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HYDROTHERMAL SYNTHESIS OF A Cs FERRUGINOUS TRIOCTAHEDRAL MICA

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ABSTRACT

Hydrothermal experiments aimed at the synthesis of trioctahedral ferruginous Cs micas were carried out at 100 MPa and a constant temperature in the range 500–710°C or in a temperature gradient. Starting mixes consisted of SiO_2, Fe_2O_3, Al_2O_3, Cs_2CO_3; there was excess water in all runs, and in some runs also an excess of CsOH or Cs_2CO_3 in solution. Two micas were grown with good yields, the Cs analog of annite and the Cs analog of tetra-ferri-annite. The former is usually accompanied by variable quantities of pollucite (± magnetite) or fayalite. An almost Al-free "Cs-tetra-ferri-annite" was synthesized from an aluminous mix in thermal gradient runs, and a pure "Cs-tetra-ferri-annite" was synthesized from an Al-free oxide mix. Rietveld refinement of the structure of "Cs-annite" shows it to be similar to the structures of annite, tetra-ferri-annite, and "Cs-tetra-ferri-annite", which has the largest unit-cell of any mica synthesized to date.

Keywords: Cs mica, synthesis, trioctahedral mica, Cs ferruginous mica.

SOMMAIRE

Nous avons effectué des expériences hydrothermales afin de synthétiser des compositions de mica trioctaédrique ferrugineux césiques à 100 MPa et une température fixe entre 500 et 710°C ou bien dans un gradient de température. Les mélanges de matériaux de départ contenaient SiO_2, Fe_2O_3, Al_2O_3, et Cs_2CO_3; il y avait un excédent d'eau dans chaque cas, et dans certains cas, un excédent de CsOH ou Cs_2CO_3 en solution. Nous avons pu synthétiser en quantités satisfaisantes deux micas, soit l'analogue césique de l'annite et de la tétra-ferri-annite. Dans le premier cas, le mica est généralement accompagné de quantités variables de pollucite (± magnétite) ou fayalite. Nous avons synthétisé la "Cs-tétra-ferri-annite" presque sans aluminium à partir d'un mélange alumineux dans un gradient de température, et la "Cs-tétra-ferri-annite" pure à partir d'un mélange d'oxydes sans Al. Un affinement de la structure de "Cs-annite" par méthode de Rietveld montre qu'il s'agit d'une structure très semblable à celles de l'annite, la tétra-ferri-annite, et de la "Cs-tétra-ferri-annite", qui possède la maille élémentaire la plus grande pour un mica synthétique connu jusqu'à maintenant.

(Traduit par la Rédaction)

Mots-clés: mica césique, synthèse, mica trioctaédrique, mica césique ferrugineux.

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INTRODUCTION

Cesium aluminosilicates are currently of interest for a number of nuclear materials applications. In addition to pollucite ($CsAlSi_2O_6$), $CsAlSiO_4$ and $CsAlSi_5O_{12}$, micas also are possible candidates for the fixation of ^{135}Cs and ^{137}Cs from nuclear waste or as solid hosts for radioactive cesium gamma-irradiation sources. Yet, few micas with Cs in the interlayer have been synthesized: Shell & Ivey (1969) reported unit-cell data for a stoichiometric synthetic Cs-fluorophlogopite, Komarneni & Roy (1986) prepared synthetic Cs-phlogopite, and Voncken *et al.* (1991) synthesized the Cs-analog of muscovite [nanpingite, $CsAl_2(Al,Si)_3O_{10}(OH)_2$]. Kopp *et al.* (1963) described the iron analog of pollucite $CsFeSi_2O_6$ in the system Cs–Fe–Si–O. The synthesis of a Cs ferruginous trioctahedral mica has not been reported previously.

