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CHEVKINITE-(Ce): CRYSTAL STRUCTURE AND THE EFFECT OF MODERATE RADIATION-INDUCED DAMAGE ON SITE-OCCUPANCY REFINEMENT

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Abstract

The crystal structure of annealed chevkinite-(Ce), ideally (REE,Ca)$_4$ Fe^{2+} (Ti,Fe^{3+},Nb)$_4$ Si$_4$ O$_{22}$, monoclinic, $C2/m$, crystal (2^{an}) a 13.400(1), b 5.7232(4), c 11.0573(9) Å, β 100.537(2)°, V 833.7(2) Å^3 and crystal (3^{an}) a 13.368(2), b 5.7243(6), c 11.041(1) Å, β 100.516(1)°, V 830.7(2) Å^3; $Z = 2$, from Mongolia, has been solved by direct methods and refined to R_1 values of 6.3 and 5.7% using 1287 and 1180 unique ($|F_o| > 4\sigma F$) reflections collected with a single-crystal diffractometer and Mo$K\alpha$ radiation. Electron-microprobe analysis gave: crystal (2^{an}) SiO_2 18.81, TiO_2 15.66, FeO 11.33, MnO 0.24, CaO 1.61, Nb_2O_5 1.55, ThO_2 0.40, Y_2O_3 0.30, Ce_2O_3 23.45, La_2O_3 13.92, Nd_2O_3 6.88, Pr_2O_3 1.95, Sm_2O_3 0.51, Gd_2O_3 0.42, HfO_2 0.01, ZrO_2 0.28, sum 97.32 wt.%, and crystal (3^{an}) SiO_2 18.53, TiO_2 16.11, FeO 12.62, MnO 0.31, BaO 0.02, CaO 1.21, Nb_2O_5 1.69, ThO_2 0.10, Y_2O_3 0.30, Ce_2O_3 24.30, La_2O_3 12.94, Nd_2O_3 8.13, Pr_2O_3 2.44, Sm_2O_3 0.82, Gd_2O_3 0.36, HfO_2 0.16, ZrO_2 0.08, Ta_2O_5 0.03, WO_3 0.02, sum 100.17 wt.%. The corresponding chemical formulae are: (2^{an}): $(Ce_{1.85}\ La_{1.11}\ Nd_{0.53}\ Pr_{0.15}\ Sm_{0.04}\ Gd_{0.03}\ Ca_{0.32}\ Th_{0.02})_{\Sigma 4.05}$ $(Fe^{2+}{}_{0.85}\ Mn^{2+}{}_{0.04}\ Zr_{0.03}\ Y_{0.03}\ Ca_{0.05})_{\Sigma 1.00}$ $(Ti_{2.54}\ Fe^{3+}{}_{1.19}\ Nb_{0.15})_{\Sigma 3.88}$ $Si_{4.06}$ O_{22} and (3^{an}): $(Ce_{1.88}\ La_{1.01}\ Nd_{0.61}\ Pr_{0.19}\ Sm_{0.06}\ Gd_{0.03}\ Ca_{0.27}\ Y_{0.03}\ Th_{0.01})_{\Sigma 4.08}$ $(Fe^{2+}{}_{0.93}\ Mn_{0.06}\ Zr_{0.01})_{\Sigma 1.00}$ $(Ti_{2.55}\ Fe^{3+}{}_{1.29}\ Nb_{0.16})_{\Sigma 4.00}$ $Si_{3.91}$ O_{22} based on 13 cations per formula unit. Infrared spectra of unannealed crystals suggest significant radiation-induced damage. The structures of two unannealed crystals were refined, but there are major discrepancies (~13%) between the sums of the site-scattering values at the octahedrally coordinated M sites and the analogous values calculated from the chemical compositions determined by electron-microprobe analysis. These discrepancies were not present when data were collected on annealed crystals, indicating that the original crystals are partly metamict and that this can significantly affect the results of site-scattering refinement. In the crystal structure of chevkinite, there are two distinct (SiO_4) tetrahedra that share one vertex to form an [Si_2O_7] group: <Si–O> = 1.614 (2^{an}) and 1.612 (3^{an}) Å, <Si(1)–O(8)–Si(2)> = 172.0° (2^{an}) and 170.6° (3^{an}). There are four octahedrally coordinated M sites that are occupied by small- to medium-sized divalent to pentavalent cations. The M(1) site is occupied dominantly by Fe^{2+} with minor Mn^{2+}, and the M(2), M(3) and M(4) sites are occupied by Ti, Fe^{3+} and Nb. There are two A-sites that are occupied by REE and minor Ca and Th, with <A–O> = 2.56 (2^{an}) and 2.55 (3^{an}) ([8]-coordinated) and 2.66 (2^{an}) and 2.55 (3^{an}) Å ([10]-coordinated). There are two crystallographically distinct rutile-like chains of octahedra ([M(3) + M(4)] and [M(2) + M(2)]) that extend in the b direction and link to form a layer of octahedra parallel to (001). The layers of octahedra link through [Si_2O_7] groups to form a framework with two interstitial A sites, CN = [8] and [10], in which Ce is dominant over other REE, Ca and Th.

Keywords: chevkinite-(Ce), Ti-silicate, crystal structure, Mongolia, radiation damage.

Sommaire

Nous avons résolu la structure cristalline de la chevkinite-(Ce) recuite (*rec*), de formule idéale (TR,Ca)$_4$ Fe^{2+} (Ti,Fe^{3+},Nb)$_4$ Si$_4$ O$_{22}$, monoclinique, $C2/m$, en utilisant un cristal (2^{rec}) a 13.400(1), b 5.7232(4), c 11.0573(9) Å, β 100.537(2)°, V 833.7(2) Å^3 et un autre (3^{rec}) a 13.368(2), b 5.7243(6), c 11.041(1) Å, β 100.516(1)°, V 830.7(2) Å^3; $Z = 2$, provenant de la Mongolie, par méthodes directes, et nous l'avons affiné jusqu'à un résidu R_1 de 6.3 et 5.7% en utilisant 1287 et 1180 réflexions uniques ($|F_o| > 4\sigma F$) prélevées sur monocristal avec un diffractomètre et un rayonnement Mo$K\alpha$. Les analyses effectuées avec une microsonde

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électronique ont donné: cristal (2^{rec}) SiO_2 18.81, TiO_2 15.66, FeO 11.33, MnO 0.24, CaO 1.61, Nb_2O_5 1.55, ThO_2 0.40, Y_2O_3 0.30, Ce_2O_3 23.45, La_2O_3 13.92, Nd_2O_3 6.88, Pr_2O_3 1.95, Sm_2O_3 0.51, Gd_2O_3 0.42, HfO_2 0.01, ZrO_2 0.28, somme 97.32% (poids), et cristal (3^{rec}) SiO_2 18.53, TiO_2 16.11, FeO 12.62, MnO 0.31, BaO 0.02, CaO 1.21, Nb_2O_5 1.69, ThO_2 0.10, Y_2O_3 0.30, Ce_2O_3 24.30, La_2O_3 12.94, Nd_2O_3 8.13, Pr_2O_3 2.44, Sm_2O_3 0.82, Gd_2O_3 0.36, HfO_2 0.16, ZrO_2 0.08, Ta_2O_5 0.03, WO_3 0.02, somme 100.17%. Les formules correspondantes sont: (2^{rec}): $(Ce_{1.85}\,La_{1.11}\,Nd_{0.53}\,Pr_{0.15}\,Sm_{0.04}\,Gd_{0.03}\,Ca_{0.32}\,Th_{0.02})_{\Sigma 4.05}\,(Fe^{2+}{}_{0.85}\,Mn^{2+}{}_{0.04}\,Zr_{0.03}\,Y_{0.03}\,Ca_{0.05})_{\Sigma 1.00}\,(Ti_{2.54}\,Fe^{3+}{}_{1.19}\,Nb_{0.15})_{\Sigma 3.88}\,Si_{4.06}\,O_{22}$ et (3^{rec}): $(Ce_{1.88}\,La_{1.01}\,Nd_{0.61}\,Pr_{0.19}\,Sm_{0.06}\,Gd_{0.03}\,Ca_{0.27}\,Y_{0.03}\,Th_{0.01})_{\Sigma 4.08}\,(Fe^{2+}{}_{0.93}\,Mn_{0.06}\,Zr_{0.01})_{\Sigma 1.00}\,(Ti_{2.55}\,Fe^{3+}{}_{1.29}\,Nb_{0.16})_{\Sigma 4.00}\,Si_{3.91}\,O_{22}$ sur une base de 13 cations par unité formulaire. Les spectres infrarouges des échantillons non chauffés indiquent la présence de dommage important dû à la radiation. Les structures de deux cristaux naturels ont été affinées, mais révèlent des différences importantes (~13%) entre les sommes des valeurs de la dispersion aux divers sites *M* à coordinence octaédrique et les valeurs analogues calculées à partir des compositions chimiques déterminées par analyse à la microsonde électronique. Ces différences ne sont pas évidentes quand les données sont prises des mêmes cristaux recuits, indication que les cristaux étaient métamictes à l'origine et que cet état peut affecter largement les résultats de l'affinement de la dispersion associée aux divers sites. Dans la structure de la chevkinite, deux tétraèdres (SiO_4) distincts partagent un vertex pour former un groupe [Si_2O_7]: <Si–O> = 1.614 (2^{rec}) et 1.612 (3^{rec}) Å, <*Si*(1)–O(8)–*Si*(2)> = 172.0° (2^{rec}) et 170.6° (3^{rec}). Il y a quatre sites *M* à coordinence octaédrique, qu'occupent des cations de petite taille ou de taille moyenne, bivalents à pentavalents. Le site *M*(1) contient surtout le Fe^{2+} avec une proportion mineure de Mn^{2+}, et *M*(2), *M*(3) et *M*(4) sont les sites de Ti, Fe^{3+} et Nb. Il y a deux sites *A* où logent les terres rares (TR) et des quantités moindres de Ca et de Th, avec <*A*–O> = 2.56 (2^{rec}) et 2.55 (3^{recc}) (à coordinence [8]), et 2.66 (2^{rec}) et 2.55 (3^{rec}) Å (à coordinence [10]). La structure contient deux chaînes distinctes d'octaèdres de type rutile ([*M*(3) + *M*(4)] et [*M*(2) + *M*(2)]) allongées selon *b* et liées pour former une couche d'octaèdres parallèles à (001). Ces couches sont liées gràce au groupes [Si_2O_7] pour former une trame ayant deux sites interstitiels *A*, à coordinence [8] et [10], dans lequel le Ce prédomine par rapport aux autres terres rares, Ca et Th.

