The location of Mn and Fe in axinite-(Fe) from Nandan, China determined by anomalous X-ray scattering (AXS)

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The distribution of Mn and Fe in axinite-(Fe) from Nandan, China, with the structural formula $\text{Ca}_2(\text{Fe}_{0.565}\text{Mn}_{0.33}\text{Mg}_{0.08}\text{Ca}_{0.025})(\text{Al}_{1.94}\text{Fe}_{0.06})\text{Si}_4\text{BO}_{15}(\text{OH})$, $Z = 2$, space group $P\bar{1}$, $a = 7.1488(4) \text{ \AA}$, $b = 9.1970(4) \text{ \AA}$, $c = 8.9688(3) \text{ \AA}$, $\alpha = 91.708(6)^\circ$, $\beta = 98.099(6)^\circ$, and $\gamma = 77.201(5)^\circ$, was determined by anomalous X-ray scattering measurements at Mn and Fe K -absorption edges. The elemental distribution map of Mn obtained by AXS analysis indicates the residence of Mn at the Y site. Conversely, the elemental map of Fe shows the location of Fe at both the Y and $Z1$ sites. XANES analysis clarifies the progressive incorporation of Fe^{3+} with decreasing Al content in axinite-(Fe). These experimental results readily suggest the substitution of Al^{3+} by Fe^{3+} at the $Z1$ site.

Keywords: Axinite, XAFS, Anomalous X-ray scattering

INTRODUCTION

The axinite group minerals typically occur in skarn and other contact metamorphic rocks with B-rich and relatively Al-poor environments (e.g., Grew, 1996). The general formula, $(\text{Ca}, \text{Mn})_2(\text{Fe}, \text{Mn}, \text{Mg})\text{Al}_2\text{Si}_4\text{BO}_{15}(\text{OH})$, was proposed by Sanero and Gottardi (1968) and later revised by Lumpkin and Ribbe (1979) and Andreozzi et al. (2004). In this paper, we utilize the site nomenclature according to the generalized structural formula: $^{\text{VI}}[\text{X}1, \text{X}2, \text{Y}, \text{Z}1, \text{Z}2]_5^{\text{IV}}[\text{T}1, \text{T}2, \text{T}3, \text{T}4, \text{T}5]\text{O}_{15}(\text{O}, \text{OH})$, where superscript VI and IV are coordination numbers; $\text{X}1 = \text{Ca}$, $\text{X}2 = \text{Ca}$, $\text{Y} = \text{Fe}^{2+}$, Mn^{2+} , Mg , $\text{Z}1 = \text{Al}$, Fe^{3+} , $\text{Z}2 = \text{Al}$, Fe^{3+} , $\text{T}1\text{--T}4 = \text{Si}$, and $\text{T}5 = \text{B}$. The three kinds of end-members for axinite minerals are classified according to the dominant cation at the Y site. Axinite-(Fe), axinite-(Mn), and axinite-(Mg) indicate the most dominant Fe, Mn, and Mg at the Y site, respectively. Tinzenite, with $2 \leq \text{Ca} \leq 4 \text{ apfu}$, prefers the location of Mn at both the $X2$ and Y sites (Basso et al., 1973; Belokoneva et al., 1997, 2001).

The crystal structure of axinite was determined by Takéuchi et al. (1974), and the structural details were well

demonstrated by Basso et al. (1973). Understanding the crystallographic location of transition metal elements is of great interest in the axinite group of minerals, since the distribution of Mg, Mn, and Fe is a key to classify the minerals. According to a variety of studies on the solid-solutions of axinite-(Mn) and axinite-(Fe), divalent iron Fe^{2+} and manganese Mn^{2+} are located at the Y site, whereas trivalent iron Fe^{3+} prefers the smaller $Z1$ site (Andreozzi et al., 2000a, 2004). The reports also demonstrate that an increase in the Mn content encourages the progressive incorporation of Fe^{3+} at the $Z1$ site. The chemical analysis and corresponding results of the ordinary single crystal X-ray diffraction well support above discussions, nevertheless direct evidence with respect to the distribution of Mn and Fe in the axinite structure has not been reported.

