THE GENESIS OF GIANT PORPHYRY MOLYBDENUM DEPOSITS

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Reno, Nevada
U.S.A., 89557-0047

ABSTRACT

Giant porphyry molybdenum deposits are best exemplified by the Climax and Henderson deposits in Colorado. The high grades of these deposits are probably inherited from magmatic molybdenum concentrations of about 4 to 5 ppm, which are high for metaluminous rhyolitic magmas that average about 2 ppm molybdenum. High magmatic molybdenum concentrations in metaluminous rocks appear to be related to high magmatic oxygen fugacities (2 or 3 log units above QFM oxygen buffer) and are correlated with high niobium concentrations. High oxygen fugacities are likely inherited from calc-alkaline or lamprophyric predecessors. High niobium and molybdenum are related to extreme fractionation of rhyolitic magmas. Much higher concentrations of molybdenum (>1,000 ppm) in the ore fluid (and the cupola magma) are probably achieved by crystallization in the deeper portions of a magma chamber accompanied by convection of the evolved liquid to the cupola and volatile fluxing.

Exploration criteria for a giant, high-grade deposit include: 1) a tectonic setting that indicates a changeover from compressional to extensional tectonics, 2) thick continental crust at the time of deposit formation may encourage extreme differentiation and crustal contamination, 3) an isotopically zoned magma chamber indicative of a long-lived heat source, 4) a large, sub-volcanic, central-vent ash flow/dome system that erupted less than 100 km³ of rhyolite, and 5) high niobium concentrations (>75 ppm) in a subalkaline, magnetite-bearing rhyolite.

INTRODUCTION

The grade and tonnage data of each deposit cited in this paper, as well as the assignment of each deposit to a general class (Table 1), is modified from the system presented in Carten et al. (in press). Deposits listed in Table 1 are geographically located in Figure 1. Deposits considered in this paper are restricted to porphyry Mo deposits which characteristically do not contain recoverable Cu and porphyry Mo-Cu deposits which contain coproduct or byproduct Cu and grades of Mo which average greater than 0.05% Mo.
Table 1. Grade and tonnage of granite-related Mo and Mo-Cu deposits (modified after Carten et al., in press).

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**GRANITE-RELATED Mo-Cu (Mo > 0.05 %)**

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1. Abbreviations as used in USGS Bulletin 1693
Figure 1. Location map for granite-related Mo and Mo-Cu deposits. Deposit numbers correspond to listing in Table 1. Spatially and temporally related deposits are combined as follows: 2 = Henderson and Urad; 6 = Mount Emmons and Redwell Basin; 11 = Questa (Sulphur Gulch, Goat Hill) and Log Cabin; 20 = Three Rivers, Cone Peak, and Rialto; 33 = Kitsault, Bell Moly, and Rouny Creek. State codes for the inset of the western United States are AZ = Arizona, CO = Colorado, ID = Idaho, MT = Montana, NV = Nevada, NM = New Mexico, TX = Texas, UT = Utah, and WA = Washington.
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Porphyry Mo deposits are further subdivided into those associated with high-silica or alkaline rhyolites which are rich in potassium, fluorine, and incompatible trace elements and are exemplified by the Climax deposit (albeit a premier example), and those associated with less silicic granitoids that exhibit average concentrations of fluorine and incompatible elements.

Examination of the grade and tonnage of 61 porphyry Mo and Mo-Cu deposits (Fig. 2) indicates that a continuum in deposit grades and tonnages may exist; however, most deposits consist of 50 to 200 million tons of ore, but only 12 deposits contain more than 200 million tons of ore. These 12 deposits can be considered "giant" in terms of tonnage, but only two deposits - Climax and Henderson - contain over 200 million tons of high-grade ore (Fig. 1 and 2). Clearly, the most economically desirable molybdenum deposit must be in this class and be "giant" in terms of both tonnage (~200 million tons) and grade (> 0.15% Mo). Processes and factors which contribute to the development of these types of deposits will be emphasized.

The genesis of these deposits in light of more recent work on the partitioning behavior and magmatic abundances of molybdenum will also be reviewed. Inasmuch as Climax-type magmas are often equated with topaz rhyolites, recent studies on the evolution of topaz rhyolites will be examined along with the volcanic rocks that are cogenetic with the Climax-type Pine Grove and Questa deposits in southwestern Utah and northern New Mexico respectively. Two large tonnage deposits that are less well characterized, but appear to not be Climax types are the Quartz Hill, Alaska deposit and Mt. Tolman, Washington deposit; processes that may have acted to produce the large tonnages with moderate-grade ores will be reviewed as well.

Several studies in recent years have clearly demonstrated that the molybdenum in porphyry deposits is derived "in toto" from the magma or the resulting stocks (Stein and Hannah, 1985; Carten et al., 1988a, 1988b; White et al., 1981). This being the case, some factors that might produce a high-grade deposit seem readily apparent. These include the initial molybdenum content of the parent magma and the increase in molybdenum content with differentiation. The source region for the magma and metal has been proposed as residing in the upper crust (Wallace et al., 1978), lower crust (White et al., 1981; Stein and Hannah, 1985), and mantle (Westra and Keith, 1981). Related factors that could control the grade of the deposit include how effectively molybdenum is sequestered by early magmatic minerals (Keith and Shanks, 1988) and how strongly it is partitioned into an evolved aqueous phase (Candela, 1989a; Keppler and Wyllie, 1991). Any discussion of what factors or processes are responsible for variations in tonnage and grade must begin with the source and differentiation processes of the magma. Processes that control the location and duration of molybdenite deposition from the aqueous phase also obviously control the grade. These include multiple stocks forming overlapping ore bodies and steep chemical and thermal gradients around the stock or pluton.

The tonnages of porphyry molybdenum deposits are also significantly affected by the factors just mentioned. However, additional factors that are perhaps more directly linked with the tonnages are the size and water content of the parent magma chamber, and the size and shape of the ensuing productive stock or cupola. For example, if mineralization occurs in a broad, shallow cupola along the roof of a large batholith, then the total amount of magmatic water and metals participating in mineralization may also be large, but unfocused. The ensuing deposit could be large, but low grade.

Most of these mineralization controls have been discussed or reviewed by other workers. However, the essential question that
remains unanswered is whether the processes that produce giant porphyry molybdenum deposits are inherently different from those which produce normal deposits. Is there a discontinuity in either sizes of parent magma chambers or the mineralizing processes associated with them? We will discuss this question along with what are the best exploration characteristics to use in finding a giant deposit.

**CLASSIFICATION AND GENERAL CHARACTERISTICS**

Most classification schemes for porphyry molybdenum deposits divide them into two main groups. These include Climax-type versus quartz monzonite type (White et al., 1981), granite versus granodiorite types (Mutschler et al., 1981), calc-alkaline versus alkali-calcic (and alkalic) types (Westra and Keith, 1981), and fluorine-enriched versus fluorine-deficient types (Theodore and Menzie, 1984). One of the two classes is generally typified by high-silica rhyolites or granites that are rich in potassium, fluorine, and incompatible trace elements. Characteristics of this class are exemplified by the Climax deposit. The other class is typified by a less silicic calc-alkaline granitoid that exhibits average concentrations of fluorine and incompatible elements. Climax-type deposits are of primary concern in this paper because they exhibit both

![Tonnage-grade diagram for granite-related Mo and Mo-Cu deposits](image-url)

**Figure 2.** Tonnage-grade diagram for granite-related Mo and Mo-Cu deposits. Deposits discussed in the text are labelled. Solid squares represent the high-silica rhyolite - alkaline suite; open circles are the differentiated monzogranite Mo suite; crosses are the Mo-Cu suite. All data are from Table 1 (Carten et al., in press).
high-grades of molybdenum and large tonnages (Sillitoe, 1980; White et al., 1981). However, both types will be examined in order to understand the processes responsible for formation of high-grade deposits.

