Abuite, CaAl$_2$(PO$_4$)$_2$F$_2$, a new mineral from the Hinomaru–Nago mine, Yamaguchi Prefecture, Japan

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Abuite was found in hydrothermally altered rocks in the Hinomaru–Nago mine, Kyo area, Abu, Abu County, Yamaguchi Prefecture, Japan (34°53′N 131°52′E). Abuite is often included in aluminum phosphate rich samples, embedded with quartz and augelite and/or trolleite, and is often accompanied by other phosphates especially apatite and crandallite. Abuite is transparent and colorless with white streak and vitreous luster. It is very difficult to find them in bare eyes, since the dominant phases in aluminum phosphate rich samples, augelite, trolleite, and quartz, are all also transparent and colorless. The empirical formula of abuite (based on 10 anions pfu, O = 8, F + OH = 2) is (Ca$_{0.99}$Sr$_{0.01}$)$_{1.00}$Al$_{1.96}$P$_{2.03}$O$_8$(F$_{1.89}$OH$_{0.11}$). H$_2$O was calculated by stoichiometry. The simplified formula is CaAl$_2$(PO$_4$)$_2$F$_2$. Abuite is the calcium analogue of SrAl$_2$(PO$_4$)$_2$F$_2$, which was synthesized by hydrothermal methods (Le Meins and Courbion, 1998). The crystal structure is orthorhombic, with space group P$_2_1$2_12. Unit cell parameters refined from the obtained X-ray diffraction pattern are $a$ = 11.818(2), $b$ = 11.993(2), $c$ = 4.6872(8) Å and $V$ = 664.3(2) Å$^3$, with $Z$ = 4.

Keywords: Abuite, Hinomaru–Nago mine, Al–phosphates, Gatumbaite, New mineral

INTRODUCTION

Various aluminum phosphates such as augelite, trolleite, scorzalite, svanbergite and florencite–(Ce) are reported from the Hinomaru–Nago mine. New mineral abuite was first reported as a ’gatumbaite–like mineral’ by Matsubara and Kato (1998) from its chemical composition and lack of X-ray diffraction pattern coinciding with the original pattern. Gatumbaite was reported by von Knorring and Fransolet (1977), with the formula CaAl$_2$(PO$_4$)$_2$(OH)$_2$·H$_2$O. However, chemical and X-ray diffraction experiments indicated that the ’gatumbaite–like mineral’ is a new mineral with completely different crystal structure from gatumbaite. The simplified formula of abuite CaAl$_2$(PO$_4$)$_2$F$_2$ is very close to gatumbaite, only differing in the amount of F and H$_2$O. The name is for the type locality, near the town of Abu, Abu County, Yamaguchi Prefecture, Japan. The mineral and mineral name have been approved by the International Mineralogical Association, Commission on New Minerals, Nomenclature and Classification (No. 2014-084). The type specimen is deposited in Kitakyushu Museum of Natural History and Human History, Kitakyushu, Japan, under the registered number KMNHM000003.

GEOLOGICAL SETTINGS

Abuite was found in hydrothermally altered rocks in the Hinomaru–Nago mine, Kyo area, Abu, Abu County, Yamaguchi Prefecture, Japan (34°53′N 131°52′E). The Hinomaru–Nago mine was described in previous studies as the ‘Hinomaru–Nako mine’ by mistake. The name of the mine comes from the company name ‘Hinomaru–Yougyou (pottery)’ which had an office in the ‘Nago’ area. There are many hydrothermal deposits in Abu County, formed by hydrothermal alteration of acidic pyroclastic rocks belonging to the Abu Group of upper Cretaceous age, caused by the intrusion of a biotite adamellite (Kamitani, 1977). The Hinomaru–Nago mine is characterized by the presence of various aluminum phosphates, aside from the aluminum silicates widely seen in Abu County (Kamitani, 1977; Matsubara and Kato, 1998). Augelite and trolleite are the most dominant Al–phosphates in the Hinomaru–Nago mine, and include other Al–phosphates.
ANALYTICAL METHODS

X-ray diffraction (XRD) data was collected on crystal fragments using a Rigaku RINT RAPIDII curved imaging plate microdiffractometer that used monochromatized CuKα radiation generated at 40 kV and 30 mA. The fragments were randomized using a Gandolfi-like motion about two axes (oscillation on ω and rotation on φ). The XRD data of abuite was indexed with the calculated data for CaAl₂(PO₄)₂F₂, using the atomic coordinates for synthetic SrAl₂(PO₄)₂F₂, PDF card; #04-011-4811 (Le Meins and Courbion, 1998).

