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Crystal structures of lizardite-*1T* and lizardite-*2H1* from Coli, Italy

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ABSTRACT

The occurrence of lizardite-*1T* and lizardite-*2H1* from Coli, Italy, is reported. The two polytypes can be identified by their morphology. The *1T* polytype occurs as truncated trigonal pyramids and the *2H1* polytype as truncated hexagonal pyramids or hexagonal plates. Lizardite-*1T* has the composition $(Mg_{2.82}Fe_{0.07}Al_{0.09})(Si_{1.94}Al_{0.06})O_5(OH)_4$, and lizardite-*2H*1 has the composition $(Mg_{2.83}Fe_{0.05}Al_{0.10})(Si_{1.93}Al_{0.07})O_5(OH)_4$.

Unit-cell parameters are $a = 5.325(5)$, $c = 7.259(7)$ Å, space group $P31m$, and $a = 5.318(4)$, $c = 14.541(7)$ Å, space group $P6_3cm$ for the *1T* and *2H1* polytypes, respectively.

The crystal structures of the two polytypes have been refined to $R = 0.074$ and 0.024 (*1T* and *2H1*, respectively). Whereas the tetrahedral-octahedral layer exhibits negative ditrigonalization in the *1T* structure ($\alpha = -1.7°$), positive distortion ($\alpha = +6.4°$) occurs in the *2H1* structure. This pattern fits the existing predictions about the layer configurations within the different polytypes of lizardite.

INTRODUCTION

Lizardite, ideally $Mg_3Si_2O_5(OH)_4$, is the flat-layer serpentine polymorph (Wicks and Whittaker, 1975). The earliest attempts to refine its crystal structure (Rucklidge and Zussman, 1965; Krstanovic, 1968) were considerably hampered by the disorder that commonly occurs in these crystals. A full three-dimensional refinement was available only recently, following the discovery of well-crystallized lizardite-*1T* in Val Sissone (Mellini, 1982).

Real trigonal symmetry and quite simple structural arrangements were the most important results of that study. In fact, lizardite-*1T* from Val Sissone closely approaches the idealized geometry of the serpentine layer, with no buckling of the atomic planes (Wicks and Whittaker, 1975; Krstanovic, 1980). Controversy over the nature of the unsubstituted (i.e., Mg end-member) lizardite structure was perhaps still possible, in that the results obtained by Mellini (1982) might be in part attributed to the particular Al-rich composition of his specimen. However, the feasibility of a simple arrangement without buckling was demonstrated from geometric considerations by Bish (1981) and later by Wicks and Hawthorne (1986) who used Mellini's (1982) results to model the end-member lizardite structure by distance least-squares refinement (Baerlocher et al., 1977). They found that the octahedral and tetrahedral sheets can be linked together without buckling.

A new occurrence of lizardite is herein reported (from Coli, Italy). Both the *1T* and the *2H1* polytypes have been identified as discrete crystals with different morphologies. The chemical substitutions are lower than in the Val Sissone specimen. Therefore these new data are useful to demonstrate the effect of different compositions within the same polytypic sequence and the effect of different stacking sequences in isochemical crystals.

OCCURRENCE AND PROPERTIES

Well-crystallized lizardite occurs in the ophiolite complex of Monte dei Tre Abati, Coli, Italy (Boscardin et al., 1982). Gray-green serpentinites were formed by low-grade metamorphic reactions under high water pressure. Chlorite, antigorite, chrysotile, lizardite, and magnetite are the most abundant replacement minerals. Lizardite occurs together with calcite as a massive filling of veins, several meters long and a few centimeters thick. Light-green lizardite crystals with dimensions smaller than 1 mm are common within the fissures of the veins. Boscardin et al. (1982) observed both trigonal and hexagonal varieties of lizardite crystals. X-ray single-crystal diffraction patterns taken from several crystals have now shown conclusively that these two varieties correspond to two different polytypes. Lizardite-*1T* crystallizes as trigonal truncated pyramids, and lizardite-*2H1* as hexagonal truncated pyramids or hexagonal plates (Fig. 1). Although the *2H1* polytype has been observed already by electron diffraction (Litsarev et al., 1984), this is the first time that ordered, discrete lizardite *2H1* crystals have been reported. The two polytypes are found within the same vein and, although they do not occur in contact with one another, they probably crystallized under common conditions.

