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A SODIAN SULFATIAN FLUORAPATITE FROM AN EPITHERMAL CALCITE–QUARTZ VEIN OF THE KUSHIKINO MINE, KAGOSHIMA PREFECTURE, JAPAN

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ABSTRACT

A sodian-sulfatian fluorapatite, a new variety of apatite, was found in sulfide concentrates of gold–silver–tellurium ores from the Shinpi No. 1 epithermal-type calcite–quartz vein of the Kushikino mine, Kagoshima Prefecture, Japan. This paper is the first detailed report on the occurrence of sulfate and sulfatian apatite from this type of ore deposit. The mineral is closely associated with quartz, interstratified chlorite–smectite, and ore minerals. The chemical composition of the mineral was determined by electron microprobe: CaO 51.51–54.30, $\mathrm{Na_2O}$ 0.13–2.26, $\mathrm{K_2O}$ 0.00–0.02, MgO 0.00–0.02, MnO 0.03–0.10, FeO 0.01–0.10, $\mathrm{P_2O_5}$ 35.09–40.82, $\mathrm{SO_3}$ 0.40–7.39, $\mathrm{SiO_2}$ 0.05–0.66, Cl 0.00–0.01, F 3.03–3.62 wt.%. The (Na + Si): S atomic ratio is close to one. The charge increase involved by the substitution of $\mathrm{(SO_4)^{2-}}$ for $\mathrm{(PO_4)^{3-}}$ is considered to be electrostatically compensated for by the concomitant substitutions of $\mathrm{Na^+}$ for $\mathrm{Ca^{2+}}$ and, although minor, of $\mathrm{(SiO_4)^{4-}}$ for $\mathrm{(PO_4)^{3-}}$. The general formula, disregarding trace to minor constituents, is expressed as follows: $\mathrm{Ca_{5-x}Na_x(P_{3-x}S_x)O_{12}\ (F_yOH_{1-y})}$, where x ranges from 0.02 to 0.41, and y, from 0.80 to 0.96. The naturally occurring sulfate and sulfatian apatites should be divided into two series, apatite–ellestadite and apatite–cesanite, on the basis of mode of substitution. These minerals form under high $f(\mathrm{O_2})$, and are rather independent of temperature, pH, $f(\mathrm{S_2})$, and halogen species in solution. The Kushikino apatite, an intermediate member of the second series, seems to have formed from a F-rich oxidizing solution at 200 to 250°C.

Keywords: apatite, new variety, sulfate, sodium, chemistry, oxidizing solution, Kushikino mine, Japan.

SOMMAIRE

On a découvert une nouvelle variété d'apatite, une fluorapatite sodique et sulfatée, dans des concentrés de sulfures des minerais Au–Ag–Te du filon de calcite + quartz Shinpi numéro 1, de type épithermal, à la mine Kushikino, préfecture de Kagoshima, au Japon. C'est la première indication d'une telle apatite dans ce genre de gisement. Elle montre une association étroite avec quartz, chlorite–smectite interstratifiée, et les minéraux du minerai. Sa composition a été déterminée à la microsonde électronique: CaO 51.51–54.30, $\mathrm{Na_2O}$ 0.13–2.26, $\mathrm{K_2O}$ 0.00–0.02, MgO 0.00–0.02, MnO 0.03–0.10, FeO 0.01–0.10, $\mathrm{P_2O_5}$ 35.09–40.82, $\mathrm{SO_3}$ 0.40–7.39, $\mathrm{SiO_2}$ 0.05–0.66, Cl 0.00–0.01, F 3.03–3.62% (en poids). Le rapport atomique (Na + Si): S se rapproche de 1. L'augmentation des charges occasionnée par le remplacement du $\mathrm{(PO_4)^{3-}}$ par le $\mathrm{(SO_4)^{2-}}$ semble compensée par une substitution concomitante de $\mathrm{Na^+}$ pour $\mathrm{Ca^{2+}}$ et, quoique moins importante, de $\mathrm{(SiO_4)^{4-}}$ pour $\mathrm{(PO_4)^{3-}}$. La formule générale, qui omet les composants à l'état de traces, serait $\mathrm{Ca_{5-x}Na_x(P_{3-x}S_x)O_{12}(F_yOH_{1-y})}$, dans laquelle x varie de 0.02 to 0.41, et y varie de 0.80 to 0.96. Nous proposons l'existence de deux séries d'apatite naturelle riche en sulfate, apatite–ellestadite et apatite–cesanite, selon le mode de substitution. Ces deux variétés seraient stables à des conditions de fugacité d'oxygène élevée, et seraient plutôt indépendantes de température, pH, $f(\mathrm{S_2})$ et espèces de halogènes en solution. L'apatite de Kushikino, membre intermédiaire de la deuxième série, se serait formée à partir d'une solution fluorée oxydante entre 200 et 250°C.

(Traduit par la Rédaction)

Mots-clés: apatite, nouvelle variété, sulfate, sodium, chimisme, solution oxydante, mine Kushikino, Japon.

INTRODUCTION

Although the ideal formula of apatite may be represented simply as $\mathrm{Ca_5(PO_4)_3(F,OH)}$, the substitution relations in the structure are highly complex, as have been investigated for near three-quarters of a century by many previous investigators (*e.g.*, Eakle & Rogers 1914, McConnell 1937, 1938, Gulbrandsen 1966, Rouse & Dunn 1982, Tazzoli 1983). Four species of sulfate and sulfatian apatite are known to occur in nature; these are ellestadite, hydroxylellestadite, "wilkeite" (now discredited by the IMA), and cesanite, in whose structures $\mathrm{(SO_4)^{2-}}$ substitutes for $\mathrm{(PO_4)^{3-}}$. Ellestadite, a sulfate silicate apatite (OH > Cl > F in atomic percent), occurs in a contact zone between crystalline limestone and granodiorite in Crestmore, California (McConnell 1937, Rouse & Dunn 1982). Hydroxylellestadite, an OH analogue of ellestadite, was reported from a skarn zone of the Chichibu pyrometasomatic iron ore deposit, Saitama Prefecture, Japan (Harada *et al.* 1971). "Wilkeite", a sulfate- and silicate-bearing fluorapatite, occurs in Crestmore (Eakle & Rogers 1914, McConnell 1937, Rouse & Dunn 1982). "Wilkeite" having Cl > OH > F (in atomic percent) was reported from the Chichibu mine (Harada *et al.* 1971), and "wilkeite" having OH ≫ F + Cl (in atomic percent) occurs in a calcite vein in skarn in crystalline limestone, Hiroshima Prefecture, Japan (Kusachi *et al.* 1982). Cesanite, a sodium sulfate hydroxylapatite, occurs in the Cesano geothermal field, Italy (Cavarreta *et al.* 1981).