In this paper, we demonstrate the distribution of Mn and Fe in axinite-(Fe) from Nandan Country, China using the results of X-ray absorption fine structure (XAFS) and anomalous X-ray scattering (AXS). The results of ordinary single-crystal X-ray diffraction assisted by the structural information around Mn and Fe are also discussed.

EXPERIMENTAL

The present axinite-(Fe) specimen found at Nandan

Table 1. Chemical compositions of three axinite-(Fe) samples

	Nandan (Nan-C)	Obira (Obi-J)	Khapalu (Kha-P)
CaO (wt%)	19.68-20.00	18.04-20.20	19.69-20.40
MnO	3.43-4.66	1.33-9.51	2.42-3.41
FeO	7.42-8.29	3.61-9.57	7.09-7.94
MgO	0.39-0.90	0.14-1.14	0.63-1.66
Al ₂ O ₃	17.06-17.52	15.68-18.26	16.92-18.39
SiO ₂	42.81-43.72	41.44-43.25	42.51-45.95
<i>apfu</i> [$\Sigma(\text{Ca}+\text{Mn}+\text{Fe}+\text{Mg}+\text{Al}) = 10$]			
Ca	4.05(3)	3.99(1)	4.06(2)
Mn	0.66(2)	0.67(5)	0.48(2)
Fe	1.25(2)	1.28(3)	1.19(2)
Mg	0.16(2)	0.18(1)	0.28(3)
Al	3.88(1)	3.87(2)	3.99(2)
Si	8*	8*	8*

* Fixed (see text).

County, Hechi Prefecture, Guangxi Zhuang Autonomous Region, China (Nan-C), consists of clove-brown-colored crystals with the typical axe-shaped habits. An electron probe micro-analyzer (EPMA: JEOL JXA-8530v at the University of Tokyo) was employed for the chemical analysis. The results are listed in Table 1, together with those for axinite samples from Obira mine, Bungo-Ohno City, Oita Prefecture, Japan (Obi-J) and Khapalu, Ganache District, Gilgit-Baltistan, Pakistan (Kha-P). Among the examined elements, the amounts of Na₂O, K₂O, and TiO₂ were lower than their respective detection limits. No further analysis of the components of B₂O₃ and H₂O was performed in this study.

Transmission XAFS spectra of Mn and Fe *K*-absorption edges were measured at BL-7C, Institute of Material Structure Science (IMSS), High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The X-rays were monochromatized with a Si (111) double-crystal monochromator. We also measured the spectrum for Mn²⁺ (rhodonite MnSiO₃, and chemical reagent MnO), Mn³⁺ (chemical reagent Mn₂O₃), Fe²⁺ (ilmenite FeTiO₃ and chemical reagent FeO), and Fe³⁺ (chemical reagent Fe₂O₃), respectively. The corresponding XANES spectra were extracted from the measured spectra using the Athena and Artemis software package (Ravel and Newville, 2005).

The anomalous X-ray scattering (AXS) study at Mn and Fe *K*-absorption edges was performed at BL-6C, IMSS. Intensity data were collected using a horizontal-type four circle diffractometer (Rigaku AFC-5). A pair of incident energies, which correspond to 25 eV and 150 eV below each *K*-absorption edge (Mn, 6539 eV; Fe, 7112 eV), were employed for the present measurements. These energies were tuned using a double-crystal Si (111) monochromator. The monochromatic incident beam was cir-

cularly polarized by a transmission-type phase retarder of (001) diamond (Hirano et al., 1995). After Lorentz and polarization corrections, an absorption correction was performed based on the size of the specimen while referring to the measured ψ -scan data. Linear absorption coefficients for the X-ray energies employed in this AXS study were calculated by using the theoretically calculated mass absorption coefficients (Waseda, 1984). The detailed procedure for AXS analysis has been well described in previous studies (Wulf, 1990; Sugiyama et al., 2010; Togashi et al., 2011). 804 and 794 reflection pairs in the full reciprocal space up to $\sin\theta/\lambda = 0.44$ were measured at the Mn and Fe *K*-absorption edges, respectively, and employed for the present data processing.

