Cation redistribution in the octahedral sheet during diagenesis of illite-smectites from Jurassic and Cambrian oil source rock shales

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ABSTRACT

During diagenesis of Jurassic and Cambrian oil source rock shales illite-smectite-vermiculite [I-S(-V)] is transformed to illite-to-belte-smectite(-vermiculite) [I-T-S(-V)]. This transformation of S layers to T layers takes place by an increase in tetrahedral charge through Al for Si substitution and subsequent fixation of interlayer NH4, accompanied by an increase in Al and a decrease in Fe and Mg in the octahedral sheet. In the present investigation, the distribution of isomorphous cations in octahedral sheets of trans-vacant I-S(-V) and I-T-S(-V) was studied by Mössbauer and Infrared (IR) spectroscopies. Mössbauer spectra have been modeled using numerical values of the Fe3+ and Fe2+ quadrupole doublets corresponding to local cation arrangements around Fe3+ and Fe2+ in octahedral sheets of micaceous minerals. To interpret IR spectra in the OH-stretching region, frequencies for each pair of cations bonded to OH groups determined for micas and I-S are used. Combination of Mössbauer and IR data by computer simulation provides two-dimensional cation distributions of octahedral cations. The Jurassic and Cambrian I-S(-V) and I-T-S(-V) have clustered octahedral sheets. Ordered clusters of mixed cation composition (Mg, Al, Fe3+, and Fe2+) with regular alternation of divalent and trivalent cations and Fe3+-clusters dispersed over an Al-matrix are found in detrital samples. In diagenetically transformed samples, ordered clusters persist while Fe3+-clusters degenerate to either short chains consisting of two Fe-Fe pairs or to isolated Fe-Fe pairs oriented along the b1, b2, and b3 directions. The release of Fe and Mg during diagenesis occurs from Fe3+ clusters and through partial destruction of ordered clusters and of b1, b2-oriented Mg-Mg pairs. However, as the cation composition and the short-range cation order within the clusters are preserved and the Al for Fe and Mg substitution occurs at cluster edges, the diagenetic transformation of S (and V) to T layers in both the Jurassic and Cambrian I-S(-V) proceeds through a solid-phase transformation and not through dissolution-reprecipitation.

Keywords: Illite-smectite, cation distribution, computer simulation

INTRODUCTION

Mixed-layer illite-smectite (I-S) is a typical component of, e.g., shales, K-bentonites, mudstones, and hydrothermally altered rocks. Transformation of smectite into illite through a series of I-S is accompanied by increasing of illite interlayers, and a tendency to ordering in the distribution of illite and smectite interlayers (e.g., Shutov et al. 1969a, 1969b; Perry and Hower 1970; Hower et al. 1976). The increase in illite layers in I-S occurs by tetrahedral Al for Si substitution and replacement of exchangeable cations by different local cation environments. Quadrupole splittings for Fe3+ cations are assumed to be due to distortions of Fe3+ octahedra by different local cation environments. Quadrupole splittings for each local cation environment have been deduced for Fe3+ (Drits et al. 1997a; Dainyak and Kheifits 1999) and, recently, for Fe2+ based on relationships between the quadrupole splitting and the corresponding local cation arrangements around these cations (Dainyak et al. 2004). These assignments allow presenting the fitted broadened doublets as groups of closely overlapping peaks. Similar presentation of the fitted doublets follows from quadrupole splitting distribution (QSD) analysis (Wivel and Morup 1981; Rancourt and Ping 1991; Rusakov 1999). It was pointed out (Rancourt 1994) that two discrete doublets in the spectra of trioctahedral biotite and ammite cannot be assigned to cis- and trans-sites and should be replaced by a QSD because the local structural disorder due to cation distribution does influence the Fe2+ Mössbauer parameters independent of the structural location.