During the course of a mineralogical study of gold–silver ores from epithermal-type calcite–quartz veins of the Kushikino mine, Kagoshima Prefecture, Japan, the present authors found sodian-sulfatian fluorapatite, a new variety of apatite (Shiga *et al.* 1985). This is the first detailed report on the occurrence of sulfate and sulfatian apatite from this type of ore deposit. In this paper, the modes of occurrence and chemical compositions of the Kushikino apatite are described, and the nomenclature of the sulfate and sulfatian apatites and the physicochemical conditions of formation of the minerals are discussed.

MODE OF OCCURRENCE AND MINERAL ASSOCIATIONS

The Kushikino gold–silver mining area lies in the northern part of Kushikino city (Fig. 1). Regional exploration for gold and silver deposits has been carried out around the mining area by the Metal Mining Agency of Japan since 1978. The Kushikino gold–silver ore deposits are representative of epithermal-type calcite–quartz veins developed in andesite of Miocene age. K–Ar ages measured on adularia from the veins are 4.0±0.3 Ma (MITI 1979). The ore mineralogy and mineralization of the deposits have been studied by many investigators (*e.g.*, Fukuyama 1954, Mukaiyama & Izawa 1964,

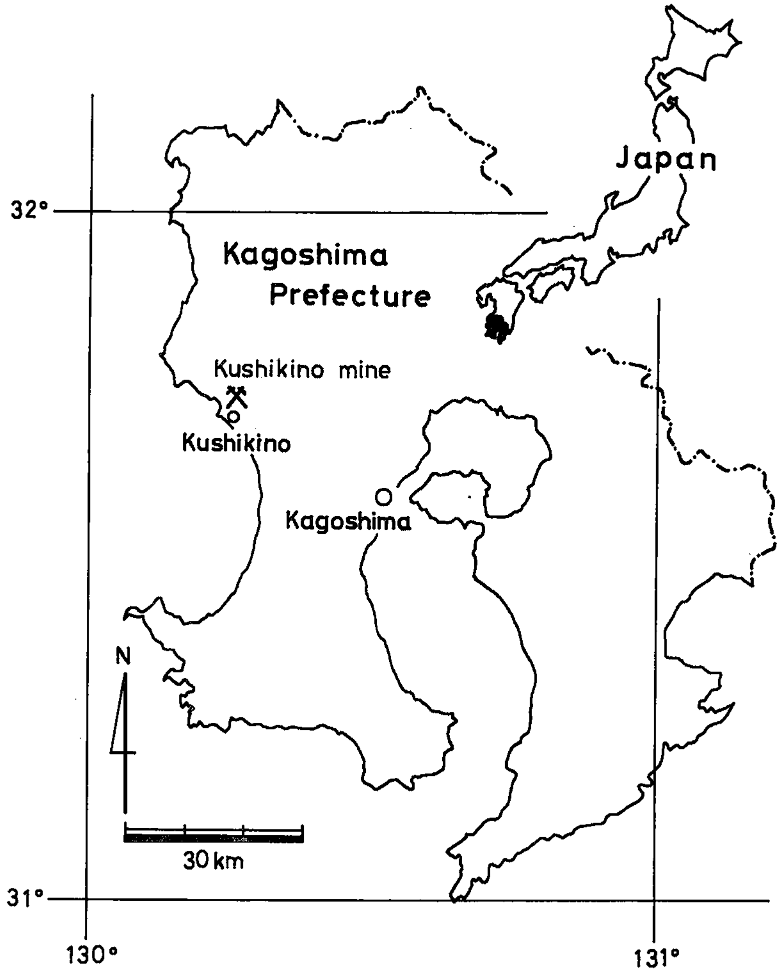

FIG. 1. Map showing location of the Kushikino mine in Kagoshima Prefecture, Japan.

