Upward flow of magmatic fluids from the Old Woman granodiorite, Old Woman Mountains, southeastern California

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Abstract. Isotopic compositions, mineral equilibrium, and field relations at the contact between the midcrustal Cretaceous Old Woman granodiorite and Paleozoic carbonates indicate that water-rich, silica-saturated magmatic fluids were transported upward, away from the pluton, across an impermeable 30- to 40-m thick marble which caps the granodiorite, to higher structural levels along a complex network of hydrologically induced fractures. Within the fractures, fluids reacted to form symmetrical radiating splays of wollastonite with minor amounts of diopside, vesuvianite, and quartz. In many cases, pegmatites are found in the center of these calc-silicate skarns. Cross-cutting pegmatites and wollastonite veins in the aureole indicate that during late stages of crystallization of the granodiorite there were multiple episodes of fluid expulsion. Above the marble layer at higher structural levels, magmatic fluids flowed both laterally and vertically, interacting with lithologies in a more pervasive manner. Values of $\delta^{18}O$ for calcite in the vein skarns average 11.8‰ and pegmatite whole rock silicate $\delta^{18}O$ values average 9.4‰. Thus oxygen isotopic compositions are consistent with a magmatic origin for the skarn-forming fluids. Away from the vein skarns, values of $\delta^{18}O$ for the capping marble range from 18.7 to 22.1‰ (avg. = 21‰) and values of $\delta^{13}C$ range from -3.8 to -3.0‰ (avg. = -3.4‰). The high $\delta^{18}O$ values provide evidence that the marble largely retained its premetamorphic isotopic composition, indicating that fluids from the granodiorite did not flow pervasively across the unit. Lithologies at higher structural levels show evidence of more pervasive interaction with magmatic fluids: forsterite-bearing calc-silicates have $\delta^{18}O$ values down to 11.8‰ and coarse-grained vesuvianite- and wollastonite-bearing skarns have $\delta^{18}O$ values of ~13‰.

Introduction

The presence of large-scale hydrothermal circulation cells surrounding epizonal intrusions has been documented by numerous stable isotopic studies [e.g., Norton and Knight, 1977; Taylor and Forester, 1979; Criss and Taylor, 1983]. In these systems, predominantly meteoric fluids flow in a circular pattern in which fluids move toward the sides of plutons then up along the margins, transporting heat upward. Further, fluid flow is generally modeled as pervasive, flowing independent of structure and lithology, in a medium of uniform porosity. These studies do not, however, address what happens to fluids forcefully discharged by plutons. With regard to magmatic fluids, Nabelek et al. [1983, 1984] showed in a detailed study of the Notch Peak aureole in Utah that country rock composition and geometry are important constraints on the flow paths, causing channelization of fluids into more permeable lithologies, and lateral outward flow from the pluton margin. Ferry [1991] and Ferry and Dipple [1992] have evaluated petrologic and isotopic data from the Notch Peak aureole in light of recent fluid flux models and suggest that outward flow of magmatic fluids (down temperature flow) is inconsistent with petrologic and isotopic data from the aureole. They suggest instead that nonmagmatic fluids flowed laterally toward the pluton, with the country rocks at the sides of the pluton recording little or no evidence of magmatic fluids. Ferry [1991] has suggested that, in general, fluids at the same level as an intrusion would flow up temperature towards the pluton.

The Old Woman granodiorite intruded at depths of ~16-18 km [Foster et al., 1992] which represents a mesozonal or midcrustal setting. Some studies have suggested that large-scale convective recirculation of fluids may not be possible at these crustal levels [e.g., Walther and Orville, 1982; Wood and Walther, 1986] and that fluids should migrate upward in a "single-pass" and escape along hydrologically induced fractures. Carbonate lithologies at the roof of the Old Woman granodiorite afford an opportunity to evaluate the nature of fluid movements in the middle crust using carbon and oxygen isotopic compositions, mineral equilibria, and field relations. This study presents such data along with field observations and interpretations.