EXPERIMENTAL

Experiments were performed in cold-seal pressure vessels at 100 MPa pressure, in sealed Ag or Au tubes. The pressure medium was pure water, and pressure was measured with a Bourdon-type gauge. Temperatures were measured with Ni–NiCr thermocouples and are accurate to ±3°C. In temperature-gradient experiments, we used the solute transport method (Vaughan & Craig 1978); the Ag tubes were 5–10 cm long, and the temperature gradient was about 10°C per cm.

The micas were synthesized from mixes of 3 SiO_2 (α-cristobalite) + 1.5 Fe_2O_3 + 0.5 Al_2O_3 (γ-alumina) + 0.5 Cs_2CO_3 or aluminum-free mixtures of 3 SiO_2 + 2 Fe_2O_3 + 0.5 Cs_2CO_3. Alpha-cristobalite was prepared from SiO_2 gel by heating for 3 hours at 1300°C. The SiO_2 gel was prepared from tetraethoxysilane (Fluka, >98%) using the method of Edgar (1973). Alumina was prepared by heating $AlCl_3{\bullet}6H_2O$ (Carlo Erba, 99.9%) in air at 700°C for 5 hours. The Cs_2O was prepared by heating Cs_2CO_3 (Merck, 99.5%) at 650°C. Before weighing, Fe_2O_3 (Koch–Light Laboratories Ltd., 99.99%) was heated in air at 800°C for several hours. The starting mixture of chemicals was homogenized and heated for 4 hours at 600°C in a stream of hydrogen. Hydrothermal gradient transport experiments were performed in an excess of 5.5 M Cs_2CO_3 or CsOH (prepared from Cs_2O) aqueous solution in Ag tubes 6–8 cm in length. Oxygen fugacity in the charge was not controlled explicitly with a buffer. However, it should be realized that the walls of the bomb maintain an oxygen fugacity close to that of the Ni–NiO buffer (Eugster & Wones 1962).

For routine X-ray powder diffraction of run products, we used two reflection-mode Bragg–Brentano diffractometers equipped with a secondary graphite monochromator and Cu or Co tubes. Polytypism and twinning of single crystals were examined by the precession method, which also permitted the selection of crystals suitable for collection of X-ray intensities.

The morphology of run products was documented on a Tesla Scanning Microscope. Electron-microprobe analyses of carbon-coated mica flakes were performed under the following conditions: Link eXL, 15 kV, 3 nA, 80 s. Kyanite was used as a standard for Si and Al, fayalite for Fe, and pollucite for Cs. The chemical composition of "Cs-annite" was also determined semiquantitatively by energy-dispersion X-ray spectroscopy (EDS) on a Philips 400T transmission electron microscope (TEM) operating at 120 kV. In this report, the Cs analogs of natural micas *annite* and *tetra-ferri-annite* were prepared synthetically. Their names are placed in quotes, to differentiate them from names of valid species of minerals.

For the TEM investigation, a small amount of the experimental charge was dispersed in distilled water (without grinding), and a few drops of the suspension were deposited on a copper mesh grid previously covered with a film of amorphous carbon (obtained by sputtering graphite under vacuum onto a clean substrate). This technique allowed a study of (001) cleavage flakes, the plane of preferred orientation in phyllosilicates. A 50 μm objective aperture was used for image formation, with a corresponding nominal point-to-point resolution close to 4 Å. Electron-diffraction patterns were obtained from selected areas 1 μm in diameter. Several flakes of mica were analyzed using an electron microprobe with a beam of approximately 1000 Å in diameter. Raw compositional data (net intensities) were corrected on the basis of J_{XSi} factors according to the method of Cliff & Lorimer (1975). According to the relation between proportionality factors and atomic numbers, an indicative factor J_{CsSi} of 0.85 was assumed. J_{XSi} factors used in our calculations were 1.05 (Al), 0.85 (Cs), and 0.76 (Fe). Inasmuch as intensity data for oxygen are strongly affected by instrumental fluctuations, chemical and mineralogical variation, and sample thickness, anhydrous formulae were calculated on the basis of 11 oxygen atoms (also assuming a theoretical 3:1 ratio for Fe^{2+}:Fe^{3+} in "Cs-tetra-ferri-annite").

