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Chevkinite-(Ce) in tuff at Heguri, Boso Peninsula, Chiba Prefecture, Japan

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Abstract Chevkinite-(Ce) occurs in the rhyolitic tuff of the Mineoka group from Boso Peninsula, Chiba Prefecture, Japan. It forms as black tiny crystals less than 100 μm across in association with zircon, quartz, K-feldspar and analcime. Optically, chevkinite-(Ce) is pleochroic in brown and blackish brown. The electron microprobe analysis gave the following empirical formula: $(Ce_{1.57}La_{0.83}Ca_{0.58}Nd_{0.56}Pr_{0.15}Y_{0.09}Th_{0.08}Sm_{0.05}Gd_{0.04}Dy_{0.02})_{\Sigma 3.97}(Ti_{2.74}Fe_{1.84}Al_{0.14}Mg_{0.05}Nb_{0.05}Mn_{0.02})_{\Sigma 4.84}Si_4O_{21.25}F_{0.18}$ on the basis of Si = 4. It is non-metamict and gives sharp X-ray diffractions. The unit cell parameters were refined from data of a single crystal on a 4-circle diffractometer; $a = 13.3949(12)$, $b = 5.7293(8)$, $c = 11.0523(10)$ Å, $\beta = 100.636(7)°$, $V = 833.62(16)$ Å^3 and $Z = 2$. The refinement of crystal structure converged to $R1 = 0.0371$ and w$R2 = 0.1304$ for 1984 independent reflections.

Key words: chevkinite-(Ce), crystal structure, Chiba, Japan, rare-earth

Introduction

Chevkinite-(Ce) is a silicate mineral of rare earth elements (REE), iron and titanium, and is a member of the chevkinite group minerals having general formula $A_4M_5Si_4O_{22}$, where A = larger cations such as REE, Sr, Ca, Th, and M = cations with octahedral coordination such as Ti, Nb, Ta, Zr; Fe, Mg, Mn, Cr. The members of chevkinite group can be classified into two groups with their crystal structures; the chevkinite-type structure in $C2/m$ and the perrierite-type structure in $P2_1/a$. The minor difference between two structures brings very similar powder X-ray diffraction patterns and makes it difficult to identify the mineral species with crystallographic data. An elaborate single crystal diffraction study is necessary to determine the crystal structure type, whereas chevkinite-(Ce) usually occurs in the metamict state giving no or poor X-ray diffraction data.

During our geological survey of the Mineoka group from Boso Peninsula, Chiba Prefecture, Japan, we recognized black fragments in the zircon-bearing heavy sand sample for the dating partitioned from pale green tuff between the shale strata at Heguri, Chiba Prefecture (35°6′13″N, 139°55′44″E). Our mineralogical investigation revealed that the fragments are non-metamict crystalline grains of chevkinite-(Ce).

Occurrence

Chevkinite-(Ce) occurs as euhedral black crystals less than 100 μm across in rhyolitic tuff in association with zircon, quartz, K-feldspar and analcime (Figs. 1 and 2). Monazite-(Ce) and fine particles of sulfides, such as galena and sphalerite, can be observed in addition to the associating minerals. The rhyolitic tuff consists of quartz, K-feldspar and volcanic glass. The almost parts of the glass were altered into analcime. Under the microscope, chevkinite-(Ce) is pleochroic in brown and blackish brown. More than 10 grains of chevkinite-(Ce) could be separated in the heavy liquid from approximate 150 g sample of

