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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_c:6 to n_c: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 $O_{10}(OH)_2$]. Lattice-fringe images have been obtained under TEM from four selected samples treated with n_c:8 and n_c: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