Ion-thinned specimens of "Cs-tetra-ferri-annite" were prepared from well-grown crystals that were glued to a copper grid (having a central hole of 200 μm). For the study of stacking sequences and polytypic disorder, the crystals had to be oriented so that [001] is parallel to the plane of the grid. The crystals were then ion-thinned (Gatan Dual Ion Mill 600) at variable conditions of voltage and incident angle, until electron-transparent areas were obtained.

RESULTS

Synthesis of "Cs-annite"

The best yields of "Cs-annite" were obtained at 610°C (Table 1). The mica is greenish grey in color, and even under an SEM, no crystal outlines can be seen at magnification 3000×. The mica is invariably accompanied by a small quantity of pollucite, and in some runs, magnetite or fayalite also were detected. Above 710°C, run products consist only of pollucite and magnetite. Owing to its fine grain-size, the mica could not be separated from the accompanying phases; for further research, we selected run products with the lowest amounts of additional phases, CS–3 (with 13% pollucite) and CS–156 (with 26% fayalite). X-ray powder-diffraction data of both micas were used for a structure refinement with the Rietveld technique. Atomic coordinates and unit-cell data appear in Tables 2 and 3, respectively.

TABLE 1. DETAILS CONCERNING SELECTED EXPERIMENTS Cs-FERRUGINOUS MICAS

run No.	duration (hrs.)	temperature (°C)	starting materials	products
CS-3	610	123	1) + H_2O	Cs-annite ≫ pol
CS-156	620	119	1) + H_2O	Cs-annite ≫ fa
CS-107	600	283	2) + H_2O	Cs-tetra-ferri-annite
CS-82	710	90	1) + H_2O	pol + mg
CS-21	552	768	3) + 5.5 M CsOH	xx mica + pol + mg
CS-20	552	768	3) + 5.5 M Cs_2CO_3	xx mica + pol + mg
CS-54	451	354	1) + 5.5 M CsOH	xx mica + pol + mg

1) 3 SiO_2 + 1.5 Fe_2O_3 + 0.5 Al_2O_3 + 0.5 Cs_2CO_3 (reduced in a stream of hydrogen); 2) SiO_2 + 2 Fe_2O_3 + 0.5 Cs_2CO_3; 3) Cs-annite. Symbols: fa: fayalite, mg: magnetite, pol: pollucite, xx: single crystals.

TABLE 2. ATOMIC COORDINATES OF "Cs-ANNITE" 1*M* (run CS-156), SPACE GROUP *C*2/*m*

atom	x/a	y/b	z/c
Cs	0.0	0.5	0.0
Fe 1	0.0	0.0	0.5
Fe 2	0.0	0.3352 (16)	0.5
Si,Al	0.0823 (48)	0.1694 (23)	0.2405 (15)
O 1	0.0687 (68)	0.0	0.1831 (49)
O 2	0.3286 (65)	0.2416 (29)	0.1738 (31)
O 3	0.1361 (93)	0.1662 (34)	0.3921 (28)
O 4	0.1204 (98)	0.5	0.3743 (41)
overall B	1.51 (6)		

