

SPECIAL COLLECTION: APATITE: A COMMON MINERAL, UNCOMMONLY VERSATILE

Column anion arrangements in chemically zoned ternary chlorapatite and fluorapatite from Kurokura, Japan

SEAN R. KELLY^{1,*}, JOHN RAKOVAN¹, AND JOHN M. HUGHES²

¹Department of Geology and Environmental Earth Science, Miami University, Oxford, Ohio 45056, U.S.A.

²Department of Geology, University of Vermont, Burlington, Vermont 05405, U.S.A.

ABSTRACT

The substitution of F, OH, and Cl in apatite has recently gained increased attention due to the complex nature of incorporation of these three constituents and the implications of apatite column anion chemistry, such as apatite's contribution to the water budget of the Moon and Mars and the use of apatite anion chemistry as an indicator of halogen and water activities. The solid solutions among F, OH, and Cl are complex because the end-member atomic arrangements cannot fully explain the ternary and binary substitutions of these constituents due to differing atomic radii and the resulting steric constraints in the structure. Three structural variations have recently been reported for the OH-Cl binary solid solution in synthetic samples. This study elucidates column anion arrangements in a chemically zoned ternary apatite from Kurokura, Japan. The structures of the compositionally different core and rim were solved ($R_1 = 0.0158$ and $R_1 = 0.0143$, respectively) in space group $P6_3/m$ using single-crystal X-ray diffraction data. The chemistry of these apatites was analyzed using electron microprobe analysis and crystal structure refinement. The core of the Kurokura crystal is a naturally occurring example of the $\text{OH} \approx \text{Cl}$ apatite structural variation in a ternary chlorapatite, with four column anion sites (one for F, two for Cl and one for *both* OH and Cl). The rim exhibits a previously unseen apatite structural variation in a ternary OH-rich fluorapatite (with only a trace Cl component) with three column anion sites (one each for F, OH, and Cl). Both structural variations show a splitting of the Ca2 site that enables reasonable column anion bond distances with Ca2 atoms. A sequence of anions that provides reasonable anion-anion distances while simultaneously enabling reversal of the anion sites relative to the mirror planes at $z = 1/4$ and $z = 3/4$ exists for both structure variations. This study demonstrates the structural complexity of natural ternary apatites, and that a structural variety of OH-Cl apatite occurs over a wider range of chemistry than initially anticipated. The results have implications regarding the poorly understood (and potentially complex) crystallization history of apatite from Kurokura, Japan.

Keywords: Apatite, ternary solid solution, chlorapatite, Kurokura, Japan

INTRODUCTION

Apatite *sensu lato* $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH},\text{F},\text{Cl})_2]$; OH = hydroxylapatite, F = fluorapatite, Cl = chlorapatite], the most abundant phosphate mineral on Earth, plays an important role across many disciplines (Hughes and Rakovan 2002, 2015; Rakovan and Pasteris 2015). Hydroxylapatite is the closest naturally occurring analog to bone material, and new insights about the occurrence of OH in bone apatite have recently been reported (Pasteris et al. 2014). Apatite is also one of the more common hydroxyl-bearing phases in extraterrestrial systems, such as the moon and Mars (McCubbin and Jones 2015; McCubbin et al. 2010; Boyce et al. 2010). Boyce et al. (2014) recently suggested that apatite plays the dominant role in fractionation of F, OH, and Cl in lunar magmatic systems. Understanding the structure and thermodynamic properties of apatite will allow better estimation of the overall H_2O content within extraterrestrial magmatic systems from measured apatite chemistries.

The F, OH, and Cl chemical variation in apatite can also

provide various geochemical information. One example is using apatite anion chemistry as a geothermometer (e.g., Stormer and Carmichael 1971). Apatite anion chemistry can also serve as an indication of magma or aqueous fluid composition from which the phase crystallized (Piccoli and Candela 2002), including the fugacity of volatiles in magmatic, metamorphic, or hydrothermal systems (Webster and Piccoli 2015; McCubbin et al. 2015; Hughes et al. 1990; Yardley 1985).

Chlorapatite, an uncommon naturally occurring apatite phase, is unique in that it can indicate unusual mineralization environments where it is found. For example, experimental work has suggested that Cl-rich apatite may be chemically associated with Pt in mineralizing hydrothermal fluids, demonstrating the significance of apatite anion chemistry to mineral exploration (Webster and Piccoli 2015).

As noted by Hughes et al. (2016), for any combination of anion occupants, the positions of the anions in the $[0,0,z]$ anion column result from several factors, including the size of the particular column anions, the nearest-neighbors in the anion column and electrostatic repulsions therefrom, any dissymmetrization (lowering of crystal symmetry) that is present in the structure, electrostatic attractions to the surrounding triangle of Ca2

* E-mail: Seanrkelly11@gmail.com

Special collection papers can be found online at <http://www.minsocam.org/MSA/AmMin/special-collections.html>.

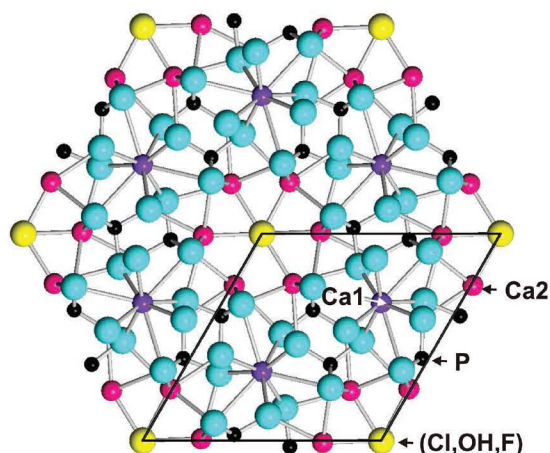


FIGURE 1. [001] projection of the crystal structure of apatite. (Color online.)

atoms, and, in hydroxyl-bearing apatite, the hydrogen bonding that occurs from the hydroxyl hydrogen to neighboring column anions. Figure 1 shows a [001] projection of the apatite atomic arrangement. Because of the steric flexibility of its structure, apatite can incorporate a large range of (F, Cl, OH) compositions in the anion column sites.