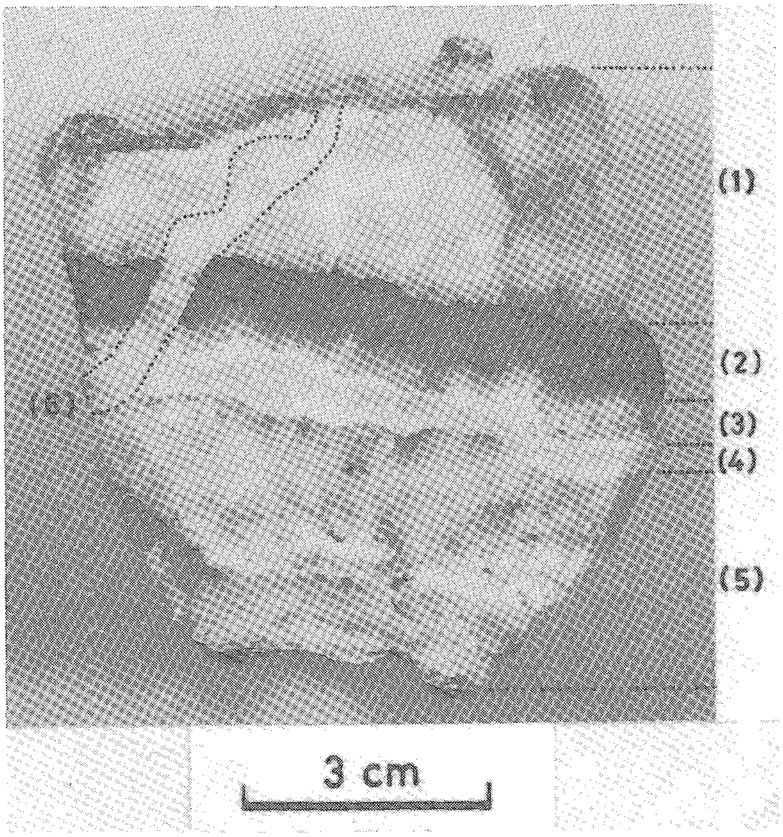

FIG. 2. Photograph of black-band ore from the Shinpi No. 1 vein of the Kushikino mine. Legend: 1 quartz zone with minor adularia partly altered to sericite, 2 ore minerals – apatite – quartz black-band zone, 3 quartz – interstratified chlorite – smectite(white) – ore minerals – apatite zone, 4 quartz(grey) – adularia(white) vein, 5 quartz – interstratified chlorite – smectite(white) – ore minerals – apatite zone, 6 post-ore quartz vein. Specimen Ku15.

Miyahisa *et al.* 1977, Takeuchi 1978, Motomura *et al.* 1981, Izawa & Hashizume 1982, Izawa & Urashima 1983). From these studies, the ores may be divided into two types based upon their mineralogical features: 1) gold–silver–antimony, and 2) gold–silver–tellurium ores. The first occur extensively in the principal veins of the mine and are characterized by the occurrence of polybasite, pearceite, pyrargyrite, stephanite, and other Au–Ag–Sb minerals (Mukaiyama & Izawa 1964, Miyahisa *et al.* 1977, Motomura *et al.* 1981, Izawa & Hashizume 1982), whereas the second occur regionally in smaller veins that contain hessite, altaite, calaverite, petzite, and other Au–Ag–Te minerals (Fukuyama 1954, Takeuchi 1978, Shiga & Urashima 1983).

Apatite occurs in the sulfide concentrates of the gold–silver–tellurium ores only from the 6th level of the Shinpi No. 1 vein, in spite of extensive examination of both types of ores. The vein, with a thickness of 2 or 3 metres, lies on the hanging-wall side of the Kushikino No. 1 champion vein, and is composed mainly of quartz, calcite, adularia and interstratified chlorite–smectite, as determined by X-ray powder-diffraction studies on untreated material. Two kinds of ores, of different texture and mineralogy, occur in the vein. One is a so-called "black band" ore (Fig. 2), in which sphalerite–galena–chalcopyrite intergrowths occur with minor to trace amounts of pyrite, tetrahedrite and tellurium-bearing minerals as black bands and films (less than 1 cm in thickness) running parallel to the boundaries between the vein and wall rock. The other is ore (Fig. 3) in which minerals such as sphalerite, chalcopyrite, clausthalite–galena solid solution, pyrite, and minor to trace amounts of tellurium-bearing minerals and electrum are disseminated in clay-rich parts composed chiefly of quartz and interstratified chlorite–smectite. Apatite occurs abundantly as euhedral to subhedral crystals in close association with both

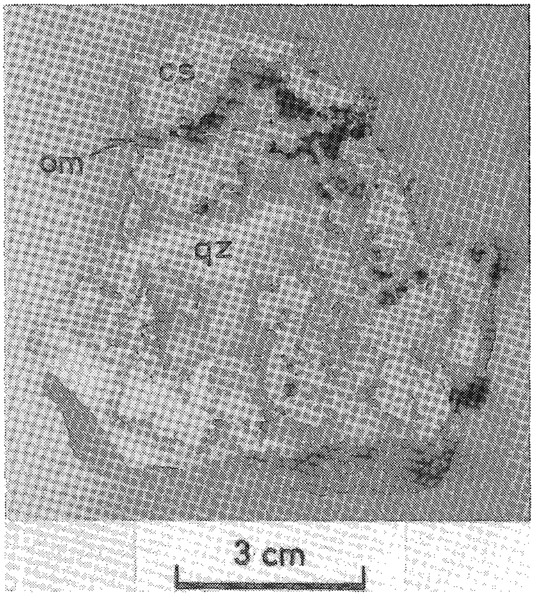

FIG. 3. Photograph of quartz–clay ore from the Shinpi No. 1 vein of the Kushikino mine. Legend: cs interstratified chlorite–smectite, om ore minerals, qz quartz. Specimen Ku04.

kinds of ores (Figs. 4, 5). In the black-band ores, fine- to medium-grained apatite crystals accumulate along the boundary between the quartz (-adularia-sericite) zone and the black-band zone (Fig. 4–1), where the crystals are rarely in contact with adularia and sericite. The crystals are concentrated also within the black-band zone (Fig. 4–2). In other parts of the ores, the mineral often occurs as thin filmy aggregates parallel to the black bands, with or without accompanying ore minerals. On the other hand, in the quartz–clay ores, rather coarse grains of apatite, 200 × 200 × 400 μm, intimately associated with interstratified chlorite–smectite and ore minerals, are dispersed in a quartz matrix (Fig. 5). Homogenization temperatures measured on fluid inclusions in quartz and calcite associated with apatite range from approximately 200 to 250°C (unpubl. data).

Megascopically, aggregates of apatite are whiter in color and more turbid than quartz. In thin section, the apatite grains are short tabular prisms. The index of refraction *n* measured by the immersion method is 1.620(2), and the birefringence is very low. The X-ray powder-diffraction pattern, indexed on a hexagonal cell, gives *a* 9.375(2), *c* 6.884(2) Å (Shiga *et al.* 1985).

