Mineralogical evolution of Fe–Si-rich layers at the olivine-water interface during carbonation reactions

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ABSTRACT

Recent studies investigating carbonation of iron-bearing silicates have shown that the rates of these reactions, although formally not depending on oxygen fugacity, are strongly different at different redox states of the system (Saldi et al. 2013; Sissmann et al. 2013). Here we provide a micro- and nanostructural characterization of the olivine/water interface during the carbonation of forsteritic olivine at 150 °C and \( P_{\text{CO}_2} = 100 \) bar. When the reaction starts under oxic conditions, the observed temporal sequence of interfacial layers consists of: a hematite/SiO\(_2\) (am) assemblage, Fe-rich phyllosilicates with mixed Fe valence and a non-passivating Fe-free amorphous SiO\(_2\) layer, which allows the formation of ferroan magnesite. In contrast, starting at micro-oxic conditions, carbonation rates are much faster, with no real evidence of interfacial layers. Separate deposits of goethite/lepidocrocite in the early stages of the reaction and then formation of magnetite are observed at these conditions, while precipitation of siderite/magnesite proceeds unhindered. The evolution of the redox conditions during the reaction progress controls the sequence of the observed reaction products and the passivating properties of Fe–Si-rich interfacial layers. These findings have important implications for modeling the carbonation of ultramafic rocks under different oxygen fugacity conditions as well as for understanding the technological implications of adding accessory gases to CO\(_2\) in carbon capture and storage mineralization processes involving ultrabasic rocks.

Keywords: Olivine carbonation, Fe–Si-rich interfacial layers, redox reactions, passivation, cronstedtite, dissolution/precipitation, Fe-oxides

INTRODUCTION

The formation of amorphous Si-rich layers and other secondary precipitates at the mineral/water interface is a well-known process that takes place during the chemical weathering of silicate minerals and can have a significant impact on their dissolution behavior (e.g., Velbel et al. 1993; White and Brantley 2003; Schott et al. 2012; Daval et al. 2013). Irrespective of the exact mechanism of their formation, it is acknowledged that Si-rich altered layers form independently of the degree of saturation of the bulk solution with respect to pure silica polymorphs (cf. Casey et al. 1993; Hellmann et al. 2012). The elementary processes that control the formation and properties of silica altered layers are complex and depend on a series of different factors, such as the structure and composition of the parent phase, the incorporation of foreign ions and the degree of hydration of the silica layers, which may decrease their solubility with respect to pure silica phases (cf. Iler 1979; Schott and Berner 1983; Daval et al. 2009, 2013; Hellmann et al. 2012). Because the development of Si-rich surface layers variably inhibits the dissolution reaction, their formation can also affect significantly a wide range of environmental and/or engineering processes, such as geological CO\(_2\) sequestration, since the rate of CO\(_2\) consumption and the extent of coupled carbonation reactions rely upon the availability of divalent cations released by the dissolution of primary silicates (cf. Oelkers et al. 2008; Guyot et al. 2011). Olivine [(Mg,Fe)\(_2\)SiO\(_4\)] is one of the most thermodynamically favorable and fastest dissolving phases (cf. Oelkers 2001; Schott et al. 2009) and for this reason, it has been the object of a relevant number of studies focusing on the elementary processes and the conditions that enhance, or limit, the overall carbonation reaction (Giammar et al. 2005; Andreani et al. 2009; Garcia et al. 2010; Gerdemann et al. 2007; Dufaud et al. 2009; King et al. 2010; Qafoku et al. 2012; Wang and Giammar 2012; Saldi et al. 2013; Sissmann et al. 2013; Johnson et al. 2014). The formation of Si-rich layers exhibiting some passivating properties on the olivine surface was investigated by several authors (e.g., Béarat et al. 2006; Davis et al. 2009; Daval et al. 2011), whose results suggest that the protective action and evolution of amorphous SiO\(_2\) layers do vary as a function of