The Henderson porphyry molybdenum deposit is one of the premier examples of a giant molybdenum deposit in terms of both tonnage and grade (727 million tons of 0.17 wt % Mo; Table 1). In addition, the most recent studies (Carten et al., 1988a; Seedorff, 1988) represent a culmination of 75 man years of geological investigation making it one of the most well-studied porphyry deposits in the world.

**MOLYBDENUM AND TUNGSTEN GEOCHEMISTRY IN IGNEOUS ROCKS**

Inasmuch as molybdenum and tungsten occur in the same group of the periodic table and exhibit many similarities in geochemical behavior, it is instructive to contrast and compare the behavior of both elements to understand the ore-forming process. For example, both molybdenum and tungsten are often sequestered by the same magmatic phases. Such a comparison is essential because the partitioning behavior of 6+ molybdenum has not been investigated experimentally; however, this is the valence that may be most important in porphyry systems and is the valence commonly exhibited by tungsten.

The concentration of both molybdenum and tungsten in the mantle is less than in C1 chondrites, indicating that a significant fraction of Earth’s original endowment of these metals now resides in the core (Newsom and Palme, 1984). Although molybdenum and tungsten generally exhibit strongly incompatible behavior in crystallizing magmas due to formation of large oxy-anions, under sufficiently reducing conditions (Fe-FeO) these metals may be strongly partitioned into a liquid metal phase, as apparently happened during core formation. The best estimates of the mantle abundance of molybdenum and tungsten are 0.059 ppm and 0.010 ppm, respectively (Newsom and Palme, 1984; Newsom et al., 1986) whereas upper crustal abundances are 1.5 ppm and 2.0 ppm, respectively (Taylor and McClennan, 1985). These data suggest that tungsten is more incompatible and therefore more enriched in the crust than is molybdenum (by a factor of 200 for W and only 25 for Mo). Newsom and Palme (1984) attribute the more strongly incompatible behavior of tungsten to an oxidation state of 6+, whereas the oxidation state of molybdenum varies from 6+ to 3+ under terrestrial conditions. Tungsten may exhibit an oxidation state of 4+ in some of the most reduced granitoid magmas (Cygan and Chou, 1987; Candela, 1988). Newsom and Palme (1984) suggest the molybdenum valences less than 5+ are perhaps more common and evidence of a 4+ valence has been observed in metal-silicate partitioning experiments. A valence of 4+ for molybdenum might indicate that its geochemical behavior would be similar to Ti (similar charge and ionic radius). A correlation in the abundance of Mo and Ti has been observed by Kuroda and Sandell (1954) for some igneous rocks.

Tacker and Candela (1987) also suggest that the dominant oxidation state for molybdenum in silicate magmas varies from 4+ to 3+ between nickel-nickel oxide and graphite-methane buffers. Molybdenum becomes more incompatible in magnetite and ilmenite as oxygen fugacity is increased (Tacker and Candela, 1987; Bouton et al., 1987).

**Associated alkaline mafic rocks**

The presence of lamprophyre dikes at Climax, Henderson, Quartz Hill, and Chicago Basin and of zoned magma chambers that are floored with alkaline mafic rocks at Pine Grove, Questa, and Grizzly Peak (mid-Tertiary volcanic field in central
Colorado) indicate that mantle-derived mafic alkaline magmas may represent a portion of the parental magma of Climax-type rhyolites. There is no isotopic constraint for eliminating them as a portion of the source material. Alkaline igneous rocks (minettes, lamproites, and nephelinites) from the Cenozoic volcanic fields in the Elkhead Mountains in Colorado, the Leucite Hills, Wyoming, and the western Colorado Plateau, Utah, have epsilon Nd and epsilon Sr values (Thompson et al., 1991; Vollmer et al., 1984; Tingey et al., 1991) that are not far removed from those exhibited by Climax-type systems. Despite the generally low concentration of molybdenum in the mantle (0.059 ppm), mantle-derived alkaline magmas formed by extremely small degrees of partial melting (<1%) have substantially higher concentrations of molybdenum that would not lower the average molybdenum content of a largely crustal melt. For example, Newsom and Palme (1984) noted that continental alkali basalts have high contents of incompatible elements including molybdenum concentrations up to 4.5 ppm (well above the crustal average of 1.5 ppm) and Newsom et al. (1986) report as much as 6.3 ppm Mo in alkaline ocean island basalt. Shoshonites, minettes, and melanephelinites from central Utah contain 0.2 to 3.0 ppm Mo (unpublished data).

The source region for mafic alkaline magmas on the continents is often proposed to be the metasomatized lithospheric mantle. Hattori et al. (1992) examined the metal content of magmatic sulfides from metasomatized (amphibole-bearing) peridotite xenoliths from a variety of localities; a xenolith from Nunivak Island, Alaska (underlain by continental crust) contained magmatic sulfide blebs with up to 60 ppm molybdenum, whereas sulfide blebs in xenoliths from other localities contained no detectable molybdenum. Insufficient data are available to speculate on whether the molybdenum content of lithospheric mantle of different Precambrian provinces may vary enough to account for the occurrence of porphyry molybdenum "provinces".

Oxidation state and molybdenum incompatibility in magmas

Perhaps the geochemical characteristic inherited from the source region that is most critical for the development of porphyry Mo magmas is the oxidation state of the magma. This parameter is fundamental because a buffer parallel oxidation state is not easily modified during magmatic fractionation (Carmichael, 1991). This characteristic may affect the oxidation state of molybdenum which in turn affects how incompatible it may behave during crystal fractionation. As previously noted, molybdenum may exhibit valences of 4+ and 3+ between nickel-nickel oxide and graphite-methane oxygen buffers (Tacker and Candela, 1987). Most subduction related (calc-alkaline) and lamprophyric magmas have oxidation states roughly 2-3 and 4-5 log units above nickel-nickel oxide respectively. If the trend of increasing incompatibility of molybdenum with increasing fO2 noted by Tacker and Candela (1987) continues, then molybdenum may become even more incompatible in calc-alkaline and lamprophyric magmas with high oxygen fugacities where molybdenum valences greater than 4+ may exist.

Evidence of variable incompatibility for molybdenum in various rock series should be noted here. Rubidium is insensitive to changes in the oxidation state of the magma and can be used in variation diagrams as a monitor of magma evolution. A plot of the abundance of tungsten versus rubidium in fresh volcanic rocks ranging in composition from mid-ocean ridge basalts to high-silica rhyolites shows linear, strongly incompatible behavior over a range of almost four orders-of-magnitude (Fig. 3). However, the enrichment of molybdenum in the same rock series is much more subdued increasing only two orders of magnitude; in addition, the
enrichment trend branches according to rock type (Fig. 3). Ocean island basalts and alkaline rocks exhibit a stronger enrichment trend than calc-alkaline (metaluminous) volcanic rocks; very reduced strongly fractionated rocks such as macusanites, ongonites, and some topaz rhyolites, such as Spor Mountain, even show sharply lower abundances of molybdenum with increased fractionation, despite strong enrichment of tungsten (up to 30-70 ppm; E. H. Christiansen, unpublished data; Pichavant et al., 1987). The differences in the behavior of molybdenum may be the result of variable oxidation states with molybdenum in a lower oxidation state ($3^+$(?)) behaving more compatibly than at higher oxidation states ($6^+$, similar to tungsten?) where molybdenum appears to be moderately incompatible.

