

A Compositional Survey of an Amorphous Aluminum Phosphate from the Ashio Mine, Tochigi Prefecture, Japan

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Abstract Microprobe analyses of a white colloform material in quartz veins traversing chert from the Ashio mine, Tochigi Prefecture, hitherto considered as “fischerite”, gave $(\text{Al} + \text{Fe})/(\text{P} + \text{S} + \text{Si}) = 1.59\text{--}1.72$, thus corresponding to that of bolivarite with $\text{Al}/\text{P} = 2$. It is amorphous to X-ray, non-birefringent and non-fluorescent under ultraviolet light. The present occurrence is an example of concentration of aluminum and phosphorus in association with silica in ore-bearing hydrothermal veins and classed with wavellite and variscite of similar mode of occurrence in Japan.

Introduction

In 1947 ITO and SAKURAI described the occurrence of a pale green vitreous crust on fissure walls in chert forming the wallrocks of the ore deposits of the Ashio mine, Tochigi Prefecture, and considered it to be fischerite or a mixture of fischerite and fluellite from two independent wet chemical analyses. However, fischerite has been discredited in favour of wavellite (FISCHER, 1955), thus reinstatement of the status of above mineral is necessary. Microprobe analyses of a material with the same mode of occurrence from the same locality owned by the third author detected major Al, P, and subordinate S, Si and Fe, giving $(\text{Al} + \text{Fe})/(\text{P} + \text{S} + \text{Si})$ ratio to range 1.59–1.72, which corresponds to 2 in bolivarite (van TASSEL, 1960). The X-ray powder pattern comprises no diffractions like bolivarite. The present material is one of the examples of aluminum and phosphorus mineralization, which is classed with the occurrences of wavellite and variscite in epithermal gold-silver vein deposits of the Kohnomai mine, Hokkaido (ITO, 1975) and of the Kawazu mine, Shizuoka Prefecture (KATO & MATSUBARA, 1981).

Description of the Studied Material

The ore deposits of the Ashio mine consist of hydrothermal veins and massive to disseminated bodies developed in Miocene pyroclastic rocks and Mesozoic sedimentary rocks, respectively (NAKAMURA & MIYAHISA, 1976). They are also famous for the occurrences of such phosphate minerals as apatite, vivianite and ludlamite, the last being uniquely known in Japan. These phosphates are exclusively found in

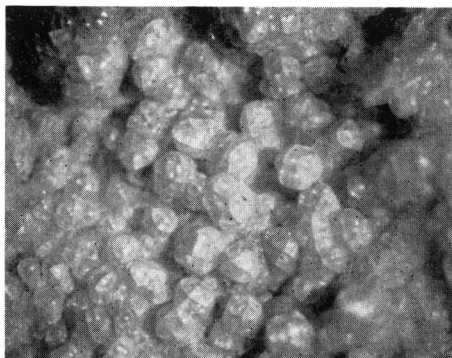


Fig. 1.

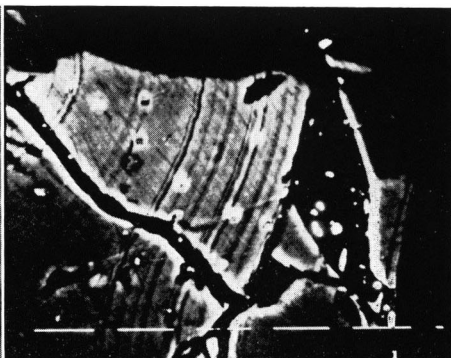


Fig. 3.