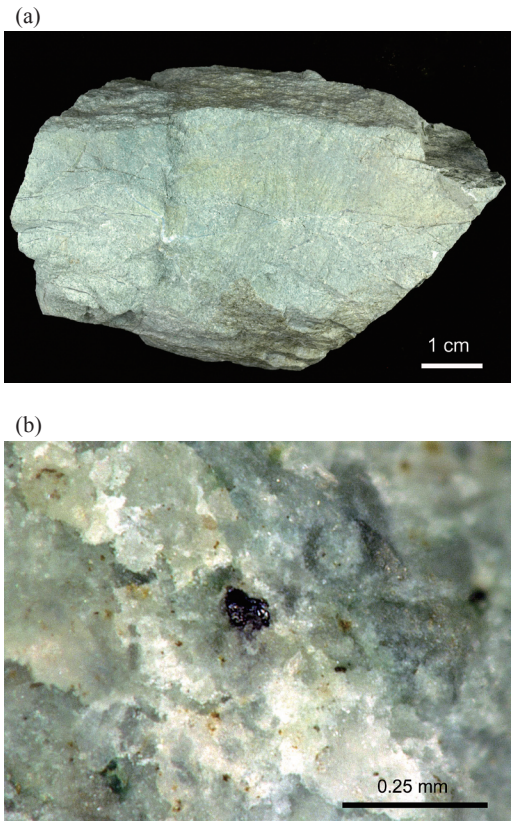

Fig. 1. The appearance of pale green rhyolitic tuff (a) and the close up view of black crystal of chevkinite-(Ce) of the rhyolitic tuff (b).

the rhyolitic tuff. The detailed geological background of chevkinite-(Ce) from rhyolitic tuff is given in Tsutsumi *et al.* (2012).

Chemical Composition

The chemical composition of chevkinite-(Ce) from Heguri was determined by means of a JEOL 8800 electron microprobe analyzer (WDS mode, 15 kV, 20 nA, and 2 μm beam diameter). The analytical standard materials are as follows; $REEP_5O_{14}$ for REE (rare earth elements), ThO_2 for Th, anatase for Ti, fayalite for Fe and Si, sillimanite for Al, forsterite for Mg, columbite for Nb, rhodonite for Mn, CaF_2 for F. The result of chemical analysis with ZAF corrections is given in Table 1. The empirical formula derived from the chemical analysis is $(Ce_{1.57}La_{0.83}Ca_{0.58}Nd_{0.56}Pr_{0.15}Y_{0.09}Th_{0.08}Sm_{0.05}Gd_{0.04}Dy_{0.02})_{\Sigma 3.97}(Ti_{2.74}Fe_{1.84}Al_{0.14}Mg_{0.05}Nb_{0.05}Mn_{0.02})_{\Sigma 4.84}Si_4O_{21.25}F_{0.18}$ on the basis of Si = 4.

