Hydrogen in spessartine-almandine garnets as a tracer of granitic pegmatite evolution

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Abstract

The hydroxide contents of spessartine-almandine garnets from the Rutherford #2 (Virginia), Himalaya (California) and George Ashley Block (California) pegmatites were determined by infrared spectroscopy. The hydroxide content of garnet increases from the wall zone to the core zone of the Rutherford #2 and Himalaya pegmatites, consistent with increasing H_2O activity during pegmatite crystallization. However, the absolute OH contents differ by about two orders of magnitude for these two suites of garnets, possibly due to the elevated Ca content of the Rutherford #2 and the differences in the depth of emplacement. The garnets from the George Ashley Block show significant excursions from this correlation at the positions within the pegmatite where Kleck and Foord (1999) identified disruptions in major- and minor-element trends that they associated with re-injections of magma and subsequent flushing of the dike system. Ease of measurement as well as a relative amplified sensitivity compared to the Mn and Fe trends, make hydrogen an excellent tracer for the evolution of granitic pegmatites.

Introduction

Concentrations of Mn and Fe^{2+} in garnets correlate with the geochemical evolution of zoned pegmatite bodies (Baldwin and Knorring 1983; Whitworth 1992). Specifically, Mn contents increase from the wall zone to the core zone, as Fe^{2+} decreases. Hydrogen in the form of OH^- is also a component of pegmatitic garnets (Aines and Rossman 1984), but no known studies have examined the relationship between H content and geochemical evolution of the pegmatite body. Work by Rossman, et al. (1988) provides background and calibration information on OH in garnets, but does not provide specific correlation to pegmatite evolution.

Hydrogen has been found in natural pyralspite garnets (pyrope, almandine, spessartine) to occur strictly as the OH species (Aines and Rossman 1984). Concentrations of OH in spessartine-almandine garnets range up to one tenth or more, expressed as wt% H_2O. In grossular garnets, OH exists as the hydrogarnet substitution, $SiO_4 = (O_4H_4)$ in higher concentrations. When the concentrations of hydrogarnet are low, other forms of substitution occur but the atomic details of the substitution have generally not been established (Cho and Rossman, 1993; Rossman and Aines 1991). Likewise the details of substitution of OH in pyralspite garnets have not been established.

In this paper we examine Mn, Fe^{2+} and H trends in spessartine-almandine garnets as they evolve through three zoned North American pegmatites: the Rutherford #2 pegmatite, George Ashley Block pegmatite, and the Himalaya Mine.

The Rutherford #2 pegmatite is a steeply dipping, symmetrically zoned, lens-shaped rare-element granitic pegmatite located near the town of Amelia in the Outer Piedmont province of central Virginia. Lumpkin (1998) reviewed much of the previous

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work on the Rutherford #2 pegmatite and provides an updated description of the mineralogy and internal evolution of this body. The George Ashley Block pegmatite (GAB) is a layered, asymmetric pocket-containing peraluminous rockslide block located in the Pala pegmatite district of Southern California. Kleck and Foord (1999) reported on its chemistry, mineralogy and petrology. The Himalaya Mine is part of the Himalaya Dike System, a group of small, relatively thin, continuous pegmatite dikes that are exposed along the east and northern flanks of Gem Hill. This dike system is located within the Cretaceous Mesa Grande pegmatite district, within the Peninsular Ranges batholith in south central San Diego County, California. Foord (1976, 1977) extensively described this system.

Experimental Methods

Sample description

A total of twenty-nine spessartine garnets were analyzed for this study (Table 1): ten from the Rutherford #2 pegmatite, fifteen from the George Ashley Block (GAB) pegmatite and four from the Himalaya Mine in the Himalaya Dike system. The Rutherford and GAB garnets are from well-constrained areas in terms of pegmatite structure, while the Himalaya garnets are from relative areas (i.e., near wall zones or near pocket zones).

