Short Communication

A sodian sulphatian fluorapatite from the Kushikino mine, Kagoshima Prefecture, Japan

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Apatite in Japanese hydrothermal ore deposits is rather accessory in quantity. The present fluorapatite is a subordinate member in a quartz-calcite vein worked for

FIG. 1. Location of the Kushikino mine.

Au-Ag ores at the Kushikino mine, Kagoshima Prefecture, and characterized by higher contents of Na₂O and SO₃ through a coupled diadochy of NaS for CaP, proving the formation of a fluorapatite solid solution containing up to about 13.5% of Na₃Ca₂(SO₄)₃F molecule. In order of cross-check of above solid solution, the measurements of refractive index and of difference between prism and basal diffractions are made.

The Kushikino mine is located in the northern part of Kushikino City, Kagoshima Prefecture, Japan (Fig. 1), and the ore deposits consist of several epithermal Au-Ag-bearing quartz-calcite veins in Miocene andesite. The described material comes from the 6th level of Shinpi No. 1 vein, where the total thickness of vein is 2 to 3 meters. Fluorapatite occurs as thin filmy aggregate of 0.1 millimeter thick along black bands (so-called "Ginguro") of less than 10 millimeters thick composed of sphalerite, chalcopyrite, galena and very small amounts of petzite, hessite and altaite with gangue

TABLE 1. Chemical analyses of the most Na₂O and SO₃-poor and -rich fluorapatites from the Kushikino mine. Numbers correspond to those in Fig. 2.

	1.			2.		
	wt. %	Recast to 100%	Atomic number	wt. %	Recast to 100%	Atomic number
CaO	54.30	55.46	4.97	51.70	52.27	4.63
Na ₂ O	0.13	0.13	0.02	2.26	2.29	0.36
MnO	0.03	0.03	0.00	0.05	0.05	0.00
FeO*	0.08	0.08	0.01	0.08	0.08	0.01
MgO	0.00	0.00	0.00	0.01	0.01	0.00
P ₂ O ₅	40.82	41.69	2.95	35.09	35.48	2.48
SO ₃	0.40	0.41	0.03	7.39	7.47	0.46
SiO ₂	0.05	0.05	0.01	0.19	0.19	0.02
F	3.33	3.40	0.90	3.26	3.30	0.86
H ₂ O**	0.18	0.18	0.10	0.25	0.25	0.14
	99.32	101.43		100.28	101.39	
-O = F ₂	-1.40	-1.43		-1.37	-1.39	
Total	97.92	100.00		98.91	100.00	

*Total Fe

**Calculated

Empirical formulae (basis: total cation = 5):

1. (Ca_{4.97}Na_{0.02}Fe_{0.01})Σ_{5.00}(P_{2.95}S_{0.03}Si_{0.01})Σ_{2.99}O_{11.98}(F_{0.90}(OH)_{0.10})Σ_{1.00}
2. (Ca_{4.63}Na_{0.36}Fe_{0.01})Σ_{5.00}(P_{2.48}S_{0.46}Si_{0.02})Σ_{2.96}O_{11.94}(F_{0.86}(OH)_{0.14})Σ_{1.00}

minerals including quartz, muscovite and minor fluorapatite. The black bands recur within the quartz-calcite vein but some of them are very thin to be rather spotty queues of ore mineral grains, which are, however, likewise surrounded by filmy fluorapatite aggregate. The vein consists principally of somewhat turbid white quartz with the black bands and light creamy earthy aggregate of interstratified chlorite/smectite. The aggregate of fluorapatite has a whiter colour and is more turbid than quartz under the binocular. In thin section, fluorapatite aggregate along black bands is composed of idiomorphic to hypidiomorphic grains of 0.0n millimeter order, they being tabular with base and prism only. The black bands include tiny subround discrete grains of fluorapatite and quartz. The fluorapatite becomes richer toward the side facing to fluorapatite aggregate, which is nearly monominerallic in adjacent to the black band, and the aggregate gets gradually sparse due to the quantitative increase of quartz to form its aggregate. It involves patchy pieces of very fine-grained mosaic aggregate of quartz and muscovite fibers, the former being less than 0.01 millimeter across and the latter of 0.0n millimeter order long. Of course, minute