(Traduit par la Rédaction)

Mots-clés: chevkinite-(Ce), silicate de Ti, structure cristalline, Mongolie, dommage dû à la radiation.

INTRODUCTION

Chevkinite-(Ce) is an accessory mineral in pegmatites associated with alkali granites and syenites; it is particularly common in associated contact-metasomatic rocks. Originally, chevkinite-(Ce) was described as perrierite by Bonatti & Gottardi (1950). Peng & Bun (1964) proposed a crystal-structure model for chevkinite-(Ce) based on structural data for perrierite-(Ce), ideally $Ce_4\,Fe^{2+}\,(Ti^{4+},Fe)_4\,Si_4\,O_{22}$ (Gottardi 1960). Chevkinite-(Ce) (space group *C*2/*m*) and perrierite-(Ce) (space group $P2_1/a$) are dimorphs. Calvo & Faggiani (1974) presented crystal-structure models for synthetic analogues of chevkinite-(Ce) and perrierite-(Ce). [We note that perrierite was redefined as perrierite-(Ce) by Nickel & Mandarino (1987)]. Usually, chevkinite-(Ce) is highly metamict, accounting for the problem in adequately characterizing its crystal structure. In addition to chevkinite-(Ce), there are two more minerals of the chevkinite-(Ce) structure-type: strontiochevkinite, ideally $(Sr,REE)_4\,Fe^{2+}\,(Ti^{4+},Fe)_4\,Si_4\,O_{22}$ (Haggerty & Mariano 1983) and polyakovite-(Ce), ideally $Ce_4\,Mg\,Cr^{3+}{}_2\,Ti^{4+}{}_2\,Si_4\,O_{22}$ (Popov *et al.* 2001), and two more minerals of the perrierite-(Ce) structure-type, rengeite, ideally $Sr_4\,Zr\,Ti_4\,Si_4\,O_{22}$ (Miyajima *et al.* 2001) and matsubaraite, $Sr_4\,Ti_5\,Si_4\,O_{22}$ (Miyajima *et al.* 2002). The crystal structures of strontiochevkinite and rengeite are not yet fully characterized. They were assigned to the chevkinite-(Ce) and perrierite-(Ce) structure types in accord with the β angle: 100.32° for strontiochevkinite and 114.26° for rengeite, as Haggerty & Mariano (1983) regarded the β angle as being the best way of distinguishing chevkinite-(Ce) ($\beta \approx 100°$) from perrierite-(Ce) ($\beta \approx 113°$). Usually, chevkinite-(Ce), strontiochevkinite, polyakovite-(Ce) and perrierite-(Ce) are highly metamict. Occurrences of non-metamict chevkinite-(Ce) (Kovalenko *et al.* 1995) and perrierite-(Ce) (Parodi *et al.* 1994) have been reported. Rengeite is very poor in U and Th, and matsubaraite does not contain any U and Th; both minerals are thus crystalline, and give excellent X-ray powder-diffraction data from unannealed material (Miyajima *et al.* 2001, 2002). Kovalenko *et al.* (1995) described crystalline chevkinite-(Ce) from the Tsahirin–Khuduk Zr–Nb–REE-ore occurrence at the northernmost part of the Northern outcrop of the Khaldzan Buragtag alkali granite, Mongolian Altay, Western Mongolia. The sample was collected from the pegmatitic zone of the alkali granite *Geophysicheskii*, in which chevkinite-(Ce) forms well-shaped prismatic crystals up to 1.0 × 0.2 × 0.1 cm. Associated minerals are orthoclase, riebeckite, quartz, fergusonite-(Y), Ta-rich fersmite and zircon. These crystals of chevkinite-(Ce) appear unaltered and do not contain any visible products of later metasomatic alteration. Chevkinite-(Ce) crystals from metasomatic assemblages are usually surrounded by a crust of secondary minerals: allanite-(Ce) , Nb-bearing ilmenite, rutile, synchysite-(Ce) and cerite-(Ce) (Kartashov 1994). Yang *et al.* (2002) reported on the structure of a sample of Fe-rich chevkinite-(Ce) from Mianning, Sichuan Province, China. Here we report results of a single-crystal study of chevkinite-(Ce), focusing on the effect of moderate radiation-damage on site-occupancy refinement, and we discuss two possible assignments of site populations and the crystal chemistry of the chevkinite-group minerals. The superscript *an* indicates that a crystal was annealed in air for 3 hours at 1100°C.

SINGLE-CRYSTAL X-RAY DIFFRACTION

Collection of X-ray data

Four sets of single-crystal X-ray data were collected for three crystals of chevkinite-(Ce). Crystals (1) and (2^{an}) were mounted on an automated four-circle *P*4 diffractometer fitted with a CCD detector [1K SMART for crystal (1), 4K APEX for crystal (2^{an})] and equipped with a Mo$K\alpha$ X-ray source. Integrated intensities were collected up to $2\theta \approx 60°$, using 60 s per frame, 0.2° framewidths, and crystal–detector distances of 4 and 5 cm for the 1K and 4K detectors, respectively. The refined cell-parameters (Table 1) were obtained from 4393 and 4103 reflections ($I > 10\ \sigma I$). An empirical absorption correction (SADABS, Sheldrick 1998) was applied. Crystals (2) and (3^{an}) were mounted on a *P*3 automated four-circle diffractometer fitted with a serial detector and using Mo$K\alpha$ X-radiation. Cell parameters were determined from 16 reflections with $7 \le 2\theta \le 25°$. Integrated intensities of 1450 and 1393 reflections with $\overline{18} \le h \le 18, 0 \le k \le 8, 0 \le l \le 15$ were collected up to $2\theta = 60.12°$ according to the procedure of Hawthorne & Groat (1985). An empirical absorption-correction using Ψ-scan data was applied, and the data were corrected for Lorentz, polarization and background effects.

INFRARED SPECTROSCOPY

Infrared spectra were collected on single grains of chevkinite-(Ce) using an Hyperion IR microscope interfaced with a Bruker Tensor 27 FTIR spectrometer fitted with a liquid-nitrogen-cooled mercury–cadmium-telluride detector. Single crystals were positioned on the microscope stage and the aperture was reduced to include only a single crystal. Thirty-two scans were collected on each of three crystals, and scans for each crystal were combined at 4 cm^{-1} resolution from 4000 to 800 cm^{-1}.

