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Crystal structure of single-layer lizardite

By **ILIJA KRSTANOVIĆ**

Department of the Geophysical Sciences, The University of Chicago*

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Auszug

Die gemessenen *x*- und *z*-Parameter des Einschicht-Lizardits von der Chromitlagerstätte von Raduša, Jugoslawien weisen auf eine Störung der Basisschicht hin, ähnlich wie sie beim Chrysotil beobachtet wurde. Für die Lizardit-Kristalle von Raduša ist ihre Zusammensetzung aus Domänen charakteristisch. Die Schichten aneinanderschließender Domänen sind um 60° oder 180° um die Basisnormale gedreht; die Anzahl der Domänen jeder Orientierung ist von Kristall zu Kristall verschieden.

Abstract

The measured *x* and *z* parameters of single-layer lizardite from Raduša chromite Mine, Yugoslavia, indicate a distortion of the basic serpentine layer similar to that found in chrysotiles. Composite crystals of lizardite from the same locality are characterized by the domains. The layers within a domain are related to those in the next one by a rotation of 60° or 180°, the number of domains in each orientation varying from crystal to crystal.

Introduction

So far, two types of serpentine minerals have been well characterized: a fibrous variety of chrysotile which has a structure based on a cylindrical lattice (WHITTAKER, 1956), and antigorite which has a superperiod along the *x* axis, and a structure based on the double half-wave pattern (ZUSSMAN, 1954; KUNZE, 1956). Recently, important structural details on another serpentine mineral, lizardite $Mg_3Si_2O_5(OH)_4$, have been obtained (RUCKLIDGE and ZUSSMAN, 1965).

The basic serpentine layer has two sets of octahedral sites which can be occupied by Mg and OH ions. This results in two orientation

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* Chicago, Illinois 60637. Permanent Address: Rudarsko-geološki Fakultet, Djusina 7, Katedra za Mineralogiju i Kristalografiju, Univerzitet u Beogradu, Beograd, Yugoslavia.

of layers (μ, γ) Fig. 1, depending on which of the octahedral sites is occupied. The layer orientations are related by a rotation of 60° or 180° about an axis parallel to z and passing through the middle of the hexagonal silicon net.

The structure of lizardite from the original locality Kennack Cove, England, is characterized by a structure with some domains consisting of a one-layer sequence in either orientation, and some in alternating sequence with a two-layer repeat (RUCKLIDGE and ZUSSMAN, 1965). Lizardite crystals from Avala Mountain, near Beograd, are characterized by equal number of domains in μ and γ orientation (KRSTANOVIĆ, to be published). More single crystals of lizardite have been found in the material collected nearby in the region of Raduša mine, and a domain structure between lizardite and six-layer orthoserpentine has been observed in one polytype.

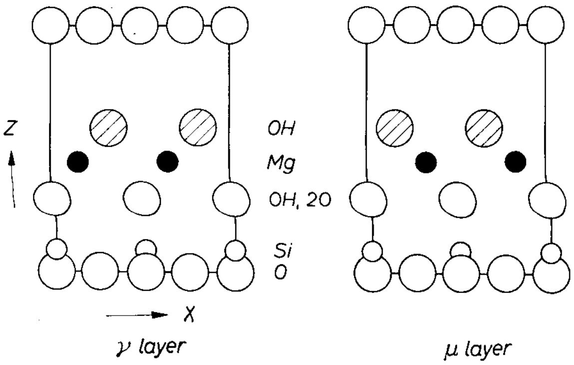

Fig. 1. Two types of serpentine layers

Experimental

From the compact serpentinite it was possible to isolate a large number of plates which were suitable for single-crystal x-ray work. Oscillation photographs were taken in order to check cell dimensions and the quality of each specimen. All the crystals were either mechanically deformed, or they had grown disordered: the pronounced shift of $\pm \frac{1}{3} b$ was observed, and all projections except that on (010) were of very little use in the structure determination. The crystals were divided subsequently into four groups:

(1) Those crystals characterized by equal $h0l$ and $h0\bar{l}$ intensities.

(2) Crystals with *h0l* reflections of unequal intensities, but with the difference in intensity far less pronounced than in group (3).

(3) Those crystals characterized by a marked difference between $I(h0l)$ and $I(h0\bar{l})$.

(4) Crystals showing a number of reflections which varied in intensity from crystal to crystal, and which could be indexed only on the basis of a six-layer cell.

