THE PROBLEM OF Na–Li SUBSTITUTION IN PRIMARY Li–Al PHOSPHATES: NEW DATA ON LACROI XITE, A RELATIVELY WIDESPREAD MINERAL

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ABSTRACT

Wet-chemical analyses and X-ray-diffraction patterns of minerals of the amblygonite–montebrasite series occurring in the Gatumba pegmatite field, Rwanda, show that an impurity is detectable on the powder pattern if Na₂O exceeds 0.2 wt.%. In a sample from Buranga with 2.05 wt.% Na₂O, this impurity was identified as lacroixite. Electron-microprobe and wet-chemical analyses of two lacroixite samples from Rusororo and one from Buranga showed them to contain Li and OH in substitution for Na and F, respectively. The two lacroixite samples from Rusororo have the following idealized formulas: (Na₆₋₆₁Li₆₋₄₁)AlPO₄(F₀.₆₁OHₐ.₄₁) and (Na₈₋₈₆Li₄₋₄₄)AlPO₄(F₀.₄₁OHₐ.₄₉). The formula of lacroixite from Buranga is (Na₆₋₇₂Li₂₋₂₂)AlPO₄(F₀.₆₅OHₐ.₄₅). The unit-cell parameters of these three samples show that b decreases with increasing Li contents. The petrographic texture of the Buranga lacroixite suggests that this mineral is either a Na-metasomatic product or an exsolved phase in its montebrasite host, whereas the decreasing Li contents of the Rusororo lacroixite samples can be tentatively related to the lowering of temperature. An X-ray-diffraction examination of the so-called “Na-rich amblygonite” from Hebron showed it to be a mixture of amblygonite and lacroixite.

Keywords: lacroixite, amblygonite–montebrasite series, Na–Li substitution, composition, X-ray data, Gatumba pegmatite field, Rwanda.

INTRODUCTION

Although amblygonite was first encountered at the Buranga pegmatite, Rwanda, in the nineteen-forties by R. de Dycker (Buttgenbach 1947), and although minerals of the LiAlPO₄(F,OH) series were extensively mined before the nineteen-sixties in several pegmatites near Buranga, in the Gatumba field, these minerals are poorly known, and the relatively few data on their mineralogical properties are dispersed in the literature (Polinard 1950, Thoreau & Bastien 1954, von Knoning 1970, Dubois et al. 1972, Fransolet & Abraham 1983).

The initial purpose of this study was to chemically determine the fluorine contents of minerals in the amblygonite–montebrasite series, collected from several phosphate-rich lithium-bearing pegmatites of the Gatumba field. The interpretation of about twenty chemical analyses, complemented by a systematic X-ray investigation to check the reliability of methods proposed to determine values of the F/OH ratio (Cernák et al. 1973, Kallio 1978), subsequently led to the identification of lacroixite from the Rusororo pegmatite and the Buranga mine.

Recently, Lahti & Pajunen (1985) reviewed the historical background of lacroixite NaAlPO₄F, published new data for this mineral, and determined its crystal structure. The present study of three lacroixite samples from the Gatumba pegmatites provides evidence of Li and OH substitution for Na and F, respectively, and warrants further discussions of the chemical composition and crystallographic properties of lacroixite, as well as the problem of Na-for-Li substitution in the amblygonite–montebrasite series.
ANALYTICAL METHODS

All minerals reported here were identified by X-ray diffraction, using Debye-Scherrer cameras and a diffractometer equipped with a Fe target and a monochromator. The d values of the lacroixite samples, corrected with a Pb(NO₃)₂ internal standard (a 7. 8568 Å) and recorded with a scanning speed of ½° 2θ/min, were used to refine the unit-cell parameters with the program of Appleman & Evans (1973) and the structural data of Lahti & Pajunen (1985). The space group C2/c, determined by the latter authors, was checked by the Weissenberg technique on the material from the Rusororo pegmatite.

The wet-chemical analyses were performed using atomic absorption for Al, Fe, Mn, Mg, Ca, Na, K and Li, colorimetry for P, direct titration with a specific electrode for F, and the Penfield method for H₂O. Lacroixite was dissolved in concentrated HCl heated at 190°C in a steel bomb lined with teflon.