Hughes et al. (1989) published one of the most recent structural analyses of the OH, F, and Cl end-members of the ternary system of anion substitution. Apatite most commonly crystallizes in space group $P6_3/m$, although subsymmetric varieties are known (Hughes and Rakovan 2015). In end-member fluorapatite, the F anion resides at (0, 0, 0.25) and (0, 0, 0.75) in the unit cell, lying on {001} mirror planes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. The larger OH and Cl (poly)anions are usually displaced off this mirror plane (ca. 0.3 and 1.3 Å, respectively), a structural response to steric interaction with the surrounding Ca cations (the Ca2 position, see Fig. 1), which also lie on the mirror planes. Figure 1 demonstrates the configuration of calcium cations surrounding the column anion. Although the substitution of these three anions is known to be extensive, the continuous solution series of these anions cannot be explained by their end-member atomic sites alone (Hughes et al. 1990).

It has been shown that novel, non-end-member atomic sites exist in the ternary solution series as well as the binary F-Cl and OH-Cl solution series (Hughes et al. 1990, 2014a, 2014b, 2016). Hughes et al. (1990) also demonstrated in natural samples that ternary solid solution can occur via ordering of OH and Cl atoms, causing symmetry reduction to $P2_1/b$. The F-OH apatite binary can exist with the end-member F and OH sites while maintaining $P6_3/m$ symmetry, as the smaller radii of these (poly)anions enable disorder about the mirror planes without necessitating new sites (Hughes et al. 1989). Hughes et al. (2016) recently demonstrated, in a series of synthetic apatites, that three different structures with distinctly different column anion sites enable solid solution along the OH-Cl binary series without reduction of symmetry due to ordering. The structure of OH-Cl apatites is influenced by column anion chemistry, with one arrangement for apatites with OH dominant, one for apatites with approximately equal OH and Cl apfu, and one for apatites with Cl dominant

in the anion column. The calcium phosphate apatite structure preferentially incorporates F over both OH and Cl (Boyce et al. 2014). In order for natural apatite dominated by OH and Cl to exist, crystal growth must have occurred from a fluid or magma substantially devoid of F relative to OH or Cl. This study presents the structure and chemistry of a natural Cl- and OH-dominant calcium phosphate apatite from Kurokura, Ashigarakami district, Kanagawa Prefecture, Japan, and an analysis of the column anion arrangement. These apatites occur in hydrothermal veins in diorite and granodiorite, in association with quartz, chlorite, talc, stilbite, and natrolite. Crystals are prismatic with well-developed {100}, {001}, and {101} faces and are typically 0.5–1.0 cm in length, but can exceed 4 cm (Fig. 2). Apatites from Kurokura were first reported to be chlorine dominant by Harada (1938). Apatites from this locality consist of two visually distinct concentric zones: a volumetrically dominant clear core and a white (cloudy) rim (Fig. 2). The rim is cloudy due to a high density of small fluid inclusions (note: the larger “bubbles” in this image occur in the epoxy rather than the mineral; the fluid inclusions in the rim are much smaller). Harada (1938) demonstrated both optically and with wet chemical analysis that the cloudy rim and clear core represent two distinct apatite chemistries. Apatite from the core is more Cl rich than that from the rim. This concentric chemical zoning may be indicative of variation in source fluid chemistry during apatite crystallization, or possibly post-growth alteration of the rim. Although the chemical analysis of Harada (1938) suggests that both the core and rim contain significant F, preliminary investigation in this study suggested that one or both of these phases is OH-rich chlorapatite.

EXPERIMENTAL METHODS

Single-crystal X-ray diffraction (SCXRD) was used as a crystal-structure analysis technique and chemical probe of the apatite samples from Kurokura in this study. There are some instances, however, where different anions are shown to occupy the same column site (Hughes et al. 2014a, 2016), causing a limitation in the accuracy of this methodology. Electron microprobe analysis (EMPA) was employed as a complementary technique for analysis of the F and Cl chemistry. Measuring O with EMPA is known to be problematic; OH chemistry is instead calculated by difference, assuming two column (poly)anions per unit cell. This method of determining OH chemistry is not ideal, particularly given the known limitations of measuring F and Cl by microprobe analysis (discussed below).

Electron microprobe analysis

A sample of Kurokura apatite was prepared for EPMA analysis by embedding the crystal in epoxy resin and slicing to achieve a (100) section. The sample was then progressively polished down to a 0.02 μm alumina paste. Measuring the Cl and F composition of apatite using EMPA is known to be problematic (Stormer et al. 1993; Stock et al. 2015), as column anion migration can lead to spurious results. One way to reduce column anion migration is to use (100) sections for analysis (Stormer et al. 1993). Six spots were measured on the polished sample, three within the clear core and three within the white rim.

Compositional analyses were acquired on a Cameca SX100 electron microprobe, at the University of Oregon's CAMCOR MicroAnalytical facility, equipped with 5 tunable wavelength-dispersive spectrometers. A 15 keV accelerating voltage and 20 nA beam current were used for measurement of Ca, F, Cl, P, and Fe, and a 20 keV accelerating voltage and a 50 nA beam current were used for measurement of S, Nd, Na, Sr, Ce, Mn, Si, Dy, and Eu. The beam size was 10 μm for all analyses. Elemental analyses were acquired using the following analyzing crystals: LIF (Fe, Dy, Eu), PET (Ca, S, Nd, Si, P), LPET (Ce, Mn, Cl), and LTAP (Sr, F, Na). The standards used were synthetic MnO (Mn), SrTiO₃ (Sr), synthetic chlorapatite (halogen corrected) (P, Ca, Cl), nepheline (partial anal.) (Na, Si), magnetite (Fe), pyrite (S), BaF₂ (F), CePO₄ (Ce), DyPO₄ (Dy), EuPO₄ (Eu), and NdPO₄ (Nd). The counting time was 60 s for F, Cl, Fe, S, Nd, Na, Sr, Ce, Mn, Dy, and Eu; 90 s for P and Ca; and 120 s for Si. The intensity data were corrected for time dependent

