Genesis and compositional heterogeneity of smectites. Part III: Alteration of basic pyroclastic rocks — A case study from the Troodos Ophiolite Complex, Cyprus

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ABSTRACT

Upper Cretaceous basic pyroclastic rocks, which overlie the Upper Pillow Lavas of the Troodos ophiolitic complex, Cyprus have been altered to bentonites. The resulting smectite is Fe-rich montmorillonite and Fe-rich beidellite, with moderate Mg contents. The smectite is trans-vacant and contains abundant exchangeable K. The presence of K is linked with hydrothermal alteration, which affected the higher members of the Troodos ophiolitic suite. The smectite displays significant compositional heterogeneity, which involves substitution of Fe for Al and to a lesser degree substitution of Mg for Al, and that reflects the influence of microenvironmental conditions on smectite formation. The layer charge of the smectite is controlled mainly by the tetrahedral charge, whereas the influence of octahedral charge is of lesser importance, because of Fe for Al substitutions, which does not create a charge deficit. Although the parent pyroclastic rocks were basic, the bentonites contain abundant Si-polymorphs and Si-rich zeolites, from dissolution of abundant radiolarian frustules, which increased the Si-activity of the pore waters, and also produced the partial replacement of smectite by palygorskite at a later stage. Dissolution of frustules was facilitated by the high heat flow from the ocean floor and by the circulation of hydrothermal fluids. The crystal chemistry of smectite and the bulk mineralogy of the bentonites influence the physical properties and industrial applications of the Cyprus bentonites, as well as their response to acid treatment.

Keywords: Troodos ophiolite, Fe-rich montmorillonite, Fe-rich beidellite, layer charge, charge heterogeneity, hydrothermal alteration, bentonite, clinoptilolite

INTRODUCTION

The compositional and structural heterogeneity of dioctahedral smectite in bentonites has been studied thoroughly in the past with various experimental techniques, including X-ray diffraction (XRD), spectroscopy (FTIR, NMR, Mössbauer, and EPR), microcalorimetry, thermal analysis, and electron microprobe analysis (Tettenhorst and Johns 1966; Lagaly and Weiss 1975; Lagaly et al. 1976; Goulding and Talibudeen 1980; Paquet et al. 1982; Talibudeen and Goulding 1983; Nadeau et al. 1985; Lim and Jackson 1986; Decarreau et al. 1987; Iwazaki and Watanabe 1988; Banfield and Eggleton 1990; Christidis and Dunham 1993, 1997; Drits et al. 1998; Cuadros et al. 1999). Although the existence of compositional heterogeneity in Al-rich smectite is well known, the factors that control it are not well understood. Weaver and Pollard (1973) assumed a complete solid solution between beidellite and montmorillonite, but Brigatti and Poppi (1981), Köster (1982), and Yamada et al. (1992) rejected this possibility. Brigatti and Poppi (1981) considered solid solutions among montmorillonite species. Previously, Grim and Kubičkí (1961) had proposed that Wyoming-type and Cheto-type montmorillonite do not form solid solutions. Decarreau et al. (1987) suggested the existence of layers or domains of different composition in Ni-Fe-Mg smectite from lateritic profiles. Finally, Meunier and Velde (1989) proposed a solid solution between high- and low-charged montmorillonite but not between montmorillonite and beidellite.

Christidis and Dunham (1993, 1997) and Christidis (2001) have shown that the chemical characteristics of smectite in bentonites are controlled by the composition of the parent rock and the pore fluid. Smectite derived from intermediate (dacitic-andesitic) precursors is extremely heterogeneous. A compositional transition exists between beidellite and Tatatilla-type (Cheto) montmorillonite, suggesting the possibility of a solid solution between the two species (Christidis and Dunham 1993). In contrast, no transition was observed either between beidellite and Wyoming-type montmorillonite, or between Cheto-type- and Wyoming-type montmorillonite. In contrast, smectite derived from acidic rocks does not necessarily display significant compositional heterogeneity. Compositionally heterogeneous systems are characterized by beidellite and Tatatilla-type montmorillonite (Christidis and Dunham 1997), whereas homogeneous systems may consist of Chambers-type montmorillonite (Christidis 2001). The observed difference in the chemistry of smectite has been attributed to the role of the pore water chemistry (Christidis 2001).

Weathering and/or hydrothermal alteration of basic rocks usually yields dioctahedral Fe-rich smectites including nontronite (Brigatti 1983; Decarreau et al. 1987; Köster et al. 1999) or saponite, which can be Fe-rich or Al-rich (Alt and Honnorez 1984;...