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Ion-microprobe analyses of Li and B in topaz from different environments

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Abstract

Ion-microprobe analyses of Li and B in topaz show a range of four orders of magnitude for Li and three orders of magnitude for B and vary as a function of association. Li (mean = 121 ppmw—parts per million by weight) and B (mean = 39 ppmw) are high in topaz from topaz rhyolites but low in pegmatites (mean Li = 1.4, B = 1.3 ppmw) and hydrothermal greisens (mean Li = 1.0, B = 1.5 ppmw). A suggestion that high Li and B in topaz are related to an igneous origin is supported by high Li and B in topaz in topazite and ongonite dikes and very low Li and B in topaz from a hydrothermal topazite.

Introduction

Topaz is a common accessory phase in F-rich rhyolites, pegmatites, and greisens. In topaz rhyolites, it crystallizes in lithophysal cavities during rapid cooling and devitrification of the extruded rhyolite in the presence of exsolved F-rich vapor (Christiansen et al., 1986). Topaz in hydrothermal greisens and pegmatites presumably formed at higher confining pressures and grew from a low-density, water-rich fluid (Burt, 1981). Probable temperatures are <700°C for the rhyolites and <500°C for the pegmatites and greisens. Topaz from rhyolites is generally more "gemmy" than that from greisens and pegmatites, in which it often occurs in massive form and may be altered to other minerals, such as micas.

The only major-element diadochy in topaz is the substitution of F^- for OH^-, although topaz with greater than 30 mol% OH substitution for F is unknown (Ribbe, 1982). Minor amounts (<500 ppm) of Fe and Cr were detected in an early electron-microprobe study (Ribbe and Rosenberg, 1971), and Ribbe (1982) referred to a spectroscopic study as showing trace amounts (<300 ppm) of Co, Ni, V, Mn, and Cu (El-Hinnawi and Hofmann, 1966). These transition elements and radiation-induced color centers are accepted as being responsible for the colors of topaz (Ribbe, 1982).

Little is known about the substitution of light trace elements in topaz, but because topaz is often associated with rocks rich in incompatible elements we undertook a reconnaissance study of the Li and B contents of topaz from different environments. In this study, we asked the following questions: (1) How do the Li and B concentrations of topaz crystals change with geologic association? (2) Can the Li and B contents of topaz (as isolated grains or in thin section) be used as a fingerprinting technique to differentiate one association from another?

Samples and localities

Topaz associations and localities are given in Table 1. The associations include topaz rhyolites, rocks with pegmatitic affinities, hydrothermal greisens, topazites, and an ongonite plus three individual specimens from other associations. Most of these were collected (or, in one case, purchased) by one of us (D.M.B.) in an on-going investigation of mineral equilibria in F-rich igneous rocks.

Topaz rhyolites

Four of the topaz rhyolite localities are from Mexico, and one is from the U.S. Topaz from Topaz Mountain and San Jorge is clear, Tepetate topaz is clear to rose, Sierra Ocote topaz is rosy to peach, and a topaz from a fumarole at San Pedro Almoyan is clear. Pink to dark red topazes (a–d, respectively, in Table 1) were found in an arroyo near the Pinos rhyolite (Mexico) from which they were almost certainly derived.

Pegmatitic affinities

Topaz specimens from the China Wall pegmatitic granite, the Brown Derby Li pegmatite, and the pegmatitic vein at Trumbull, Connecticut, are all massive and colorless. Large, colorless single crystals occur at the pegmatoid locality at the Shizhuyuan tungsten mine in China. A bluish crystal was broken off a large aggregate of columnar topaz (var. pycnite) occurring with quartz and zinnwaldite in a purchased specimen from Altenberg, German Democratic Republic (Erzgebirge district).

Hydrothermal greisens

Clear to rosy crystals of topaz occur at the China Wall, Burnt Hill, and Sherlovaya Gora greisens, whereas Piaotang topaz is mostly massive and colorless.