TABLE 3. IMPORTANT CRYSTALLOGRAPHIC DATA FOR FOUR FERRUGINOUS MICAS

	annite[1]	tetra-ferri-annite[2]	"Cs-annite"[3]	"Cs-tetra-ferri-annite"[4]
unit cell				
a, Å	5.3860 (9)	5.430 (2)	5.4065 (1)	5.487 (1)
b, Å	9.3241 (7)	9.404 (5)	9.3829 (2)	9.506 (2)
c, Å	10.2683 (9)	10.341 (3)	10.7993 (3)	10.826 (6)
β,°	100.63 (1)	100.07 (17)	99.637 (2)	99.83 (3)
V, Å^3	506.8 (1)	519.9 (5)	540.10 (2)	556.4 (3)
arc cos ($a/3c$),°	100.05	100.08	99.61	99.73
interlayer				
MEFBL[5], Å	3.175	3.144	3.280	3.375
ECoN[5]	11.91	10.81	11.64	12.00
M1 octahedron				
MEFBL[5], Å	2.121	2.104	2.178	2.130
ECoN[5]	6.00	5.97	5.87	5.99
ψ,°	58.63	59.33	56.35	59.42
M2 octahedron				
MEFBL[5], Å	2.100	2.104	2.162	2.124
ECoN[5]	5.99	5.97	5.89	6.00
ψ,°	58.30	59.31	56.02	59.34
δ,°	0.87	0.03	0.83	0.21
sheet thickness, Å	2.207	2.148	2.424	2.168
tetrahedron				
MEFBL[5], Å	1.660	1.686	1.672	1.688
ECoN[5]	4.00	4.00	3.85	4.00
sheet thickness, Å	2.252	2.314	2.228	2.284
α,°	1.57	6.37	2.58	0.24

[1] Hazen & Burnham (1973)

[2] Donnay *et al.* (1964)

[3] run CS-156, present paper

[4] Mellini *et al.* (1996)

[5] *ECoN* is the effective coordination number of Hoppe (1979), *MEFBL* is effective bond length obtained from individual cation-oxygen bond lengths by the same weighing as defined by Hoppe for *MEFIR*

Synthesis of "Cs-tetra-ferri-annite"

The synthesis of tetra-ferri-annite was described by Veres *et al.* (1955) and Wones (1959, 1963). Its Cs analog was synthesized from an Al-free oxide mix under conditions similar to those in which we grew "Cs-annite". Runs starting with a reduced oxide mix produced 100% mica. "Cs-tetra-ferri-annite" forms aggregates of fine brownish flakes.

Hydrothermal growth of single crystals of "Cs-tetra-ferri-annite"

Both "Cs-annite" and "Cs-tetra-ferri-annite" can be synthesized easily, so we attempted to grow single crystals suitable for single-crystal X-ray-diffraction analysis. The starting mix used for synthesis of "Cs-annite" was allowed to crystallize in excess of 5.5 M CsOH or Cs_2CO_3 aqueous solution. At the cold end of the tubes, mica crystallized as hexagonal plates or aggregates of flakes, accompanied by octahedra of magnetite and trapezohedra of pollucite (Figs. 1, 2). Under these conditions, the composition of the product mica could not be controlled and had to be determined with a microprobe. Seventeen analyses of three crystals from CS–21 gave the following results: SiO_2 29.93(1.04), Al_2O_3 0.38(0.23), FeO(total) 47.68(1.19), Cs_2O 20.69(0.19)%. Mica crystals are chemically homogeneous; the composition of mica crystals from several runs was found to be identical within the error of measurement. Assuming 22(+) charges, we varied the proportion of divalent and trivalent iron and imposed an additional condition of full occupancy of the octahedral sites. The corresponding formula of "Cs-tetra-ferri-annite" is $Cs_{0.89}Fe^{2+}_{2.96}Fe^{3+}_{0.04}Si_{3.07}Fe^{3+}_{0.90}Al_{0.03}O_{10.0}(OH)_{2.0}$. This phase is the Cs analog of tetra-ferri-annite $KFe^{2+}_3(Fe^{3+}Si_3)O_{10}(OH)_2$. There is relatively poor

