YTTRIAN MILARITE

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ABSTRACT

Milarite from the Jaguaragri pegmatite, Minas Gerais, Brazil, and from the Strange Lake peralkaline complex, Labrador-Quebec border, contains up to 7.90 wt. % Y2O3 and 5.10 wt. % ∑REE2O3. The Strange Lake milarite shows moderate concentric or sector zoning. The Jaguaragri milarite shows enrichment in (Y,REE) in the outermost zones, in networks of fracture-filling and replacement veinlets of a (Y,REE)-rich phase in the primary (Y,REE)-poor interior, and, to a degree, in (Y,REE)-poor pinacoidal caps. The principal substitution is that of \( \text{AY,REE}^{3+} + \text{Be}^{2+} + \text{Ca}^{2+} + 2\text{Al}^{3+} \), leading from the ideal composition \( \text{KCa}_2(\text{Be}_2\text{Al})\text{Si}_2\text{O}_{30} \) to \( \text{K(CaY)(Be)}_2\text{Si}_2\text{O}_{30} \). However, the A position also shows minor vacancies (<9%) that increase with the (Y,REE) content. The above substitution strongly modifies intensities of X-ray diffraction maxima, and reduces the unit-cell dimensions. Additional occurrences of yttrian milarite can be expected in (Y,REE)-rich miarolitic peralkaline intrusions and related hydrothermal environments. An extension of the substitution from \( \text{K(CaY)(Be)}_2\text{Si}_2\text{O}_{30} \) to \( \text{(Y,REE)}_2\text{Si}_2\text{O}_{30} \) is a possibility.

Keywords: milarite, yttrium, rare-earth elements, Labrador, Brazil.

INTRODUCTION

The double-ring silicate milarite, ideally \( \text{Na}_2\text{Ca}_2(\text{Be}_2\text{Al})\text{Si}_2\text{O}_{30} \cdot 2\text{H}_2\text{O} \), was described as a new mineral species 130 years ago: the complex history of its study was reviewed by Černý et al. (1980); see their Fig. 1 for structure and site symbolism. These authors recognized a wide range of Be/Al proportions in this mineral, from about \( \text{Be}_{1.9}\text{Al}_{1.1} \) to \( \text{Be}_{2.55}\text{Al}_{0.45} \), resulting from the substitution

\[ \text{T}^{2+}\text{Be}^{2+} + \text{C}^{(B)}(\text{Na,K})^{+} = \text{T}^{2+}\text{Al}^{3+} + \text{C}^{(B)}\Box. \]

These authors also reviewed the relationships among structure, chemistry, unit-cell dimensions, and optical properties in both natural and heated specimens of milarite from 16 localities. Additional data on milarite have been reported recently by Janczew (1986), Armbruster et al. (1989) and Kimata & Hawthorne (1989).

Yttrium was reported in trace to minor quantities in milarite from several localities (Sosedko 1960, Černý 1960, 1967, 1968, Sosedko & Telesheva 1962, Stanek 1964, Chistyakova et al. 1964, Iovcheva et al. 1966, Novikova 1972). However, significant

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yttrium content, estimated by emission spectrographic analysis, was known only for the milarite from Grorud, Norway (Oftedal & Saebø 1965).

In 1986, one of us (J.L.J.) obtained electron-microprobe data on milarite from the Strange Lake peralkaline complex, Québec-Labrador border, which turned out to have high levels of Y, REE and (calculated) Be, but low Ca and Al contents, and unit-cell dimensions distinctly different from the previously established range. Recently, we recorded analogous unit-cell dimensions, and an unusual distribution of X-ray powder-diffraction intensities, for a milarite sample from the Jaguaráçu granitic pegmatite, Brazil (supplied by Dr. R.V. Gaines). As this locality is famous for its high concentration of Y (Foord et al. 1986), enrichment of milarite in Y was considered a distinct possibility.

We report here the results of our study on the Jaguaráçu and Strange Lake samples of milarite, both of which have proven to be Y-rich. More detailed examination of the Strange Lake milarite has shown the presence of even higher Y contents than those revealed by the 1986 analyses.

**SAMPLES EXAMINED**

At Strange Lake, Québec-Labrador border, milarite occurs in an extensively mineralized peralkaline granite, in part pegmatitic (e.g., Miller 1989, Boily et al. 1990). The milarite is found in three associations: (i) as anhedral grains associated with quartz, albite, and K-feldspar in a medium-grained granitic assemblage that also contains armstrongite, titanite, gittinsite, aegirine and fluorite (drill core sample SL-60D-18.3); (ii) as euhedral columnar crystals with prismatic, pyramidal and basal pinacoid faces, measuring up to 0.15 x -0.50 mm in size, in miarolitic vugs lined with quartz and albite crystals, all locally dusted with hematite (drill-core sample SL-258-71), and (iii) as clear, white, purplish to reddish euhedral columnar crystals with a well-defined dominant core and subordinate outer zones, in small vugs lined with powdery xenotime (drill-core sample SL-258-75.2).

