Compositional End Members and Thermodynamic Components of Illite and Dioctahedral Aluminous Smectite Solid Solutions

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[2]In accord with the classification system established by the AIPEA (Bailey *et al*., 1984), the terms smectite and illite are used in the present communication to refer to two separate mineral groups that have specific crystallographic and chemical characteristics that distinguish the species in one group from those in the other.

Abstract: Consideration of XRD, TEM, AEM, and analytical data reported in the literature indicates that dioctahedral aluminous smectite and illite form two separate solid solutions that differ chemically from one another primarily by the extent of Al substitution for Si, the amount of interlayer K, and the presence of interlayer H_2O. The data indicate that limited dioctahedral-trioctahedral and dioctahedral-vacancy compositional variations occur in both minerals. Excluding interlayer H_2O and based on a half unit cell [i.e., $O_{10}(OH)_2$], natural dioctahedral smectite and illite solid solutions fall within the compositional limits represented by $A_{0.3}$ R 1.9 3+ $Si_4O_{10}(OH)_2$-$AR^{2+}R^{3+}Si_4O_{10}(OH)_2$-$A_{0.25}$ R 0.3 2+ R 1.8 3+ $Al_{0.25}Si_{3.75}O_{10}(OH)_2$ for smectites and $A_{0.8}$ R 1.9 3+ $Al_{0.5}Si_{3.5}O_{10}(OH)_2$-$A_{0.55}$ R 0.45 2+ R 1.55 3+ $Al_{0.1}Si_{3.9}O_{10}(OH)_2$-$A_{0.9}$ R 0.3 2+ R 1.8 3+ $Al_{0.9}Si_{3.1}O_{10}(OH)_2$ for illites, where A represents either monovalent cations or divalent cations expressed as their monovalent equivalent (e.g., $Ca^{2+}/2$); R^{2+} stands for the divalent cations Mg^{2+} and Fe^{2+} and R^{3+} refers to the trivalent cations Al^{3+} and Fe^{3+}. Taking account of these compositional limits, smectite and illite solid solutions can be described in terms of nine and six thermodynamic components, respectively, all of which are consistent with both the law of definite proportions and the concept of a unit cell. Thermodynamic components that can be used to describe natural smectite solid solutions in terms of a half unit cell [i.e., $O_{10}(OH)_2$] can be expressed as $NaAl_3Si_3O_{10}(OH)_2$, $NaAl_3Si_3O_{10}(OH)_2 \cdot 4.5H_2O$, $Al_2Si_4O_{10}(OH)_2$, $Fe_2Si_4O_{10}(OH)_2$, $Mg_3Si_4O_{10}(OH)_2$, $Fe_3Si_4O_{10}(OH)_2$, $K_3AlSi_4O_{10}(OH)_2$, $KAl_3Si_3O_{10}(OH)_2$, and $Ca_{0.5}Al_3Si_3O_{10}(OH)_2$. Of these, $NaAl_3Si_3O_{10}(OH)_2 \cdot 4.5H_2O$ provides explicitly for the presence of interlayer H_2O in the mineral. Thermodynamic components representing illite solid solutions in natural systems can be written for a half unit cell as $KAl_3Si_3O_{10}(OH)_2$, $KMg_3AlSi_3O_{10}(OH)_2$, $KFe_3AlSi_3O_{10}(OH)_2$, $Al_2Si_4O_{10}(OH)_2$, $KFe_2AlSi_3O_{10}(OH)_2$, and $K_3AlSi_4O_{10}(OH)_2$. The calculations and observations summarized below indicate that neither smectite nor illite occur in nature as stoichiometric phases and that the two minerals do not form a mutual solid solution corresponding to mixed-layered illite/smectite.

Key Words: Clay minerals • Composition • End members • Illite • I/S clays • Mixed-layered clays • Smectite • Stoichiometry • Structural formula • Thermodynamic components • Thermodynamic status

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