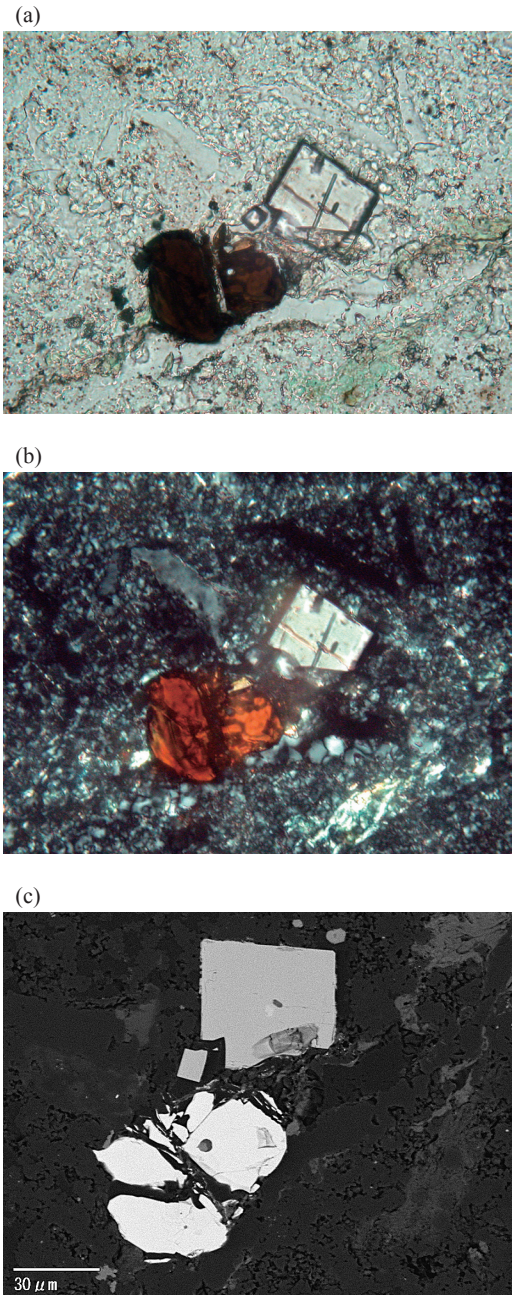

Fig. 2. Photomicrographs [plane polarized light (PPL) (a) and crossed polars (CPL) (b)] and back scattered electron image (c) of chevkinite-(Ce) [brown in PL and pale gray in BSE] and zircon [colorless in PL and gray in BSE] in the rhyolitic tuff.

Table 1. Chemical composition of chevkinite-(Ce) from Heguri.

CaO	2.68	Ca	0.58
Sc_2O_3	0.02	Sc	0.00
ThO_2	1.70	Th	0.08
Y_2O_3	0.81	Y	0.09
La_2O_3	11.24	La	0.83
Ce_2O_3	21.31	Ce	1.57
Pr_2O_3	2.05	Pr	0.15
Nd_2O_3	7.75	Nd	0.56
Sm_2O_3	0.79	Sm	0.05
Gd_2O_3	0.57	Gd	0.04
Dy_2O_3	0.30	Dy	0.02
		Σ*A*	3.97
TiO_2	18.14	Ti	2.74
Nb_2O_5	0.50	Nb	0.05
Ta_2O_5	0.00	Ta	0.00
FeO	10.96	Fe	1.84
MnO	0.14	Mn	0.02
MgO	0.15	Mg	0.05
Al_2O_3	0.58	Al	0.14
		Σ*M* (*BC*)	4.84
SiO_2	19.92	Si	4
F	0.28	F	0.18
O = F	− 0.12		
Total	99.77		

X-ray crystallography

Powder X-ray diffraction data of chevkinite-(Ce) from Heguri were obtained with a 114.6 mm Gandolfi camera. A fragment of chevkinite-(Ce) which was chemically analyzed was picked up from the thin section, and mounted on a glass fiber of 10 μm diameter. The Debye-Sheller ring images were recorded on an imaging plate (IP) in the Gandolfi camera using Ni-filtered Cu$K\alpha$ radiation for a few days. Two exposures for measurement were carried out with and without Si standard material for X-ray diffraction angle calibration. The data were processed with a Fuji BAS-2500 bio-imaging analyser using a computer program written by Nakamuta (1999). The reflections were indexed according to the observed single crystal X-ray diffraction data and

Table 2. The powder X-ray diffraction data of chevkinite-(Ce) from Heguri.

