Lizardite-chlorite structural relationships and an inferred high-pressure lizardite polytype

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ABSTRACT

We determined details of the layer stackings in lizardite (variety: baltimorite) and chlorite in a splintery sample from a massive serpentinite. Based on high-resolution transmission electron microscopy (HRTEM) and image simulations, we localized the positions of projected columns of tetrahedral (T) and octahedral (O) cations that allow determination of the nature of the transformation of lizardite to chlorite and the structural formula of the chlorite. The lizardite stacking is of an unexpected type because adjacent layers are in non-hydrogen-bonded placements, a configuration that permits easy, strain-free transformation to chlorite. We conclude that the lizardite-chlorite transformation was isochemical and at constant volume. A consequence is that the product chlorite consists of neutral brucite- and talc-type layers and so can be regarded as a 1:1 interstratification of brucite and talc. Both the T and the O sheets in talc-type layers contain M3+ (M = Al, Fe, Cr, …) cations. An implication of our results combined with high-pressure studies of chlorite and TO silicates is that lizardite stacking sequences can indicate whether a given crystal has been subjected to high pressures. Lizardite in non-hydrogen-bonded sequences presumably has this configuration because of its prior exposure to elevated pressures and can thus be added to the list of indicators of past high pressure. Calibration of this new geobarometer remains for the future.

INTRODUCTION

The serpentine minerals and chlorite are major phases in hydrated mafic and ultramafic rocks, and their physical behavior is of considerable importance in geodynamic processes. They may be major carriers of water to the mantle via subduction (Peacock 1990a, 1990b; Ulmer and Trommsdorf 1999), contribute to the source mechanism of earthquakes (Peacock 2001; Dobson et al. 2002), and influence the rheology of subduction zones (Guillot et al. 2001). The Mg chlorite end-member, clinochlore, is the variety that is most relevant to mantle geophysics (Welch and Marshall 2001). The similarities in structure, composition, and geological occurrence of lizardite and clinochlore make them common mineralogical associates. Their behavior in response to high pressure is important during subduction, and so considerable attention has been given to changes that might occur with increases in pressure (Hofmeister et al. 1999; Welch and Marshall 2001; Kleppe et al. 2003; Theye et al. 2003).

Major differences in compressibility normal to the structural layering exist between brucite and clinochlore, and talc is roughly twice as compressible as clinochlore (Pawley and Wood 1995; Welch and Marshall 2001; Welch and Crichton 2002). Little information is available regarding the details of interstratified lizardite-clinochlore and how it would respond to changes in pressure. A first step toward understanding that relation is knowledge of the structural and crystal-chemical details of such interstratification. We show that the type of stacking between adjacent layers is an important variable that can have major effects on their compressibilities.

Lizardite is the most abundant serpentine mineral exposed in Earth’s upper crust, has the most straightforward structure, and is the standard for comparison for estimates of the structures of the other serpentine forms. Its ideal composition is \(\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4\), where \(\text{M}^{2+}\) = Al, Fe, Cr, and \(x\) lies between 0 and 0.5, with a usual value around 0.1. Its structure consists of a tetrahedral (T) silicate sheet joined by apical O atoms to form a continuous, Mg-centered octahedral (O) sheet (Rucklidge and Zussman 1965; Krstanovic 1968; Mellini 1982) (Fig. 1). Although the symmetry of the TO structural layer is \(P31m\), a C-centered orthogonal unit cell \(a_{\text{orthogonal}} = a_{\text{tetragonal}} = a_0, b_{\text{orthogonal}} = b_{\text{tetragonal}} = \sqrt{3}a_{\text{tetragonal}}\) is widely used for easier indexing of selected-area electron-diffraction (SAED) patterns and comparing polytypes. Hereafter all indices refer to this setting, for which the <100> and <110> directions are symmetrically equivalent, as are <010> and <310>.

Early structure determinations of lizardite and lizardite analogue TO phyllosilicates led to recognition that stacking disorder and polytypism (periodic stacking of different sequences) is common (Steadman and Nuttal 1962; 1963; 1964; Rucklidge and Zussman 1965). The relative positions of the layers determine the several lizardite polytypes and led to a distinction between so-called “standard” and “nonstandard” polytypes. Zvyagin et al. (1965) and Bailey (1969) derived what they called “standard” lizardite polytypes on the assumption that a/3 and b/3 shift vectors (and equivalent directions in \(P31m\)) of adjacent layers do not occur within the same crystal. They used the term “nonstandard polytypes” for structures in which no shift, a/3, and b/3 shift vectors occur in the same crystal. Polytype derivations