LETTER

Zäirite in quartz veins from Ishidera area, Wazuka, Kyoto Prefecture, Japan

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Zäirite was found from the quartz vein penetrating into the metamorphosed mudstone of the Wazuka Unit in Ishidera area, Wazuka-cho, Kyoto Prefecture, Japan, which is the first occurrence in Japan. Zäirite occurs as bright-yellow granular crystals (20–30 μm) in a cavity formed by the leaching of fluorapatite with native bismuth inclusion. The chemical composition of zäirite from Ishidera was closer to the ideal chemical composition, comparing with the zäirite from type locality including Al. The empirical formula from electron probe micro-analyzer (EPMA) analysis on the basis of O = 8, $\text{OH}^- = 6$ was $(\text{Bi}_{0.70}\text{Ca}_{0.23})_{\Sigma 0.93}\text{Fe}_{2.91}^{3+}(\text{P}_{2.04}\text{S}_{0.09}\text{O}_8)(\text{OH})_6$. The unit cell parameters obtained from the X-ray diffraction (XRD) pattern were $a = 7.311(3)$ Å and $c = 16.407(7)$ Å, larger than the type locality due to difference in chemical composition.

Keywords: Zäirite, Waylandite, Plumbogummite group, Ishidera, Wazuka

INTRODUCTION

The Wazuka district, located in southern Kyoto Prefecture, is situated at the northern margin of the Cretaceous Ryoke low-pressure/temperature (low- P/T) metamorphic belt stretching along the Median Tectonic Line, Southwest Japan. In this district, the Late Jurassic accretionary complex of the Tamba belt (Wazuka Unit) is widely distributed as the protolith of the low- to high-grade metamorphic rocks (Wang et al., 1986; Takeuchi and Wang, 1999; Ozaki et al., 2000). The Wazuka Unit is mainly composed of mudstone and bedded chert. Ozaki et al. (2000) studied the paragenesis of pelitic and psammitic metamorphic rocks in the Wazuka district and divided into four mineral zones; chlorite zone, chlorite-biotite zone, biotite zone, and sillimanite zone, in order of increasing metamorphic grade. In the northern area of the district, Late Cretaceous granitic rocks (the Younger Ryoke granitic rocks) were intruded discordantly into the regional metamorphic rocks. Contact aureole is recognized as a cordierite zone

between biotite and sillimanite zones (Ozaki et al., 2000). At the present sampling locality in the Ishidera area, corresponding to the cordierite zone, a number of quartz veins penetrates into the metamorphosed mudstone of the Wazuka Unit. These quartz veins are grayish and mainly composed of quartz and minor amount of muscovite, feldspar, fluorapatite, scheelite, beryl, tourmaline, pyrite, and native bismuth. Some secondary minerals are reported; phosphates (cacoxenite, phosphosiderite, strengite, and waylandite), tungsten minerals (ferritungstite, russelite, anthoinite, and mpororoite), bertrandite, and goethite (Tsuruta et al., 2008; Shimobayashi et al., 2012; Shirose et al., 2018). We have newly found a secondary phosphate mineral ‘zäirite’ formed by alteration of fluorapatite in the quartz veins in the Ishidera area, which is the first occurrence in Japan.

Zäirite $[\text{BiFe}_3^{3+}(\text{PO}_4)_2(\text{OH})_6]$ was first found in the weathering zone of quartz veins mineralized in wolframite at Eta-Etu, North Kivu, Zaïre (now the Democratic Republic of the Congo) by Wambeke (1975). Wambeke considered this greenish-colored mineral as the ferric iron analogue of waylandite, both of which belongs to the crandallite series (space group: $R\bar{3}m$), plumbogummite group mineral. Wambeke (1975) derived its structural formula

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Figure 1. Photographs of zaïrite from the Ishidera area, Wazuka, Japan. (a) Bright-yellow granular crystals in a cavity formed by the leaching of fluorapatite. (b) Secondary electron image of zaïrite showing aggregated crystals. (c) Secondary electron image of zaïrite showing a short hexagonal prismatic crystal. Color version is available online from <https://doi.org/10.2465/jmps.201130d>.

from the chemical analysis as $[\text{Bi}_{0.76}(\text{Ba}, \text{Ca}, \text{Cu}, \text{Zn})_{0.23} \text{H}_{0.23}] [\text{Fe}_{2.38} \text{Al}_{0.65}] [(\text{PO}_4)_{1.91} (\text{XO}_4)_{0.09}] (\text{OH})_6$, where $X = \text{Si}, \text{S}, \text{Te}, \text{H}_4$, and its unit cell parameters as $a = 7.015(5) \text{ \AA}$ and $c = 16.365(15) \text{ \AA}$. Geological setting of this type material is granite pegmatite. After its discovery in 1975, the occurrence of zaïrite has been reported from a few localities in the world. The mineralogical properties, especially unit cell parameters, of zaïrite from Ishidera was quite different from the type locality. For further understanding of the mineralogical properties of zaïrite and plumbogummite group mineral, the present paper reports the occurrence and mineralogical properties of zaïrite from Ishidera area, Wazuka-cho, Kyoto Prefecture, Japan.