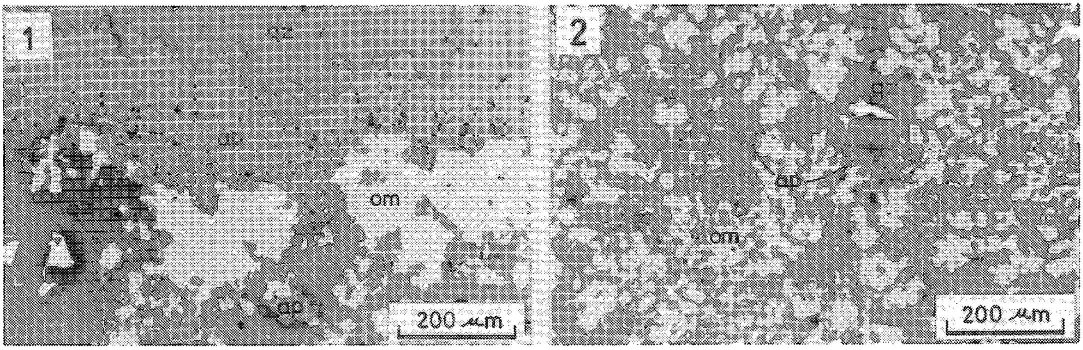

FIG. 4. Photomicrographs of polished surfaces of a black-band ore from the Shinpi No. 1 vein of the Kushikino mine, showing the mode of occurrence of apatite. Legend: 1 upper part of Zone 2 shown in Figure 2, 2 central part of Zone 2 shown in Figure 2, ap apatite, om ore minerals, qz quartz. Uncrossed nicols. Specimen Ku15.

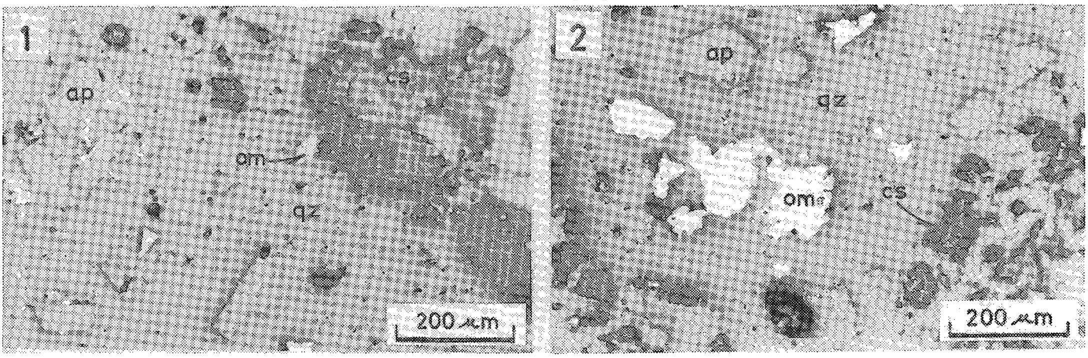

FIG. 5. Photomicrographs of polished surfaces of a quartz–clay ore from the Shinpi No. 1 vein of the Kushikino mine, showing the mode of occurrence of apatite. Legend: ap apatite, om ore minerals, qz quartz, cs interstratified chlorite–smectite. Uncrossed nicols. Specimen Ku01.

CHEMICAL COMPOSITION OF THE APATITE

Chemical analyses of the Kushikino apatite were performed with an ARL–Shimadzu X-ray microanalyzer, model EMX–SM. Line-scan analyses on more than ten single crystals from different modes of occurrence revealed that most of them are markedly heterogeneous in distribution of constituents (Fig. 6), similar to apatite from other localities (*e.g.*, Nedachi & Ueno 1981, Tsusue *et al.* 1981).

Instrumental conditions for microprobe analyses were: 15 kV excitation voltage, 2×10^{-8} A sample current on a natural apatite standard, 5 μm beam diameter, 20 s count times on samples and standards. The following materials were utilized as standards: apatite for Ca, P, F and Cl, anhydrite for S, albite for Na, biotite for Si, Fe, Mg and K, pyrosmalite for Mn. Data were reduced using the Bence & Albee method (1968). The results thus obtained are as follows: CaO 51.51–54.30, Na_2O 0.13–2.26, K_2O 0.00–0.02, MgO 0.00–0.02, MnO 0.03–0.10, FeO 0.01–0.10, P_2O_5 35.09–40.82, SO_3 0.40–7.39, SiO_2 0.05–0.66, Cl 0.00–0.01, F 3.03–3.62 wt.% (Table 1). Structural formulae calculated from the analytical data are presented in Table 2.

In sulfur-bearing apatite, the S, Na and Si contents are of particular importance, as discussed later. The S and Na contents of this apatite show apparent negative correlations with the P and Ca contents, respectively (see the line-scan profiles, Fig. 6). The SiO_2 content, although generally low (less than 0.7 wt.%), does not show any distinct correlation with other constituents. The material is also characterized by a high but variable F-content and by a low Cl-content. No relationship between the F and Cl contents is apparent.

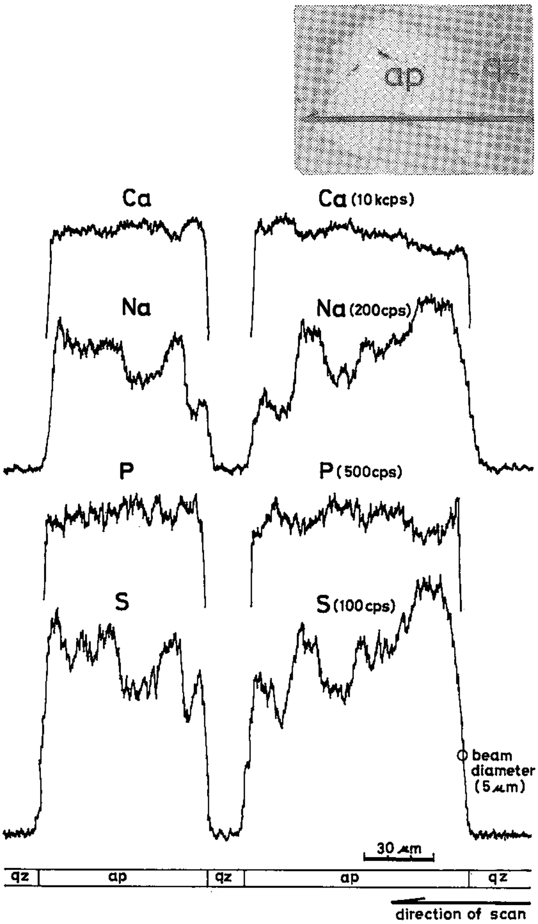

FIG. 6. Line-scan profiles, showing the variation in intensities of characteristic *Kα* X-rays along the line drawn on the photomicrograph. Symbols: ap apatite, qz quartz.