In the Jaguaráçu pegmatite, Minas Gerais, Brazil, milarite forms pale greenish yellow or pale brown euhedral columnar crystals, up to 10 x 30 mm in size, with colorless and clear caps in pinacoidal terminations. Milarite is associated with adularia, albite, hematite, muscovite, quartz and minasgeraisite (Y₂CaBe₂Si₃O₁₀; Foord et al. 1986). Two milarite-bearing samples were examined in the present study: one with associated minasgeraisite, and the other from a specimen devoid of this Y-rich mineral.

**EXPERIMENTAL METHODS**

Electron-microprobe analyses were carried out with a JEOL 733 electron microprobe, equipped with three spectrometers, utilizing an accelerating voltage of 12 kV, a beam current of 25 nA, and a beam diameter of less than 1 µm. Raw data were reduced using Tracor Northern's "Task" ZAF program. The following standards and X-ray emission lines were used: synthetic NaNO₃ (NaKα), orthoclase (KKα, AlLα, SiKα), titanite (CaKα), synthetic YbFeO₃ (Ybα), synthetic YFeO₃ (YLaα), synthetic CeO₂ (CeLα), synthetic NdAlO₃ (Ndα), synthetic ErAlO₃ (ErLα), and synthetic glass REE4 (DyLα).

No elements were detected in quantitatively determinable amounts except those for which the X-ray emission lines are quoted here. Table 1 summarizes the localities and sample-plus-analysis numbers, and Figure 1 shows the location of different analyzed fragments of one of the Jaguaráçu specimens.

**TABLE 1. LIST OF MULARITE SAMPLES**

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Locality</th>
<th>Source</th>
<th>Analysis #</th>
</tr>
</thead>
<tbody>
<tr>
<td>MI-1A, 8</td>
<td>Jaguaráçu, Brazil; associated with minasgeraisite</td>
<td>R.V. Gaines</td>
<td>MI-1A-1, MI-1A-2 to -4; MI-1A-3-5 to -9; MI-1B-1 and Z</td>
</tr>
<tr>
<td>MI-2 to 7</td>
<td>Jaguaráçu, Brazil</td>
<td>R.V. Gaines</td>
<td>MI-2-1 to -2; MI-3-1 and -2; MI-4-1 and -2; MI-5-1 and -2; MI-6-1 and -2; MI-7-1 and -2</td>
</tr>
<tr>
<td>SL-600-18.3</td>
<td>Strange Lake, Labrador-Québec; thin section</td>
<td>J.L. Jambor</td>
<td>SL-600-19.3-1 and -2</td>
</tr>
<tr>
<td>SL-258-71</td>
<td>Strange Lake, Labrador-Québec; crystals in vugs</td>
<td>J.L. Jambor</td>
<td>71-1 and 71-2</td>
</tr>
<tr>
<td>SL-258-75.2</td>
<td>Strange Lake, Labrador-Québec; crystals in vugs</td>
<td>J.L. Jambor</td>
<td>75-1 to -8</td>
</tr>
</tbody>
</table>

Potassium and sodium began to migrate significantly after 50 seconds of beam exposure. To eliminate errors due to alkali mobility, the concentrations of K and Na were always determined first; counting periods for all elements were limited to 40 seconds, and the beam position was moved by 2-3 µm every 80 seconds to prevent sample decomposition. With these analytical conditions, the following limits of detection apply: Na 0.05, Al 0.02, Y 0.04, Dy 0.15, and Ce, Nd, Er, Yb 0.1 wt. %.

Beryllium and water cannot be determined by electron-microprobe analysis. Consequently, the compositions of yttrian milarite are treated here on an anhydrous basis, and Be was calculated to fill the (Al + Be)-populated T(2) sites (cf. "Chemical Composition" below). Structure refinement of
some of the analyzed samples shows that the Be contents derived from electron densities at the $T(2)$ sites are in good agreement with those calculated here (Hawthorne et al. 1991).