The oxidation states of most porphyry molybdenum systems are not well constrained. Keith (1982) demonstrated that the oxygen fugacity of the Pine Grove magma was about 2 log units above nickel-nickel oxide (similar to most calc-alkaline rocks). Christiansen et al. (1986) found that the magmatic oxygen fugacity of the topaz-bearing Chalk Mountain rhyolite (comagmatic with Climax) was also about 2-3 log units above nickel-nickel oxide. However, some topaz rhyolites from west-central Utah (including Spor Mountain) were found to be substantially more reduced, with magmatic $f_O_2$ values 2 units below nickel-nickel oxide. Therefore, this is permissive evidence that Climax-type magmas would exhibit modest enrichment of molybdenum with continued fractionation, probably along the trend of other metaluminous (apparently more oxidized) magmas (Fig. 3), rather than depletion as found in more reduced magmas.

From the incompatible trace element systematics, we conclude that magmatic concentrations of Mo in metaluminous, calc-alkaline magmas are generally quite low. This is indicated by the average molybdenum content of continental crust and granitoids (1.5 ppm, Taylor and McLennan, 1985). More importantly, because the enrichment trend of molybdenum in metaluminous rocks is relatively flat through the granitoid region (Fig. 3), an approximate magmatic molybdenum concentration (between 1 and 5 ppm with an uncertainty of only a few ppm) can be inferred from the granitoid’s rubidium concentration. Rhyolites or granites with rubidium concentrations of over 1000 ppm are rare and commonly are reduced types that display molybdenum depletion with fractionation. Even if highly evolved oxidized granitic magmas existed with concentrations of Rb as high as 2000 ppm, magmatic Mo concentrations predicted by this trend would still be less than 6 or 7 ppm. Moreover, a survey of the molybdenum contents of subalkaline volcanic rocks worldwide indicates that concentrations in excess of 10 ppm have not been found (Smith, 1985). This does not include potentially large enrichments of molybdenum that are inferred to occur at the apices of Climax-type intrusions (13,000 ppm, Carten et al., 1988a) due to accumulation of a separate aqueous phase (discussed later), but only to molybdenum enrichment due to crystal fractionation.

Molybdenum and niobium

Another explanation of the moderately incompatible behavior of molybdenum is that its magmatic fractionation is similar to niobium. Molybdenum and niobium may commonly exist as cations of approximately similar size and charge in magmas. Ocean island basalts and continental alkaline magmas (excluding minettes) exhibit higher concentrations of niobium than do calc-alkaline magmas at the same rubidium concentrations (Fig. 3). In addition, niobium concentrations probably decrease with continued evolution in macusanite, ongonites, and the most evolved topaz rhyolites (Christiansen et al., 1986; Pichavant et al., 1987; Congdon and Nash, 1991) as does
Figure 3. Concentrations of Rb versus W, Mo, and Nb. A) Concentrations of Rb and W in fresh terrestrial volcanic rocks are strongly correlated over almost 5 orders of magnitude showing that W generally behaves as a strongly incompatible element. Mid-ocean ridge basalts (MORB) and ocean island basalts (OIB) form distinct but nearly continuous fields (stippled). The field for andesites, dacites, and rhyolites (ADR) extends from but overlaps the upper end of the field for ocean island basalts (OIB). For rhyolites, only data collected from glassy samples has been included. B) Concentrations of Rb and Mo in most fresh terrestrial volcanic rocks are strongly correlated showing that Mo generally behaves as a moderately incompatible element. Mid-ocean ridge basalts (MORB) and ocean island basalts (OIB) form distinct but nearly continuous fields. At a given Rb content, the Mo enrichment in andesites, dacites, and rhyolites (ADR) from subduction zones or continental settings is less than in (OIB). Highly evolved rhyolites that crystallized under reducing conditions (macusanites and some topaz rhyolites; stippled pattern, "low fO₂ trend") have even lower Mo/Rb ratios, apparently as a result of magmatic depletion of molybdenum. For rhyolites, only data collected from glassy samples has been included. C) Concentrations of Rb and Nb in fresh terrestrial volcanic rocks reveal a pattern similar to that for Rb and Mo in that andesites, dacites, and rhyolites (ADR) from continental and subduction zone settings are depleted in Nb compared to ocean island basalts (OIB) and even some mid-ocean ridge basalts (MORB). Although apparently more incompatible than Mo in most magmas, Nb behaves like Mo in that low Nb/Rb ratios are found in highly evolved rhyolitic rocks indicated by magmatic depletion of Nb in these rocks. Data from Newsom et al. (1986), Govindaraju (1989), Christiansen et al. (1986), Kovalenko et al. (1978, 1981), Pichavant et al. (1987), Congdon and Nash (1991), Turley and Nash (1983), Mahood (1981), Hildreth (1981) and our own unpublished analyses.

Molybdenum. For example, the strongly reduced macusanite glasses also show a decoupling of the behavior of niobium and tantalum resulting in a very low Nb/Ta ratio of 1.7 (Pichavant et al., 1987). Whether the behavior of niobium can be ascribed to a change in oxidation state from 5+ to 4+ in reduced magmas is unknown. But whatever magmatic phases control the abundance of niobium may also control that of molybdenum.

In summary, ocean island basalts and continental alkali basalts may inherit modestly high molybdenum and niobium concentrations from their sources. However, the high oxygen fugacities inherited from the source regions of minettes and calc-alkaline magmas may be of fundamental importance in allowing molybdenum concentrations to increase during crystal fractionation of magmas related to porphyry molybdenum deposits.

Preservation of magmatic molybdenum and tungsten concentrations

There are several reasons to believe the tungsten and molybdenum concentrations of many silicic igneous rocks often do not represent magmatic values. Perhaps most importantly, both elements are substantially partitioned into an aqueous phase when one is evolved from a crystallizing granitic magma (Candela, 1989a). If an aqueous phase escapes from a pluton, then the tungsten and molybdenum content of a granitoid will be reduced whereas country rock might become enriched by deposition of these metals from that fluid. The very process that makes mineralization possible, makes determination of original magmatic values almost unattainable. In this regard, Ivanova (1963) studied the distribution of tungsten in biotite granites and correlative greisens and concluded that tungsten content of the rocks is
Figure 4. Concentrations of Rb versus W and Mo for volcanic and granitoid rocks. A) Concentrations of W in fresh granitoids from western North America are generally depleted compared to fresh terrestrial rocks of the same Rb content, including the andesites, dacites, and rhyolites (ADR) commonly associated with tungsten deposits. B) Concentrations of Mo in fresh granitoids from western North America are generally depleted compared to fresh terrestrial rocks with similar Rb concentrations, including the andesites, dacites, and rhyolites (ADR) commonly associated with porphyry molybdenum deposits. C) Judging from the correlation of Rb and Mo in glassy rhyolitic rocks, the Mo concentrations in the rhyolitic magma at Pine Grove may have been as high as 3 ppm. However, concentrations of Mo in the volcanic rocks range to as low as 0.2 ppm as a result of post-magmatic losses including loss of a volatile phase during eruption and meteoric leaching (Keith and Shanks, 1988). Includes unpublished data of J. D. Keith.

primarily a function of alteration. Keith et al. (1989) made the same conclusion from a study of the CanTung granitoids, Northwest Territories. Figure 4 illustrates that the tungsten content of granitoids from western North America (Keith, unpublished data) scatter above and mostly below the trend established for fresh andesites, dacites, and rhyolites. Keith et al. (1989) also examined the molybdenum content of barren and tungsten-related granitoids from western North America. No correlation of molybdenum content with degree of differentiation, size of associated deposit, or other trace element concentrations was found. As was the case for tungsten, the molybdenum concentrations in these granitoids generally are substantially less than those of fresh andesites, dacites, and rhyolites (Fig. 4).