SAMPLES AND METHODS

Sample description

The samples used in this study are collected from the grayish quartz vein including muscovite and fluorapatite. The grayish quartz at this locality is characterized by including the numerous fine particles ($<10 \mu\text{m}$) of graphite. In addition to sulfide minerals such as pyrite and chalcopyrite, aggregates of native sulfur are often observed in the grayish quartz vein. There are some cavities formed by the leaching of fluorapatite out from the quartz vein. Zaïrite occurs in this type of cavity, as aggregates of bright-yellow granular crystals ($<20 \mu\text{m}$) with glassy luster (Fig. 1a). Other secondary phosphate minerals such as strengite and beraunite are also coexistent in the cavity.

Analytical methods

Chemical analyses were performed on a JEOL JXA-8105 electron probe micro-analyzer (EPMA) equipped with a wavelength dispersive X-ray spectrometer. Quantitative analyses were performed at an accelerating voltage of 15 kV, beam current of 3 nA, and probe diameter of 3 μm .

The standard materials were bismuth selenide (for $\text{BiM}\alpha$), corundum (for $\text{AlK}\alpha$), hematite (for $\text{FeK}\alpha$), diopside (for $\text{CaK}\alpha$), jadeite (for $\text{NaK}\alpha$), apatite (for $\text{PK}\alpha$) and sphalerite (for $\text{SK}\alpha$). The ZAF method was used for data correction. Morphological observations were carried out using a JEOL JSM-6060 scanning electron microscope (SEM). X-ray diffraction (XRD) data of this mineral was collected by using a randomized Gandolfi-like motion by two axes (oscillation on ω and rotation on ϕ) in a Rigaku RINT RAPID II curved imaging plate microdiffractometer at Kyushu University, with utilized monochromatized $\text{CuK}\alpha$ radiation generated at 40 kV and 30 mA.

DESCRIPTION OF MINERALS

Morphological observation with SEM shows that zaïrite occurs as short hexagonal prismatic crystal up to $20 \mu\text{m}$ in size (Figs. 1b and 1c). As shown in Figure 2, zaïrite occurs in association with other bismuth phosphates less than $10 \mu\text{m}$, in the cracks and cavities formed by the leaching of fluorapatite including native bismuth as an inclusion ($<10 \mu\text{m}$). This indicates the formation of zaïrite by the

Figure 2. Backscattered electron image of zaïrite and associated minerals. Ap, fluorapatite; Ms, muscovite; Qtz, quartz.

Table 1. Representative XRD data for zäirite

<i>h k l</i>	1		2	
	<i>d</i> _{meas.}	<i>I</i>	<i>d</i> _{meas.}	<i>I</i>
1 0 1	5.890	100	5.710	95
0 1 2	5.011	3	4.870	10
1 1 0	3.641	19	3.500	40
0 2 1	3.098	14		
1 1 3	3.031	89	2.945	100
2 0 2	2.944	12	2.851	15
0 0 6	2.739	13	2.727	20
0 2 4	2.502	12	2.440	10
1 2 2	2.353	2		
2 0 5	2.285	2		
1 0 7	2.199	26	2.184	10
1 1 6			2.158	15
0 3 3	1.963	12		
3 0 3			1.897	15
2 2 0	1.821	13	1.754	10
2 0 8	1.719	8		
2 2 3			1.670	5
1 1 9	1.631	5		
1 0 10	1.589	1		
2 2 6	1.516	7		
0 2 10	1.457	14		
<i>a</i> = 7.311(3) Å			<i>a</i> = 7.015(5) Å	
<i>c</i> = 16.407(7) Å			<i>c</i> = 16.365(15) Å	

1. Zäirite from Ishidera, Wazuka, Japan (Present work).

2. Zäirite from Eta-Etu, northern Kivu, Congo (Wambeke, 1975; ICDD-PDF 00-029-0226).

alteration of fluorapatite, pyrite, and native bismuth.

The XRD pattern of zäirite from Ishidera does not well match the XRD pattern of zäirite from type locality described by Wambeke (1975) or PDF card #00-029-0226, due to the difference in chemical composition, which will be explained in the discussion section. The obtained peaks were indexed using a simulated crystal structure of zäirite based on the atomic parameter of waylandite, an Al analogue of zäirite (Mills et al., 2010). The unit cell parameters of zäirite from Ishidera were obtained as trigonal cell: *a* = 7.311(3) Å, *c* = 16.407(7) Å, and *V* = 759.5(6) Å³ (Table 1).

The chemical composition of zäirite from Ishidera was closer to the ideal chemical composition, comparing with the zäirite from type locality including Al. The empirical formula from EPMA analysis on the basis of O = 8, OH[−] = 6 was (Bi_{0.70}Ca_{0.23})Σ_{0.93}Fe_{2.91}³⁺(P_{2.04}S_{0.09}O₈)(OH)₆ (Table 2). Al was not measured in quantitative analysis because it was not detected in qualitative analysis. The total was 92 wt% including calculated H₂O, and this lower value may be due to minor beam damage, as in the case of waylandite reported by Mills et al. (2010), which belongs to the same group with zäirite. Some grains of zäirite show slight chemical zoning along the shape of the crystal.