Unit-cell dimensions of the Jaguaraçu milarite were calculated from X-ray powder-diffraction data obtained with a Philips PW1710 X-ray diffractometer, using graphite-monochromated CuKα radiation at 40 kV and 40 mA, with a scan speed of 0.5° 2θ/min and annealed CaF$_2$ ($a = 5.46379(4)$ Å; Erict 1986) as an internal standard. From 13 to 22 powder reflections between 10° and 60° 2θ were used for the least-squares refinement, using a modified version of the program CELREF (Appleman & Evans 1973). Because of a very limited quantity of material, the Strange Lake milarite SL–258–71.5 mm Debye–Scherrer camera using Fe-filtered CoKα radiation; intensities were estimated from a 114.6-mm Gandolfi camera film obtained after additional material was added to the original spindle mount. A modified least-squares program (Gabe et al. 1989) was used to refine unit-cell dimensions from 19 diffraction maxima between 3.206 and 1.697 Å. Unit-cell dimensions of the Strange Lake milarite SL–258–71, and other structural data from single-crystal fragments, were obtained on a Nicolet R3m automated four-circle diffractometer, using graphite-monochromated MoKα radiation at ~50 kV and 35 mA.

Chemical composition

Yttrian milarite is chemically very heterogeneous in samples from both localities examined in the present study. Concentric zoning, sector zoning and replacement veining all are observed, both individually and in combination.

The Jaguaraçu milarite exhibits thin subsurface zones of increased $(Y,REE)$ contents on the prismatic faces (Figs. 2A,D), rarely with a reversal to reduced $(Y,REE)$ contents (Fig. 2B). This zoning is broader but not so $(Y,REE)$-enriched in the clear (001) caps of these crystals (Fig. 2C). The main body of each crystal is veined by $(Y,REE)$-rich milarite that corresponds in chemical composition to the $(Y,REE)$-rich subsurface zones (Figs. 2A,B,D). This network of veinlets extends from the subsurface zones, follows fractures in the homogeneous primary milarite, and is clearly a replacement, not a fissure-filling.

Milarite crystals from Strange Lake sample SL–258–71 show concentric zonal growth, with two distinct $(Y,REE)$-rich compositions that predominate over a $(Y,REE)$-poor composition. This latter composition is also dispersed in somewhat irregular streaks parallel to c throughout most of the crystal (Fig. 2E). The crystals also are corroded parallel to c, with the $(Y,REE)$-rich cores having been preferentially attacked; the outer zones, however, remain relatively unaffected.

Milarite crystals from Strange Lake sample SL–258–75.2 display sector zoning, with oscillatory compositional variations within the sectors (Fig. 2F). The (001) growth sectors are distinctly more enriched in $(Y,REE)$ than are the sectors underlying the (001) pinacoids.

Table 2 lists the results of electron-microprobe analyses representative of the milarite occurrences examined; some of the analyzed spots are marked in Figure 2. A complete set of compositional data collected during this study is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

All crystals show similar compositional trends, irrespective of locality. The broadest and most informative range of data is provided by the Jaguaraçu milarite, whereas the data for the Strange Lake milarite are much more restricted. Figure 3A shows a well-defined negative correlation between Ca and $(Y + REE)$, and Figure 3B shows a poorer but statistically significant positive correlation of $(Y + REE)$ with Be/(Be + Al). The Be/(Be + Al) ratio also is affected by the substitution

$$^{8}Na^{+} + ^{7(2)}Be^{2+} → ^{8}Na^{+} + ^{7(2)}Al^{3+}$$
(Černý et al. 1980); thus we do not expect the data to fall along the ideal line in Figure 3B, as the analytical data also indicate significant variations in the extent of this (Y, REE)-free substitution.

The cation contents corresponding to the chemical compositions given in Table 2 were calculated on the basis of 30 oxygen anions (excluding H₂O) with the constraint that Be + Al equal 3.00 apfu (atoms per formula unit). It is obvious that some kind of systematic error is present, either in the analytical data or in our understanding of the milarite structure. First, the Si content exceeds the ideal value of 12.00 apfu, and this observed excess shows a positive correlation with the (Y,RE) content. Adjustment of the SiO₂ wt.% of several compositions to produce 12.00 apfu Si brings the
TABLE 2. CHEMICAL COMPOSITION

<table>
<thead>
<tr>
<th>Locality</th>
<th>Analysis</th>
<th>Jaguaraçu</th>
<th>Strange Lake</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MI-8-1</td>
<td>MI-8-2</td>
<td>MI-7-1</td>
</tr>
<tr>
<td>SiO₂</td>
<td>70.00</td>
<td>73.40</td>
<td>72.70</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.23</td>
<td>5.10</td>
<td>3.40</td>
</tr>
<tr>
<td>BeO</td>
<td>7.11</td>
<td>5.10</td>
<td>5.36</td>
</tr>
<tr>
<td>CaO</td>
<td>6.40</td>
<td>10.90</td>
<td>9.50</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.19</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.70</td>
<td>4.80</td>
<td>5.10</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>5.20</td>
<td>n.d.</td>
<td>1.80</td>
</tr>
<tr>
<td>Ca₂O₃</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>MgO</td>
<td>0.20</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.50</td>
<td>n.d.</td>
<td>0.20</td>
</tr>
<tr>
<td>Er₂O₃</td>
<td>0.80</td>
<td>n.d.</td>
<td>0.20</td>
</tr>
<tr>
<td>Er₂O₃</td>
<td>2.40</td>
<td>n.d.</td>
<td>0.60</td>
</tr>
<tr>
<td>total</td>
<td>97.73</td>
<td>99.30</td>
<td>99.36</td>
</tr>
</tbody>
</table>

