SACROFANO COMPLEX, A NATURAL LABORATORY FOR THE SYNTHESIS OF NEW MATERIALS

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Abstract. Sacrofano caldera is a remarkable mineralogical object. Of about 70 species described here, 10 species belong to the cancrinite group. The minerals of this group have zeolite-like frameworks built by layers consisting of six-membered rings of SiO$_4$ tetrahedra. There are three modes of stacking of neighbouring layers denoted by the letters A, B and C. Most wide spread species belonging to the cancrinite group have the simplest structure, with the stacking sequence $(AB)_6$ and small hexagonal unit cells with the parameters: $a = 12.7$-$12.9$ Å, $c = 5.2$-$5.4$ Å. Some of them (cancrinite, vishnevite) are even known as rock-forming minerals. However such minerals are surprisingly rare in Sacrofano area. All of them (except davyne that is relatively rare in this area) have unit cells with $c$ varying from 15.93 Å (for liottite) to 79.605 Å (for biachellaite). The latter mineral is characterized by the largest stacking sequence $(ABCABCACBACBCACBCACBCACBCACBCAC)$.$^6$. Outstanding mineral diversity of Sacrofano volcano, in particular the presence of large-period cancrinite-group minerals, can be connected with unusual conditions of their formation, including high gradients of temperature and concentrations of mineral-forming components in alkaline lava.

The caldera of Sacrofano volcano located about 25 km to the north of Rome city is one of significant mineralogical objects (Chukanov, Allori, 2008). Of about 70 species described here, 10 species belong to the cancrinite group, and of 7 new species first discovered in the Sacrofano caldera, 5 minerals (sacrofanite, giuseppettite, marinellite, alloriite and biachellaite) have cancrinite-like crystal structures. Sacrofano caldera is also the type locality of peprossiite-(Ce) and mottanaite-(Ce).

Table 1. New mineral species discovered in the caldera of Sacrofano and role of mineral collectors in their finding.

<table>
<thead>
<tr>
<th>New species</th>
<th>Year of description</th>
<th>Collector involved in the discovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sacrofanite</td>
<td>1980</td>
<td>Ezio Curti, who found the species</td>
</tr>
<tr>
<td>Giuseppettite</td>
<td>1981</td>
<td>Luciano Liotti, who found the species</td>
</tr>
<tr>
<td>Peprossiite-(Ce)</td>
<td>1993</td>
<td>Giorgio Penco, who found the species</td>
</tr>
<tr>
<td>Mottanaite-(Ce)</td>
<td>2002</td>
<td>No collector directly involved. Holotype comes from a large old set of specimens from Mt.Cavalluccio</td>
</tr>
<tr>
<td>Marinellite</td>
<td>2003</td>
<td>Luciano Liotti, who found the specimen of giuseppettite on which marinellite was detected</td>
</tr>
<tr>
<td>Alloriite</td>
<td>2007</td>
<td>Roberto Allori, who found the species</td>
</tr>
<tr>
<td>Biachellaite</td>
<td>2008</td>
<td>Ezio Curti, who found the specimen of sacrofanite on which biachellaite was detected</td>
</tr>
</tbody>
</table>

CANCRRNITE-GROUP MINERALS

The minerals belonging to the cancrinite group are trigonal or hexagonal aluminosilicates whose zeolite-like frameworks are composed of layers consisting of six-membered rings of SiO$_4$ tetrahedra. In cancrinite-group minerals (as well as many other framework silicates), three modes of stacking of neighbouring layers are distinguished and denoted by the letters A, B and C. The sequence of layers in the unit cell is a peculiar “genetic code” of the mineral. The simplest two-layer sequence $(AB)_6$ characterizes cancrinite, vishnevite, hydroxycancrinite, cancrisilite, pitiglianoite, davyne, microsommite and quadridavyne. Other cancrinite-group minerals are characterized by longer and more complex sequences.
Depending on the type of layer stacking, cancrinite-group minerals can contain channels composed of different cavities. The latter host alkaline- and alkaline-earth cations (mainly Na⁺, K⁺, Ca²⁺), various anions (SO₄²⁻, S²⁻, CO₃²⁻, Cl⁻, F⁻, OH⁻) and water molecules. Five types of cavities are known in cancrinite-group minerals: cancrinite-type, sodalite-type, liottite-type, losod-type and giuseppettite-type.

Large cavities (liottite, losod and giuseppettite) are present only in minerals with complex structures based on more than two-layer sequences. Such minerals are very rare (except afghanite) and are known only in special types of formations (some types of effusive rocks or lazurite-bearing metasomatites). The number of layers in complex cancrinite-like species can vary from 4 to 30. Most of such minerals have been found in the Sacrofano caldera. The presence of different cancrinite-group minerals in one association is common: marinellite associates with giuseppettite, the ejectum with sacrofanite contains also biachellaite, liottite and a mineral of the alloriite-afghanite series, etc.

