intrusive centers, although the ore zones are themselves composite features, created by overlap of ore shells formed about each mineralizing stock. A thin arrow from an open circle enclosing Mo points to each of the filled black circles. The sizes of the black circles are scaled roughly to the Mo content of each ore zone. Around each black dot, there are open white arrows representing the principal directions that ore fluids initially were directed, based on orientations and relative abundances of veins. B. Qualitative distribution of W, present predominantly in the moderate-temperature assemblage TPZ-PY, based on the distribution and abundance of TPZ-PY logged in drill core. Open pentagons enclosing W are placed at the approximate centers of the overlapping tungsten zones, one over the Henderson center and the other over the Seriate center. C. Qualitative distribution of Pb-Zn, present predominantly in the low-temperature assemblage SPHAL, based on distribution and abundance of SPHAL logged in drill core. Open rectangles enclosing Pb-Zn are placed at the approximate centers of the three Pb-Zn zones, one over each of the three intrusive centers. D. Qualitative distribution of Mn, present predominantly in the low-temperature assemblages GAR and RHOD, based on distribution and abundance of GAR and RHOD logged in drill core. Open triangles enclosing Mn are placed at the approximate centers of the three Mn zones, one over each of the three intrusive centers.
Results and interpretation

Results of microthermometric measurements are presented in Figures 7 and 8. An unconventional approach, similar to that of Preece and Beane (1982, fig. 16, p. 1634) and Shaver (1984a, b) but unlike that of most fluid inclusion studies, is adopted to interpret the results. The approach involves a geologic deduction of which fluid inclusions in a sample, if any, might be representative of the fluids from which a particular assemblage formed. Deduction follows from (1) measurements made on individual samples (Fig. 7, left side, and Fig. 8); (2) geologic relationships regarding the distribution and relative age of formation of assemblages (documented in Seedorff and Einaudi, 2004), which are used to help identify possible sources of secondary inclusions in a given sample (right side of Fig. 7); and (3) comparison of data obtained from different samples so that the data gathered from samples containing only the youngest events can be used to strip off effects of younger events (i.e., secondary inclusions) superimposed on older events. A review of the results and interpretations (summarized in Table 1) follows, proceeding from lower to higher temperatures.

Samples in which the low-temperature group of assemblages was targeted exhibit a surprisingly large proportion of halite-bearing fluid inclusions (salinities as high as 37 wt % NaCl equiv). Fluids with temperature-salinity characteristics similar to those of the low-temperature assemblages appear to be represented in the data gathered from samples in which other, earlier assemblages were targeted (Figs. 7–8).

Among the moderate-temperature assemblages, fluid inclusions attributed to the SER-PY assemblage (in veins without inner envelopes of TPZ-PY) exhibit similar salinities but
The temperatures (310°–470°C) and salinities (generally 29–36 wt % NaCl equiv or roughly 6–10 m NaCl solutions; all fluid inclusions homogenized by vapor disappearance) of the SER-PY assemblage are considerably higher than the values reported for sericitic alteration in most porphyry deposits (e.g., 250°–350°C, <20 wt % NaCl equiv; Beane and Titley, 1981, p. 253–254; Hedenquist et al., 1998, p. 385). Where the SER-PY assemblage fringes an inner envelope of the TPZ-PY assemblage (Figs. 7–8), the inferred temperatures are even higher, approaching 500°C, and salinities locally exceed 50 wt percent NaCl + KCl equiv (sylvite may be present at room temperature and some inclusions homogenize by halite dissolution). Neither daughter salt is present in fluid inclusions from the TPZ-PY assemblage in vein types where envelopes of the GREEN BIO assemblage fringe the TPZ-PY assemblage, although the homogenization temperatures are comparable (Fig. 7; Table 1). Moderate-temperature assemblages that are members of the suite on the flanks of the Seriate center (TPZ-MT, SER-MT, GREEN BIO) appear to be associated with fluid inclusions that lack daughter salts. Most of the low-temperature fluid inclusions in samples from this region of the deposit similarly lack such daughters (Fig. 7).

Data from samples in which moderately high temperature assemblages were targeted are difficult to interpret, although it is apparent that most fluid inclusions studied probably are secondary fluid inclusions related to assemblages formed at lower temperatures. For the BIO-KSP assemblage, some fluid inclusions probably are secondary fluid inclusions that were contributed by fluids associated with high-temperature assemblages (QTZ-FL and QTZ-KSP-MO) of a younger intrusive hydrothermal cycle associated with the underlying Vasquez stock. Although none was present in the samples studied, high-temperature veins related to the Vasquez center are present in the regions from which all of the BIO-KSP assemblage samples were collected (Figs. 3, 7). For the sample in which the MOTTLED KSP-QTZ assemblage is the targeted assemblage (and for four other histograms of Fig. 7), none of the fluid inclusions is thought to be representative of the fluids from which the assemblage(s) formed. If one were to assume that the fluid inclusions measured for the MOTTLED KSP-QTZ assemblage are representative of the fluids from which the assemblage formed, then the earlier, K-feldspar-bearing

### Table 1. Reconnaissance Fluid Inclusion Study of Lower Temperature Assemblages

<table>
<thead>
<tr>
<th>Group</th>
<th>Assemblage</th>
<th>Temperature</th>
<th>Salinity</th>
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<tbody>
<tr>
<td>Moderately high temperature</td>
<td>MOTTLED KSP-QTZ</td>
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<td>No data</td>
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<td></td>
<td>MT-KSP</td>
<td>460–530</td>
<td>&lt;29</td>
</tr>
<tr>
<td></td>
<td>BIO-KSP*</td>
<td>500–600?</td>
<td>Mostly &lt;29?</td>
</tr>
<tr>
<td></td>
<td>TZT-BIO-MT*</td>
<td>No data</td>
<td>No data</td>
</tr>
<tr>
<td>Moderate temperature</td>
<td>TZT-PY (with an outer envelope of SER-PY)</td>
<td>400–500</td>
<td>Mostly 30–65</td>
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<tr>
<td></td>
<td>TZT-PY (with an outer envelope of GREEN BIO)</td>
<td>410–510</td>
<td>&lt;29</td>
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<td></td>
<td>SER-PY (beyond an inner envelope of TZT-PY)</td>
<td>400–500</td>
<td>Mostly 30–65</td>
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<td></td>
<td>SER-PY (without an inner envelope of TZT-PY)</td>
<td>310–470</td>
<td>Mostly 29–36</td>
</tr>
<tr>
<td></td>
<td>TPZ-MT* (without an outer envelope of SER-MT)</td>
<td>No data</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td>TPZ-MT* (with an outer envelope of SER-MT)</td>
<td>400–530</td>
<td>&lt;29</td>
</tr>
<tr>
<td></td>
<td>SER-MT* (beyond an inner envelope of TPZ-MT)</td>
<td>400–530</td>
<td>&lt;29</td>
</tr>
<tr>
<td></td>
<td>SER-MT* (without an inner envelope of TPZ-MT)</td>
<td>No data</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td>GREEN BIO* (beyond an inner envelope of TZT-PY)</td>
<td>410–510</td>
<td>&lt;29</td>
</tr>
<tr>
<td></td>
<td>GREEN BIO* (without an inner envelope of TPZ-PY)</td>
<td>No data</td>
<td>No data</td>
</tr>
<tr>
<td>Low temperature</td>
<td>PO*</td>
<td>No data</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td>PY-CLAY</td>
<td>200–330</td>
<td>Mostly &lt;29–35</td>
</tr>
<tr>
<td></td>
<td>SPHAL (without an outer envelope of GAR)</td>
<td>210–370, mostly 280–330</td>
<td>Mostly 28–37</td>
</tr>
<tr>
<td></td>
<td>SPHAL (with an outer envelope of GAR)</td>
<td>200–380, mostly 200–300</td>
<td>Mostly 28–36</td>
</tr>
<tr>
<td></td>
<td>GAR (beyond an outer envelope of SPHAL)</td>
<td>200–380, mostly 200–300</td>
<td>Mostly 28–36</td>
</tr>
<tr>
<td></td>
<td>RHOD</td>
<td>200–390</td>
<td>&lt;29</td>
</tr>
<tr>
<td></td>
<td>Propylitic</td>
<td>210–320</td>
<td>&lt;29</td>
</tr>
</tbody>
</table>

1. See Figure 2 and Seedorff and Einaudi (2004, table 1) for definitions and abbreviations of assemblages (except propylitic—see text); an asterisk (*) denotes a member of the suite of assemblages on the flanks of the Seriate center; the remaining assemblages are members of the suite of assemblages above intrusive centers; for this compilation, compositions of fluids are assumed to have been similar from the vein filling to the edge of an alteration envelope so that microthermometric data are applied to all assemblages in a zoned envelope, regardless of the position of the fluid inclusions that were measured.

2. Interpreted range of homogenization temperatures (°C).

3. Interpreted range of salinities, in wt percent NaCl equiv and wt percent NaCl + KCl (see App.).

4. None of the fluid inclusions measured in the sample targeted for this assemblage is thought to be related to this assemblage.

5. Not a targeted assemblage in any sample, but secondary inclusions in some samples are interpreted to be related to this assemblage.
Inclusion containing halite daughter mineral that homogenizes by L + hal + V → L + V → L
Inclusion containing halite daughter mineral that homogenizes by L + hal + V → L + V → L
Inclusion containing halite and sylvite daughter minerals that homogenizes by L + hal + syl + V → L + hal + syl → L + hal → L
Inclusion containing halite and sylvite daughter minerals that homogenizes by L + hal + syl + V → L + hal + syl → L + hal → L
Inclusion containing halite and halite daughter mineral that homogenizes by L + hal + V → L + hal + V → L + V → V

Note: Daughter minerals other than those mentioned above may be present in any type of inclusion.
assemblage of MOTTLED KSP-QTZ would have formed at temperatures <370°C, which is substantially below that of the later, feldspar-destructive assemblages TPZ-PY (400°–500°C) and SER-PY (310°–440°C). This latter alternative is rejected because it is geologically less probable. The argument for the former, preferred alternative is strengthened by the number of low-temperature assemblages (inferred to be responsible for the fluid inclusions that were measured; Fig. 7) that were superimposed on the same general region where the MOTTLED KSP-QTZ assemblage was developed, near the apices of intrusions (Fig. 3). The spatial distribution of the assemblage and its texture also point to the possibility that fluids boiled during its formation (Seedorff and Einaudi, 2004).