h	*k*	*l*	I/I_0	$d_{obs.}$	$d_{calc.}$	*h*	*k*	*l*	I/I_0	$d_{obs.}$	$d_{calc.}$	*h*	*k*	*l*	I/I_0	$d_{obs.}$	$d_{calc.}$
0	0	1	9	10.9	10.9	$\bar{3}$	1	3	7	2.34	2.34				9 q	1.542	
2	0	0	6	6.58	6.59	$\bar{4}$	0	4	12	2.31	2.32	0	2	6	5	1.528	1.530
0	0	2	23	5.43	5.43	$\bar{3}$	1	4			2.31	$\bar{3}$	1	6	8	1.517	1.517
$\bar{2}$	0	1	5	5.21	5.22				6 q	2.28		$\bar{3}$	1	7	11	1.501	1.502
$\bar{1}$	1	1	23	4.87	4.87	0	2	3			2.25	$\bar{4}$	2	6	5	1.476	1.479
1	1	1	35	4.60	4.60	4	0	3	18 q	2.24	2.24	2	2	6	5	1.442	1.441
			15 q	4.26		$\bar{6}$	0	1			2.23	0	4	0	12	1.432	1.431
$\bar{1}$	1	2	4	3.92	3.92	$\bar{4}$	2	1	33	2.17	2.17	$\bar{3}$	3	5	5	1.415	1.415
2	0	2	5	3.86	3.85	4	2	0			2.16	8	2	1	8	1.383	1.387
0	0	3	21	3.62	3.62				5 q	2.13		7	1	4			1.385
$\frac{3}{3}$	1	0	21	3.47	3.48	$\bar{4}$	2	2	11	2.10	2.10	$\bar{6}$	2	4	10 q	1.376	1.377
	1	1			3.47	6	0	1	8	2.07	2.08	$\bar{7}$	3	2	10	1.340	1.343
			76 q	3.34		4	2	1			2.07	$\bar{7}$	3	0			1.340
3	1	1	61	3.18	3.18	$\bar{3}$	1	4	17	2.00	2.00	$\bar{4}$	4	2	5	1.298	1.298
$\bar{3}$	1	2	49	3.15	3.15	$\bar{3}$	1	5	33	1.971	1.978	$\bar{4}$	4	1	7	1.291	1.292
$\bar{1}$	1	3	33	3.08	3.09	0	2	4			1.970	$\bar{8}$	2	5			1.292
$\bar{4}$	0	2			3.08	$\bar{2}$	2	4	25	1.958	1.961	6	2	5	11	1.268	1.271
4	0	1	23	3.00	3.00	1	1	5			1.956	0	4	4			1.266
2	0	3	7	2.95	2.95	1	3	1	6	1.853	1.852	$\bar{6}$	2	7	9	1.253	1.254
1	1	3	18	2.88	2.88	2	2	4	16 q	1.819	1.821	0	2	8	4	1.226	1.226
0	2	0	25	2.87	2.86	$\bar{7}$	1	2	5	1.799	1.794	3	3	6	5	1.214	1.214
$\frac{3}{3}$	1	2	50	2.76	2.75	4	2	3	10	1.762	1.763	$\bar{3}$	1	8	11	1.205	1.206
	1	3	100	2.72	2.72	$\bar{6}$	2	1			1.761	$\bar{3}$	3	7			1.206
0	0	4			2.71	$\bar{6}$	2	2	19	1.734	1.735	$\bar{3}$	1	9	7	1.196	1.196
2	2	0	10	2.62	2.62	$\bar{4}$	0	6	20	1.729	1.727	4	2	7			1.193
$\frac{4}{2}$	0	2	12	2.61	2.61	$\bar{6}$	0	5			1.711	$\bar{11}$	1	1	8	1.185	1.189
	2	1			2.60	$\bar{3}$	3	1	20	1.707	1.708	$\bar{7}$	1	8			1.186
0	2	2	16	2.53	2.53	$\bar{3}$	3	2			1.703	7	1	6	5	1.173	1.173
$\frac{2}{1}$	2	1	9	2.51	2.51	6	2	1			1.682	7	3	4	6	1.143	1.143
	1	4	4	2.49	2.49	$\bar{4}$	0	5	18 q	1.676	1.676	$\bar{8}$	0	6	5	1.118	1.119
			6 q	2.46		$\bar{8}$	0	1			1.675	$\bar{4}$	4	6	6	1.102	1.102
$\bar{2}$	2	2	5	2.43	2.43	$\bar{5}$	1	4	15	1.662	1.662	$\bar{6}$	4	5	5	1.097	1.098
$\bar{5}$	1	1			2.42	$\bar{3}$	3	3	16	1.625	1.623	3	5	1			1.097
5	1	0	3	2.40	2.39	6	2	2	5	1.593	1.592						

q: quartz

$a = 13.405(6)$, $b = 5.7242(15)$, $c = 11.050(3)$ Å, $\beta = 100.69(3)^\circ$, $V = 833.2(5)$ Å^3, $Z = 2$.

calculated X-ray diffraction pattern simulated from the subsequent result of crystal structure analysis. The unit-cell parameters were refined from the powder X-ray diffraction data using the computer program of Toraya (1993) and are: $a = 13.405(6)$, $b = 5.7242(15)$, $c = 11.050(3)$ Å, $\beta = 100.69(3)°$, $V = 833.2(5)$ Å^3 and $Z = 2$. X-ray powder diffraction data are given in Table 2.

