The dehydroxylation of serpentine group minerals

ALESSANDRO F. GUALTIERI,1 CARLOTTA GIACOBBE,1,2* AND CECILIA VITI3

1Dipartimento di Scienze della Terra, University of Modena and Reggio Emilia, Via S. Eufemia 19, I-41000 Modena, Italy
2Dipartimento di Scienze della Terra, University of Siena, Via Laterina 8 1-53100 Siena, Italy
3Dipartimento di Scienze della Terra, University of Siena, Via Laterina 8 I-53100 Siena, Italy

ABSTRACT

The thermal transformation, stability field, and reaction kinetics of serpentine minerals (antigorite, chrysotile, and lizardite) have been studied to draw a comprehensive model for their dehydroxylation and recrystallization reactions. In situ X-ray powder diffraction (XRPD) and kinetic studies were combined with transmission electron microscopy (TEM) observations to describe the mechanisms of dehydroxylation and later high-temperature crystallization. During dehydroxylation, a metastable transition phase with a characteristic peak around 9 Å was observed in antigorite and, to a minor extent, in lizardite. Rietveld refinements confirmed that the 9 Å phase actually possesses a talc-like structure. The appearance of this phase is controlled by structure and kinetic factors.

The kinetic parameters and reaction mechanism for lizardite and antigorite dehydroxylation in air at ambient pressure were calculated using the Avrami models and compared to those of chrysotile. For both lizardite and antigorite, the kinetics of dehydroxylation is controlled by diffusion. Apparent activation energy of the reaction in the temperature range 612–708 °C was 221 and 255 kJ/mol for lizardite and antigorite, respectively. The reaction sequences of chrysotile, lizardite, and antigorite leading to the formation of stable high-temperature products (i.e., forsterite and enstatite) are described taking into account previous topotactic and dissolution-recrystallization models.

Keywords: Main serpentine minerals, dehydroxylation, reaction kinetics, Avrami, metastable phases

INTRODUCTION

Serpentine minerals are phyllosilicates formed during the hydration of basic and ultrabasic rocks. They are rather abundant in the oceanic lithosphere, and play an important role in the global water cycle (Scambelluri et al. 1995; Ulmer and Trommsdorff 1995; Wunder and Schreyer 1997; Iwamori 1998; Schmidt and Poli 1998). Serpentine is a 1:1 layer silicate characterized by stacked tetrahedral (T) and octahedral (O) sheets, with ideal chemical formula Mg3Si4O10(OH)8. The T sheet is formed by the two-dimensional polymerization of Si-centered tetrahedra sharing three out of four oxygen atoms with other tetrahedra. The unshared oxygen atoms are bonded to Mg atoms of the octahedral sheet. To a very first approximation, the different structural arrangement in the serpentine group minerals seems to be caused by the misfit between the tetrahedral and the octahedral sheets (Wicks and O’Hanley 1988). As a matter of fact, because the TO unit is polar and a misfit exists between the smaller parameters of the T sheet and the larger ones of the O sheet (Bailey 1988), a differential strain occurs between the two sides of the layer. In chrysotile, the strain is relieved by rolling the TO layers around the fiber axis. Thus, the structure of chrysotile fibrils is composed of layers curved concentrically or spirally around the fiber axis, producing a tubular fibrous habit (Yada 1971). Lizardite displays a planar structure, with tetrahedral and octahedral substitutions promoting interlayer hydrogen bonds (Mellini 1982; Mellini and Viti 1994) and eventually strain in the lattice. Antigorite is actually not a serpentine sensu stricto because of the discrete Mg(OH)2 depletion (Capitani and Mellini 2004). It has a modulated structure with periodic inversions in the tetrahedral sheet polarity. Wicks and Whittaker (1975) and Krstanovic (1968) have discussed the distortions of both the tetrahedral and octahedral sheets of a pure lizardite 17 with limited substitutions for Si or Mg. In antigorite, which is, similar to lizardite and chrysotile, usually found as an alteration product of olivine-rich rocks like dunites and other peridotites (Trommsdorff and Evans 1974; Frost 1975; Worden et al. 1991), the tetrahedral sheet is always on the convex side of the wave and, consequently, flips at each inversion point to the opposite side of the octahedral sheet.

Because serpentine minerals are important components of the oceanic crust and play a chief role in lithosphere dynamics, their structural and mineralogical modifications with temperature have major implications. Thermal behavior of serpentine group minerals has been widely studied in the past but major attention was given to chrysotile (Aruja 1943; Hey and Bannister 1948; Bowen and Tuttle 1949; Brindley and Ali 1950; Jolicoeur and Duchesne 1981; Khorami et al. 1984; Datta et al. 1986; Suquet 1989; MacKenzie and Meinhold 1994; Gualtieri and Tartaglia 2000; Dellisanti et al. 2002; Cattaneo et al. 2003; Candela et al. 2007; Gualtieri et al. 2008). Detailed models for chrysotile dehydration and dehydroxylation mechanisms and high-T crystallization are reported in Ball and Taylor (1963), Brindley and Hayami...