Crystal structures of lizardite-IT and lizardite-2HI from Coli, Italy

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ABSTRACT

The occurrence of lizardite-IT and lizardite-2HI from Coli, Italy, is reported. The two polytypes can be identified by their morphology. The IT polytype occurs as truncated trigonal pyramids and the 2HI polytype as truncated hexagonal pyramids or hexagonal plates. Lizardite-IT has the composition \((\text{Mg}_{0.43} \text{Fe}_{0.08} \text{Al}_{0.06})\text{Si}_{1.92} \text{Al}_{0.06} \text{O}_{4} \text{OH})_4\), and lizardite-2HI has the composition \((\text{Mg}_{0.83} \text{Fe}_{0.06} \text{Al}_{0.11})\text{Si}_{1.92} \text{Al}_{0.07} \text{O}_{4} \text{OH})_4\).

Unit-cell parameters are \(a = 5.325(5)\) Å, \(c = 7.259(7)\) Å, space group \(P31m\), and \(a = 5.318(4)\), \(c = 14.541(7)\) Å, space group \(P6_3cm\) for the IT and 2HI polytypes, respectively.

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

INTRODUCTION

Lizardite, ideally \(\text{Mg}_3\text{Si}_2\text{O}_5\text{(OH)}_4\), 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-IT in Val Sissone (Mellini, 1982).

Real trigonal symmetry and quite simple structural arrangements were the most important results of that study. In fact, lizardite-IT 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 IT and the 2HI 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-IT crystallizes as trigonal truncated pyramids, and lizardite-2HI as hexagonal truncated pyramids or hexagonal plates (Fig. 1). Although the 2HI polytype has been observed already by electron diffraction (Litsarev et al., 1984), this is the first time that ordered, discrete lizardite 2HI 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...
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, \((\text{Mg}_{2.7} \text{Fe}_{0.7} \text{Al}_{0.6})_2 \leq 2.98 (\text{Si}_{1.9} \text{Al}_{0.07})_2 \leq 2.00 (\text{OH})_4\), does not differ much from the formula for the 2H1 polytype, \((\text{Mg}_{2.9} \text{Fe}_{0.1} \text{Al}_{0.1})_2 \leq 2.94 (\text{Si}_{1.97} \text{Al}_{0.07})_2 \leq 2.00 (\text{OH})_4\). Comparison with the Val Sissone lizardite-1T, \((\text{Mg}_{2.7} \text{Fe}_{0.3} \text{Al}_{0.07})_2 \leq 2.96 (\text{Si}_{1.9} \text{Al}_{0.1})_2 \leq 2.00 (\text{OH})_4\), 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 3m for the 1T polytype and 6/mmm for the 2H1 polytype, with no systematic extinctions in lizardite-1T and \(h0l\) present for \(l = 2n\) in lizardite-2H1. Symmetries, morphologies, and systematic extinctions are in agreement with the space groups of the ideal polytypes, \(P3_1m\) and \(P6_3m\) for 1T and 2H1, respectively.

The unit-cell parameters (Table 2) were determined using the \(\omega\)-scan 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 MoKα radiation (\(\lambda = 0.71069\,\text{Å}\)) 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° \(\theta\). 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 \(R_{\text{exp}}\) of 0.086 and 0.024, respectively. Structure refinement was performed starting from the idealized structure models.
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

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.

### 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 (O)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 = −1.7° and +6.4° in the 1T and 2H1 polytypes, respectively), the tetrahedral sheets of the two