Ordinary single-crystal X-ray diffraction using MoK α radiation was also performed in this study. Intensity measurement was carried out using an X-ray diffractometer equipped with an imaging plate and a conventional X-ray tube and Lorentz, polarization and absorption corrections were conducted (Rigaku R-Axis RAPID). Scattering factors for neutral atoms and anomalous dispersion coefficients were adopted from Volume C of the International Tables for Crystallography (1992). The least-squares refinement was carried out using the software program SHELXL (Sheldrick, 2008) implemented in WinGX (Farrugia, 2012). Detailed information on the data collection is listed in Table 2.

STRUCTURE ANALYSIS

The crystal structure of axinite is described as an alternation of a tetrahedral layer and octahedral layer in Figure 1 (Takéuchi et al., 1974; Andreozzi et al., 2000b). A tetrahedral layer is composed of isolated B₂Si₈O₃₀ [*T*₅₂(*T*₁, *T*₂, *T*₃, *T*₄)₈O₃₀] planar units, where the two kinds of di-silicate groups of *T*₁*T*₂O₇ and *T*₃*T*₄O₇ are connected by two *T*₅ tetrahedra. Another octahedral layer consists of a six-fold finite chain of octahedra with a sequence of *Y*-*Z*₁-*Z*₂-*Z*₁-*Y* linked by heavily distorted octahedra around *X*₁ and *X*₂, filled by Ca with relatively large ionic radii. The positional parameters given by Andreozzi et al. (2004) were used as starting parameters for a full-matrix least-squares refinement. As for the octahedral sites, *X*₁ and *X*₂ sites are modeled by the full occupation of Ca, the *Y* site is modeled by the mixed occupation Mg/Fe, and *Z*₁ and *Z*₂ are modeled by Al. *T*₁, *T*₂, *T*₃, and *T*₄ were modeled by the full occupation of Si, and *T*₅ was fully occupied by B. The obtained structural parameters gave average distances of between 1.62 and 1.63 Å for the tetrahedral *T*₁, *T*₂, *T*₃, and *T*₄ sites. This result readily supports the full occupation of Si at these four tetrahedral sites, together with the almost stoichiometric silicon for

Table 2. Crystal data and structural analysis summary of axinite-(Fe) from Nan-C

Structural model	$\text{Ca}_2(\text{Fe}_{0.565}\text{Mn}_{0.33}\text{Mg}_{0.08}\text{Ca}_{0.025})(\text{Al}_{1.94}\text{Fe}_{0.06})\text{Si}_4\text{BO}_{15}(\text{OH})$ ($Z = 2$)
Wavelength	0.71069 Å
Device	Rigaku R-Axis RAPID
Method	Oscillation
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell constants	$a = 7.1488(4)$ Å, $\alpha = 91.708(6)^\circ$ $b = 9.1970(4)$ Å, $\beta = 98.099(6)^\circ$ $c = 8.9688(3)$ Å, $\gamma = 77.201(5)^\circ$
Volume	$569.29(4)$ Å ³
Density (calculated)	3.317 Mg/m ³
Absorption coefficient	2.816 mm ⁻¹
Theta range	3.23 to 30.50°
Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 13$, $-12 \leq l \leq 12$
Measured reflections	7131
$R_{\text{int}}/R_{\text{sigma}}$	0.0362/0.0279
Data/parameters	3431/236
Goodness of fit in F^2	1.23
Extinction parameter	0.0160(17)
R indices $I > 2$	$R_1 = 0.0319$, $wR_2 = 0.0852^*$
R indices (all data)	$R_1 = 0.0431$, $wR_2 = 0.0885^*$
Diff. peak and hole	0.797 and -0.815 e/Å ³

* $w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.1257P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Figure 1. The crystal structure of axinite with (a) a tetrahedral layer of a $T5_2(T1, T2, T3, T4)_8O_{30}$ planar unit and (b) an octahedral sequence of $Y-Z1-Z2-Z2-Z1-Y$ with $X1$ and $X2$ (Dowty, 2006). Color version is available online from <https://doi.org/10.2465/jmps.190110>.