The electron-microprobe analyses were done with Camebax equipment using the ZAF correction procedure of Henoc & Tong (1977) and the following standards: synthetic berlinite (P and Al), Fe₂O₄ (Fe), metallic Mn, MgO (Mg), albite (Na), wollastonite (Ca), and topaz (F).

MINERALOGICAL DATA

Lacroixite from the Rusororo pegmatite

Near the quarry of Rusororo, briefly described by Bertossa (1960) and cited as the "Amblygonite mine of Rongi" by Varlamoff (1961,1973), now deserted and overgrown since the end of the mining activities, some boulders of montebrasite displaying complex replacement textures are still visible. Around the cores of montebrasite is an alteration rim, up to 30 cm wide, that consists mainly of an intimate mixture of abundant berline fite and of faintly bluish lacroixite. The individual grains of lacroixite (up to 10 mm) display a vitreous to pearly luster on the cleavages (as in montebrasite). Many of the alteration rims are interrupted by irregular masses of bluish white lacroixite in close association with deep blue scorzalite, easily recognized in the field. Both lacroixite and scorzalite occur as irregular veinlets, pods, or diffuse specks. Berlineite is seldom present in this second association.

Thin sections containing the two types of association show that the bluish color of lacroixite is caused by minute inclusions of scorzalite (10 to 50 µm) that look like exsolution products. The lacroixite grains are generally turbid and are locally stuffed with other undetermined minute inclusions. In the first association, however, berlineite occurs as a mosaic, and lacroixite has a poikiloblastic-like texture and appears rather transparent at the contact with the embedded globular grains (200 µm to 1 mm) of berlineite.

The mean of several microprobe analyses of the lacroixite (Ru-I) containing embedded berlineite is given in Table 1. On the basis of 1 (PO₄)³⁻ per formula unit (f.u.), the main cation numbers show a distinct nonstoichiometric ratio, in contrast with the results of Lahti & Pajunen (1985). Attempts at purification did not succeed in complete separation of berlineite from lacroixite in this assemblage, and several wet-chemical analyses indeed gave an excess of Al₂O₃ and P₂O₅. These analyses, however, showed Li and H₂O to be present in the mixtures. These results allowed me to complete the microprobe analytical data by calculating the Li₂O and H₂O contents to render stoichiometric the formula for lacroixite Ru-I, as indicated in Table 1. The simplified formula of this mineral is (Na₀.₆₁Li₀.₃₉)AlPO₄(F₀.₇₉OH₄.₄₄).

Lacroixite Ru-II, which occurs in the scorzalite-rich veinlets of the second type of association and cross-cuts the association rich in berlineite, was purified by hand-picking under a binocular microscope. All minute inclusions of scorzalite could not be eliminated, but X-ray examination showed that impurities other than scorzalite are absent. The results of a wet-chemical analysis of lacroixite Ru-II are given in Table 2. Because Mg was not detected either in lacroixite Ru-I (Table 1) or the Buranga lacroixite (see below), the MgO content of 0.29 wt.% is assigned to scorzalite. The composition of the scorzalite inclusions was determined by microprobe analysis; the composition of lacroixite Ru-II was deduced (Table 2) to be (Na₀.₈₆Li₀.₁₄)AlPO₄(F₀.₈₃OH₀.₁₉).

| TABLE 1. MICROPROBE DATA ON LACROIXITE FROM RUSORORO |
|-----------|-------------------------------|-------------------------------|
| Ru-I (n=19) | Ru-I (n=7) |
| P₂O₅ | 1.000 | 1.000 |
| Al₂O₃ | 1.016 | 1.040 |
| FeO | 0.000 | 0.000 |
| MnO | 0.008 | 0.009 |
| CaO | 0.000 | 0.000 |
| Na₂O | 0.584 | 0.758 |
| Li₂O | 0.370 | 0.219 |
| H₂O | 0.410 | 0.347 |
| F | 0.590 | 0.652 |
| Total | 1.000 | 1.000 |
| Na/ (Na+Li) | 0.612 | 0.776 |