Three additional interpretations are drawn from the results (Table 1). First, there appears to be a difference in the salinities of fluids that formed the two suites of assemblages. High-salinity (i.e., halite saturated at room temperature) fluids commonly are associated with the suite of assemblages that formed above intrusive centers (Figs. 2–3, 7–8). Liquid-rich fluid inclusions without halite or sylvite daughter minerals (Fig. 7) appear to characterize the suite of assemblages on the flanks of the Seriate center. These compositional differences may be inherited from higher temperatures, because Carten (1987) has identified two types of high-temperature fluids that have different spatial distributions—one a Cl-rich fluid, the other a low-Cl, F-rich, Fe- and K-bearing aluminosilicate fluid. Lower temperature fluids on the flanks of the Seriate center may represent evolved versions of the low Cl, F-rich fluid, whereas those above intrusive centers may be dominated by contributions from the Cl-rich fluid (R. B. Carten, pers. commun., 1987).

Second, four vapor-rich fluid inclusions were observed in one sample for which BIO-KSP was the targeted assemblage (Fig. 7). The same sample also contains the only fluid inclusion that appeared to homogenize by critical behavior. It is uncertain as to which assemblage these two types of fluid inclusions are related, because these two types did not occur in any other samples, including two others with the same target assemblage. This constitutes permissive evidence for phase separation during lower temperature evolution of the hydrothermal system, although there are no saline fluid inclusions with similar homogenization temperatures as the vapor-rich fluid inclusions in that sample.

Third, none of the 300 fluid inclusions (including those hosted by quartz phenocrysts) of this study homogenized at temperatures below 200°C (Fig. 7). In addition, the histogram of White et al. (1981, fig. 30) shows roughly 200 homogenization temperatures, with none below 225°C. Either fluids cooler than 200°C were present but were not trapped as fluid inclusions or cooler fluids may not have circulated through the mineralized core of the hydrothermal system (Seedorff and Einaudi, 2004). Homogenization temperatures of fluid inclusions from base and precious metal veins at the periphery of the district (Corbeta, 1986) do include some values below 200°C, although most are between 200° and 300°C—roughly comparable to values observed at Henderson from a sample that exhibits propylitic alteration (Fig. 7).

**Depth Constraints and Pressure Estimates**

Early geologic reconstructions made by Ogden Tweto were used to place the top and base of the Henderson orebody at depths of 1.7 and 2.3 km, respectively (Wallace, 1974; White et al., 1981, p. 287), below a paleosurface that is likely to have been a rhyolite dome field with associated ash-flow tuffs (e.g., Keith et al., 1986; Stein and Crock, 1990). In light of the effects of subsequently identified postore faulting and tilting in the region, these paleodepths have been revised by Geraghty et al. (1988) to 2.8 km for the top of the Henderson and Seriate centers and 3.1 km for the top of the Vasquez center. Considering the types of igneous and hydrothermal textures observed in the deposit (Wallace et al., 1978; White et al., 1981; Carten et al., 1988b), both estimates are within reason. Geologic evidence indicates that the Urad orebody formed in a shallower environment than Henderson (Wallace et al., 1978, p. 364–365), so major uplift did not occur at Red Mountain concurrent with hydrothermal activity. According to Carten et al. (1988b), high-temperature fluids were at or above lithostatic pressures. Further, moderately high temperature assemblages generally are associated with discontinuous, thin veins (Seedorff and Einaudi, 2004, table 2), suggesting that pressures also may have been near lithostatic when they developed. Commencing with deposition of moderate-temperature assemblages, veins became more through going, and the upper limit of alteration migrated to higher levels during deposition of moderate- and low-temperature assemblages (Seedorff and Einaudi, 2004).
Fig. 8. Temperature vs. salinity diagrams for selected fluid inclusion samples. Geologic data pertinent to interpretation and a key to symbols are contained in Figure 7. Where a number also appears in a box, this indicates the number of points associated with the symbol plotted at that location. All liquid-rich inclusions are simply plotted at the appropriate temperature, in the manner of a histogram, below the horizontal line at the bottom of each diagram; for the system H2O-NaCl-KCl, these would have salinities of less than 29 wt percent. For CX-158-1416, fields of points are outlined for obviously secondary fluid inclusions (many displaying negative crystal habits) that were assigned to two particular planes during petrographic examination made prior to heating. Note that the salinity scale is condensed by 50 percent in the upper two diagrams compared to the lower three. For samples illustrated from the suite of assemblages above intrusive centers (bottom four diagrams), there is a general trend of decreasing temperature and decreasing maximum salinity in the sequence from top to bottom after geologic constraints (Fig. 7) are considered.

fibs. 10, 12). This increase in fracture permeability may have coincided with a transition from lithostatic to hydrostatic conditions (e.g., Gustafson and Hunt 1975; Fournier, 1999), although it is possible that even some of the low-temperature assemblages formed under a lithostatic regime. Geraghty et al. (1988) calculated lithostatic pressures of approximately 0.7 to 0.8 kbars for the region near the tops of the principal mineralizing intrusions. The actual fluid pressure may have declined during deposition of the final, low-temperature assemblages if hydrostatic conditions were reached.

Even at the highest possible estimated pressure (<1.0 kbar), pressure corrections on homogenization temperatures of fluid inclusions from Henderson fluids would be small, particularly for the most saline inclusions (Potter, 1977). For calculation of phase equilibria, uncorrected homogenization temperatures are used, a pressure of 0.5 kbar is considered as a first approximation for moderately high and moderate-temperature assemblages, and the effect of declining pressure from this value is examined.

**Geochemical Evolution and Mass Transfer of Nonore Components**

*Types of geochemical paths and means of illustration*

The mineralogy, sequence, and distribution of hydrothermal mineral assemblages, thermally calibrated by fluid inclusion results, mark the trail of geochemical evolution of hydrothermal fluids and provide qualitative insight into mass transfer at Henderson. We describe two types of geochemical paths with different frames of reference, one from the rock perspective and the other from the fluid perspective (see also Seedorff and Einaudi, 2004).

The rock perspective, with its coordinate system fixed in space, is useful when fluids are evolving over narrow intervals of time and temperature. Conventional displays of phase equilibria, such as activity-activity diagrams, can be used to illustrate quasi-isothermal paths quantitatively from the rock perspective.

The fluid perspective, in contrast, is most appropriate for describing the evolution of fluids over longer times and distances and uses a coordinate system that follows the fluid. Temperatures of fluids in porphyry systems range over many hundreds of degrees Celsius, beginning above the solidus of magmas, so deposit-scale geochemical paths are a challenge to display. The first strategy is to plot temperature on one of the axes of a diagram (sacrificing display of a chemical variable) because the locations of phase boundaries shift with temperature (although the topology of the phase diagram may remain unchanged). Second, conventional activity-activity diagrams may still be used quantitatively under certain circumstances without sacrificing a chemical variable if diagrams can be complexly stacked or contoured. Third, paths from the fluid perspective can be superimposed on the topology of the phase diagram, without labeling the values on the axes, if the purpose is to illustrate the succession of phase boundaries crossed. In this case, however, the directions of the arrows have no meaning relative to a fixed set of axes in an isothermal view; they have meaning only relative to the succession of phase fields crossed. We use all three types of diagrams to display the polythermal geochemical evolution at
Henderson, where there are two principal deposit-scale fluid trajectories to describe—one for each of the two suites of assemblages (Fig. 2).

**Paths on activity-activity diagrams**

Figures 9 and 10 show deposit-scale evolutionary paths (wide arrows) in activity-activity diagrams. Because the same assemblages were produced at high temperatures along each of these two evolutionary paths, it is assumed initially that the two paths had a common starting composition (dark circles of Figs. 9–10). A second family of paths (thin arrows) is shown that begins at selected points along the deposit-scale evolutionary paths. The paths shown by thin arrows illustrate the quasi-isothermal and -isobaric activity gradients during diffusion of fluid from channel way to alteration front on the scale of an alteration envelope (centimeters in width), as recorded by zoned alteration envelopes.

The deposit-scale paths for both suites evolve from K-feldspar to topaz to sericite with time and decreasing temperature (Fig. 9A–B). Hydrothermal fluids that evolve on the flanks of the Seriate center follow the K-feldspar-topaz boundary, whereas fluids above intrusive centers cross the K-feldspar-topaz boundary at values of $a_{K^+)/a_{H^+}$ greater than the K-feldspar-topaz-sericite invariant point. After the fluids saturate with respect to topaz and then sericite, the two paths merge at low temperatures (not shown in phase diagrams) as the fluids eventually reattain equilibrium with K-feldspar in the host rocks. The paths associated with both suites of assemblages provide the opportunity to develop zoned envelopes on single veins that contain inner topaz and outer sericite zones (paths 1-1’ in Fig. 9A and 4-4’ in B). Only deep fluids on the flanks of the Seriate center have ample opportunity to develop topaz-bearing alteration envelopes without an outer sericite envelope as relative values of $a_{K^+}/a_{H^+}$ remain higher than in the regions above intrusive centers (e.g., path 3-3’ in Fig. 9B).

A biotite field can be displayed if iron is added to the system (Fig. 9C–D). In high-temperature assemblages, early QTZ-FL lacks biotite, whereas later QTZ-KSP-MO locally contains brown biotite. At moderately high temperatures, the potassic alteration path for fluids above intrusive centers only rarely reaches the K-feldspar-biotite boundary as it evolves along small increments of a polythermal evolutionary path and the spatial sequence of assemblages (proximal to distal) in a single zoned envelope. Polythermal paths here are diagrammatic because the absolute position of the invariant point in activity space shifts as a function of temperature relative to a fixed origin. The topology of the diagram, which is all that is of interest here, remains similar for various temperatures, although the diagram was constructed at 400°C (within the range of moderate-temperature assemblages). Wide arrows describe the geochemical paths of packets of fluid that evolve in space and time (the fluid perspective), with a concomitant decline in temperature, for the two suites. Compositions of the initial fluids are presumed to be similar for the two suites of assemblages, although the fluids evolve along different paths. Thin, numbered arrows show the quasi-isothermal and -isobaric activity gradients from vein filling toward alteration front with fresh, K-feldspar-bearing wall rock, as deduced from the sequence of mineral assemblages in zoned alteration envelopes. Slopes of the narrow lines are schematic; they are drawn at shallow angles to activity-activity coordinate lines (Fig. 9, thin arrows).