Table 3. Atomic positions and equivalent displacement parameters of axinite-(Fe) from Nand-C

Site	Occupation	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
<i>X</i> 1	Ca	0.7461(1)	0.3481(1)	0.3953(1)	0.0096(1)
<i>X</i> 2	Ca	0.1827(1)	0.1007(1)	0.0842(1)	0.0100(1)
<i>Y</i>	Fe _{0.565} Mn _{0.33} Mg _{0.08} Ca _{0.025}	0.7683(1)	0.5907(1)	0.1122(1)	0.0102(1)
<i>Z</i> 1	Al _{0.94} Fe _{0.06}	0.0525(1)	0.8011(1)	0.2537(1)	0.0055(2)
<i>Z</i> 2	Al	0.3519(1)	0.9362(1)	0.4210(1)	0.0045(1)
<i>T</i> 1	Si	0.2115(1)	0.4502(1)	0.2350(1)	0.0062(2)
<i>T</i> 2	Si	0.2193(1)	0.2747(1)	0.5236(1)	0.0056(2)
<i>T</i> 3	Si	0.6995(1)	0.2558(1)	0.0116(1)	0.0061(2)
<i>T</i> 4	Si	0.6413(1)	0.0192(1)	0.2302(1)	0.0057(2)
<i>T</i> 5	B	0.4615(4)	0.6349(3)	0.2866(3)	0.0063(5)
<i>O</i> 1	O	0.0555(3)	0.6034(2)	0.1900(2)	0.0086(4)
<i>O</i> 2	O	0.2328(3)	0.3385(2)	0.0967(2)	0.0113(4)
<i>O</i> 3	O	0.4193(3)	0.4871(2)	0.3123(2)	0.0083(4)
<i>O</i> 4	O	0.1364(3)	0.3735(2)	0.3708(2)	0.0120(4)
<i>O</i> 5	O	0.0218(3)	0.2421(2)	0.5637(2)	0.0086(4)
<i>O</i> 6	O	0.3269(3)	0.3793(2)	0.6455(2)	0.0077(4)
<i>O</i> 7	O	0.3806(3)	0.1274(2)	0.4957(2)	0.0071(4)
<i>O</i> 8	O	0.5371(3)	0.3436(2)	0.8770(2)	0.0086(4)
<i>O</i> 9	O	0.8765(3)	0.1544(2)	0.9338(2)	0.0077(4)
<i>O</i> 10	O	0.7692(3)	0.3660(2)	0.1395(2)	0.0108(4)
<i>O</i> 11	O	0.6039(3)	0.1347(2)	0.0871(2)	0.0114(4)
<i>O</i> 12	O	0.4365(3)	0.9816(2)	0.2439(2)	0.0079(4)
<i>O</i> 13	O	0.7212(3)	0.0996(2)	0.3844(2)	0.0076(4)
<i>O</i> 14	O	0.7939(3)	0.8748(2)	0.1776(2)	0.0088(4)
<i>O</i> 15	O	0.3255(3)	0.7469(2)	0.3550(2)	0.0065(4)
<i>O</i> 16	O	0.0972(3)	0.9955(2)	0.3228(2)	0.0079(4)
H16*	H	0.0071	1.0404	0.3644	0.012

* See text

Nan-C. Additionally, the averaged *T*5-O bond length (1.486 Å) could be a sufficient reason for the full occupation of B at the *T*5 site. The converged isotropic displacement parameter of the *Z*1 site was obviously smaller than that of the *Z*2 site. This may indicate the possible distribution of a heavy metal cation at the *Z*1 site. Finally, the structural information obtained by AXS and XANES analysis allows us to make a final structural model, and the full-matrix least-squares refinement of all parameters converged at *R* = 0.0319 for the observed 3016 reflections. The anisotropic displacement model was introduced for non-hydrogen atoms, and the isotropic displacement parameter of *U*_{iso}(H16) = 1.5*U*_{eq}(O16) was used for H16 in the refinement. Final atomic coordinates, together with the equivalent displacement parameters and the anisotropic displacement parameters, are shown in Tables 3 and 4, respectively.