The chemical data (Table 1) were collected on a Philips 501 scanning-electron microscope, equipped with an EDAX 9100/60 energy-dispersive analyzer, on the same crystal

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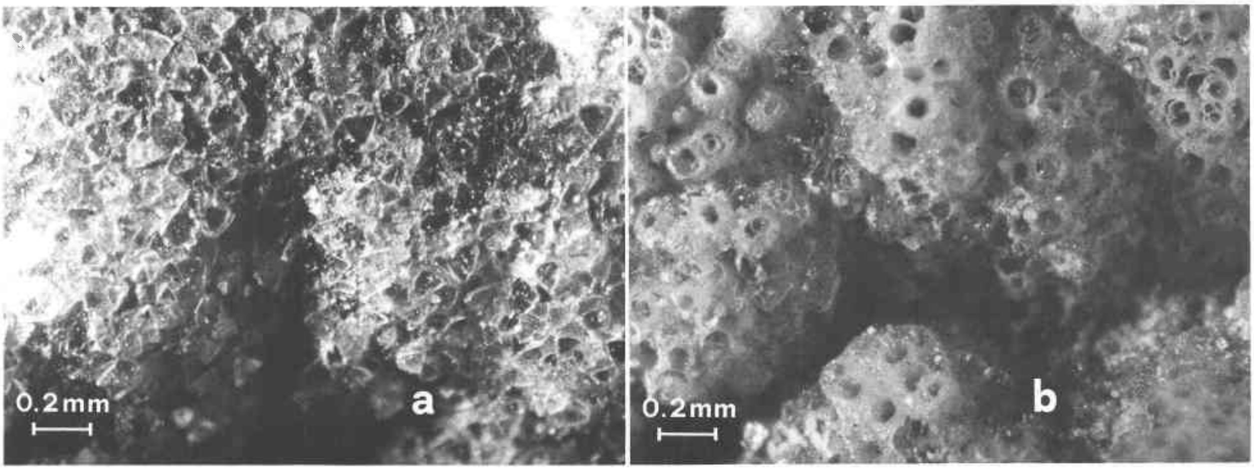

Fig. 1. Microphotographs of lizardite from Coli: (a) lizardite-*1T*; (b) lizardite-*2H1*.

fragments later used for the structure refinements, using silicate minerals as standards. No chemical heterogeneity was observed within the grains. The water values were computed by assuming two water molecules per formula unit, and the oxide sum was normalized to 100 wt%. The chemical formula for the *1T* polytype, $(Mg_{2.82}Fe_{0.07}Al_{0.09})_{\Sigma=2.98}(Si_{1.94}Al_{0.06})_{\Sigma=2.00}O_5(OH)_4$, does not differ much from the formula for the *2H1* polytype, $(Mg_{2.83}Fe_{0.05}Al_{0.10})_{\Sigma=2.98}(Si_{1.93}Al_{0.07})_{\Sigma=2.00}O_5(OH)_4$. Comparison with the Val Sissone lizardite-*1T*, $(Mg_{2.79}Fe^{2+}_{0.04}Fe^{3+}_{0.10}Al_{0.07})_{\Sigma=3.00}(Si_{1.83}Al_{0.17})_{\Sigma=2.00}O_5(OH)_4$, shows less chemical substitution for the Coli specimens, which approach the end-member composition especially for the tetrahedral cations. Both lizardite-*1T* and lizardite-*2H1* from Coli produce very sharp diffraction spots, with rare streaking or diffuseness. The Laue symmetry is $\bar{3}m$ for the *1T* polytype and $6/mmm$ for the *2H1* polytype, with no systematic extinctions in lizardite-*1T* and $h\bar{h}0l$ present for $l = 2n$ in lizardite-*2H1*. Symmetries, morphologies, and systematic extinctions are in agreement with the space groups of the ideal polytypes, $P31m$ and $P6_3cm$ for *1T* and *2H1*, respectively.

The unit-cell parameters (Table 2) were determined using the LAT routine of the Philips PW1100 single-crystal diffractometer. Both the Coli polytypes have layer-to-layer separation along [001] greater than the Val Sissone specimen. This feature is related to the lower Al content (Chernovsky, 1975), which has the effect of decreasing H bonding across the interlayer zone and allows a progressively increasing interlayer distance to develop (Mellini, 1982). The *2H1* polytype from Coli is slightly expanded along [001] with respect to the isochemical *1T* polytype from the same occurrence. However, the volume per formula unit remains almost constant, as a and c vary in opposite sense (Table 2).