TABLE 1. CHEMICAL COMPOSITION OF APATITE FROM THE SHINPI NO.1 VEIN OF THE KUSHIKINO MINE

	Ku(1)	Ku(2)	Ku(3)	Ku(4)	Ku(5)	Ku(6)	Ku(7)	Ku(8)	Ku(9)	Ku(10)	Ku(11)	Ku(12)	Ku(13)	Ku(14)
CaO	51.91	52.54	52.66	52.05	53.03	54.02	52.40	55.18	51.51	52.79	54.30	51.70	52.72	54.30
Na_2O	1.99	1.51	0.98	2.23	1.61	0.33	2.22	0.15	2.22	1.62	0.33	2.26	2.13	0.13
K_2O	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.00	0.02	0.02	0.00	0.01	0.01	0.00
MnO	0.06	0.03	0.10	0.04	0.10	0.05	0.07	0.03	0.04	0.10	0.05	0.05	0.07	0.03
FeO*	0.05	0.06	0.04	0.01	0.10	0.08	0.08	0.08	0.01	0.10	0.09	0.08	0.08	0.08
P_2O_5	38.39	39.04	40.27	35.42	37.66	40.70	36.64	40.14	35.80	37.19	40.43	35.09	37.17	40.82
SO_3	6.33	5.19	2.89	6.68	5.39	1.03	6.56	0.41	6.36	5.37	1.04	7.39	5.97	0.40
SiO_2	0.13	0.33	0.37	0.16	0.24	0.66	0.09	0.05	0.20	0.23	0.66	0.19	0.14	0.05
Cl	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00
F	3.16	3.05	3.17	3.39	3.22	3.35	3.29	3.62	3.58	3.03	3.11	3.26	3.46	3.33
H_2O**	0.28	0.33	0.25	0.20	0.27	0.17	0.25	0.07	0.09	0.36	0.29	0.25	0.18	0.17
Sum	102.33	102.12	100.74	100.19	101.64	100.40	101.63	99.73	99.83	100.82	100.30	100.28	101.94	99.31
less O=F,Cl	1.33	1.29	1.33	1.43	1.36	1.41	1.39	1.52	1.51	1.28	1.31	1.37	1.46	1.40
Total	101.00	100.83	99.41	98.76	100.28	98.99	100.24	98.21	98.32	99.54	98.99	98.91	100.48	97.91

Determined by electron microprobe (in wt. percent). * Total Fe as FeO. ** Calculated on the basis of Cl+F+OH=1.000 in the structural formula.

TABLE 2. STRUCTURAL FORMULAE OF APATITE OBTAINED FROM THE CHEMICAL COMPOSITIONS GIVEN IN TABLE 1

	Ku(1)	Ku(2)	Ku(3)	Ku(4)	Ku(5)	Ku(6)	Ku(7)	Ku(8)	Ku(9)	Ku(10)	Ku(11)	Ku(12)	Ku(13)	Ku(14)
Ca	4.665	4.744	4.826	4.636	4.725	4.936	4.632	4.968	4.633	4.722	4.937	4.625	4.648	4.969
Na	0.324	0.247	0.163	0.359	0.260	0.054	0.355	0.024	0.360	0.262	0.054	0.365	0.340	0.022
K	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mg	0.003	0.001	0.001	0.001	0.001	0.001	0.002	0.000	0.003	0.002	0.000	0.002	0.001	0.000
Mn	0.004	0.002	0.007	0.003	0.007	0.003	0.005	0.002	0.003	0.007	0.003	0.003	0.005	0.003
Fe	0.004	0.004	0.003	0.001	0.007	0.006	0.006	0.006	0.001	0.007	0.006	0.005	0.006	0.006
	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
P	2.726	2.785	2.916	2.493	2.652	2.938	2.559	2.856	2.545	2.629	2.904	2.480	2.590	2.952
S	0.354	0.292	0.165	0.371	0.299	0.059	0.361	0.023	0.356	0.299	0.059	0.411	0.328	0.023
Si	0.011	0.028	0.031	0.013	0.020	0.056	0.007	0.004	0.017	0.019	0.056	0.016	0.011	0.005
	3.091	3.105	3.112	2.877	2.971	3.053	2.927	2.883	2.918	2.947	3.019	2.907	2.929	2.980
Cl	0.001	0.001	0.000	0.000	0.001	0.000	0.001	0.000	0.001	0.001	0.000	0.000	0.001	0.001
F	0.839	0.812	0.857	0.891	0.847	0.904	0.858	0.962	0.949	0.800	0.834	0.862	0.901	0.900
OH*	0.160	0.187	0.143	0.109	0.152	0.096	0.141	0.038	0.050	0.199	0.166	0.138	0.098	0.099
	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

* Calculated on the basis of Cl+F+OH=1.000.

DISCUSSION

Chemistry of the sulfate and sulfatian apatite

Ellestadite is an end member of the substitution of $(SO_4)^{2-}$ and $(SiO_4)^{4-}$ for $(PO_4)^{3-}$ (McConnell 1937), and hydroxylellestadite is an OH analogue of ellestadite (Harada *et al.* 1971). Cesanite, a sodium sulfate hydroxylapatite, is an end member of the substitution of $(SO_4)^{2-}$ for $(PO_4)^{3-}$, in whose structure the charge increase is made up by the substitution of Na^+ for Ca^{2+} (Cavarretta *et al.* 1981, Tazzoli 1983).