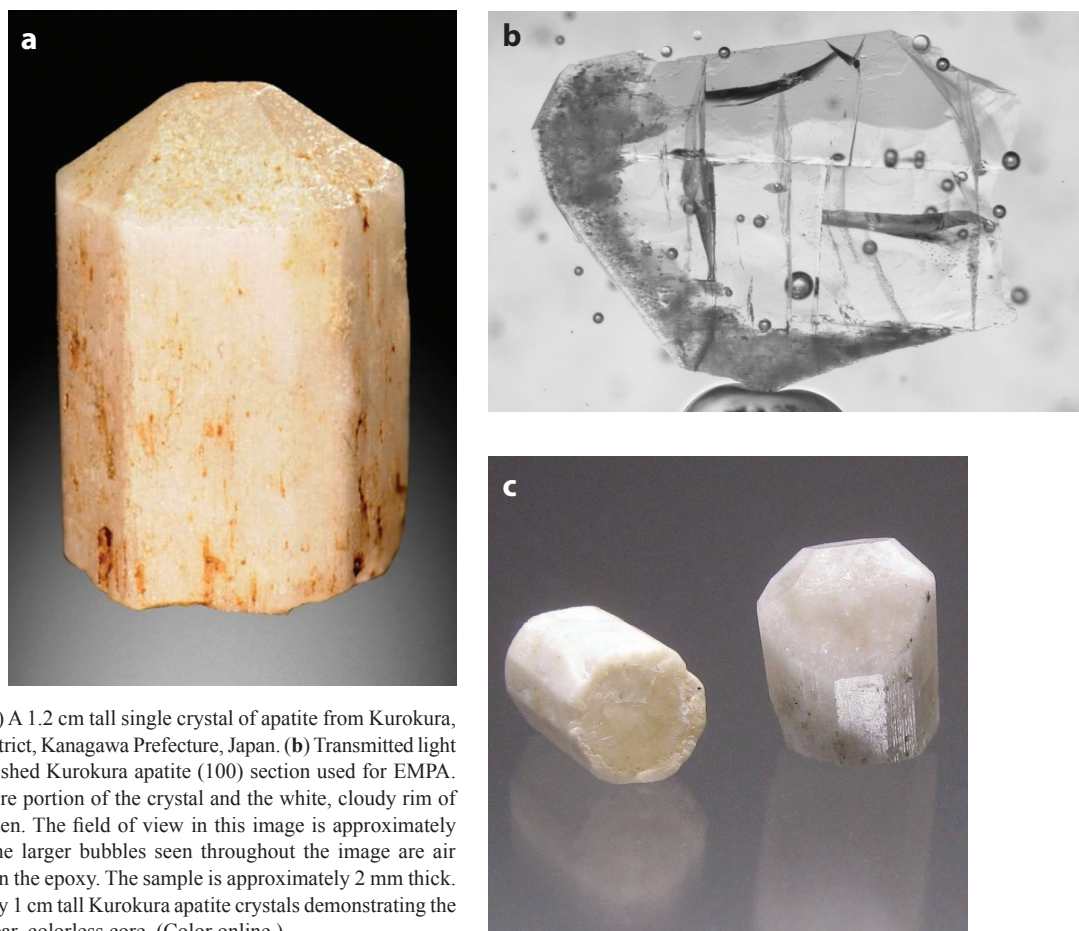


FIGURE 2. (a) A 1.2 cm tall single crystal of apatite from Kurokura, Ashigarakami district, Kanagawa Prefecture, Japan. (b) Transmitted light image of the polished Kurokura apatite (100) section used for EMPA. Both the clear core portion of the crystal and the white, cloudy rim of the crystal are seen. The field of view in this image is approximately 5 mm across. The larger bubbles seen throughout the image are air bubbles trapped in the epoxy. The sample is approximately 2 mm thick. (c) Approximately 1 cm tall Kurokura apatite crystals demonstrating the white rim and clear, colorless core. (Color online.)

intensity (TDI) loss (or gain) using a self-calibrated correction for Ca, F, Cl, P, and Fe. This correction accounts for the known variation of F and Cl peak intensity over time in apatite due to anion migration. The off-peak counting time was 30 s for Ca and P; 60 s for Cl, F, Fe, S, Nd, Na, Sr, Ce, Mn, Dy, and Eu; and 120 s for Si. Interference corrections were applied to F (P, Ce, Eu, and Nd), Cl (Nd), Nd (Ce and Eu), Sr (Si), Ce (Sr), Mn (Nd and Eu), Dy (Mn, Eu, and Fe), and Eu (Mn and Nd). Oxygen was calculated by cation stoichiometry and included in the matrix correction. Oxygen-equivalence from halogens (F/Cl/Br/I), was not subtracted in the matrix correction. Hydrogen was calculated by difference. Further details of the EMPA experimental methods used in this study can be found in Armstrong (1988) and Donovan et al. (1993, 2011).

Single-crystal X-ray diffraction

X-ray diffraction data were collected with a Bruker Apex II CCD single-crystal diffractometer using graphite-monochromated MoK α radiation; complete details of crystal data and data collection for each of the two crystals described herein have been deposited.¹ For each sample, redundant data were collected for a sphere of reciprocal space (4500 frames, 0.20° scan width, average redundancy ≈ 16) and were integrated and corrected for Lorentz and polarization factors and absorption using the Bruker Apex2 package of programs. The atomic arrangement was refined in space group $P6_3/m$, on F^2 , with SHELXL-97 (Sheldrick 2008) using neutral atom scattering factors and full-matrix least-squares, minimizing the function $\sum w(F_o^2 - F_c^2)^2$ with no restraints. All atoms were refined with anisotropic temperature factors except the column anions. As noted previously (e.g., Hughes

et al. 1990, 2014a, 2016) use of anisotropic atomic displacement factors for the column anions yields unreasonable values of U_{33} , an anisotropy that masks the positions of anion sites occupied by small fractions of a column anion. The occupancy values of the column anions were not constrained.