CHEMICAL ANALYSIS

The crystals used for X-ray diffraction were mounted in a perspex disc, ground, polished and coated with carbon for chemical analysis using a Cameca SX–50 electron microprobe. Ten points were analyzed on each crystal using the following conditions: excitation voltage: 15 kV, specimen current: 20 nA, beam size 5 μm. The following standards and crystals were used: diopside: Si, Ca, titanite: Ti, spessartine: Mn, fayalite: Fe, $MnNb_2O_6$: Nb, $LaPO_4$: La, $CePO_4$: Ce, $NdPO_4$: Nd, REE3: YiPr, REE2*: Sm, REE1*: Gd [REE 1–3: synthetic Ca–Al-silicate glasses to which 3–4 wt.% REE has been added (Drake & Weill 1972)], chromite: Cr, $ZrSiO_4$: Zr, barite: Ba, $HfSiO_4$: Hf, $CaWO_4$: W, ThO_2: Th, UO_2: U, manganotantalite: Ta. The formulae (Table 2) were calculated on the basis of 13 cations per

TABLE 1. MISCELLANEOUS STRUCTURE-REFINEMENT INFORMATION FOR CHEVKINITE-(Ce)

	(1)	(2)	(2^{an})	(3^{an})
a (Å)	13.4319(8)	13.534(3)	13.400(1)	13.368(2)
b	5.7628(3)	5.789(1)	5.7232(4)	5.7243(6)
c	11.0914(7)	11.159(2)	11.0573(9)	11.041(1)
β (°)	100.629(1)	100.57(2)	100.537(2)	100.516(1)
V ($Å^3$)	843.8(1)	859.5(3)	833.7(2)	830.7(2)
Space group	*C*2/*m*	*C*2/*m*	*C*2/*m*	*C*2/*m*
Z	2	2	2	2
Absorption coefficient (mm^{-1})	13.80	13.15	13.56	13.92
F(000)	1228.9	1147.1	1147.1	1157.7
D(calc) ($g.cm^{-3}$)	5.017	4.858	5.009	5.078
Crystal size (mm)	0.08 x 0.10 x 0.12	0.08 x 0.08 x 0.16	0.06 x 0.07 x 0.16	0.08 x 0.10 x 0.12
Radiation	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$
2θ-range for data collection (°)	60.06	60.12	59.98	60.12
R(int) (%)	2.3	6.8	1.9	1.7
Reflections collected	7154	1450	5599	1393
$\|F(obs)\| > 4\sigma F$	4325	–	3208	–
Unique reflections	1342	1397	1320	1331
$F(obs) > 4\sigma F$	1182	1090	1287	1180
Refinement method	Full-matrix least-squares on F^2; fixed weights proportional to $1/\sigma(F^2)$			
Goodness of fit on F^2	1.15	1.12	1.24	1.13
Final *R* index (%) [$F_o > 4\sigma F$]	4.7	6.5	6.3	5.7
R index (%) (all data)	5.3	8.0	6.5	6.1
wR^2	14.7	20.5	16.1	18.3

TABLE 2. CHEMICAL COMPOSITION (wt.%)* AND EMPIRICAL FORMULA (*apfu*) OF CHEVKINITE-(Ce)

	(1)	(2)	(2^{an})	(3^{an})		(1)	(2)	(2^{an})	(3^{an})
SiO_2	18.56	18.89	18.81	18.53	Si	3.99	4.01	4.06	3.91
TiO_2	16.11	16.49	15.66	16.11					
FeO	11.44	11.12	11.33	12.62	Ti	2.61	2.63	2.54	2.55
MnO	0.31	0.27	0.24	0.31	Fe^{3+}	1.25	1.21	1.31	1.29
CaO	1.11	1.64	1.61	1.21	Nb	0.14	0.16	0.15	0.16
Nb_2O_5	1.48	1.69	1.55	1.69	Σ	4.00	4.00	4.00	4.00
ThO_2	n.d.	0.48	0.40	n.d.					
Y_2O_3	0.28	0.31	0.30	0.30	Fe^{2+}	0.81	0.76	0.73	0.93
Ce_2O_3	24.37	23.48	23.45	24.30	Mn^{2+}	0.04	0.05	0.04	0.06
La_2O_3	13.59	14.18	13.92	12.94	Hf	0.01	0.01	0.00	0.00
Nd_2O_3	7.78	6.72	6.88	8.13	Zr	0.01	0.03	0.03	0.01
Pr_2O_3	2.22	2.08	1.95	2.44	Y	0.03	0.04	0.03	0.03
Sm_2O_3	0.72	0.64	0.51	0.82	Ca	0.10	0.11	0.16	0.00
Gd_2O_3	0.37	0.42	0.42	0.36	Σ	1.00	1.00	0.99	1.03
HfO_2	0.14	0.18	0.01	0.16					
ZrO_2	0.08	0.28	0.28	0.08	Ce	1.92	1.83	1.85	1.88
Total	98.56	98.873	97.32	100.00	La	1.08	1.11	1.11	1.01
					Nd	0.60	0.51	0.53	0.61
					Pr	0.17	0.16	0.15	0.19
					Sm	0.05	0.05	0.04	0.06
					Gd	0.03	0.03	0.03	0.03
					Ca	0.16	0.26	0.21	0.27
					Th	–	0.02	0.02	–
					Σ	4.01	3.97	4.00	4.05

* Cr, Mg, Ba, U, Mg, Ta, W not detected

formula unit, as this method does not require prior knowledge of the Fe^{3+}:Fe^{2+} ratio of the crystal.

STRUCTURE SOLUTION AND REFINEMENT

The crystal structure of chevkinite-(Ce) was solved by direct methods; the SHELXTL 5.1 system of programs (Sheldrick 1997) was used for solution and refinement of the structure. Scattering factors for neutral atoms were taken from the International Tables for X-Ray Crystallography (1992). Details of the structure refinement are given in Table 1. The crystal structure of chevkinite-(Ce) was refined to R_1 indices of 4.7–6.5% and a GoF of 1.12–1.24 for a total of 115 refined parameters. Residual weak maxima [about 2.5 *e* for crystal (1) and 3.5–4.2 *e* for crystals (2), (2^{an}) and (3^{an})] were found to be present in difference-Fourier maps calculated at the final stages of refinement. Final atom parameters are given in Table 3, selected interatomic distances are presented in Table 4, refined site-scattering values are given in Table 5, comparison of total *M*-scattering is given in Table 6, and bond-valence analyses of crystals (2^{an}) and (3^{an}) are shown in Table 7. Structure factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

DESCRIPTION OF THE STRUCTURE

Coordination of the cations

In the crystal structure of chevkinite-(Ce), there are two unique *Si* sites, each occupied by Si and surrounded by four O atoms in a tetrahedral arrangement. For crystals (1) and (2), <*Si*(1)–O> varies from 1.620 to 1.625 Å and <*Si*(2)–O> varies from 1.618 to 1.623 Å. For the annealed crystals (2^{an}) and (3^{an}), <*Si*(1)–O> varies between 1.612 and 1.614 Å, and <*Si*(2)–O> varies between 1.616 and 1.609 Å. There are four *M* sites, each coordinated by six O atoms in an octahedral arrangement and occupied by intermediate to small divalent to tetravalent cations. There are two *A* sites (CN = [8] and [10]) occupied by REE, Ca and Th. The interatomic distances vary from 2.469 to 2.811 Å at *A*(1) and 2.437 to 3.003 Å at *A*(2).

Site-scattering refinement

Solution and refinement of the structure of crystal (1) resulted in a major discrepancy between the number of electrons at the *M* sites determined directly from site-scattering refinement and derived from the chemical composition determined by electron-microprobe analysis: there is a 10% difference between these two values (133.9 *versus* 122.1 *epfu*, respectively, Table 6). This difference is much larger than expected for these two methods (*i.e.*, of the order of a few %). Moreover, there was an unsatisfactory aspect to the unit formula in that the number of *M*-site cations is significantly less than 5 *apfu* whereas the number of large cations ($r > 0.9$ Å) is significantly greater than 4 *apfu* (Table 2). Moreover, this problem is not confined to the unit formula. The refined site-scattering value at the *M*(1) site (Table 5) is 31.7 *epfu*, and yet the dominant cation at this site *must* be Fe (or Ti) with only a small amount of Nb as a possible constituent. The atomic number of Fe is 26, and the *M*(1) octahedron is too small to contain any REE cations; hence the refined site-scattering value at the *M*(1) site is incompatible with the chemical composition of the crystal. These problems prompted us to repeat the X-ray and electron-microprobe data-collections on a second crystal [crystal (2)]. The results (Table 3b) for crystal (2) are very similar to those for crystal (1), and the problem with the high value of the refined scattering at the *M*(1) site is even greater than that observed for crystal (1) (Table 5).