The chemical compositions of the Kushikino apatite (Table 2) indicate that $(SO_4)^{2-}$ substitutes for $(PO_4)^{3-}$ and that electrostatic neutrality is balanced chiefly by the substitution of Na^+ for Ca^{2+}, similar to that for cesanite. The general formula of the material, disregarding trace and minor constituents, is: $Ca_{5-x}Na_x(P_{3-x}S_x)O_{12}(F_yOH_{1-y})$, where x ranges from 0.02 to 0.41, and y ranges from 0.80 to 0.96.

Cavarretta *et al.* (1981) regarded cesanite as "the end member of the apatite–ellestadite series". After that, Tazzoli (1983) also considered this mineral to be "one member of the apatite–ellestadite series". Since the charge increase resulting from the substitution of $(SO_4)^{2-}$ for $(PO_4)^{3-}$ in the sulfate and sulfatian apatites is compensated by two clearly different schemes of substitution, $(SiO_4)^{4-}$ for $(PO_4)^{3-}$ and Na^+ for Ca^{2+}, it seems more appropriate to divide them into two series: 1) apatite–ellestadite $Ca_5P_3O_{12}(F,OH,Cl)$ – $Ca_5S_{1.5}Si_{1.5}O_{12}(F,OH,Cl)$ and 2) apatite – cesanite $Ca_5P_3O_{12}(F,OH,Cl)$ – $Ca_2Na_3S_3O_{12}(F,OH,Cl)$ series, not considering anions. The general formula of the first series is expressed as follows: $Ca_5(P_{1-2x}S_xSi_x)_3O_{12}(F,OH,Cl)$, where x ranges from 0 (apatite) to 0.5 (ellestadite). A similar formula was proposed by Harada *et al.*

TABLE 3. REVIEW OF CHEMICAL COMPOSITION OF NATURAL APATITE (IN WT. PERCENT)

	Locality	Na_2O	SO_3	SiO_2	Cl	F	Reference
1. igneous rock							
shonkinite	Shonkin Sag, Montana	0.15-0.35	0.15-0.30	0.45-0.65	0.12-0.34	2.1-2.7	Nash 1972
syenite	Shonkin Sag, Montana	0.14-0.34	0.15-0.22	0.56-0.81	0.11-0.23	3.1-3.3	Nash 1972
Skaergaard intrusion	Skaergaard, Greenland	0.03-0.12	0.02-0.07	0.29-0.73	0.08-0.85	1.92-3.37	Nash 1976
iron deposit	Avnik, Turkey	0.00-0.21	0.10-0.22	0.13-0.42	0.00-0.10	0.00-4.22	Helvaci 1984
2. carbonatite							
carbonatite	Ontario, Canada	0.18	<0.03	0.15	<0.002	4.0	Gulbrandsen *et al.* 1966
3. metamorphosed rock							
marble	north-central Ceylon	-	-	-	2.31	1.05	Cooray 1970
4. hydrothermal ore deposit and hydrothermally altered rock							
skarned limestone	Crestmore, California	-	20.69	17.31	1.64	0.57	McConnell 1937
	Crestmore, California	-	4.2-21.2	3.8-16.8	0.4-1.7	0.3-2.8	Rouse & Dunn 1982
	Tojyo, Hiroshima Prefecture, Japan	0.20-0.35	16.58-17.21	13.16-14.18	0.08*	<0.1*	Kusachi *et al.* 1982
pyrometasomatic ore deposit	Uzunosawa, Chichibu mine, Japan	0.11	trace	0.64	2.38	1.08	Harada *et al.* 1971
	Takiue, Chichibu mine, Japan	0.06	13.47	11.99	1.44	0.43	Harada *et al.* 1971
	Doshinkubo, Chichibu mine, Japan	0.34	21.56	17.30	0.91	0.28	Harada *et al.* 1971
explosive breccia	Cesano geothermal field, Italy	23.3	52.6	0.0	0.44	0.25	Cavarretta *et al.* 1981
epithermal vein	Kushikino mine, Japan	0.13-2.26	0.40-7.39	0.05-0.66	0.00-0.01	3.03-3.62	Present study
5. sedimentary rock							
phosphorite	Montana, Idaho *etc.*	0.2-1.2	0.3-3.1	-	-	3.8-4.2	Gulbrandsen 1966
phosphate rock	various localities	0.13-1.65	0.17-0.84	-	-	3.10-4.93	McClellan & Lehr 1969

- No data. * Analyst:M. Nedachi.

(1971) and Rouse & Dunn (1982). The chemical compositions of this series reported so far (Table 3) suggest the possibility of a continuous solid solution. On the other hand, the general formula of the second series is represented as follows: $Ca_{5-3x}Na_{3x}(P_{1-x}S_x)_3O_{12}(F,OH,Cl)$, where x ranges from 0 (apatite) to 1 (cesanite). It is not yet evident whether this series is completely continuous. However, the Kushikino material proves the existence of a solid solution containing nearly 14% of the $Ca_2Na_3S_3O_{12}(F,OH,Cl)$ end member (Table 2). Apatite with small amounts of S and Na reported by Brauns (1917) and Vasil'eva *et al.* (1958) are not referred to here because of the lack of complete analytical data.

The Na:S atomic ratio in members of the second series should be equal to unity. However, this ratio in the Kushikino material is somewhat less than one in most cases (Table 2). Values of the (Na + Si):S atomic ratio are close to one, especially in the Na and S-rich samples. This finding indicates the existence of substitution of $(SiO_4)^{4-}$ for a part of $(PO_4)^{3-}$ in the material and suggests a certain extent of overlap of the two series.

