Liottite, a new mineral in the cancrinite–davyne group

STEFANO MERLINO AND PAOLO ORLANDI

Istituto di Mineralogia e Petrografia, Università di Pisa
Via S. Maria 53, 56100 Pisa (Italy)

Abstract

A new mineral, liottite, was found in Pitigliano (Tuscany, Italy). It occurs, as flattened hexagonal prisms up to 1 cm in diameter, inside cavities of ejected blocks in a pumice deposit. The space group is P6m2; a = 12.842, c = 16.091 Å. Optical data ω = 1.530, ε = 1.528. The density is 2.56 g cm⁻³. The strongest lines in the powder patterns are: 4.84(36), 3.715(100), 3.315(75), 2.686(10), 2.471(10), 2.141(24), 1.801(10). The chemical formula (Ca₁₀₋₇₆Na₉₋₇₆K₉₋₇₆Fe₀₋₇₆Si₈₋₇₆Al₁₇₋₇₆O₇₋₇₆(SO₄)₃₋₇₆(CO₃)₁₋₇₆Cl₁₋₇₆(OH)₉₋₇₆·1.8₆H₂O, the hexagonal symmetry, and the lattice dimensions show that liottite is a new member of the cancrinite group.

Introduction

Pitigliano (Tuscany, Italy) is a locality well known to collectors and students of minerals, because of the occurrence of a rich variety of well-crystallized minerals. Within a program of reexamination of Tuscan mineralogy, a study of the various mineral phases of that locality was undertaken. The study was fruitful because at least three different minerals of the cancrinite–davyne group were found: one was identified as afghanite and two appeared to be new mineral species on the basis of space group and cell dimensions. The aim of the present paper is the description and discussion of one of these new minerals, which was named liottite in honor of Luciano Liotti, enthusiastic and well-informed collector, who kindly gave us the material in which liottite was first found.

The new mineral and its name were approved by the New Minerals and Mineral Names Commission of I.M.A. Type material is deposited in the museums of Instituto di Mineralogia e Petrografia dell’ Università di Pisa (Italy) and Istituto di Mineralogia dell’ Università di Modena (Italy).

Paragenesis

The sample studied is one of numerous ejected blocks found in a pumice deposit, which is indicative of the explosive activity of a small volcanic center set up in the Pleistocene on the rims of the great Latera caldera. These blocks are the product of a synectic between the carbonate rocks which make up the walls of the vent of the magmatic reservoir and a trachytic magma. The most common mineral assemblage, which is also characteristic of the specimen from which the new species was obtained, is vesuvianite, garnet (grossular and andradite), pyroxene, and, subordinately, melilite, latiumite, anorthite, and brandsite.

Crystallographic and physical properties

Liottite is transparent and colorless. The crystals occur as well-developed flattened hexagonal prisms, up to one centimeter in diameter, inside the cavities of the blocks. Measurement by two-circle optical goniometer indicated hexagonal symmetry. No evidence contrary to dihexagonal dipyramidal symmetry was discovered in morphology; the various forms were then indexed assuming 6/mmm symmetry. The habit of the crystals is illustrated in Figure 1. Other minor forms appearing in the crystal on which we made our goniometric measurements were: {120}, {121}, {112}, {113}. They were not included in the drawing because of their minor development.

Weissenberg and precession photographs indicated Laue symmetry 6/mmm, with a ≈ 12.9 and c ≈ 16.1 Å. As no systematic absences were observed, possible space groups are P6/mmm, P6m, P62m, P6m2, and P622.

The X-ray powder data (Table 1) were obtained by means of a Phillips diffractometer, scanning speed 1/2° 2θ per min, Ni-filtered Cu radiation (λ = 1.54051 Å). The powder pattern was readily indexed using prominent reflections on the single-crystal pho-
Chemical composition

The chemical composition was obtained in the following way: CaO, Na₂O, and K₂O were determined by atomic absorption spectrometry using a Perkin Elmer 303 instrument. CO₂ and H₂O were obtained by the microdetermination of carbon and hydrogen carried out with the Carlo Erba elemental microanalyzer 1104 instrument. Cl and SO₄ were determined by X-ray fluorescence spectrometry, using as reference standard samples of analyzed cancrinite to which known quantities of sulphur and chlorine were added. Starting from the known quantities of the other elements, SiO₂, Al₂O₃, and Fe₂O₃ were determined by X-ray fluorescence spectrometry according to the method of Franzini and Leoni (1972), introducing the appropriate correction factors for sulphur and chlorine and assuming that the sum of the weight percentages was 100.0. The results of the analyses are given in the first column of Table 2.