General Geology

The Old Woman Mountains are located in the Mojave Desert region of southeastern California (Figure 1a). Early
Figure 1. (a) Simplified geologic map of the Old Woman Mountains [from Miller et al., 1982]. (b) Detailed geologic map of the relations exposed in the Scanlon Gulch area from J.L. Anderson (unpublished data, 1992) and Rothstein [1990]. Sample localities (solid squares) are designated by numbers and are keyed to specific samples in Table 1.
Proterozoic gneisses, which comprise most of the pre-batholithic rocks in the Old Woman Mountains, were first metamorphosed at ~1.70 Ga [Miller et al., 1982; Wooden and Miller, 1990]. These Proterozoic gneisses are overlain by Paleozoic sedimentary rocks, which correlate with the classic Grand Canyon lithostratigraphic sequence of western Arizona [Stone et al., 1983; Brown, 1984]. During Mesozoic time, the Proterozoic basement and overlying sediments were buried and extensively deformed and metamorphosed. Regional peak-metamorphic temperatures and pressures are estimated at ~650 ± 50°C and 3.6 to 5.0 kbar [Hoisch et al., 1988; Miller et al., 1990; Foster et al., 1992]. Two suites of broadly synkinematic to postkinematic granitic magmas, a metallocuminate suite and a peraluminous suite, were intruded at 74 ± 3 Ma [Wooden et al., 1988; Miller et al., 1990; Foster et al., 1992].

The Old Woman granodiorite (K granodiorite, Figure 1a) and the Sweetwater Wash monzogranite (K 2-mica granite, Figure 1a) are the major plutons of the Cretaceous granitic suite. These Cretaceous granites comprise ~50% of the rocks exposed in the Old Woman Mountains. In the central Old Woman Mountains, the two plutons are separated by and intrude a shallowing dipping, sheeltake zone of deformed and thrust-faulted schists, gneisses, and Paleozoic metasedimentary rocks, termed the Scanlon shear zone [Rothstein, 1990]. The Old Woman granodiorite lies structurally below the 1- to 2-km thick shear zone and the Sweetwater Wash pluton lies structurally above. The lower section of the Scanlon shear zone is heavily injected by dikes and pegmatites emanating from the Old Woman granodiorite. Northwest tilting has exposed structurally lower rocks to the southeast and structurally higher rocks to the northwest.

Within the shear zone, the Scanlon thrust juxtaposed an upright section of upper Paleozoic metasedimentary rocks beneath a recumbent folded and overturned package of Proterozoic schists, gneisses and lower Paleozoic metasedimentary rocks. The upper Paleozoic metasedimentary rocks are ~300 m thick and contain lithologies that range in age from Mississippian through Triassic [Stone et al., 1983; Rothstein, 1990].

Contact relations exposed in the Scanlon Gulch area of the central Old Woman Mountains (Figure 1b) are the focus of this study. Work to date has been confined within the upright sequence of upper Paleozoic metasediments, within ~60 m of the main upper contact of the Old Woman granodiorite. Along its upper contact, the granodiorite has intruded against a 30- to 40-m thick virtually pure calcite marble that correlates with the Mississippian Redwall limestone (Figure 1b). The intrusive contact is broadly concordant and is characterized by local development of a variable thickness garnet + epidote skarn. At higher structural levels, the Redwall marble includes other, more heterogeneous skarns composed of variable amounts of wollastonite, vesuvianite, calcite, grossular, diopside, quartz and potassium feldspar. Above these skarns, but below the Scanlon thrust, are stratigraphic equivalents of Permian Hermit Shale, Permian Coconino Sandstone, Permian Kaibab Limestone, and Triassic Moenkopi Formation. These units now occur as schist, quartzite and calc-silicate lithologies.