**MI-2-2**: (Y,REE)-poor clear core; **MI-7-1** and **-2**: main body of the crystal (Fig. 3A); **71-1** and **-2**: darker and lighter area, respectively, of zoned crystal (Fig. 3E); **75-1, -6 and -8**: darkest core/lightest zone in termination and most Ce-enriched spot, respectively, on the sector-zoned crystal (Fig. 3F). n.d. = not detected.

**X-ray diffraction**

Table 3 lists X-ray powder-diffraction data for both the Strange Lake and Jaguaraçu samples of yttrian milarite, compared to those of the classic, optically "anomalous" milarite (Guanaquito #25) and the optically hexagonal milarite with positional disorder of Ca and increased B-site occupancy (Vězná #29; from Table 10 in Černý et al. 1980). Figure 4 shows the distinctly different distributions of intensities in the X-ray powder-diffraction patterns of all three types.

Whereas Černý et al. (1980) ascribed the differences in diffraction intensities between the
Fig. 3. A. Ca versus (Y + REE) (apfu) in yttrian milarite. Note that the data plot consistently below the line that marks the ideal correlation. Circles: Jaguaragri; X: Strange Lake. B. (Y + REE) versus Be/(Be + Al) (apfu) in yttrian milarite. Note that the data plot below the line that marks the ideal substitution. Symbols as in Figure 3A. C. (Ca + Y + REE) versus Be/(Be + Al) (apfu) in yttrian milarite. Difference between 2.00 and (Ca + Y + REE) equals "vacancies" in the A site. Symbols as in Figure 3A.

Fig. 4. X-ray powder diffractogram of Jaguaragri milarite M1-7 compared to those of Guanajuato milarite #25 and Vežná milarite #29 (Cerný et al. 1980).

Guanajuata and Vežná specimens to the higher alkali and H₂O content of the latter, the difference between these two and the Jaguaragri yttrian milarite is not so easily clarified. The lack of quantitative data on H₂O contents of yttrian milarite is the main obstacle. Nevertheless, we expect that the substitution of Y (Z = 39) for Ca (Z = 20) at the A sites is in part responsible, as well as the increased Be/Al ratio at T(2).

Unit-cell dimensions of yttrian milarite listed in Table 4 are compared with those of other samples of milarite in Figure 5. In Y-poor milarite, a and c decrease with increasing Be/Al at T(2); c decreases and a increases with increasing H₂O (Cerný et al. 1980).
In unheated natural Y-poor milarite, the increase in Be/Al and H$_2$O is roughly parallel. The combined effects of these two variables result in a range (Fig. 5). It is again difficult to interpret these results. The c dimension falls in the middle of the known range (compounded effects of both).

For details of data collection, see "Experimental Methods".
The unit-cell dimensions of milarite samples close to the Be\(^{2+}\) + Na\(^{+}\) Al\(^{3+}\) substitution series (Černý et al. 1980) compared to those of yttrian milarite. Dotted rectangle marks unit-cell dimensions characteristic of the composition KCaz(BezAl)Si12O30. Vectors parallel to the coordinates indicate changes in unit-cell dimensions resulting from different substitutions. Arrow indicates reduction in unit-cell dimensions from the KCaz(BezAl)Si12O30 composition to the Jaguaraguí (circles) and Strange Lake (crosses) milarite.

Milarite from (Y,REE)-poor parageneses typically contains minor quantities of Y. This fact, plus its high Y,(H)REE contents in lanthanide-rich environments, indicate that milarite is a sink for these elements. Additional occurrences of yttrian milarite can be expected, particularly in vugs and fissures of peralkaline intrusive bodies similar to the Grorud nordmarkite in Norway, and in hydrothermal orebodies related to alkaline intrusive complexes of the Strange Lake type (Trueman et al. 1988). The Jaguaraguí granitic pegmatite seems to be too much of a geochemical oddity (enriched in both rare alkalis and Y,REE) to predict further finds of yttrian milarite in granitic pegmatites in general.

It is quite possible that the composition of yttrian milarite will extend into the K(CaY)Be3Si12O30 - (Yz)(Bez)Si12O30 range at one or another locality, defining a new species with Y > Ca.

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