RESULTS AND DISCUSSION

Chemical composition of axinite-(Fe) sample

The chemical composition of Nan-C is relatively homogeneous in comparison with the other two axinite-(Fe)

samples, and its octahedral sites are occupied by $3.98 < \text{Ca} < 4.08$, $1.18 < \text{Fe} < 1.33$, $0.55 < \text{Mn} < 0.75$, $3.85 < \text{Al} < 3.91$, and $0.11 < \text{Mg} < 0.25$, and a negligible amount of Ti, Na, and K (all in *apfu*). Because the ordinary single-crystal structural analysis of Nan-C indicates the full occupation of Si at the *T*1, *T*2, *T*3, and *T*4 sites and the stoichiometric distribution of B at the *T*5 site, the present analysis normalizes the number of each element in the octahedral sites to meet the equation $\Sigma_{\text{apfu}}(\text{Ca} + \text{Mn} + \text{Fe} + \text{Al} + \text{Mg}) = 10$. The averaged numbers of these cations are listed in Table 1 together with their standard deviations in brackets. The structural formula of axinite-(Fe) for Nan-C could be described as $\text{Ca}_2(\text{Fe}_{0.565}\text{Mn}_{0.33}\text{Mg}_{0.08}\text{Ca}_{0.025})(\text{Al}_{1.94}\text{Fe}_{0.06})\text{Si}_4\text{BO}_{15}(\text{OH})$ with a Fe^{3+}/Fe ratio of 0.096. The formula indicates the possible distribution of Ca at the *Y* site; nevertheless, the present authors maintain a view that the experimental error for the obtained CaO content led to this structural formula.

Valence states of Mn and Fe

The measured XANES spectra for Mn and Fe *K*-absorption edges are shown in Figures 2a and 2b, respectively. The XANES spectra of Mn for the three axinite-(Fe)

Table 4. Anisotropic displacement parameters of axinite-(Fe) from Nan-C

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
X1	0.0107(3)	0.0082(3)	0.0089(3)	0.0019(2)	-0.0007(2)	-0.0012(2)
X2	0.0106(3)	0.0098(3)	0.0092(3)	0.0024(2)	-0.0028(2)	-0.0036(2)
Y	0.0074(2)	0.0137(2)	0.0100(2)	0.0028(2)	0.0008(2)	-0.0028(2)
Z1	0.0059(3)	0.0059(3)	0.0050(3)	0.0004(2)	0.0007(2)	-0.0016(3)
Z2	0.0049(4)	0.0047(4)	0.0043(4)	-0.0001(3)	0.0004(3)	-0.0017(3)
T1	0.0071(3)	0.0057(3)	0.0057(3)	0.0007(2)	-0.0002(2)	-0.0016(3)
T2	0.0051(3)	0.0057(3)	0.0059(3)	0.0002(2)	0.0005(2)	-0.0013(3)
T3	0.0064(2)	0.0065(2)	0.0051(2)	0.0012(1)	0.0006(1)	-0.0009(2)
T4	0.0053(3)	0.0065(3)	0.0054(3)	0.0005(2)	0.0009(2)	-0.0016(3)
T5	0.0065(13)	0.0070(13)	0.0056(13)	0.0002(9)	0.0003(9)	-0.0021(10)
O1	0.0094(9)	0.0059(9)	0.0100(9)	0.0003(7)	0.0001(7)	-0.0015(7)
O2	0.0138(10)	0.0099(10)	0.0103(10)	-0.0020(7)	0.0020(7)	-0.0026(8)
O3	0.0077(9)	0.0065(9)	0.0107(9)	0.0014(7)	-0.0003(7)	-0.0022(7)
O4	0.0112(10)	0.0151(10)	0.0103(10)	0.0060(7)	-0.0001(7)	-0.0044(8)
O5	0.0070(9)	0.0121(10)	0.0074(9)	0.0015(7)	0.0012(6)	-0.0033(7)
O6	0.0054(9)	0.0079(9)	0.0099(9)	-0.0021(7)	-0.0001(6)	-0.0025(7)
O7	0.0055(9)	0.0073(9)	0.0086(9)	0.0001(7)	0.0011(6)	-0.0013(7)
O8	0.0089(9)	0.0095(9)	0.0067(9)	0.0016(7)	0.0019(7)	0.0002(7)
O9	0.0074(9)	0.0087(9)	0.0063(9)	-0.0002(7)	0.0011(6)	-0.0003(7)
O10	0.0122(10)	0.0127(10)	0.0076(9)	-0.0016(7)	0.0004(7)	-0.0033(8)
O11	0.0120(10)	0.0127(10)	0.0104(10)	0.0041(7)	0.0015(7)	-0.0042(8)
O12	0.0065(9)	0.0103(9)	0.0074(9)	0.0010(7)	0.0007(6)	-0.0027(7)
O13	0.0081(9)	0.0096(9)	0.0060(9)	-0.0006(7)	0.0012(6)	-0.0037(7)
O14	0.0081(9)	0.0109(10)	0.0073(9)	-0.0011(7)	0.0016(7)	-0.0013(7)
O15	0.0062(9)	0.0064(9)	0.0068(9)	-0.0005(6)	0.0010(6)	-0.0011(7)
O16	0.0071(9)	0.0089(9)	0.0075(9)	-0.0012(7)	0.0021(7)	-0.0004(7)