**Analytical Techniques**

Carbon and oxygen isotopic compositions of calcite in marble, calc-silicate, and skarn were determined using the technique described by McCrea [1950]. Calcite was reacted with H3PO4 at 25°C for 8 hours. Water and noncondensable gases were removed, and the yield of CO2 was determined manometrically. Whole rock oxygen isotopic compositions of silicates in the pegmatites was determined using the method outlined by Clayton and Mayeda [1963] using BrF5 as the oxidizing reagent. Whole rock powders from the pegmatites (composed predominantly of feldspar + quartz) were heated in Ni-velocity reactors at 550°C for 12 hours. The liberated oxygen gas was converted to CO2 and the amount of gas was measured manometrically. Isotopic compositions were measured on a VG PRISM gas ratio mass spectrometer at the University of Southern California. All δ18O values are reported relative to V-SMOW (Vienna-Standard Mean Ocean Water) and values of δ13C are reported relative to PDB (Peedee Belemnite). All δ values are in standard per mil notation.

Analysis of NBS-18 (carbonatite) yields an average δ13C of -0.01% and an average δ18O of +7.21% (accepted values are -5.00 and +7.20, respectively). Replicate analysis of our internal laboratory standard, USC-CC1, yields an average δ13C of 3.01 ± 0.08 and an average δ18O of 19.88 ± 0.10. To test within-sample isotopic heterogeneity of the skarns, four discrete, ~20 mg aliquots of calcite were drilled from sample 90-OW-1 and analyzed individually. The results (90-OW-1A through -1D in Table 1) document carbon isotopic homogeneity (average δ13C = -5.4 ± 0.1) and oxygen isotope heterogeneity (average δ18O = 11.2 ± 0.7). Replicate analyses of NCSU-quartz during the course of this study yield an average δ18O = 11.69 ± 0.17 (n = 14), and analysis of NBS-28 (African Sand) yields an average δ18O of 9.6‰.

**Petrology and Phase Equilibria**

Isotopic and petrologic studies have been conducted on four country rock lithologies: (1) calcite marble, (2) forsterite-bearing calc-silicate, (3) skarn, and (4) pegmatite. Sample locations are shown in Figure 1 and are keyed to individual samples in Table 1. Two distinct types of skarn have been identified on the basis of field occurrence: massive skarns and dike selvage or vein skarns. Massive skarns are characterized by zones up to 2 m thick consisting of wollastonite + vesuvianite + calcite + diopside ± sphene ± garnet ± potassium feldspar. They are generally coarse-grained, with some vesuvianite crystals ranging up to 15 cm in length. Internally, massive skarns contain 5- to 15-cm thick layers of >90% wollastonite and layers of virtually pure calcite.

The dike selvage and vein skarns are strikingly similar in terms of both mineralogy and occurrence. Both consist of generally symmetrical radiating splays of wollastonite ± diopside ± vesuvianite ± quartz ± calcite. Wollastonite is predominant, comprising >90% of the skarn. The skarns range in width from ~10 to 250 cm. The principal difference between dike selvage skarns and vein skarns is that the latter emanate from healed fractures, and the dike selvage skarns are cored by granitic pegmatites. A characteristic example of a dike selvage skarn is shown in Figure 2, where 10- to 30-cm wide selvages of wollastonite + quartz + diopside are developed around a granitic dike in a relatively pure (>98%) calcite marble. There is no correlation between the width of the pegmatite and the width of the selvage skarns.

The occurrence of wollastonite + calcite + quartz in the skarns enables estimation of fluid composition from the reaction calcite + quartz = wollastonite + CO2. At 4.5 kbar and
### Stable isotopic compositions and sample mineralogy