TABLE 1. Topaz associations, localities, and compositions

I.D.	Ore (prospect)	Locality		Concentrations in ppmw Li	B	Na
		Topaz rhyolite association				
1	Gems	Topaz Mountain	Thomas Range, Utah	79	3.6	11.6
2	Gems	San Jorge Topaz mine	Guanajuato, Mexico	155	48.6	10.0
3	Gems	Tepetate	San Luis Potosi, Mexico	132	1.4	4.6
4	Sn placer	Sierra Ocote	Guanajuato, Mexico	68	17.0	16.0
5	Sn	San Pedro Almoyan (fumarole)	Guanajuato, Mexico	234	34.4	5.7
6	Sn placer	Pinos (mean)	Zacatecas, Mexico	59	128	164
		a		43	39.2	21.5
		b		45	16.4	19.2
		c		67	272	463
		d		82	184	151
				121*	39*	35*
		Pegmatite affinities				
7	Be (W)	China Wall cupola	Tarryall, Colorado	0.7	2.0	4.3
8	Li (Ta)	Brown Derby mine	Gunnison, Colorado	1.0	1.2	3.6
9	W	Trumbull	Connecticut	0.6	0.9	5.6
10	W (Sn)	Shizhuyuan mine	Hunan Province, south China	0.6	2.0	16.6
11	Sn (W)	Pycnite (Erzgebirge district)	Altenberg, DDR	3.9	0.5	2.4
				1.4*	1.3*	6.5*
		Hydrothermal greisen association				
12	Be (W)	China Wall cupola	Tarryall, Colorado	0.4	1.0	3.4
13	W (Be, Bi)	Burnt Hill mine	New Brunswick, Canada	0.4	0.8	5.2
14	W (Sn, Be)	Piaotang mine	Jiangxi Province, south China	2.9	0.6	5.4
15	Be (Sn)	Sherlovaya Gora	Transbaikalia, USSR	0.3	3.6	5.8
				1.0*	1.5*	5.0*
		Ongonite and topazite association				
16	Be	Flying W Range (ongonite)	Young, Arizona	72	9.8	—
17	Be	Flying W Range (topazite)	Young, Arizona	19	5.2	20.0
18	W	Torrington (topazite)	N.S.W., Australia	0.03	0.1	0.7
		Other associations				
19	(Au)	Brewer mine	Chesterfield County, South Carolina	2.5	26.4	25.5
20	(Be)	Honeycomb Hills	Utah	44	0.7	4.4
21	Mo (W, Sn)	Porphyry molybdenite	Henderson, Colorado	17	0.7	10

* Mean.

Ongonite and topazites

Quartz-topaz dikes sampled in this study included a very fine-grained ongonite (abundant albite, quartz, and topaz) and a fine-grained topazite (little or no albite). Both are from the Flying W Ranch area near Young, Arizona, and are discussed in Kortemeier and Burt, 1985. In the ongonite, tiny (<15 μm in the longest direction) acicular topaz crystals abound. Larger acicular crystals (up to 500 μm) were observed in the topazite. A sugary-textured, hydrothermally altered topazite dike (locally referred to as "silexite") was donated to us (reportedly from a dike mined for tungsten in Torrington, N.S.W., Australia) and contained 1-mm yellowish euhedral topaz.

Other associations

Metamorphic topaz from Brewer mine, South Carolina, is cryptocrystalline. Large pinkish crystals occur in a pegmatitic granite xenolith in rhyolite from Honeycomb Hills, Utah, and 100-μm crystals are common in a topaz-quartz alteration adjacent to a quartz-pyrite vein from the Henderson porphyry molybdenite deposit, Colorado.

