

A CO₃-bearing member of the hydroxylapatite–hydroxyllellstadite series from Tadano, Fukushima Prefecture, Japan: CO₃-SO₄ substitution in the apatite–ellestadite series

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ABSTRACT

A CO₃-bearing member of the hydroxylapatite–hydroxyllellstadite series occurs as a Si-rich part of a hydroxylapatite–hydroxyllellstadite series mineral (hydroxylapatite_{ss}) in a skarn xenolith from Tadano, Fukushima Prefecture, Japan. Hydroxylapatite_{ss} is composed of Si-poor and Si-rich parts. The Si-poor part is F-rich hydroxylapatite. The infrared spectrum of the Si-rich part demonstrates the presence of B-type CO₃. A representative analysis of the Si-rich part yielded the empirical formula Ca_{4.989}[(PO₄)_{1.315}(SiO₄)_{0.848}(SO₄)_{0.368}(CO_{2.943})_{0.480}]_{Σ3.011}(OH_{0.629}Cl_{0.264}F_{0.107})_{Σ1.000} on the basis of 8 cations, assuming Si = S + C. There is a very strong inverse correlation between Si and P in both the Si-poor and Si-rich parts. These data indicate that the substitution mechanism (SO₄,CO₃)²⁻ + (SiO₄)⁴⁻ = 2(PO₄)³⁻ probably occurs in hydroxylapatite_{ss}. Therefore, it was concluded that the Si-rich part corresponds to a CO₃-bearing hydroxylapatite–hydroxyllellstadite series mineral with CO₃ partially replacing SO₄. Most of the Si-rich part shows CO₃ > SO₄ and its composition approaches Ca₅(SiO₄)_{1.5}(CO₃,SO₄)_{1.5}(OH,Cl,F).

KEYWORDS: hydroxylapatite, hydroxyllellstadite, skarn, CO₃-SO₄ substitution, vibrational spectra, Tadano, Japan.

Introduction

HYDROXYLAPATITE, fluorapatite and chlorapatite (hereafter simply written as apatite, the root name) are common accessory minerals in rocks of almost all types and the apatite structure allows various chemical substitutions. Carbonate-bearing apatite, known as ‘carbonate-apatite’, is well recognized as the major constituent of phosphorite and is the main component of bone and dental enamel (Pan and Fleet, 2002). The CO₃²⁻ ions in

carbonate-bearing apatite are classified into an A-type with CO₃²⁻ ions in the *c* axis anion channels, and a B-type with CO₃²⁻ ions substituting for tetrahedral PO₄³⁻ groups (Elliott, 1994). Although there are many studies on carbonate-bearing apatite from synthetic, biological and geological samples (Elliott, 1994; Chang *et al.*, 1996; Fleet, 2014), CO₃-, Si-, and S-bearing apatite is rarely described. CO₃-, Si-, and S-bearing apatite occurs as an accessory mineral in carbonatites and characteristically contains small amounts of rare-earth elements (*REE*) and Na (Sommerauer and Katz-Lehnert, 1985; Liu and Comodi, 1993; Comodi and Liu, 2000). Sommerauer and Katz-Lehnert (1985) and Liu and Comodi (1993) reported the

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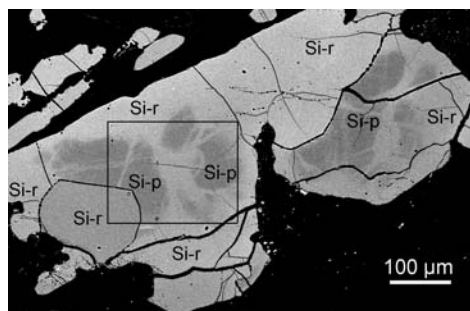


FIG. 1. Backscattered-electron image of hydroxylapatite_{ss}. Si-p = Si-poor part, Si-r = Si-rich part. The rectangle indicates the location of elemental X-ray mapping images shown in Fig. 4.

substitutions $\text{CO}_3^{2-} + \text{SiO}_4^{4-} = 2\text{PO}_4^{3-}$ and $(\text{SO}_4, \text{CO}_3)^{2-} + \text{SiO}_4^{4-} = 2\text{PO}_4^{3-}$, respectively, indicating the presence of B-type CO_3 in Si- and S-bearing apatite. Until recently, there have been no reports of A-type CO_3 in natural mineral apatites; however, the presence of both A-type and B-type CO_3 in Si- and S-bearing apatite from carbonatites was confirmed by Comodi and Liu (2000). Therefore, CO_3 substitution in Si- and S-bearing apatite remains controversial.

