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Neutron-diffraction study on the orientation of hydroxyl groups in margarite

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Abstract. The crystal structure of margarite $2M_1$ was refined in space group *Cc* from neutron and X-ray data on a crystal from Greiner, Zillertal, Austria, $a = 5.108(1)$ Å, $b = 8.844(2)$ Å, $c = 19.156(3)$ Å, $\beta = 95.48(2)^\circ$. Almost complete Si/Al ordering was found for the tetrahedral position.

The hydroxyl group exhibits two different orientations: one is close to those commonly found in dioctahedral and the other to those characteristic of trioctahedral micas. About 79 % of the O–H bonds are located in the first oritentation, whereas 21 % are found in the second. The second orientation agrees with a cationic occupation of about 21 % in the M(1) site in the structure of the Zillertal margarite.

Introduction

The structure of the brittle mica margarite was first described by Takéuchi (1965) in space group $C2/c$ based on X-ray film intensity data. Guggenheim and Bailey (1975, 1978) refined the structure of margarite in a subgroup symmetry *Cc*, and found essential ordering of tetrahedral and octahedral cations, so that in the tetrahedral sheet the Al–O–Al avoidance rule (Loewenstein, 1954) is obeyed. The present neutron diffraction study was performed to determine the hydrogen positions and the Si/Al ordering, as the difference in scattering power of Si and Al is more pronounced for neutrons ($b_{Si} = 4.149$ fm; $b_{Al} = 3.449$ fm) than for X-rays. A complementary X-ray diffraction study was performed in order to refine the occupation of the M(1) position unambiguously.

Experimental

Crystals of margarite from Greiner, Zillertal, Tirol, were used for the present study. A wet chemical analysis of the material revealed that the number of the octahedral cations per octahedral sheet exceeded four by 0.42 (Table 1), the excess cations being presumably located at the M(1) positions which are otherwise vacant for dioctahedral micas. The composition is then $(Ca_{1.45}Na_{0.42})$ $(Al_{3.92}Fe_{0.06}Mg_{0.20}Li_{0.23})$ $(Si_{3.84}Al_{4.16})O_{20}(OH)_{4.24}$. If the above formula is idealized to a content of O_{20} and $(OH)_4$, then the composition is given by $(Ca_{1.46}Na_{0.42})$ $(Al_{4.01}Fe_{0.06}Mg_{0.20}Li_{0.23})$ $(Si_{3.87}Al_{4.13})O_{20}(OH)_4$. A crystal with the shape of an equilateral triangle of edge length 1.66 mm and thickness 0.45 mm was selected. Reflections with $k \neq 3n$ showed no diffuseness indicating the well ordered structure of the crystal. The cell dimensions were refined by least-squares procedures from the setting angles of 25 independent X-ray reflections measured with graphite-monochromated MoKα radiation ($\lambda = 0.7107$ Å). They are $a = 5.108(1)$ Å, $b = 8.844(2)$ Å, $c = 19.156(3)$ Å and $\beta = 95.48(2)°$. Neutron data were collected on the D8 four-circle diffractometer at the HFR of the Institut Laue-Langevin, Grenoble. A wavelength $\lambda = 1.2686$ Å from a Cu(200) monochromator was used. About 1300 reflections up to $\sin\theta/\lambda = 0.67$ Å^{-1} were measured resulting in a unique set of 1037 reflections, 1003 of these with intensities greater than $2\sigma(F^2)$ were used for the structure refinement.

A crystal with dimensions 0.1 × 0.3 × 0.37 mm was chosen for X-ray diffraction. A total of 3000 intensities were collected on a Syntex $P2_1$ diffractometer with MoKα radiation, 1260 were symmetry independent. The intensities were corrected for Lorentz-polarization and for absorption ($\mu = 14$ cm^{-1}). A set of 1185 reflections with intensities greater than $2\sigma(F_o^2)$ were used for structure refinement.