ANALYTICAL METHODS

Analyses for Li and B were performed on a Cameca IMS 3f ion microprobe using glass standards for the light elements. Conditions were as follows: The primary beam was mass-analyzed $^{16}O^-$ with an impact energy of 17 keV. Primary currents were 8–12 nA, and the beam was focused to a 20–30 μm spot. Positive secondary ions were collected using the 25-μm transfer lens and a 750-μm field aperture to restrict the analyzed area to a 10-μm diameter within the sputtered crater. However, for the tiny crystals of topaz in the ongonite, a 100-μm field aperture was used to reduce the analyzed area to <2 μm in diameter. Standard intensity ratios taken at these conditions were identical to data taken with a 10-μm diameter analyzed area, but intensities were reduced by almost a factor of 100. The energy window was left wide open but translated to discriminate against low energy (gas phase) ions.

A separate study (Hervig, 1985) showed a linear relation between secondary ion intensity for B and Li (normalized to ^{28}Si) and concentration for glasses along the binary joins $NaAlSi_3O_8$-$NaBSi_3O_8$, SiO_2-$NaBO_2$, $NaAlSi_3O_8$-$LiAlSi_3O_8$, and $KAlSi_3O_8$-$LiAlSi_3O_8$. At these conditions, secondary-ion intensity ratios for B are the same on crystalline and glassy $NaBSi_3O_8$; for these compositions using glass standards does not introduce a system-

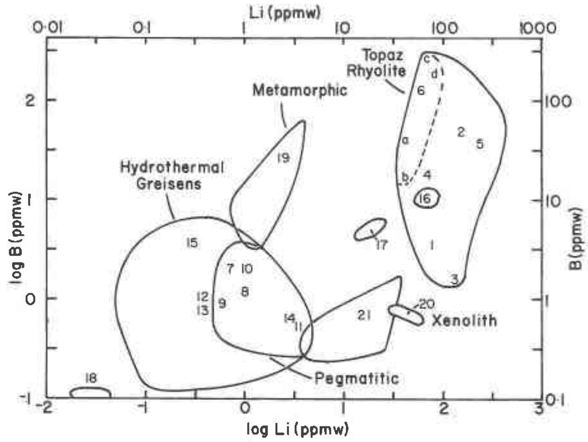

Fig. 1. Variation of the log of Li content vs. log of B content in topaz in parts per million by weight (ppmw). Numbers are placed at the mean composition for each locality, and solid lines encompass all analyses from an association. The areas labeled 16, 17, and 18 represent an ongonite and a topazite from Arizona and a topazite from N.S.W. Australia, respectively. Sample 21 is from the Henderson porphyry molybdenite deposit. See Table 1 for other localities.

atic error. No comparison between glasses and crystals has been made for Li, but Ray and Hart (1982) found 40% lower ratios of Na/Si for glasses than for crystals of the same composition. Note also that in her discussions with reviewers, Havette (1985) suggested that this was due to charge-induced migration of ions away from the ion beam in the glass. Differential charging between crystals and glasses may also lead to different intensity ratios if the energy distributions of the isotope of interest and the normalizing isotope are different and change with matrix composition.

Although there are still unanswered questions concerning the use of glasses as ion-microprobe standards, the problem is least serious for B. As a worst case, if Li secondary-ion intensities of glasses relative to topaz crystals are systematically low by the same factor as Ray and Hart (1982) noted for Na in clinopyroxene-composition crystals and glass, then the given analyses are overestimating Li by about 45%. The conclusions of this study are based on relative abundances in topaz and so are not affected.

Replicate analyses of topaz from Topaz Mountain on three different analysis sessions over seven months showed Li reproducible to ±10% (8 ppmw) and B to ±25% (0.9 ppmw). Replicate analyses for B in cryptocrystalline topaz from the Brewer mine showed constantly increasing values over seven months. No other topaz crystals showed this feature, but their grain size was always larger than the beam diameter. The samples were repolished during this time; perhaps B in the polishing medium became embedded in the interstices and contaminated the secondary-ion beam during analyses of topaz from the Brewer mine.