Hydroxyllellastadite and fluorellastadite (hereafter, ellestadite) commonly contains small amounts of carbon, up to 2.18 wt.% as CO_3 (McConnell, 1937; Harada *et al.*, 1971; Chesnokov *et al.*, 1987). In the empirical formulae reported by McConnell (1937) and Harada *et al.* (1971), carbon was allotted not only to the tetrahedral site but also to the calcium site. Rouse and Dunn (1982) pointed out that the assignment of C^{4+} to the calcium site is chemically unrealistic. Because ellestadite contains minor CO_3 , its substitution in the mineral has not been discussed adequately.

We found a CO_3 -bearing member of the hydroxylapatite–hydroxyllellastadite series in a skarn xenolith from Tadano, Japan. It contains no detectable amounts of REE or Na, so the effect of coupled substitution involving these elements can be ignored. The mineral from Tadano is therefore one of the most suitable samples for characterizing CO_3 substitution in Si- and S-bearing apatite and ellestadite. We present mineral data for the CO_3 -bearing member of the hydroxylapatite–hydroxyllellastadite series, including vibrational spectra, and discuss CO_3 substitution in the mineral. The specimen studied is stored at the Geological Museum, Geological Survey of Japan, AIST, Tsukuba, registration number GSJ M42086.

Occurrence

The CO_3 -bearing mineral was found in a specimen of skarn xenolith within Tertiary andesite in a quarry in Tadano, Fukushima Prefecture, Japan ($37^\circ 23' 38''\text{N}$ $140^\circ 15' 21''\text{E}$). The skarn xenolith consists mainly of wollastonite, grossular, andradite, gehlenite, vesuvianite and a member of the hydroxylapatite–hydroxyllellastadite solid-solution series (hereafter, hydroxylapatite_{ss}). Hydroxylapatite_{ss} occurs as subhedral to anhedral crystals, up to 700 μm long. Backscattered-electron images indicate that hydroxylapatite_{ss} is composed of parts that are Si-poor (hydroxylapatite) and Si-rich (the CO_3 -bearing member of the hydroxylapatite–hydroxyllellastadite series), respectively (Fig. 1). The Si-poor core is surrounded by a Si-rich rim. An additional Si-rich part cuts the Si-poor host to form veins. This texture indicates that the Si-poor parts formed earlier than the Si-rich parts. It also suggests that the Si-rich parts may have formed by metasomatic alteration of an originally Si-poor fraction.

Wollastonite occurs as prismatic crystals up to 1.6 mm long. Gehlenite occurs as subhedral to anhedral crystals up to 2.6 mm long and is partly replaced by unidentified, fine-grained minerals. Vesuvianite inclusions have been observed in wollastonite. Grossular is colourless, forming aggregates of anhedral crystals up to 0.2 mm across. Andradite is yellowish green or brown (the Ti-bearing variety, 'melanite') and occurs as discrete anhedral crystals up to 0.1 mm in size.

Raman spectroscopy

Micro-Raman spectra of hydroxylapatite_{ss} were collected using a JASCO NRS-5100 spectrophotometer with a 532 nm laser, collecting 2 scans over a range of $3775\text{--}56\text{ cm}^{-1}$ with a resolution of 7 cm^{-1} . The output power of the laser beam was 11.8 mW and the diameter of the focal spot on the sample was $\sim 1\text{ }\mu\text{m}$. Single crystals in polished thin sections were selected for measurements. The spectra of hydroxylapatite_{ss} cut nearly perpendicular to the *c* axis are shown in Fig. 2*b*. We assigned the Raman spectra on the basis of data from Elliott (1994), Comodi *et al.* (1999), and Comodi and Liu (2000) (see Fig. 2). The spectrum of the Si-rich part shows bands at 1076, 1010, and 864 cm^{-1} attributed to the $\nu_1\text{ CO}_3$, $\nu_1\text{ SO}_4$ and $\nu_1\text{ SiO}_4$ modes, respectively. Penel *et al.* (1998) pointed out that types A and B ν_1 carbonate bands were detected