The X-ray diffraction intensity data of the single crystal selected for structure analysis were collected using a Rigaku RASA-7R four-circle diffractometer employing graphite-monochromatized Mo$K\alpha$ radiation from a rotating anode (50 kV and 200 mA). Experimental details of the data collection are given in Table 3. Data reduction to F_o^2 with Lorentz and polarization corrections and correction for absorption (ϕ-scan procedure) were carried out with a computer program by Prof. Kazumasa Sugiyama of Tohoku University (pers. comm.). The SHELXL-97 software package (Sheldrick, 2008) was employed to refine the crystal structure. The scattering factors for the neutral atoms and anomalous dispersion factors were taken from the International Tables for X-ray Crystallography, Volume C (1992). Full-matrix least-squares refinement was performed by refining the positional parameters, scale factor, and displacement parameters.

The single crystal X-ray diffraction data showed the chevkinite-type *C*-lattice with extinction rules consistent with the space group *C*2/*m*. The atomic positional parameters of chevkinite-(Ce) "Crystal 1" (Sokolova *et al.*, 2004) were used for the starting model. Although chevkinite-

Table 3. Crystallographic data of chevkinite-(Ce) and experimental details.

Temperature	298 K
a (Å)	13.3949(12)
b (Å)	5.7293(8)
c (Å)	11.0523(10)
β (°)	100.636(7)
V (Å^3)	833.62(16)
Space group	$C2/m$
Z	2
Formula	$(Ce_{0.83}Ca_{0.15}Y_{0.02})_4Fe(Fe_{0.686}Al_{0.314})_2Ti_2Si_4O_{22}$
D_{calc} (g/cm^3)	4.795
μ (cm^{-1})	12.587
Crystal dimension (mm)	0.15 × 0.07 × 0.03
Diffractometer	Rigaku AFC-7R
Radiation	Mo$K\alpha$ (graphite-monochromatized)
Scan mode, rate (°/min in ω)	2θ–ω, 2
2θ range (deg.)	5–70
Reflection range	$-21 \le h \le 21$
	$0 \le k \le 9$
	$-17 \le l \le 8$
No. of measured reflections	2238
No. unique reflections	1984
No. of observed reflections [$I > 2\sigma(I)$]	1750
R_{int}	0.0158
No. of variable parameters	101
$R1$ [$I > 2\sigma(I)$], R1(all reflections)	0.0296, 0.0371
w$R2$ (all reflections)	0.1304
Weighting parameters, a, b	0.1, 0
Goodness of fit	1.111
Final $\Delta\rho_{min}$ (e/Å^3)	−2.976
Final $\Delta\rho_{max}$ (e/Å^3)	1.432

$R1 = \Sigma \, | \, |F_o| - |F_c| \, | \, / \, \Sigma \, |F_o|$

$wR2 = \{\Sigma \, [w(F_o^2 - F_c^2)_2^2] \, / \, \Sigma \, [w(F_o^2)^2]\}^{0.5}$

$w = 1 \, / \, [\sigma^2(F_o^2) + (aP)^2 + bP]$

$P = [2F_c^2 + F_o^2] \, / \, 3$

Table 4. Final atomic coordinates and displacement parameters (Å^2).