Table 1. Wet chemical analysis of margarite

Weight percent		Calculation for 24 oxygens		
SiO_2	28.98	Si	3.84	8.00^{IV}
Al_2O_3	51.82	Al	4.16	
			3.92	4.42^{VI}
TiO_2	0.11	Ti	0.01	
Fe_2O_3	0.41	Fe^{3+}	0.04	
FeO	0.21	Fe^{2+}	0.02	
MgO	1.01	Mg	0.20	
Li_2O	0.43	Li	0.23	
CaO	10.23	Ca	1.45	1.87^{XII}
Na_2O	1.63	Na	0.42	
$H_2O^{(+)}$	4.80	(OH)	4.24	
MnO, K_2O, BaO, SrO, P_2O_5	< 0.03			
Total	99.69			

Structure refinement

Refinement of the neutron data started in the centric space group $C2/c$. The least-squares calculations were carried out with the CRYLSQ link of the X-RAY-SYSTEM (Stewart et al., 1972); a weighting scheme was employed of the form $w(F_o) = [\sigma(F_o) + 0.001\, F_o^2]^{-1}$. The neutron scattering lengths were $b_{Li} = -2.03$, $b_{Ti} = -3.37$, $b_{Mg} = 5.38$, $b_{Al} = 3.449$, $b_{Fe} = 9.54$, $b_{O} = 5.803$, $b_{Si} = 4.149$, $b_H = -3.7409$ (in fm) Koester (1977). Values for the occupancy of individual tetrahedra were obtained by a variation of the relevant scattering lengths. The refinement with $C2/c$ converged to give $R = 0.066$. A difference-Fourier synthesis revealed a weak but significant negative peak at the position expected for hydrogen atoms in trioctahedral micas in addition to a strong negative peak at the hydrogen position in dioctahedral micas. This suggests a distribution of hydrogens in two different positions in this Zillertal margarite. The trioctahedral position mentioned first is denoted H(B) and the dioctahedral one H(A). The occupancy refinement in $C2/c$ symmetry revealed the hydrogen content in H(A) and H(B) sites to be 79(3) % and 21(3) %. The difference Fourier, however, did not show any significant peak at the M(1) position where the excess octahedral cations are expected. This result implies that this specific position would be occupied by two types of cations, one having negative neutron scattering length such as Li and Ti (Table 1) and the other positive neutron scattering length such as Mg. The occupancies of both types of cations in the M(1) site would be such that the scattering lengths just cancel out. The possible occupation of M(1) therefore has to be studied by X-rays as will be shown later.

The structure was then furtherrefined in the subgroup symmetry Cc. The tetrahedral site T(1) in the $C2/c$ splits in Cc into two non-equivalent sites. We denote these sites T(11) and T(12). Likewise, T(2) in $C2/c$ splits into T(21) and T(22). Atomic notations similar to these are adopted for oxygen and hydrogen atoms in the acentric structure; note that there are four hydrogen positions in the Cc structure: H(11A), H(11B), H(12A), and H(12B). In the least-squares refinement of the acentric structure, we simultaneously varied all positional parameters (including those of Si and Al, and all pseudosymmetrically related parameters), anisotropic thermal and population parameters [except H(B)]. During the refinement we noted high correlations between thermal parameters and occupancy values of the hydrogen atoms at both B positions. The occupancy of H(B) was therefore fixed to 21 % according to the results of the centric refinement and the chemical analysis.

Table 2. Atomic parameters refined in space group *Cc* by neutron diffraction except M(1), which is from X-ray refinement

