Determination of the content and distribution of fixed ammonium in illite-smectite by X-ray diffraction: Application to North Sea illite-smectite

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ABSTRACT

A new X-ray diffraction method for the determination of the amount and distribution of fixed NH4+ in illite-smectite has been developed. Illite-smectite was saturated with K+ and heated at 150 °C. The 002 and 005 reflections were recorded with steps of 0.01° 2θ, and the experimental d values and the values for full-width at half-height (FWHH) were determined using a peak-profile-fitting procedure. Peak profiles were calculated with the NEWMOD program for illite structures having different amounts of NH4+ and different patterns for the distribution of NH4+ in interlayers. For Upper Jurassic illite-smectite from North Sea oil source rocks, the amount and the distribution of NH4+ in illite interlayers were determined by comparing the experimental values for d_005 and FWHH with the values calculated for the selected illite structures. The amounts of NH4+ determined in this manner correlate well with the amounts determined by an isotopic dilution method. The results demonstrate that these illite-smectite samples have K end-member illite and NH4+ end-member illite (tobelite) layers and that the illite layers formed during diagenesis and oil generation actually are tobelite layers.

INTRODUCTION

Smectite illitization is accompanied by formation of mixed-layer illite-smectite (I-S) or illite-smectite-vermiculite (I-S-V) having different interstratified interlayer types. In oil source rocks, diagenetic alterations of I-S and I-S-V often take place simultaneously with oil generation. For example, in the Upper Jurassic oil source rocks in the North Sea, the increase in the number of illite layers and the ordering of I-S take place simultaneously with oil generation (Hansen and Lindgreen 1989). In this Upper Jurassic shale, illitization is the transformation of single smectite interlayers to illite interlayers in I-S-V (Drits et al. 1997) through tetrahedral substitution of Al for Si and subsequent fixation of K+ and NH4+ (Lindgreen et al. 1991; Lindgreen 1991).

Generally, the fixed cation in illite interlayers in I-S is assumed to be K+. However, Stevenson (1960) found a significant amount of fixed NH4+ (0.2–0.5% N) in clay minerals from Paleozoic shale and suggested that during smectite illitization NH4+ released from the decomposition of organic matter can be fixed in illite interlayers as NH4+. According to Stevenson (1960), the presence of fixed NH4+ in clay-mineral structures may be considered as evidence of oil generation. Cooper and Abedin (1981) found that the amount of fixed NH4+ in Tertiary Gulf Coast shales increased with depth and eventually constituted 7% of the fixed interlayer cations in clay fractions. Williams et al. (1989, 1992) investigated NH4+-bearing sandstones and mudstones from Gulf Coast Tertiary sediments and concluded that NH4+, released during oil generation from organic matter, migrated with oil through sandstones to become incorporated into clay-mineral structures.

Recently, Lindgreen (1994), using an isotopic dilution method, studied NH4+-bearing I-S formed during diagenesis in Upper Jurassic shales that are the main source rocks for oil in the North Sea. Lindgreen (1994) found that with increasing depth of sample, the ratio NH4+/K+ for soluble cations in the pore fluids of core samples increased as did the same ratio for fixed cations in interlayers of the I-S structures. Lindgreen concluded that NH4+ fixation may be a general process during burial diagenesis in oil source rocks.

The presence of NH4+ in mineral structures cannot be detected by most microprobes, which usually determine elements atomic number 11 and higher. Nor can NH4+ be detected by atomic absorption spectrometry, another method commonly applied in elemental analysis of rocks. IR spectroscopy is a very useful technique for detection of NH4+ (Vedder 1965) but is difficult to use for quantitative determination of NH4+ (Sterne et al. 1982). The isotopic dilution method requires a very small amount (≈5 mg) of sample and is highly accurate (Middelboe 1977; Middelboe and Johansen 1991), but the procedure requires special equipment. Because of these analytical difficulties, fixed NH4+ in I-S is often not detected.

Fixed NH4+ in illite interlayers of I-S should modify the structure and the diffraction patterns of these minerals. Thus, natural and synthetic NH4+-bearing dioctahedral micas are different from pure K end-member illite and mus-