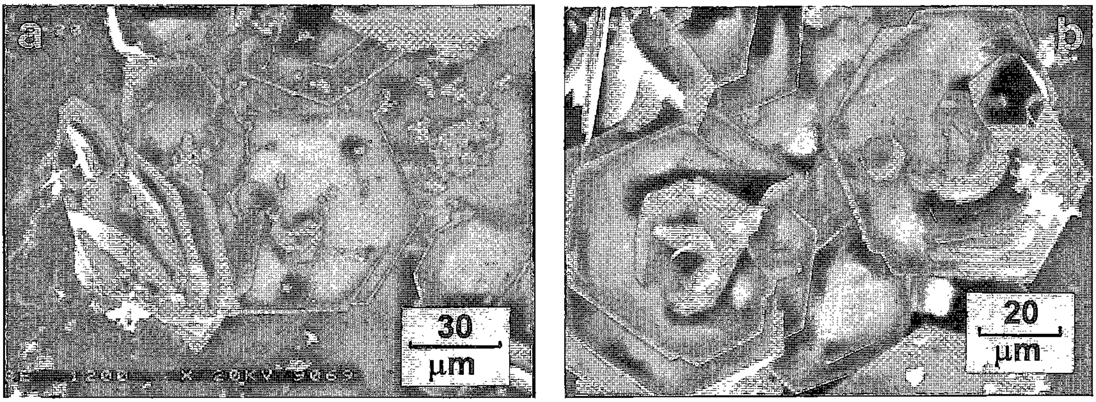

FIG. 1. SEM photographs of products of run CS–20. (a) Mica crystals plus a crystal of pollucite (lower right); (b) mica crystals plus an octahedron of magnetite (center, right).

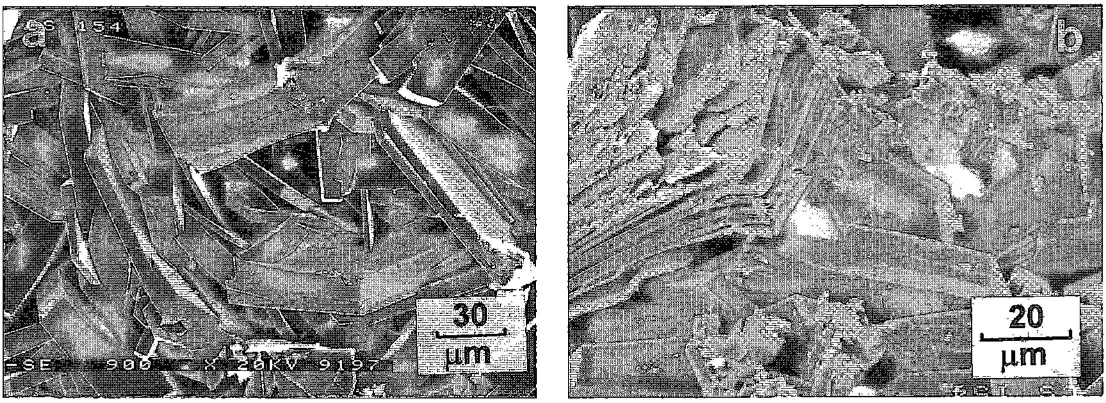

FIG. 2. SEM photographs of products of run CS–54 showing different types of aggregates on tube wall.

agreement of measured (3.36 g cm^{-3}) and calculated density (3.68 g cm^{-3}) of "Cs-tetra-ferri-annite", but owing to the nature of the material, the error on the determination is large, and correcting the formula on the basis of measured density would probably not be meaningful.

Single crystals of "Cs-tetra-ferri-annite" were examined for polytypism and twinning and used for the collection of single-crystal intensities and a refinement of its crystal structure (Mellini *et al.* 1996).

TEM investigation of Cs-ferruginous micas

"Cs-annite" (powder sample). Separate flakes gave electron-diffraction patterns **a*b*** that have sharp and intense reflections, with no evidence of disorder. There possibly are weak extra reflections owing to layer rotations about [001] (twinning?). The crystals exhibit a euhedral shape (more or less perfect pseudo-hexagonal flakes) up to 4–5 μm in diameter. Pseudo-hexagonal flakes commonly show rounded edges and internal heterogeneities revealed by contrast. Prismatic crystals also are present, up to 0.5 μm long and thicker than the hexagonal flakes. At this point, we have no data indicating possible chemical differences between crystals of different shapes. The EDS-based composition refers to the largest pseudo-hexagonal crystals; the mean formula (anhydrous basis) is $Cs_{1.00}Fe_{3.06}(Al_{1.01}Si_{2.96})O_{11.00}$.