STRUCTURE REFINEMENTS

Intensity data were gathered using Mo$K\alpha$ radiation (λ = 0.71069 Å) from a trigonal plate 0.2 mm on edge and 0.1 mm thick and from a hexagonal plate 0.15 mm on edge and 0.1 mm thick for lizardite-*1T* and lizardite-*2H1* respectively. A total of 845 and 1652 symmetry-related reflections were measured for the *1T* and *2H1* polytypes, respectively, in the range 2–30° θ. Collection parameters, data reduction, and absorption-correction procedures were applied as described by Mellini (1982). The independent reflections were 293 (*1T*) and 366 (*2H1*), with discrepancy factors among symmetry-related reflections R_{sym} of 0.086 and 0.024, respectively. Structure refinement was performed starting from the idealized structure models,

TABLE 1. Chemical data for lizardite from Coli

	1T		*2H1*	
	Wt%	Atomic ratio	Wt%	Atomic ratio
MgO	40.69	2.82	40.93	2.83
FeO	1.81	0.07	1.30	0.05
Al_2O_3	2.79	0.15	3.16	0.17
SiO_2	41.80	1.94	41.68	1.93
H_2O	12.90	4.00	12.93	4.00

TABLE 2. Lattice parameters (Å) and unit-cell volumes (Å³) for lizardite from Val Sissone and Coli

	Lizardite-*1T* Val Sissone	Lizardite-*1T* Coli	Lizardite-*2H1* Coli
a	5.332 (5)	5.325 (5)	5.318 (4)
c	7.233 (7)	7.259 (7)	14.541 (7) = 7.270 × 2
V	178.1 (5)	178.3 (5)	356.2 (5) = 178.1 × 2

Note: The esd's are in parentheses.

TABLE 3. Final atomic positional and thermal parameters for lizardite-*1T* and lizardite-*2H1* from Coli

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
				Lizardite-*1T*					
Si	⅓	⅔	0.0748(13)	6(8)	6(8)	234(15)	0	0	3(4)
Mg	0.3322(5)	0	0.4557(12)	28(10)	31(12)	242(14)	0	26(9)	16(6)
O(1)	⅓	⅔	0.2920	−60(19)	−60(19)	405(44)	0	0	−30(10)
O(2)	0.5045(11)	0	−0.0082(16)	147(27)	76(28)	147(25)	0	−45(27)	38(14)
O(3)	0.6655(12)	0	0.5899(15)	109(25)	127(30)	257(35)	0	28(22)	64(15)
O(4)	0	0	0.3080(17)	84(27)	84(27)	108(37)	0	0	42(14)
H(3)	0.580(7)	0	0.738(7)	U = 0.022(7)					
H(4)	0	0	0.200(7)	U = 0.023(7)					
				Lizardite-*2H1*					
Si	⅓	⅔	0.0360	53(3)	53(3)	72(5)	0	0	26(1)
Mg	0.3324(3)	0	0.2266(1)	58(4)	56(6)	121(5)	0	4(5)	28(3)
O(1)	⅓	⅔	0.1462(2)	62(8)	62(8)	83(12)	0	0	31(4)
O(2)	0.4838(7)	0	−0.0047(2)	90(10)	75(11)	137(10)	0	39(16)	38(6)
O(3)	0.6657(5)	0	0.2934(2)	91(8)	77(11)	111(12)	0	17(13)	38(6)
O(4)	0	0	0.1502(3)	84(11)	84(11)	88(17)	0	0	42(6)
H(3)	0.620(5)	0	0.365(4)	U = 0.048(5)					
H(4)	0	0	0.081(2)	U = 0.030(5)					

Note: Anisotropic thermal factors (× 10^4) are in the form $\exp[-2\pi^2(\Sigma_i \Sigma_j h_i h_j a_i^* a_j^* U_{ij})]$. Esd's in parentheses. The negatively defined ellipsoid for the O(1) atom in lizardite-*1T* is likely due to stacking faults.

