XRD-TEM-AEM comparative study of n-alkylammonium smectites and interstratified minerals in shallow-diagenetic carbonate sediments of the Basque-Cantabrian Basin

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ABSTRACT

The validity of the application of the n-alkylammonium method to carbonate-rich lithologies was checked by means of a double comparison: First, the method was applied to samples studied by XRD and HRTEM. Second, these results were compared with the chemical compositions obtained independently by analytical electron microscopy (AEM) from single grains of smectites and I/S. Marl and marly limestone samples corresponding to the R0 and R1 illite/smectite mixed-layer (I/S) stages of diagenetic evolution have been analyzed by the n-alkylammonium method. Forty samples were taken and analyzed by routine X-ray diffraction (XRD) methods. The complete series from n\textsubscript{6} to n\textsubscript{18} has been used for XRD determination on eight samples, yielding layer charges of 0.32 to 0.39 apfu for the expandable component [formula based on O\textsubscript{10}(OH)\textsubscript{2}]. Lattice-fringe images have been obtained under TEM from four selected samples treated with n\textsubscript{8} and n\textsubscript{14} alkylammonium, which are the best chain lengths for discrimination, according to the XRD results. The same type of interlayer configuration (mono-, bi-, or pseudo-tri-layer) has been found by XRD and TEM in all cases. A comparison of the alkylammonium method layer charges with those calculated from formulas determined by AEM on single clay particles has revealed a good general agreement between the two independent methods; however, results from the alkylammonium method are 3 to 14% lower than those from AEM. This disparity is qualitatively in agreement with the literature, but the difference is clearly lower, presumably due to the use of specific in situ analyses (which are contamination-free) instead of whole analyses of separates. The good agreement among the three methods validates their use for carbonate-rich lithologies. Layer charge increases with depth through the R0 stadium, but stabilizes, with no further increase, when the R1 stadium is reached; this change in behavior may be related with qualitative differences in the transformation mechanism.

Keywords: Illite-smectite mixed-layer, diagenesis, layer charge, marl, limestone

INTRODUCTION

Layer charge is a significant parameter in smectites and related minerals. It plays a fundamental role in edaphic environments as it determines the exchange capacity between the mineral component and fluids of soils. The diagenetic environment is characterized by the evolution from smectite (a low-charge 2:1 phyllosilicate) to high-charge micas. Therefore, the transition from one configuration to another occurring for different lengths of the alkylammonium chain, depending on the layer charge. A complete determination would require sample treatment with all the n-alkylammonium (hereafter, n\textsubscript{c} refers to the number of C atoms in the alkylammonium chain); the identification of n\textsubscript{c} for which the transitions occur would allow a determination of the layer charge. Due to heterogeneities in the layer charge at the sample level, the transition can occur in the range between two non-consecutive n\textsubscript{c} alkylammoniums.

The method has been applied to the expandable component of illite-smectite mixed-layers (I/S) (Lagaly 1979; Cetin and Huff 1995; Inoue et al. 2005). In such cases, a good knowledge of the proportion of S layers in the I/S is necessary to calculate the resulting d\textsubscript{001} for the different alkylammonium configurations.

In HRTEM images, layer spacing can be directly measured. Smectites or I/S treated with alkylammonium are able to main-