Table 2. Chemical compositions of zäirite

	1		2	
	Average of 7 points	Standard deviation		
Wt %				
Bi ₂ O ₃	24.44	0.98		28.71
BaO	-	-		1.98
CaO	1.90	0.46		0.72
CuO	-	-		0.82
ZnO	-	-		0.82
Fe ₂ O ₃	34.77	1.25		30.75
Al ₂ O ₃	*n.d.	*n.d.		5.35
P ₂ O ₅	21.65	0.78		21.93
SiO ₂	-	-		0.33
SO ₃	1.04	0.28		0.29
TeO ₃	-	-		0.20
H ₂ O	**8.09	**0.28		9.05
Total	91.89	2.50		100.18
Mole ratios (basis: O = 8, OH [−] = 6)				
Bi	0.70	0.04		0.760
Ba	-	-		0.080
Ca	0.23	0.05		0.080
Cu	-	-		0.064
Zn	-	-		0.004
Fe ³⁺	2.91	0.03		2.380
Al	*n.d.	*n.d.		0.650
P	2.04	0.02		1.910
Si	-	-		0.034
S	0.09	0.08		0.023
Te	-	-		0.007
OH [−]	6	-		6

1. Zäirite from Ishidera, Wazuka, Japan (Present work).

2. Zäirite from Eta-Etu, northern Kivu, Congo (Wambeke, 1975).

* Al was not measured in quantitative analysis because it was not detected in qualitative analysis.

** H₂O was calculated by stoichiometry.

DISCUSSION

The general chemical formula of plumbogummite group minerals is *AB*₃(*XO*₄)₂(OH, H₂O)₆, where *A* is a large cation site occupied by Bi, REE, Ca, Sr, Ba, and Pb; *B* is an octahedral site occupied by Al, Fe³⁺, and V³⁺; *X* is a tetrahedral site occupied by P, minor S and As (Mills et al. 2010). Zäirite [BiFe₃³⁺(PO₄)₂(OH)₆] and waylandite [BiAl₃(PO₄)₂(OH)₆] are plumbogummite group minerals including Bi and P. Zäirite was originally described from Eta-Etu (Congo) reported by Wambeke (1975). Since then, a few locations had been reported in the world. Waylandite was first described by von Knorring and Mrose (1963), which was well reviewed by Clark et al. (1986) and Mills et al. (2010). The original zäirite reported by Wambeke (1975) included Al, replacing 22% of the Fe³⁺ site. On the other

hand, zaïrite from Ishidera reported in this paper did not include any Al. This difference in chemical composition caused the difference in unit cell parameter, especially the *a*-axis. The unit cell parameters of waylandite are $a = 6.9834(3) \text{ \AA}$, $c = 16.175(1) \text{ \AA}$ (Clark et al., 1986), which are smaller than those of zaïrite from Ishidera. Waylandite is composed of (001) sheets of corner-shared AlO_6 octahedra and PO_4 tetrahedra, stacked along the *c*-axis, with Bi atoms in icosahedral (12-fold coordinated) sites between the sheets (Mills et al., 2010). In the substitution of Fe^{3+} and Al, the octahedral frame work in the (001) sheet become larger with the increase in Fe^{3+} , which had larger ionic radius than Al, resulting as the elongation of the *a*-axis. Same trend can be seen in unit cell parameters of plumbogummite $[\text{PbAl}_3(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})_6]$ as $a = 7.017(1) \text{ \AA}$ and $c = 16.75(1) \text{ \AA}$ (Slansky, 1977); kintorenite $[\text{PbFe}_3^{3+}(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})_6]$ as $a = 7.2963(5) \text{ \AA}$ and $c = 16.8491(5) \text{ \AA}$ (Grey et al., 2009), and the unit cell parameters (*a*- and *c*-axis length) of kintorenite are larger than those of plumbogummite. In the Bi site, because the ionic radius of Bi is similar to that of Ca, the substitution of Bi and Ca did not cause much change of the unit cell parameters, as you can see from the unit cell parameters of crandallite $[\text{CaAl}_3(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})_6]$ as $a = 7.005(15) \text{ \AA}$ and $c = 16.192(32) \text{ \AA}$ (Blount, 1974), which are very close to that of waylandite.

Plumbogummite group minerals take wide variation of chemical compositions accepting variable elements, which reflects the formation condition during hydrothermal alteration. In Ishidera area, florencite-(Ce) including REE also occurs as a plumbogummite group mineral similar to zaïrite and waylandite. Further study, including a reexamination of zaïrite from a type locality and a crystal structure analysis of zaïrite, is required to reveal their relationships and formation conditions.

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SUPPLEMENTARY MATERIAL

Color version of Figures 1 is available online from <https://doi.org/10.2465/jmps.201130d>.

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