Because the first example of group (1) crystals came from Avala Mountain, this division is named the Avala-type lizardite. The crystals are built of equal number of μ and γ domains. They represent by far the largest number of crystals investigated so far. Crystals from group (2) were investigated in some detail: over-exposed x-ray photographs revealed no weak or diffuse reflections such as those indicating a two-layer domain structure in the lizardite from Kennack Cove. Therefore, unequal number of two types of domains (μ, γ) are stacked along the z axis, the size of the individuals being so large that no coherency is practically retained among the x-ray beams from different individuals. The results of the detailed examination of crystals of group (4) will be discussed in a subsequent publication. Intensity measurement and subsequent calculations of the structure factors indicate that the crystals from group (3) consist of one type of layer only. Crystals showing hexagonal morphology with the approximate dimensions 0.1 × 0.1 × 0.4 mm were mounted, and oscillation photographs were taken about the three axes. More accurate cell dimensions were obtained from powder photographs measured with the Straumanis technique (Table 1). Two sets of intensity data were obtained from two crystals of slightly different shape which were found on two different specimens from the Raduša-mine locality. One of the crystals was later analyzed on an electron microprobe, and the total amount of cations other than Si and Mg was found to be less than $1\,^0/_0$ by weight.

Table 1. *Lizardite powder pattern*

Fe*K*α radiation. Camera: diameter 11.46 cm. $a = 5.301 \pm 0.003$ Å, $b = 9.186 \pm 0.006$ Å, $c = 7.281 \pm 0.005$ Å

d_{obs}	d_{calc}	hkl	I
7.31 Å	7.28 Å	001	100
4.59	4.59	020	50
3.87	3.88	021	15
3.64	3.64	002	100
2.655	2.651	200 130	30
2.494	2.491	201 131	100
2.430 Å	2.427 Å	003	25
2.296	2.296	040	10
2.143	2.143	202 132	60
2.100	2.107	140	10
1.822	1.820	004	10
1.790	1.790	203 133	50
1.731 Å	1.735 Å	310	20
1.690	1.692	311 114	10
1.531	1.531	060	75
1.503	1.498	061 331 204	60
1.459	1.456	005	10
1.414 Å	1.411 Å	062 332 313	20
1.328	1.325	400	25
1.306	1.304	401 261 342	60
1.298	1.295	063 333	5

Multiple-film technique using both Ni-filtered Cu, and Zr-filtered Mo radiation was used in collecting intensity data. The usual corrections were made for Lorentz and polarization factors but no absorption correction was made: the atomic scattering factors were those from International Tables. In the present structure determination the first set of structure factors was calculated on the basis of trigonal coordinates, assuming that the symmetry of the basic serpentine layer is trigonal as was determined by Rucklidge and Zussman on the composite crystals from Kennack Cove. With the overall temperature factor $B = 2.0$ an R value of $26\,^0/_0$ was obtained. Furthermore, the differences between several F_0 and F_c values were of such a magnitude that this could not possibly be ignored. For this reason the space group was changed to *Cm*; the refinement of the parameters was carried out on an IBM 7090 computer with a full-matrix least-squares program ORFLS (Busing, Martin and Levi, 1962) and constant weighing. The restricted number of reflections used in this work did not allow simultaneous refinement of the positional and thermal parameters. It has been shown by several investigators (Danner, Frazer and Pepinsky, 1960; Geller, 1961; Megaw, 1962), that the positional parameters can be obtained with fair accuracy even when the thermal parameters are doubtful. We have however adopted the following procedure. Individual isotropic temperature factors were estimated from the Fourier map and from the structure of similar type for which such data were available (Shirozu and Bailey, 1966). These values of assumed B were split in four sets: the difference in B for a particular atom in each set was 0.3 for Si, 0.5 for Mg and 1.0 for O and OH ions. Therefore the refinement of the positional parameters was carried out in four stages, each stage

Table 2. *Atomic parameters*

Atom	x	z	B
Si	−0.003 ± 0.005	0.075 ± 0.004	0.5 Å^2
O(1)	−0.036 0.024	−0.031 0.019	2.0
O(2)	0.238 0.015	0.024 0.010	2.0
OH	0.023 0.015	0.326 0.010	2.0
O(3)	−0.008 0.030	0.289 0.006	2.0
Mg(1)	0.328 0.006	0.444 0.005	1.0
Mg(2)	0.333 0.017	0.500 0.013	1.0
OH(1)	0.170 0.017	0.604 0.012	2.0
OH(2)	0.210 0.031	0.602 0.013	2.0