Physicochemical conditions of formation of the sulfate and sulfatian apatites

The sulfate and sulfatian apatites have been investigated so far with special attention to the chemistry and crystal structure; their contribution to an understanding of ore formation and petrogenesis has been rather limited. In order to deduce aspects of the physicochemical conditions of formation of those minerals, the literature on chemical composition of natural apatite was extensively reviewed (Table 3). Apatite commonly occurs as an accessory mineral in various rocks and ore deposits. In igneous rocks, carbonatite, and sedimentary rocks, the mineral is generally poor in SO_3. The sulfate and sulfatian apatites tend to occur in hydrothermal ore deposits and hydrothermally altered rocks, although apatite in such ore deposits and rocks is not always rich in SO_3, like apatite from the Uzunosawa ore deposit of the Chichibu mine, Japan.

Based on the equilibria in sulfur-containing aqueous solutions (*e.g.*, Figs. 6–8 of Barnes & Kullerud 1961), $(HSO_4)^-$- or $(SO_4)^{2-}$-predominant solutions, from which the sulfate and sulfatian apatites are considered to precipitate, are stable under high $f(O_2)$ and wide ranges of temperature, pH, and $f(S_2)$. The $f(O_2)$, therefore, appears to be a more important factor for controlling the formation of those minerals than the others. This study supports the previous suggestion that epithermal-type gold–silver quartz veins, including the Kushikino ore deposits, may form under oxidizing condition (*e.g.*, Shikazono 1978, Izawa & Urashima 1983, Izawa 1984).

Apatite is also of interest in that it generally contains elevated amounts of the halogens fluorine and chlorine, believed in many cases to be carriers of ore-forming metals. The F, Cl and OH contents of natural apatite are distinctly variable (Table 3). The partitioning of halogens between apatite and solution is said to be controlled by temperature, pressure and pH (*e.g.*, Stormer & Carmichael 1971, Latil & Maury 1977, Argiolas & Baumer 1978). Latil & Maury (1977) noted, based on their studies under hydrothermal conditions, that F^- displaces Cl^- and OH^- in the apatite structure and that Cl^- has no influence on proportion of F^- and OH^-. From the point of view of crystal chemistry, it is difficult for Cl^- to enter the apatite structure, especially at low temperature, because of its large ionic radius (1.81 Å) relative to that of F^- and OH^- (1.33 and 1.36 Å, respectively). The following relations on halogens between apatite and hydrothermal solution may be pointed out: 1) fluorapatite indicates a F-rich solution, but it is not evident whether the solution is rich or not in Cl (*e.g.*, Kushikino apatite); 2) chlorine-rich apatite indicates a Cl-dominant, F-poor solution (*e.g.*, some of the Crestmore and Chichibu apatite), and 3) hydroxylapatite probably indicates a F-poor solution, but it is not evident whether the solution is rich or not in Cl (*e.g.*, Tojyo apatite).

CONCLUSIONS

The Kushikino sodian-sulfatian fluorapatite is an intermediate member of the apatite–cesanite (strictly speaking, fluorapatite–"fluorcesanite") series. The mineral is considered to have formed at 200 to 250°C from a F-rich oxidizing solution.

The variety of chemical compositions of natural apatite indicates a flexibility in composition according to and dependent on the geochemistry and physical chemistry of the solution from which the mineral formed. Thus apatite is expected to provide useful information on the environment of formation of the mineral and of ores and rocks containing it. The sulfate and sulfatian apatites appear to form under high $f(O_2)$, rather independent of temperature, pH, $f(S_2)$, and halogen species in solution. These minerals therefore are unlikely to occur in ore deposits and rocks that form under reducing condition (*e.g.*, pyrrhotite-containing ore). Apatite in such ore deposits and rocks is probably deficient in SO_3.

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REFERENCES

ARGIOLAS, R. & BAUMER, A. (1978): Synthèse de chlorapatite par voie hydrothermale: étude de l'influence de la sursaturation sur l'évolution des faciès des cristaux. *Can. Mineral.* **16**, 285-290.

BARNES, H.L. & KULLERUD, G. (1961): Equilibria in sulfur-containing aqueous solutions, in the system Fe-S-O, and their correlation during ore deposition. *Econ. Geol.* **56**, 648-688.

BENCE, A.E. & ALBEE, A.L. (1968): Empirical correction factors for the electron microanalysis of silicates and oxides. *J. Geol.* **76**, 382-403.

BRAUNS, R. (1917): Über den Apatit aus dem Laacher Seegebiet. Sulfatapatit und Carbonatapatit. *Neues Jahrb. Mineral. Geol., Beil. B.* **41**, 60-92.

CAVARRETTA, G., MOTTANA, A. & TECCE, F. (1981): Cesanite, $Ca_2Na_3[(OH)(SO_4)_3]$, a sulphate isotypic to apatite, from the Cesano geothermal field (Latium, Italy). *Mineral. Mag.* **44**, 269-273.

COORAY, P.G. (1970): A carbonate-bearing fluor-chlor-hydroxyapatite from Matale, Ceylon. *Amer. Mineral.* **55**, 2038-2041.

EAKLE, A.S. & ROGERS, A.F. (1914): Wilkeite, a new mineral of the apatite group, and okenite, its alteration product, from southern California. *Amer. J. Sci.* **187**, 262-267.

FUKUYAMA, K. (1954): Geology and ore deposits of the Arakawa mine, Kagoshima Prefecture, Japan. *J. Sci., Kumamoto Univ., Ser.* **B.** 19-89.

GULBRANDSEN, R.A. (1966): Chemical composition of phosphorites of the Phosphoria Formation. *Geochim. Cosmochim. Acta* **30**, 769-778.

______, KRAMER, J.R., BEATTY, L.B. & MAYS, R.E. (1966): Carbonate-bearing apatite from Faraday Township, Ontario, Canada. *Amer. Mineral.* **51**, 819- 824.

HARADA, K., NAGASHIMA, K., NAKAO, K. & KATO, A. (1971): Hydroxylellestadite, a new apatite from Chichibu mine, Saitama Prefecture, Japan. *Amer. Mineral.* **56**, 1507-1518.