separately, at 1103 and 1071 cm⁻¹, respectively. In our data, the presence of a band at 1076 cm⁻¹ and the absence of a band at ~1103 cm⁻¹ indicate that the Si-rich part contains B-type carbonate. Nelson and Williamson (1982) reported that very weak ν_3 CO₃ bands (1495, 1465 and 1410 cm⁻¹) in a carbonated apatite spectrum were observed only when the slits were opened to give a slit width of ~5 cm⁻¹. The ν_3 CO₃ bands in the Si-rich part spectrum could not be detected because of their weakness (Fig. 2b). Penel *et al.* (1998) also reported no detectable ν_3 CO₃ bands in Raman spectra of carbonate-bearing apatite. A broad band at ~1507 cm⁻¹ in the Si-rich part of the spectrum (Fig. 2b) is due to photoluminescence, because it was not observed using a source excitation of 633 nm. Although obvious bands in the range 3600–3500 cm⁻¹ were not measured from the crystal, bands at ~3550 cm⁻¹

in the spectra of both Si-poor and Si-rich parts were observed from the prismatic crystal that was set with the *c* axis nearly parallel to the polarization direction of the incident laser (Fig. 2a). Bands at ~3550 cm⁻¹ can be attributed to OH stretching vibrations.

Infrared (IR) spectroscopy

Micro-IR spectra of hydroxylapatite *s.s.* (Fig. 3) were recorded using a JASCO FT/IR-6700 with IRT-7200, employing a reflection method that collected 64 scans over the range of 4500–650 cm⁻¹ with 8 cm⁻¹ resolution. Aperture-size was 12 $\mu\text{m} \times 12 \mu\text{m}$. The spectra from a single crystal, cut nearly perpendicular to the *c* axis, in polished thin section are shown in Fig. 3. The spectra are assigned by referring to the data of

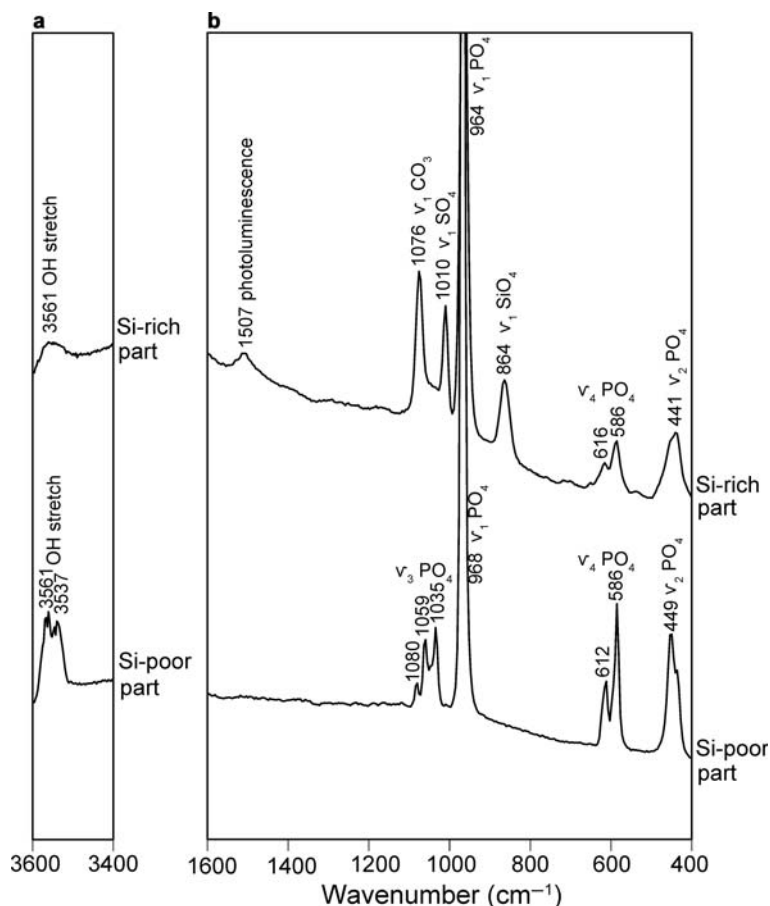


FIG. 2. Raman spectra of Si-poor and Si-rich parts of hydroxylapatite_{ss} crystals.

