Experimental investigation of smectite interaction with metal iron at 80 °C: Structural characterization of newly formed Fe-rich phyllosilicates

BRUNO LANSON,1,* SÉBASTIEN LANTENOIS,2 PETER A. VAN AKEN,3 ANDREAS BAUER,4 AND ALAIN PLANÇON2

1ISTerre, Grenoble University, CNRS, F-38041 Grenoble, France
2Institut des Sciences de la Terre d’Orléans (ISTO), Orléans University, CNRS, F-45071 Orléans, France
3Stuttgart Center for Electron Microscopy, Max Planck Institute for Intelligent Systems, D-70569 Stuttgart, Germany
4Institut für Nukleare Entsorgung, Karlsruhe Institute of Technology, D-76021 Karlsruhe, Germany

ABSTRACT

Interactions between metallic iron and clay minerals have been extensively studied under low-temperature anoxic conditions owing to their potential impact on the long-term safety of high-level nuclear waste disposal in deep geological repositories. To complement the studies investigating the destabilization mechanisms and rates of various initial clay minerals, the prediction of the storage long-term performance requires a comprehensive characterization of the reaction products. The Fe-rich 1:1 phyllosilicates resulting from interactions at 80 °C and in the absence of O2 between metallic iron and smectites with contrasting compositions are thus characterized chemically and structurally using various experimental techniques (X-ray and electron diffractions, infrared, energy-dispersive, and electron energy loss spectroscopies, and high-resolution electron microscopy). Cronstedtite and odinite are the two Fe-rich 1:1 phyllosilicates formed under the experimental conditions investigated, both species differing from their relative contents and the average valence state of structural Fe. No parental link has been evidenced between the two minerals despite their contrasting crystal morphologies and thermodynamical predictions. The formation of the 1:1 phyllosilicates apparently results from the destabilization of the initial smectite through the formation of an intermediate gel.

Keywords: Iron-clay, nuclear waste, smectite, serpentine, berthierine, cronstedtite, odinite

INTRODUCTION

Multi-barrier concepts are envisaged in most countries for the long-term underground storage of high- and intermediate-level and/or long-lived nuclear waste. To prevent the release of radionuclides to the biosphere, metallic containers filled with nuclear waste are possibly placed in an engineered confinement barrier, which is itself surrounded by the geological barrier. Depending on the countries, canisters could be made of carbon steel, stainless steel, or copper, whereas bentonite is universally considered as the major component of engineered barriers (Gates et al. 2009). Bentonite’s main constituent, smectite, combines swelling and self-healing abilities with high cation retention and surface sorption capacities, thus ensuring mechanical stability, low hydraulic conductivity, and minimum release of radionuclides. In some concepts, such as the one currently envisaged by the French agency Andra, the engineered barrier is absent, but smectite is present however as a major component of the geological barrier. However, the safety of the whole concept depends strongly on the long-term stability of smectite in response to thermal and chemical perturbations induced by the waste storage. The formation of non-swelling phyllosilicates and/or of phyllosilicates with low-sorption capacity at the expense of smectite would be detrimental to the storage performance. For example, a wealth of literature has been devoted to the impact of the high-pH plume resulting from cement alteration on the clay mineralogy of both engineered and geological barriers (Chermak 1992, 1993; Claret et al. 2002; Ramirez et al. 2005; Bauer et al. 2006; Charpentier et al. 2006; Sanchez et al. 2006; Devol-Brown et al. 2007; Savage et al. 2007; Cuisinier et al. 2008; Honty et al. 2010).

Similarly, metallic iron-clay, and more specifically metallic iron-smectite, interactions have been thoroughly investigated both experimentally and through thermodynamical modeling. Both approaches are consistent in that they report the destabilization of dioctahedral smectite under neutral to alkaline pH conditions if the metallic iron:clay ratio exceeds a threshold value (~1.5 at 80 °C, Lantenois et al. 2005; Bildstein et al. 2006; Wilson et al. 2006b; Perronnet et al. 2008; Mosser-Ruck et al. 2010; Osacky et al. 2010; Savage et al. 2010; De Combarieu et al. 2011). However, the influence of the chemical composition of smectite, and more especially of its iron content, remains controversial as thermodynamical modeling predicts a higher stability for iron-rich dioctahedral smectite (nontronite; Wilson et al. 2006b) in contradiction with experimental evidence (Lantenois et al. 2005). At temperatures exceeding 150°C, experimental metallic iron-smectite interactions lead to the formation of iron-rich smectites (di- and/or trioctahedral) and/or of chlorite (Guillaume et al. 2003, 2004; Charpentier et al. 2006; Wilson et al. 2006a; Mosser-Ruck et al. 2010). Over the 50–100 °C range predicted...