1. Analytical results (Analyst: Prof. K. Abraham) n = number of point analyses * calculated wt. % for stoichiometry
2. Cation number on the basis of 1 (PO₄)³⁻ per formula unit.
TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR LACROIXITE FROM BURANGA

<table>
<thead>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<tbody>
<tr>
<td>P2O5</td>
<td>42.24</td>
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<td>42.98</td>
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<tr>
<td>Al2O3</td>
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<td>FeO</td>
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<tr>
<td>K2O</td>
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<tr>
<td>Li2O</td>
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<td>-</td>
<td>1.21</td>
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<tr>
<td>H2O4</td>
<td>1.51</td>
<td>0.50</td>
<td>1.10</td>
</tr>
<tr>
<td>H2O³</td>
<td>0.40</td>
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<tr>
<td>F</td>
<td>8.78</td>
<td>-</td>
<td>9.60</td>
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<tr>
<td>Total</td>
<td>104.36</td>
<td>-</td>
<td>104.07</td>
</tr>
<tr>
<td>O = F - 3.69</td>
<td>-</td>
<td>4.03</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100.89</td>
<td>-</td>
<td>99.99</td>
</tr>
</tbody>
</table>

1. Analysis of lacroixite Ru-II
2. Impurity of scorzalite calculated on the basis of the electron microscope analysis:
   42.39% P2O5; 31.74% Al2O3; 16.02% FeO; 0.13% Na2O; 0.37% MgO
   (Analyst: Prof. K. Abraham).
3. Analysis "I" recalculated to 100%.
4. Cation numbers on the basis of 1(P04)5-
   per formula unit.

This wet-chemical analysis provides an important argument to justify the addition of appropriate amounts of Li2O and water to complete the mineral formula unit. In this case, the idealized composition for lacroixite from Buranga pegmatite is Na0.78Li0.22AlPO4(F0.65OH0.35).

Although the X-ray powder-diffraction data obtained from lacroixite Ru-I are in good agreement with the results of Lahti & Pajunen (1985), a new list of indexed diffraction peaks for lacroixite rich in Li and OH seems in order because several d values have significantly shifted as a result of a noticeable shortening of the b parameter (Tables 3, 4). For example, 040 and 242 occur as additional peaks, and the indexing of a few other lines has been slightly modified (e.g., indices for 2.054 and 1.657 Å).

Lacroixite from the Buranga pegmatite

A pale greyish blue sample of montebrasite from the Buranga pegmatite, replaced by pure white montebrasite, gave 2.05 wt.% Na2O (Table 5), rather similar to the Na content quoted for Hebron amblygonite (Černá et al. 1973). However, the X-ray pattern of the Buranga sample showed 6 readily discernible diffraction peaks attributable to lacroixite (Fig. 1). These d values were used to calculate the unit-cell dimensions of this lacroixite (Table 4), whose occurrence can be added to the long list of phosphate minerals known for this famous pegmatite.

In thin sections the greyish blue montebrasite looks turbid or cloudy from place to place, particularly along some directions corresponding roughly to the main cleavages. Observation at high magnification shows minute grains (up to 10 x 75 μm) with a lower birefringence than that of the host material, and with uniform optical orientation (Fig. 2). As is evident in Figure 3, the backscattered-electron image as well as the mapping of Na in such a “turbid zone” provide evidence for the existence of minute inclusions of a Na-rich mineral within a Na-free host.

The analytical results obtained with the electron microscope corroborate the presence of lacroixite within montebrasite (Tables 1, 5). The interpretation of the microprobe analysis of lacroixite (Table 1) again suggests the presence of additional Li and OH to maintain stoichiometry. On the basis of 1(P04)5-
   p.f.u., the idealized composition for this Buranga lacroixite is Na0.78Li0.22AlPO4(F0.65OH0.35).
   A similar heterogeneous distribution of Na within
### TABLE 5. CHEMICAL COMPOSITION OF RHEOGISOCRUSTE LA4Al5O14(P2,21) MINERALS

