Katayamalite and baratovite are structurally identical

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Abstract: An investigation of the crystal structure of the mineral katayamalite, $KLi_3Ca_7Ti_2[Si_6O_{18}]_2(OH,F)_2$, shows that it is best described as monoclinic in space group $C2/c$, and not as centrosymmetrically triclinic as originally proposed. Moreover, a comparison of the crystal structures of katayamalite and baratovite, $KLi_3Ca_7(Ti,Zr)_2[Si_6O_{18}]_2(OH,F)_2$, shows them to be identical within experimental error. The only difference between the two minerals is the slightly different chemical composition. Therefore katayamalite and baratovite are structurally identical minerals.

Key-words: Katayamalite, baratovite, symmetry, crystal structure, ring silicate.

Introduction

Baratovite was described as a new monoclinic mineral by Dusmatov *et al.* (1975). Its crystal structure was determined by Sandomirskii *et al.* (1976) and refined by Menchetti & Sabelli (1979) in space group $C2/c$. The basic feature of the crystal structure is a ring of six SiO_4 tetrahedra. The idealized chemical formula of baratovite proposed by these authors is $KLi_3Ca_7(Ti,Zr)_2[Si_6O_{18}]_2F_2$, but the only available chemical analysis indicates insufficient presence of fluorine to justify two atoms of fluorine per twelve silicon atoms. The chemical formula of baratovite should be $KLi_3Ca_7(Ti,Zr)_2[Si_6O_{18}]_2(OH,F)_2$.

Murakami *et al.* (1983) described katayamalite as a new triclinic mineral, related to baratovite, but clearly different because of its lower symmetry. On the basis of a chemical analysis and a crystal structure determination (Kato & Murakami, 1985) the formula $(K_{0.89}Na_{0.11})Li_3Ca_7(Ti_{1.95},Fe_{0.05})[Si_6O_{18}]_2(OH_{1.76}F_{0.24})$ was suggested. Since Na and Fe were also identified as minor constituents in baratovite, the main differences between the chemical compositions are that the minor replacement of Ti by Zr is not observed in katayamalite and that the hydroxyl content in the latter may be slightly higher. According to Kato & Murakami (1985) the basic difference between the two minerals lies in their symmetry and a distortion of the crystal structure of katayamalite relative to baratovite. Thus the two minerals would appear to be polymorphs of one compound.

Table 1. Cell constants of katayamalite (original, Kato & Murakami, 1985) and transformed, and of baratovite (Menchetti & Sabelli, 1979); the transformation matrix triclinic to monoclinic is (0 1 0/1 0 0/-0.5 -0.5 -1).

	Katayamalite		Baratovite
	original in $C\bar{1}$	transformed in $C2/c$	
a (Å)	9.721(2)	16.923(3)	16.941(3)
b (Å)	16.923(3)	9.721(2)	9.746(2)
c (Å)	19.942(3)	20.909(3)	20.907(3)
α (°)	91.43(10)	89.98(10)	90
β (°)	104.15(11)	112.40(10)	112.50(10)
γ (°)	89.94(10)	89.94(10)	90

The monoclinic description of the crystal structure of katayamalite

The unit cell of katayamalite can be shown by standard methods (Baur & Tillmanns, 1986) to correspond, well within the estimated standard deviations of the angles reported by Kato & Murakami (1985), to a C-centered monoclinic unit cell (Table 1). The transformation matrix from the triclinic setting preferred by Kato &

Murakami to the monoclinic setting proposed here is (0 1 0/1 0 0/-0.5 -0.5 -1).

A corresponding transformation of the coordinates of the atomic positions in the triclinic unit cell into the monoclinic description shows that all atoms of the triclinic cell can be projected pairwise onto each other in the monoclinic cell. The mean distance between the averaged positions and the individual atom positions in katayamalite is only 0.011 Å, which is much less than

Table 2. Positional coordinates ($\times 10^5$) for katayamalite as transformed into the monoclinic setting from the values of Kato & Murakami (1985) using the transformation matrix (0 1 -0.5/1 0 -0.5/0 0 -1) and then averaged, and for baratovite taken from Menchetti & Sabelli (1979).