Baumer *et al.* (1990), Liu and Comodi (1993), Regnier *et al.* (1994), Santos and Clayton (1995), Comodi *et al.* (1999) and Comodi and Liu (2000) (see Fig. 3). The IR spectrum of the Si-rich part of the crystal exhibits the ν_3 mode of the carbonate group at 1454 and 1417 cm^{-1} . The A- and B-type carbonates have characteristic IR absorption features of the ν_3 mode; the former has doublet bands in the range 1549–1450 cm^{-1} , whereas the latter has doublet bands in the range 1465–1412 cm^{-1} (Elliott, 1994; Santos and Clayton, 1995; Fleet *et al.* 2004). Doublet bands at 1454 and 1417 cm^{-1} observed in our data demonstrate that the Si-rich

part of the crystal contains B-type carbonate, in agreement with Raman spectroscopy.

Mineral chemistry

Chemical analyses were performed using a JEOL JXA-8800R electron microprobe. Accelerating voltage and specimen current were kept at 15 kV and 12 nA on the Faraday cup, respectively. A beam diameter of 5 μm was used for analyses of hydroxylapatite_{ss}, and 2 μm for silicate minerals. Synthetic wollastonite (for Ca), celestine (S), KTiOPO_4 (P), F-phlogopite (F), natural kyanite (Si), and Cl-rich hastingsite (Cl) were used as standards for hydroxylapatite_{ss}. Synthetic quartz (for Si), rutile (Ti), corundum (Al), Cr_2O_3 (Cr), MnO (Mn), hematite (Fe), periclase (Mg), wollastonite (Ca), natural albite (Na), and adularia (K) were used as standards for silicate minerals. ZAF and Bence and Albee (1968) methods were used for matrix corrections for hydroxylapatite_{ss} and silicate minerals, respectively. Detection limits for Cl and F were ~ 0.02 and 0.11 wt.% (3 σ level), respectively.

Hydroxylapatite_{ss}

According to the most recent nomenclature for the apatite supergroup minerals (Pasero *et al.*, 2010), we use a generic chemical formula $M_5(\text{TO}_4)_3X$ ($Z=2$) in this study. The Si-poor part of hydroxylapatite_{ss} is F-rich hydroxylapatite that contains small amounts of SiO_2 (≤ 1.59 wt.%) and SO_3 (≤ 1.18 wt.%). Its average composition is SiO_2 0.29, CaO 55.93, SO_3 0.17, P_2O_5 41.48, F 1.53, Cl 0.34, $\text{H}_2\text{O}(\text{calc.})$ 0.98, $\text{O} = \text{F} + \text{Cl} - 0.72$, total 100.00 wt.%, corresponding to $\text{Ca}_{5.022}(\text{P}_{2.943}\text{Si}_{0.024}\text{S}_{0.011})\Sigma 2.978\text{O}_{11.960}(\text{OH}_{0.546}\text{F}_{0.406}\text{Cl}_{0.048})\Sigma 1.000$ on the basis of 8 cations, assuming $\text{OH} + \text{F} + \text{Cl} = 1$ atom per formula unit (apfu), with OH derived by calculation from this constraint.

Qualitative analyses by microprobe confirmed that O, F, Si, P, S, Cl, and Ca were present in the Si-rich part of hydroxylapatite_{ss}. The presence of B-type CO_3 , which occupies the tetrahedral anion site, in the Si-rich part was confirmed by Raman spectroscopy and IR spectroscopy. An average composition of the Si-rich part is SiO_2 7.24, CaO 55.87, SO_3 4.00, P_2O_5 25.54, F 0.79, Cl 1.14, $\text{O} = \text{F} + \text{Cl} - 0.59$, total 93.99 wt.%. The low analytical total is due mostly to the fact that CO_2 and H_2O contents were not determined. The Si-rich part has a wide range of compositions, with $\text{SiO}_2 = 3.65$ –11.12, $\text{SO}_3 = 1.44$ –7.32, and $\text{P}_2\text{O}_5 = 15.89$ –33.94 wt.%.