Secondary-ion intensities were collected for F^+. Comparison with electron-microprobe analyses revealed that these intensities were not linear with F concentration under the above conditions. Recently we have found that a −50-V offset on the sample voltage gives a fair linear correlation between F^+ and concentration; however, this leads to a hundredfold reduction in the secondary ion signal. We are studying this effect further (see Hinthorne and Andersen, 1975, and Jones and Smith, 1984, for earlier studies).

RESULTS

The analyses of Li and B (Table 1) in 17 different topaz localities are shown in a log Li vs. log B plot (Fig. 1). Numbers identify the locality from Table 1 and are placed at the mean value. Topaz analyses are grouped by associations: topaz rhyolite, hydrothermal greisen, pegmatitic affinity, ongonites and topazites, and others for which only single samples are available. Individual analyses (a–d) are shown for four topaz from the Pinos rhyolite flow. Bold lines show the range of analyses for each association.

Topaz in rhyolites (either from lithophyses or fumaroles) is about 100 times richer in Li than topaz from hydrothermal greisens or pegmatitic rocks (means are 121, 1, and 1.4 ppmw, respectively). B in topaz from rhyolites overlaps with values from other associations but is higher on average (see mean values in Table 1). Topaz from the Pinos rhyolite locality shows high Li and the highest B of any topaz. The letters a to d indicate increasingly darker red color in these samples.

Only one analyses could be taken on the ongonite dike. The ion-microprobe is a surface analytical technique, and only a few grains of topaz intersected the surface of the 30-μm thick section. Of these, only one was large enough to analyze. It also shows high Li and B similar to the rhyolitic topaz. Topaz from the fine-grained topazite from Arizona showed less Li and B than that from the ongonite, but more than was found in pegmatitic and hydrothermal associations. The topaz from the coarser-grained Australian hydrothermal topazite gave the lowest Li and B of any sample.

The metamorphic topaz is variable in B (see earlier) and low in Li. Topaz from a granitic xenolith in rhyolite is high in Li but quite low in B. Topaz from an alteration vein adjacent to a pyrite vein from Henderson showed variable chemistry, from quite rich in Li to values closer to the hydrothermal greisens and pegmatitic groups.

Na secondary-ions were collected on all topaz except the ongonite, where stray Na ions from the surrounding albite made quantitative analyses impossible. Concentrations are given in Table 1. The highest Na was recorded in the darker red topaz crystals from the Pinos rhyolite (150–400 ppmw Na). Most other topaz had 3–17 ppmw, but metamorphic topaz was high, and one topaz crystal from the Henderson sample had >20 ppmw Na.

K was analyzed in the Pinos detrital topaz. It was <0.1 ppmw in the palest crystals and increased to 0.3 ppmw K in the darkest samples.

Other ions studied included the first-row transition metals in the Pinos topaz and the colorless Topaz Mountain sample. No Cr or V was detected at the 10 ppmw level, but Ti, Mn, and Fe were present. As the color darkened in the Pinos topaz, Ti was constant, but Mn and especially Fe increased. A peak at mass 93 (Nb) was observed in two different topaz analyses but has not been studied in detail.

DISCUSSION

Crystal chemistry

Substitution of Li and B into topaz is puzzling from a crystal-chemical viewpoint. Barring the presence of microinclusions in the analyzed volume of crystal, Li and B must be charge-balanced by (1) coupled substitution of F^- for O^{2-}, (2) coupling with defects or vacancies, and/or (3) coupled substitution with higher-valence cations.

It is difficult to see excess F in topaz because of its abundance and because all topaz has at least a trace of OH component. However, Rosenberg (1972) synthesized topaz with excess Al and F so that a similar substitution with $B^{3+} + F^-$ for $Si^{4+} + O^{2-}$ can be imagined.

Defects or vacancies in the topaz structure can be called upon for the substitution of B and Li, but in the context of the present data set, their existence cannot be proven. We can speculate that the quickly cooled, disequilibrium environment of the lithophyses in the rhyolites might lead to a higher percentage of defects than slow cooling in pegmatites and hydrothermal greisens.