The Rutherford #2 pegmatite is subdivided into seven major zones, six of which contain garnet (Glass, 1935; Lemke et al., 1952; Sinkankas, 1968; Lumpkin, 1998). We examined samples from five of these zones. Wall Zone samples (2) are euhedral crystals, red in color; vary in size from 2-10 mm, and are associated with oligoclase, microcline,

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muscovite, quartz, fergusonite and tourmaline. Second Intermediate Zone samples contain red-brown to red-orange 2-10 mm euhedral garnet crystals (4) with associated albite-oligoclase, muscovite, ferrocolumbite, fergusonite, microlite, and monazite associations. Middle Intermediate Zone samples contain red-orange to orange 5-15 mm subhedral crystals (2), with associated albite, muscovite, ferrocolumbite, microlite, and quartz. Inner Intermediate Zone samples contain orange to pale-orange 5-25 mm subhedral crystals (1), with albite, muscovite, manganotantalite, microlite, cassiterite, and fluorite. The Core Zone contains pale orange 5-15 mm subhedral crystals (1), with associated quartz, microcline, albite, muscovite, and apatite.

The George Ashley Block garnet samples were collected across a fully exposed cross section of the pegmatite body by Kleck, as reported in Kleck and Foord (1999). Collection started at the lower contact of the wall (border zone), designated in our tables as 0 cm, and continued approximately every 30 or 60 cm there after until the top was reached (810 cm), the core (pocket) zone being at 360 cm. Garnets range in color from red to orange, and in size from 0.5 mm to 1.5 mm. The majority of the garnets are euhedral with well-developed crystal faces. Associated minerals through most of the traverse are quartz, potassium feldspar, Na-rich plagioclase, muscovite, and biotite, with tourmaline crystallizing instead of biotite as the main Fe-bearing mineral nearest to the core zone.

The Himalaya Mine samples were not collected from a continuous traverse across the pegmatite body, rather they were collected from the mine dumps. Three whole rock samples were collected to represent various zones within the pegmatite, one showing a boundary contact with the host rock, one from near an intermediate zone, and one from

near the pocket zone. Four garnet grains were extracted from these. The two garnet

grains extracted from the boundary rock are red in color and range in size from 1 mm to 5

mm. One garnet grain from the intermediate zone is pale orange in color and was 2 mm

in diameter. One garnet grain from the pocket zone area is pale orange in color and 10

mm diameter. Associated minerals are quartz, Na-rich plagioclase, albite, muscovite,

lepidolite (pocket zone), and tourmaline.

OH determination

       To determine the OH contents of the garnets, infrared spectral measurements were

obtained on a Nicolet Magna 860 Fourier Transform Infrared Spectrometer operating at 4

cm^{-1} resolution. With detection limits of about one ppm H_2O, and samples ranging in

size from 1 to 10 mm in diameter, it was necessary to thin the samples to keep the spectra

on scale. Each sample was doubly polished to an approximate 0.2 mm thick slab, and

mounted over steel pinhole apertures (0.2- 0.4 mm diameters), which defined the region

of interest. To determine if the grains were zoned, multiple measurements were taken

covering the rim to the center of the Rutherford and Himalaya Mine grains. The

diameters of the GAB grains were so small that the rim and the center measurements of

the grains overlapped.

       Among pyralspite garnets from pegmatites, spessartine has the greatest amount of

OH, commonly found in concentrations up to hundreds of ppm. The OH content,

expressed as weight % H_2O is based on the spessartine calibration in Rossman et al.

(1988), where the weight percent water $= 0.0000375 \times$ [integrated absorbance per cm

sample thickness in the 3750 to 3450 wavenumber (cm^{-1}) range]. Because a new

instrument was used in the current analyses, one of the original calibration samples was thinned to 0.183 mm and re-analyzed. The new calibration coefficient was 0.0000365. With just a 2.7% change in the sample calibration, we were unable to determine if this is a true revision of the calibration, a manifestation of heterogeneity within the sample, or experimental uncertainty in the determination. Throughout this paper the most recent calibration was used to determine H contents of all garnet samples analyzed.

Infrared spectral measurements in the 5200 cm^{-1} region were also acquired. Molecular H_2O, if present, would show up as a combination bend and stretch mode. No bands in this region were observed in the sample used for this study.