<table>
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<tr>
<th>Sample</th>
<th>Calcite $\delta^{18}O$</th>
<th>Calcite $\delta^{13}C$</th>
<th>Silicate $\delta^{18}O$</th>
<th>Mineralogy</th>
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<td>-5.4</td>
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<td>Kfs, Scp, Spn, Di</td>
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<td>Kfs, Scp, Spn, Di</td>
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<tr>
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<td></td>
<td>+9.4</td>
<td>Kfs, Scp, Spn, Di</td>
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<td>-3.0</td>
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<td>-3.2</td>
<td>...</td>
<td>Cal, Ap, Qtz, Chl (trace)</td>
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<tr>
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<td>-3.5</td>
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<td>-3.8</td>
<td>...</td>
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<tr>
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<td>+1.1</td>
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<td>-0.4</td>
<td>...</td>
<td>Cal, Chl, Fo, Ap</td>
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</table>

Abbreviations: Cal, calcite; Qtz, quartz; Di, diopside; Ves, vesuvianite; Ap, apatite; Chl, clinochlore; Dol, dolomite; Fo, forsterite; Srp, serpentine; Tr, tremolite; Scp, scapolite; Gnt, garnet; Spn, spheine; Kfs, potassium feldspar; Ep, epidote; Wol, wollastonite; and Pl, plagioclase feldspar. Texturally secondary minerals are listed in parentheses.

*Sample location numbers are keyed to Figure 1.

At 650°C, the equilibrium fluid composition is $X_{H_2O} = 0.93$, based on the thermodynamic data of Berman [1988] and the equation of state for mixed H$_2$O-CO$_2$ fluid from Kerrick and Jacobs [1981]. The assemblage wollastonite + calcite + quartz is widespread in the skarns, indicating that the skarn fluids were water-rich, which is consistent with a derivation from the granite. Further, coexisting wollastonite + vesuvianite in both the selvage and massive skarns also indicates that fluids were extremely H$_2$O-rich. Valley et al. [1985] argued that in the system CaO-MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O-CO$_2$, the coexistence of Mg-vesuvianite and wollastonite requires a virtually pure H$_2$O fluid (generally $X_{H_2O} > 0.97$). Although this esti-
Figure 2. Photograph of a typical dike selvage skarn. Darkened central portion is a granitic pegmatite (gr) which consists predominantly of feldspar and quartz, surrounded by wollastonite selvages (Wol). The pegmatite and skarns are developed in virtually pure calcite marble (Cal).

Stable Isotopic Compositions

Values of δ¹⁸O and δ¹³C for the four lithologies are plotted in Figure 3. Values of δ¹⁸O are plotted on the upper histogram, and values of δ¹³C are plotted on the lower histogram. Calcite δ¹⁸O and δ¹³C values are shown for marble, skarn, and calc-silicate, and whole rock silicate δ¹⁸O values are shown for pegmatite. The highest and lowest values of δ¹⁸O are from calcite marble and pegmatite, respectively. Calcite marble has an average δ¹⁸O of 20.9 ± 1.5‰, while pegmatite has an average δ¹⁸O of 9.4 ± 0.3‰. Skarn and calc-silicate have intermediate δ¹⁸O values. Carbon isotopic compositions of the calc-silicates (avg. δ¹³C = 0.0 ± 0.7‰) are distinctly higher than those of marble and skarn (avg. δ¹³C = -4.9 ± 1.3‰). These isotopic heterogeneities among the four lithologies document selective preservation of premetamorphic isotopic compositions and channelized fluid flow.

Calcite Marbles

Detailed mapping in the Scanlon Gulch area by Rothstein [1990] identified the massive marble unit adjacent to the Old Woman granodiorite as Mississippian Redwall Limestone. Despite the fact that no equivalent unmetamorphosed limestones are exposed in the immediate area, a reasonable range of premetamorphic carbon isotopic values can be estimated from the data of Veizer and Hoefs [1976]. Values of δ¹⁸O for Carboniferous calcite (the most similar precursors of the calcite marbles) range from 17 to 29‰ with a mode at 23-24‰ [Veizer and Hoefs, 1976]. Values of δ¹³C range from -5 to +4‰ with a mode at +2‰. This range in premetamorphic isotopic compositions is illustrated in Figure 4. The 12‰ range in δ¹⁸O (17 to 29‰) and 9‰ range in δ¹³C (-5 to +4‰) likely reflect a combination of (1) local or regional variations in original depositional conditions (such as temperature and water isotopic composition) and (2) variable diagenetic overprints. Values of δ¹⁸O and δ¹³C for the calcite marble from this area of the Old Woman Mountains are within this range.
range and thus are interpreted to have largely preserved their original isotopic compositions. The preservation of sedimentary compositions indicates that the calcite marble was not pervasively infiltrated by significant quantities of magmatic fluid.