<table>
<thead>
<tr>
<th></th>
<th>Buranga (UsNM 621521)</th>
<th>Amblygonite (UsNM 62576)</th>
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<tr>
<td></td>
<td>1</td>
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<tr>
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<td>P2O5</td>
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<td>1.000</td>
<td>0.976</td>
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<td>Al2O3</td>
<td>1.000</td>
<td>0.991</td>
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<td>Fe2O3</td>
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<td>MgO</td>
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<td>0.03</td>
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<tr>
<td>CaO</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Li2O</td>
<td>1.68</td>
<td>3.77</td>
</tr>
<tr>
<td>H2O</td>
<td>1.28</td>
<td>1.28</td>
</tr>
</tbody>
</table>

1. Bulk composition: wet-chemical analysis by J.-M. Speerjean. 2. Microprobe analysis of montebrasite hosting lacroixite. Analy- list: Prof. R. Abrahams (see Fig. 3). 3. Composition recalculated to 100% assuming that Na is derived only from lacroixite, as given in Table 1. 4. Cation numbers on the basis of 1(RNa)²⁺ per formula unit. 5. Results of wet-chemical analysis by J.-M. Speerjean. 6. Cation numbers on the basis of 1(RNa)²⁺ per formula unit.

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**Fig. 1.** Selected portions of powder diffractograms showing typical lacroixite (L) peaks separated by shading from those of montebrasite from Buranga (A), and those of amblygonite from Hebron (B). Two additional peaks attributed to an undetermined impurity are present on diffractogram (B).

**Fig. 2.** Photomicrograph (crossed nicols) of the Buranga montebrasite, showing a "cloudy zone" rich in minute lacroixite grains (white), as well as the typical polysyn- thetic twins of montebrasite (upper left).

**Fig. 3.** Back-scattered electron (a) and sodium distribution (b) pictures of a portion of Buranga montebrasite invaded by a "cloudy zone" (see Fig. 2). The brighter areas on the sodium map show the shape of the lacroixite grains within montebrasite.
montebrasite associated with triplite and graphite was described in the Buranga pegmatite (Fransolet & Abraham 1983). However, the presence of lacroixite could not be verified.

**Discussion**

The new data on lacroixite from two pegmatites in the Gatumba field invite several comments and expand our knowledge of this mineral.

From infrared spectral results, Lahti & Pajunen (1985) considered that only a very limited substitution of OH for F in lacroixite may be possible. The wet-chemical and electron-microprobe analytical data in the present study indicate that Li and OH may occur in major quantities in lacroixite. In addition, marked variations of Na/(Na+Li) and F/(F+OH) have been noted (Table 1), even from one association to another in the Rusororo pegmatite. Although the available data are still too scarce, it seems that these variations affect the unit-cell parameters of lacroixite. To test this possibility further, the unit-cell dimensions given in Table 4 have been plotted against Na/(Na+Li) (Fig. 4). Whereas the a and c parameters seem relatively unaffected by the substitution of Li for Na, b decreases significantly as Li increases, possibly because of the smaller ionic radius of Li compared to Na. This conclusion, based on only four data-points, admittedly is tenuous, especially as F-for-OH substitution affects the unit-cell values in a similar way (Fig. 4).

The wet-chemical and the microprobe analyses both indicate a persistent presence of Fe, Mn and Ca, in contrast with the chemical data for lacroixite from Greifenstein (Lahti & Pajunen 1985). As the octahedral sites populated by Al are either filled completely, or Al is in excess (possibly because of analytical error), it is reasonable to accept that Ca, Mn and also Fe occupy the larger alkali positions. Such a hypothesis implies a coupled substitution to maintain the charge balance of the chemical formula, i.e., Na\(^+\) + (F,OH)\(^-\) → R\(^{2+}\) + O\(^2-\). The anion involved in this coupled substitution occupies the non-tetrahedral oxygen position of the titanite structure. Therefore, the water contents calculated for stoichiometry (Table 1) are a little too high. In the case of lacroixite Ru-I, the presence of 0.046ivalent cations in the alkali positions implies 0.046 oxygen with 0.590 F and 0.364 OH p.f.u. From this OH content, one deduces 2.04 wt.% H\(_2\)O. Following the same argument, the lacroixite from Buranga contains 1.78 wt.% H\(_2\)O. The analytical error associated with a determination of H\(_2\)O by the Penfield method is relatively high, however, so that this argument cannot be corroborated by the results of the wet-chemical analysis (Table 2).