The presence of high valence ions, such as Nb, provide one mechanism for Li substitution with the exchange reaction $Li^+ + Nb^{5+} = 2Al^{3+}$. However, the 100 ppmw of Li in rhyolitic topaz would require about 1300 ppmw of Nb for complete charge balance, and the secondary-ion signals observed for Nb and other high-valence ions do not support these high abundances.

Probably all three mechanisms play a role in balancing the charges of trace Li and B in topaz. At the 1 ppmw level for these elements, major amounts of excess F, defects, or high-valence impurities are not required.

Relation of Li and B to formation conditions

Pegmatites and some hydrothermal greisens have high bulk Li, but topaz occurrences in these environments are very low in Li. Topaz rhyolites have only about 100 ppmw Li (Christiansen et al., 1984) but show high Li in their topaz. Topaz in the ongonite dike and the Arizona topazite dike is also Li-rich. The common thread among the associations with high-Li topaz is high temperature, fast cooling rates, and low pressure of origin relative to the rocks containing low-Li topaz. In contrast to topaz from the Arizona topazite dike, topaz from the Australian topazite is extremely Li- and B-poor. This rock has apparently undergone hydrothermal alteration that replaced some topaz with muscovite, recrystallized quartz and formed wolframite (Eadington and Nashar, 1978). This alteration is, in all likelihood, responsible for the depletion of the topaz in both Li and B.

It is difficult to determine the relative importance of *P* and *T* in controlling topaz chemistry. Low *P* may be most important in that it precludes stable growth of Li-rich micas that are abundant in hydrothermal greisens and pegmatites. As speculated above, the high temperature and fast cooling rates may be necessary to produce abundant defect sites for Li substitution.

The topaz from a pegmatitic granite xenolith in rhyolite from Honeycomb Hills, Utah, and low Li relative to the igneous samples (44 ppmw). Large topaz crystals in this xenolith probably grew prior to eruption. We suggest that the intermediate Li content of this topaz reflects growth at higher pressure than other igneous associations.

Problems with possible contamination make reasonable speculations on the meaning of the trace-element chemistry of the metamorphic topaz difficult. Perhaps the high Na content (consistent values were obtained over seven months) is an important signature of the conditions under which this topaz grew.

Trace elements in topaz as a fingerprinting technique

The data displayed in Figure 1 support a distinction between topaz from igneous vs. hydrothermal associations. Our sample population is generally restricted to large, gemmy crystals whose associations with hydrothermal or igneous rocks are clear. The distinction we are able to make between the mineralogically similar Arizona topazite (igneous) and Australian topazite (hydrothermal) suggests that this technique may also be useful in determining the genesis or subsequent history of ambiguous topaz-bearing rocks. Interpreting some data may prove difficult. For example, the small crystals of topaz coating a pyrite vein from the Henderson porphyry molybdenite deposit (sample 21) show variable Li and B contents. Does the large range in chemistry relate to gross changes in *P* or *T* during the last stages of hydrothermal activity? Specifically, could a sudden decompression of the hydrothermal system generate an environment more akin to topaz rhyolites—thus crystallizing Li-rich topaz? These speculative questions cannot be answered at the moment.

The following question relates to using trace elements as a fingerprinting technique for determining the petrogenesis of topaz: Could trace element analyses of alluvial topaz be used as a prospecting tool? From Figure 1 and Table 1, it would appear that the topaz with low Li and B is most commonly associated with rocks with economic concentrations of Sn, W, Be, Ta, and Nb.

CONCLUSIONS

The Li content of topaz varies over four orders of magnitude. There is a distinct division that correlates high-Li topaz with rhyolitic and other igneous associations and low-Li topaz with hydrothermal or pegmatitic rocks. B is generally higher in igneous topaz but overlaps with analyses from other associations.

At the moment, we can only speculate on substitution mechanisms for Li and B and suggest excess F, defects, and high-valence elements as possibilities.

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