**Fig. 9.** Evolutionary paths of fluids on schematic activity diagrams. This figure displays the contrasting paths for the two suites of assemblages and illustrates the similarity between the temporal sequence of assemblages (early to late) along small increments of a polythermal evolutionary path and the spatial sequence of assemblages (proximal to distal) in a single zoned envelope. Polythermal paths here are diagrammatic because the absolute position of the invariant point in activity space shifts as a function of temperature relative to a fixed origin. The topology of the diagram, which is all that is of interest here, remains similar for various temperatures, although the diagram was constructed at 400°C (within the range of moderate-temperature assemblages). Wide arrows describe the geochemical paths of packets of fluid that evolve in space and time (the fluid perspective), with a concomitant decline in temperature, for the two suites. Compositions of the initial fluids are presumed to be similar for the two suites of assemblages, although the fluids evolve along different paths. Thin, numbered arrows show the quasi-isothermal and -isobaric activity gradients from vein filling toward alteration front with fresh, K-feldspar-bearing wall rock, as deduced from the sequence of mineral assemblages in zoned alteration envelopes. Slopes of the narrow lines are schematic; they are drawn at shallow angles to $a_{K^+}/a_{H^+}$, but the actual paths are unknown. A and B portray equilibria in the vicinity of the invariant point involving K-feldspar (ksp), sericite (ser), and topaz (tpz), with separate diagrams for each suite. C and D depict equilibria involving K-feldspar (ksp) or sericite (ser), biotite (bio), andalusite (al), and topaz (tpz). Each diagram contains paths for both suites, but C applies to potassic (transitional to sodic) assemblages (i.e., $a_{K^+}/a_{H^+}$ sufficient to stabilize K-feldspar instead of sericite), whereas D shows sericite (rarely transitional to potassic and sodic) assemblages (i.e., $a_{K^+}/a_{H^+}$ appropriate for stability of sericite instead of K-feldspar, andalusite, or pyrophyllite).
toward the topaz field (Fig. 9C). For fluids on the flanks of the Seriate center, the path follows the K-feldspar-biotite univariant line toward higher $a_{\text{Fe}^2+} / a_{\text{H}^+}$ (Fig. 9C).

During sericitic alteration (Fig. 9D), the path for fluids above intrusive centers is not well constrained in the iron-bearing system, but it must have evolved to values of $a_{\text{Fe}^2+}/a_{\text{H}^+}$ that were low enough such that a fluid in the topaz field (Fig. 9D) could develop an outer sericitic envelope that replaced both magmatic K-feldspar and magmatic biotite (reaction path 1-1’). On the other hand, the path for fluids on the flanks of the Seriate center must have moved to higher values of $a_{\text{Fe}^2+}/a_{\text{H}^+}$, relative to the topaz-biotite-sericite invariant point in order to intersect the biotite field again. These fluids, while in the topaz field (Fig. 9D), developed zoned envelopes with outer zones of either sericite (reaction path 4-4’ with SER-MT) or biotite (reaction path 5-5’ with GREEN BIO).

A projection illustrating $a_{\text{Fe}^2+}/a_{\text{H}^+}$ and $a_{\text{K}^+}/a_{\text{H}^+}$ (Fig. 9A) shows that the GREEN BIO assemblage, which does rarely contain sericite, can be classified as a sericitic-type assemblage (Seedorff and Einaudi, 2004) because values of $a_{\text{K}^+}/a_{\text{H}^+}$ are appropriate for sericite, just as certain chlorite-bearing assemblages can be classified as sericitic (Seedorff, 1991).

The difference in the geochemical paths of the two suites probably can be accounted for largely by greater production of $\text{H}^+$ by fluids evolving above intrusive centers than by fluids evolving on the flanks of the Seriate center. Fluid inclusion data from high-temperature assemblages (Carten, 1987) suggest that concentrations of HCl, rather than H$_2$S, probably are most responsible for that difference. Concentrations of K$^+$ and Fe$^{2+}$ in the fluid may have been similar in both suites.

A field for albite appears upon consideration of the Na$_2$O component (Fig. 10B-C). Fluids above intrusive centers appear to have evolved at lower $a_{\text{Na}_2\text{O}}/a_{\text{H}^+}$ than fluids on the flanks of the Seriate center. The path for fluids above intrusive centers misses the albite field. Fluids on the flanks of the Seriate center straddle the albite-K-feldspar boundary at moderately high temperatures but leave the albite field upon forming the TPZ-MT assemblage, so the path reflects $a_{\text{Na}_2\text{O}}/a_{\text{H}^+}$ values lower than the albite-K-feldspar-sericite invariant point (Fig. 10B). The path locally reaches the sericite-albite boundary in the SER-MT assemblage (Fig. 10B) in the rare cases where both muscovite and albite occur together. The projection used in Figure 10C depicts equilibria involving topaz as well as K-feldspar, biotite, and albite. Path differences in terms of $a_{\text{K}^+}/a_{\text{H}^+}$ and $a_{\text{Na}_2\text{O}}/a_{\text{H}^+}$ (Fig. 10B) probably result from slight contrasts in the directions of flow for the two fluids relative to the orientation of isotherms.

**Mass transfer and topaz saturation**

Figure 11 summarizes the mass transfer that occurred during evolution of fluids associated with the two suites of assemblages. The alkalis underwent a complex history of mass transfer. In the suite above intrusive centers, sodrum probably was leached from the rock in all assemblages. On the other hand, it is unknown whether there was net removal or addition of sodium on the flanks of the Seriate center, the path follows the K-feldspar-biotite univariant line toward higher $a_{\text{Fe}^2+} / a_{\text{H}^+}$ (Fig. 9C).
the Seriate center. Above intrusive centers, potassium initially was leached at high temperatures in the QTZ-FL assemblage, then added to the rock in the QTZ-KSP-MO assemblage, and may have been added in the MOTTLED KSP-QTZ and MT-KSP assemblages. At moderate temperatures, potassium must have been strongly leached in the TPZ-PY assemblage, probably was slightly leached in the SER-PY assemblage (White et al., 1981, p. 305), and may have been slightly leached at low temperatures. The mass transfer of potassium as a function of declining temperature appears to be qualitatively similar in the suite formed on the flanks of the Seriate center.

The local presence of Na-rich feldspars in the suite formed on the flanks of the Seriate center raises the possibility that fluids that produced these assemblages followed a prograde thermal path (e.g., Hemley et al., 1980; Carten, 1986). Chessboard twinning, a characteristic of replacement of K-feldspar by albite during sodium metasomatism (Carten, 1986, p. 1502), has not been observed at Henderson. In contrast to the sodic-calcic and sodic assemblages that formed deep in the Yerington porphyry copper system (Carten, 1986), the sodic plagioclase-bearing assemblages at Henderson contain K-feldspar and biotite; hence, they are assigned to a transitional potassic-sodic type of alteration (fig. 7 of Seedorff and Einaudi, 2004). No magma was present to the deepest observed levels of exposure at the time when these assemblages formed; nonetheless, fluids may have been flowing toward the most recent intrusion. Because of the mineralogy and

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**Figure 11.** Schematic representation of mass transfer of nonore components and metals at Henderson. Single-headed arrows represent mass transfer of components between fluids and rocks during evolution of fluids along two evolutionary paths (shaded light and dark). The paths begin with injection of juvenile magmatic hydrothermal fluids and progress from proximal to distal products, diverging at higher temperatures and merging at low temperatures. The generalized evolutionary path above intrusive centers is most applicable to the Henderson and Seriate centers, as some assemblages failed to form above the Vasquez center.
space-time relationships, these fluids probably did not follow a strictly prograding thermal path, although they probably were flowing at low angles to isotherms. Sodic hydrothermal alkali feldspars, including ones of intermediate Na-K compositions, are reported by John (1989, p. 595, 598–599) in type 2 veins in the Park Premier system, and John (1989) concluded that they, too, do not represent a prograding thermal path.

Effects of temperature and solid solution in topaz and sericite on the evolutionary path are explicitly displayed in Figure 12, which is otherwise equivalent to Figure 9A and B. This analysis, utilizing compositions of topaz and homogenization temperatures from fluid inclusions, reveals that the entire path can be traced at nearly constant log \( \frac{a_{K^+}}{a_{H^+}} \approx -3 \), with the suite above intrusive centers following a path at slightly lower \( \frac{a_{K^+}}{a_{H^+}} \).

To enter the topaz field from the K-feldspar field following an isobaric path, a fluid must outrun an advancing front of topaz stability (Fig. 12). Migration of invariant points to higher values of \( a_{K^+}/a_{H^+} \) with a decrease in temperature from 600°C to 300°C is even more pronounced at lower pressures (Fig. 13). The effect of a decrease in pressure from 0.5 to 0.3 kbars, which is dramatic above 350°C, is highly effective at driving a fluid into the topaz field (Fig. 13). There is geologic evidence at Henderson for a decrease in pressure with evolution of the fluids (discussed above); decline in pressure (overpressured lithostatic to lithostatic, or lithostatic to hydrostatic) may have contributed to saturating the fluid with respect to topaz. The pressure effect on K-feldspar-sericite equilibria is minor (Fig. 13), indicating that a drop in temperature, not pressure, promoted change from potassic to sericitic alteration (Fig. 12).