After structure solution and initial refinement, the column anion positions were analyzed by difference maps. In this way, positions along the anion column were modeled and refined one at a time, as they sequentially appeared as the highest peaks in the difference maps. Disorder of the Ca2 site was also modeled in this fashion, as sites Ca2 and Ca2'. When disorder of the Ca2 site was modeled, the sum of the Ca2 and Ca2' site occupancy was constrained to total 1.00 and the two sites were also constrained to have identical thermal parameters. An extinction coefficient was also refined in both samples. Using previous literature, anion positions were named and assigned an anion scattering factor (Cl, O, or F). Anion selection was then evaluated using the calculated total anion apfu based on the refinement.

RESULTS

Electron microprobe analysis

Table 1 shows the chemistry results from EMPA data for each portion of the crystal. Figure 3 shows the column anion chemistry results from each of the six individual analysis spots, as well as average anion chemistry for the core and two averages for the rim. The average core anion chemistry is $[\text{Cl}_{0.93}(\text{OH})_{0.66}\text{F}_{0.38}]$ and the average rim anion chemistry is $[\text{F}_{0.97}(\text{OH})_{0.88}\text{Cl}_{0.24}]$. As determined by Harada (1938), the apatite core has a higher Cl concentration than the rim. Figure

¹Deposit item AM-17-45825, CIF/Supplemental Material. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2017/Apr2017_data/Apr2017_data.html).

TABLE 1. Electron microprobe chemical analysis of the Kurokura apatite

Oxide (wt%)	Kurokura Core (n = 3)	Kurokura Rim (n = 3)
CaO	53.404 ± 0.328	54.998 ± 0.363
F	0.716 ± 0.134	1.843 ± 0.689
Cl	3.244 ± 0.055	0.848 ± 1.005
P ₂ O ₅	40.5 ± 0.122	40.886 ± 0.672
FeO	0.119 ± 0.037	0.03 ± 0.045
S	0.045 ± 0.018	0.01 ± 0.009
Nd ₂ O ₃	0.291 ± 0.048	0.136 ± 0.042
Na ₂ O	0.168 ± 0.03	0.036 ± 0.052
SrO	0.024 ± 0.003	0.018 ± 0.005
Ce ₂ O ₃	0.36 ± 0.054	0.113 ± 0.022
MnO	0.229 ± 0.003	0.092 ± 0.094
SiO ₂	0.279 ± 0.043	0.196 ± 0.054
Dy ₂ O ₃	0.051 ± 0.031	0.042 ± 0.024
Eu ₂ O ₃	0.013 ± 0.008	0.004 ± 0.004
HO ^a	0.557 ± 0.1	0.75 ± 0.598
Total	100	100.002

Apatite structural formula^b

Ca	9.659	9.792
Na	0.055	0.012
Fe	0.017	0.004
Mn	0.033	0.013
Sr	0.003	0.002
Dy	0.003	0.002
Eu	0.001	0.000
Ce	0.022	0.007
Nd	0.018	0.008
Subtotal	9.810	9.840
P	5.788	5.753
Si	0.047	0.032
S	0.014	0.003
Subtotal	5.849	5.788
Cl	0.928	0.240
F	0.382	0.966
OH ^a	0.664	0.875
Subtotal	1.975	2.082

Notes: Each is an average of the three spots measured in the core and rim.

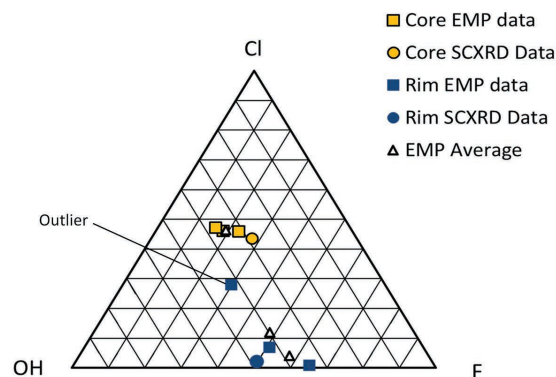
^a HO wt% and proportion in structural formula is calculated by difference.

^b Apatite structural formula was calculated using atom% values. Using net negative charge is problematic given OH substitution for F and Cl.

3 demonstrates a notable presence of column anion chemical heterogeneity in the Kurokura apatite, particularly in the rim. One of the three spots where rim chemistry was measured has anion values much more similar to the core than the other two rim spots (Fig. 3; see labeled outlier spot). Although this may simply represent heterogeneity in the rim, the outlier may also be the result of collecting data across the boundary between the core and rim. Because of this possibility, an average rim chemistry from EMPA not including the outlier is also shown in Figure 3. Comparison of EMPA data to anion chemistry determined by crystal-structure analysis is given below.

Crystal structure refinements

The structures of the clear apatite core and cloudy rim were solved and refined using SCXRD data to R1 values of 0.0158 and 0.0143, respectively. Both samples were successfully modeled in space group $P6_3/m$. Tables 2 and 3 contain the atomic coordinates and equivalent atomic displacement parameters for the core and rim, respectively. From the refined atomic arrangement, the core anion chemistry is $[\text{Cl}_{0.87}(\text{OH})_{0.58}\text{F}_{0.55}]_{\Sigma 2.00}$ and the rim apatite's chemistry is $[\text{F}_{1.05}(\text{OH})_{1.02}\text{Cl}_{0.04}]_{\Sigma 2.12}$. These results are plotted on Figure 3, alongside the results from EMPA. There is some disagreement between anion chemistry determined by SCXRD and EMPA, primarily for the rim sample. This difference may be the result of analytical error, particularly with EMPA due to the known limitations in

**FIGURE 3.** Ternary plot of the column anion chemistry (percent of total column occupancy) of the apatite rim and core from both structure refinement (SCXRD data) and electron microprobe analysis. Two averages for the rim EMPA column anion chemistry are shown, one including the outlying data point and one without. (Color online.)**TABLE 2.** Atomic coordinates and equivalent isotropic atomic displacement parameters ($\text{\AA}^2$) for the Kurokura core sample

