Experimental determination of solubility constants of saponite at elevated temperatures in high ionic strength solutions

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ABSTRACT

Saponite occurs in a wide range of environments from hydrothermal systems on the Earth to surface deposits on Mars. Of practical importance is that Mg-saponite forms when glasses for nuclear waste are altered in Mg-bearing aqueous solutions. In addition, saponite is favorably considered as candidate buffer material for the disposal of high-level nuclear waste and spent nuclear fuel in harsh environments. However, the thermodynamic properties, especially for Mg-saponites, are not well known. Here the author synthesized Mg-saponite (with nitrate cancrinite) following a previously reported procedure and performed solubility experiments at 80 °C to quantify the thermodynamic stability of this tri-octahedral smectite in the presence of nitrate cancrinite. Then, in combination with the equilibrium constant at 80 °C for the dissolution reaction of nitrate cancrinite from the literature, the author determined the solubility constant of saponite at 80 °C based on the solution chemistry for the equilibrium between saponite and nitrate cancrinite, approaching equilibrium from the direction of supersaturation, with an equilibrium constant of –69.24 ± 2.08 (2σ) for dissolution of saponite at 80 °C. Furthermore, the author extrapolated the equilibrium constant at 80 °C to other temperatures (i.e., 50, 60, 70, 90, and 100 °C) using the one-term isocoulombic method. These equilibrium constants are expected to have applications in numerous fields. For instance, according to the extrapolated solubility constant of saponite at 50 and 90 °C, the author calculated the saturation indexes with regard to saponite for the solution chemistry from glass corrosion experiments at 50 and 90 °C from the literature. The results are in close agreement with the experimental data. This example demonstrates that the equilibrium constants determined in this study can be used for reliable modeling of the solution chemistry of glass corrosion experiments.

Keywords: Glass corrosion, Mars, nuclear waste management, buffer materials, hydrothermal alteration of basalt, disposal in salt formations, disposal in clay formations

INTRODUCTION

Saponite, a tri-octahedral smectite, occurs in a wide range of environments. For instance, it occurs in igneous rocks as hydrothermal alteration products (e.g., Kohyama et al. 1973; April and Keller 1992; Garvie and Metcalfe 1997; Tao et al. 2019), and in metamorphosed dolomitic limestone as hydrothermal products (e.g., Post 1984). It also occurs as lake sediments and in volcanic rocks on seafloor (e.g., Desprairies et al. 1989; Cuevas et al. 2003; Kadir and Akbulut 2003). Its occurrence in the martian meteorites and its proposed occurrence in Mawrth Vallis region and Yellowknife Bay, Gale Crater on Mars (e.g., Bishop et al. 2003; Kadir and Akbulut 2003). Its occurrence in the martian meteorites and its proposed occurrence in Mawrth Vallis region and Yellowknife Bay, Gale Crater on Mars (e.g., Bishop et al. 2013; Hicks et al. 2014; Bristow et al. 2015) generated enormous scientific interest. Most recently, saponite was also observed in an analog study of the hydrothermal alteration in the martian subsurface (e.g., Sueoka et al. 2019; Calvin et al. 2020).

Additionally, of practical importance and therefore particular interest is that saponite is relevant to the geological disposal of nuclear waste, as Mg-saponite has been observed as an alteration product when a borosilicate glass for nuclear waste is corroded (Thien et al. 2010) in Mg-containing solutions, as detailed below.

Mg-bearing groundwaters are common in the disposal concepts in various rock formations. For instance, salt formations have been recommended for nuclear waste isolation since the 1950s by the U.S. National Academy of Sciences Committee on Waste Disposal (1957). Because of their excellent properties of high-heat conduction, low permeability, and a propensity to self-seal, rock salt is a viable candidate for a nuclear waste repository. Salt formations contain brines, which have relatively high concentrations of magnesium (Nishri et al. 1988; Schuessler et al. 2001; Xiong and Lord 2008). For instance, the Q-brine at Asse, Germany, has a magnesium concentration of 4.47 mol·kg⁻¹ (Nishri et al. 1988; Schuessler et al. 2001). When high-level waste (HLW) glass is corroded in Mg-rich brines, Mg-bearing phyllosilicates form as part of the secondary phase assemblage (Strachan 1983; Strachan et al. 1984; Grannell and Müller 1989; Maeda et al. 2011). Although previously, and tentatively, identified as sepiolite (a member of the palygorskite family), more recent investigations have identified trioctahedral smectites, such as saponite with various stoichiometries, e.g., \((\frac{1}{2}Ca,Na)_{0.66}Mg_{2}[(Si_{7.34}Al_{0.66})O_{20}](OH)_{4}\) (e.g., Abdelouas et al. 1997; Thien et al. 2010; Zhang et al. 2012; Fleury et al. 2013;