At this stage, we began to suspect that this sample of chevkinite-(Ce) is not completely crystalline, as partial metamictization can affect the X-ray scattering characteristics of crystals (*e.g.*, Hawthorne *et al.* 1991). Examination of grains by transmission electron spectroscopy was unsuccessful owing to the very small grain-size, grain-shape and paucity of material. However, infrared spectroscopy was more revealing. The spectra of

TABLE 3. ATOM COORDINATES AND DISPLACEMENT PARAMETERS (Å^2) FOR CHEVKINITE-(Ce)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
					Crystal (1)					
A(1)	0.35601(6)	0	0.73503(7)	0.0180(4)	0.0181(4)	0.0182(4)	0	0.0036(3)	0	0.0181(3)
A(2)	0.06863(6)	0	0.74067(7)	0.0146(4)	0.0366(5)	0.0150(4)	0	0.0037(3)	0	0.0219(3)
M(1)	1/2	0	1/2	0.0328(16)	0.0188(13	0.0137(12)	0	0.0049(10)	0	0.0217(9)
M(2)	1/4	1/4	0	0.0175(10)	0.0145(10)	0.0130(10)	–0.0002(7)	0.0022(7)	0.0005(7)	0.0151(6)
M(3)	0	0	0	0.0142(16)	0.0155(16)	0.0126(15)	0	0.0045(11)	0	0.0139(10)
M(4)	1/2	0	0	0.0184(13)	0.0166(13)	0.0171(13)	0	0.0023(10)	0	0.0175(6)
Si(1)	0.2008(3)	–1/2	0.7312(3)	0.0318(16)	0.0272(15)	0.0294(15)	0	0.0067(12)	0	0.0293(7)
Si(2)	0.3567(3)	–1/2	0.5465(3)	0.0344(17)	0.0319(17)	0.0300(16)	0	0.0069(13)	0	0.0320(7)
O(1)	0.4775(5)	0.2539(12)	0.8734(6)	0.015(3)	0.016(3)	0.014(3)	–0.003(2)	0.004(2)	–0.004(3)	0.0149(13)
O(2)	0.1460(7)	0	0.9767(8)	0.013(4)	0.012(4)	0.013(4)	0	0.006(3)	0	0.0121(17)
O(3)	0.1843(8)	0	0.5969(9)	0.021(5)	0.015(4)	0.010(4)	0	0.003(3)	0	0.0154(18)
O(4)	0.3479(7)	0	0.9895(8)	0.012(4)	0.010(4)	0.015(4)	0	0.003(3)	0	0.0122(17)
O(5)	0.4245(6)	0.2739(14)	0.5973(7)	0.030(4)	0.019(4)	0.019(3)	0.002(3)	–0.003(3)	0.011(3)	0.0235(16)
O(6)	0.2285(6)	–0.7349(12)	0.8139(6)	0.027(3)	0.010(3)	0.009(3)	0.002(2)	0.002(2)	0.003(3)	0.0151(13)
O(7)	0.0818(8)	–1/2	0.6726(11)	0.010(5)	0.060(9)	0.027(6)	0	–0.001(4)	0	0.033(3)
O(8)	0.2648(11)	–1/2	0.6237(12)	0.033(7)	0.068(10)	0.024(6)	0	0.023(5)	0	0.040(3)
					Crystal (2)					
A(1)	0.35496(9)	0	0.73642(11)	0.0304(6)	0.0248(6)	0.0308(6)	0	0.0086(4)	0	0.0283(4)
A(2)	0.06918(8)	0	0.74232(10)	0.0242(6)	0.0462(8)	0.0254(6)	0	0.0073(4)	0	0.0316(4)
M(1)	1/2	0	1/2	0.053(2)	0.0286(17)	0.0234(16)	0	0.0095(13)	0	0.0347(11)
M(2)	1/4	1/4	0	0.0284(13)	0.0204(13)	0.0206(12)	0.0003(9)	0.0045(8)	0.0005(9)	0.0231(8)
M(3)	0	0	0	0.024(2)	0.019(2)	0.0222(2)	0	0.0085(15)	0	0.0209(13)
M(4)	1/2	0	0	0.0301(19)	0.0215(17)	0.0277(19)	0	0.0041(15)	0	0.0266(8)
Si(1)	0.2020(3)	–1/2	0.7317(4)	0.041(2)	0.0303(19)	0.040(2)	0	0.0088(17)	0	0.0370(9)
Si(2)	0.3576(4)	–1/2	0.5470(4)	0.046(2)	0.041(2)	0.038(2)	0	0.0093(18)	0	0.0416(10)
O(1)	0.4776(6)	0.2532(16)	0.8744(8)	0.023(4)	0.026(4)	0.020(4)	–0.005(3)	0.0078(3)	–0.006(3)	0.0223(17)
O(2)	0.1468(9)	0	0.9786(11)	0.021(6)	0.017(5)	0.023(6)	0	0.006(5)	0	0.020(2)
O(3)	0.1827(11)	0	0.5957(12)	0.036(7)	0.019(6)	0.019(6)	0	0.008(5)	0	0.025(3)
O(4)	0.3486(9)	0	0.9886(11)	0.024(6)	0.019(6)	0.019(6)	0	0.005(5)	0	0.021(2)
O(5)	0.4247(8)	0.273(2)	0.5985(9)	0.040(6)	0.037(6)	0.031(5)	0.003(4)	–0.005(4)	0.0172(5)	0.037(2)
O(6)	0.2286(7)	–0.7354(14)	0.8138(7)	0.036(5)	0.010(3)	0.012(3)	0.000(3)	0.004(3)	0.003(3)	0.0193(16)
O(7)	0.0831(11)	–1/2	0.6737(18)	0.016(7)	0.083(15)	0.053(11)	0	–0.004(7)	0	0.052(5)
O(8)	0.2654(15)	–1/2	0.6254(17)	0.044(10)	0.083(15)	0.039(9)	0	0.030(8)	0	0.053(5)