HELVACI, C. (1984): Apatite-rich iron deposits of the Avnik (Bingöl) region, southeastern Turkey. *Econ. Geol.* **79**, 354-371.

IZAWA, E. (1984): Gold-silver mineralization in southern Kyushu, and the related igneous activities and geothermal system. *Mining Geol.* **34**, 66-67 (abstr.). (In Japanese).

______ & HASHIZUME, M. (1982): Mineralogy of the gold-silver quartz veins of the Kushikino mine, Kagoshima Prefecture, Japan. *Mining Geol.* **32**, 170 (abstr.). (In Japanese).

______ & URASHIMA, Y. (1983): Gold-silver deposits in southern Kyushu, Japan. *Proc. Mining Metall. Inst. Japan/Australaisian Inst. Mining Metall. Symp.*, 97-111.

KUSACHI, I., HENMI, C. & HENMI, K. (1982): Occurrence of wilkeite from skarnized crystalline limestone in Tojyo, Hiroshima Prefecture, Japan. *Coll. Abstr. Autumn Joint Meet. Mineral. Soc. Japan, Soc. Mining Geol. Japan, Japan. Assoc. Mineral. Petrology Econ. Geol.,* **C-49**, 153 (abstr.). (In Japanese).

LATIL, C. & MAURY, R. (1977): Contribution à l'étude des échanges d'ions OH^-, Cl^- et F^- et de leur fixation dans les apatites hydrothermales. *Soc. franç. Minéral. Crist. Bull.* **100**, 246-250.

MCCLELLAN, G.H. & LEHR, J.R. (1969): Crystal chemical investigation of natural apatites. *Amer. Mineral.* **54**, 1374-1391.

MCCONNELL, D. (1937): The substitution of SiO_4- and SO_4-groups for PO_4-groups in the apatite structure; ellestadite, the end-member. *Amer. Mineral.* **22**, 977-986.

______ (1938): A structural investigation of the isomorphism of the apatite group. *Amer. Mineral.* **23**, 1-19.

MITI (1979): Report on the regional exploration researches of the Hokusatsu-Kushikino region (1978). *Ministry of International Trade and Industry*, 1-92. (In Japanese).

MIYAHISA, M., KATO, A., MATSUTOYA, S. & MOTOMURA, Y. (1977): Pyrostilpnite from the east silver – black ore body of No. 1 Vein, Kushikino Mine, Kagoshima Prefecture, Japan. *J. Mineral. Soc. Japan* **13**, 209-219. (In Japanese).

MOTOMURA, Y., YAMAMOTO, S., WAKABAYASHI, K. & HIROWATARI, F. (1981): Gold-silver ores from the Arakawa No. 3 vein of Kushikino mine, Kagoshima Prefecture. *Mining Geol., Spec. Issue* **10**, 15-23. (In Japanese, with Engl. abstr.).

MUKAIYAMA, H. & IZAWA, E. (1964): The gold-silver ores from the Kushikino mine, Kagoshima Prefecture, Japan, with special reference to the occurrence of naumannite. *Mining Geol.* **14**, 191-199. (In Japanese, with Engl. abstr.).

NASH, W.P. (1972): Apatite chemistry and phosphorus fugacity in a differentiated igneous intrusion. *Amer. Mineral.* **57**, 877-886.

______ (1976): Fluorine, chlorine, and OH-bearing minerals in the Skaergaard intrusion. *Amer. J. Sci.* **276**, 546-556.

NEDACHI, M. & UENO, H. (1981): Chlorine and fluorine in apatites from the Orikabe granitic rocks, Kitakami Mountains, Japan. *Mining Geol., Spec. Issue* **10**, 219-225. (In Japanese, with Engl. abstr.).

ROUSE, R.C. & DUNN, P.J. (1982): A contribution to the crystal chemistry of ellestadite and the silicate sulfate apatites. *Amer. Mineral.* **67**, 90-96.

SHIGA, Y. & URASHIMA, Y. (1983): Au-Ag-Pb-Te mineralization in the Kushikino ore deposits. *Coll. Abstr. Autumn Joint Meet. Mineral. Soc. Japan, Soc. Mining Geol. Japan, Japan. Assoc. Mineral. Petrology Econ. Geol.* **C-25**, 123 (abstr.). (In Japanese).

______, ______ & KATO, A. (1985): A sodian sulphatian fluorapatite from the Kushikino mine, Kagoshima Prefecture, Japan. *Mineral. J.* **12**, 269-274.

SHIKAZONO, N. (1978): Selenium content of acanthite and the chemical environments of Japanese vein-type deposits. *Econ. Geol.* **73**, 524-533.

STORMER, J.C. & CARMICHAEL, I.S.E. (1971): Fluorine-hydroxyl exchange in apatite and biotite: a potential igneous geothermometer. *Contr. Mineral. Petrology* **31**, 121-131.

TAKEUCHI, K. (1978): On Ag-Te minerals from the Arakawa No. 5 vein of the Kushikino mine, Kagoshima Prefecture, Japan. *Mining Geol.* **28**, 42-43 (abstr.). (In Japanese).

TAZZOLI, V. (1983): The crystal structure of cesanite, $Ca_{1+x}Na_{4-x}(SO_4)_3(OH)_x \cdot (1-x)H_2O$, a sulphate isotypic to apatite. *Mineral. Mag.* **47**, 59-63.

TSUSUE, A., NEDACHI, M. & MIZUTA, T. (1981): On the granitic rocks of the Tsumo mining district, especially on the halogen contents of rock-forming minerals. *Mining Geol., Spec. Issue* **9**, 15-22. (In Japanese, with Engl. abstr.).

VASIL'EVA, Z.V., LITSAREV, M.A. & ORGANOVA, N.I. (1958): Natural sulfate-apatite. *Dokl. Akad. Sci. SSSR* **118**, 577-580. (In Russ.).

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