Electron microprobe chemical analysis

The Rutherford #2 pegmatite and the Himalaya Mine garnets were analyzed for major elemental chemical compositions on Caltech's JOEL JXA-733 electron microprobe equipped with 5 wavelength-dispersive spectrometers, and a Tracor Northern energy-dispersive spectrometer operating at 15 kV accelerating potential, 25 nA beam current, and 10 micrometer beam size. Analyses were acquired using the Probe for Windows operating system, interfaced to the Tracor 5600 microprobe automation. For instrument calibration well-characterized garnet and metal oxide standards were used. The GAB pegmatite garnets analyses are taken from Kleck and Foord (1999), where an average of two to three grains were used for each analysis.

Results

Compositional results

Chemical compositional analyses obtained at Caltech are reported in Table 1. Foord (1977) reported the chemical analysis of Himalaya Mine almandine-spessartine garnets in the wall zone to intermediate zones. They range in composition from $Alm_{78}Sps_{24}Py_3$ to $Alm_{49}Sps_{50}Py_1$, and within the pocket (core) zone, $Alm_{0.5}Sps_{99.5}Py_0$. Data collected at Caltech are in general agreement with the more extensive chemical study of garnets in the Himalaya Mine by Foord (1977). Furthermore, analyses of the Rutherford # 2 pegmatite garnets are generally similar to the Himalaya dike garnets in their respective zones.

Plots of weight percent oxide chemical compositions as a function of elevation into the pegmatite body (wall to core (pocket) zone) for the Rutherford and Himalaya systems, display patterns of increasing Mn and decreasing Fe^{2+} towards the pegmatite core (Figs. 1 and 2). The GAB on the other hand, displays a more complex pattern (Fig. 3). Rather than monotonically increasing to the core zone (360 cm), it undergoes a reversal to near original compositional levels at approximately 150 and 550, with another small reversal at 700 cm.

OH content

The infrared spectra of the garnets yield OH absorption bands that are similar in shape and number to published spectra of OH in spessartine garnets (Aines and Rossman 1984), with prominent bands at 3580 cm^{-1}, 3634 cm^{-1}, 3624 cm^{-1} (Figs. 4, 5, 6a, and 6b). No features of molecular H_2O were observed in the 5200 cm^{-1} region of the spectra. H

contents are presented in Table 1 and plotted against sample position for all three

pegmatites. The Rutherford and Himalaya plots reveal that the H content increases from

wall to core zones (Figs. 7 and 8). The GAB displays a more complex trend, where

increases in H content are followed by sudden decreases around the core zone (360 cm)

at 150 cm and 550 cm, along with another oscillation at 700 cm (Fig. 9).

Discussion

This study was conducted to determine if the amount of H is correlated with the

geochemical evolution of three zoned pegmatites. For the Rutherford #2 pegmatite, the

general pattern of increasing H_2O content from the wall zone inward through the

intermediate zones to the core is consistent with the mineralogical and textural evolution.

In reviewing the internal evolution of the pegmatite, Lumpkin (1998) proposed that the

magma was initially H_2O-undersaturated and that the activity of the H_2O increased

gradually through the outer zones, ultimately reaching saturation during crystallization of

the intermediate zones. The results of this study indicate a fairly rapid increase in the

H_2O content of garnet after the formation of the wall zone. This observation may be a

direct indication of the effect of crystallization of apatite, fluorite, and tourmaline noted

by Lumpkin (1998). Results clearly show there is a general trend of increasing H content

towards the core of the pegmatites. In the case of the GAB, previous studies (Kleck and

Foord, 1999) show a multi event growth history; the H trend shows this same complexity.

Mn and Fe also track the evolution of the pegmatite from wall to core, a

comparison of Figures 3,4 and 5, to 7,8 and 9, shows that H content has proportionally a

much greater change than the Mn or Fe content. In garnets from simple pegmatite

systems, the wall to mid zone trends are that of generally rising H contents that generally

mimic a corresponding trend of Mn contents. Ca also tracks the pegmatite evolution in the Rutherford #2 garnets, decreasing from about 5.5 wt% (X_{grs} approx. 0.12) to less than 1.0 wt% (X_{grs} approx. 0.02) from wall zone to core (Figure 1). In the case of the GAB, the variation in H content vs. sample position is much more complex. Initially there is an increase as the garnets are extracted further from the wall, punctuated by an abrupt decrease in content at 150 cm followed by a rise to the core zone at 360 cm, then a fall at 550 cm, another rise then a fall at 700 cm, then a final rise to 810 cm. The 150 and 550 cm falls mirror each other around the core zone (360 cm). These are the same ranges where Kleck and Foord (1999) suggested resetting occurred in the magma. We note that H is a particularly sensitive component due to its proportionally greater range of variation.