Table 3. *Observed and calculated structure factors*

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
0 0 1	129	136	2 0 0	74	54	2 0 8	35	37	2 0 $\bar{8}$	30	48	4 0 $\bar{1}$	207	178	6 0 2	46	39
2	221	211	1	261	229	$\bar{1}$	110	101	4 0 0	102	86	$\bar{2}$	70	49	3	22	47
3	93	90	2	170	172	$\bar{2}$	68	68	1	117	74	$\bar{3}$	132	145	4	17	17
4	104	89	3	124	152	$\bar{3}$	49	51	2	95	103	$\bar{4}$	41	74	$\bar{1}$	54	47
5	115	118	4	99	89	$\bar{4}$	129	155	3	20	22	$\bar{5}$	24	56	$\bar{2}$	43	53
6	91	80	5	51	62	$\bar{5}$	105	129	4	102	120	$\bar{6}$	21	47	$\bar{3}$	17	43
7	62	47	6	81	68	$\bar{6}$	42	29	5	64	56	6 0 0	120	97	$\bar{4}$	11	25
8	68	57	7	35	68	$\bar{7}$	52	61	6	19	37	1	54	30			

being characterized by the fixed set of thermal parameters. The lowest R value of 19.1 $^0/_0$ for one set of intensity data, and 19.4 $^0/_0$ for the other, was obtained for the B values given in Table 2. Further attempts to reduce the discrepancy between observed and calculated structure factors were unsuccessful. On the basis of previous experience with the visual intensity measurement, it is believed that the accuracy achieved here is somewhat less than that obtained with good single crystals. In addition, measurement of the intensity of $60l$ and $60\bar{l}$ reflections was difficult because of overlap.

Discussion

The y and z projections of the serpentine layer of lizardite are shown in Fig. 2; the displacement of the atoms from the idealized coordinates is indicated by the arrows. The z coordinates of the O(1) and O(2) atoms at the base of the tetrahedral layer differ by 0.4 Å. A definitive explanation of this difference requires the knowledge of the y coordinates, which is not available at this time. However, the difference indicates that O(1) is situated in the groove between the hydroxyl groups below it, while O(2) is situated approximately

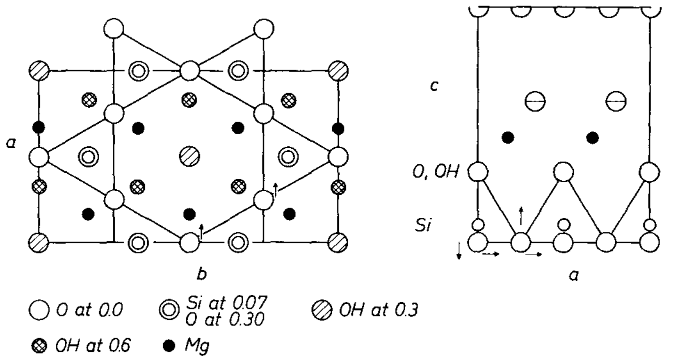

Fig. 2. Projection of the lizardite structure on the (001) and (010) planes. The arrows indicate the shift of the coordinates

over the row of hydroxyl ions. At the same time both oxygens are shifted along the axis from the initial coordinates. A similar separation of the basal oxygens has been observed in the structure of chrysotiles by Whittaker (1956), who suggested that the separation was caused by the different radii of successive cylindrical layers. Since lizardite has a single-layer non-cylindrical structure, it is clear that the position of O(1) is not the only factor controlling the stacking of basic serpentine layers in chrysotiles, and that this distortion does not necessarily lead to a one-layer or a multiple-layer monoclinic structure.

The structural features of lizardite do not preclude the possibility of existence of a two-layer serpentine structure, not based on a cylindrical lattice, with perhaps a slightly different value for the angle β than the value found in clinochrysotile (Krstanović and Pavlović, 1964). However, the distortion of the idealized net may help to explain the small number of serpentine polytypes as compared to the other trioctahedral minerals, such as cronstedtite, for which no significant distortion the basic structural unit is observed.

The interatomic distances Si—O (calculated with the y parameters of the ideal net) range from 1.54 Å to 1.72 Å, while the Mg—O distances range from 2.04 Å to 2.17 Å, with the mean value of 2.14 Å. However, one set of Mg—OH distance is 2.5 Å. These values suggest that the y parameters in the structure of lizardite must differ from those of the idealized net. The significance of these results is not now apparent, and must await more detailed study.

It is interesting to speculate that the shift of O(1) toward the groove between the hydroxyl groups below it may be related to the observed difference in the z coordinate of the Mg ions. This difference, which amounts to 0.4 Å, is considered to be significant. A somewhat similar effect, related to the oxygen shifts, has been reported in the structure of several polytypes of cronstedtite (Steadman and Nuttall, 1963).

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