FIG. 2. Correlation diagram of Na and SO₄ contents (basis: total cation = 5) of fluorapatites from the Kushikino mine. Numbers correspond to those in Table 1. Line is drawn to indicate the relation Na:SO₄ = 1:1 in mole ratio.

discrete grains of fluorapatite are dispersed in the aggregate of quartz without any ore minerals.

The fluorapatite is non-fluorescent under short wave ultraviolet light. The refractive index measured by the immersion method on the grains adjacent to the spotty queues of sphalerite grains is $n = 1.620$ (2) with very low birefringence, and the optically examined material was subjected to the X-ray powder diffraction study as stated later.

The microprobe analyses of 14 different points in fluorapatite aggregate along the black bands reveal a reciprocal relation of Na_2O and SO_3 against CaO and P_2O_5 up to 2.26 and 7.39 wt. %, respectively (Table 1), proving the materials to be fluorapatite

TABLE 2. X-ray powder diffraction patterns of synthetic $\text{Ca}_5(\text{PO}_4)_3\text{F}$ and of sodian sulphatian fluorapatite from the Kushikino mine

1.		2.				1.		2.			
I	d(Å)	I	d _{obs}	d _{calc}	hkl	I	d(Å)	I	d _{obs}	d _{calc}	hkl
8	8.12	5	8.11	8.111	10 $\bar{1}$ 0	4	1.862	2	1.864	1.862	32 $\bar{5}$ 0
4	5.25	2	5.25	5.249	10 $\bar{1}$ 1	30	1.837	30	1.837	1.838	21 $\bar{3}$ 3
1	4.684	2	4.70	4.688	11 $\bar{2}$ 0	16	1.797	14	1.799	1.798	32 $\bar{5}$ 1
8	4.055	5	4.06	4.059	20 $\bar{2}$ 0	14	1.771	10	1.772	1.772	41 $\bar{5}$ 0
8	3.872	7	3.88	3.875	11 $\bar{2}$ 1	14	1.748	10	1.749	1.750	30 $\bar{3}$ 3
1	3.494			3.496	20 $\bar{2}$ 1					1.748	4042
40	3.442	70	3.445	3.442	0002	16	1.722	30	1.721	1.721	0004
14	3.167	7	3.173	3.169	10 $\bar{1}$ 2	1	1.684			1.684	10 $\bar{1}$ 4
10	3.067	15	3.070	3.069	21 $\bar{3}$ 0	6	1.637		*	1.638	32 $\bar{5}$ 2
100	2.800	100	2.801	2.803	21 $\bar{3}$ 1	4	1.607	5	1.608	1.607	3143
55	2.772	30	2.776	2.775	11 $\bar{2}$ 2	5	1.580	½	1.580	1.580	50 $\bar{5}$ 1
30	2.624	26	2.626	2.625	20 $\bar{2}$ 2	1	1.562			1.563	33 $\bar{6}$ 0
6	2.517	5	2.521	2.519	30 $\bar{3}$ 1	6	1.534		*	1.534	42 $\bar{6}$ 0
8	2.289		*	2.291	21 $\bar{3}$ 2	4	1.524	3	1.523	1.524	33 $\bar{6}$ 1
20	2.250	10	2.251	2.252	3140	4	1.501	4	1.502	1.501	2134
4	2.218	10	*	2.218	2241	4	1.497	1	1.498	1.498	4161
6	2.140		*	2.140	3141	8	1.468	5	1.468	1.469	5052
4	2.128		*	2.128	3032	4	1.426	4	1.426	1.427	5161
6	2.061	5	2.063	2.061	1123	4	1.422	2	1.422	1.423	3362
2	2.028	1	2.031	2.030	4040	2	1.4015	1	1.402	1.402	4153
4	1.997	2	1.999	1.998	2023	2	1.3418			1.343	5162
25	1.937	17	1.937	1.937	2242	1	1.3336			1.335	4370
14	1.884	8	1.885	1.884	3142	3	1.3095	2	1.310	1.310	4371