A fluid would have a higher probability of saturating with respect to topaz if its initial fluorine content and its capacity to generate hydrogen ion were high. High initial magmatic fluorine contents at Henderson (Carten, 1987; Carten et al., 1988b) probably are most responsible for evolutionary paths that traverse from K-feldspar to topaz to sericite, i.e., evolve on the K-feldspar-topaz side of the migrating invariant point topaz-sericite-K-feldspar. In contrast, the paths for topaz-bearing deposits that are less fluorine rich than Henderson, such as Butte, Montana (Meyer et al., 1968; Howard, 1972), generally evolve from K-feldspar through sericite, andalusite, pyrophyllite, and/or kaolinite before saturating with respect to topaz, i.e., tend to evolve on the K-feldspar-sericite side of the invariant point (Seedorff, 1986).

Fluids on the flanks of the Seriate center entered the topaz field at an earlier stage in their evolution than fluids above intrusive centers (Figs. 2, 9–10, 12). One might expect, on the basis of the \( a_{K^+}/a_{H^+} \) values of the two paths (Figs. 9A-B, 12), that the fluids on the flanks were less, rather than more, acid than fluids above intrusive centers; further, these deeper fluids would tend to reach lower pressures later, rather than sooner, compared to the other suite. Processes that operated at moderately high and moderate temperatures, therefore, probably cannot explain the earlier appearance of topaz on the flanks of the Seriate center. This implies that the paths of the two fluids began to diverge at high temperatures or that the fluids on the flanks of the center may have been preferentially enriched in fluorine at the

![Figure 12. Temperature effect on geochemical evolutionary paths. Figure is produced by stacking phase diagrams for multiple temperatures. Locations of points that are plotted along the evolutionary paths for fluids that formed the two suites of mineral assemblages (Fig. 2) are based on homogenization temperatures of fluid inclusions and analyzed compositions of topaz from various assemblages (table 6 of Seedorff and Einaudi, 2004). Points are labeled with assemblages appropriate to the temperatures shown. The quantitative paths shown here in the stacked diagrams are equivalent to the schematic paths shown in the single diagrams of Figures 9A-B. Abbreviations are as in Figures 2, 9–10. Diagram uses proton avoidance model for solid solution in topaz (Barton, 1982), ideal site solution model for activity of hydroxyl muscovite, an average composition appropriate for sericite/muscovite from Henderson, and assumes unit activity and equilibrium state of order of K-feldspar. Diagram is plotted at P\(_T\) = P\(_{H_2O}\) = 0.5 kbar in the presence of quartz, activity of water = 1, and activity of OH muscovite in muscovite solid solution = -0.5. The composition of topaz solid solution at invariant points is insensitive to pressure.](https://pubs.geoscienceworld.org/segweb/economicgeology/article-pdf/99/1/39/3498427/39.pdf)
outset. The latter hypothesis is consistent with fluid inclusion results from high-temperature assemblages (Carten, 1987).

Fluorine was continuously added to wall rocks along the entire length of the evolutionary paths of fluids forming both suites of assemblages (Fig. 11), as fluorite was newly forming in every assemblage and significant fluorine was being fixed in numerous other hydrothermal phases, including topaz, mica, and garnet (Fig. 2). Although migration of hydrothermal fluids and their continual reaction with wall rocks caused fluorine to be widely dispersed, geochemical analyses indicate that the strongest fluorine enrichment is inside the Mo orebody and that, on the deposit scale, F content varies directly with Mo content (Bright, 1974).

Mineralogic evidence indicates that iron was leached as hydrothermal fluids evolved at high to moderately high temperatures—in wall rocks with low total iron contents. Above intrusive centers, iron was leached during formation of the QTZ-FL, QTZ-KSP-MO, and MOTTLED KSP-QTZ assemblages, as evidenced by destruction of magmatic magnetite and biotite and general absence of hydrothermal iron-bearing phases; iron was first added to the rock as magnetite in the MT-KSP assemblage and subsequently was fixed mostly as pyrite (Fig. 11). On the flanks of the Seriate center, leaching of iron terminated earlier in the evolutionary sequence (Fig. 11), as magnetite and Fe-bearing silicates began to be deposited in the BIO-KSP assemblage and were deposited in abundance in the TPZ-BIO-MT and TPZ-MT assemblages (Fig. 2).

On the scale of an individual vein, it is obvious from hand specimens and petrographic observations that wall-rock reactions between fluid and feldspar phenocrysts were important to precipitation of magnetite and pyrite, in a manner similar to the promotion of molybdenite deposition at high temperatures by wall-rock reactions between fluid and K-feldspar (Carten et al., 1988b). In turn, magnetite appears to have played a role in fixing sulfur in the rock, because iron sulfides (pyrite, pyrrhotite) that were deposited at intermediate to deep levels in the system at moderate and low temperatures were localized by interaction of fluids with precursor hydrothermal magnetite.

**Oxidation and sulfidation states**

Although the Henderson deposit does not contain a wealth of minerals that are useful for specifying oxidation and sulfidation states of fluids, coexisting minerals in assemblages (Fig. 2), when coupled with information on evolutionary paths and temperatures from fluid inclusion studies (Table 1), nonetheless provide important constraints (Fig. 14). Note that molybdenite does not occur in equilibrium with pyrite in either suite of assemblages (Fig. 2), although the two minerals commonly occur together in the same sample due to superimposed events at Henderson and were coprecipitated in many other porphyry deposits. For the suite above intrusive centers, pertinent observations are the following; pyrrhotite is not present; the transition from magnetite- to pyrite-bearing assemblages (at inception of deposition of the TPZ-PY assemblage) took place at approximately 450° to 500°C; hematite locally accompanies pyrite in the PY-CLAY and SPHAL assemblages; sphalerite occurs with chalcopyrite and

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**Fig. 13.** Pressure effect on topaz equilibria. All conditions, assumptions, and abbreviations of Figure 12 apply except for differences in pressures. If a point within the K-feldspar field at 400°C and the specified values of $a_{K^+}/a_{H^+}$ and $a_{F^-}a_{H^+}$ were subjected to an instantaneous drop in pressure from 0.5 to 0.3 kbars, its position would then lie well inside the stability field of topaz solid solution.
pyrite in the SPHAL assemblage; and rare barite has been observed in the SPHAL assemblage (but only in occurrences from high levels in the deposit).

For the suite on the flanks of the Seriate center, magnetite-bearing assemblages are relatively abundant, and pyrrhotite locally occurs at the transition from magnetite- to pyrite-bearing assemblages (Fig. 2). The temperature of deposition of the PO assemblage can be estimated, though only indirectly through its age relative to other assemblages whose temperatures are known (Table 1), as 350° to 400°C. The first deposition of pyrite-bearing assemblages (PY-CLAY) along this evolutionary path was at approximately 350°C. Although the two suites merged at low temperatures, the pyrite- and locally hematite-bearing assemblages that formed at low temperatures were deposited in relatively low abundances at intermediate to deep levels of the deposit (along the flanks of the Seriate center and in the vicinity of the Vasquez center) compared to above the Henderson and Seriate centers.

These constraints imply that the evolutionary path of fluids on the flanks of the Seriate center was more reduced in terms of sulfidation and oxidation states than the path of fluids above intrusive centers (Fig. 14). The more reduced path also evolved at a slightly higher temperature than the path of fluids above the Henderson and Seriate centers. The more reduced path also evolved at a slightly higher temperature than the path of fluids above intrusive centers (Fig. 14).

Space-Time Constraints on Introduction and Deposition of Metals

Mapped alteration-mineralization relationships that can be correlated in time across much of the deposit, as documented by Carten et al. (1988b) and Seedorff and Einaudi (2004), place important constraints on the timing of introduction and deposition of Mo, W, Pb, Zn, Cu, and Mn at Henderson, as shown in Figures 15 and 16.

Carten et al. (1988b) demonstrated that juvenile hydrothermal fluid was introduced at high temperatures and that Mo was deposited in numerous cycles, each corresponding to emplacement and crystallization of a mineralizing stock. Molybdenum largely remained in solution through formation of the QTZ-FL assemblage, but most of the Mo that was precipitated was deposited in the assemblage QTZ-KSP-PO (Figs. 2–4, 11, 15A-B, E, 16).

The metals deposited at moderate and low temperatures were precipitated principally from fluids in assemblages that formed above intrusive centers, which were more saline and followed the more oxidized evolutionary path (Table 1; Figs. 11, 14). Because of constraints provided by spatial correlation of temporal events at Henderson (Seeedorff and Einaudi, 2004), W was introduced at high temperatures by each mineralizing stock of the first two intrusive centers and remained in solution through formation of all high- and moderately high temperature assemblages, with minor exceptions (Fig. 2).

Tungsten was deposited primarily in the moderate-temperature assemblage TPZ-PY in one major event prior to intrusion of stocks of the Vasquez center, but deposition took place simultaneously in two zones (Seeedorff and Einaudi, 2004, table 7), one each over the Henderson and Seriate intrusive centers (Figs. 5, 15C). The paucity of moderately high and moderate-temperature assemblages (and thus W) in the Vasquez center remains problematic (see Seeedorff and Einaudi, 2004).

Similarly, Zn, Pb, and Cu were introduced at high temperatures by each mineralizing stock, and time lines suggest that these metals remained in solution, with minor exception (Fig. 2), through formation of all high-, moderately high, and moderate-temperature assemblages (Fig. 11). The metals Zn, Pb, and trace Cu were deposited primarily in the high-temperature assemblage SPHAL in one event after all 12 stocks were emplaced but in three discrete zones (Figs. 15F, 16; Seeedorff and Einaudi, 2004, table 7), one each over the Henderson and Seriate intrusive centers and Vasquez intrusive centers. The precipitation of galena and sphalerite only at low temperatures is expected from the solubility relationships of Pb and Zn (Hemley et al., 1992). Nonetheless, the high salinities of the associated fluids (Table 1) and discreetness of the three zones—in spite of their simultaneous formation—are remarkable.