Related compounds and structural considerations

The chemical data reported in Table 2, together with the hexagonal symmetry and the cell parameters, clearly show a close relationship with the minerals of the cancrinite–vishnevite–davyne series with chemical composition (Na, Ca, K)₈₋₉Al₉Si₆O₂₄(CO₃, SO₄, Cl, OH)₁₋₁₋₉H₂O. On this basis the unit-cell contents of liottite were calculated assuming 36(Si + Al) and are given in Table 2. From the excess of oxygen atoms over 72, a content of 3.58 hydroxyl anions can be inferred; in fact, hydroxyl ions are present in cancrinite minerals as indicated by chemical analyses and structural studies and were actually found in liottite by crystal-structure determination (Merlino and Mellini, 1976). The following chemical formula was thus calculated for liottite: (Ca₀.₇₀Na₀.₂₉K₀.₅₂Fe₀.₅₂)(Si₁₈.₃₄Al₁₇.₆₆)O₇₂(SO₄)₉₀.₉₁(CO₃)₁.₇₂Cl₁₂.₆₁(OH)₁₈.₅₈·1.₈₃H₂O. Liottite contains calcium as its dominant cation, a relation which was not found in any mineral of the cancrinite group except one microsommitite, as shown in Figure 2.

The crystal structure of cancrinite, space group P6₃, a = 12.75, c = 5.14 Å, was determined by Pauling (1930) and refined by Jarchow (1965). It is made up of six-fold rings of tetrahedra: each ring is linked to three rings in the preceding layer and to
three other rings in the succeeding one, in a threedimensional framework. The layers succeed each other along the \(c\) axis, according to the stacking sequence \(ABAB\ldots\).

The diffraction pattern of the specimen used by Jarchow (1965) to refine the structure of cancrinite showed diffuse spots symmetrically disposed relative to the sharp ones at \(\pm 3/7\,c^*\) in reciprocal space.
(satellite reflections), thus indicating some kind of superstructure. Foit et al. (1973) and Brown and Cesbron (1973) studied “cancrinites” from different sources, finding superstructures characterized by values of \( c \) parameter equal to 5\( c \), 8\( c \), 11\( c \), 16\( c \), and 21\( c \), where \( c = 5.13 \text{ Å} \). The diffraction patterns of all these cancrinites differ as regards the much weaker diffuse reflections but do not differ in the positions and intensities of the sharp spots. This indicates, as the authors remark, that they have the same aluminosilicate framework structure, differing only in the ordering of the cations outside the framework, which leads to the appearance of the satellite reflections.

Natural and synthetic compounds exist which, although structurally related to cancrinite, have a different aluminosilicate framework. Bariand et al. (1968) found and studied afghanite, a new aluminosilicate with unit-cell content \((\text{Na,Ca,K})_{66}(\text{Si,Al})_{66}\text{O}_{182}(\text{Cl,SO}_{4},\text{CO}_{3})_{12} \cdot 1.8\text{H}_{2}\text{O}\). Chemical composition and crystallographic data, reported in Table 3, indicated afghanite as a member of the cancrinite group, with an 8-layer sequence of six-membered rings. Recently Sieber and Meier (1974) prepared and studied Losod, a compound with idealized formula \( \text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 18\text{H}_{2}\text{O} \). Its cell data, also reported in Table 3, indicated it is a member of the cancrinite group with a 4-layer sequence \( ABAC \).