Molybdenum concentrations of rocks from a porphyry molybdenum deposit would always be suspect of being either enriched (especially within 300 m of an ore zone, Mutschler et al., 1981) or depleted by hydrothermal leaching or loss of a molybdenum-rich aqueous phase. Even fresh volcanic rocks may exhibit molybdenum concentrations lower than pre-eruption magmatic values due to loss of a molybdenum-bearing aqueous phase or to leaching by meteoric fluids. Keith and Shanks (1988) documented that at least 90% of the molybdenum in the non-welded tuff of Pine Grove was leached by meteoric water; in addition, they inferred that very fresh comagmatic rhyolite cobbles eroded from an extrusive dome had lost ~70% of their original molybdenum content due to escape of magmatic volatiles (Fig. 4). Although measured molybdenum concentrations in fresh Pine Grove rocks range from 0.20 to 1.82 ppm, the pre-eruption magmatic level may have been as high as ~3 ppm (Fig. 4); the difference may have been lost to meteoric leaching or degassing of the ash flow tuff shortly after eruption. Consequently, it is difficult to determine the magmatic tungsten and molybdenum concentrations of evolved water-rich granites and rhyolites. Molybdenum has been found in fumarolic crusts associated with similar rhyolitic tuffs (Zies, 1929). Even strongly differentiated rhyolitic magmas such as those that formed the molybdenite deposits at Climax and Henderson, may originally have contained only about 4 ppm molybdenum; magmas with lower rubidium and niobium - such as those from Quartz Hill and Mount Tolman - may have originally had molybdenum concentrations closer to ~2 ppm. Actual magmatic concentrations of molybdenum for these deposits may be unattainable for the reasons just outlined. If such molybdenum-niobium-rubidium correlations have some validity, then the more niobium-rubidium-rich magmas might be expected to produce larger tonnages of higher grade molybdenum ore. Figure 5 illustrates that deposits with higher
Figure 5. Rb and Nb concentrations in silicic igneous rocks associated with porphyry molybdenum deposits in western North America are similar to other members of the andesite, dacite, rhyolite group world wide. Granitic rocks at Urad/Henderson are the most fractionated (indicated by their high concentrations of the incompatible elements Rb and Nb) and host the highest grade Mo deposit. Rb, Nb, and Mo ore grade decrease regularly in the sequence Pine Grove, Questa, Quartz Hill, and Mt. Tolman.

niobium and rubidium concentrations do have larger tonnages of high grade ore.

PETROGENESIS OF MAGMA RELATED TO CLIMAX-TYPE MOLYBDENUM DEPOSITS

Lower and upper crustal sources

Do the igneous rocks associated with giant porphyry molybdenum deposits inherit a special composition from their magma source region that distinguishes them from lesser deposits? Is there a unique tectonic setting or epoch for their development? In this regard, White et al. (1981) proposed that because the Colorado Rocky Mountain region exhibits many deposits or mineral occurrences enriched in molybdenum, tungsten, and fluorine, this indicates a "long-term source" for these elements in the underlying continental lithosphere (1.7 Ga). They suggested that Climax-type magmas were generated by fractional melting of the lower crust followed by fractional crystallization of each batch of magma as it diapirically rose through the crust. White et al. (1981) suggest the magmas would be enriched in molybdenum and other incompatible trace elements as a consequence. What levels of molybdenum enrichment would be achieved by this process are not specified, but they suggest that Climax-type granitoids are "rather like" the topaz rhyolites of Burt et al. (1982). Extensive data on the molybdenum content of topaz rhyolites are not available, but Keith and Shanks (1988) found that fresh topaz rhyolite from southwestern Utah with niobium and rubidium concentrations similar to those at Henderson contained 3.3 (+/- 0.2) ppm molybdenum. Turley and Nash (1983) found from 2 to 6 (+/- 1.5) ppm molybdenum in vitrophyres from topaz rhyolite lavas at Smelter Knoll, Utah. There is no evidence that topaz rhyolites generally contain higher concentrations of molybdenum than these values.

Stein (1988) investigated the lead, strontium, sulfur, and oxygen isotope ratios and rare earth-element compositions of ores, and of volcanic and plutonic rocks from the Colorado mineral belt; the genesis of Climax-type systems was of particular concern. Her data were interpreted to indicate that all the Laramide-Tertiary intermediate to felsic magmas (including calc-alkaline) had a lower crustal origin; however, Climax-type granites were proposed to have originated from a unique lower crustal source (not related to calc-alkaline magmatism). The magmatic characteristics critical to Climax-type mineralization acquired from this unique source are not specified.

In their review of the Henderson deposit, Carten et al. (1988b) suggest that a unique magma that contained high concentrations of ore components was not required to form the deposit. They argue that the initial concentration of molybdenum in the ore-related magma is not as critical to ore formation as the type and duration of fractionation processes in a high-level magma chamber.

The average molybdenum content of the lower and upper crust is estimated to be 0.8 and 1.5 ppm respectively (Taylor and
McLennan, 1985). One of the first attempts to define a special molybdenum-rich source for Climax-type deposits was analysis of the molybdenum content of Idaho Springs Formation and the Silver Plume Granite; Zahoney (1968) found an average of 5 ppm and 2-3 ppm Mo in these respective rock types. On this basis, Wallace et al. (1978) suggested that the tungsten and molybdenum of the Climax and Henderson deposits were derived from these upper crustal host rocks. However, later isotopic studies (White et al., 1981; Stein, 1988) have demonstrated that Climax-type magmas and ore deposits in the Colorado mineral belt could not have incorporated any appreciable amount of these upper crustal rocks.

Most recent workers have proposed that the magma source of Climax-type systems and topaz rhyolites is in the lower crust (White et al., 1981; Christiansen and Wilson, 1982; Christiansen et al., 1988; Stein, 1988) although enriched upper mantle has been proposed also (Westra and Keith, 1981). White et al. (1981) noted that the initial $^{87}\text{Sr}/^{86}\text{Sr}$ values for "unaltered" Climax and Henderson rocks varies between 0.705 - 0.710. Stein (1988) found significantly higher and widely varying values of 0.7085 to 0.740 for Climax and Henderson rocks. Chalk Mountain rhyolite is a relatively unaltered topaz-bearing extrusive dome that is comagmatic with the Climax rhyolites (Burt et al., 1982). Stein (1988) reported a $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.7085 for Chalk Mountain and 0.710 - 0.711 for Climax samples. Fused ash-flow tuff associated with the Climax-type Pine Grove deposit in Utah, which is underlain by Proterozoic crust of the same age as Climax, has an initial $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.7099 (Christiansen and Wilson, 1982).

Although sparse, Nd isotopic data may reveal more about the source(s) of Climax type rhyolites, because they are probably less affected by hydrothermal alteration and wall-rock contamination than Sr isotope ratios. Farmer and DePaolo (1984) reported the compositions of 3 samples from Henderson. Epsilon Nd for these samples ranged from -9.5 to -9.9. These values are indistinguishable from the high end epsilon Nd of Precambrian (1.6 to 1.8 Ga) basement rocks, suggesting to Farmer and DePaolo (1984) that the "granitic magmas were derived exclusively from mid-Proterozoic crust". However, it should be noted that DePaolo (1981) observed that Proterozoic crust in Colorado could have had epsilon Nd as low as -14 during the middle Tertiary. If such crust was involved in the genesis of Climax-type rhyolites then a significant mantle component with higher epsilon Nd must have been present even in this magma system. Moreover, the occurrence of igneous rocks with epsilon Nd values as low as -13 (Johnson and Fridrich, 1990) in the same region and broadly coeval with Henderson is consistent with the involvement of significant mantle-derived magma at Henderson. As noted below, Johnson et al. (1989) also propose a similar mixed (mantle and crustal) heritage for the magmas that led to the formation of the Questa deposit.