MINERAL SPECIES OF THE CANCRINITE GROUP FIRST DISCOVERED IN THE SACROFANO’S CALDERA

Sacrofanite (IMA 1979-058). The primary specimen with sacrofanite was found at the end of seventies by E.Curti, a well known researcher and passionate collector of Latium minerals, in a quarry opened in Biachella valley, not far from Sacrofano, Rome province, Latium region, Italy. When sacrofanite was found, in Biachella valley two small quarries had been opened to dig out black lapilli. Both in the yellow tuff block and even loose on the ground it was possible to detect volcanic ejecta, mainly metamorphosed, pyroxenic and calcareous ones. Consequently, in the quarries and just nearby, mineral research was comparatively easy and, usually, fruitful enough (Liotti, Tealdi, 1983; Stoppani, Curti, 1982).

The original specimen with sacrofanite was an ejectum of atypical “sanidinite” composed mainly of sanidine with minor amounts of brown andradite, dark green diopside (fassaite), pale blue-greyish haüyne and leucite. The rock looked greyish, finely granular and contained cavities incrusted with crystals of late sanidine, diopside, andradite, haüyne and a cancrinite-group mineral forming colourless hexagonal prismatic crystals up to 2 cm in size, flattened along the basal pinacoid.

The latter mineral has been investigated at the Institute of Mineralogy and Petrography, University of Rome “La Sapienza”, and at the Institute of Mineralogy, State University of Perugia, (Burragato et al., 1980). Single-crystal investigations demonstrated that it is a new member of the cancrinite group with an exceptionally large hexagonal unit cell (the unit-cell dimensions are: \(a = 12.865\) and \(c = 74.240\ \text{Å}\)). This mineral was approved by the IMA CNMMN with the name sacrofanite, from the name of the volcanic area where it was found (Burragato et al., 1980). Sacrofanite has been characterized by optical, IR spectroscopic, thermal and other data (Table 3). Its empirical formula is \((Z = 14)\):

\[
(Na_{6.25}Ca_{1.83}K_{1.30}Fe_{0.05})(Si_{5.26}Al_{5.74}O_{24})(SO_4)_{1.14}(CO_3)_{0.27}Cl_{0.20}(OH)_{2.69}H_{0.27}O.
\]

Type specimen of sacrofanite is now preserved at the Mineralogical Museum of the University of Rome “La Sapienza” with the reference number 24322.

Recently, the crystal structure of sacrofanite has been modelled on the basis of HRTEM images and refined vs. synchrotron radiation data (Ballirano, Bonaccorsi, 2005). It corresponds to the following 28-layer stacking sequence: \(\text{ABCABACABACBACBACABACBC}\), where A, B and C designate the positions of six-member rings in each layer. The framework of sacrofanite contains sodalite-, cancrinite-, losod- and liottite-type cages. The space group is \(P-62c\), the single-crystal unit-cell parameters are: \(a = 12.903\) and \(c = 74.284\ \text{Å}\).

Giuseppettite (IMA 1979-064) was discovered in the Biachella valley (Mazzi, Tadini, 1981). This mineral occurs as blue-violet veinlets in sanidine volcanic ejecta, in the association with potassic feldspar, nepheline, haüyne, biotite and kalsilite. Blue-violet crystals of giuseppettite are known from Mt. Cavalluccio. Giuseppettite is one of the most sulfur-rich minerals of the cancrinite group. Its approximate empirical formula is: \((Na_{3.9}K_{1.8}Ca_{1.0})(Si_{5.95}Al_{0.05}O_{24})(SO_4)_{1.8}Cl_{0.25}\). High content of sulfur is connected with a specific
structural feature of the mineral: it contains a large giuseppettite cavity that can host up to four \( \text{SO}_4 \) groups. Giuseppettite is characterized by the 16-layer stacking sequence \( \text{ABABACBABABABC} \).

Type material is deposited in the Civic Museum of Natural History, Milan (Museo Civico di Storia Naturale), specimen number M 23737, and in the University of Pavia.

Marinellite (IMA 2002-021). Type specimen of marinellite comes from the Biachella valley (Bonaccorsi, Orlandi, 2003) and was identified in the same ejectum in which also giuseppettite was detected. It forms anhedral colourless individuals associated with giuseppettite, sanidine, haüyne, biotite and kalsilite. Marinellite (Table 3) has approximately the same unit-cell parameters as tounkite, another cancrinite-group mineral, but is characterized by a different 12-layer stacking sequence: \( \text{ABCBCBACBCBC} \). The empirical formula of marinellite calculated on \( Z = 6 \) is close to that of giuseppettite: \( \text{(Na}_{5.3}\text{Ca}_{1.0}\text{K}_{1.8})\text{(Si}_{6.0}\text{Al}_{6.0}\text{O}_{24})(\text{SO}_4)_{1.4}\text{Cl}_{0.3} \cdot 0.6\text{H}_2\text{O} \).