In common with the other metals, Mn was introduced at high temperatures by each mineralizing stock. Although minor Mn was fixed in micas in various assemblages formed at higher temperatures, the low-temperature assemblages GAR and RHOD are the most important hosts of Mn (Figs. 2–4, 11; see also Seeedorff and Einaudi, 2004, table 6). There is a single zone of concentration of the GAR assemblage (Fig. 15G), which Seeedorff and Einaudi (2004) consider is probably related to evolution of fluids from the Henderson center.
The RHOD assemblage is widely distributed, forming a pattern reminiscent of the distribution and abundance of the SPHAL assemblage in three zones, although less clearly defined than those of the SPHAL assemblage (Figs. 3–4, 15C). The RHOD assemblage was deposited in one event after all 12 stocks were emplaced, immediately following deposition of the GAR assemblage, but from fluids that contained less than 29 wt percent NaCl equiv (Table 1).

**Assessing the Possibility of Recycling Ore Components**

Early-deposited metals conceivably can be hydrothermally leached, concentrated in the fluid, and reprecipitated, where there is extensive spatial overlap of different mineral assemblages in a single, evolving hydrothermal system or where there is extensive overlap of two temporally distinct, genetically unrelated hydrothermal systems. Considering the multiplicity of mineralizing intrusions at Henderson, the possibility that the ore metals (Mo, W) that were deposited prior to emplacement of the final intrusive center, Vasquez, were recycled warrants evaluation.

At Henderson, textural observations indicate that neither molybdenite grains, which mostly are related to the assemblage QTZ-KSP-MO, nor wolframite grains, which occur largely in the assemblage TPZ-PY, are generally affected where superimposed by alteration envelopes related to younger veinlets. Nonetheless, centimeter-scale redistribution of molybdenum is locally observed with the moderately high temperature, spatially restricted, assemblage MOT-TLED KSP-QTZ (Fig. 17A) and even more rarely where earlier molybdenite grains are overprinted by exceptionally intense versions of the moderate-temperature assemblage TPZ-PY (Fig. 17C-D). Most lower temperature assemblages contain no molybdenite (Fig. 2), and collectively they contain a very small fraction (<0.1 vol %) of the molybdenite in the entire deposit. Likewise, the patterns of abundance of younger alteration types show no effect on molybdenite grade patterns, on the scale of single 10-ft assay intervals or the scale of the deposit (Figs. 3–4). One of the most clear cases is where isopleths of the greatest abundance of the TPZ-PY assemblage on the 490-H section cut across molybdenite grade isopleths at high angles without any change in molybdenite grade in an area with grades >0.7 percent.

**Origin of sericitic and intermediate argillic alteration**

The potassic-sericitic transition has a rich mineralogic record at Henderson compared to many other porphyry-related deposits (e.g., presence of feldspars, micas, and topaz, all of variable composition). This record permits closer monitoring of geochemical conditions across this transition at Henderson than does the mineralogy of Transitional-stage quartz sulfide B veins at many porphyry copper deposits. Interpretations of the onset of sericitic alteration generally call on the incursion of low-temperature, low-salinity meteoric water (Sheppard et al., 1971; Hall et al., 1974; Gustafson and Hunt, 1975; Mutschler et al., 1981; Westra and Keith, 1981; Beane, 1983). Some invoke quasi-isothermal changes in a K+/H+ of an evolving fluid (Beane and Tittley, 1981, p. 260) and others call upon renewed influx of juvenile magmatic fluids, albeit of a different character than earlier juvenile fluids (Hedenquist et al., 1998; Muntean and Einaudi, 2001, fig. 17). These interpretations are not applicable to Henderson, where phase equilibrium suggest heat and hydrothermal fluids followed essentially constant values of aK+/aH+ and that the potassic to sericitic transition largely was promoted by a decline in temperature. Furthermore, fluid inclusion results indicate that fluids that evolved above intrusive centers were saline during sericitic alteration and remained saline into intermediate argillic alteration. This persistence of high-salinity fluids suggests that Henderson is likely among the most magmatic water-dominated porphyry systems documented to date and that incursion of meteoric water probably was not an important factor in the potassic to sericitic transition (which is supported by reconnaissance stable isotope analyses; M. Barton and E. Seedorff, unpub. data, 1989).

**Discussion and Application to the Origin of Porphyry Systems**

**Geologic significance of fluid inclusion data**

Early veins in porphyry systems, which have textures and mineral assemblages that are indicative of high (>500°C) temperatures, contain fluid inclusions of inferred primary origin that commonly show a wide spread in homogenization temperatures from >550°C to <350°C (e.g., Almald and Rose, 1980, fig. 6; Bloom, 1981, fig. 2; Bowman et al., 1987, fig. 6). Numerous possible explanations for this variability have been offered (e.g., Bodnar and Beane, 1980, p. 883–884; Almald and Rose, 1980, p. 239). This investigation indicates that the inability to identify unambiguously those fluid inclusions that are related to the geologic event of interest likely is a major cause of variability in homogenization temperatures, although some workers have downplayed this possibility (Ahmad and Rose, 1980, p. 242; Bloom, 1981, p. 1915–1916).

Samples—even those as small as thin section billets—from porphyry deposits generally contain mineralogical and textural evidence of two or more events, even when samples chosen for fluid inclusion study are selected with great care (Fig. 7). Hence, a cloud of uncertainty hovers over any fluid inclusion measurement to a specific geologic event. On geologic grounds it can be argued—as is done here for some samples—that all of the fluid inclusions measured in a given sample could be related to later, commonly lower temperature, events rather than the targeted assemblage (Fig. 5, Table 1). Because many measured fluid inclusions may not represent the fluid of interest, early, high-temperature alteration-mineralization events in some porphyry deposits probably formed at much higher temperature than those that have been inferred by other workers (e.g., Climax: Hall et al., 1974, table 5). The underlying causes of preserving, modifying, or destroying fluid inclusions in porphyry-related deposits in general are imperfectly known.
different types of porphyry deposits and between different examples of each type, in part depending on timing of ingress of external fluids. The mineralogy of Henderson, its moderate sulfide content, abundance of halite daughter minerals in fluid inclusions related to sericitic alteration, and lack of evidence for high sulfate content imply that Henderson was a relatively low sulfate, high chloride, fluoride-bearing magmatic hydrothermal system. Sericitic alteration at Henderson may be regarded as the chloride-fluoride fluid end member among porphyry deposits, which generated only a moderate volume of sericitic alteration.

Degree of recycling of ore components

Centimeter-scale redistribution of copper inside sericitic and advanced argillic envelopes is observable in most porphyry copper deposits, but the process rarely has been proven to be a significant ore former at the deposit scale, in part because alteration envelopes of given vein sets commonly do not sufficiently overlap and coalesce. The most convincing case for remobilization has been made at Butte, based on the geologic relationship (e.g., Brimhall, 1979, fig. 13, p. 582) and subsequent lithologic analysis and theoretical modeling (Brimhall,
1979, 1980; Brimhall and Ghiorso, 1983; Woitschekowskaya and Hemley, 1995) that demonstrate the thermodynamic validity and mass-transfer efficacy of such a process in forming Main-stage ore by hypogene dissolution, deposit-scale transport, and redeposition of pre-Main-stage Cu.

Evidence is lacking for either leaching or deposit-scale recombination of Mo or W by any younger assemblages at Henderson (Fig. 47). The contrasting importance of hydrothermal recycling of metals at Butte versus Henderson can be rationalized on two accounts. First, the metals deposited relatively early and at high to moderate temperatures at Henderson, Mo and W, are less soluble at moderate temperatures than is Cu (e.g., Wood et al., 1987; Wood and Vlassopoulos, 1989; Wood and Samson, 1998); indeed, molybdenite apparently was inert at Butte (Brimhall, 1979, p. 582). Second, the fluids at Henderson and many other porphyry-related deposits worldwide did not evolve to conditions characteristic of advanced argillic alteration (Fig. 12), which, even for Cu, may be required for effective leaching and redeposition of earlier deposited metals (Brimhall and Ghiorso, 1983; Brimhall, 1989).

**Timing of magmatic volatile fluxing into the environment of deposition**

Inspired by numerical models of magmatic fractionation processes (e.g., Candela, 1989; Cline and Bodnar, 1991), numerous recent authors have called upon varying compositions of progressively evolved juvenile magmatic hydrothermal fluids to account for different hydrothermal mineral assemblages or veins formed over time. For instance, Dilles and Profetti (1995) proposed that multiple influxes of juvenile fluids with variable initial compositions may account for differences in metal ratios in successive vein generations within the same intrusive center at the Ann-Mason porphyry copper deposit.

Alternatively, such variations might be explained by evolution of fluids within the environment of deposition, without new influxes of juvenile fluid. Notwithstanding the conflicting interpretations of the mechanism for volatile concentration and initial Mo concentration of magmas and fluids in porphyry molybdenum deposits (Carter et al., 1988a, b; Keith and Shank, 1988; Lowenstern, 1994; Shinozuka et al., 1995),

