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	承認日Date of Approval 2016/09/13 承認者Approver Takanori Hattori 提出日Date of Report 2016/09/13
課題番号 Project No. 2015A0034 実験課題名 Title of experiment Compositional and structural problems of chevkinite 実験責任者名 Name of principal investigator Mariko NAGASHIMA 所属 Affiliation Graduate School of Sciences and Technology for Innovation, Yamaguchi University	装置責任者 Name of responsible person Dr. Takanori Hattori 装置名 Name of Instrument/(BL No.) BL11 実施日 Date of Experiment 2015/10/31 9:00 ~ 2015/11/1 9:00

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)  
 Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form. Natural mineral: Chevkinite (powder) from Cape Ashizuri, Japan and from Haramosh, Pakistan The REE-Fe-Ti-rich silicate with simplified formula $(\text{REE}, \text{Ca})_4\text{Fe}^{2+}(\text{Ti}, \text{Fe}^{3+}, \text{Nb}^{5+})_4\text{Si}_4\text{O}_{22}$ ( $Z = 2$ , monoclinic) The chemical compositions analyzed by electron microprobe analyzer is as follows; $(\text{Ce}_{1.46}\text{La}_{0.93}\text{Ca}_{0.68}\text{Pr}_{0.11}\text{Nd}_{0.35}\text{Sm}_{0.04}\text{Eu}_{0.01}\text{Gd}_{0.11}\text{Th}_{0.14}\text{Y}_{0.06}\text{Dy}_{0.01}\text{U}_{0.01} \square_{0.09})_{\Sigma 4.00}(\text{Ti}_{2.46}\text{Fe}^{2+}_{1.91}\text{Nb}_{0.22}\text{Al}_{0.04}\text{Mg}_{0.02} \square_{0.35})_{\Sigma 5.00}\text{Si}_4\text{O}_{21.06}$ from Cape Ashizuri, Japan and $(\text{Ce}_{1.73}\text{La}_{0.76}\text{Nd}_{0.55}\text{Ca}_{0.48}\text{Gd}_{0.18}\text{Pr}_{0.15}\text{Ba}_{0.05}\text{Sr}_{0.01}\text{Sm}_{0.01}\text{Y}_{0.01}\text{Dy}_{0.01} \square_{0.06})_{\Sigma 4.00}(\text{Ti}_{2.58}\text{Fe}^{2+}_{2.01}\text{Mg}_{0.12}\text{Mn}_{0.07}\text{Al}_{0.03}\text{Cr}_{0.01}\text{Ni}_{0.01}\text{P}_{0.01} \square_{0.16})_{\Sigma 5.00}\text{Si}_4\text{O}_{21.09}$ from Pakistan.
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2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。) Experimental method and results. If you failed to conduct experiment as planned, please describe reasons. <b>Main purpose:</b> This experiment is going to determine the presence of hydrogen atoms and the site occupancies of Ti and Fe in the octahedral sites in order to examine the different interpretations among previous studies. The determination of cation-anion distribution in chevkinite is extremely difficult because of (i) the similar X-ray scattering factors between Fe and Ti, (ii) the presence of the four octahedra M1-M4 (their volume and the deformation of the M2-M4 octahedra are very similar), and (iii) the oxidation states of Fe (both ferrous and ferric irons are present). Furthermore, Zhuming et al. (2008) suggested the partial substitution of hydroxyl group for $\text{O}^{2-}$ in chevkinite-(Ce) from the aegirine-alkali granite, Mianning, China using IR-spectrum and bond-valence sum calculation. However, the presence (atomic position) of H atom was not confirmed. <b>Experimental with BL11:</b> <ul style="list-style-type: none"> <li>• Powder samples contained in V capillary</li> <li>• Measurement condition: 1 atom and room temperature.</li> <li>• Crystal structures were refined with Z-code.</li> </ul> /
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## 2. 実験方法及び結果(つづき) Experimental method and results (continued)

### Result

The data were successfully measured with BL11. The crystal structure obtained from the refined result is shown in Fig. 1. Structural formula is represented as  $A_4M_1M_2M_3M_4(Si_2O_7)_2O_8$ , where  $A = REE^{3+}, Ca, Sr, Th$ ;  $M_1 = Fe^{2+}$ ,  $M_2$  and  $M_3 = Fe^{3+}, Fe^{2+}, Mn, Mg, Zr, Nb$ , and  $M_4 = Ti$  (e.g. Ito and Arem, 1971). Chevkinite group minerals are subdivided into chevkinite- and perrierite-subgroups, which are distinguished with  $\beta$  angle:  $\sim 100^\circ$  (chevkinite) and  $\sim 114^\circ$  (perrierite) (e.g. Hagatty and Mariano, 1983). Crystal structure of chevkinite is characterized by 8- and 10-coordinated large polyhedra (A1 and A2), four octahedra (M1-M4) and  $Si_2O_7$ -disilicate (Fig. 1).