TABLE 3. continued

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
					Crystal (2^{an})					
A(1)	0.35648(8)	0	0.73698(9)	0.0162(5)	0.0150(5)	0.0129(5)	0	0.0031(3)	0	0.0146(3)
A(2)	0.07064(8)	0	0.74336(9)	0.0128(5)	0.0263(6)	0.0129(5)	0	–0.0005(3)	0	0.0177(3)
M(1)	1/2	0	1/2	0.0141(17)	0.0151(17)	0.0049(15)	0	–0.0022(11)	0	0.0119(10)
M(2)	1/4	1/4	0	0.0129(11)	0.0110(12)	0.0055(11)	–0.0003(8)	0.0004(7)	0.0001(9)	0.0100(7)
M(3)	0	0	0	0.014(2)	0.02479	0.010(2)	0	0.0023(14)	0	0.0163(14)
M(4)	1/2	0	0	0.012(2)	0.022(3)	0.011(2)	0	–0.0012(15)	0	0.0156(14)
Si(1)	0.2020(3)	–1/2	0.7312(4)	0.030(2)	0.0248(19)	0.0240(18)	0	0.0031(15)	0	0.0265(8)
Si(2)	0.3596(3)	–1/2	0.5442(4)	0.032(2)	0.032(2)	0.0252(19)	0	0.0027(16)	0	0.0302(9)
O(1)	0.4781(6)	0.2522(16)	0.8732(7)	0.007(3)	0.017(4)	0.009(3)	–0.003(3)	0.000(3)	–0.003(3)	0.0109(15)
O(2)	0.1467(9)	0	0.9786(10)	0.009(5)	0.008(5)	0.009(5)	0	0.000(4)	0	0.009(2)
O(3)	0.1872(10)	0	0.5963(10)	0.021(6)	0.013(5)	0.000(4)	0	0.001(4)	0	0.012(2)
O(4)	0.3478(8)	0	0.9886(9)	0.003(4)	0.007(5)	0.004(4)	0	–0.002(3)	0	0.0048(19)
O(5)	0.4279(7)	0.269(2)	0.5905(8)	0.019(4)	0.030(5)	0.012(4)	0.008(4)	0.000(3)	0.010(4)	0.021(2)
O(6)	0.2277(6)	–0.7360(14)	0.8142(7)	0.021(4)	0.006(3)	0.003(3)	0.001(3)	0.002(3)	0.001(3)	0.0098(15)
O(7)	0.0851(10)	–1/2	0.6660(14)	0.006(5)	0.048(10)	0.024(7)	0	–0.010(5)	0	0.028(3)
O(8)	0.2734(12)	–1/2	0.6308(15)	0.027(8)	0.054(11)	0.028(8)	0	0.025(7)	0	0.034(4)
					Crystal (3^{an})					
A(1)	0.35694(6)	0	0.73625(7)	0.0216(5)	0.0207(5)	0.0125(4)	0	0.0029(3)	0	0.0183(3)
A(2)	0.07052(6)	0	0.74265(7)	0.0178(4)	0.0334(5)	0.0114(4)	0	0.0012(3)	0	0.0211(3)
M(1)	1/2	0	1/2	0.0208(15)	0.0226(15)	0.0079(13)	0	0.0013(9)	0	0.0173(9)
M(2)	1/4	1/4	0	0.0176(9)	0.0144(10)	0.0057(9)	0.0006(6)	0.0007(6)	0.0001(7)	0.0127(6)
M(3)	0	0	0	0.0143(17)	0.026(2)	0.0050(15)	0	0.0011(11)	0	0.0152(11)
M(4)	1/2	0	0	0.0186(17)	0.029(2)	0.0094(16)	0	–0.0003(12)	0	0.0194(11)
Si(1)	0.2014(3)	–1/2	0.7310(3)	0.0333(16)	0.0318(17)	0.0233(15)	0	0.0038(12)	0	0.0296(7)
Si(2)	0.3588(3)	–1/2	0.5447(3)	0.0368(17)	0.0385(18)	0.0227(15)	0	0.0013(12)	0	0.0332(8)
O(1)	0.4780(5)	0.2517(13)	0.8734(6)	0.0141(3)	0.020(3)	0.010(3)	–0.002(3)	0.004(2)	–0.001(3)	0.0148(13)
O(2)	0.1461(7)	0	0.9780(8)	0.012(4)	0.013(4)	0.008(4)	0	0.002(3)	0	0.0115(16)
O(3)	0.1872(8)	0	0.5969(9)	0.023(5)	0.020(5)	0.008(4)	0	0.003(3)	0	0.0168(19)
O(4)	0.3479(7)	0	0.9886(9)	0.017(4)	0.010(4)	0.011(4)	0	0.008(3)	0	0.0126(17)
O(5)	0.4264(6)	0.2708(17)	0.5915(7)	0.027(4)	0.038(5)	0.014(3)	0.007(3)	–0.002(3)	0.013(3)	0.0272(17)
O(6)	0.2273(5)	–0.7351(12)	0.8137(5)	0.026(3)	0.014(3)	0.000(2)	0.002(2)	0.001(2)	0.003(3)	0.0132(12)
O(7)	0.0833(9)	–1/2	0.6683(11)	0.016(5)	0.054(8)	0.016(5)	0	–0.007(4)	0	0.030(3)
O(8)	0.2719(10)	–1/2	0.6291(12)	0.031(6)	0.077(11)	0.021(6)	0	0.021(5)	0	0.041(4)

unannealed chevkinite-(Ce) (Fig. 1) shows a very strong absorption with a maximum at ~3400 cm^{-1} and extending down to ~2400 cm^{-1}, with a very asymmetric envelope. This feature is very similar to absorption in partly metamict titanite (Hawthorne *et al.* 1991) and zircon (Aines & Rossman 1986), which, like chevkinite-(Ce), are also nominally anhydrous minerals. The presence of small amounts of Th (and possibly U) in chevkinite-(Ce) (Table 2) and the similarity of its infrared spectrum in the principal OH-stretching region to those of metamict titanite and zircon suggest very strongly that the crystals of chevkinite-(Ce) examined here are partly metamict. Hence we annealed crystal (2) and a third crystal [crystals (2^{an}) and (3^{an})] in air for 3 h up to 1100°C, and then repeated the data collection for these crystals. The refined site-scattering values at the *M* sites are 128.2 (2^{an}) and 123.4 (3^{an}) *epfu* (Table 6) and the

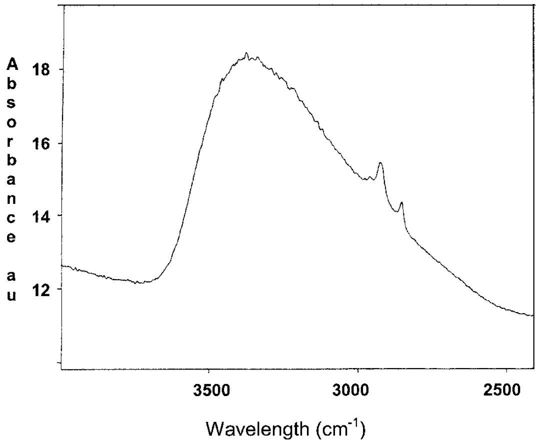

FIG. 1. Infrared-absorption spectrum of unannealed chevkinite-(Ce).

TABLE 4. SELECTED INTERATOMIC DISTANCES (A) AND ANGLES (°) IN CHEVKINITE-(Ce)

		(1)	(2)	(2^{an})	(3^{an})			(1)	(2)	(2^{an})	(3^{an})
A(1)–O(1)	x2	2.497(7)	2.517(8)	2.472(8)	2.469(7)	*A*(2)–O(1)	x2	2.518(6)	2.534(9)	2.503(8)	2.507(7)
A(1)–O(3)		2.522(10)	2.561(14)	2.505(12)	2.498(11)	*A*(2)–O(2)		2.633(9)	2.653(13)	2.614(11)	2.610(9)
A(1)–O(4)		2.844(9)	2.831(12)	2.806(10)	2.811(9)	*A*(2)–O(3)		2.423(9)	2.441(13)	2.453(12)	2.437(10)
A(1)–O(5)	x2	2.488(8)	2.507(12)	2.546(10)	2.522(9)	*A*(2)–O(5)	x2	2.616(8)	2.642(12)	2.660(11)	2.654(9)
A(1)–O(6)	x2	2.566(7)	2.561(8)	2.555(8)	2.565(7)	*A*(2)–O(6)	x2	2.639(7)	2.647(9)	2.593(9)	2.590(7)
<*A*(1)–O>		2.559	2.570	2.557	2.553	*A*(2)–O(7)	x2	2.992(3)	3.009(6)	3.003(15)	2.991(4)
						<*A*(2)–O>		2.659	2.676	2.659	2.653
M(1)–O(5)	x4	2.256(8)	2.271(11)	2.159(10)	2.181(9)	*M*(2)–O(2)	x2	1.990(6)	1.995(8)	1.975(8)	1.978(6)
M(1)–O(7)	x2	2.024(12)	2.055(18)	1.976(14)	1.984(11)	*M*(2)–O(4)	x2	1.968(6)	1.988(8)	1.960(7)	1.958(6)
<*M*(1)–O>		2.179	2.199	2.098	2.115	*M*(2)–O(6)	x2	2.033(6)	2.046(7)	2.023(1)	2.025(6)
						<*M*(2)–O>		1.997	2.010	1.986	1.987
M(3)–O(1)	x4	1.980(7)	1.986(8)	1.978(8)	1.977(7)	*M*(4)–O(1)	x4	2.012(7)	2.012(9)	1.996(9)	1.991(7)
M(3)–O(2)	x2	2.024(9)	2.044(12)	2.023(12)	2.011(9)	*M*(4)–O(4)	x2	2.025(9)	2.030(12)	2.020(10)	2.015(9)
<*M*(3)–O>		1.995	2.005	1.993	1.988	<*M*(4)–O>		2.016	2.018	2.004	1.999
Si(1)–O(6)	x2	1.639(7)	1.645(8)	1.634(8)	1.627(7)	*Si*(1)–O(8)–*Si*(2)		163.8(1.1)	164.1(1.5)	172.0(1.3)	170.6(1.1)
Si(1)–O(7)		1.610(12)	1.621(16)	1.600(13)	1.605(11)						
Si(1)–O(8)		1.593(11)	1.587(16)	1.593(14)	1.594(11)						
<*Si*(1)–O>		1.620	1.625	1.612	1.614						
Si(2)–O(3)		1.585(10)	1.585(14)	1.565(12)	1.573(11)						
Si(2)–O(5)	x2	1.629(8)	1.640(11)	1.635(10)	1.623(9)						
Si(2)–O(8)		1.627(12)	1.650(16)	1.629(14)	1.617(12)						
<*Si*(2)–O>		1.618	1.623	1.616	1.609						