Atom	x/a	y/b	z/c	U_{eq}^a
Ca1	2/3	1/3	0.99794(5)	0.01099(10)
Ca2	0.2417(4)	0.9969(3)	1/4	0.0076(3)
Ca2'	0.2676(4)	0.9946(5)	1/4	0.0076(3)
P	0.62949(4)	0.03123(4)	1/4	0.00684(9)
O1	0.51310(13)	0.84692(12)	1/4	0.01300(19)
O2	0.53517(14)	0.12404(13)	1/4	0.0165(2)
O3	0.73872(10)	0.08624(10)	0.06902(13)	0.02106(19)
F	0	0	1/4	0.0130(19)
ClB	0	0	0.0942(9)	0.0106(12)
ClOH	0	0	0.1662(10)	0.0159(12)
ClA	0	0	0	0.028(10)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Atomic coordinates and equivalent isotropic atomic displacement parameters ($\text{\AA}^2$) for the Kurokura rim sample

Atom	x/a	y/b	z/c	U_{eq}^a
Ca1	2/3	1/3	0.99875(5)	0.00896(8)
Ca2	0.2433(3)	0.99335(6)	1/4	0.0074(2)
Ca2'	0.275(6)	0.991(2)	1/4	0.0074(2)
P	0.63123(4)	0.02980(4)	1/4	0.00520(8)
O1	0.51536(13)	0.84289(13)	1/4	0.00972(19)
O2	0.53395(14)	0.12201(14)	1/4	0.0120(2)
O3	0.74258(10)	0.08495(10)	0.07029(12)	0.01393(16)
F	0	0	1/4	0.0097(14)
OH	0	0	0.193(3)	0.008(2)
Cl	0	0	0.113(13)	0.010(15)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

quantifying F and Cl (and the inability to measure OH). The discrepancy may also be in part due to heterogeneity in the samples; the data from EMPA and SCXRD were collected on different individual crystal fragments.

The clear core has the same column anion arrangement reported in Hughes et al. (2016) that exists for OH-Cl apatites with OH occupancy approximately equal to Cl occupancy in the anion column. Conversely, the cloudy rim was found to have a new column anion arrangement for ternary apatites that are predominantly F and OH. The column anion arrangements of each zone of the crystal are discussed further below.

TABLE 4. Values of z for column anions in (0, 0, z) sites and percentage of total column anion occupancy of each corresponding site for the core structural analysis of apatite from Kurokura

Sample	F	% Sites	Cl _a	% Sites	Cl _b	% Sites	ClOH ^a	% Sites	Column occupancy ^b
Kurokura Core	1/4	27.7	0	3.0	0.094	25.4	0.166	44.00	F _{0.55} (OH) _{0.58} Cl _{0.87}

^a ClOH site: 65% OH, 35% Cl.^b Constrained to 2.00 column anions/formula unit.

Clear apatite core

Four anion column sites were refined for the sample of the clear core portion of the Kurokura apatite, yielding a column anion arrangement almost identical to the Cl $\approx$ OH apatite structure published in Hughes et al. (2016). The position and occupancy of the four sites are given in Table 4.

Two distinct Cl sites were found at $z = 0$ and $z = 0.094$. The site at $z = 0$ represents a unique Cl position only found in binary F-Cl and OH-Cl calcium phosphate apatites (Hughes et al. 2014, 2016). The site at $z = 0.094$ is nearly equivalent to the Cl atomic site in end-member chlorapatite, only slightly less displaced from the mirror planes at $z = 1/4$ and $z = 3/4$ than the typical end-member Cl site ($z \approx 0.068$; Hughes et al. 1989). This site has an acceptable bond distance to Ca2' of 2.878 Å.

Another column anion site was found in the clear apatite core samples at $z = 0.166$. This site is particularly interesting, having only recently been documented in Hughes et al. (2016). As is the case in Hughes et al. (2016), here it is demonstrated that this site represents a special site with mixed occupancy of *both* OH and Cl.

For OH and Cl (poly)anions with significantly different radii (Cl = 1.72 Å, OH = 1.33 Å; Jenkins and Thakur 1979) to occupy the same atomic site, they must both achieve acceptable bond distances with the neighboring Ca2 site. This requires the splitting of the Ca2 site into two distinct sites, which was found in this structure refinement (Ca2 and Ca2'; Table 2). The ClOH site has a distance of 2.387 Å to the Ca2 site (acceptable for OH) and 2.637 Å to the Ca2' site (acceptable for Cl). These interatomic distances are almost identical to those found in Hughes et al. (2016) (2.404 Å to Ca2 and 2.647 Å to Ca2'). Further supporting mixed occupancy of the site at $z = 0.166$ is that the sum of the site occupancies of the column anions (which should be approximately 2 anions per unit cell) is substantially *below* 2.00 when the ClOH site is modeled as Cl (1.70 atoms per unit cell) and substantially *above* 2.00 when the ClOH site is modeled as OH (2.39 atoms per unit cell). Because of this, as in Hughes et al. (2016), a total column occupancy of 100% (2.00 atoms per unit cell) was used to calculate the proportion of the ClOH site occupied by each anion (Table 4).

A final site was found at $z = 1/4$, directly centered among three Ca2 cations on the mirror plane at $z = 1/4$ and $z = 3/4$ and concordant with the F position in end-member fluorapatite. However, Hughes et al. (2016) found that in their synthetic apatite where OH $\approx$ Cl (with anion sites identical to those published here) OH can occupy this site. Dual occupancy of this site by F and OH makes fractional occupancy determination via SCXRD difficult, because the scattering factors of O²⁻ and F⁻ are nearly identical as they are isoelectronic. However, EMPA data from the Kurokura core (Table 1; Fig. 3) indicates 16–23% F occupancy of the anion column. This occupancy coincides closely with the refined site occupancy at $z = 1/4$ in the structure (28% occupied, Table 4), suggesting that this site is exclusively (or almost exclusively)

occupied by F in the Kurokura core. No OH was modeled at this site in the refinements. This demonstrates that the OH $\approx$ Cl apatite structural result found in Hughes et al. (2016) occurs over a wider range of apatite anion chemistry than just in the OH-Cl binary, and that this structure variant, i.e., column anion arrangement, is found in nature.