the H atoms were located by ΔF Fourier syntheses, and anisotropic thermal motion was used for all the atoms apart from the H atoms. Final R discrepancy factors were 0.074 for the *1T* polytype and 0.024 for the *2H1* polytype. The atomic positional parameters and temperature factors are given in Table 3. Lizardite-*1T* from Coli exhibits a pronounced anisotropic thermal ellipsoid, strongly elongated along [001]. Most probably this is the result of disorder rather than actual motion and is related to the slightly worse quality of the Coli lizardite-*1T* crystal relative to that of the Val Sissone lizardite-*1T* or to the Coli lizardite-*2H1*. Observed and calculated structure-factor amplitudes are reported in Table 4.[1]

STRUCTURE DESCRIPTION

The structure refinements of lizardite-*1T* and lizardite-*2H1* from Coli are in excellent agreement with many of the results obtained for lizardite-*1T* from Val Sissone. First of all, nearly ideal 1:1 tetrahedral-octahedral layers with well-defined trigonal symmetries occur in the three structures (see Fig. 2 in Mellini, 1982). Buckling is restricted to the O(1) and O(4) atoms, as required by the symmetry restrictions. The independent atoms (O)1 and 0(4) differ in z height by 0.064 Å in lizardite-*1T* from Val Sissone, by 0.116 Å in lizardite-*1T* from Coli, and by 0.058 Å in lizardite-*2H1* from Coli. The main structural differences depend on the different stacking operators; whereas direct overlap of adjacent T-O layers occurs in the *1T* polytype, 60° rotation relates adjacent layers in the *2H1* polytype (Fig. 2). Owing to the small ditrigonal distortion (α is −1.7° and +6.4° in the *1T* and *2H1* polytypes, respectively), the tetrahedral sheets of the two

TABLE 5. Selected interatomic distances (Å) and calculated bond strengths (valence units) in lizardite

	Lizardite-*1T* Val Sissone		Lizardite-*1T* Coli		Lizardite-*2H1* Coli	
	Bond length	Bond strength	Bond length	Bond strength	Bond length	Bond strength
Si–O(1)	1.616(5)	1.016	1.577(10)	1.128	1.602(3)	1.055
–O(2)	1.646(3) × 3	0.939 × 3	1.651(2) × 3	0.927 × 3	1.648(1) × 3	0.934 × 3
avg. Si–O	1.639	$\Sigma a_v = 3.833$	1.632	$\Sigma a_v = 3.908$	1.636	$\Sigma a_v = 3.857$
Mg–O(3)	2.021(5)	0.389	2.024(7)	0.387	2.021(3)	0.389
–O(3)	2.026(5) × 2	0.386 × 2	2.025(7) × 2	0.386 × 2	2.021(3) × 2	0.389 × 2
–O(4)	2.082(5)	0.343	2.069(6)	0.352	2.087(3)	0.339
–O(1)	2.121(3) × 2	0.316 × 2	2.139(5) × 2	0.305 × 2	2.125(2) × 2	0.314 × 2
avg. Mg–O	2.067	$\Sigma a_v = 2.136$	2.070	$\Sigma a_v = 2.134$	2.067	$\Sigma a_v = 2.134$
O(3)–H(3)	0.84(6)		1.16(5)		1.07(5)	
O(4)–H(4)	0.79(6)		0.81(5)		1.01(2)	
O(2)···O(3)	3.03(1)		3.04(1)		3.09(1)	