TABLE 5. REFINED SCATTERING VALUES (*epfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*) FOR *M*-SITES IN CHEVKINITE-(Ce)

	Crystal	Refined site-scattering	Assigned site-population	Predicted site-scattering	<*M*–O>$_{calc}$** (Å)	<*M*–O> (Å)
M(1)	(1)	31.7(4)	np[+]	–	–	2.179
	(2)	35.3(6)	np[+]	–	–	2.201
	(2^{an})	28.2(5)	0.85 Fe^{2+} + 0.05 Ca + 0.04 Mn + 0.03 Y + 0.03 Zr	26.5	2.150	2.098
	(3^{an})	27.2(4)	0.93 Fe^{2+} + 0.06 Mn^{2+} + 0.01 Zr	26.1	2.163	2.115
M(2)	(1)	53.2(6)	–	–	–	1.997
	(2)	55.7(7)	–	–	–	2.010
	(2^{an})	54.5(7)	1.19 Fe^{3+} + 0.57 Ti + 0.16 Nb + 0.08 □	50.0	2.012	1.986
	(3^{an})	52.7(6)	1.29 Fe^{3+} + 0.55 Ti + 0.16 Nb	52.2	2.014	1.987
	(3^{an})*	52.7(6)	1.00 Ti + 0.84 Fe^{3+} + 0.16 Nb	50.4	2.005	1.987
M(3)	(1)	23.0(4)	–	–	–	1.995
	(2)	22.3(5)	–	–	–	2.005
	(2^{an})	23.5(6)	1.00 Ti	22.0	1.985	1.993
	(3^{an})	21.2(4)	1.00 Ti	22.0	1.985	1.988
M(4)	(1)	26	–	–	–	2.016
	(2)	26	–	–	–	2.018
	(2^{an})	22.0(6)	1.00 Ti	22.0	1.985	2.004
	(3^{an})	22.3(5)	1.00 Ti	22.0	1.985	1.999
	(3^{an})*	22.3(5)	0.55 Ti + 0.45 Fe^{3+}	23.8	2.003	1.999

[+] not possible to assign site-populations as there is insufficient scattering in the formulae (Table 2);
* alternate possible site-populations for (3^{an});
** calculated by summing the constituent ionic radii using values from Shannon (1976).

analogous values derived from the unit formula are 118.8 (2^{an}) and 122.3 *epfu* (3^{an}), differences of 7.9 and 1.1%, respectively. Also, the refined scattering values at the *M*(1) sites (Table 5) are 28.2 (2^{an}) and 27.2 (3^{an}) *epfu*, much less than the values of 31.7 and 35.3 *epfu* for crystals (1) and (2), and more in accord with the constituent *M*-site cations available for assignment to this site.

The valence state of Fe

The chemical formulae of crystals (2^{an}) and (3^{an}) (Table 2) leave us with a residual problem: the resultant structures have net positive charges of 2.97^+ and 3.37^+ to be assigned to 1.31 (2^{an}) and 1.29 Fe (3^{an}) at the *M*(2,3,4) sites. This results in contents of ($Ti^{4+}_{2.54}$ $Fe^{3+}_{0.35}$ $Fe^{2+}_{0.96}$ $Nb_{0.15}$) and ($Ti^{4+}_{2.55}$ $Fe^{3+}_{0.79}$ $Fe^{2+}_{0.50}$ $Nb_{0.16}$) for crystals (2^{an}) and (3^{an}), respectively. We may also examine the possible oxidation state of Fe at these sites *via* the hard-sphere model relating mean bond-length and constituent ionic radius. Although this model is not highly accurate in an absolute sense, it can give a reasonable indication of site constituents, particularly where the potential differences in size involved (*i.e.*, 0.645 Å for Fe^{3+} and 0.78 Å for Fe^{2+}) are substantial. We will consider three models: (1) all Fe^{3+}, (2) Fe^{3+} : Fe^{2+} required for electroneutrality (see above), and (3) all Fe^{2+}. The mean coordination of anions (calculated from Table 7) is [3.5], giving a mean anion radius of 1.37 Å (Shannon 1976). The resulting calculations for crystal (3^{an}) are shown in Table 8 [those for crystal (2^{an}) are fairly similar]. The closest agreement occurs for an all-Fe^{3+} model, agreement for a neutral model is (just about) acceptable, whereas the agreement for the all-Fe^{2+} model is not sufficiently close for this model to be considered acceptable.

TABLE 6. COMPARISON OF TOTAL *M*-SITE SCATTERING VALUES (*epfu*) FROM SREF AND EMPA

	(1)	(2)	(2^{an})	(3^{an})
ΣM^{SREF}	133.9	139.3	128.2	123.4
ΣM^{EMPA}	122.1	118.8	118.8	122.3

Assignment of site populations

We will assign site populations for crystals (2^{an}) and (3^{an}), for which there is better agreement between the refined site-scattering values and the analogous values calculated from the unit formulae. The *M*(1) octahedron is large (2.098 and 2.115 Å) and the remaining octahedra are small (1.994 and 1.991 Å), indicating that Ti

TABLE 7. BOND-VALENCE TABLE* FOR CHEVKINITE-(Ce) CRYSTALS (2^{an}) AND (3^{an})

	Si(1)	*Si*(2)	*M*(1)	*M*(2)	*M*(3)	*M*(4)	*A*(1)	*A*(2)	Σ
					Crystal (2^{an})				
O(1)					$0.62^{x4}\downarrow$	$0.59^{x4}\downarrow$	$0.40^{x2}\downarrow$	$0.37^{x2}\downarrow$	1.98
O(2)				$0.58^{x2}\downarrow\rightarrow$	$0.55^{x2}\downarrow$			0.28	1.99
O(3)		$1.17^{x2}\downarrow$					0.37	0.42	1.96
O(4)				$0.60^{x2}\downarrow\rightarrow$		$0.56^{x2}\downarrow$	0.18		1.94
O(5)		0.97	$0.36^{x4}\downarrow$				$0.33^{x2}\downarrow$	$0.26^{x2}\downarrow$	1.92
O(6)	$0.97^{x2}\downarrow$			$0.51^{x2}\downarrow$			$0.32^{x2}\downarrow$	$0.29^{x2}\downarrow$	2.09
O(7)	1.06		$0.59^{x2}\downarrow$					$0.11^{x2}\downarrow\rightarrow$	1.87
O(8)	1.08	0.98							2.06
Σ	4.08	4.29	2.62	3.38	3.58	3.48	2.65	2.76	
					Crystal (3^{an})*				
O(1)					$0.62^{x4}\downarrow$	$0.60^{x4}\downarrow$ (0.57)	$0.43^{x2}\downarrow$	$0.39^{x2}\downarrow$	2.04 (2.01)
O(2)				$0.59^{x2}\downarrow\rightarrow$ (0.61)	$0.57^{x2}\downarrow$			0.26	2.01 (2.05)
O(3)		$1.09^{x2}\downarrow$					0.44	0.48	2.01
O(4)				$0.62^{x2}\downarrow\rightarrow$ (0.64)		$0.57^{x2}\downarrow$ (0.53)	0.14		1.95 (1.95)
O(5)		0.94	$0.31^{x4}\downarrow$				$0.36^{x2}\downarrow$	$0.27^{x2}\downarrow$	1.88
O(6)	$1.00^{x2}\downarrow$			$0.52^{x2}\downarrow$ (0.54)			$0.33^{x2}\downarrow$	$0.31^{x2}\downarrow$	2.16 (2.18)
O(7)	1.13		$0.52^{x2}\downarrow$					$0.11^{x2}\downarrow\rightarrow$	1.87
O(8)	1.04	1.08							2.12
Σ	4.17	4.20	2.28	3.46	3.62	3.54	2.82	2.90	

* Bond-valence curves (*vu*) from Brown (1981);
values in parentheses are for the site populations labelled (3^{an})* in Table 5.

occurs at *M*(2,3,4) and not at *M*(1). This assignment is also in accord with the refined site-scattering values at these sites (Table 5). The large size of the *M*(1) octahedron indicates that the *M*(1) site must be dominated by the divalent cations of the unit formula. Moreover, the fact that the refined scattering at *M*(1) exceeds 26 *epfu*, the scattering value for Fe^{2+}, indicates that the small amounts of large heavy cations in the structure (*i.e.*, Zr and Y) must occur at the *M*(1) site. The predicted mean bond-lengths for the *M*(1) site in crystals (2^{an}) and (3^{an}) are significantly greater (2.150 and 2.163 Å) than the corresponding observed values (2.098 and 2.115 Å), suggesting that some of the Fe at the *M*(1) site may be Fe^{3+}: 0.54 Fe^{2+} + 0.31 Fe^{3+} for crystal (2^{an}), and 0.69 Fe^{2+} + 0.24 Fe^{3+} for crystal (3^{an}). These values produce an even larger excess positive charge on the formulae than already caused by the assignment of all Fe as Fe^{3+} at the *M*(2,3,4) sites, indicating that there are still residual-damage effects in the annealed structures.