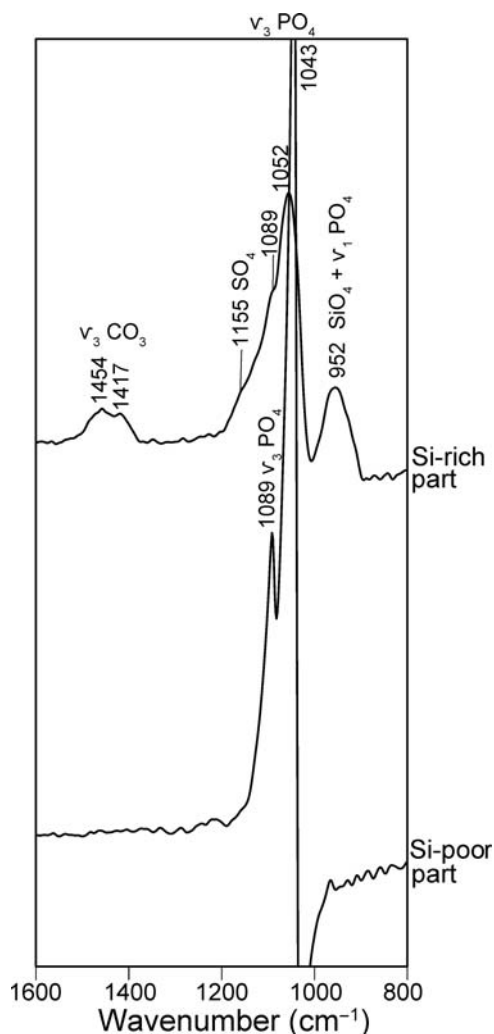


FIG. 3. Infrared spectra of Si-poor and Si-rich parts of hydroxylapatite_{ss} crystals.

Other minerals

Grossular exhibits a zoned structure, with an Fe³⁺-poor core ($X_{\text{Adr}} = 0.00\text{--}0.09$ and $X_{\text{Grs}} = 0.91\text{--}0.94$) and an Fe³⁺-rich rim ($X_{\text{Adr}} = 0.09\text{--}0.12$ and $X_{\text{Grs}} = 0.85\text{--}0.87$). The compositional range of andradite is $X_{\text{Adr}} 0.81\text{--}0.91$, $X_{\text{Grs}} 0.07\text{--}0.18$, $X_{\text{Alm}} 0.00\text{--}0.01$, $X_{\text{Prp}} 0.01$; TiO₂ contents of 'melanite' reach 8.60 wt.%. Gehlenite comprises 28–43% åkermanite and vesuvianite contains up to 2.49 wt.% TiO₂.

X-ray diffraction data

Fragments of hydroxylapatite_{ss} were carefully handpicked from the thin section and analysed using X-ray diffraction. Powder X-ray diffraction data of the fragments were obtained using a 114.6 mm diameter Gandolfi camera employing Ni-filtered CuK α radiation. Data were recorded on an imaging plate and processed with a Fuji BAS-2500 bio-image analyser using a computer program written by Nakamuta (1999). Observed diffraction angles were calibrated by a Si-standard material (NBS, #640b) on the sample fragments. Parameters of the hexagonal unit cell refined using a computer program written by Toraya (1993) from the powder X-ray diffraction data are as follows: $a = 9.4114(14)$, $c = 6.9018(16)$ Å, and $V = 529.4(2)$ Å³ for the Si-poor part, and $a = 9.4410(19)$, $c = 6.9003(19)$ Å, and $V = 532.6(3)$ Å³ for the Si-rich part. The length of the a axis for the Si-rich part is slightly longer than that for the Si-poor part.