"Cs-tetra-ferri-annite" (ion-thinned specimen). We mainly studied the **b*c*** electron-diffraction patterns. Reflections are sharp and intense; there is no evidence of streaking along **c***; random polytypic stacking thus is ruled out. There are sharp extra reflections along **c*** due to twinning. The (001) lattice fringes are regularly stacked over large fields, up to 1 μm wide, with no bending or interlayer parting. Nonetheless, some structural irregularities can be observed, most commonly twinning (with contrast reversal at twin boundary), local stacking errors, lateral termination of lattice fringes, or characteristic step-wise fracturing within the crystals, parallel and perpendicular to (001). Finally, if tilted out of the **b*c*** orientation, the crystals display elongate spots roughly parallel to (001); this may be due to small inclusions in the interlayer. The mean EDS-based composition (anhydrous basis) is $Cs_{1.02}Fe^{2+}_{3.00}(Fe^{3+}_{0.99}Si_{3.00})O_{11.00}$.

Rietveld refinement of the structure of 1M "Cs-annite"

Step-scanned diffraction data (range 7.0 – 157.0°, step = 0.02°2θ, exposure 20 s per step) were collected with graphite-monochromatized cobalt radiation. The refinement was performed with the WYRIET Version 3 program package (Schneider 1994). The pattern of sample CS–3 reveals a mixture of mica and pollucite, whereas that of CS–156 reveals a mixture of mica and fayalite. Atomic coordinates of pollucite and fayalite were obtained from Beger (1969) and Birle *et al.* (1968), respectively, and were not refined. As starting coordinates for the mica, we used those of "Cs-tetra-ferri-annite" (Mellini *et al.* 1996). By analogy with the structures of annite, tetra-ferri-annite and "Cs-tetra-ferri-annite" and in the absence of evidence to the contrary, we assumed polytype 1*M* and space group *C*2/*m* in the refinement.

After obtaining the experiment-related variables (scale factors, FWHM parameters V, W, zero point, unit-cell parameters, asymmetry and mixing parameter NA), atomic coordinates were gradually refined, and so was the constant G_1 for preferred orientation along (001). The refinement converged smoothly, but the data for CS–3 did not make it possible to refine temperature factors for each atom, just an overall *B*. For CS–156, values of atomic *B* could be obtained, but some of them were found to be negative. Thus, in the end, an equivalent overall *B* was calculated. The total number of variables refined simultaneously in the two data sets were 27 and 32, respectively. The FWHM parameter V (absolute term) had to be refined separately (strong correlation with *W*, first-order trigonometric term). At first, the background was determined using the manual mode of the BAPL program; later, linear filtering was used. Refinement (ended by convergence indicated by a program message) and background filtering were repeated until a stable solution was obtained.

During the calculations, we varied the assumed composition of the mica so as to reflect the quantities of additional phases present in the run products, but, surprisingly, none of the models proved preferable to stoichiometric $CsFe^{2+}_{3.0}(AlSi_3)O_{10}(OH)_2$. There are, however, clear differences between the results obtained for CS–3 and CS–156. For CS–3, the *x* coordinates of oxygen atoms (particularly O3 and O4) are associated with large uncertainties and are responsible for unusual distortions of coordination polyhedra in the sheets of octahedra and tetrahedra. For instance, Hoppe's (1979) *effective coordination number* (*ECoN*) for *M*1, *M*2 and *T* positions are, respectively, 5.33, 5.84, and 2.87, among which the last one is particularly unlikely. On the contrary, results for CS–156 appear considerably more plausible (Tables 2, 3). A likely cause of this paradoxical conclusion is that the overlap of mica peaks with peaks of pollucite is more serious than the overlap with peaks of fayalite.