This lack of isotopic change is consistent with the unreactive mineralogy of the Redwall marble. Rumble and Spear [1983] suggested that mineralogically unreactive marble is relatively impermeable to fluid flow. They concluded that metamorphic volatilization reactions can increase permeability by generating an intergranular fluid, but in the absence of internally generated fluids, marbles may act as impermeable barriers. The calcite marbles in this study offer no mineralogic evidence for volatilization. Additionally, they are devoid of any visible (>5 μm diameter) fluid inclusions, whereas the calc-silicates and skarns contain abundant fluid inclusions.

Calc-Silicates

The forsterite-bearing calc-silicates are interpreted to correlate with the Permian Kaibab "limestone" of the Grand Canyon sequence which includes facies of siliceous dolomitic and calcitic-limestone [Stone et al., 1983]. Metamorphic mineralogy indicates that initially dolomite + quartz + potassium feldspar were present and reacted to form forsterite via the reaction tremolite + dolomite = forsterite + calcite + CO₂ + H₂O. Values of δ¹⁸O for Permian dolomite range from 18 to 30‰ but are strongly negatively skewed to values between 25 and 30‰, so it is likely that the original dolomite in the forsterite-bearing marbles had values of δ¹⁸O ≥ −24 [Veizer and Hoefs, 1976, Figure 4]. Since equilibrium volatilization will not result in decreases in δ¹⁸O of >2 to 3‰ [Valley, 1986], the average δ¹⁸O depletion of 9‰ is interpreted to indicate that the forsterite-bearing calc-silicates experienced both volatilization (documented by forsterite + calcite) and the infiltration of externally derived fluids. If the protolith δ¹⁸O was ≥ 24‰, and 2 to 3‰ of the decrease resulted from equilibration volatilization, then the remaining 5 to 9‰ decrease in δ¹⁸O is best explained by the infiltration of magmatic fluid.

Unmetamorphosed Permian dolomites have δ¹³C values between -4 and +6‰. Although the range of δ¹³C values for Permian dolomites and Carboniferous calcites are similar (Figure 4), the distribution of δ¹³C values in Permian dolomites is strongly negatively skewed with a mode at +4‰ [Veizer and Hoefs, 1976]. Thus it is likely that the protolith δ¹³C was > 0 and possibly as high as +5‰. As depicted in Figure 3, the average δ¹³C of the forsterite-bearing calc-silicates (0.0 ± 0.7) is ~5‰ higher than the skarns (avg. δ¹³C = -5.2 ± 1.2) and ~3.5‰ higher than the marbles (avg. δ¹³C = -3.4 ± 0.4). The difference in δ¹³C between the forsterite-bearing calc-silicates and other lithologies is due largely to differences in protolith composition.

Skarns

The development of extensive calc-silicate skarns, as well as the evidence for infiltration of magmatic fluids into forsterite-bearing calc-silicates, indicates that despite the presence of the impermeable capping marble, magmatic fluids escaped from the granodiorite and moved to higher structural levels of the aureole. Evaluation of field relations, isotopic compositions and mineral equilibrium of the vein and selvage skarns indicates that they deliniate the fractures along which magmatic fluids flowed to higher structural levels.