**Tectonic setting**

Sillitoe (1980) subdivided porphyry molybdenum deposits into rift-related and subduction-related deposits that correspond fairly well to Climax-type and the "other" categories respectively. Several authors have recognized that few Mo deposits occur in young island arc settings (i.e. Canicanian, Table 1), and almost always in areas underlain by at least thin continental crust (Sillitoe, 1980; Westra and Keith, 1981; Christiansen and Wilson, 1982). Although some have claimed that Climax-type systems correlate with thicker continental crust, others suggest that they are independent of crustal thickness (Westra and Keith, 1981). Perhaps the most commonly suggested tectonic setting for Climax-type systems is during the changeover from compressional to extensional tectonics...
SEG SP-2 GIANT ORE DEPOSITS

(Sillitoe, 1980; Westra and Keith, 1981; Mutschler et al., 1981; White et al., 1981; Bookstrom, 1981). Some authors prefer to consider this setting as "atectonic" or back-arc spreading rather than simply rift-related.

The "changeover" tectonic setting has also recently been documented for the Coulee Dam intrusive suite (Carlson and Moye, 1990) that hosts the Cu-rich Mt. Tolman deposit whose ore-related granite porphyry clearly evolved from a dominant volume of granodiorite (Carlson and Moye, 1990). Additionally, a "post-orogenic", extension-related setting has been proposed for the Quartz Hill deposit (Hudson et al., 1981). The Quartz Hill intrusive complex was emplaced in the Coast batholith after it had been extensively uplifted and eroded. A regional extension-related joint system controls emplacement of many lamprophyre dikes as well the Quartz Hill intrusions. However, the initial $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.7051 for the Quartz Hill intrusions do not differ significantly from those of the older subduction-related plutonic rocks. Additionally, the Quartz Hill intrusions show minimal enrichment of $\text{K}_2\text{O}$, fluorine, and other incompatible elements (Hudson et al., 1981).

Crystal fractionation from calc-alkaline predecessors

Despite accumulation of a large amount of data on the petrogenetic and isotopic evolution of Climax-type rhyolites, a number of differing source rocks are permissible. Questa and Pine Grove show many petrogenetic similarities. Pine Grove (23-22 Ma; Fig. 1) is located in the Indian Peak volcanic field that produced dominantly high-K calc-alkaline dacitic ash flows from 32 to 27 Ma (Best et al., 1989). More than 50,000 km$^3$ of ash flow tuff was erupted. Smaller volumes of high-K calc-alkaline rhyolite, trachyandesite, and minor dacite were erupted near the Indian Peak volcanic field at 18-23 Ma and are roughly contemporaneous with the inception of extension in the area (Best et al., 1987). The Pine Grove porphyry molybdenum deposit occurs in the eroded vent of an ash-flow/dome complex just east of the rim of the Indian Peak caldera complex. Initial eruptions began with high-silica rhyolite and later eruptions simultaneously vented rhyolitic and dacitic magma. High-silica rhyolite subsequently filled the vent to form domes and intruded to shallow levels to form a Climax-type deposit. The co-erupted dacitic magma exhibits a mode and major-element composition very similar to the voluminous dacitic ash-flows that were emplaced during the Oligocene and to other intermediate volcanic rocks of the same age (23-21 Ma) to the west (Best et al., 1992). Shortly after complete crystallization of the magma chamber, trachyandesitic magma intruded the vent and other portions of the crust and covered the tuff of Pine Grove across the region. Keith (1982) demonstrated that 60% fractionation of dacitic magma, using observed phenocryst proportions and compositions, could produce the major-element composition of the Pine Grove rhyolite. The available Sr isotopic data are consistent with this idea; no significant differences exist between the Sr-isotopic compositions of the Pine Grove magma and the older dacites of the Indian Peak volcanic field.

Johnson and Lipman (1988) investigated the origin of the metaluminous and alkaline volcanic rocks of the Latir volcanic field, host of the Questa deposit (Fig. 1), in the Rio Grande rift near the Colorado-New Mexico border. Magmatism in the Latir field (22 - 28.5 Ma and 11-15 Ma) is approximately coeval with Climax-type systems (i.e. Climax, Henderson, Mt. Emmons) farther north along the Rio Grande rift. In addition, the age of magmatism spans the inception of rifting in the area (26 Ma). Molybdenum mineralization is associated with waning stages of caldera magmatism. The
highest grades of ore are associated with the Sulphur Gulch pluton (23-25 Ma) that intruded the southern rim of the Questa caldera (Johnson et al., 1989). Johnson and Lipman (1988) suggested that 60% fractionation of a parental magma similar to the Cabresto Lake monzogranite, a slightly older resurgent pluton, could produce the major- and trace-element composition of the Sulphur Gulch pluton. They suggest that a "base level" intermediate composition magma, exemplified by the majority of the local volcanic and plutonic rocks, persisted in the area for 6 m.y. The inferred monzogranite parent is very similar to the dacite co-erupted with the rhyolitic Pine Grove magma and the "base level" composition of the Indian Peak volcanic field (Best et al., 1989).

A critical question that should be asked is whether the petrogenetic processes exemplified by Pine Grove and Questa magmatism operated at other Climax-type porphyry Mo systems. Bookstrom (1981) states that the Climax-type deposits in the Colorado mineral belt occur along the axes of slightly older calc-alkaline plutons (mostly less than 40 Ma). There are about 30 molybdenum prospects with up to ~0.1% MoS₂ mineralization in the mineral belt and most of these are associated with broadly calc-alkaline igneous rocks and appear to be subduction related. He notes that the "Climax-like" rhyolite porphyries of the Winfield prospect (35-38 Ma) formed within a granodioritic pluton well before initial rift-related basaltic volcanism (~24-26 Ma). These data would suggest that Climax-type rhyolites and calc-alkaline intermediate plutons may be comagmatic. A similar temporal association of broadly calc-alkaline magmas (50 to 45 Ma), topaz-bearing granites and rhyolites (48 Ma), and a Climax-type Mo deposit at Big Ben (48.5 Ma), Montana, has been noted by Christiansen et al. (1986).

The petrogenesis of the igneous rocks at Climax and Henderson is difficult to interpret when generally only high-silica rhyolites are exposed. The published analyses carry all the earmarks of strongly fractionated magma: low concentrations of compatible elements (notably Sr, Mg, and Ti) and high concentrations of incompatible elements like Rb and Nb. Thus the nature of their more mafic predecessors is difficult to deduce. Isotopic, major- and trace-element compositions of the rhyolitic rocks present no reason to exclude the possibility that they evolved by crystal fractionation from high-K calc-alkaline magma (which itself was partially derived from lower crustal and mantle sources).

One of the reasons that White et al. (1981) exclude magma evolution from calc-alkaline parents is that one of the Climax-type deposits, Mt. Emmons, is much younger (17 Ma) than the cessation of apparently subduction-related magmatism (~26 Ma). However, non-subduction-related volcanic rocks with calc-alkaline characteristics are present elsewhere in the Tertiary of the western United States. For example, a 16.5 Ma volcanic center in the Gold Springs and Stateline districts of Utah and Nevada exhibits a complete spectrum of compositions ranging from 68 to 77% SiO₂. The lower-silica rocks have the calc-alkaline characteristics of steep REE patterns, abundant magnetite, and nonevolved trace element abundances. The culminating events of the volcanic center were eruption of a high-silica ash-flow tuff and emplacement of a dome of topaz rhyolite in the vent. The latter hosts a gold-bearing fluorite pipe and quartz-sericite-pyrite and argillic alteration; precious-metal veins occur adjacent to the vent. Both older (18-21 Ma) and younger (10-12 Ma) topaz rhyolites occur nearby (Best et al., 1992; Best et al., 1987).

