Dissolution-reprecipitation and self-assembly of serpentine nanoparticles preceding chrysotile formation: Insights into the structure of proto-serpentine

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ABSTRACT

Any poorly crystalline serpentine-type mineral with a lack of recognizable textural or diffraction features for typical serpentine varieties (i.e., chrysotile, lizardite, and antigorite) is usually referred to as proto-serpentine. The formation of the so-called proto-serpentine seems ubiquitous in serpentinization reactions. It is related to dissolution-precipitation of strongly reactive particles prior to true serpentine formation (e.g., in veins where both chrysotile and proto-serpentine are described). However, the structural characteristics of proto-serpentine and its relation with serpentine crystalline varieties remain unclear. In this study a model describing the transformation from proto-serpentine to chrysotile is presented based on experimental chrysotile synthesis using thermogravimetric analyses, transmission electron microscopy, and high-energy X-ray diffraction with pair distribution function analyses. The combination of the high-resolution TEM and high-energy X-ray diffraction enables to resolve the local order of neo-formed particles and their structuration processes occurring during pure chrysotile formation (i.e., during the first three hours of reaction). The formation of individual nanotubes is preceded by the formation of small nanocrystals that already show a chrysotile short-range order, forming porous anastomosing features of hydrophilic crystallites mixed with brucite. This is followed by a hierarchical aggregation of particles into a fiber-like structure. These flake-like particles subsequently stack forming concentric layers with the chrysotile structure. Finally, the individualization of chrysotile nanotubes with a homogeneous distribution of diameter and lengths (several hundreds of nanometer in length) is observed. The competitive precipitation of brucite and transient serpentine during incipient serpentinization reaction indicates that both dissolution-precipitation and serpentine-particle aggregation processes operate to form individual chrysotile. This study sheds light into mineralization processes and sets a first milestone toward the identification of the factors controlling polymorph selection mechanisms in this fascinating system.

Keywords: Proto-serpentine, pair distribution function, chrysotile, stacking, simulation

INTRODUCTION

Serpentine is a common mineral containing structural water with an ideal chemical formula Mg₃Si₂O₅(OH)₄. The serpentine group of minerals contains different varieties, among which the most common forms are antigorite, consisting of periodic modulated layers (Kunze 1956), lizardite, consisting of flat periodic layers (Wicks and O’Hanley 1988), and chrysotile and polygonal serpentine, consisting in fibers (Yada 1967; Middleton and Whittaker 1976). Serpentines are mainly found in altered Earth oceanic lithosphere. Lizardite and chrysotile are both involved in hydrothermal systems and are found in the same stability domains (moderate temperature, bellow 400 °C), whereas antigorite is the high-pressure and high-temperature serpentine variety (Evans et al. 1976; Evans 2004; Wunder and Schreyer 1997). Chrysotile is one of the most common and studied cylindrical fibrous serpentine and consists in the succession of tetrahedral sheets inserted between brucite-type magnesian octahedral layers. The structural misfit between tetrahedral and octahedral sheets induces a concentric or spiral curvature around the x or y axis (Whittaker 1956b, 1956c, 1956a; Middleton and Whittaker 1976) with a fivefold symmetry (Cressey and Whittaker 1993; Cressey et al. 2010) and with the tetrahedral sheet inside (Pauling 1930). Chrysotile is considered as a thermodynamically metastable serpentine variety having a strong chemical reactivity toward the formation of lizardite, even in the pure Mg system (Grauby et al. 1998; Evans 2004). The relationships between layered and tubular serpentine minerals, the overlap between individual polymorphs and the frequent occurrence of turbostratism in serpentine minerals (Trittschack et al. 2012) are of great interest in natural settings where both lizardite and chrysotile coexist. Moreover, an advanced understanding of the atomic scale mineral transformation mechanisms in the serpentine system remains