**Fig. 15.** Seven, nearly instantaneous and two cumulative time panels, showing development of metal zones on bent section 52N-N63E-58N, emphasizing decoupling of introduction of components by juvenile magmatic hydrothermal fluids released from various stocks and deposition of the metals Mo, W, Pb-Zn, and Mn. Compare to present-day distribution pattern of Figure 4. Panels A through G represent a sequence of fairly narrow time intervals. Filled black circles in panels A, B, and E correspond to centers of ore shells formed by each mineralizing stock (numbered); sizes of filled black circles are scaled to Mo content of ore shells. Panels A, B, and E show introduction of fluids at high temperature from the apex of each intrusion; directions that fluids were injected for the principal mineralizing intrusion in each intrusive center, based on orientation and abundance of high-temperature veins, are shown by open white arrows. Juvenile magmatic hydrothermal fluids were sourced from individual stocks of the three intrusive centers but coalesced at high to moderately high temperatures into more diffusely defined reservoirs where fluids were reacting with rocks about the three centers, Henderson (H), Seri- ate (S), and Vasquez (V). Panels C, D, F, and G are a series of snapshots that capture the location of the reservoirs, which migrated slowly over time concurrent with evolution of fluids in temperature and composition and formed zones of concentration of other metals as temperature declined. Open symbols of various shapes, filled with letter abbreviations of elements, are placed at the center of each metal zone, as in Figure 4. The distribution of the SER-PY assemblage is inserted in its proper temporal position between W and Pb-Zn to provide continuity of spatial patterns because of relatively large-time gap between deposition of W and Pb-Zn. A. Mo zone for Henderson intrusive center, showing upper limit of molybdenite. This Mo zone is a composite feature produced by successive, discrete periods of introduction of metal by successively emplaced stocks (primarily Phantom, Henderson, and Primos; contributions from Berthoud and Arapaho are negligible), with formation of each stock's ore shell prior to emplacement of next stock. B. Mo zone for Seriate intrusive center, showing upper limit of molybdenite. Seriate ore zone was produced by successive, discrete periods of introduction of metals and deposition of Mo upon emplacement and cooling of East Lobe, Seriate, Ruby, and Nystrom stocks. C. Essentially simultaneous deposition of two, partially coalesced W zones, one each related to Henderson and Seriate centers. D. Distribution of two, partially coalesced zones of concentration of the SER-PY assemblage that formed essentially simultaneously. E. Mo zone for Vasquez center, produced almost solely by introduction of metals and deposition of Mo upon emplacement and cooling of Vasquez stock (negligible contributions from the Dalley and Ute stocks, whose locations are poorly known, are not shown). F. Deposition of three, remarkably distinct Pb-Zn zones, one each related to the Henderson, Seriate, and Vasquez centers. These three are interpreted to have formed essentially simultaneously, as isotherms collapsed across the three reservoirs of evolved magmatic hydrothermal fluids. G. Deposition of three, partially coalesced Mn zones. Highest Mn zone, interpreted to be related to the Henderson center, is a composite of subequal contributions from the GAR and RHOD assemblages; note that the RHOD is superimposed on the GAR and that on the eastern side of the section the upper limit of the younger RHOD assemblage is below the upper limit of the GAR assemblage. Two lower Mn zones, related to the Seriate and Vasquez centers, are related primarily to the RHOD assemblage. All three RHOD zones formed essentially simultaneously. H. Time-integrated view showing inferred flow paths of fluids. To aid visualization of the two-dimensional migration paths of fluids that deposited the various metal zones through time, the labels for each zone are linked by lines, with arrows showing the order in which the patterns developed, one path for each intrusive center. The Henderson path changes little during formation of the Mo and W zones, then migrates upward as the SER-PY assemblage is formed, then farther upward and easterly until the Pb-Zn zones formed, then descended slightly as the Mo zone formed during deposition of first the GAR and then the RHOD assemblage. The Seriate path migrates upward from Mo to W to SER-PY—although not as much as in Henderson, then collapses downward as the Pb-Zn and Mn zones form. The Vasquez patterns are weakly developed and show minimal migration. I. Summary diagram showing sites of introduction of fluids and metals and deposition of Mo at high temperature (from panels A, B, and E) and deposition of a representative low-temperature zone (Pb-Zn from panels F), emphasizing the similarity in timing of shapes of metal zones formed at low temperature with the shapes of the high-temperature ancestors from which they evolved. The Henderson patterns are displaced from, but broadly mimic the shape of the, ore zone of the Henderson center. The Seriate metal patterns tend to retain the donkey ears shape of the ore shell related to the Seriate stock. The Vasquez patterns are crudely donal.
Fig. 16. Simplified evolutionary tree and space-time diagrams for Henderson, showing decoupling of the introduction of components by juvenile magmatic hydrothermal fluids by various stocks and successive deposition of the metals Mo, W, Pb-Zn, and Mn. Diagrams are recast from figures 12 and 13 of Seedorff and Einaudi (2004), with conversion of assemblages to alteration types in both diagrams and addition of inferred temperature contours based on fluid inclusion temperatures of this study. A. Evolutionary tree diagram shows the geochemical evolutionary paths, keyed to alteration types, and various metal depositional events. Inset shows general trajectory of fluids in each intrusive center. B. Space-time diagram shows evolution of mineral assemblages along a vertical line in the center of the hydrothermal system along cross section 52N-N63E-58N, showing inferred flow paths of fluids and formation of the multiple spatial zones: numerous for Mo, two for W, and three each for Pb-Zn and Mn. Note that multiple zones of metal concentration of metals deposited at moderate to low temperatures (W, Pb-Zn, and Mn) formed during essentially one depositional event for each metal.
The field relationships at Henderson documented by Carten et al. (1988a, b) regarding the introduction of components and timing of formation of high-temperature Mo-bearing veins are clear: fluxing of magmatic volatiles into the environment of deposition must have been nearly instantaneous. Introduction of components was inversely proportional to the level of crystallization of the stocks—greatest for crystallization of the apex of the stock where brain rock is present (e.g., Carten et al., 1988b, Figs. 9–10) and complete by the time each stock had crystallized downward to the lowest layer of unidirectional solidification textures only ~200 m below the apex of each intrusion. The rock beneath the last unidirectional solidification textures layer has no aplitic groundmass, is hypidiomorphic granular, and is remarkably fresh and free of veins (Carten et al., 1988b).

Temporal relationships established at Henderson imply that all metals contained in lower temperature assemblages (e.g., W, Pb, Zn, and Mn) were introduced synchronous with...
Mo, as discussed above (Fig. 16). An influx of a W- and F-rich fluid—distinct from the fluids that produced Mo ore shells—to form the wolframite-bearing TPZ-PY assemblage and related W halo at Henderson can be ruled out, as no evidence has been observed that juvenile magmatic hydrothermal fluids were entering the environment of deposition when the most abrupt shift in the Mo/W ratio of veins occurred between formation of the Mo ore shells of the Nystrom and Vasquez stocks (initial deposition of the TPZ-PY assemblage). Similarly, juvenile fluids also were not entering when the large shift in Zn/Mn ratios of veins occurred during the onset of deposition of the RHOD assemblage (Fig. 16).

Our suggestion that metals deposited at moderate to low temperatures (W, Pb, Zn, and Mn at Henderson but including Mo in many porphyry copper systems) are introduced at high temperatures with the metals that are deposited at high temperatures (Mo at Henderson, but Cu ± Au in porphyry copper deposits) is consistent with microanalysis of fluid inclusions from porphyry deposits. For example, high-temperature fluid inclusions associated with ore at Bingham, Butte, Grasberg, and Bajo de la Alumbrera have Pb, Zn, and Mn concentrations that are as much as an order of magnitude higher than the concentrations of Cu (Anderson et al., 1989; Bödner, 1995; Heinrich et al., 1999; Ulrich et al., 1999, 2001), even though Pb, Zn, and Mn minerals are not reported in more than trace amounts in the associated high-temperature mineral assemblages. Virtually all metals ultimately deposited in the system probably were present in the high-temperature fluids.

Although it is tempting to assume that components deposited at lower temperature (or later) were introduced later than components deposited at higher temperature (or earlier), we attribute changes in metal ratios in successive vein sets at Henderson to thermal and compositional evolution of previously introduced magmatic fluids (see below) and suggest that other porphyry-related systems may have behaved similarly.

Change in composition of juvenile magmatic fluid evolved over time

Only slight variations are observed in the sequences and abundances of lower temperature assemblages formed above the Henderson and Seriate centers. For example, brown biotite is more abundant in the QTZ-KSP-MO and MT-KSP assemblages around the Seriate center than around the Henderson center, and hydrothermal garnet is present in a distinct, low-temperature garnet-rich assemblage (GAR) above the Henderson center but is a minor component of many moderately high to low-temperature assemblages around the Seriate center (Fig. 2; Seedorff and Einaudi, 2004). The similarity in assemblages developed around the two centers suggests minimal change in the initial compositions of juvenile hydrothermal fluids introduced by stocks of the Henderson versus the Seriate center.

The initial compositions of fluids ultimately may have changed upon initiation of the Vasquez center, because moderately high and moderate-temperature assemblages and W mineralization are nearly absent above the Vasquez center, and low-temperature assemblages occur in distinctly lower abundances there than above the Henderson and Seriate centers (Fig. 3; Seedorff and Einaudi, 2004). Initiation of the Vasquez center coincides with a district-wide shift in composition of intrusive rocks from the potassic series to the sodic series of Carten et al. (1985b, p. 276-284).

The near absence of moderately high and moderate-temperature assemblages above the Vasquez center is perplexing; perhaps the initial composition of these fluids was less acidic than the Henderson and Seriate fluids, permitting the Vasquez fluids to miss the sericite and/or muscovite field upon cooling. An analogous situation has been observed at the Buffalo Valley deposit, a porphyry copper system with late veins that was mined for gold. There, late dikes that contain secondary biotite (though barren of copper) are cut by gold-bearing pyrite veins that lack alteration envelopes (Seedorff et al., 1991), which would be roughly comparable to a hypothetical sequence at Henderson of a fluid skipping directly from the QTZ-KSP-MO to the SPHAL assemblage.

Hence, changes in initial composition of fluids over time at Henderson probably are slight and occur on time scales comparable to the emplacement of several intrusive centers. If the Henderson interpretation were applied to other porphyry districts, such as Yerington (Dilles, 1987; Dilles and Proffett, 1995; Dilles et al., 2000b), the analogy would be that changes in the composition of fluids derived from a large evolving magma chamber may account for differences between intrusive centers, such as differences in metal content between the Yerington deposit (mineralized with Cu but virtually free of Mo) and the Ann-Mason deposit (a Cu-(Mo) deposit).

Mode of release of magmatic hydrothermal fluids between intrusive centers

The majority of juvenile, Cl-rich hydrothermal fluid released from the apices of intrusions at Henderson generally escaped upward, marked by high-temperature, steep, generally thin, radial replacement veinlets (Carten et al., 1985a, b). We conclude that these same fluids (samples of which are trapped in high-temperature fluid inclusions; Carten, 1987) evolved to form the suite of lower temperature assemblages above intrusive centers. Fluid inclusion results (Table 1) indicate that the fluids remained highly saline from potassic through intermediate argillic alteration.