For this apatite sample to maintain the hexagonal symmetry of space group $P6_3/m$, it must be demonstrated that a sequence of atoms exists, given the refined atomic sites in the anion column, to reverse the ordering of sites from above the mirror planes at $z = 1/4$ and $z = 3/4$ to below these mirror planes, such that throughout the crystal the occupancies are averaged half above and half below. Hughes et al. (2016) proposed a model for reversal of the anion column with acceptable anion-anion distances for this particular apatite structure. This model is shown in Figure 4, with the only difference being F occupancy of the site at $z = 1/4$ and $3/4$. The c dimension of the structure from this paper is only 0.002 Å larger than that used in the model from Hughes et al. (2016), and the interatomic distances are effectively identical. As mentioned in Hughes et al. (2016), OH must occupy the Cl_a and Cl_b site in trace quantities to enable this reversal sequence. Given the constraints proposed in Mackie and Young (1974): (1) the interatomic distances between occupants of the anion column must be of reasonable length, (2) the anions must occupy positions found in the structure refinement, and (3) F [and OH] can occupy a Cl site but Cl cannot occupy an F [or OH] site because of the resulting short Ca-Cl distances, it is reasonable to propose that *both* F and OH can occupy the Cl_a and Cl_b sites (F and OH are both smaller than Cl), making reversal of the anion column via the sequence in Figure 4 possible.

White apatite rim

The structure of the white outer rim of the apatite crystal (Fig. 2) was found to have three column anion sites, with the overall chemistry being that of a OH-rich fluorapatite (almost identical OH and F concentrations) with a small chlorine component. The unit-cell fractional coordinates of these column anion sites and their occupancy factors are given in Table 5.

One column anion site was modeled at $z = 1/4$, identical to the end-member fluorapatite column site. This site is considered here to be occupied by F, as with the core refinement there is no reason to suggest it is occupied by OH. The EMPA data demonstrate high F in the apatite rim (Table 1), supporting the occupancy of the $z = 1/4$ site by F. Another site was refined at $z = 0.19$. This was modeled as an OH site, as it is close to the end-member hydroxylapatite column site ($z \approx 0.20$, Hughes et al. 1989). A third site was modeled at $z = 0.11$, which is slightly less offset from the mirror planes at $z = 1/4$ and $z = 3/4$ than the end-member chlorapatite site ($z \approx 0.068$). This site was modeled as a Cl site.

A splitting of the Ca2 site into Ca2 and Ca2' was also modeled in this sample. The F and OH sites have acceptable bond distances to the Ca2 site of 2.32 and 2.35 Å, respectively. The

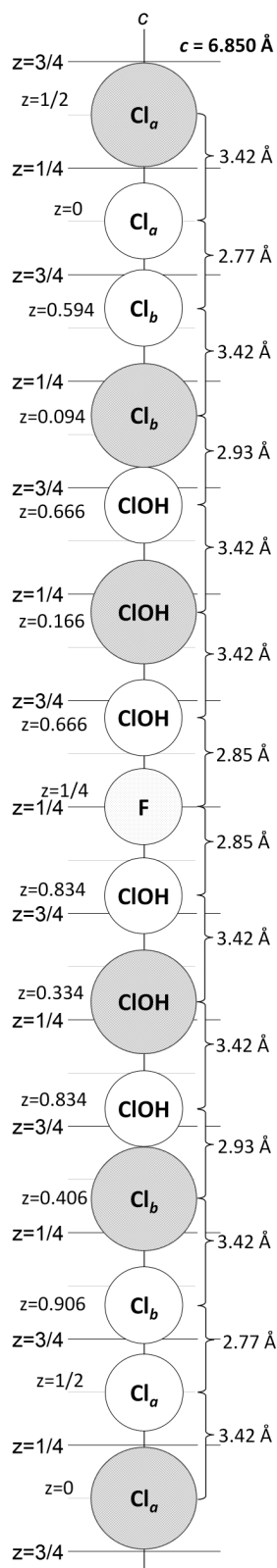


FIGURE 4. Sequence of atoms demonstrating a permissible reversal sequence of sites from above to below the mirror plane at $z = 1/4$ and $z = 3/4$ to maintain $P6_3/m$ symmetry in the Kurokura core apatite structure.

TABLE 5. Values of z for column anions in $(0, 0, z)$ sites and percentage of Total column anion occupancy of each corresponding site for the rim structural analysis of apatite from Kurokura

Sample	F	% Sites	Cl _b	% Sites	OH	% Sites	Column occupancy
Kurokura Rim	1/4	52.6	0.113	2.1	0.193	51.0	$F_{1.05}(\text{OH})_{1.02}\text{Cl}_{0.04}$

Cl site is prohibitively close to the Ca2' site (2.51 Å), but has an acceptable bond distance of 2.79 Å to the Ca2' site, making the Ca2' site a necessary component of this apatite structure. The short Ca2' to O2 distance (2.11 Å) indicates the requirement of an O2' site for the Ca2' site to be feasible. The highest peak in the difference map ($0.51 \text{ e}/\text{\AA}^3$) is an O2' site that when modeled provides an acceptable Ca2'-O2' distance (2.39 Å), affirming the O2 disorder. However, the data could not successfully support the modeling of disordered O2 and the concomitant disordering of P, and thus it was not modeled.

The combined column anion site occupancy refined to 2.12 sites per unit cell, slightly over the 2.00 sites per unit cell mandated by the apatite structure. This indicates a potential inaccuracy in the refinement. One possible explanation for the over occupancy of the anion column in the rim refinement is that there is Cl occupying the OH or F site that is not being accounted for in the model. The interatomic distances between the Ca2' site and the F/OH sites (Ca2'-OH: 2.66 Å; Ca2'-F: 2.63 Å) are both large enough to ideally accommodate Cl. This suggests that there may be a small amount of Cl occupancy in either (or both) the F and OH sites (more likely the OH site) that is accounting for the over occupancy of the anion column in the model. Adding Cl occupancy at the F and OH sites moves the SCXRD anion chemistry closer to the anion chemistry determined by EMPA, as EMPA found substantially more Cl than SCXRD (2.1 vs. 12% of total column occupancy, respectively). However, the very small occupancy of the Ca2' site (3.49% occupied) suggests that only a very small amount of substitution of Cl into the OH or F sites may be occurring, if any. As mentioned in Hughes et al. (2016), there should be a 1:1 linear relationship between the occupancy of the Ca2' site and the occupancy of the column anion sites that require the Ca2' site to have reasonable bond distances. The Cl site in this structure is 2.12% occupied, leaving 1.37% possible occupancy of the F and OH sites by Cl.