The *M*(2,3,4) sites have refined site-scattering values of 54.5(7), 23.5(6) and 22.0(6) for crystal (2^{an}) and of 52.7(6), 21.2(4) and 22.3(5) for crystal (3^{an}) *epfu*, respectively (Table 5), indicating that the strongest scatterers at these sites (*i.e.*, Nb and Fe^{3+}) must be assigned to the *M*(2) site. This is in accord with the observation that the refined site-scattering values at the *M*(3) and *M*(4) sites are 23.5(6) and 22.0(6) for crystal (2^{an}), and 21.2 and 22.3 *epfu* for crystal (3^{an}), respectively, and in accord with these two sites being completely occupied by Ti. The resulting site-populations for the *M*(2,3,4) sites [labeled (2^{an}) and (3^{an}) in Table 5] show close agreement for the site-scattering values but significant differences between the observed and calculated mean bond-lengths at the *M*(2) and *M*(4) sites: *e.g.*, Δ = 0.5 and 0.3 *epfu*, and Δ' = 0.027 and 0.014 Å, respectively, for crystal (3^{an}), where Δ is the difference between the refined and EMPA site-scattering values, and Δ' is the difference between the observed and calculated mean bond-lengths. An alternative site-assignment is given for the *M*(2) and *M*(4) sites [labeled (2^{an}) and (3^{an})' in Table 5]. Here, Δ = 2.3 and 1.5 *epfu*, and Δ' = 0.018 and 0.004 Å, respectively for crystal (3^{an}); model (3) shows closer agreement with the refined site-scattering values, whereas model (3)' shows closer agreement with the observed mean bond-lengths. We find no compelling argument to prefer either assignment (2^{an}) or (2^{an})', (3^{an}) or (3^{an})', and hence present both possibilities in Table 5.

TABLE 8. OBSERVED AND CALCULATED <*M*(2,3,4)–O> DISTANCE FOR CRYSTAL (3^{an}) WITH DIFFERENT Fe^{2+} AND Fe^{3+} CONTENTS

	All Fe^{3+}	Neutral	All Fe^{2+}
<r> (Å)	0.619	0.636	0.663
<r> + r_{anion} (Å)	1.989	2.006	2.033
<*M*(2,3,4)–O> (Å)	1.990	1.990	1.990
Δ (Å)	0.001	0.016	0.043

The effect of partial metamictization on site-scattering refinement

A comparison of the results of site-scattering refinement and electron-microprobe analysis for unannealed crystals (1) and (2) shows major and systematic differences. The total amount of refined scattering at the *M* sites exceeds that indicated by the unit formula calculated from the chemical composition by ~13%, an amount considerably greater than that expected for these experimental methods. Annealing a crystal [*i.e.*, crystals (2 and 3)] reduced this discrepancy, producing an agreement between the two methods of ~7 and 1% (Table 6) for crystals (2^{an}) and (3^{an}). These discrepancies are not uniformly distributed across all four of the *M* sites in the unannealed crystals; in particular, the refined scattering at the *M*(1) site is not possible, given the chemical composition of the crystal, and yet it is reproducible.

These observations indicate that small amounts of radiation damage can lead to erroneous site-scattering values (and hence erroneous site-populations), and that the effect is reproducible. It is rather intriguing that the site-scattering values are differentially affected by radiation damage; this finding implies that displacements (around the *M* sites) associated with small amounts of radiation damage are significantly different for the *M*(1) site than for the *M*(2,3,4) sites. In this regard, Lian *et al.* (2003) reported that in ion-irradiated pyrochlore, anion disorder precedes cation disorder in the radiation-induced transition from an ordered-pyrochlore superstructure to a cation-disordered defect-fluorite structure-type. Thus there seems to be some evidence that radiation-induced disorder does not proceed homogeneously in all structures.

These results have two implications: (1) structural studies on crystals that are suspected of being slightly radiation-damaged should involve heating of the crystal prior to X-ray data collection to avoid this systematic error; (2) the diffraction data contain information on the atom displacements associated with radiation damage, although it is not yet clear how to extract more quantitative information than the qualitative conclusions that are reached here.

Structure topology

Subsequent to determination of the crystal structure of perrierite-(Ce) (Gottardi 1960), Peng & Bun (1964) proposed a model for the crystal structure of chevkinite-(Ce) of composition $\{REE_{3.47}\ Ca_{0.74}\ Th_{0.01})_{\Sigma 4.22}\ Fe^{2+}$ $(Ti_{2.72}\ Fe^{3+}_{0.44}\ Fe^{2+}_{0.41}\ Al_{0.33}\ Mg_{0.08})_{\Sigma 3.98}\ (O_{7.92}\ OH_{0.08})$ $[(Si_{1.855}\ Al_{0.145})_{\Sigma 2.00}\ O_7]_2$. They predicted a structure based on analysis of the P(*uvw*) map and reported the space group as *C*2/*m*. Topologically, this model corresponds to the crystal structure determined for chevkinite-(Ce) in this work.

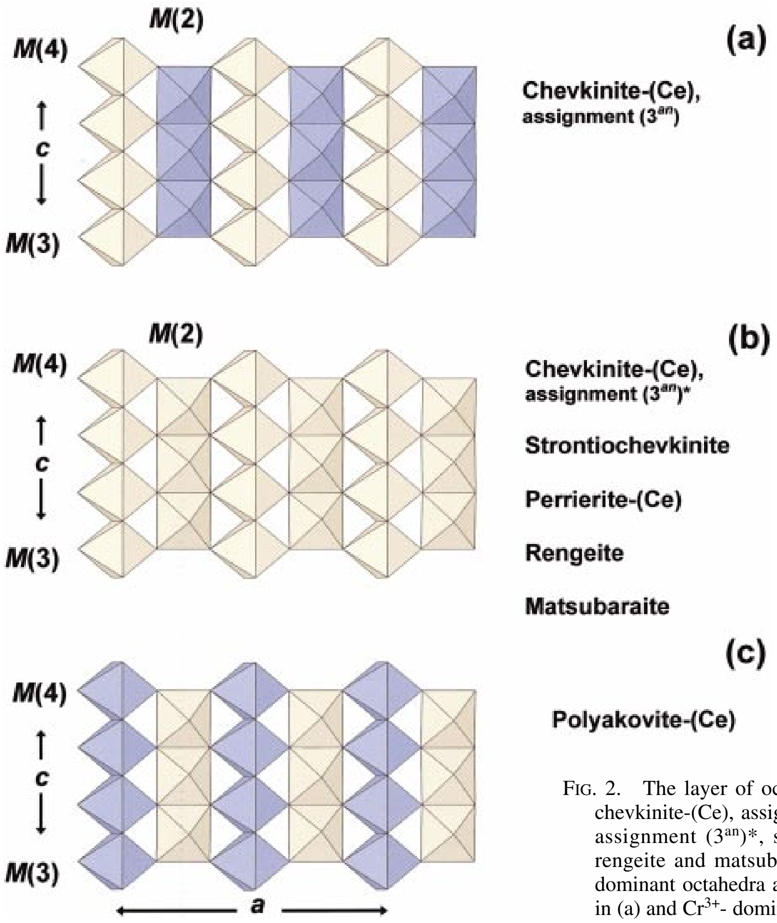

FIG. 2. The layer of octahedra projected onto (001) (a) in chevkinite-(Ce), assignment (3^{an}); (b) in chevkinite-(Ce), assignment (3^{an})*, strontiochevkinite, perrierite-(Ce), rengeite and matsubaraite; (c) in polyakovite-(Ce). Ti-dominant octahedra are yellow, Fe^{3+}-dominant octahedra in (a) and Cr^{3+}- dominant octahedra in (c) are blue.