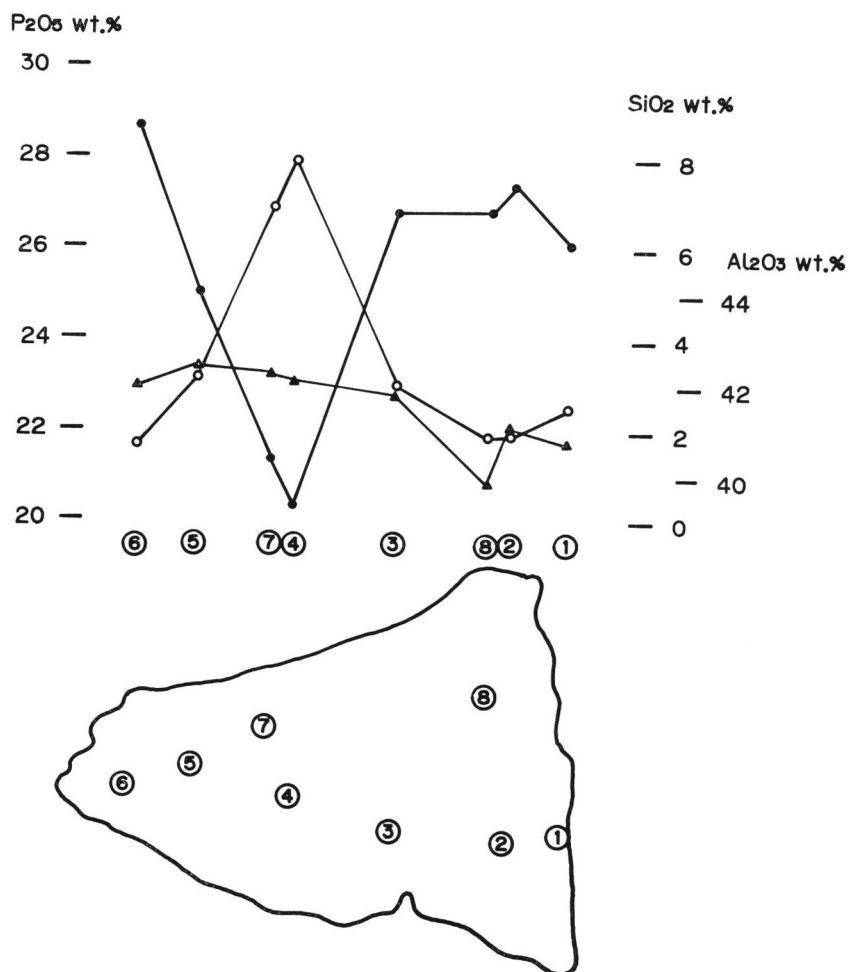


Fig. 2.

massive to disseminated bodies formed in chert after the solution of siliceous material by hydrothermal fluid containing phosphoric acid. Although the exact locality of studied material is unknown, it is evident that it comes from one of the massive or disseminated bodies, since it comprises a fragment of chert.

The fragment is dark grey in appearance and composed of aggregate of fine quartz grains possibly produced by a hydrothermal recrystallization. It is traversed by veinlets of a millimeter order wide including idiomorphic quartz, grains of chalcopyrite and sphalerite and a white semi-transparent crust with a colloform to mammillary surface (Fig. 1). It covers all the other minerals as films and the mammillae are generally fractured to suggest a trace of volume contraction due to the release of a watery component after the formation. The relative quantity of this mineral to quartz is variable in some veinlets, where all the quartz crystals are perfectly covered by it. The crust has a minute banding texture under the binocular, and it is responsible for the compositional variation as stated later.

It is rather soft and cleavable along the fractures as well as banding. The hardness is about $4\frac{1}{2}$ in Moh's scale. Under the microscope, it is colourless and non-birefringent. Mean refractive index measured by the immersion method is 1.510 (2). X-ray powder study provided no diffractions, indicating its amorphous nature. It is non-fluorescent under the short wave ultraviolet light.

Chemical Analysis

Microprobe analyses using the energy dispersive type instrument of Link Co. Ltd. were made on eight spots in the section perpendicular to the banding as given in Table 1, where the chemical analyses referred to by ITO and SAKURAI (1947) and of bolivarite (van TASSEL, 1960) are also compared, since the latter is compositionally most related to the present material in Al/P etc. mole ratio among known amorphous hydrous phosphates of aluminum. The most conspicuous compositional variations are seen in P_2O_5 and SiO_2 contents, which are in reciprocal relation (Fig. 2). In Fig. 3, the correspondence of variation to the banding texture is clearly seen in the back-scattered images. Even after the employment of lower excitation voltage, bombardment pits are formed due to the superficial disintegration coming from the loss of volatile component.

The calculation of ratio of total (Al+Fe) to total anion on respective analysis gives the range 1.59–1.72, which corresponds to that of bolivarite, 2 (van TASSEL, 1960). Such minor components as Na and Zn are ignored for the present time. If

Fig. 1. A colloform to mammillary surface of amorphous aluminum phosphate from the Ashio mine, Tochigi Prefecture, Japan. Field views approx. 5×7 mm.

Fig. 2. The compositional variations in P_2O_5 , SiO_2 and Al_2O_3 contents. The numbers in sketch show bombardment pits in Fig. 3, where the measurements were made. solid circle: P_2O_5 , open circle: SiO_2 , solid triangle: Al_2O_3 .