Figure 2. (a) Mn and (b) Fe K-edge XANES spectra of axinite-(Fe) together with standard samples. The positions of the absorption edges shown in brackets were defined as half the normalized edge jump.

Figure 3. The Mn distribution maps at (a) $z = 0.11$ and (b) $z = 0.26$ analyzed by AXS measurement at the Mn K -absorption edge. The contours are drawn at an interval of $0.14 \text{ e}/\text{\AA}^3$: negative contours are in broken lines, while zero-contours are omitted.

samples are almost superimposed, and their edge positions are similar to those of rhodonite and MnO. This result readily suggests that most of the Mn atoms in axinite-(Fe) are in a divalent state and provides a reasonable agreement with the general discussion of Mn in the axinite structure. In the case of Fe-XANES, the edge positions for the axinite-(Fe) samples are located near those of ilmenite and FeO, suggesting the overall preference for divalent Fe^{2+} . However, the edge positions shift toward the higher energy side in the order Kah-P, Obi-J, and Nan-C. This shift suggests an increase in the Fe^{3+} fraction as a substitute for Al^{3+} . The relationship between Fe^{3+} and Al in the axinite structure is attributed well to the discussion found in the previous literature (Andreozzi et al., 2000a, 2004).

Distribution map of Mn and Fe obtained by AXS measurements

Classical single-crystal X-ray diffraction is one of the most powerful tools for determining the atomic distribution in crystals. However, the discrimination of Mn and Fe is very difficult only using ordinary X-ray diffraction because the atomic scattering factors for Mn and Fe are similar to each other. Anomalous X-ray scattering at energies near the absorption edge is one way to circumvent this difficulty by analyzing an appropriate difference in the measured structure factors (Wulf, 1990; Sugiyama et al., 2010; Togashi et al., 2011). Figures 3a and 3b show

the distribution map for Mn at $z = 0.11$ and 0.26 obtained by Fourier synthesis of the difference in structure factors measured at the Mn K -absorption edge. The distribution of Mn can be observed at the Y site, whereas it is not found at the Z1 site. These feature simply the preferred distribution of Mn at the Y site. Figures 4a and 4b show the distribution map for Fe at $z = 0.11$ and 0.26 obtained by Fourier synthesis of the difference in structure factor measured at the Fe K -absorption edge. Although the anomalous dispersion terms of Mn just below the Fe K -absorption edge more or less contribute to the distribution map of Fe, the effect is expected to produce a negative peak at the Y site where Mn resides. Therefore, the distinct positive peaks at the Y site and Z1 site definitely imply the distribution of Fe at these sites. It should be noted that we could find no significant contribution at the X2 site in the distribution map of Mn and at the Z2 site in the distribution map of Fe. These findings allow us to make a superior structural model in which the X2 and Z2 sites are fully occupied by Ca and Al, respectively.