Although isotopic signatures of Climax-type rhyolites are marginally permissive of purely crustal sources, well-studied rhyolitic ash-flow systems that erupted a spectrum of cogenetic magma compositions suggest that other interpretations
are also possible. For example, the 34 Ma Grizzly Peak Tuff, located approximately 80 km southwest of the Climax deposit, varies in composition from high-silica rhyolite at the base to low-silica rhyolite at the top of a single eroded cooling unit; two heterogeneous tuff layers also contain dacite to mafic latite fiamme (Johnson and Fridrich, 1990). Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range from 0.7170 to as low as 0.7099 and epsilon Nd values vary between -13.0 and -11.3; similar variations are exhibited by Pb and O isotopes. Johnson and Fridrich (1990) point out that the most mafic composition (57 wt% SiO$_2$) is too mafic to be a partial melt of crustal rocks; this magmatic composition is best explained by approximately 50 wt% crystal fractionation of basaltic magma, accompanied by 20 to 40 wt% assimilation of Proterozoic crust. The more silicic portions of the magma were modeled to have formed by crystal fractionation accompanied by late-stage crustal assimilation. Evidence for late-stage assimilation included isotopic disequilibrium between whole-rock fiamme and early- and late-crystallizing phenocrysts separated from the same fiamme. They note that without the fortuitous eruption of the more mafic portions of the magma chamber, they would have drawn the erroneous conclusion that the tuff was generated by 100% crustal melting. The high-silica portion of the Grizzly Peak Tuff would fit all of the isotopic criteria for derivation from a "Climax-type source" (Stein, 1988; Stein and Crock, 1990), in spite of its inferred mantle heritage.

**Isotopically zoned magma chambers**

Plutonic and volcanic rocks related to the Questa caldera and porphyry molybdenum deposit also show evidence of derivation from chemically and isotopically zoned magma chambers. The Questa caldera formed upon eruption of $>500$ km$^3$ of the high-silica peralkaline Amalia Tuff (Johnson and Lipman, 1988). Pre-caldera intermediate composition volcanic rocks have relatively uniform initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of approximately 0.7055 (identical to the intermediate lavas of the San Juan volcanic field; Lipman et al., 1978; Johnson et al., 1990). Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the Amalia Tuff increases monotonically with decreasing Sr content from 0.7057 to 0.7098, the Sr-poor tuff representing the early eruptions. Late-stage roofward assimilation of Proterozoic rocks is proposed as the preferred explanation of the increasing initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios; convincing evidence of this model is the roofward increase in the proportion of zircons with Proterozoic cores relative to Tertiary zircons with no Proterozoic cores. The Mo-mineralized Sulphur Gulch pluton exhibits an analogous trend of decreasing initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (from 0.7085 to 0.7067) with increasing Sr content. The inferred parent (Cabresto Lake pluton) has an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7053 (Johnson et al., 1990). Late-stage roofward contamination may also cause some of the large variations in initial $^{87}\text{Sr}/^{86}\text{Sr}$ noted in the Climax, Henderson, and Mt. Emmons rhyolites (Stein, 1988). Stein and Crock (1990) reject that possibility because the inferred proportions of wallrock needed to produce the variations are substantially different for the Nd, Sr, and Pb isotopic constraints. However, Johnson et al. (1990) encountered very similar isotopic inconsistencies in modeling the late-stage assimilation of the Sulphur Gulch (Questa) pluton.

Not all high-level magma chambers or post-caldera plutons show evidence of late-stage assimilation. If late-stage roofward assimilation is a common process in Climax-type magma chambers, then what process is responsible for causing assimilation? Ultimately, the answer is related to heat, whether by crystallization or by underplating or injection of new magma. The fact that Climax-type magmas may show consistent isotopic evidence of late-stage assimilation of roof rocks should not be
surprising inasmuch as one of the most widely recognized characteristics of this deposit type is the occurrence of multiple intrusions and ore bodies that are generally emplaced by assimilation and stoping.

Chondrite-normalized rare-earth element patterns from Climax, Henderson, Questa, and Pine Grove (discussed in a later section) show evidence of some crystallization and fractionation of the parent magmas between intrusive units; this could be one source of heat for assimilation. All four of these deposits were apparently developed during the change from subduction-controlled to extensional tectonics. Thompson et al. (1991) suggested that extension-related mafic magma associated with the Rio Grande rift played a substantial role in extending the life of "pre-rift" volcanism approximately by 3 m.y. For example, the Sulphur Gulch pluton (23-25 Ma), which hosts the Questa deposit, may have evolved from pre-rift magmas that were kept "alive" by basaltic magmatism related to rifting (26 Ma). Therefore, underplated mafic magma at Questa may have been responsible for the gradual elevation in initial $^{87}\text{Sr}/^{86}\text{Sr}$ associated with roofward assimilation.

Evidence for extension-related trachyandesite underplating of the Pine Grove chamber is perhaps even more conclusive in substantiating a role for extension-related magmas. Trachyandesitic magmas were clearly associated with extensional tectonics from 22 to 18 Ma across the Pioche-Marysvale volcanic belt. Trachyandesite magma co-erupted with the tuff of Pine Grove and intruded the vent just after final consolidation of the magma chamber. Keith and Shanks (1988) suggested that the trachyandesitic magma may have provided the heat to allow the water-rich Pine Grove magma to ascend to slightly higher levels in the crust without solidifying.

White et al. (1981) and Stein and Crock (1990) point out that assimilation of highly radiogenic country rocks around Climax and Henderson could not have been a very significant magma modifying process. However, even a trivial amount of assimilation (0-2% of Silver Plume Granite, Bookstrom et al., 1988) may explain the monotonic increase in initial $^{87}\text{Sr}/^{86}\text{Sr}$ values between comagmatic rhyolite intrusions. We do not propose that late-stage assimilation is adding anything "special" to the magma chamber, but it may point to a long-lived heat source at the base of the system that permits extended crystal fractionation, volatile loss, and perhaps volatile fluxing without rapidly solidifying the entire chamber. Isotopic zonation of the high-level magma chamber may be one signature of that heat source.

White et al. (1981) also note that basaltic volcanism is not associated, on a local scale, with Climax-type systems. However, felsic rocks at Climax, Henderson, and Chicago Basin are contemporaneous with minor volumes of cross-cutting biotite-rich lamprophyre dikes (Bookstrom, 1981; Bookstrom et al., 1988). Additionally, mildly alkaline to transitional basalts (24-20 Ma) interfinger with basin-fill sedimentary rocks of the Browns Park Formation west of the Colorado mineral belt (Thompson et al., 1991). Bookstrom (1981) suggests that the lamprophyres represent "a different type of bimodal suite." Some have suggested that lower thermal input may result in selective partial melting of less refractory "plums" in a "plum pudding" mantle with the resulting melt being isotopically enriched and of alkaline affinity (Thompson et al., 1991; Perry et al., 1987). Climax, Henderson, and Chicago Basin are sufficiently removed from areas of substantial rifting that rift-related thermal input may have been low, but sufficient to extend the life of the magma chambers.

In summary, when only high-silica rhyolite is erupted or exposed for examination, the petrogenesis is ambiguous (Christiansen and Wilson, 1982; Johnson and Fridrich, 1990). Inasmuch as high-silica rhyolitic magmas lie near the ternary
minimum, a variety of source materials and petrogenetic paths may yield essentially the same bulk composition. We see no reason that topaz and Climax-type rhyolites could not be developed by either partial melting of lower crustal felsic granulite (Christiansen et al., 1988; Stein, 1988; Stein and Crock, 1990; White et al., 1981), differentiation of subduction-related high-K calc-alkaline magmas (Keith et al., 1986; Westra and Keith, 1981), or extreme fractionation of rift-related basaltic magma significantly contaminated by lower crust. However, rhyolites generated by these processes may not be equally capable of generating a giant deposit.