Atom	k#	t#	katayamalite			baratovite		
			x/a	y/b	z/c	x/a	y/b	z/c
Ti	1,2	1,2	33500	7050	25200	33460	7052	25190
Ca1	3,6	4,1	22050	-7250	51300	22017	-7256	51329
Ca2	5,7	-4,-3	14550	28350	50700	14518	28319	50695
Ca3	4,8	4,-3	7200	63900	50000	7260	63830	50006
Ca4	1,2	1,2	0	0	0	0	0	0
K	-	1,2	0	7100	25000	0	7116	25000
Si1	6,10	4,-1	61400	26500	36000	61404	26552	36061
Si2	1,9	4,-1	43100	32350	36000	43105	32388	36004
Si3	2,8	4,-1	36850	63500	35900	36923	63544	35952
Si4	3,7	4,-1	49100	88000	36000	49150	87983	36058
Si5	4,12	4,-1	67350	81550	35900	67409	81512	35930
Si6	5,11	4,-1	73900	50800	36200	73852	50777	36230
O1	16,31	4,-1	65850	40350	34500	65859	40248	34516
O2	18,30	4,-1	65900	22350	44100	65949	22375	44124
O3	17,29	4,-1	61250	14350	30800	61253	14422	30831
O4	1,28	4,-1	51525	30975	34050	51498	30992	34054
O5	2,26	4,-1	35350	23900	30600	35284	24005	30572
O6	3,27	4,-1	45200	28300	43900	45297	28340	43964
O7	4,25	4,-1	41025	48775	35050	41045	48836	35154
O8	5,23	4,-1	27350	65300	30400	27384	65317	30411
O9	6,24	4,-1	37850	65150	43800	37909	65109	43871
O10	7,22	4,-1	42675	74875	34050	42732	74862	34060
O11	9,21	4,-1	52125	91975	44150	52081	92000	44137
O12	8,20	4,-1	44850	450	30900	44899	464	30851
O13	10,19	4,-1	57250	82050	34500	57291	82063	34558
O14	12,36	4,-1	72800	85450	43800	72900	85295	43888
O15	11,35	4,-1	69500	90700	30400	69539	90634	30421
O16	13,34	4,-1	69250	65750	34500	69225	65698	34453
O17	14,32	4,-1	78550	47600	31000	78585	47590	31054
O18	15,33	4,-1	80050	49850	44200	80087	49875	44299
F1	Oh1,Oh2	4,-1	10100	6850	45700	10199	6911	45949
Li1	3,3	1,2	50000	8350	25000	50000	8430	25000
Li2	1,2	4,1	24625	31675	24850	24650	31810	24880

The original numbering of the atomic positions in katayamalite is given in column k#. The code in column t# indicates how the coordinates of katayamalite must be transformed in the monoclinic system in order to coincide with the values for baratovite: 1: x,y,z; 2: -x,y,1/2-z; 3: 1/2+x,1/2+y,z; 4: 1/2-x;1/2+y,1/2-z. Negative numbers indicate centrosymmetrically related position.

the experimental error with which the atomic positions were determined by Kato & Murakami (1985). The individual distance differences between pairs of atoms range from 0.0 to 0.068Å, where the largest value refers to the distance between the positions of Li(1) to Li(2). However, the error in the determination of the Li positions is particularly large. In fact *all* estimated standard deviations of these individual distance differences are larger than the distances themselves, indicating that within experimental error the crystal structure of katayamalite is best described as monoclinic. Table 2 lists the transformed and averaged positional coordinates of all atoms in the new description of katayamalite.

Comparison of the crystal structures of baratovite and katayamalite

The monoclinic cell of katayamalite is extremely similar to the unit cell of baratovite (Menchetti & Sabelli, 1979; see Table 1). The slightly larger cell constants of baratovite are most likely due to the partial replacement of titanium atoms by zirconium in that mineral (more than one eighth of the titanium is so replaced). On the other hand, the systematic errors in the determination of unit cell constants by single crystal methods are usually much larger than the statistical errors would indicate; thus the difference in the cell constants of katayamalite and baratovite is of little significance and need not concern us.

Table 2 lists also the positional coordinates determined by Menchetti & Sabelli (1979) for baratovite. A comparison of the atomic positions in the two minerals shows that they are extremely similar. The mean distance of corresponding atoms from each other is 0.012Å, thus it is even smaller than between the two triclinic halves of katayamalite projected into the monoclinic unit cell. The distance differences range between 0.0 and 0.049Å, where the largest deviation is found for the (OH,F) site. Possibly this reflects the different fluorine content of the two samples. Again *all* the distance differences are much smaller than the corresponding pooled estimated standard deviations of atomic positions in katayamalite and baratovite. However, since the precision of the crystal structure determination of baratovite is much higher than that achieved in the refinement of katayamalite, it is mainly the comparison with the statistical errors in the crystal structure determination of katayamalite that matters.

Discussion

A close look at the crystal structures of katayamalite and baratovite shows that:

1) katayamalite is best described as monoclinic in space group $C2/c$, and not as centrosymmetrically triclinic as originally proposed;

2) the crystal structures of katayamalite and baratovite are identical within experimental error. The main difference between the two descriptions is a slightly different chemical composition, namely a partial replacement of titanium by zirconium and possibly a different proportion of OH versus F in baratovite.

Mistakenly triclinic descriptions of substances crystallizing in space group $C2/c$ are the second most common error found in a sample of 221 wrongly assigned space groups (Baur & Kassner, 1992). It is comparable to the overlooking the inversion center in $P\bar{1}$, and it occurs half as often as the oversight of an inversion center in space group $C2/c$.

Minor chemical differences between different occurrences of a mineral are common. The chemical differences between katayamalite and baratovite are small when compared with similar differences known from other minerals.

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