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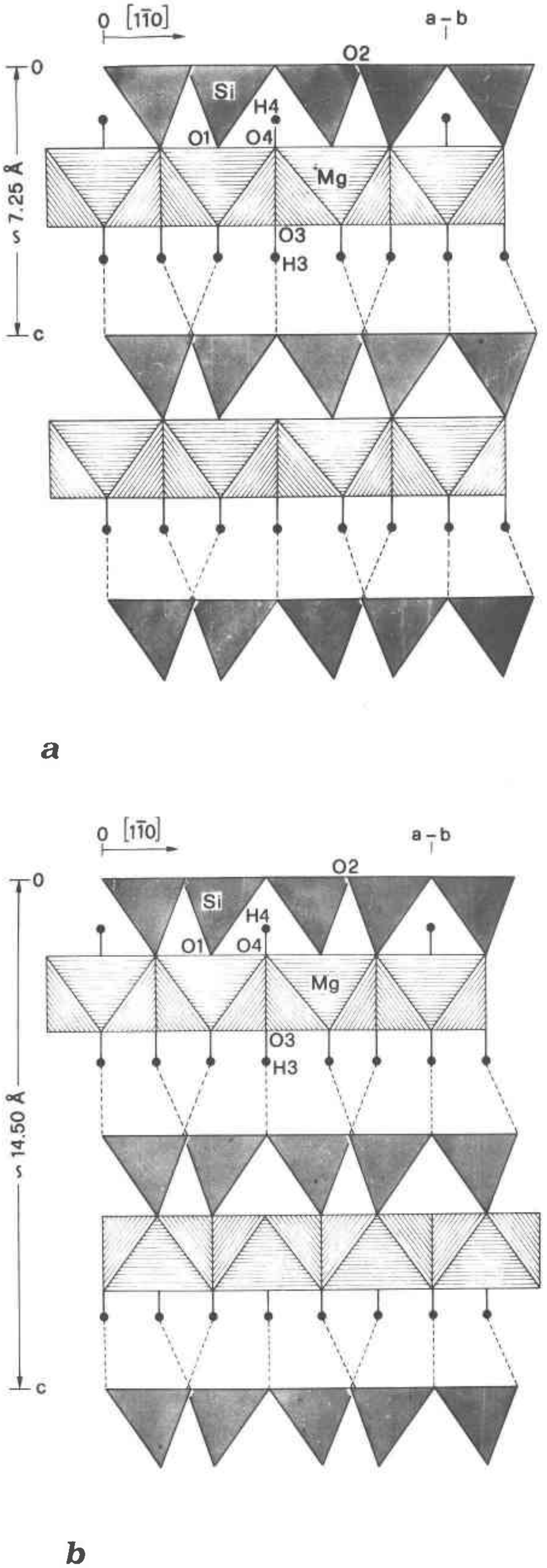
[1] To obtain a copy of Table 4, order Document AM-87-352 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.



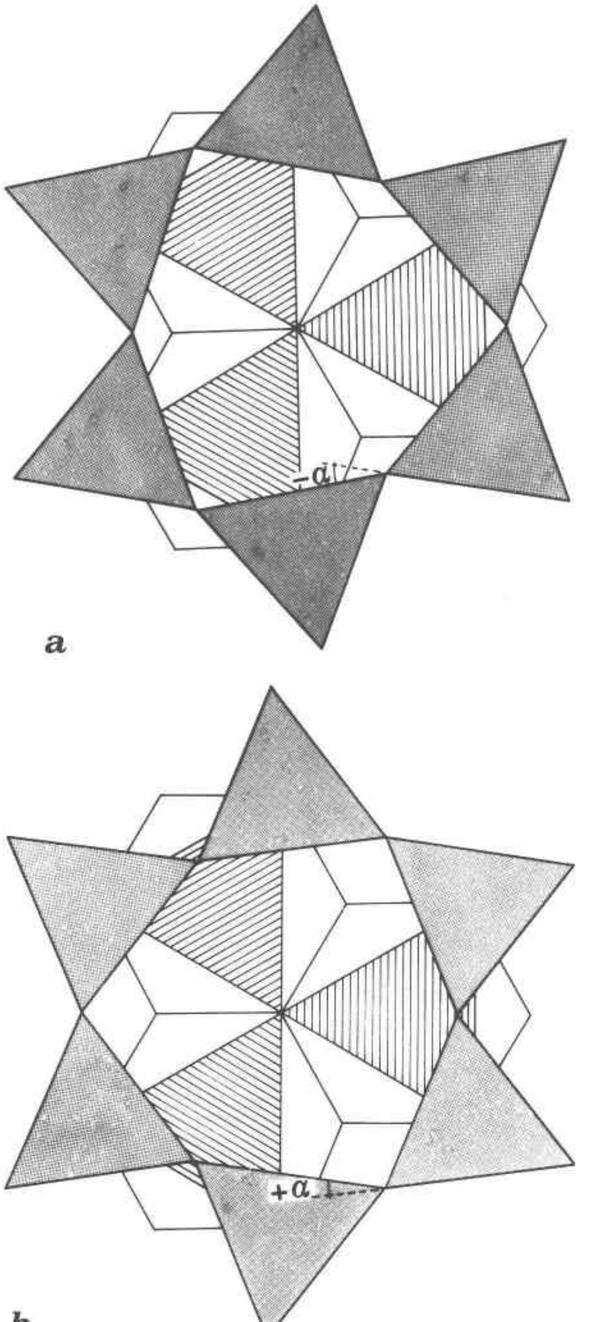


Fig. 3. Schematic representation of (a) negative and (b) positive ditrigonal distortion in the T-O layer of lizardite. Opposite movement of the bridging oxygen atoms is shown, away from and toward the octahedral cations of the same layer, respectively.