		occupancy	x	y	z	U_{eq}
Ce1	*A*1	$Ce_{0.83}Y_{0.02}Ca_{0.15}$	0.35634(2)	0	0.73373(3)	0.01315(12)
Ce2	*A*2	$Ce_{0.83}Y_{0.02}Ca_{0.15}$	0.06982(2)	0	0.74050(3)	0.01681(12)
Fe1	*B*(*M*1)	Fe	0.5	0	0.5	0.00745(18)
Fe2	*C*1(*M*2)	$Fe_{0.686(8)}Al_{0.314}$	0.25	0.25	0	0.0071(2)
Ti3	*C*2a(*M*2)	Ti	0	0	0	0.0095(2)
Ti4	*C*2b(*M*3)	Ti	0.5	0	0	0.0096(2)
Si1		Si	0.20107(10)	0.5	0.73167(11)	0.0065(2)
Si2		Si	0.35743(10)	0.5	0.54576(12)	0.0078(2)
O1		O	0.47764(19)	0.2519(5)	0.8741(2)	0.0107(4)
O2		O	0.1462(3)	0	0.9777(4)	0.0100(6)
O3		O	0.1859(3)	0	0.5981(3)	0.0126(6)
O4		O	0.3477(3)	0	0.9906(4)	0.0106(6)
O5		O	0.4264(3)	0.2720(6)	0.5943(3)	0.0214(6)
O6		O	0.2284(2)	−0.7353(5)	0.8146(2)	0.0118(4)
O7		O	0.0845(3)	0.5	0.6708(4)	0.0257(11)
O8		O	0.2685(4)	0.5	0.6282(5)	0.0356(14)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ce1	0.01331(18)	0.01482(18)	0.01094(17)	0	0.00127(12)	0
Ce2	0.01025(17)	0.0306(2)	0.00995(18)	0	0.00271(12)	0
Fe1	0.0098(4)	0.0078(4)	0.0042(3)	0	−0.0001(3)	0
Fe2	0.0078(3)	0.0096(4)	0.0041(3)	0.0000(2)	0.0010(2)	0.0002(2)
Ti3	0.0098(5)	0.0120(5)	0.0074(4)	0	0.0031(4)	0
Ti4	0.0085(5)	0.0106(5)	0.0094(5)	0	0.0006(4)	0
Si1	0.0073(5)	0.0061(5)	0.0062(5)	0	0.0014(4)	0
Si2	0.0089(5)	0.0098(5)	0.0048(5)	0	0.0013(4)	0
O1	0.0094(10)	0.0130(11)	0.0102(9)	−0.0021(9)	0.0035(8)	−0.0026(8)
O2	0.0069(13)	0.0111(14)	0.0125(14)	0	0.0034(11)	0
O3	0.0178(16)	0.0139(16)	0.0055(13)	0	0.0000(12)	0
O4	0.0077(13)	0.0089(14)	0.0146(15)	0	0.0006(11)	0
O5	0.0271(15)	0.0236(15)	0.0127(11)	0.0060(11)	0.0015(11)	0.0153(12)
O6	0.0191(11)	0.0082(10)	0.0082(10)	0.0013(8)	0.0027(8)	0.0030(8)
O7	0.0092(16)	0.054(3)	0.0129(18)	0	−0.0017(13)	0
O8	0.028(3)	0.064(4)	0.021(2)	0	0.020(2)	0

(Ce) showed a complex chemistry of isomorphous substitutions, simplified occupancy parameters were employed in the initial cycles of the refinement calculations; $Ce_4Fe_3Ti_2Si_4O_{22}$ as the structural formula. Although Fe and Ti have the similar scattering properties, the former was adopted to the Fe1 (*B* or *M*1) and Fe2 (*C*1 or *M*2) sites, whereas the latter was employed for the Ti3 (*C*2, or *M*3 and *M*4) sites, in reference to the previous studies on the crystal structure of chevkinite-(Ce) (Yang *et al.*, 2002, 2007; Sokolova *et al.*, 2004). In the next stage of refinement cycles, the occupancy parameters for the *A* (REE) sites were fixed as $Ce_{0.83}Y_{0.02}Ca_{0.15}$ according to the chemical composition. In the further refinement cycles, Al, as the representative of Mg and Al, was introduced into the octahedral Fe1, Fe2, Ti3 and Ti4 sites to refine the occupancy parameters against to the Ti or Fe, the representative of Ti, Mn and Fe. The refined occupancy parameters indicated the partial (0.3) substitution of Al(Mg) for Fe only at the Fe2 site, whereas no substitution at the other octahedral sites. In the final cycles of refinements, the occupancy parameters of Al and Fe at the Fe2 site were refined. The final positional parameters and anisotropic displacement parameters with equivalent isotropic displacement parameters are given in Table 4. Selected interatomic distances are summarized in Table 5.