In contrast, a significant fraction of the fluid released from the apex of the Seriate stock was injected downward and outward from the apex, because of the bulletlike geometry of the stock and fluid pressures in excess of lithostatic (Carten et al., 1985a, b). This mode of fluid release is marked by high-temperature, gently outward dipping concentric, open-space and replacement veins, with the open-space veins tending to be wide. Fluids that were injected downward and outward evolved to form the distinctive suite of lower temperature assemblages on the flanks of the Seriate center (Figs. 2–3, 16). The suite is characterized by less-saline fluid inclusions (Fig. 7, Table 1), produces contrasting mass transfer effects (Fig. 11), and defines an evolutionary path at different sulfidation and oxidation stages and cation activity ratios than fluids above intrusive centers (Fig. 14). Fluids on the flanks of the Seriate center could represent evolved versions of the low Cl, F-rich, Fe- and K-bearing aluminosilicate fluid inclusion population.
observed in high-temperature veins (Carten, 1987; R. B. Carten, pers. commun., 1987).

The Henderson case suggests that the mode of accumulation and release of magmatic hydrothermal fluids from the apices of mineralizing intrusions influences their subsequent evolution and is a source of diversity of hydrothermal mineral assemblages. Other porphyry deposits that have both high-angle radial and low-angle, outward-dipping, high-temperature veins might also display contrasting paths of fluid evolution related to different vein sets.

**Evolution of hydrothermal fluids, deposition of components at moderate and low temperatures, and origin of metal zonation**

Porphyry deposits typically involve a series of porphyry intrusions and a complex sequence of hydrothermal mineral assemblages and associated metals. At Henderson, there were numerous periods of Mo deposition at high temperatures during intense potassic alteration in multiple ore shells related to separate stocks, one significant W depositional event at moderate temperatures primarily in a topaz-bearing sericitic assemblage in two zones above the Henderson and Seriate centers, and one Pb-Zn and Mn depositional event at low temperatures during intermediate argillic and carbonate alteration above each of the three intrusive centers (Fig. 16). Hence, the temporal sequence of metal deposition with decrease in temperature at Henderson is Mo, followed by W, then Pb + Zn ± (Cu), and finally Mn (Figs. 15–16). The spatial arrangement of metals from proximal to distal depends in part on the flow directions of fluids over time, but the zonation patterns commonly, but not in every case (exceptions are where arrows turn downward in Fig. 15H), mimic the temporal sequence of deposition, i.e., proximal Mo, followed by W, then Pb + Zn ± (Cu), and distal Mn.

The deposition of Pb and Zn at low temperatures at Henderson is particularly instructive. Pb and Zn were deposited principally in the SPHAL assemblage in essentially a single event at low temperatures but in three separate spatial zones (Figs. 15F, 16). Each Pb-Zn zone can be readily related to the migration of fluids from each of the three intrusive centers (Fig. 15I); Pb and Zn remained in solution during protracted evolution of these fluids, while higher temperature assemblages developed, until the temperature declined to 380 to 200°C (Fig. 16, Table 1). Magmatic hydrothermal fluids released from the Seriate and Henderson stocks were the principal sources of Pb-Zn, even though all Pb-Zn zones formed after emplacement of the younger stocks of the Las Vegas center. As suggested by Wallace et al. (1978, p. 347–348) and M. D. Barton (pers. commun., 2001), cooling of the principal host rock (Urad porphyry), rather than cooling of the host, but smaller, mineralizing stocks, may have controlled deposition of low-temperature mineral assemblages and metals.

The sequences and patterns of metal deposition differ only slightly between different intrusive centers at Henderson (Fig. 15). Although there is variation, the sequences and patterns of metal deposition tend to be similar between deposits of the same type (e.g., between Climax-type porphyry molybdenum deposits). Greater differences in the sequence and pattern of metal deposition are observed between different types of porphyry deposits. For example, the relative spatial positions of Mo versus W and of Mo versus Cu at the Turquoise Gulch porphyry copper deposit at El Salvador (Gustafson and Quiroga G., 1995, p. 12) are both reversed from those documented at Henderson. We suggest that, in spite of these variations, the operative processes of metal introduction and deposition may be similar among porphyry-related deposits.

The Henderson case emphasizes the distinction between the processes of introduction and deposition of components during primary dispersion (see also Hemley and Hunt, 1992, p. 40). Fluids evolve in the environment of deposition as they migrate—rising upward, collapsing downward, and flowing inward or outward—by reacting with wall rocks, boiling, mixing with other fluids, and cooling. A variety of processes are potentially involved, but some degree of spatial (and temporal) separation between the site (and time) of introduction of components and the eventual deposition of various metals is expected as fluids evolve. The separation results from different initial concentrations of the various metals, solubilities of metals, water/rock ratios, and solubility responses to changes in temperature, pressure, and composition of fluids (Hemley et al., 1967, 1986, 1992; Barnes, 1975, 1979; Hemley and Hunt, 1992; Reed, 1997). As a result, the youngest intrusion cut by a given mineral assemblage is not necessarily the only, or even dominant, source of magmatic components deposited in that assemblage, as at Henderson. The same may be true at other porphyry deposits where metals deposited at low temperature (and late) commonly have been interpreted as having been introduced at the time of late intrusions (e.g., Late Barren stage at Climax, Wallace et al., 1968; late Sn-Pb-Zn-Cu mineralization at Mt. Pleasant, Kooiman et al., 1986; relatively late Mo at Bingham, Redmond et al., 2001). Decoupling of the introduction and the deposition of components deposited at low temperatures, such as Pb, Zn, Mn, Ag, and Au, may be most pronounced in porphyry districts that have well developed distal halos of these metals, such as Bingham (Babcock et al., 1995), Butte (Meyer et al., 1968), and Yauricocha (Petersen, 1965; Alvarez and Noble, 1988).

**Degree of decoupling of introduction and deposition of metals as a geochemical classification tool in porphyry deposits**

The evidence that the majority of Mo at Henderson was deposited at high temperatures is compelling: most molybdenite is in veinlets with K-feldspar envelopes; veinlets exhibit a strong spatial and temporal relationship to crystallization of individual mineralizing stocks; and Mo-grade contours are closely spaced and geometrically related to apices of stocks (Carten et al., 1988b; Seedorff and Einaudi, 2004, figs. 2–3). This relationship seems to hold for other Climax-type deposits.

Mineral assemblages, crosscutting relationships, and grade distributions are less well documented in most porphyry copper deposits, but the deposition of Cu tends to be less restricted to a single assemblage or vein type. The relative timing and temperature of Cu deposition in most porphyry copper deposits is controversial. One view (Fig. 15A) holds that most of the Cu is deposited relatively early, at relatively high temperatures (commonly >400°C) as chalcopyrite ± (bournite + digenite) ± magnetite synchronous with potassic
alteration (e.g., Hemley and Hunt, 1992; Gustafson et al., 1999; Dilles et al., 2000a), resulting in the orebody being largely within the zone of potassically altered rocks. This view is supported by studies of deposits such as Bingham (Atkinson and Einaudi, 1978; Phillips et al., 1997; Redmond and Einaudi, 2000). El Salvador (Gustafson and Hunt, 1975; Gustafson and Quiroga G., 1995), Yerington (Proffett, 1979; Carten, 1986; Dilles et al., 2000b), Dos Pobres (Langton and Williams, 1982), Lakeshore (Huyck, 1990), and Bajo de la Alumbrera. Each view may be correct at the deposits in question. If Cu is of magmatic origin and all three views are correct in at least some deposits (Fig. 18), then we suggest that differing initial compositions of fluids and contrasting evolutionary paths between deposits may produce differing relative amounts of separation in space and time between introduction and deposition of a single component (Cu), just as evolution of hydrothermal fluids with decline in temperature produces separation in space and time of different metals in a given deposit such as Henderson. As a first step, the degree of decoupling between introduction and deposition of Cu might be used as a geochemical classification tool for well-studied deposits. The observational underpinnings of past attempts to model deposit-scale zoning (e.g., Barnes, 1975) understate the diversity of deposition of metals in porphyry deposits (Fig. 19). Hence, the abundance, timing of deposition, and spatial distributions of Mo and Au relative to Cu in various
Deposition of topaz, geochemical paths, and similarities of alteration-mineralization with other deposits

Nowhere at Henderson is topaz present in high-temperature assemblages of the silicic and intense potassic types, which contain the vast majority of molybdenite. Saturation with respect to topaz occurred subsequently upon decrease in temperature and may have been promoted by a decrease in pressure. In both suites of assemblages, the evolutionary paths of fluids eventually passed again into the topaz-absent field during sericitic and intermediate argillic alteration.

In the suite of assemblages that formed above intrusive centers at Henderson, topaz was deposited almost exclusively in a single, sericitic-type assemblage. This suite is similar to alteration-mineralization assemblages of many porphyry molybdenum deposits associated with high-silica rhyolites, including Urad, Climax, and Questa (Table 2), although the key minerals magnetite, topaz, and fluorite are not all reported from each deposit.

In the suite of assemblages formed on the flanks of the Seriate center, the flanks of the Seriate center (Table 2). Those deposits contain abundant biotite, in part coexisting with topaz, but the associated fluids had even lower oxidation and sulfidation states than fluids on the flanks of the Seriate center. Most of the above deposits are granite-related Mo deposits of the high-silica rhyolite-alkaline suite of Carten et al. (1993).

Carten et al. (1993) also defined two other types of porphyry molybdenum deposits, granite-related Mo deposits of the differentiated monzogranite suite (e.g., Quartz Hill, Endako, Cannivan Gulch, and East Kounrad) and granite-related Mo-Cu deposits (e.g., Mount Tolman, Hall, Buckingham, El Crestón (Opodepe), Cumobabi, and Mocoa). These two types of porphyry molybdenum deposits generally lack hydrothermal topaz. Although a few of those deposits contain fluorine anomalies and accessory fluorite (e.g., Hall: Shaver, 1986, 1991), most tend to be fluorine poor (Theodore and Menzie, 1984; Carten et al., 1993). Their alteration-mineralization products do not have much in common with either suite of assemblages at Henderson and have greater similarity to alteration-mineralization in porphyry copper deposits or tin-tungsten vein and greisen deposits.

The similarities and contrasts between deposits and in different parts of the Henderson deposit underscore the importance of defining the geochemical environment of wall-rock alteration and ore deposition on the basis of mineral assemblages as a step toward systematization and classification of mineral deposits.