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Fig. 2. The crystal structure of lizardite, as seen along [110]: (a) *1T* polytype; (b) *2H1* polytype. Octahedra are lined, tetrahedra are shaded, and H bonds are schematically indicated.

structures are similar. The main difference occurs in the *2H1* polytype in which O(3)–H(3) hydroxyl groups exchange their positions from layer to layer.

Selected bond lengths are reported in Table 5, together with the corresponding bond strengths (calculated for the idealized serpentine composition following the procedure of Brown and Wu, 1976). Very minor modifications affect the bond lengths from structure to structure. The octahedral size is almost constant, whereas the average tetrahedral size decreases with decreasing Al content. The most sensitive parameter is the short Si–O(1) bond length, that ranges from 1.616 to 1.577 Å. It is dubious, however, whether this is an actual variation in bond distance or an artifact arising from the strongly anisotropic thermal ellipsoids that are elongated parallel to [001], the Si–O(1) bond direction.

The six-membered tetrahedral ring of the layer silicates is usually distorted to a ditrigonal configuration (Mellini, 1982). In this way, the tetrahedral net is able to provide the best position for H bonding between adjacent layers. The rotation angle (α) may assume positive or negative values depending on whether the bridging oxygen moves toward or away from the octahedral cations of the same T-O layer (Fig. 3). The alternative convention by Franzini (1969) denoted positively or negatively distorted layers as A or B layers, respectively. Mellini (1982) proposed that the polytypes of lizardite with 60° rotation from layer to layer should be characterized by the occurrence of A layers, whereas B layers should be present in polytypes with no such rotation within the stacking operator. This hypothesis was based on the few available data and on the assumption that the formation of the best possible interlayer H bonding might control the movement of the bridging oxygen atoms. This prediction is fulfilled in the case of Coli polytypes. The *1T* structure is still characterized by the occurrence of B layers as in the Val Sissone lizardite-*1T*. In contrast, A layers ($\alpha = +6.4$) occur in the *2H1* polytype, as required by the presence of 60° rotation within the stacking operator. The occurrence of positive ditrigonalization in slightly substituted Coli lizardite-*2H1* conflicts with the CNDO/2 molecular-orbital calculations by Peterson et al., 1979. According to these authors, only negative α values are to be expected when the average Si–O distance is 1.62 Å, whereas positive and negative α values may occur for more substituted tetrahedra. Most probably the disagreement arises because the CNDO/2 model used for the calculations does not account for interlayer effects. The possible effect of nearest-neighbor interactions between adjacent layers may be found also in the magnitudes of distortion. Whereas the Coli *1T* polytype has α lower than in the Val Sissone *1T* specimen, the isochemical Coli *2H1* polytype, with a different stacking sequence, shows greater α distortion. At the same time, the *2H1* polytype exhibits H-bonding connections weaker than in the polytype, as shown both by the expanded basal spacing (Table 2) and by the longer O(2)···O(3) distance (Table 5).

DISCUSSION AND CONCLUSIONS

The usual disorder found in the serpentine minerals depends on several factors. One of them is to be found in the low crystallization temperature and in the absence of important annealing phenomena under the usual formation conditions. A second one is well documented in the literature (Wicks and Whittaker, 1975) and arises from the ill-fitting dimensions of pure Mg and Si octahedral and tetrahedral layers. A third factor is the occurrence of a bidimensional net of chemical bonds with no strong link along the third direction. All these factors allow for the easy occurrence of many possible defects (e.g., small crystal size, easy deformability and bending, stacking faults, intergrowth of different structures). However, crystalline lizardite does exist and, as shown by the new occurrence at Coli, offers a wealth of information about the actual structural arrangements. Data obtained from poorly crystalline material must be considered with suspicion and should not be used to define the details of the crystal-chemical principles and the structural arrangements of serpentine. In particular, both the experimental structural determinations (Mellini, 1982; this work) and theoretical modeling (Bish, 1981; Wicks and Hawthorne, 1986) do not show any buckling of the atomic planes in lizardite. The individual layers show trigonal symmetry, with ditrigonal distortion depending largely upon interlayer effects, either as regards direction and magnitude. The interlayer effects arise mostly by H bonding, and H bonding is favored by heterovalent chemical substitutions.

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