This apatite column anion arrangement has not previously been documented. However, comparison below demonstrates that the structure may represent a low Cl analog to the hexagonal structure of a ternary apatite collected from "ash F" in the Gunnison Formation near Jackson Peak, southwestern Utah, published in Hughes et al. (1990). That structure has identical F and OH sites, as well as splitting of the Ca2 site (with a short 2.16 Å Ca2'-O2 distance). The only structural difference is that, unlike the structure published here, Hughes et al. (1990) documented a splitting of the Cl site into two: one at $z = 0.132$ and another at $z = 0.06$. Splitting of the Cl site was proposed due to the abnormally large U_{33} value (0.098 Å²). The U_{eq} value for the Cl site in the rim structure in this paper is not unusually large (0.01045), and thus a split is not considered. A key difference that likely explains this observation is the different chemistry of these apatites.

The apatite described herein is approximately a pure binary F-OH apatite, with only 0.04 Cl atoms per unit cell. The small occupancy on the Cl site in this structure provides uncertainty as

to the legitimacy of the site. The site was included in the model, however, due to EMPA data showing substantial Cl, the presence of the Ca2' site, and that removal of the Cl site from the refinement leads to a higher R value (0.0149) and the appearance of an electron density peak of $0.64 \text{ e}^-/\text{\AA}^3$ in the difference map near $z = 0.10$ (near the Cl site).

The ternary apatite from Hughes et al. (1990) has a much higher Cl occupancy of 0.63 Cl atoms per unit cell. The greater proportion of Cl in the apatite from Hughes et al. (1990) may be what causes the splitting of the Cl site. Furthermore, a greater Cl occupancy can also make it easier to resolve a splitting of the Cl site. The very low Cl occupancy of the Kurokura rim structure is effectively a limitation in observing this split if it does exist.

A model demonstrating a possible reversal of the column anion occupancy necessary to maintain $P6_3/m$ symmetry using the sites found in this study is shown in Figure 5. As seen in Figure 5, the most prohibitive anion-anion distance necessary to enable disorder of anion sites from one side of the mirror plane at $z = 1/4$ and $z = 3/4$ to the other is an OH-Cl distance of 2.89 Å. This distance is greater than an OH-Cl distance proposed in Hughes et al. (2016) (2.85 Å), and is considered acceptable.

IMPLICATIONS

This study presents two structural variations of apatite, within compositionally different concentric zones of the same crystal, which have previously not been documented in natural samples. Whereas a naturally occurring OH-Cl binary apatite was not found, the clear core portion of these apatite crystals represents the first naturally occurring example of the $\text{OH} \approx \text{Cl}$ OH-Cl apatite structure variety first published in Hughes et al. (2016). The fact that this structure was found in an apatite with a significant F component demonstrates that this structural result occurs over a wider range of apatite chemistries than documented in Hughes et al. (2016) using pure Cl-OH synthetic crystals. The rim represents an F- and OH-dominant ternary apatite with a new structural variety closely resembling previously documented hexagonal ternary apatite (Hughes et al. 1990).

The distinct difference in chemistry from the core and rim suggests that the two zones of the crystal represent either two distinct mineralization events/fluids or one mineralization event that was later metasomatically altered. The rim representing an alteration phase is consistent with the substantial chemical heterogeneity of the rim observed in the microprobe data (Fig. 3).

Further investigation will be necessary for addressing the petrological questions posed herein. New analyses, such as an elemental map documenting the chemistry variation over a section of a crystal, or analysis of the fluid inclusions present in the rim, may elucidate the cause of the anion chemistry variation from the rim to the core. Understanding the petrogenic history of this apatite is pertinent to the interpretation of these results from a petrological standpoint. It is possible that the two different apatite structural varieties presented here are affected both by variation in chemistry (evident given the difference in anion chemistry in each phase) and variation in temperature, particularly given the possibility that the rim may represent a lower temperature alteration of the original apatite phase.

There is little background literature on the crystallization events of the Kurokura region, making it impossible to put

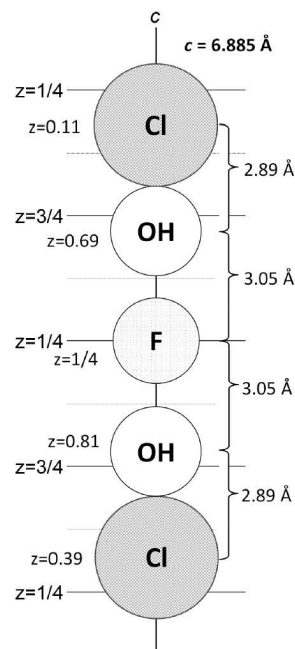


FIGURE 5. Sequence of atoms demonstrating a permissible reversal sequence of sites from above to below the mirror plane at $z = 1/4$ and $z = 3/4$ to maintain $P6_3/m$ symmetry in the Kurokura rim apatite structure.

the work of this paper into the context of the greater geology of Kurokura. Further studies of this region will help to better characterize the unique formation conditions responsible for formation of apatite at Kurokura.

ACKNOWLEDGMENTS

Support for this work was provided by the National Science Foundation through grant EAR-1249459 to J.M.H. and EAR-0952298 to J.R. Reviews by Francis McCubbin, Jill Pasteris, and an anonymous reviewer improved this manuscript significantly.