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

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U12</th>
<th>U13</th>
<th>U23</th>
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<tr>
<td>Si</td>
<td>1/2</td>
<td>1/2</td>
<td>0.0748(13)</td>
<td>6(8)</td>
<td>6(8)</td>
<td>234(15)</td>
<td>0</td>
<td>0</td>
<td>3(4)</td>
</tr>
<tr>
<td>Mg</td>
<td>0.3322(5)</td>
<td>0</td>
<td>0.4557(12)</td>
<td>28(10)</td>
<td>31(12)</td>
<td>242(14)</td>
<td>0</td>
<td>26(9)</td>
<td>16(6)</td>
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<tr>
<td>O(1)</td>
<td>1/2</td>
<td>1/2</td>
<td>0.2920</td>
<td>-60(19)</td>
<td>-60(19)</td>
<td>405(44)</td>
<td>0</td>
<td>0</td>
<td>-30(10)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.5045(11)</td>
<td>0</td>
<td>-0.0085(18)</td>
<td>147(27)</td>
<td>75(28)</td>
<td>147(25)</td>
<td>-45(27)</td>
<td>0</td>
<td>38(14)</td>
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<tr>
<td>O(3)</td>
<td>0.6655(12)</td>
<td>0</td>
<td>0.5899(15)</td>
<td>109(25)</td>
<td>127(30)</td>
<td>257(35)</td>
<td>28(22)</td>
<td>64(15)</td>
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<tr>
<td>O(4)</td>
<td>0</td>
<td>0</td>
<td>0.3080(17)</td>
<td>84(27)</td>
<td>84(27)</td>
<td>108(37)</td>
<td>0</td>
<td>0</td>
<td>42(14)</td>
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<tr>
<td>H(3)</td>
<td>0.58(7)</td>
<td>0</td>
<td>0.738(7)</td>
<td>U = 0.022(7)</td>
<td>U = 0.023(7)</td>
<td>U = 0.023(7)</td>
<td></td>
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<tr>
<td>H(4)</td>
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<td>0</td>
<td>0.200(7)</td>
<td>U = 0.022(7)</td>
<td>U = 0.023(7)</td>
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<table>
<thead>
<tr>
<th></th>
<th>lizardite-2H1</th>
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<tbody>
<tr>
<td>Si</td>
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<tr>
<td>Mg</td>
<td>0.3324(3)</td>
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<tr>
<td>O(1)</td>
<td>1/2</td>
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<tr>
<td>O(2)</td>
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<tr>
<td>O(3)</td>
<td>0.6657(5)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0</td>
</tr>
<tr>
<td>H(3)</td>
<td>0.620(5)</td>
</tr>
<tr>
<td>H(4)</td>
<td>0</td>
</tr>
</tbody>
</table>

*Note: Anisotropic thermal factors (×10⁴) are in the form exp[−2π²(U11a₁² + U22a₂² + U33a₃² + U12a₁a₂ + U13a₁a₃ + U23a₂a₃)]. Esd’s in parentheses. The negatively defined ellipsoid for the O(1) atom in lizardite-1T is likely due to stacking faults.*

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

<table>
<thead>
<tr>
<th></th>
<th>Lizardite-1T Val Sissone</th>
<th>Lizardite-1T Coli</th>
<th>Lizardite-2H1 Coli</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O(1)</td>
<td>1.616(5)</td>
<td>1.016</td>
<td>1.577(10)</td>
</tr>
<tr>
<td>Si-O(2)</td>
<td>1.646(3) x 3</td>
<td>0.939 x 3</td>
<td>1.851(2) x 3</td>
</tr>
<tr>
<td>Si-O(3)</td>
<td>1.639</td>
<td>3a = -3.933</td>
<td>1.632</td>
</tr>
<tr>
<td>Mg-O(3)</td>
<td>2.02(6)</td>
<td>0.389</td>
<td>2.024(7)</td>
</tr>
<tr>
<td>Mg-O(4)</td>
<td>2.02(5)</td>
<td>0.386 x 2</td>
<td>2.02(7) x 2</td>
</tr>
<tr>
<td>Mg-O(11)</td>
<td>2.12(3) x 2</td>
<td>0.316 x 2</td>
<td>2.13(6) x 2</td>
</tr>
<tr>
<td>avg. Mg-O</td>
<td>2.067</td>
<td>3a = -2.136</td>
<td>2.070</td>
</tr>
<tr>
<td>O(3)-H(3)</td>
<td>0.84(6)</td>
<td>1.16(5)</td>
<td>1.07(5)</td>
</tr>
<tr>
<td>O(4)-H(4)</td>
<td>0.79(6)</td>
<td>0.81(5)</td>
<td>1.01(2)</td>
</tr>
<tr>
<td>O(2)-O(3)</td>
<td>3.03(1)</td>
<td>3.04(1)</td>
<td>3.09(1)</td>
</tr>
</tbody>
</table>
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.

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 ex-
change 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 octa-
hedralsizeis almost constant, whereas the average tet-
rahedral 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 el-
loids 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
forward or backward from the octahedral chains of the same
T-O layer (Fig. 3). The alternative convention by Fran-
zini (1969) denoted positively or negatively distorted lay-
ers 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 charac-
terized by the occurrence of B layers as in the Val Sissone
lizardite-1T. In contrast, A layers (α = +6.4°) occur in the
2H1 polytype, as required by the presence of 60° rotation
within the stacking operator. The occurrence of positive
distortion 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 in-
terlayer 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 speci-
emen, 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 ex-
panded 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 for-
mation 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, crys-
talline lizardite does exist and, as shown by the new oc-
currence 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 di-
trigonal distortion depending largely upon interlayer ef-
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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