Second discovery of marinellite was made on a specimen collected in 1982 by the mineral collector L.Mattei, near a small quarry located at the border area of Sacrofano caldera between Fosso Attici and Biachella valley (Bellatreccia et al., 2006). The specimen represents a fragment of fine-grained sanidinite containing rare grains of biotite and small black crystals of augite. Imperfect (almost anhedral) light-blue to blue crystals of marinellite up to 2 mm in size are present in small cavities of the rock. Its approximate empirical formula is \( Z = 6 \): \( \text{(Na}_{4.8}\text{Ca}_{1.9}\text{K}_{0.9})\text{(Si}_{6.4}\text{Al}_{5.6}\text{O}_{24})(\text{SO}_4)_{1.8}(\text{CO}_3)_{0.1}\text{Cl}_{0.1} \cdot 0.7\text{H}_2\text{O} \), or, ideally, \( \text{Na}_{5}\text{Ca}_{2}\text{K} \text{(Si}_{5}\text{Al}_{6}\text{O}_{24})(\text{SO}_4)_{2} \cdot \text{H}_2\text{O} \). It differs from the type sample by the ratio \( \text{Ca}:\text{K} \). However unit-cell parameters refined from the powder X-ray diffraction data \( a = 12.881, c = 31.764 \, \text{Å} \) are very close to that for the holotype (see Table 3).

Alloriite (IMA number 2006-020 – Chukanov et al., 2007) was found by R.Allori at Monte Cavalluccio. The mineral was formed on a late stage of crystallization, within cavities in a volcanic sanidinite ejectum. Associated minerals are: sanidine, biotite, andradite, apatite. Alloriite forms short-prismatic and tabular colourless to very pale lilac crystals up to 1.5 × 2 mm. Its empirical formula is \( Z = 4 \): \( \text{(Na}_{4.5}\text{K}_{1.6}\text{Ca}_{1.2})\text{(Si}_{6.3}\text{Al}_{5.7}\text{O}_{24})(\text{SO}_4)_{1.2}(\text{CO}_3)_{0.2}\text{Cl}_{0.1} \cdot (\text{OH})_{0.2} \cdot 1.2\text{H}_2\text{O} \).

The crystal structure of alloriite is based on the same tetrahedral framework as that of afghanite. It is characterized by the ABABACAC stacking sequence and ordering of Si and Al.
The framework contains two types of channels. One of them contains liottite-type and cancrinite-type cages. The liottite-type cage can host up to three SO₄ groups. The cancrinite-type cage can contain [Ca·Cl]⁺ clusters (in davyne, microsommite, quadridavyne and afghanite), or [Na·H₂O]⁺ clusters (in cancrinite, vishnevite, pitiglianoite and alloriite). A distinctive feature of alloriite is the predominance of OH groups over Cl in the smaller (cancrinite-type) cages of wide channels. In afghanite, Cl is the main anion in these cages. The composition of the cancrinite-type cage is Ca₄Cl₂ for afghanite and Ca₄(OH)₁.66Cl₀.34 for alloriite.

The cage sequence of the second type forms a narrow cancrinite-type channel. In afghanite, a part of Ca and Cl is situated within narrow channels forming chains ⋯Ca-Cl-Ca-Cl⋯. In alloriite, sodium-water chains (ideally, ⋯Na-H₂O-Na-H₂O⋯) are situated in analogous channels.
Holotype specimen of alloriite is deposited in the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with registration number 3459/1.

**Biachellaite** (IMA number 2007-044) has been detected in a specimen preserved, since more than twenty five years, in a private collection and presumed to be sacrofanite. Its origin goes back to L.Liotti, well known researcher and collector of Latium’s minerals. Accordingly to his statement, the specimen is a part of the same volcanic ejectum on which sacrofanite was detected.

![Fig. 4. Crystals of biachellaite. Рис. 4. Кристаллы бьякеллаита.](image)

The investigated sample, sizing about 4.5 × 4.5 cm, consists of tabular, glassy, translucent white to colourless crystals, often in “accordeon-like” aggregates. Associated minerals are brown andradite, dark green diopside (fassaite) and sanidine. In association with biachellaite, also other cancrinite-group minerals have been identified. In particular, liottite with unit-cell dimensions $a = 12.884$, $c = 15.931$ Å forms intergrowth with biachellaite (personal communication by R.K.Rastsvetaeva).