Chemical analyses were also performed by a JEOL JXA8530F electron probe microanalyzer (EPMA). Quantitative analyses were performed at an accelerating voltage of 15 kV, beam current of 5 nA and prove diameter of 20 µm. The standard materials were apatite (CaKα, Pβα, Fβα), celestine (SrLα), and corundum (AlKα). H₂O contents were calculated by stoichiometry. The ZAF method was used for data correction.

OCURRENCE

The hydrothermally altered rocks of the Hinomaru–Nago mine can be roughly divided into three groups as in Matsubara and Kato (1998); white fine-grained rock, light grey less fine-grained rock, and white coarser-grained rock. Fine-grained white rock is mainly composed of quartz, andalusite, and clay minerals such as pyrophyllite, kaolinite, and muscovite, and devoid of any aluminum phosphates. Light grey less fine-grained rock and white coarser-grained rock are mainly composed of quartz, andalusite, and aluminum phosphates, the latter involving more aluminum phosphates in quantity. They come in close relation, and the white coarser-grained parts are seen as small patches in outcrops of light grey less fine-grained part. Not every sample of these types includes aluminum phosphates, and the blue tints of lazulite–scorzalite, or the cleavage of augelite can be the clue to determine. Abuite is often included in aluminum phosphate rich samples. Abuite is embedded with quartz and augelite and/or trolleite, and is often accompanied by other phosphates especially apatite and crandallite (Fig. 1). Abuite occurs as grains of 100–500 µm in size, and sometimes makes aggregates with other minerals, up to 2 mm in size. Abuite was probably formed during hydrothermal alteration of pre-existing minerals.

PHYSICAL AND OPTICAL PROPERTIES

Abuite is transparent and colorless with white streak and vitreous luster. Cleavage is not observed. It is very difficult to find them in bare eyes, since the dominant phases in aluminum phosphate rich samples, augelite, trolleite, and quartz, are all also transparent and colorless. No fluorescent was seen. Density could not be measured due to small amount of the mineral. The calculated density is 3.214 g cm⁻³ using the empirical formula and refined unit cell parameters.

CHEMICAL COMPOSITION

The empirical formula of abuite (based on 10 anions pfu, O = 8, F + OH = 2) is (Ca₀.₉₉Sr₀.₀₁)₁₀₀Al₁₀₀P₂₀₃O₈(F₁.₈₉OH₀.₁₁) (Table 1). H₂O was calculated by stoichiometry. The simplified formula is CaAl₂(PO₄)₂F₂, which requires CaO 17.42, Al₂O₃ 31.67, P₂O₅ 44.08, F 11.80, O = F -4.97, total 100.00 wt%. Abuite is mostly homogeneous, and slight compositional inhomogeneity by Sr is seen in some samples (Fig. 2 and Table 1). As noted in the next section, Sr analog of abuite is already synthesized, so Sr analog of abuite may also exist in nature.

| Table 1. Chemical compositions of abuite from the Hinomaru-Nago mine |
|------------------------|--------|--------|--------|--------|--------|
|                        | 1 (n = 21) | 2 (n = 4) | 3 (n = 4) | 4 (n = 4) | 5 (ideal) |
| P₂O₅                  | 45.04   | 45.38   | 41.87   | 42.78   | 44.08   |
| Al₂O₃                 | 31.26   | 30.81   | 30.26   | 30.28   | 31.67   |
| CaO                   | 17.29   | 16.28   | 16.24   | 13.60   | 17.42   |
| SrO                   | 0.22    | 1.78    | 5.39    |         |         |
| F²                    | 11.24   | 10.17   | (11.21) | (11.37) | 11.80   |
| O = F                 | 4.73    | 4.28    | (4.91)  | (4.91)  | 4.97    |
| H₂O**                 | 0.31    | 0.81    | 0.00    | 0.00    |         |
| Total                  | 100.63  | 100.95  | (94.67) | (98.51) | 100.00  |


* For 3 and 4, F content was calculated on the assumption that F = 2 apfu, for comparison with present study, since F was not analyzed in Matsubara and Kato (1998).
** H₂O was calculated by stoichiometry.
Abu is the calcium analogue of SrAl$_2$(PO$_4$)$_2$F$_2$, which was synthesized by hydrothermal methods (Le Meins and Courbion, 1998). SrAl$_2$(PO$_4$)$_2$F$_2$ is orthorhombic, space group $P2_12_12_1$ with unit cell parameters $a = 12.026(1)$, $b = 12.199(1)$ and $c = 4.666(1)$ Å. The Sr phase has not been found to occur in nature to date. The XRD pattern of abuite was calculated using the atomic coordinates for SrAl$_2$(PO$_4$)$_2$F$_2$. The calculated XRD pattern conforms closely to the observed pattern.