The fact that lacroixite is characterized by a titanite-type structure (Lahti & Pajunen 1985), which is rather flexible in accepting various coupled substitutions, could explain why lacroixite contains the highest weight-percentages of FeO of any Al-rich phosphate minerals occurring in the two pegmatites (except, of course, the minerals of the scorzalite – lazulite and the childrenite – eosphorite series). Whereas 1.56% FeO was detected in lacroixite Ru-I (Table 1), the FeO contents determined previously for these Al phosphates have never exceeded 1 wt.%, e.g., 0.18% as an upper limit in montebrasite, 0.27% in trolite, 0.08% in brazilianite (wet-chemical procedure), 0.26% in augelite, and 0.85% in bertossait (electron microprobe) (unpublished results).

From a genetic point of view, the two different values of the Na/(Na+Li) ratio reported for lacroixite from Rusororo are puzzling. Lacroixite Ru-I associated with berlinite replaced montebrasite, and was replaced in turn by another association charac-

![Figure 4](image-url)
terized by lacroixite Ru-II, with abundant scorza-
lite and a small amount of berlinite. This observa-
tion suggests that the decreasing Li contents perhaps
relate to a lowering of the temperature. However,
more data are required to ascertain whether Li con-
tents may serve as a geothermometer for lacroixite
formation; interestingly, Li-free lacroixite from
Greifenstein occurs in druses of a lithium-bearing
granite, associated with other phosphate minerals
that are typical of a low-temperature hydrothermal
environment (Lahti & Pajunen 1985).

The Buranga montebrasite - lacroixite association
raises another problem, critical for both the crystal
chemistry and genesis of the LiAlPO₄(F,OH)
minerals. The petrographic texture exhibited by the
lacroixite grains within montebrasite suggests an
analogiy with chessboard albite, or exsolution (Figs.
2, 3).

In the first case, lacroixite would be taken to
represent a product of Na metasomatism that
affected the amblygonite – montebrasite masses, as
reported by Moore (1973). This evolutionary stage
of Al-rich phosphate associations could be related
to the same event of Na metasomatism that is known
to transform the Li(Fe,Mn) PO₄ mother-phases into
alluaudite in Fe-Mn phosphate associations (Moore

The second alternative is that lacroixite and mon-
tebrasite are the exsolution products of a pre-existing
homogeneous (Li,Na)AlPO₄(OH,F) phase, thereby
requiring a miscibility gap in the binary Li-Na monte-
brasite solid-solution series. If natromontebrasite
(“fremontite”) described by Schaller (1911, 1914)
and Na-bearing ambygonite from Hebron (Černá et
al. 1973) are actually homogeneous, a closure of the
miscibility gap must be inferred to exist at higher
temperatures. All the ambygonite – montebrasite
samples initially studied here, however, were found
to contain lacroixite impurities if the bulk samples
contain more than 0.20 wt.% Na₂O. Consequently,
a sample of the Na-bearing ambygonite from Hebron
was re-examined. The wet-chemical results from a
fragment of this sample (U.S.N.M. 62570
accompany those obtained from the Buranga
material (Table 5). The X-ray powder pattern (Fig. 1)
clearly demonstrates that the mineral from Hebron
contains lacroixite in amounts roughly similar to
those observed in the Buranga material.

Several occurrences of lacroixite in close associa-
tion with ambygonite from various localities in
Czechoslovakia are known (F. Čech, written comm.
1987), and lacroixite thus may be much more
widespread than was considered previously. The pos-
sibility of a miscibility gap in the Na-Li montebra-
site solid solution requires much additional study.
A reinvestigation of the type natromontebrasite of
Schaller (1911) is in progress to answer the impor-
tant question of its validity as a mineral species.

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author is also indebted to F.N.R.S., Belgium, for
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