Fig. 3. Back-scattered image of analysed sample. Bar indicates 100 μ m.

Table 1. Chemical analyses and number of molecules of “fischerite”, “fischerite+fluellite”, bolivarite, and the present mineral.

CHEMICAL ANALYSES												
	a.	a'.	b.	c.	1.	2.	3.	4.	5.	6.	7.	8.
Al ₂ O ₃	34.88	35.35	43.68	36.2	40.74	41.09	41.95	42.10	42.32	41.96	42.26	39.85
Fe ₂ O ₃			0.31				0.49			0.45	0.34	0.37
P ₂ O ₅	24.84	27.31	25.13	24.9	26.09	27.43	26.84	20.36	25.04	28.70	21.37	26.82
SO ₃					3.21	3.37	3.74	3.74	2.95	3.65	3.63	3.42
SiO ₂					2.56	1.99	3.00	7.99	3.18	1.69	6.93	1.89
Na ₂ O					0.41	0.71	0.72	0.70	0.70	0.99	0.86	0.61
CaO					0.18	0.21	0.20	0.19	0.26	0.15	0.16	0.15
ZnO											1.62	0.74
F			8.32									
H ₂ O	31.22	34.33	26.94	39.5								
—O=F ₂			3.59									
total	90.94	99.99	100.99	100.6	73.19	74.80	76.94	75.08	74.45	77.59	76.97	73.85

NUMBER OF MOLECULES (basis: P+S+Si=1)												
	a'.	b.	c.	1.	2.	3.	4.	5.	6.	7.	8.	
Al	1.95	2.43	2.02	1.63	1.60	1.59	1.64	1.72	1.58	1.66	1.59	
Fe		0.01				0.01			0.01	0.01	0.01	
P	1	1	1	0.81	0.83	0.79	0.61	0.79	0.84	0.65	0.83	
S				0.09	0.09	0.09	0.10	0.08	0.09	0.09	0.09	
Si				0.11	0.09	0.12	0.29	0.13	0.07	0.26	0.08	
Na				0.03	0.05	0.05	0.05	0.05	0.06	0.06	0.04	
Ca				0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
Zn										0.04	0.02	

- a. “Fischerite”. Ashio mine, Tochigi Prefecture, Japan. After ITO & SAKURAI (1947).
- a'. Ditto. Recalculated to 100%.
- b. “Fischerite+fluellite”. ditto. After ITO & SAKURAI (1947).
- c. Bolivarite. Pontevedra, Spain. After van TASSEL (1960).
- 1.~8. The present mineral. Ashio mine, Tochigi Prefecture, Japan.

they are added to the cations, above stated range comes closer to 2. The analysis No. 5 has the highest ratio and is closest to 2. Therefore, the present material may be called “a cation depleted bolivarite” or its lower hydrate, unless any additive components playing an important role are overlooked.

Geological Implications

In Japan some hydrothermal veins comprise hydrous aluminum phosphates and they are with or without ore minerals. Wavellite and variscite from the Kohnomai mine, Hokkaido (ITO, 1975) and from the Kawazu mine, Shizuoka Prefecture (KATO & MATSUBARA, 1981) are the examples of ore-bearing veins, where they are the products

of the latest stage of vein formation principally composed of quartz with minor sulphides. The present material is also the product of the latest stage of quartz vein formation produced as a part of massive or disseminated orebody, which is considered to have been formed under the presence of PO_4^{3-} that solved a siliceous wallrock away.

As to the estimation of temperature of formation, variscite dehydrated at 180°C (PALACHE *et al.*, 1951) and about 2/3 of ignition loss of bolivarite is occupied by H_2O heated at 110°C (van TASSEL, 1960). Seeing from the colloform nature of the present mineral, above stated temperatures serve to the setting of temperature range of formation.

In certain Japanese hydrothermal veins, it is now evident that the concentration of aluminum and phosphorus is so prominent in the later stage of formation where the temperature is under approximately 200°C . Under such circumstances wavellite and variscite are formed when the circumstance is rich in phosphorus, whereas such an amorphous material as here described is formed when it is poorer in phosphorus relative to aluminum accompanied by abundant siliceous material. Also, the formation of amorphous material might have been favoured by rather a rapid cooling. On account of less outstanding feature and amorphous nature, it may be overlooked. So, the real occurrence will be more common than considered.

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