Crystal structures of chevkinite from Ashizuri and Pakistan were refined with space groups  $C2/m$  and  $P2_1/m$ , respectively, on a basis of the results of X-ray single-crystal method.  $R_{wp}$  and  $R_e$ -factors are converged to 6.10% and 3.51% for Ashizuri, and 7.64% and 6.88% for Pakistan, respectively. The cell-parameters and atomic positions obtained from each specimen using X-ray single-crystal method were used as the initial parameters. The refined unit-cell parameters are as follows;  $a=13.439(5)$ ,  $b=5.760(2)$ ,  $c=11.083(4)$ ,  $\beta = 100.692(3)$  for Ashizuri, and  $a = 13.396(4)$ ,  $b = 5.739(2)$ ,  $c = 11.068(3)$ ,  $\beta = 100.622(4)$  (with  $C2/m$  setting) for Pakistan. They are almost consistent with those obtained from X-ray single-crystal method. It was also confirmed that hydroxyl group and  $H_2O$  molecule were NOT present in chevkinite structure. Determined site occupancies in this study is listed in Table 1. The Fe and Ti distributions at M1-M4 were refined using Z-code, whereas the Ca and Ce at A1 and A2 were fixed with the occupancies determined by the X-ray single-crystal method.

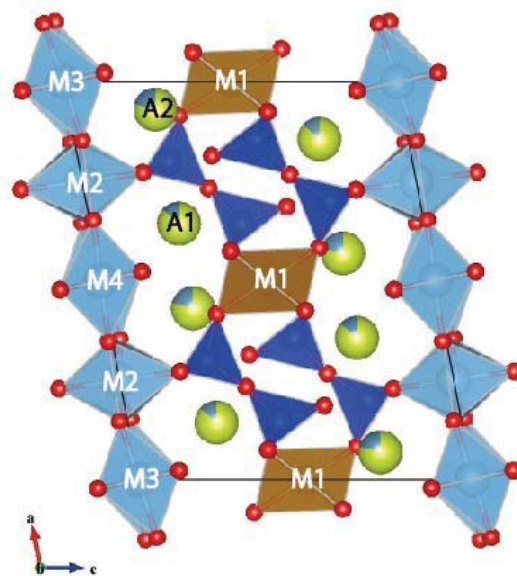


Fig. 1 Crystal structure of chevkinite-group minerals drawn with VESTA3 (Momma and Izumi 2011)

**Table 1. Refined site occupancies of chevkinite specimens**

Site	Ashizuri, Japan	Tangir, Pakistan	Determined by
A1	Ce0.866+Ca0.134	Ce0.900+Ca0.100	X-ray single-crystal method
A2	Ce0.800+Ca0.200	Ce0.836+Ca0.164	X-ray single-crystal method
M1	Fe0.94+Ti0.06	Fe0.87+Ti0.13	TOF neutron
M2	Ti0.67+Fe0.33	Ti0.55+Fe0.45	TOF neutron
M3	Ti0.70+Fe0.30	Ti0.72+Fe0.28	TOF neutron
M4	Ti0.62+Fe0.38	Ti0.87+Fe0.13	TOF neutron

Although the Fe occupancies were determined at M1-M4, the oxidation state of Fe should be considered. As the results of  $^{57}Fe$  Mössbauer spectra,  $Fe^{2+}/total\ Fe$  was 0.70 in Ashizuri and 0.36 in Pakistan. Because the both spectra were composed of five doublets and charge transfer, the assignment of Mössbauer doublets is not straight forward. Two possible site occupancies at M1-M4 of Ashizuri chevkinite can be proposed due to different Mössbauer assignments: (1)  $M_1(Fe^{2+}_{0.94}Ti_{0.06})M_2(Fe^{3+}_{0.33}Ti_{0.67})M_3(Fe^{2+}_{0.16}Fe^{3+}_{0.14}Ti_{0.70})M_4(Fe^{2+}_{0.38}Ti_{0.62})$ , and (2)  $M_1(Fe^{2+}_{0.94}Ti_{0.06})M_2(Fe^{2+}_{0.18}Fe^{3+}_{0.15}Ti_{0.67})M_3(Fe^{3+}_{0.30}Ti_{0.70})M_4(Fe^{2+}_{0.38}Ti_{0.62})$ . The site occupancy of Pakistani chevkinite is  $M_1(Fe^{2+}_{0.87}Ti_{0.13})M_2(Fe^{3+}_{0.415}Ti_{0.55})M_3(Fe^{3+}_{0.28}Ti_{0.72})M_4(Fe^{2+}_{0.13}Ti_{0.87})$ .

This study concluded that chevkinite is anhydrous, and determined Fe-Ti distribution among octahedral M1-M4 in chevkinite. The result in this study contributes to settle a dispute about cation-anion distributions in chevkinite. However, the Mössbauer assignment and site occupancies are still scope for improvement.