

PERSPECTIVES

Resolving the conundrum of equilibrium solubility of smectites

STEPHEN U. AJA^{1,*}

¹Department of Earth and Environmental Sciences, Brooklyn College & The Graduate Center, City University of New York, 2900 Bedford Avenue, Brooklyn, New York 11210-2889, U.S.A

ABSTRACT

Smectites are common clay minerals in surface and near surface terrestrial environments and have recently been shown to be ubiquitous on Mars. Because these minerals are products of water-rock interaction, the thermodynamics of their interaction with fluids constitutes a vital part of resolving the utility of smectite mineralizations as petrogenetic and paleoenvironmental indicators on both Mars and Earth's near surface environments. Smectites, and other clay minerals of comparable compositional complexity, have been purported to be disequilibrium solids whose complexity derives from steep chemical gradients in their environments of formation rather than from crystal-chemical constraints. Solubility investigations of several natural smectites wherein none exhibited the predicted inverse correlation between $\text{pH}-\frac{1}{2}\text{pAl}$ and $\text{pSi}(\text{OH})_4$ were adduced by May et al. (1986) as empirical proof of the disequilibrium solid concept, and hence they asserted unequivocally that "it is obviously impossible to obtain valid ion activity quotients for smectite solubilities in these systems." However, the unattainability of equilibrium smectite solubility in those experimental systems was probably an artifact of the extremely high fluid-to-solid ratios employed therein. In subsequent experimental studies using significantly lower fluid-to-solid ratios, smectite-fluid interactions (Kittrick and Peryea 1989; Gaboreau et al. 2020), and chlorite-fluid interactions (Aja and Dyar 2002) yielded solubility data amenable to laws of chemical thermodynamics and thus invalidated the disequilibrium solid model. Therefore, the notion of smectite metastability and/or instability anchored on the disequilibrium solid model is false and warrants a more constrained definition of smectite metastability.

Keywords: Smectite, metastability, disequilibrium solid, fluid-to-solid ratio, reversibility, solubility equilibrium, colloidal electrolyte