XRD-Rietveld and RMC analysis of the aging process in glauconites

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Glauconites work as open systems at seawater-sediment interface leading to simultaneous chemical and structural re-arrangements on aging. A precise knowledge of this process, usually termed as *glauconite maturity,* is of interest for oceanographers and sedimentologists in order to characterize paleoenvironmental changes and to stimate sedimentary conditions for sequence stratigraphic studies.

Usual models are based on empirical markers as are the colour, K^+ contents, distance between the 001, 020 reflections from XRD patterns, magnetic susceptibility, etc. Nevertheless, a complete characterization of evolutionary stages of glauconite must able to relate the chemical changes taking place during the growth process with the structural variability, from a nearly amorphous initial stage to a highly evolved glauconite, as function of both the variation on stoichiometry and the structural disorder.

In this work, the aging process in glauconites has been examined using the XRD-Rietveld analysis to characterize the average structural disorder associated with several compositional variations in the glauconite formula. This was done by simultaneous constrained refinement of both the occupancy factors and the crystallite-size domains, as a measure of the cristallinity degree. The celadonite atomic coordinates were used as starting structural model. Fifty glauconite samples located at the NW of Spain continental shelf, with several maturity degrees were employed in the refinements and to perform geochemical mapping relating the space distribution of the glauconite maturity to the chemical variability.

The results show that although the rise in K^+ in the structure is the driving variable in the ordering process this is coupled with simultaneous loss in Fe, given a progressive tendence towards the enrichment of Al^{3+} and Mg^{2+}.

The previous study leads an average characterization de ordering process. Nevertheless several local mechanisms, like layer interstratification or stacking faults dues to layer rotation (Drits and Tchoubar, 1990) have been proposed. Then, to analyse detailed aspects of the local structural disorder, adittional Reverse Montecarlo (RMC) calculations based on the average structure previously obtained from Rietveld analysis have been performed.

References

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Sorption of Pb^{2+} on barite and crystallisation of $(Ba,Pb)SO_4$ in aqueous environments

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Sorption of lead ions on barite surface by precipitation of $(Ba,Pb)SO_4$ solid solutions represents a potential removal process of this contaminant in aqueous environments.

Thermodynamics models for the $(Ba,Pb)SO_4$-H_2O system reveal that this solid solution presents a wide miscibility gap (Kornicker et al., 1991). Moreover, the low solubility of barite compared to lead sulphate involves a strong preferential partitioning of Ba to the solid phase. However, under non-equilibrium conditions the complete solid solution series can be crystallised (Takiyama and Kozuki, 1969) and the preferential partitioning of Ba to the solid becomes less important.

We present experimental work on (i) crystallisation of $(Ba,Pb)SO_4$ solid solutions, and (ii) sorption of lead on barite in aqueous environments.

Crystallization experiments have been carried out by counter-diffusion of (Pb^{2+},Ba^{2+}) and SO_4^{2-} in a silica hydrogel column. The gel reduces the nucleation density and favours the development of relatively large crystals. Representative single crystals of the complete solution series were obtained and the evolution of both morphology and composition during the growth process was studied.

In addition, two different kinds of sorption experiments have been performed. In a first set, Pb-containing aqueous solutions were placed in contact with barite grains in a stirred reactor to study the decrease in $(Pb^{2+})_{aq}$ concentration as a function of time. Moreover, assuming that sorption occurs by surface precipitation of Pb-bearing solids, a second set of experiments were carried out in a gel medium. This procedure increases the size of the sorbed entities, that were then characterized as nearly two-dimensional $(Ba,Pb)SO_4$ crystallites that grow epytaxialy onto the {001} barite cleavage surfaces.

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