DISCUSSION AND CONCLUSIONS

It is interesting to compare the crystal structures for four ferruginous trioctahedral micas refined to date, annite (Hazen & Burnham 1973), tetra-ferri-annite (Donnay *et al.* 1964), "Cs-annite" (present study), and "Cs-tetra-ferri-annite" (Mellini *et al.* 1996), interrelated by the substitutions K ⇔ Cs and $^{IV}Al \Leftrightarrow {}^{IV}Fe^{3+}$. Completely or almost completely occupied with divalent iron, the sheets of octahedra in the four micas should be a constant common feature. Variability can be expected

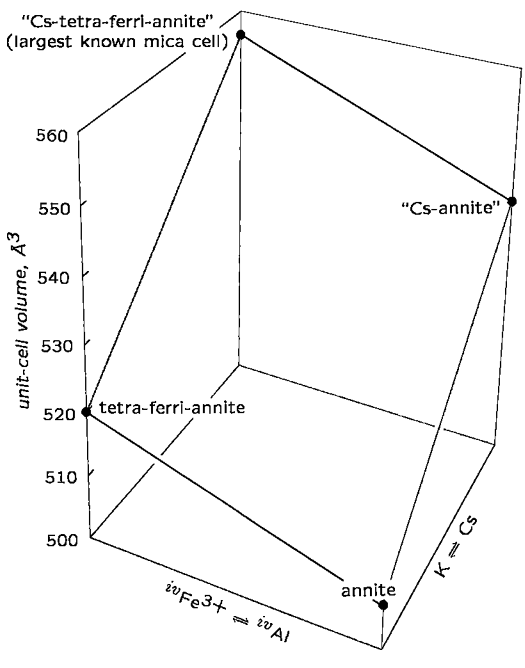

FIG. 3. Unit-cell volumes of four ferruginous micas.

in the sheets of tetrahedra because tetrahedra occupied with (Al,Si_3) will be smaller than those occupied with (Fe^{3+},Si_3), and in the interlayer, where K or Cs will demand different tetrahedron-rotation angles and thus different coordinations.

Even though the precision of Rietveld data is decidedly lower than that of the three single-crystal refinements, the effects illustrated in Table 3 essentially follow expectations. Clearest is the behavior of unit-cell volumes (Fig. 3). Also an interesting observation is the thickness of the 1*M* layer, about the same in both Cs micas, but the incorporation of Fe^{3+} in tetrahedra expands considerably the dimensions along **a** and **b**. Also, the size of Cs, in conjunction with the large (Fe^{3+},Si_3) tetrahedra, produces a sheet of tetrahedra with only a small rotation angle α and a quasi-ideal coordination of oxygen atoms in "Cs-tetra-ferri-annite"; this is almost emulated in annite by the smaller potassium and the smaller (Al,Si_3) tetrahedra. The flattening angles ψ of octahedra in all structures show some differences, but they span only the central part of the range known from refined structures (Weiss *et al.* 1985, Fig. 3). With respect to the "Cs-annite" itself, the bond lengths in octahedra *M*1 and *M*2 are close to each other and indicate a rather regular sheet of octahedra.

This project was initiated as a search for phases suitable for the fixation of radioactive waste Cs isotopes. Such phases should be stable under conditions in a repository, where, among others, a high fugacity of oxygen can be expected. In terms of the conditions of synthesis, both "Cs-annite" and "Cs-tetra-ferri-annite" grow well in the temperature range 500–600°C and at a confining pressure of 100 MPa, but the latter, whose Al^{3+} is replaced by Fe^{3+}, seems to grow more easily. Further experiments would be needed to determine the extent of thermodynamic stability of these two micas, but their behavior indicates that both might serve well for the fixation of Cs. However, under conditions of high oxygen fugacity, the ferriferrous "Cs-tetra-ferri-annite" might be preferable.

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