Table 5. Interatomic distances (Å).

Ce1	− O5	2.494(3)	Ce2	− O3	2.408(4)
	− O5	2.494(3)		− O1	2.530(3)
	− O3	2.489(4)		− O1	2.530(3)
	− O1	2.490(3)		− O6	2.616(3)
	− O1	2.490(3)		− O6	2.616(3)
	− O6	2.569(3)		− O5	2.620(4)
	− O6	2.569(3)		− O5	2.620(4)
	− O4	2.863(4)		− O2	2.632(4)
mean		2.557		− O7	2.9824(14)
				− O7	2.9824(14)
			mean		2.654
Fe1	− O7	2.014(4)	Fe2	− O4	1.956(2)
	− O7	2.014(5)		− O4	1.956(2)
	− O5	2.206(3)		− O2	1.980(2)
	− O5	2.206(3)		− O2	1.980(2)
	− O5	2.206(3)		− O6	2.018(2)
	− O5	2.206(3)		− O6	2.018(2)
mean		2.142	mean		1.985
Ti3	− O1	1.973(3)	Ti4	− O1	1.988(3)
	− O1	1.973(3)		− O1	1.988(3)
	− O1	1.973(3)		− O1	1.988(3)
	− O1	1.973(3)		− O1	1.988(3)
	− O2	2.018(3)		− O4	2.024(4)
	− O2	2.018(3)		− O4	2.024(4)
mean		1.988	mean		2.000
Si1	− O7	1.582(5)	Si2	− O3	1.589(4)
	− O8	1.583(5)		− O8	1.628(5)
	− O6	1.633(3)		− O5	1.632(3)
	− O6	1.633(3)		− O5	1.632(3)
mean		1.608	mean		1.620

Discussion

Chevkinite-(Ce) from the rhyolitic tuff, Heguri, Chiba Prefecture, Japan, shows a chondrite-normalized lanthanides distribution pattern with simple decay with increasing atomic number (Fig. 3). This is a typical pattern for the Ce-dominant rare earth minerals. Although the trace amount lanthanides, such as Eu and Er, could not determined by the electron microprobe owing to their low contents, we can estimate their concentrations in chevkinite-(Ce) from this liner trend; Eu_2O_3 0.23, Tb_2O_3 0.07, Ho_2O_3 0.04, Er_2O_3 0.09, Tm_2O_3 0.01, Yb_2O_3 0.04 wt%, and others are less than 0.01 wt%. The value for Eu must be an overestimation, because the electron microprobe detected the negligible weak signal of the Eu analytical line. The Eu anomaly is suggested as the spike in Fig. 3. Eventually, only the $Er_{0.01}$ can be estimated among the trace lanthanoids into the empirical formula; $(Ce_{1.57}La_{0.83}Ca_{0.58}Nd_{0.56}Pr_{0.15}Y_{0.09}Th_{0.08}Sm_{0.05}Gd_{0.04}Dy_{0.02}Er_{0.01})_{\Sigma 3.98}(Ti_{2.74}Fe^{3+}_{1.34}Fe^{2+}_{0.50}Al_{0.14}Mg_{0.05}Nb_{0.05}Mn_{0.02})_{\Sigma 4.84}Si_4O_{21.82}F_{0.18}$.

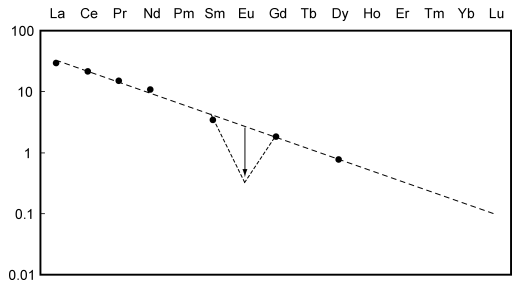

Fig. 3. Chondrite-normalized lanthanide distribution pattern of chevkinite-(Ce) from Heguri. The dashed line indicates a fitted line estimated from the values of La, Ce, Pr, Nd, Sm, Gd and Dy.