Atom	$b[10^{-15}\text{m}]$	Population	x	y	z
Ca	4.45	1.001(7)	0.00	0.0929(1)	0.25
M(1)[a]		0.21	0.258(6)	0.242(2)	0.504(1)
M(2)	3.449	0.99(1)	0.7480(4)	0.9169(2)	0.9998(1)
M(3)	3.449	1.00(2)	0.2522(4)	0.0851(2)	0.0003(1)
T(11)	3.449	1.04(2)	0.4636(4)	0.9279(3)	0.1425(1)
T(12)	4.149	1.00(1)	0.5350(3)	0.0747(2)	0.8553(1)
T(21)	4.149	1.04(1)	0.4546(3)	0.2565(2)	0.14486(9)
T(22)	3.449	1.00(1)	0.5468(4)	0.7438(2)	0.8579(1)
O(11)	5.803		0.9611(2)	0.4455(1)	0.05259(5)
O(12)			0.0451(2)	0.5618(1)	0.94059(6)
O(21)			0.3953(2)	0.2545(1)	0.06003(6)
O(22)			0.6200(2)	0.7497(1)	0.94772(6)
O(31)			0.3636(2)	0.0978(1)	0.17757(6)
O(32)			0.6376(2)	0.9181(1)	0.82274(6)
O(41)			0.2674(2)	0.7786(1)	0.16830(6)
O(42)			0.7122(2)	0.2156(1)	0.83231(6)
O(51)			0.2882(3)	0.3906(2)	0.17847(7)
O(52)			0.7352(3)	0.6036(2)	0.82142(7)
O(61)			0.4547(3)	0.5670(2)	0.05169(7)
O(62)			0.5489(3)	0.4361(2)	0.94891(7)
H(11)	−3.741	0.77(1)	0.3663(7)	0.6550(5)	0.0620(3)
H(12)		0.79(2)	0.6325(9)	0.3452(5)	0.9396(4)
H(21)		0.21	0.439(3)	0.591(2)	0.098(1)
H(22)		0.21	0.561(4)	0.399(3)	0.905(1)

[a] By X-ray

All other parameters were successfully refined to a final $R = 0.017$. The atomic parameters are given in Tables 2 and 3. The least-squares calculation of the X-ray data were performed in the same way as for the neutron data. Atomic scattering factors for the ionic state were from *International Tables for X-ray Crystallography* (1974). Refinement in space group *Cc* converged to $R = 0.024$. A difference Fourier revealed an electron density of approximately 1 $e\text{Å}^{-3}$ at M(1). The occupancy was fixed at 21 % and a form factor was calculated based on an occupation of M(1) by Li and Mg. An attempt to refine the occupancy further was unsuccessful.

Results and discussion

Orientation of hydroxyl groups

The refinement of the neutron data gave occupancies of hydrogens H(11A) and H(12A) as 77(1) % and 79(2) %, respectively. This implies a hydrogen occupancy of H(11B) of 23 % and of H(12B) of 21 %, based on four hydroxyl groups per unit cell. The latter value for H(12B) agrees well with the occupancy of 21 % based on the chemical composition (Table 1) and on the refinement of the site occupancy of H(B) in *C*2/*c* space group. The difference in occupancy between H(11A) and H(12A) is insignificant and we may regard 79 % H of each hydroxyl group in the A position and 21 % in the B position.

Table 3. Anisotropic temperature factor coefficients (× 100)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	0.90(6)	1.12(6)	1.12(6)	0.12(6)	0.21(4)	−0.05(7)
M(1)[a]	2.3(4)	2.3(5)	2.1(6)	0.1(3)	0.5(4)	0.5(4)
M(2)	0.25(11)	0.47(11)	0.58(12)	−0.00(6)	0.07(7)	0.01(7)
M(3)	0.52(11)	0.42(11)	0.54(11)	−0.09(7)	0.03(7)	0.18(7)
T(11)	0.76(11)	0.48(11)	0.53(11)	−0.05(7)	0.17(6)	0.01(7)
T(12)	0.23(8)	0.44(9)	0.62(9)	0.04(5)	0.02(5)	−0.03(6)
T(21)	0.64(9)	0.61(9)	0.57(9)	−0.01(5)	0.03(5)	−0.02(6)
T(22)	0.38(10)	0.29(11)	0.61(11)	−0.04(6)	0.05(6)	0.09(7)
O(11)	0.65(5)	0.67(4)	0.69(5)	0.06(4)	0.26(4)	−0.04(4)
O(12)	0.51(4)	0.72(4)	0.61(5)	0.20(4)	0.14(4)	0.19(3)
O(21)	0.86(5)	0.55(5)	0.59(5)	−0.06(4)	−0.23(4)	0.01(3)
O(22)	0.79(5)	0.41(5)	0.67(5)	−0.03(4)	0.06(4)	−0.12(3)
O(31)	0.82(5)	0.50(4)	0.84(5)	0.01(3)	0.38(4)	0.09(3)
O(32)	0.94(5)	0.50(5)	0.89(5)	0.03(4)	0.32(4)	0.03(4)
O(41)	0.55(5)	0.76(5)	0.95(5)	−0.18(4)	0.01(4)	0.09(4)
O(42)	0.53(5)	0.70(4)	1.09(5)	−0.14(4)	0.07(4)	0.29(4)
O(51)	0.53(6)	0.90(5)	0.81(6)	0.27(4)	−0.05(5)	−0.18(4)
O(52)	0.59(5)	0.85(5)	0.80(7)	0.19(4)	0.00(5)	−0.13(4)
O(61)	0.65(6)	0.90(6)	0.69(7)	−0.16(5)	0.14(5)	−0.27(6)
O(62)	0.73(5)	0.87(7)	1.00(7)	−0.33(6)	0.29(5)	−0.22(6)
H(11)	1.6(2)	2.2(2)	6.1(4)	0.4(2)	0.9(2)	−1.8(2)
H(12)	3.3(2)	1.8(2)	5.6(4)	0.2(2)	2.0(2)	−1.1(2)
H(21)	2.5(7)	5.3(12)	3.0(9)	−0.1(7)	1.6(6)	−1.8(7)
H(22)	5.1(10)	4.4(11)	2.2(8)	−3.5(8)	1.9(7)	−2.5(8)