Single-crystal X-ray diffraction

Thanks to the structural information acquired from EX-AFS and AXS measurements together with the ordinary single crystal X-ray diffraction, the structural refinement could be performed using the reasonable structural model with the complete occupancy of the T1 to T4 sites by Si, of the T5 site by B, of the X1 and X2 sites by Ca, and of

Figure 4. The Fe distribution maps at (a) $z = 0.11$ and (b) $z = 0.26$ analyzed by AXS measurement at the Fe K -absorption edge. The contours are drawn at an interval of $0.14 \text{ e}/\text{\AA}^3$; negative contours are in broken lines, while zero-contours are omitted.

Table 5. Interatomic distances ($\text{\AA}$) and site volume ($\text{\AA}^3$) of tetrahedral sites

	<i>T</i> 1	<i>T</i> 2	<i>T</i> 3	<i>T</i> 4	<i>T</i> 5
O1	1.613(2)				
O2	1.589(2)				
O3	1.649(2)				1.487(3)
O4	1.635(2)	1.631(2)			
O5		1.597(2)			
O6		1.655(2)			1.528(3)
O7		1.611(2)			
O8			1.645(2)		1.488(3)
O9			1.626(2)		
O10			1.608(2)		
O11			1.637(2)	1.645(2)	
O12				1.599(2)	
O13				1.640(2)	
O14				1.626(2)	
O15					1.439(3)
O16					
Average	1.622	1.624	1.629	1.628	1.486
Volume	2.18	2.17	2.21	2.20	1.67

Table 6. Interatomic distances ($\text{\AA}$) and volume ($\text{\AA}^3$) of octahedral sites

	<i>X</i> 1	<i>X</i> 2	<i>Y</i>	<i>Z</i> 1	<i>Z</i> 2
O1			2.101(2)	1.887(2)	
O2		2.290(2)	2.000(2)		
O3	2.427(2)				
O4					
O5	2.348(2)			1.871(2)	
O6	2.473(2)		2.358(2)		
O7					1.907(2)
					1.919(2)
O8			2.147(2)		
O9		2.363(2)			
		2.472(2)		1.905(2)	
O10	2.336(2)		2.087(2)		
O11					
O12		2.242(2)			1.867(2)
O13	2.330(2)				1.948(2)
O14		2.398(2)	2.701(2)		
O15	2.585(2)			1.995(2)	1.862(2)
O16		2.578(2)		1.953(2)	1.878(2)
Average	2.417	2.390	2.232	1.922	1.897
Volume	15.50	15.39	13.30	9.24	9.04

the Z2 site by Al. The constituents for the *Y* site and Z1 site were fixed as $\text{Fe}_{0.565}\text{Mn}_{0.33}\text{Mg}_{0.08}\text{Ca}_{0.025}$ and $\text{Al}_{0.94}\text{Fe}_{0.06}$, respectively, using the chemical information listed in Table 1. Because the structural features of Nan-C are similar to those of axinite in Figure 1, the detailed interatomic distances associated with the elemental distribution are discussed in this paper. Interatomic distances for octahedral and tetrahedral sites are summarized in Tables 5 and 6, along with calculated site volumes.

As shown in Figure 1, the *X*1 and *X*2 sites for Ca indicate a significant distortion, and the geometry of *X*1 could be described as a trigonal-antiprism rather than the common octahedron, in particular (Takéuchi et al., 1974). The *X*2 site is smaller than the *X*1 site, and the excess amount of Mn was suggested to reside at this site (Basso et al., 1973; Belokoneva et al., 1997, 2001). However, the

present EPMA analysis of Nan-C suggests the full occupation of Ca at the *X2* site, and the introduction of a chemically disordered model for Ca/Mn at this site did not improve the results of the structural refinement. This conclusion is also supported by AXS analysis with respect to the Mn distribution.