Discussion

Raman and IR spectra obtained from the Si-rich part of hydroxylapatite_{ss} demonstrate that it contains B-type carbonate. Pan and Fleet (2002) summarized the chemical substitutions in synthetic and natural apatite supergroup minerals. They proposed seven charge-compensating mechanisms for B-type CO₃ substitution, as follows.

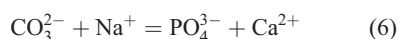
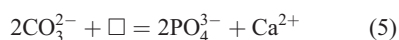
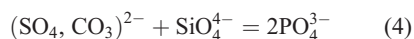
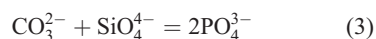
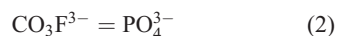
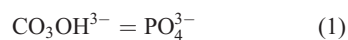


Table 1 lists representative chemical compositions of hydroxylapatite_{ss} from Tadano. The data indicate that the SO₃ content increases, but the P₂O₅ content decreases, with increasing SiO₂ content. This corresponds to substitution (4) $(\text{SO}_4, \text{CO}_3)^{2-} + \text{SiO}_4^{4-} = 2\text{PO}_4^{3-}$. The elemental X-ray mapping images of the hydroxylapatite_{ss} studied are in Fig. 4, showing a fairly homogeneous distribution of Ca, irrespective of the heterogeneous distribution of C. This indicates that the effect of the coupled

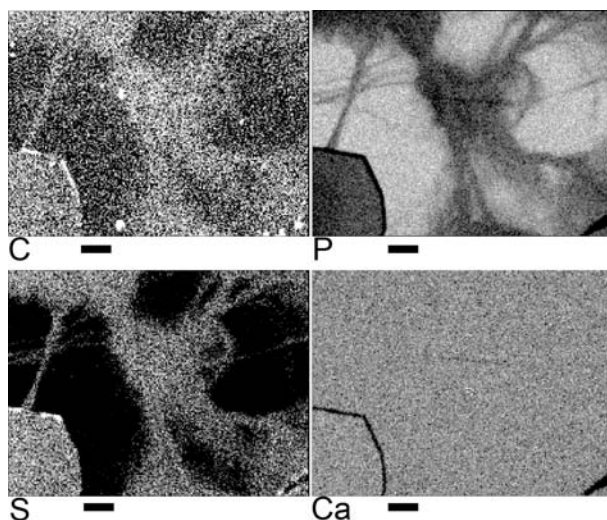


FIG. 4. Elemental X-ray mapping images of hydroxylapatite_{ss}. Brighter shades indicate heavier elemental content. Scale bars represent 20 μm .

substitutions involving Ca [substitutions (5)–(7)] is not significant. Although the sample was carbon-coated, the pattern in the mapping image for C is similar to those in the mapping images for S and P. This indicates that the pattern for C is not an artifact and the C-concentration map actually reflects C contents in hydroxylapatite_{ss}. Therefore, the chemical formulae of the Si-rich part were calculated on the basis of 8 cations, assuming Si = S + C, with C derived by calculation from this constraint (Table 1). The H₂O calculation was based on the assumption F + Cl + OH = 1 apfu. The averaged composition for the Si-rich part gives the empirical formula Ca_{4.990}(P_{1.803}Si_{0.604}S_{0.250}C_{0.353})Σ_{3.010}O_{11.661}(OH_{0.631}F_{0.208}Cl_{0.161})Σ_{1.000}. The total number of tetrahedral cations is 3.01 apfu, close to ideal. This supports the assumption that Si = S + C. Chemical variations of hydroxylapatite_{ss} are shown in Fig. 5, which displays a very strong inverse correlation between Si and P. The regression equation is $P = -1.97Si + 2.99$ ($r^2 = 0.98$). These data indicate that the substitution mechanism (SO₄, CO₃)²⁻ + (SiO₄)⁴⁻ = 2(PO₄)³⁻ most probably occurs in the mineral. Therefore, it is concluded that the Si-rich part of hydroxylapatite_{ss} from Tadano corresponds to a CO₃-bearing hydroxylapatite–