[a] By X-ray

The A position is very close to the hydrogen position reported for a $2M_1$ muscovite (Rothbauer, 1971). Let the hydrogen position be defined by a polar coordinate system ϱ, φ as given in Figure 1. Then we find $\varrho = 78.0°$ and $\varphi = 30.0°$ for the O–H orientation in Rothbauer's muscovite; these values should be compared with those of O(61)–H(11A) and O(62)–H(12A) for margarite (Table 6). On the other hand, the B position is far away from the octahedral sheet (Table 6) and closer to the hydrogen position found for phlogopite (Joswig, 1972), in which the O–H vector is parallel to *c* and hence $\varrho = 0$. The structure of Zillertal margarite may then be regarded as having 79 % "dioctahedral character" and 21 % "trioctahedral character". The

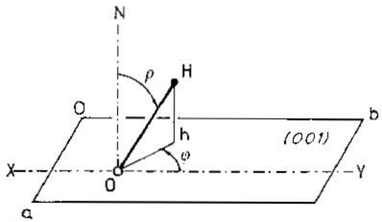

Fig. 1. Polar coordinate system to specify the location of the proton, H, of a hydroxyl group. XY is a line that is parallel to the *b* axis and passes through the oxygen atom, indicated by a small open circle, of the hydroxyl group, ON being a normal to the (001) plane

larger values of ϱ for O(61)−H(11B) and O(62)−H(12B) compared with phlogopite may be related to the situation that the major contents in M(1) are Li and Mg with nearly the same fraction. For the case in which a triplet of octahedral cations bound to OH are Al, Al, and Li, the value of ϱ has been calculated to be 67° (Giese, 1979). Although the calculated O−H orientation is not available for a triplet of Al, Al, and Mg, the value of ϱ would be much closer to $\varrho = 0°$. The existence of Na (about 20 %) at the interlayer cation positions may also be responsible for the orientation of the trioctahedral O−H in the margarite structure.

General structural features

The lengths and angles of individual bonds in all tetrahedra are given in Table 4. The values of Table 4 are based on the neutron refinement. Regarding the crystal structure as a whole, we find no significant difference in configuration between the upper and lower tetrahedral sheets of mica layer in contrast to the results given by Guggenheim and Bailey (1978). Thus, for example, the rotation angle α, which adjusts the difference in dimension between the tetrahedral and octahedral networks, shows essentially the same value for the upper and lower tetrahedral sheets, and both tetrahedral sheets have the same thickness (Table 5).

The acentric nature of the margarite structure is basically characterized only by the perfect ordering of tetrahedral and octahedral cations as revealed by the neutron diffraction study (Table 3). The accuracy of the refined occupancies of tetrahedral cations is somewhat biased by relatively high correlation effects of the parameters due to the pronounced pseudosymmetry; the greatest correlation coefficient observed was 0.663 for the pair of z parameters of M(2) and M(3). An additional information on the ordering of tetrahedral cations may be provided by mean bond-lengths of individual tetrahedra. They are: T(11) 1.748 Å, T(12) 1.628 Å, T(21) 1.626 Å, and T(22) 1.748 Å (Table 4). As Baur (1981) gave 1.623 Å for Si−O and 1.753 for Al−O (Takéuchi et al., 1980, experimentally provided a value of Al−O = 1.752 Å), we may estimate the ordering to be 96 % for the four tetrahedra in fairly good agreement with the refinement of the population numbers.