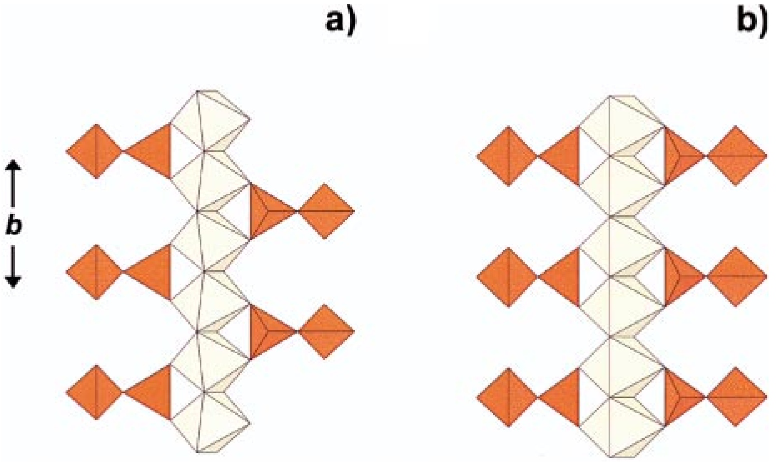

FIG. 3. Linkage of (SiO_4) tetrahedra and *M*(2) octahedra in the crystal structure of (a) chevkinite-(Ce), assignment (3^{an})*; (b) perrierite-(Ce). Legend as in Figure 1; (SiO_4) tetrahedra are orange.

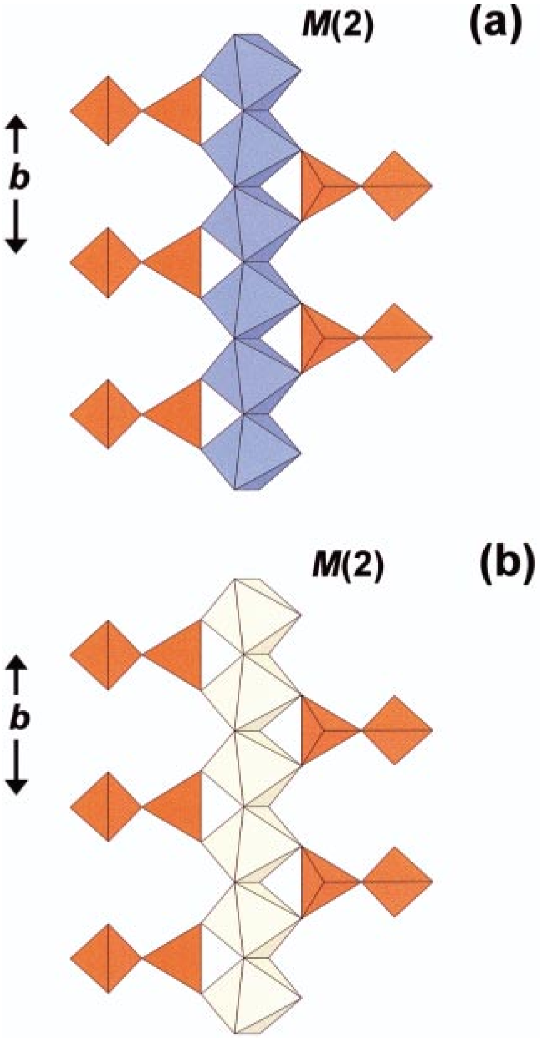

FIG. 4. The linkage of (SiO_4) tetrahedra and $M(2)$ octahedra in the crystal structure of chevkinite-(Ce). (a) Assignment (3^{an}), see Table 5; (b) assignment (3^{an})*. Legend as in Figure 2.

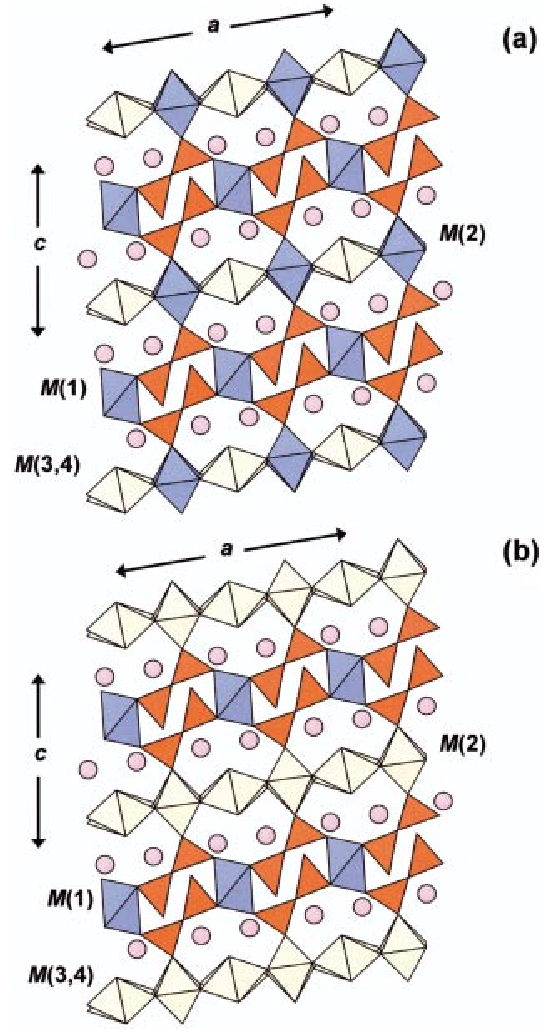

FIG. 5. The crystal structure of chevkinite-(Ce) viewed down [010]. (a) Assignment (3^{an}); (b) assignment (3^{an})*.

The principal unit of the chevkinite-(Ce) structure is a layer of octahedra parallel to (001) (Figs. 2a, b). This layer consists of two distinct rutile-like chains of octahedra in which each octahedron shares two *trans* edges with adjacent octahedra; the first chain involves $M(2)$ octahedra, and the second chain involves $M(3)$ and $M(4)$ octahedra. Chains of each type alternate within the layer, and are connected through common vertices. On the basis of the latest data for the chevkinite-group minerals (Macdonald *et al.* 2002), it is probable that strontiochevkinite and rengeite, as well as perrierite-(Ce) (neglecting the fact that perrierite-(Ce) has an $M(3)$ site with a multiplicity of 4; Gottardi 1960), have the same type of layer in their structure (Fig. 2b).

The two site-assignments described above (Table 5) result in two different layers of octahedra with regard to their arrangements of (TiO_6) octahedra. Figure 2a shows the layer of octahedra corresponding to assignment (3). Ti is dominant at the $M(3^{an})$ and $M(4)$ sites, and Fe^{3+} is dominant at the $M(2)$ site. Ideally, the layer consists of regularly alternating $[TiO_4]^{4-}$ and $[Fe^{3+}O_4]^{5-}$ chains. Figure 3a shows the layer of octahedra corresponding to assignment (3^{an})* (Table 5). Ti is dominant at the $M(2–4)$ sites, producing a layer of corner- and edgesharing (TiO_6) octahedra. On the other hand, polyakovite-(Ce) has a different arrangement of (TiO_6) octahedra: Ti^{4+} and (Cr^{3+}, Fe^{3+}) occur at the octahedrally coordinated M(2–4) sites (Popov *et al.* 2001) (Fig. 2c).

Chevkinite-(Ce) [plus strontiochevkinite and polyakovite-(Ce)] and perrierite-(Ce) [plus rengeite and matsubaraite] are structural dimorphs. They differ in the linkage of (SiO_4) tetrahedra and M(2) octahedra (Figs. 3a, b). Figure 3a also applies to polyakovite-(Ce): M(2) octahedra are Ti-dominant, as in perrierite-(Ce). Assignments (3^{an}) and (3^{an})* suggest that, in the chevkinite-(Ce) structure, (SiO_4) tetrahedra might be linked either to a chain of Fe^{3+}-dominant octahedra (Fig. 4a) or to a chain of Ti-dominant octahedra (Fig. 4b).

Intercalated between these layers are heteropolyhedral chains of [Si_2O_7] groups and M(1) octahedra (Figs. 5a, b) that extend in the *a* direction. Two outer vertices of one tetrahedron of the [Si_2O_7] group link to the apical vertices of M(2) octahedra to form a fairly open heteropolyhedral framework. Regular arrangement of M(2) and M(3,4) octahedra within the layer results in relatively large cages that contain the A(1) and A(2) sites (CN = [8] and [10], respectively) (Figs. 5a, b). Structure models presented in Figures 5a, b differ in the degree of polymerization of (TiO_6) octahedra. There are rutile-like (TiO_6) chains in the structure shown in Figure 5a, and there is a sheet of (TiO_6) octahedra in the structure shown in Figure 5b. Polymerization of (TiO_6) octahedra is a significant feature of Ti-silicate minerals; we consider this issue elsewhere (Sokolova & Hawthorne 2004).

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