The development of wollastonite vein and selvage skarns in thick layers of virtually pure calcite marble necessitates the influx of Si-saturated H₂O-rich fluids. The average oxygen isotopic composition of calcite in the skarns (both vein and selvage) is 11.8 ± 1.8‰ and values range from 8.6 to 13.8‰. These data are best explained by exchange between magmatic fluid derived from the Old Woman granodiorite and marbles. H₂O in equilibrium with the granodiorite at 600 to 700°C would have a δ¹⁸O of 8-10‰. The range in calcite δ¹⁸O values in the skarns is consistent with variable time-integrated fluxes of magmatic fluids with values of δ¹⁸O of 8-10‰ through individual vein systems.

Whether the dike selvage skarns could have been generated by the in situ crystallization of pegmatites is an important question. Material balance calculations which model the amount of wollastonite precipitated by the crystallization of pegmatite in a host of pure calcite marble indicate that crystallization of the pegmatites alone cannot provide sufficient Si
to generate the observed wollastonite. Thus magmatic fluids (or possibly magma) must have flowed along the pegmatite-marble contact, either before or after crystallization of the pegmatite. In a model volume of pegmatite measuring 2 x 30 x 30 cm (dimensions similar to pegmatite-skarn system illustrated in Figure 2), composed of quartz and plagioclase with 6 wt. % H$_2$O, crystallization of the pegmatite will release ~16 moles of H$_2$O. If the H$_2$O contains the maximum amount of soluble SiO$_2$ (1.6 wt. % SiO$_2$ at 650°C and 0.45 GPa) [Anderson and Burnham, 1965] then only 0.08 moles of SiO$_2$ will be in solution in the fluid. Reaction stoichiometry dictates that this SiO$_2$ can produce a maximum of 0.08 moles or ~9 grams of wollastonite. Typical selvage skarns surrounding 2 cm wide pegmatites are between 1 and 4 cm thick (e.g. Figure 2). To produce a 2 cm thick skarn on both sides of the volume of pegmatite modeled above (3600 cm$^3$ or 10,450 grams wollastonite), 90 moles of SiO$_2$ are required. Thus, the amount of wollastonite that could be generated by the crystallization of the in situ pegmatite alone (0.08 moles) is at least 3 orders of magnitude less than the amount of wollastonite observed (90 moles). This simplified calculation is consistent with the conclusion that pegmatite injection into fractures was either the culmination of extensive fluid and/or magma flow through the fractures or that following crystallization, Si-saturated fluids continued to flow along the pegmatite-marble contact. Calculation of time-integrated fluid fluxes using the reaction progress method (Baumgartner and Ferry, 1991) cannot be applied to the wollastonite because the method assumes that all cation constituents are immobile.

**Conclusions**

The initial development of discrete fractures in the capping marble through which magmatic fluids escaped must have required the development of fluid pressures high enough to hydrofracture the marble. The impermeable capping marble would have prevented the escape of fluids being evolved by crystallization of the magma, resulting in an increase in fluid pressure along the boundary between the marble and granodiorite. Hydrofracturing may have created the fractures into which dikes were subsequently injected. Epidote-gossansular skarns that range in width from ~10 to 30 cm occur along the main contact between the granodiorite and the capping marble and document the presence of fluids along the boundary. Multiple generations of pegmatite in the aureole and the extensive fluid-rock interaction indicated by the selvage and vein skarns require a protracted series of fluid expulsions from the granodiorite.

In the Scanlon Gulch area, where magmatic fluids are expelled at the roof of a mesozonal pluton, no evidence of convective recirculation was found. Rather, the evidence supports a simple upward migration of magmatic fluids. Fluid migration occurred along both cross-cutting and layer-parallel hydrofractures. In this regard, the mode of fluid escape is similar to that seen in epizonal plutons. This is interesting despite the significantly different rheological properties of aureole rocks, dominantly brittle in epizonal settings and dominantly ductile in the mesozonal setting. This study documents that forcefully discharged magmatic fluids tend to escape through channels, either lithologically controlled [Nabelek et al., 1983, 1984] or hydrologically induced in all settings, rather than flowing pervasively through an interconnected porosity.

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