CONCENTRATION AND TRANSPORTATION MECHANISMS

Wallace et al. (1968) emphasized that 100-125 km³ of magma is needed to supply the molybdenum found in the Climax ore bodies. Carten et al. (1988a) concluded that enrichment of ore components in the cupola occurs prior to the onset of crystallization and that the initial concentration of molybdenum in the parent magma chamber is not as significant to ore formation as the type and duration of processes that deliver molybdenum to the cupola. Intermingled barren and productive stocks at Henderson have the same isotopic composition (Farmer and DePaolo, 1984) and probably represent successive draughts from a large, persistent magma chamber that was contiguous with each intrusion. Carten et al. (1988a) also concluded that either variations in residence time or variations in the efficiencies of fractionation processes could account for the intermingling of barren and productive stocks.

Crystallization

Candela (1989a) states that partitioning of molybdenum into an aqueous phase is most efficient when an initially dry melt fractionates at shallow depth or when melt evolves water at great depth, he suggests that in either case evolution of vapor during crystallization (second boiling) is more effective in removing Mo from the melt than any reasonable first boiling scenario. However, there is no reason to believe the Climax-type rhyolitic magmas are dry (~1% H₂O) and do not evolve an aqueous phase until the last few percent of the magma crystallizes. Keith and Shanks (1988) documented a high water fugacity and content for the Pine Grove rhyolites; most rhyolitic magmas are probably saturated or nearly saturated with water when they erupt. In addition, rhyolites that appear to have erupted from Pine Grove, Questa, Climax, and Henderson have less than 35% phenocrysts.

The alternative Candela (1989a) proposes for generating a molybdenum-rich magma--evolving an aqueous phase at great depth--may have some application to crystallization of drier, intermediate-or-mafic magma at the roots of a stratified magma system. If buoyant fluids that evolved as a result of crystallization at depth can extract molybdenum from the magma they traverse and then collect efficiently in a high-level cupola, then they may form a molybdenum-rich magma and consequently contribute to ore formation.

Some have proposed that little additional crystallization or differentiation of the parent magma chamber occurred from the time of emplacement of one stock to the next (Keith and Shanks, 1988; Carten et al., 1988a). For example, zirconium and niobium concentrations are approximately the same for all stocks at Henderson. However, relatively constant concentrations of these elements are perhaps not unusual for metaluminous magmas; crystal fractionation can occur and maintain relatively constant values for zirconium, niobium, and molybdenum.
Variations in vapor/melt partitioning

In orthomagmatic hydrothermal fluids, Mo does not appear to be complexed and transported with either Cl or F; in fact, Keppler and Wyllie (1991) found that molybdenum is most strongly partitioned into an aqueous phase ($K_p=5.5$) when Cl and F are absent. Consequently, if our conclusions regarding the maximum enrichment, ~5 ppm, of molybdenum in magmas are correct, none of the experimentally determined vapor/melt partition coefficients for molybdenum would produce an extremely molybdenum-rich ore fluid (one with thousands of ppm Mo) from a water-rich rhyolitic melt at shallow depths (Keppler and Wyllie, 1991; Tacker and Candela, 1987).

Lowenstem et al. (1991) investigated the copper content of melt inclusions in quartz phenocrysts from the peralkaline rhyolites from Pantelleria. They found 3 ppm copper in matrix glass and in melt inclusions with fractures to the crystal surface. Non-degassed melt inclusions contained 20 ppm copper and melt inclusions that also contained large vapor bubbles contained up to 300 ppm copper. They calculated that the vapor/melt partition coefficients for copper may be well over 1000; this value is much higher than those determined experimentally (~50; Candela and Holland, 1984). Lowenstem et al. (1991) propose that the stronger partitioning of copper into the fluid phase could be due to more "available Cl" in the fluid phase than in the experiments. This might have been caused by a high $CO_2/H_2O$ ratio, rendering HCl more dissociated. They also emphasize that crystallization-induced volatile saturation (second-boiling) may not be necessary for the production of Cu-rich fluids. Exsolved volatiles were present in pantellerite magma with only 10% crystals and in rhyolite from the Valley of Ten Thousand Smokes with only 2% phenocrysts (Lowenstem et al., 1991).

Similarly, there are several reasons why the vapor/melt partitioning coefficients of molybdenum in natural systems may be significantly higher than experimentally determined values. For instance, porphyry molybdenum systems have $fO_2$ conditions of calc-alkaline rocks (about 2 log units above NNO) that are well above the $fO_2$'s investigated experimentally; the trends of the experimental data suggest that molybdenum should be even more strongly partitioned into the aqueous phase under such high $fO_2$ conditions. Candela (1989b) also speculates that if the oxidation state of molybdenum in the aqueous phase is higher than in the melt, then the tendency of molybdenum to enter the vapor phase may be compounded.

Keith and Shanks (1988) reviewed the evidence that extension-related trachyandesitic magmas were episodically injected into the base of the Pine Grove magma chamber. If such magmas are injected into the base of a dacitic or rhyolitic magma chamber, they would quench or crystallize and release volatiles that could be fluxed through the magma chamber. Lamprophyric magmas or less primitive K-rich mafic magmas that are generally volatile-rich, may have interacted with Climax, Henderson, Quartz Hill, and other porphyry molybdenum systems to produce similar volatile fluxing.

If such a molybdenum-transporting magmatic fluid phase existed and was $CO_2$-rich, then evidence of $CO_2$ in high-temperature fluid inclusions should perhaps be found. Linnen and Williams-Jones (1990) note that aqueous-carbonic fluid inclusions are common in fluorine-deficient molybdenum deposits, but are scarce in fluorine-rich deposits. However, White et al. (1981) note that a carbonate daughter mineral is present in some fluid inclusions from Henderson. Seedorff (1988) found similar daughter minerals in fluid inclusions from a rhodochrosite-bearing alteration assemblage at Henderson. Thus, $CO_2$-rich fluid inclusions have been observed at Climax and Henderson, but are not abundant (Seedorff, 1988; Hall et al. 1974). Hypersaline fluid inclusions are
rare in the F-deficient deposits, but common in Climax-type systems (Linnen and Williams-Jones, 1990). These data suggest that volatile fluxing by a CO$_2$-rich fluid phase in Climax-type systems may not be a significant process.

Analysis of volcanic gas emissions from active volcanoes indicates that sulfurous gases are emitted upon the inferred arrival of new magma at the base of a magma chamber. At the fO$_2$ conditions of calc-alkaline magmas, SO$_2$ and H$_2$S would be present with about sub-equal fugacities (Whitney, 1988). The low solubility of SO$_2$ in magmas may allow a flux of SO$_2$-bearing volatiles to rise through a zoned magma chamber and perhaps scavenge molybdenum. Molybdenum is not complexed with sulfur; but the partitioning behavior of molybdenum relative to a fluid phase that is rich in an oxidized sulfur species has not been investigated. Indeed, fluxing of S-rich fluids through a magma is probably required to account for large amount of magmatic sulfur associated with a giant porphyry molybdenum deposit. The low solubility of sulfur in high-silica rhyolitic melts argues for such a process, but mass balance calculations to test this scenario would involve much uncertainty.