Table 4. Interatomic distances (Å) and bond angles (°) of margarite

Bond lengths		Edge lengths		Bond angles
Tetrahedron about T(11):				
T(11)−O(31)	1.743(3)	O(31)−O(41)	2.868(2)	110.1(1)
−O(41)	1.757(3)	O(31)−O(51)	2.838	108.0
−O(51)	1.765(3)	O(41)−O(51)	2.828	106.8
−O(11)	1.727(2)	O(11)−O(31)	2.833	109.4
		−O(41)	2.914	113.5
		−O(51)	2.842	108.9
mean	1.748	mean	2.854	109.5
Tetrahedron about T(21):				
T(21)−O(31)	1.623(2)	O(31)−O(41)	2.629(2)	107.9(1)
−O(41)	1.630	O(31)−O(51)	2.618	107.3
−O(51)	1.628	O(41)−O(51)	2.665	109.8
−O(21)	1.624	O(21)−O(31)	2.662	110.1
		−O(41)	2.684	111.2
		−O(51)	2.671	110.4
mean	1.626	mean	2.655	109.5
Tetrahedron about T(12):				
T(12)−O(32)	1.626(2)	O(32)−O(42)	2.662(2)	109.9(1)
−O(42)	1.625	O(32)−O(52)	2.628	107.9
−O(52)	1.625	O(42)−O(52)	2.620	107.4
−O(12)	1.634	O(12)−O(32)	2.672	110.1
		−O(42)	2.687	111.0
		−O(52)	2.676	110.4
mean	1.628	mean	2.658	109.5
Tetrahedron about T(22):				
T(22)−O(32)	1.761(2)	O(32)−O(42)	2.835(2)	107.7(1)
−O(42)	1.750	O(32)−O(52)	2.826	107.0
−O(52)	1.755	O(42)−O(52)	2.875	110.2
−O(22)	1.727	O(22)−O(32)	2.828	108.3
		−O(42)	2.905	113.3
		−O(52)	2.853	110.1
mean	1.748	mean	2.854	109.4

Some other features of the structure include:

(1) The apical bonds of the T(11) and T(22) tetrahedra, both occupied essentially by Al, are significantly shorter than the basal bonds. This feature is rationalized by the deficiency in Pauling's valence sum at the apical oxygen

Table 5. Characteristic features of the structure

	Sheet 1 [contains T(11), T(21)]		Sheet 2 [contains T(12), T(22)]
Rotation angle of the tetrahedra α_{tet} (°)	20.92		20.87
Sheet thickness (Å)			
tetrahedral	2.259		2.262
octahedral		2.079	
interlayer		2.874	
Basal oxygen ΔZ_{aver} (Å) "corrugation"	0.186		0.195

Table 6. Distribution of the hydrogen atoms in margarite

O – H group			O – H bond		
Oxygen site	Hydrogen site		Bond length	Orientation	
	Notation	Occupancy		ϱ	φ
O(61)	H(11A)	77(1) %	0.931(5) Å	77.8(2)°	31.1(2)°
	H(11B)	21	0.92(2)	17(1)	37(1)
O(62)	H(12A)	79(2)	0.935(5)	100.9(2)	−151.1(2)
	H(12B)	21	0.91(2)	157(1)	−157(1)

atoms; the deficiency is balanced by the contractions of bonds in which the apical oxygen atoms are involved (Table 5).

(2) If we define the elongation of a tetrahedron in terms of a ratio between mean length of the pyramidal edges and that of the basal edges, the ratios are 1.006, 1.016, 1.013 and 1.006 for T(11), T(12), T(21) and T(22), tetrahedra, respectively. The tetrahedra about T(12) and T(21), both occupied by Si, are significantly elongated compared to the tetrahedra about Al.

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