It is particularly satisfying that the H content responds at the same positions at which Kleck and Foord (1999) interpreted the chemical compositions to reset by multiple stages of magma injections and subsequent flushings. No textural or mineralogical variation was observed at these specific levels during field examination (W. Kleck, personal communication), but their presence in trace element signatures, particularly H, is obvious. It must be noted that another interpretation of the complexity of the GAB evolution exists (Webber et al., 1997 and 1999), that suggests that variations in the overall volatile content of the GAB as it crystallized could explain the fluctuations. While our data directly support the Kleck and Foord (1999) model, the implications of the Webber et al. model for variation in the H content have not been evaluated. Because of the widespread occurrence of garnets in many pegmatites, the study of H may have wide applications as a tracer for the evolution of pegmatites.

The absolute concentration of H in the three pegmatites varies by two orders of magnitude. The question remains whether these differences are related to differences in the absolute H content in the magma at the time of emplacement, or to other chemical variations in the garnet. Hopefully, further investigations into this subject will answer this question.

Depth of emplacement may well be a factor. The Rutherford #2 was probably emplaced at a moderate level in the crust following the Barrovian metamorphism in central Virginia at pressure, 3-4 kbar, typical of rare element pegmatites (Cerny, 1989). In contrast, the miarolitic, Li rich pegmatites of the Mesa Grande and Pala districts may have been emplaced at a shallower level in the crust, 1-2 kbar, (Cerny 1989). We note that garnets in all three pegmatites have about the same Mn/Fe ratio, so the differences cannot be due to that ratio alone. The correlation of minor and trace elements with the OH content was also examined. Previous work has shown that generally higher concentrations of Ca correlate with higher concentrations of OH in both grossular and andradite garnets (Rossman and Aines 1991). It is reasonable to expect that in almandine-spessartine garnets this would also hold true. In fact, the exact opposite was found. While the Rutherford #2 pegmatite does have higher H and Ca contents than the other two localities (Table 1), increases in H do not correlate with an increase in Ca at this locality. Furthermore, neither does H correlate with the Ca content at the other two localities. Although a correlation between H and Ca was not found, the elevated levels of Ca in the Rutherford #2 could have still facilitated the overall increase in H for these garnets. We also investigated the volatile F (Table 1), and found that there is no correlation between all three pegmatites with H content. The Rutherford #2 was the only

one that had F increase along with H as the pegmatite progressed from rim to core. These studies have not identified any viable minor or trace component with which hydrogen is clearly associated. However, the sensitivity of hydrogen as a tracer and its correlation with the evolution of simple pegmatites raises the question whether other anhydrous phases such as quartz and feldspar might also show similar correlations.

Acknowledgments

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Figure Captions

Figure 1. Composition versus sample position for the Rutherford #2 garnets.

Figure 2. Composition versus sample position for the Himalaya Mine garnets.

Figure 3. Composition versus sample position for the GAB garnets.

Figure 4. Rutherford #2 garnet OH absorbance.

Figure 5. Himalaya Mine garnet OH absorbance, 1) 5 mm from wall contact, 2) 40 mm

from wall contact, 3) near intermediate zone, 4) near pocket zone.

Figure 6a. GAB garnet OH absorbance 0-330 cm (wall to core).

Figure 6b. GAB garnet OH absorbance 420-810 cm (core to wall).

Figure 7. Rutherford #2 garnet wt% H_2O vs. sample position.

Figure 8. Himalaya Mine garnet wt% H_2O vs. sample position.

Figure 9. GAB garnet wt% H_2O vs. sample position.