The averaged *Y*-O distance is 2.232 Å, and the longest *Y*-O(14) bond is 2.701 Å. This heavily distorted feature of octahedra is common to every axinite structure. The averaged distance is associated with the effective ionic radius of constituent elements, and the mean *Y*-O distance (2.232 Å) and polyhedron volume at the *Y* site (13.30 Å³) of Nan-C are larger than that of the end-member axinite-(Mg) (12.56 Å³) (Andreozzi et al., 2000b). Similarly, the averaged *Y*-O distance indicates close similarity with those of axinite-(Fe) No.30 and No.35, with the *Y* site filled by Fe_{0.67}Mn_{0.205}Mg_{0.12}Al_{0.005} and Fe_{0.425}Mn_{0.37}Mg_{0.195}, respectively (Andreozzi et al., 2004). The unit-cell parameters in Table 2 are close to the published values for the typical axinite-(Fe) samples, indicating a relatively smaller volume in comparison with axinite-(Mn). This is also attributed to the presence of smaller divalent cations of Fe and Mg at the *Y* site of axinite-(Fe) (Andreozzi et al., 2000a, 2004).

The averaged distances for the *Z1* and *Z2* sites are 1.922 Å and 1.897 Å, respectively. Because the averaged size of 1.906 Å and 1.894 Å with full occupation of Al sites were reported in axinite-(Mg) (Andreozzi et al., 2000b), the larger averaged distance and the corresponding volume of the *Z1* site for Nan-C are consistent with the partial occupation of Fe at the *Z1* site. It may be noted that further structural refinement with a mixed occupation model of Al/Fe at the *Z2* site suggested no significant occupation of Fe at the *Z2* site.

The averaged distances for the *T1* to *T4* sites with Si range between 1.622 and 1.628 Å, corresponding well with the well-compiled data reported by Andreozzi et al. (2004). Similarly, no significant features those suggest the occupation of Al, Si or Fe could be found in the local coordination features around the *T5* site. These structural features on tetrahedral sites support the stoichiometric distribution of Si and B in the structure of axinite-(Fe) of Nan-C.

It should be added that a hydrogen position of H16 was safely determined in difference Fourier maps. H16 is bonded to O16 at 0.82 Å and makes a hydrogen bridge with O13 with the distance of 2.77 Å (Takéuchi et al., 1974; Swinnea et al., 1981; Belokoneva et al., 1997; Andreozzi et al., 2000b).

CONCLUDING REMARKS

The distribution of Mn and Fe in axinite-(Fe) from Nan-

dan County, Hechi Prefecture, Guangxi Zhuang Autonomous Region, China was investigated by the two advanced analytical methods of XANES and AXS. The XANES spectra of axinite-(Fe) samples at Mn and Fe *K*-absorption edges indicate the overall preference for Mn²⁺ and Fe²⁺; however, the edge positions of the Fe *K*-absorption edge shift toward the high-energy side, in particular. This information and the results of EPMA allow us to suggest that the fractional Fe³⁺ content of axinite-(Fe) increases as the Al content decreases. The elemental distribution maps of Mn and Fe obtained by AXS analysis clearly indicate the distribution of Mn at the *Y* site and of Fe both at the *Y* site and *Z1* site. The structural model with direct observation with respect to the distribution of Mn and Fe was subsequently employed for single-crystal X-ray diffraction, and the converged results were discussed along with previous data. The present authors would like to stress here that single-crystal AXS analysis is concluded to be a very powerful tool for obtaining direct structural information concerning interesting elements, even though the next-neighboring atoms coexist in the structure.

ACKNOWLEDGMENTS

This research project was performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2016G571).

SUPPLEMENTARY MATERIAL

Color version of Figure 1 is available online from <https://doi.org/10.2465/jmps.190110>.

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Manuscript received January 10, 2019

Manuscript accepted January 6, 2020

Published online June 13, 2020

Manuscript handled by Takahiro Kuribayashi