The empirical formula of biachellaite is ($Z = 15$):

$$(\text{Na}_{3.76}\text{Ca}_{2.50}\text{K}_{1.44})_{2.70}(\text{Si}_{6.06}\text{Al}_{5.94}\text{O}_{24})(\text{SO}_{4})_{1.84}\text{Cl}_{0.15}(\text{OH})_{0.43}·0.81\text{H}_{2}\text{O}.$$  

The crystal structure of biachellaite is characterized by the 30-layer stacking sequence (ABCABCACACBABCACBACBABCACBACBACBACBACBABC). The tetrahedral Al, Si, O framework contains cavities of four types: cancrinite, sodalite, losod and liottite ones.
Fig. 5. Narrow channel (a) and fragment of framework (b) in biachellaite. Cancrinite (C), sodalite (S), liottite (Lt) and losod (Ld) cavities are shown.

Рис. 5. Узкий канал (а) и фрагмент каркаса (б) в бьякеллаите. Показаны канкринитовая (C), содалитовая (S), лиоттитовая (Lt) и лосодовая (Ld) полости.

Holotype sample is deposited in the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with registration number 3642/1.

OTHER CANCRINITE-GROUP MINERALS KNOWN IN THE SACROFANO CALDERA

Franzinite. This 10-layer cancrinite-group mineral, was found by L.Liotti and investigated by S.Merlino and P.Orlandi (1977) in ejected blocks in a pumice deposit (the Case Collina quarry, Pitigliano, Grosseto, Toscana, Italy). It forms white crystals up to 1 cm in the association with grossular, “apatite”, fassaitic diopside and vesuvianite. Type material from Pitigliano is deposited in the Museum of Natural History (Museo di Storia Naturale e del Territorio), University of Pisa, with the number 3208.

However crystal structure of franzinite was investigated on a specimen collected “near Sacrofano” (Ballirano et al., 2000) and preserved in the Mineralogical Museum of the University of Rome under the number 24340.

Pitiglianoite. Monte Cavalluccio is the second occurrence of this rare mineral of the cancrinite group (Bonaccorsi, Orlandi, 1996), the first one being within ejected metasomatic blocks in the pumice quarry of Case Collina, near Pitigliano, Grosseto, Toscana, Italy (Merlino
et al., 1991). At Case Collina it occurs as vitroes, colourless hexagonal prism up to 4 mm associated to “apatite”, diopside, grossular.

Investigated pitiglianoite from Monte Cavalluccio occurs within a sanidine-rich volcanic ejected block. It forms prismatic, clearly hexagonal elongated crystals both colourless and white-pale bluish in colour and it is associated with clinopyroxene, titanite, zircon, magnetite, nepheline, a hellandite-group mineral and peprossiite-(Ce). Its approximate crystal-chemical formula is: (Na$_{4.7}$K$_{2.7}$Ca$_{0.1}$)(Si$_{6.1}$Al$_{5.9}$O$_{24}$)(SO$_4$)$_{0.8}$·2H$_2$O.

As it was shown using IR spectroscopy, pitiglianoite from Monte Cavalluccio contains CO$_2$ molecules within the structural channels (Della Ventura et al., 2005).

Afghanite was first discovered in the lazurite deposit Sar-e-Sang, Badakhshan prov., Afghanistan, 40 years ago. (Bariand et al., 1968). This Cl-bearing 8-layer cancrinite-group mineral is a rather typical feldspathoid of lazurite-bearing metasomatic rocks.

Later afghanite was found in different Italian volcanogenic localities: Monte Somma, Case Collina quarry near Pitigliano as well as in Fosso Attici and Valle Biachella in the Sacrofano Caldera. It forms both platy and barrel-like glassy hexagonal crystals, either single or in swarm-like aggregates, from white-greyish to very pale blue, associated to pyroxens (augite, “fassaite”), micas, hauyne, “horneblende”, tuscanite.

Davyne was first discovered on Monte Somma/Vesuvio and investigated by T.Monticelli and N.Covelli in 1825. Unlike most other cancrinite-group minerals known in the Sacrofano Caldera (except pitiglianoite), davyne is characterized by a simple two-layer structure. Its specific feature is high content of chlorine.

This mineral was noted in Valle Biachella and Monte Cavalluccio. It occurs as prismatic hexagonal crystals up to 4 mm both freely scattered on the matrix and grouped together. Colour is from white-greyish to pale blue, waxy, very pale pink fluorescent. Associations are “horneblende”, titanite, sodalite, sanidine.

Liottite. Also this species was found by L.Liotti in the ejected blocks in the pumice deposit of Case Collina, Pitigliano, Grosseto, Toscana, Italy. It forms colourless to white hexagonal crystals in association with grossular, vesuvianite, “apatite” and fassaitic diopside.

As noted above, liottite is one of cancrinite-group minerals associated with sacrofanite in the type specimen form Valle Biachella. It forms intergrowths with biachellaite. Findings of this mineral have been noted also in other areas of the Sacrofano caldera.

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