**Figure 1.** Occurrence of abuite from the Hinomaru-Nago mine. (a) BSE image and (b) photomicrograph (crossed nicols) of abuite. (c) BSE image of abuite occurring with lazulite-scorzalite. (d) BSE image of abuite occurring with apatite and alunite super group minerals. Abu, abuite; Agl, augelite; Ap, apatite; Cdl, crandallite, Gcx, gorceixite; Laz, lazulite; Qtz, quartz; Rt, rutile; Scz, scorzalite; Sv, svanbergite; Trl, trolleite.

**Figure 2.** BSE image and X-ray mapping images (CaK$\alpha$, SrL$\alpha$, AlK$\alpha$, PK$\alpha$ and FK$\alpha$) of abuite including Sr. Abu, abuite; Agl, augelite; Ap, apatite; Qtz, quartz.

**X-RAY CRYSTALLOGRAPHY**

Abu is the calcium analogue of SrAl$_2$(PO$_4$)$_2$F$_2$, which was synthesized by hydrothermal methods (Le Meins and Courbion, 1998). SrAl$_2$(PO$_4$)$_2$F$_2$ is orthorhombic, space group $P2_12_12_1$ with unit cell parameters $a = 12.026(1)$, $b = 12.199(1)$ and $c = 4.666(1)$ Å. The Sr phase has not been found to occur in nature to date. The XRD pattern of abuite was calculated using the atomic coordinates for SrAl$_2$(PO$_4$)$_2$F$_2$. The calculated XRD pattern conforms closely to the observed pattern.
to the observed data (Fig. 3). Data were indexed using the calculated data for CaAl$_2$(PO$_4$)$_2$F$_2$ and are listed in Table 2 (in Å for CuK$\alpha$) in comparison with SrAl$_2$(PO$_4$)$_2$F$_2$, PDF card; #04-011-4811 (Le Meins and Courbion, 1998). The unit cell parameters of abuite refined from the obtained XRD pattern are $a = 11.818(2)$, $b = 11.993(3)$, $c = 4.6872(8)$ Å and $V = 664.3(2)$ Å$^3$ with $Z = 4$.

Abuite have similar atomic coordinates to SrAl$_2$(PO$_4$)$_2$F$_2$, estimated from the resemblance of the calculated XRD pattern for CaAl$_2$(PO$_4$)$_2$F$_2$ to the observed XRD pattern of abuite. The crystal structure of SrAl$_2$(PO$_4$)$_2$F$_2$ (Le Meins and Courbion, 1998) consists of infinite chains of cis-linked Al octahedra along [001] by sharing two fluorine atoms. Two different chains are linked by PO$_4$ tetrahedra, giving rise to channels along [001] delimited by a helical distribution of oxygen anions in which the Sr cations are found.

**DISCUSSION**

The chemical composition of abuite is similar to gatumbaita (Table 3). The only difference is the presence of fluorine and H$_2$O content. Gatumbaita is a very rare mineral which is reported in only four localities (von Knorring and Fransolet, 1977; Duggan et al., 1990; Ek and Nysten, 1990; Breiter et al., 2009). However, XRD pattern is only obtained in two localities (von Knorring and Fransolet, 1977; Ek and Nysten, 1990), and data only written in type locality. Also, F is detected in the sample from Vernéřov, Bohemia, Czech Republic (Breiter et al., 2009). Though more investigation is essential, it is possible that abuite was described as gatumbaita in some localities.

Abuite occurs in hydrothermally altered rocks of the Hinomaru–Nago mine, and gatumbaita is reported from pegmatites and hydrothermal deposits (von Knorring and Fransolet, 1977; Duggan et al., 1990; Ek and Nysten, 1990; Breiter et al., 2009). Augelite occurs in all localities, with accompanying berlinite and/or trolleite. The occurring species of these Al–phosphates differ by temperatures, in the descending order; berlinite, augelite, trolleite (Wise and Loh, 1976). Augelite is stable in narrow range around 400–500°C in low pressure, which is relatively high temperature for hydrothermal deposits. In addition, Al–silicates such as andalusite or kyanite are widely found in the hydrothermal deposits, indicating the presence of large volume acidic fluids (Wise, 1975). So relatively high temperature acidic environments may
be required for formation of abuite and gatumbait. Also, the amount and activity of Ca and F contents within the alteration fluid, and the balance with coexisting minerals such as apatite, crandallite and topaz, could be the key to their formation and distinction.
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<td>1</td>
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<td>1.388 2</td>
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<td>1.411</td>
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* Calculated X-ray diffraction data for synthesized SrAl2(PO4)2F2 (PDF #04-011-4811). Overlapped reflections are given an ‘m’ qualifier. This is because the instrumental resolution is assumed to be insufficient to resolve the overlapped reflections.
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