Semiquantitative determination of trans-vacant and cis-vacant 2:1 layers in illites and illite-smectites by thermal analysis and X-ray diffraction

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ABSTRACT

Interstratified illite-smectites (I/S) and illite-smectite-vermiculites (ISV) representing both hydrothermal and diagenetic transformations and having different degrees of structural order were investigated for cis-trans occupancy in the octahedral sheet by X-ray diffraction (XRD) and by differential thermal analysis (DTA) in combination with evolved water analysis (EWA) using an infrared detector. By XRD, the amounts of cis ($w_{cv}$) and trans ($w_{tv}$) vacant 2:1 layers were determined for the three-dimensionally ordered samples using both the WILDFIRE simulation program and calculations based on positions of the 11l and 11r reflections. Based on the EWA curves, the I/S and ISV could be divided into three groups having (1) one strong and one or more weak EWA peaks; (2) two well-resolved peaks; and (3) a complex EWA curve. The amounts of cis- and trans-vacant sites were determined by peak fitting of the total dehydroxylation curve. The complex EWA curves were, however, in addition split into separate dehydroxylation processes during a step-heating technique. If the EWA peaks below and above 600 °C were attributed to trans vacant (tv) and cis vacant (cv) octahedra, respectively, the $w_{cv}$ values determined by XRD and by EWA were in agreement. For the three-dimensionally ordered minerals, both XRD and EWA should be used, whereas the EWA method can be applied to the structurally disordered samples having no diagnostic 11r reflections. Accordingly, a combination of XRD and EWA for the determination of $w_{cv}$ and $w_{tv}$ supports an evaluation of the mechanism of illitization in various geological environments. Thus, significant changes in $w_{cv}$ and $w_{tv}$ during illitization are likely due to a dissolution-precipitation, whereas almost constant values indicate a solid-state transformation.

INTRODUCTION

Interstratified illite-smectite (I/S) is present in different geological environments, and the structure (amount of illite interlayers and ordering of the interlayer types) is an indicator of the degree of transformation both during burial diagenesis and hydrothermal activity (Burst 1969; Shutov et al. 1969; Hower et al. 1976; Bethke and Altaner 1986; Nadeau and Bain 1986; Inoue et al. 1988; Eberl 1993).

Characterization of I/S and the mechanisms of I/S formation at different stages of postsedimentary and hydrothermal alteration of rocks have been extensively studied (Shutov et al. 1969; Hower et al. 1976; Pevear et al. 1980; Reynolds 1980; Šrodon 1980, 1984). Until recently, mainly the mixed-layering of the I/S structure has been studied through investigation of basal reflections by X-ray diffraction (XRD) and through attempts to image the distribution of illite and smectite interlayers using high resolution transmission electron microscopy (Ahn and Peacor 1986a, 1986b, 1989; Bell 1986; Klementidis and MacKinnon 1986; Hansen and Lindgreen 1987, 1989; Guthrie and Veblen 1989; Ahn and Buseck 1990; Veblen et al. 1990; Lindgreen and Hansen 1991; Šrodon et al. 1992; Sucha et al. 1996). Furthermore, electron microscopy has been used to determine shape and thickness of particles (Nadeau et al. 1984, 1985; Inoue et al. 1987; Lanson and Champion 1991; Sucha et al. 1992; Inoue and Kitagawa 1994).

Tsipursky and Drits (1984) showed that in the 2:1 layers of montmorillonite, as a rule, one of two symmetrically independent cis-octahedra is vacant, whereas illites normally have trans-vacant (tv) 2:1 layers. Accordingly, a formation of illite 2:1 layers from smectite 2:1 layers should lead to an increase in proportion of tv 2:1 layers. Investigations of the change in amount of cis-vacant (cv) and tv 2:1 layers in I/S during transformations should accordingly be important for understanding the mechanisms and dynamics of this process. For example, Drits