Convection and volatile fluxing

There are several reasons to suspect that the process of metal enrichment involves convection and volatile fluxing through a large volume of the chamber. Keith et al. (1986) document that large blocks of biotite-rich (5-7%) dacitic magma from the base of the Pine Grove magma chamber were rafted to the top of the cupola just prior to the main episode of ore formation. Individual blocks are surrounded by rhyolitic magma and successive intrusions are rhyolitic. Because of the higher density of dacitic magma relative to rhyolitic magma, emplacement of dacitic blocks at the top of a rhyolitic intrusion would not be expected to occur. One mechanism for reducing the density of dacitic magma below that of the rhyolite is by exsolution of volatiles in the dacitic magma. Crystallization, magma mixing, and/or arrival of mafic magma at the base of the chamber may have helped create a flux of components with low solubility such as CO$_2$ or SO$_2$; exsolved bubbles of these gases would contain some water and other ore constituents such as molybdenum. Evidence of similarly rafted blocks in other porphyry systems may often go unrecognized. As a possible example, White et al. (1981) describe a textural variant of the Late rhyolite at Climax wherein blocks of biotite-rich (3-5%) rock, 2 m to 1 cm in size, occur as inclusions within the main phase. Carter et al. (1988a) propose that convection could augment the transport of ore components as dissolved or undissolved volatiles. These data indicate that a stream of undissolved volatiles could begin at the deepest levels of the magma chamber.

Central vent architecture

Magmatic volatile collection associated with both porphyry copper and molybdenum deposits often appears to be channelled to a vent associated with prior eruptions; such is clearly the case with Henderson and Climax. Although many authors lament the loss of volatiles and ore constituents associated with opening a vent, it may be a critical positive feedback mechanism. Subsequent volatiles could be collected from the roof zone by a single, flaring funnel, eroded into the wall rocks during eruption. Volatiles collected in the sub-volcanic pipe could experience a pressure drop to hydrostatic values more readily than any other portion of the roof zone. If the pipe geometry is lacking, then the ore zone may be more sheetlike extending along the roof of the chamber as seen at Mt Tolman (W. Utterback, unpublished report). The same volume of magma that could be "seen" by the vent during eruption may also be seen during collection of volatiles. The larger the volume of magma seen by one vent
during fluid collection, then the larger, or higher grade, the deposit could be. Certainly a single, well-situated vent would be optimal.

Smith (1979) pointed out that central vent volcanoes do not erupt more than about 100 km$^3$ of ash flow tuff; larger eruption volumes are related to calderas where multiple vents are probably involved, as is the case of the 500 km$^3$ Amalia Tuff expelled from the Questa caldera. Several resurgent (or slightly younger) plutons occur along the ring fracture and elsewhere; all of the intrusions are variably mineralized with molybdenite (Johnson et al., 1989). In addition, the molybdenite-bearing Sulphur Gulch and Bear Canyon plutons connect at depth (Leonardson et al., 1983), but only the Sulphur Gulch pluton is ore-grade. Multiple vents or caldera-related systems may not be as likely to produce a single giant deposit.

The 10:1 ratio of chamber volume to eruption volume (Smith, 1979) suggests that a central vent volcano that erupts the maximum 100 km$^3$ could "see" no more than ~1000 km$^3$, but much less may be required considering that 150 km$^3$ of magma stripped of 3 ppm of molybdenum would supply all the metal needed to form the Henderson deposit.

CHARACTERISTICS OF THE DEPOSITIONAL SITE

There is no evidence to indicate that Climax-type systems more efficiently deposit molybdenum from a magmatic ore fluid than other types; but they may do it in a smaller volume of rock to produce a higher grade. Carten et al. (1988a) identified one of the primary controls for the deposition of molybdenite at Henderson as the presence of K-feldspar along vein margins. Westra and Keith (1981) noted a linear correlation between K$_2$O content of hydrothermally altered rock and grade. K$_2$O-rich stocks may have equilibrated with a larger volume of magmatic water prior to consolidation, and thereby originally contained a greater amount of molybdenum (White et al., 1981). However, on a fine scale, molybdenite crystals are preferentially deposited along K-feldspar crystals relative to quartz or other minerals. Sericite separates molybdenite from the K-feldspar. The high modal abundance of K-feldspar in some Climax-type stocks may be, in part, a depositional control to their grade.

Climax-type deposits may also be high-grade due to deposition from a purely magmatic aqueous phase that begins deposition at the magma-wallrock interface. The ore-fluid for F-deficient deposits may be a mixture of magmatic and meteoric water and, at deposits such as Trout Lake, must have cooled at least a few hundred degrees prior to mineralization (Linnen and Williams-Jones, 1990). This amount of cooling and mixing may result in deposition over a larger volume of rock resulting in lower grades. Deposition of molybdenite from the ore fluid in both Climax- and F-deficient-type deposits is related to decreasing temperature and/or pH (Linnen and Williams-Jones, 1990).

Processes that control the location and duration of molybdenite deposition from the aqueous phase would also obviously control the grade. These would include multiple stocks forming overlapping ore bodies and high chemical and thermal gradients around the stock or pluton.

SUMMARY MODEL AND EXPLORATION CRITERIA

From the foregoing discussion it is apparent that the most significant process (or problem) in the formation of Climax-type deposits is scavenging a few ppm molybdenum from a large chamber eventually to yield an ore fluid with thousands of ppm molybdenum. A Mo-rich magma would be formed in the cupola during this process due to equilibration with the fluid after its arrival and prior to release during mineralization.
The following processes appear to have acted together to produce a molybdenum-rich cupola of magma:

1. Crystallization along the walls or floor of the magma chamber would account for the gradually reduced REE content of the magma between successive intrusions. The successively deeper U-shaped REE patterns are not unique to Climax-type systems, but have been noted in comagmatic intrusions from other non-mineralized granitoids (Johnson et al., 1989). Gradual accumulation of water and fluorine along the chamber roof may lower the solidus, prevent crystallization, and permit assimilation.

2. Underplated or injected mafic magmas may play several roles. They may melt the lower crust and mix with lower crustal melts to provide an oxidized magma in which molybdenum would behave incompatibly during fractionation. They may provide heat for: a) convective transport of dissolved and undissolved volatiles to the cupola, b) assimilation of roof rocks and the cores of older stocks, c) extension of the life of the chamber to allow generation of a large volume of rhyolitic magma and emplacement of multiple intrusions. They may also supply some flux of less soluble, especially sulfurous, gases.

Examination of the histories of most volcanoes reveals that they tend to be complex rather than simple, with the common occurrence of repeated injections of magma, storage of magma at different levels, and magmatic degassing occurring during periods of relative quiescence or activity. Ore deposits would be far more common if simple passive crystallization of modestly water-rich magma near the surface produced an ore deposit. In terms of increased complexity beyond simple crystallization of cupola magma, this model only suggests that convection aids the transport of volatiles produced by crystallization along the walls and floor and from underplated mafic magma. The processes of convection and volatile fluxing may have helped transform Mo-poor magma (3 ppm) into Mo-rich magma (> 1000 ppm), an enrichment that otherwise would be impossible by crystal fractionation alone. Similar processes may have operated in the parent magma chambers of many porphyry Mo systems, although the evidence for these processes often cannot be found in mineralized cupolas alone. Geochemical data reviewed here suggest that initially high incompatible trace element abundances may be much less a "cause" of mineralization than the above processes. However, fluorine and water may be important positive feedback parameters; as their concentrations increase, they reduce the viscosity of the magma and allow more rapid convection and accumulation of ore fluid components in the cupola.

Exploration criteria for a giant, high-grade deposit include:

1. a tectonic setting that indicates a changeover from compressional to extensional tectonics,

2. thick continental crust at the time of deposit formation may encourage extreme differentiation and crustal contamination,

3. an isotopically zoned magma chamber indicative of a long-lived heat source,

4. a large, sub-volcanic, central-vent ash flow/dome system that erupted less than 100 km³ of rhyolite, and
5. high niobium concentrations (>75 ppm) in a subalkaline, magnetite-bearing rhyolite.

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