1. Synthetic $\text{Ca}_5(\text{PO}_4)_3\text{F}$. JCPDS Card No. 15-876. Cu/Ni radiation. $a = 9.3689$, $c = 6.8841$ Å.

2. Fluorapatite. Kushikino mine, Kagoshima Prefecture. Cu/Ni radiation. Diffractometer method. $a = 9.375(2)$, $c = 6.884(2)$ Å.

*: diffractions masked by those of quartz or sphalerite.

solid solutions containing $\text{Na}_3\text{Ca}_2(\text{PO}_4)_3\text{F}$ molecule up to about 13.5%. This formula corresponds to the fluorine analogue of ideal cesanite (Cavarretta et al., 1981). The possibility of CO_3^{2-} in the examined materials could not be excluded, but the content

FIG. 3. Comparative representation of X-ray powder diffraction peaks of synthetic $\text{Ca}_5(\text{PO}_4)_3\text{F}$ and fluorapatite from the Kushikino mine with the external standard of (1122) of quartz. All the diffraction angles were calculated from their unit cell parameters. No reference to relative intensities is made in the figure.

S: synthetic $\text{Ca}_5(\text{PO}_4)_3\text{F}$. K: fluorapatite from the Kushikino mine. q: quartz. f: fluorapatite. Underlined diffractions form a pair to find the compositional variation as seen in the text.

is considered to be of negligible order, since a near linear relation is seen in the variation of Na and SO_4 contents on analysed grains (Fig. 2).

As to the presence of Na_2O in the minerals of apatite series, dehrnite had been known to contain higher content than the present maximum. However, the Na_2O has now been ascribed to contaminants (Dunn, 1978). While SO_4^{2-} substituting PO_4^{3-} in the minerals of apatite series is known in wilkeite, which contains no essential Na_2O . The present description is thus one of the examples to account for the manner of valency compensation coming from the substitution of Na for Ca.

A small amount of fluorapatite aggregate developed along the spotty queues of ore mineral grains was subjected to the X-ray powder study for measurement of unit cell parameters, which are expected to reflect the compositional deviation from $\text{Ca}_5(\text{PO}_4)_3\text{F}$. Although small amounts of quartz and sphalerite are included, the separated material provided a pattern indexed on a hexagonal cell with $a = 9.375(2)$ and $c = 6.884(2)\text{\AA}$ (Table 2), where a is slightly longer than that of synthetic $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (JCPDS Card No. 15-876), whereas c is equal to that of above compound. The powder pattern difference from the pure $\text{Ca}_5(\text{PO}_4)_3\text{F}$ is very small and may be overlooked unless careful comparison is made. It must be focused to find a pair of prism and basal diffractions, and $(41\bar{5}0) - (0004)$ is the best one, since the difference of d -values or diffraction angles between them can be precisely calibrated after the employment of the diffraction $(11\bar{2}2)$ of quartz (Fig. 3). The lack of unit cell data for $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$ makes it meaningless to figure the variation diagram including those of the present material. The natural cesanite is not a mere OH analogue of above compound but contains excess Na beyond the $\text{Na}:\text{Ca} = 3:2$ through the valency adjustment coming from the substitution of H_2O for OH after the structure analysis of Tazzoli (1983), who designates the ideal formula of cesanite to be $\text{Ca}_{1+x}\text{Na}_{4-x}(\text{SO}_4)_3(\text{OH})_x \cdot (1-x)\text{H}_2\text{O}$.

References

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