Conclusions

1. A geologic evaluation of the fluid inclusion results suggests that we failed to gather data for several of the hydrothermal mineral assemblages that were targeted (i.e.,
inclusions measured were unrelated, secondary inclusions). The moderately high temperature group of assemblages probably formed at 600° to 400°C, the moderate-temperature assemblages at 530° to 310°C, the low-temperature assemblages at 390° to 200°C, and propylitic alteration at 320° to 210°C. The fluid inclusions from the suite of assemblages formed on the flanks of the Seriate center generally are not halite saturated, whereas many of the inclusions related to assemblages formed above intrusive centers commonly contain halite (± sylvite). High salinities persisted through sericitic and intermediate argillic alteration, indicating lack of significant dilution by meteoric waters during this portion of the evolution of hydrothermal fluids.

2. Phase equilibria indicates that fluids followed essentially constant $a_{K^+}/a_{H^+}$ during the transition from potassic to sericitic alteration, such that the transition was promoted by a decline in temperature, consistent with the fluid inclusion results.

3. Fluorine was continuously added to wall rocks along the entire evolutionary paths of both suites of assemblages. The alkalis underwent a complex history of mass transfer, with the behavior of potassium fluctuating between periods of strong leaching and strong addition to the rock. Iron was leached at high to moderately high temperatures and then fixed in the rock at lower temperatures.

4. There is no evidence of deposit-scale leaching or redistribution of Mo or W during evolution of the hydrothermal system.

5. Integration of space-time relationships indicates that metal-bearing volatiles could have been fluxed into the environment of deposition only during the crystallization of the tops of mineralizing intrusions.

6. Compositions of juvenile hydrothermal fluids were similar between successive mineralizing stocks through stocks of the Henderson and Seriate intrusive centers but may have changed upon initiation of the Vasquez center.

7. A significant fraction of the fluid released from the Seriate stock was injected downward and outward from the apex along gently outward-dipping, concentric veins. These fluids evolved to form a distinctive suite of lower temperature assemblages on the flanks of the Seriate center.

8. Metals deposited at moderate to low temperatures (W, Pb-Zn, and Mn) were introduced synchronous with Mo at high temperatures but were not deposited until fluids evolved to lower temperatures. The delayed deposition of some metals relative to others, coupled with flow of fluids, led to a spatial zonation. There was progressively greater decoupling between the times of introduction and deposition of metals from those deposited at high temperatures (e.g., Mo) to those deposited at low temperatures (e.g., Mn). This time delay lengthened for metals introduced by an earlier intrusion compared to the same metal introduced by a later intrusion. The degree of decoupling of introduction and deposition of metals may be useful as a classification tool in porphyry copper deposits.

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Exploration, development, and mine geologists at the Urad and Henderson mines made this study possible; Will White, Rick Carter, Bob Kamilli, and Bruce MacKenzie deserve special note in the context of this paper. Judy Hannah, Jeff Keith, Mark Hammington, Carten, Gail Mahood, George Parks, Mark Barton, Dave John, Mark Sander, Paul Zweng, and Holly Stein read various sections and versions of the manuscript and catalyzed its improvement. The phase equilibria involving topaz was made possible by Barton’s experimental work, and he helped make the thermodynamic data set used in this work internally consistent. This study benefited from the assistance of Dennis Bird, Don Burt, Mike Gutierrez, Ken Jackson, and Perfecto Mari and discussions with Frank Mazdab. We extend special thanks to Carten, John, Barton, John Dilles, Lew Gustafson, John Proffett, Jeff Keith, and Steve Shaver for their decades of contribution to our inquiry into the origin of porphyry deposits. Seedorff acknowledges Rick Carter’s unwavering professional support, mentoring, and generosity.

<table>
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<td>Pine Grove, Utah</td>
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TABLE 2. Alteration-Mineralization Suites at Henderson Compared to Other Deposits
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Sample selection

Samples for fluid inclusion investigation were sought that represented a minimum number of geologic events. Detailed petrography was conducted on 36 doubly polished wafers of the most promising samples. Microthermometric measurements were conducted on 14 wafers, the locations of which are shown in Figure A1, resulting in data on 300 fluid inclusions.

Methodology

Microthermometric studies of fluid inclusions were performed on a Fluid Inc. modified version of the USGS gas-flow heating/freezing system calibrated with synthetic fluid inclusions and operated using standard techniques (Roedder, 1984, p. 196–201). The combined errors of thermocouples, temperature indicators, and thermal gradients in the sample chamber limit the estimated accuracy of homogenization temperatures to ±2° at 200°C to approximately ±10° at 600°C (e.g., Fasteris, 1983; Smith, 1983; Bodnar et al., 1985, p. 1864). Uncertainties in laboratory measurements used to calculate salinity from salt daughter mineral dissolution and freezing temperatures probably are a few percent. The conversion of those data to salinity using model chemical systems typically introduces considerable uncertainty, although it is minimal for Henderson et al. (1983; Smith, 1983; Bodnar et al., 1985, p. 1864). Uncertainties in temperature and salinity. Samples are described in greater detail in Seedorff (1987, app. B). Documentation of each run and additional information on fluid inclusion procedures are contained in Seedorff (1987, app. C).

Classification

The various types of fluid inclusions that were observed, based on the identity of contained phases and their behavior upon heating, are shown at the bottom of Figure 7. The shapes of fluid inclusions range from irregular to negative crystal forms (the latter are common); the usual precautions were taken to avoid fluid inclusions that may have necked off. For the 300 fluid inclusions for which microthermometric data were obtained, the range in sizes (max dimension; 1-µm size intervals) is 4 to 29 µm, the mean is 9.5 µm, the median is 8 µm, and the mode is 6 µm.

The criteria of Roedder (1984, p. 43–45) were used as a guide to classify the origin of fluid inclusions as primary, pseudosecondary, or secondary, except that large size and negative crystal shape were not used as criteria for primary fluid inclusions because these attributes characterized many inclusions that clearly are of secondary origin. The material available in this study, however, precludes objective assignment of many fluid inclusions to any category with confidence, in part because of the absence of growth zoned minerals in the veinlets of interest and because of the high abundance of (mostly small) fluid inclusions. Although all of the fluid inclusions hosted by quartz phenocrysts probably are of secondary origin, fluid inclusions were termed secondary only if they could be assigned to a planar array with the characteristics noted by Roedder (1984). For many fluid inclusions, including those hosted by vein-filling minerals, it is difficult to decide to which plane, if any, a given inclusion belongs. Because the fluid inclusions are neither clearly of secondary origin nor meet Roedder’s (1984) criteria for primary or pseudosecondary origins, all remaining fluid inclusions (of ambiguous origin) are termed secondary(?) fluid inclusions.

Characteristics

Liquid-rich fluid inclusions are common, but many fluid inclusions contain daughter salts that indicate that the fluids were brines. Vapor-rich fluid inclusions were observed in one sample, which also contains the only fluid inclusion that appeared to homogenize by critical behavior.
The salt-bearing fluid inclusions contain halite, and several also contain sylvite. Most halite-bearing fluid inclusions homogenized by vapor disappearance after halite dissolution (bottom of Fig. 7). Hematite (which did not dissolve upon heating) is common, particularly in halite-bearing inclusions. A rhombohedral, highly birefringent daughter mineral that dissolved prior to vapor disappearance, presumably a carbonate, is present in some of the fluid inclusions in the sample in which RHOD is the targeted assemblage. Several unidentified daughter minerals were observed (Seedorff, 1987, app. C), including a small cubic phase that did not dissolve upon heating (fluorite?) and at least two opaque phases, one of which (e.g., in samples where BIO-KSP is the target assemblage) could be molybdenite (see Kamilli, 1978; White et al., 1981, p. 299).

Model geochemical systems

Fluids from the Henderson deposit should be the best natural analogue of the system H2O-NaCl-KCl, given that both wall rocks and mineralizing intrusions are high-silica rhyolites that are poor in Ca, Mg, and Fe, although other components must be present in minor amounts. Phase equilibria of this system (Roedder, 1984, p. 245) indicate that an inclusion theoretically could have a salinity exceeding 29 wt percent NaCl + KCl without precipitating either halite or sylvite daughters at room temperatures; salinities, therefore, are reported in Figures 7 and 8 as <29 wt percent equiv if freezing data are not available and neither halite nor sylvite were observed. Salinities are reported in terms of wt percent NaCl + KCl equiv. (Roedder, 1984, p. 245) if both halite and sylvite were present, but in terms of wt percent NaCl equiv if only halite was present at room temperature (Potter et al., 1977). In the H2O-NaCl-KCl system, fluids could contain as much as 11 percent KCl (depending on NaCl content and homogenization temperature) without being saturated with respect to sylvite at room temperature. Hence, the salinity expressed as wt percent NaCl + KCl equiv could be several percent higher than the estimates reported as wt percent NaCl equiv. For the few successful freezing runs (not available for samples shown in Fig. 8), salinities are calculated in terms of wt percent NaCl equiv (Potter et al., 1978).

Considering that iron-bearing hydrothermal phases are present at Henderson (Fig. 2), FeCl2 is almost certainly present in the fluids, thereby reducing solubilities of NaCl and KCl by the salting out effect and resulting in overestimation of Na and K abundances based on microthermometry (Cline and Vanko, 1995, p. 167). The actual FeCl2 contents of Henderson fluids have not been determined but are expected to be lower than those at the Granisle porphyry copper (Quan et al., 1987) and Questa porphyry molybdenum (Cline and Boddnar, 1994; Cline and Vanko, 1995) deposits because the stocks and wall rocks at Henderson are Fe poor.

Henderson fluids are considered to have been relatively poor in CO2, particularly relative to fluids associated with fluorine-poor porphyry molybdenum deposits (Theodore and Menzie, 1984; Theodore et al., 1992), so the effect of CO2 on phase equilibria is assumed to be minimal. Nonetheless, a finite amount of CO2 must have been present, at least in the low-temperature fluids, for rhodochrosite to have been deposited. Liquid CO2 was not observed in this study, although R. J. Kamilli (oral commun., 1986) and R. B. Carten (oral commun., 1987) have observed rare fluid inclusions from Henderson with liquid CO2.