REFERENCES CITED

- Armstrong, J.T. (1988) Quantitative analysis of silicate and oxide materials: comparison of Monte Carlo, ZAF, and phi-rho-z procedures. *Microbeam Analysis*, 239–246.
- Boyce, J.W., Liu, Y., Rossman, G.R., Guan, Y., Eiler, J.M., Stolper, E.M., and Taylor, L.A. (2010) Lunar apatite with terrestrial volatile abundances. *Nature Letters*, 466, 466–469.
- Boyce, J.W., Tomlinson, S.M., McCubbin, F.M., Greenwood, J.P., and Treiman, A.H. (2014) The lunar apatite paradox. *Science*, 344, 400–402.
- Donovan, J.J., Snyder, D.A., and Rivers, M.L. (1993) An improved interference correction for trace element analysis. *Microbeam Analysis*, 2, 23–28.
- Donovan, J.J., Lowers, H.A., and Rusk, B.G. (2011) Improved electron probe microanalysis of trace elements in quartz. *American Mineralogist*, 96, 274–282.
- Harada, Z. (1938) Beiträge zur Kenntnis der optischen und chemischen Eigenschaften der Apatite von Kurokura, Kanagawa Präfektur. *Journal of the Faculty of Science, Hokkaido Imperial University. Series 4, Geology and Mineralogy*, 4, 11–16 (in German).
- Hughes, J.M., and Rakovan, J. (2002) The crystal structure of apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH}, \text{Cl})$. In M. Kohn, J.F. Rakovan, and J.M. Hughes, Eds., *Phosphates: Geochemical, Geobiological and Materials Importance*, 48, p. 1–12. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Chantilly, Virginia.
- (2015) Structurally robust, chemically diverse: Apatite and apatite supergroup minerals. *Elements*, 11, 167–172.
- Hughes, J.M., Cameron, M., and Crowley, K.D. (1989) Structural variations in natural F, OH and Cl apatites. *American Mineralogist*, 74, 870–876.
- (1990) Crystal structures of natural ternary apatites: solid solution in the $\text{Ca}_5(\text{PO}_4)_3\text{X}$ (X = F, OH, Cl) system. *American Mineralogist*, 75, 295–304.
- Hughes, J.M., Nekvasil, H., Ustunisik, G., Lindsley, D.H., Coraor, A.E., Vaughn,

- J., Phillips, B., McCubbin, F.M., and Woerner, W.R. (2014a) Solid solution in the fluorapatite-chlorapatite binary system: High-precision crystal structure refinements of synthetic F-Cl apatite. *American Mineralogist*, 99, 369–376.
- Hughes, J.M., Heffernan, K.M., Goldoff, B., and Nekvasil, H. (2014b) Fluor-chlorapatite, devoid of OH, from the Three Peaks Area, Utah: The first reported structure of natural fluor-chlorapatite. *Canadian Mineralogist*, 52, 643–652.
- Hughes, J.M., Harlov, D.H., Kelly, S.R., Rakovan, J., and Wilke, M. (2016) Solid solution in the apatite OH-Cl binary system: compositional dependence of solid solution mechanisms in calcium phosphate apatites along the Cl-OH binary. *American Mineralogist*, 101, 1783–1791.
- Jenkins, H.D.B., and Thakur, K.P. (1979) Reappraisal of thermochemical radii for complex anions. *Journal of Chemical Education*, 56, 576–577.
- Mackie, P.E., and Young, R.A. (1974) Fluorine-chlorine interaction in fluor-chlorapatite. *Journal of Solid State Chemistry*, 11, 319–329.
- McCubbin, F.M., and Jones, R.H. (2015) Extraterrestrial apatite: Planetary geochemistry to Astrobiology. *Elements*, 11, 183–188.
- McCubbin, F.M., Steele, A., Hauri, E.H., Nekvasil, H., Yamashita, S., and Hemley, R.J. (2010) Nominally hydrous magmatism on the Moon. *Proceedings of the National Academy of Science*, 107, 11,223–11,228.
- McCubbin, F.M., Vander Kaaden, K.E., Tartese, R., Boyce, J.W., Mikhail, S., Whitson, E.S., Bell, A.S., Anand, M., Franchi, I.A., Wang, J.H., and Hauri, E.H. (2015) Experimental investigation of F, Cl, and OH partitioning between apatite and Fe-rich basaltic melt at 1.0–1.2 GPa and 950–1000 °C. *American Mineralogist*, 100, 1790–1802.
- Pasteris, J.D., Yoder, C.H., and Wopenka, B. (2014) Molecular water in nominally unhydrated carbonated hydroxylapatite: The key to a better understanding of bone mineral. *American Mineralogist*, 99, 16–27.
- Piccoli, P.M., and Candela, P.A. (2002) Apatite in igneous systems. In M. Kohn, J.F. Rakovan, and J.M. Hughes, Eds., *Phosphates: Geochemical, Geobiological and Materials Importance*, 48, p. 255–292. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Chantilly, Virginia.
- Rakovan, J., and Pasteris, J.D. (2015) A technological gem: Materials, medical, and environmental mineralogy of apatite. *Elements*, 11, 195–200.
- Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, A64, 112–122.
- Stock, M.J., Humphreys, M.C.S., Smith, V.C., Johnson, R.D., Pyle, D.M., and EIMF (2015) New constraints on electron beam induced halogen migration in apatite. *American Mineralogist*, 100, 281–293.
- Stormer, J.C., and Carmichael, I.S.E. (1971) Fluorine-hydroxyl exchange in apatite and biotite: A potential igneous geothermometer. *Contributions to Mineralogy and Petrology*, 31, 121–131.
- Stormer, J.C., Pierson, M.L., and Tacker, R.C. (1993) Variation of F and Cl X-ray intensity due to anisotropic diffusion in apatite during electron microprobe analysis. *American Mineralogist*, 78, 641–648.
- Webster, J.D., and Piccoli, P.M. (2015) Magmatic apatite: A powerful, yet deceptive, mineral. *Elements*, 11, 167–172.
- Yardley, B.W.D. (1985) Apatite composition and the fugacities of HF and HCl in metamorphic fluids. *Mineralogical Magazine*, 49, 77–79.

MANUSCRIPT RECEIVED APRIL 25, 2016

MANUSCRIPT ACCEPTED DECEMBER 3, 2016

MANUSCRIPT HANDLED BY GREGORY DUMOND