hydroxyllestadite series mineral with CO₃ partially replacing SO₄. The empirical formula of the Si-rich part with SiO₂ = 10.30 wt.%, as shown in Table 1, can be expressed as Ca_{4.989}[(PO₄)_{1.315}(SiO₄)_{0.848}(SO₄)_{0.368}(CO_{2.943})_{0.480}]Σ_{3.011}(OH_{0.629}Cl_{0.264}F_{0.107})Σ_{1.000}. The relationship between Si and B-type CO₃ of the Si-rich part is shown in Fig. 6. Data for CO₃-bearing apatite and ellestadite, whose B-type CO₃ is mainly controlled by the substitution mechanism (SO₄, CO₃)²⁻ + (SiO₄)⁴⁻ = 2(PO₄)³⁻, from the literature are also plotted in Fig. 6. The CO₃ and SO₄ contents in the Si-rich part are controlled by the coupled substitutions CO₃²⁻ + SiO₄⁴⁻ = 2PO₄³⁻ and SO₄²⁻ + SiO₄⁴⁻ = 2PO₄³⁻, respectively. Therefore, in this system, two end-members, apatite [Ca₅(PO₄)₃X (X = OH, F, Cl)] and ellestadite [Ca₅(SiO₄)_{1.5}(SO₄)_{1.5}X], and one hypothetical end-member [Ca₅(SiO₄)_{1.5}(CO₃)_{1.5}X] can be plotted. Most of the Si-rich part shows CO₃ > SO₄ and its composition points towards Ca₅(SiO₄)_{1.5}(CO₃,SO₄)_{1.5}X (X = OH, F, Cl).

The CO₃²⁻ ion has never been found to be the dominant anion species substituting for tetrahedral groups (or in the *c*-axis anion channel) in natural carbonate-bearing apatite (Pan and Fleet, 2002). Figure 6 implies that maximum occupancy of the

TABLE 1 Compositions (wt.%) of hydroxylapatite_{ss}*

	Si-p	Si-p	Si-r	Si-r	Si-r	Si-r
CaO	55.81	55.53	56.43	56.35	56.89	56.55
P ₂ O ₅	42.36	41.43	26.28	24.21	20.90	18.86
SiO ₂	n.d.	0.35	7.00	7.93	9.60	10.30
SO ₃	n.d.	0.22	4.14	4.78	5.05	5.95
CO ₂ **			2.85	3.18	4.26	4.27
F	1.79	1.41	0.84	0.65	0.54	0.41
Cl	0.23	0.38	1.20	1.40	1.30	1.89
–O = F + Cl	0.81	0.68	0.62	0.59	0.52	0.60
H ₂ O***	0.89	1.02	1.11	1.15	1.25	1.15
Total	100.27	99.66	99.23	99.06	99.27	98.78
Composition calculated on the basis of eight cations						
Ca	5.001	5.006	5.001	4.993	4.984	4.989
P	2.999	2.951	1.840	1.695	1.447	1.315
Si		0.029	0.579	0.656	0.785	0.848
S		0.014	0.257	0.297	0.310	0.368
C			0.322	0.359	0.475	0.480
Total	2.999	2.994	2.999	3.007	3.016	3.011
F	0.473	0.375	0.220	0.170	0.140	0.107
Cl	0.033	0.054	0.168	0.196	0.180	0.264
OH	0.494	0.571	0.612	0.634	0.680	0.629

*Si-p = Si-poor part, Si-r = Si-rich part, n.d. = not detected. **CO₂ calculation for Si-rich part based on the assumption of Si = S + C. ***H₂O calculation based on the assumption of OH + F + Cl = 1 apfu.

