Formation of mixed-layer sulfide-hydroxide minerals from the Tochilinite-Valleriite group during experimental serpentinization of olivine

THOMAS M. MCCOLLOM1,*, TORI HOEHLLER2, DAVID A. FIKE3, JENNIFER L. HOUGHTON3, AARON BELL4, FRIEDER KLEIN5, BRUCE MOSKOWITZ6, AND PETER SOLHEID6

1Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, Colorado 80309, U.S.A.
2NASA Ames Research Center, Moffett Field, California 94035 U.S.A.
3Department of Earth and Planetary Sciences, Washington University in St. Louis, St. Louis, Missouri 63130, U.S.A.
4Department of Geological Sciences, University of Colorado, Boulder, Colorado 80309, U.S.A.
5Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, U.S.A.
6Department of Earth and Environmental Sciences and Institute for Rock Magnetism, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.

ABSTRACT

We report the formation of minerals from the tochilinite-valleriite group (TVG) during laboratory serpentinization experiments conducted at 300 and 328 °C. Minerals in the TVG are composed of a mixture of sulfide and hydroxide layers that can contain variable proportions of Fe, Mg, Cu, Ni, and other cations in both layers. Members of this group have been observed as accessory minerals in several serpentinites, and have also been observed in association with serpentine minerals in meteorites. To our knowledge, however, TVG minerals have not previously been identified as reaction products during laboratory simulation of serpentinization. The serpentinization experiments reacted olivine with artificial seawater containing 34S-labeled sulfate, with a small amount of solid FeS also added to the 300 °C experiment. In both experiments, the predominant reaction products were chrysotile serpentine, brucite, and magnetite. At 300 °C, these major products were accompanied by trace amounts of the Ni-bearing TVG member haapalaite, Ni,Fe-sulfide (likely pentlandite), and anhydrite. At 328 °C, valleriite occurs rather than haapalaite and the accompanying Ni,Fe-sulfide is proportionally more enriched in Ni. Reduction of sulfate by H2 produced during serpentinization evidently provided a source of reduced S that contributed to formation of the TVG minerals and Ni,Fe-sulfides. The results provide new constraints on the conditions that allow precipitation of tochilinite-valleriite group minerals in natural serpentinites.

Keywords: Tochilinite, valleriite, haapalaite, serpentinization, sulfate reduction

INTRODUCTION

Tochilinite and valleriite are the most common representatives of a structurally related group of minerals that are composed of alternating sulfide and hydroxide layers (referred to herein as the tochilinite-valleriite group, or TVG; Organova et al. 1971; Makovicky and Hyde 1981; Zolensky 1987; Beard 2000). Minerals in this group have a nominal composition of 2(Fe,Cu,Ni) S·1.67(Mg,Fe)OH, although TVG minerals exhibit substantial variability in the relative abundances of Fe, Mg, Ni, and Cu and, in many instances, include additional components such as Al, Ca, Cr, and CO3 (e.g., Huhma et al. 1973; Zolensky 1987; Beard 2000; Mücke 2017; Mikhlin et al. 2022a). Several compositional end-members within the group have been defined (e.g., Evans and Allmann 1968; Organova et al. 1971; Huhma et al. 1973), but the extent of solid solution among these end-members remains poorly understood.

Several studies have reported TVG minerals as accessory components of serpentinite (Chamberlain and Delabio 1965; Jambor 1969; Clark 1970; Organova et al. 1971; Harris and Vaughan 1972; Huhma et al. 1973; van de Vusse and Powell 1983; Matsubara and Kato 1992; Alt and Shanks 1998; Beard 2000; Beard and Hopkinson 2000; Dietze and Konnly 2011; Boschi et al. 2017; Mücke 2017; Mikhlin et al. 2022b; note that in some early studies TVG minerals were identified as “fibrous Fe sulfide”). In at least some cases, TVG minerals are sufficiently abundant to be considered as rock-forming minerals or to be the predominant reservoir of S in serpentinite (e.g., Beard 2000). Tochilinite, the Fe-rich end-member of the group, is also a common secondary alteration component of carbonaceous chondrite meteorites, where in many cases it occurs in close association with the Fe-rich serpentine mineral crosnstedite (e.g., Zolensky 1987; Zolensky et al. 1993; Palmer and Lauretta 2011; Pignatelli et al. 2017).

Few experimental studies have investigated the circumstances under which TVG minerals precipitate in geologic environments, and these have primarily examined formation of tochilinite during alteration of native metal alloys relevant to meteorite parent bodies (e.g., Peng et al. 2007; Peng and Jing 2014; Vacher et al. 2019). To our knowledge, formation of TVG minerals has not previously been reported during experimental serpentinization of ultramafic rocks or their constituent minerals. As a consequence, current experimental data provide only very limited insight into the circumstances under which TVG minerals form in natural serpentinite.

Here, we report precipitation of the TVG minerals haapalaite and valleriite during experimental serpentinization of olivine following reaction with artificial seawater at 300 and 328 °C. The results provide insight into possible pathways for formation of TVG minerals in serpentinite. The experiments were part of a series designed to investigate the temperature dependence of sulfate reduction rates during serpentinization. The present communication focuses only on documentation of the occurrence of TVG minerals...