Yang, *et al.* (2002) pointed out the deficiencies of cations at the *A* and *BC* (*M*) sites in their Fe-rich chevkinite-(Ce). A slight deficiency can be observed for each site in the empirical formula of chevkinite-(Ce) from Heguri. It is worth noting that chevkinite-(Ce) from Heguri contains small amounts of Al and Mg, and differs from chevkinite-(Ce) from China (Yang *et al.*, 2002) and Mongolia (Sokolova *et al.*, 2004).

Chevkinite-(Ce) from Heguri is characteristic in the Fe-rich chemistry. The concentration of Fe is comparable to that in chevkinite-(Ce) from the aegirine-alkali granite, Mianning, Sichuan Province, China (Yang *et al.*, 2002, 2007). The Fe constituent in chevkinite-(Ce) from Heguri is estimated as divalent FeO, although no valency determination, such as Mössbauer analysis, was carried out. However, chevkinite-(Ce) from Heguri possibly consists of both Fe^{2+} and Fe^{3+}, as the Fe-rich chevkinite-(Ce) from China (Yang *et al.*, 2002, 2007). A tentative estimation of Fe^{2+}/Fe^{3+} partition on the basis of Si = 4 and (O,F) = 22 *apfu* gave a formula; $(Ce_{1.57}La_{0.83}Ca_{0.58}Nd_{0.56}Pr_{0.15}Y_{0.09}Th_{0.08}Sm_{0.05}Gd_{0.04}Dy_{0.02})_{\Sigma 3.97}(Ti_{2.74}Fe^{3+}_{1.34}Fe^{2+}_{0.50}Al_{0.14}Mg_{0.05}Nb_{0.05}Mn_{0.02})_{\Sigma 4.84}Si_4O_{21.82}F_{0.18}$.

The crystal structure of chevkinite-(Ce) consists of two kinds of sheets; one is a sheet of octahedral cations (Fe2, Ti3 and Ti3), and the other is a sheet of Fe1 octahedra and corner shar-

ing two silicate tetrahedra, Si_2O_7. The sheets are parallel to the *ab* plane, and stack alternately in the c^* direction to form a three-dimensional framework. The resulted structural formula is therefore $(Ce_{0.83}Ca_{0.15}Y_{0.02})_4Fe(Fe_{0.686}Al_{0.314})_2Ti_2Si_4O_{22}$. An approximation of minor atoms into the structural formula leads to the formula $(Ce_{0.83}Ca_{0.15}Y_{0.02})_4(Fe_{0.98}Mn_{0.02})(Fe_{0.43}Ti_{0.40}Al_{0.07}Mg_{0.03}\square_{0.07})_2(Ti_{0.97}Nb_{0.03})_2Si_4O_{22}$, suggesting a fractional vacancy at the Fe2 site. Whereas the Ti and Fe are simply allocated into Ti3, Ti4 and Fe1 sites, respectively, in this approximation, a complex mixing of Fe and Ti is probable at the octahedral sites in chevkinite-(Ce) from Heguri, as the site population in the Fe-rich chevkinite-(Ce) from China assigned by Yang *et al.* (2007).

The present chevkinite-(Ce) is the second occurrence in Japan, following to the first occurrence from alkaline dike in Cape Ashizuri, Kochi Prefecture, Shikoku, Japan (Imaoka and Nakashima, 1994). Chevkinite-(Ce) occurs in pumice fragments and air-fall ash, as well as in alkali granite and syenite pegmatites. The occurrence mode at Heguri is similar to the former type. The X-ray fluorescence whole rock analysis (Table 2 in Tsutsumi *et al.*, 2012) indicated considerable abundances of Y (101 ppm) and Ce (144 ppm) in the chevkinite-(Ce) bearing pale green rhyolitic tuff from Heguri. These rare earth elements are considered to be concentrated into the crystals of chevkinite-(Ce) and the associating monazite-(Ce). The source magma of rhyolitic tuff should be as rich in the rare earth as the tuff. It is worth to note that such a REE-rich volcano once existed within or close to Japanese Islands, whereas the position of volcano can not be identified.

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