Liottite is another member of this group. Cell data pointed to a 6-layer sequence of six-membered rings; this has been confirmed by a crystal structure determination (Merlino and Mellini, 1976), which has led to the space group \( P\overline{6}m2 \) and indicated the stacking sequence \( ABABAC \). The structure refinement is in progress.

Table 2. Chemical data and unit-cell contents in liottite

<table>
<thead>
<tr>
<th></th>
<th>wt.%</th>
<th>cell contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SiO}_2 )</td>
<td>30.51</td>
<td>( \text{Si} ) 18.34</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>24.92</td>
<td>( \text{Al} ) 17.66</td>
</tr>
<tr>
<td>( \text{Fe}_2\text{O}_3 )</td>
<td>0.36</td>
<td>( \text{Fe}^{3+} ) 0.16</td>
</tr>
<tr>
<td>( \text{CaO} )</td>
<td>15.71</td>
<td>( \text{Ca} ) 10.76</td>
</tr>
<tr>
<td>( \text{Na}_2\text{O} )</td>
<td>7.97</td>
<td>( \text{Na} ) 9.29</td>
</tr>
<tr>
<td>( \text{K}_2\text{O} )</td>
<td>4.98</td>
<td>( \text{K} ) 3.82</td>
</tr>
<tr>
<td>( \text{SO}_3 )</td>
<td>8.66</td>
<td>( \text{SO}_4 ) 3.91</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>2.1</td>
<td>( \text{CO}_3 ) 1.72</td>
</tr>
<tr>
<td>( \text{Cl} )</td>
<td>2.57</td>
<td>( \text{Cl} ) 2.61</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>1.8</td>
<td>( \text{H}_2\text{O} ) 3.62</td>
</tr>
</tbody>
</table>

Table 3. Crystallographic data of compounds in the cancrinite group

<table>
<thead>
<tr>
<th>Source</th>
<th>Davyne Bariand et al. (1968)</th>
<th>Sieber and Meier (1974)</th>
<th>Liottite This paper</th>
<th>Afghanite Bariand et al. (1968)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>( P\overline{6}3 )</td>
<td>( P\overline{6}3\text{mmc} )</td>
<td>( P\overline{6}m2 )</td>
<td>( P\overline{6}3\text{mmc},P\overline{6}3\text{mc} )</td>
</tr>
<tr>
<td>( a(\text{Å}) )</td>
<td>12.70(0.03)</td>
<td>12.906(0.003)</td>
<td>12.842(0.003)</td>
<td>12.77(0.03)</td>
</tr>
<tr>
<td>( c(\text{Å}) )</td>
<td>5.33(0.02)</td>
<td>5.341(0.003)</td>
<td>5.391(0.005)</td>
<td>5.36(0.04)</td>
</tr>
<tr>
<td>( D_{\text{calc.}}(\text{g.cm}^{-3}) )</td>
<td>-</td>
<td>2.21</td>
<td>2.61</td>
<td>2.65</td>
</tr>
<tr>
<td>( D_{\text{meas.}}(\text{g.cm}^{-3}) )</td>
<td>-</td>
<td>2.15</td>
<td>2.56</td>
<td>2.55</td>
</tr>
<tr>
<td>( \mu^\text{*} )</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>8</td>
</tr>
</tbody>
</table>

* number of layers of six-membered rings in the sequence.
**Fig. 2.** Cation chemistry of liottite, compared with that of the other minerals in cancrinite group. The data are from Deer et al. (1962) and Bariand et al. (1968), excluding the analyses with cation sums less than 6 on the basis of 12 (Si + Al).

- **Cancrinite**
- **Vishnevite**
- **Microsommitite**
- **Davyne**
- **Afghanite**
- **Liottite**

**Acknowledgments**

Thanks are due to Mr. R. Cioni and Dr. L. Leoni who made respectively the absorption spectrometry and X-ray fluorescence spectrometry analyses. Particularly helpful were the suggestions and comments by A. Kato. The financial support of Consiglio Nazionale delle Ricerche, Roma, is also kindly acknowledged.

**References**


Franzini, M. and L. Leoni (1972) A full matrix correction in X-ray


Manuscript received, April 9, 1976; accepted for publication, September 15, 1976.