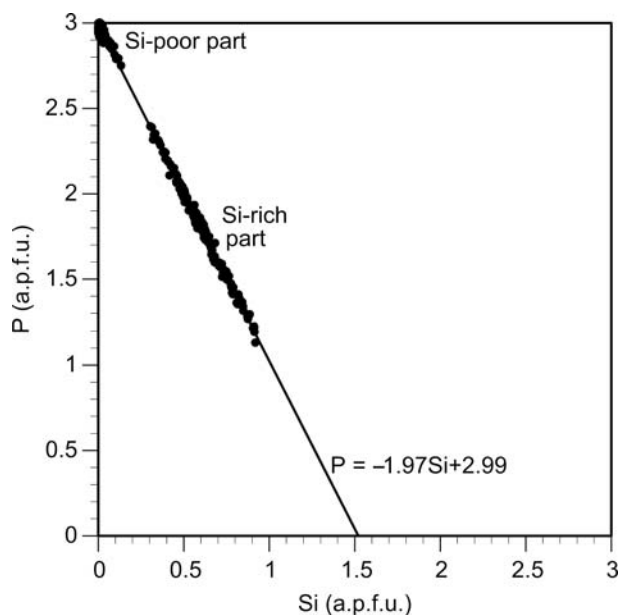
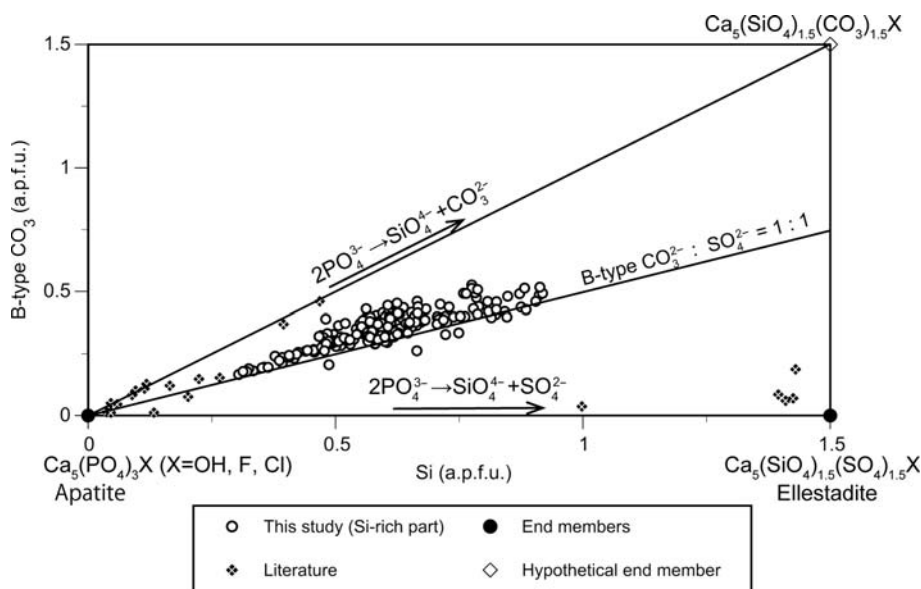
FIG. 5. Si vs. P plots of hydroxylapatite_{ss}.

FIG. 6. Si vs. B-type CO₃ plots of the Si-rich part of hydroxylapatite_{ss} in this study. B-type CO₃ means CO₃ which occupies the tetrahedral anion site in the apatite structure. Plots of CO₃-bearing apatite and ellestadite, whose B-type CO₃ is controlled mainly by the substitution mechanism $(\text{SO}_4, \text{CO}_3)^{2-} + (\text{SiO}_4)^{4-} = 2(\text{PO}_4)^{3-}$, from the literature are also shown. Data are from McConnell (1937), Harada *et al.* (1971), Rouse and Dunn (1982), Sommerauer and Katz-Lehnert (1985) and Chesnokov *et al.* (1987).

CO₃ triangle in the tetrahedral anion site in CO₃-bearing apatite and ellestadite, whose CO₃ is controlled mainly by the substitution mechanism

$(\text{SO}_4, \text{CO}_3)^{2-} + (\text{SiO}_4)^{4-} = 2(\text{PO}_4)^{3-}$, is ~20%. Comodi and Liu (2000) pointed out that due to the entry of non-trivalent ions such as SiO₄⁴⁻ and CO₃²⁻ for the

trivalent PO_4^{3-} ions in apatite, the periodicity of the structure is progressively lost, long-range translational symmetry is destroyed, and tetrahedral distortion increases. The increasing structural distortion of the tetrahedral site with increasing SiO_4^{4-} and CO_3^{2-} substitution for PO_4^{3-} can explain why B-type CO_3 occurs as a subordinate component in the apatite–ellestadite series.

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