4.2.P15

The evolution of REE and other trace element patterns in the course of glauconitization

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The glauconitization process

Glauconite is an Fe^{3+}-rich dioctahedral interlayer deficient mica series (IMA definition). It forms on the ocean floor in the form of grains (appr. size range 63 μm–1 mm), which is a quite unusual feature for clay minerals, providing an excellent chance for separation.

The process of glauconitization can be described as follows: different kinds of substrates (e.g. biogenic test fillings, faecal pellets, rock fragments) turn gradually from a mixed-layer mica-smectite phase into a more micaceous phase. In the course of evolution the amounts of K and Fe (Fe^{3+}, Fe^{2+}) increase while that of Al decreases. The amount of expanding layers is decreasing while density is increasing.

Materials and methods

The glauconitization process was traced by the study of three glauconite populations, originating from different horizons of the Upper Oligocene Eger Formation (south-western foreland of the Bükk Mountains, North Hungary). A novel approach has been applied: beside separation upon grain size and magnetic property, grains were also separated upon density. In the 2.83–2.33 g/cm^3 density range, density steps of 0.05 g/cm^3 were used. The resulting glauconite fractions represent different stages of glauconitization of the same starting material.

The trace element content of the hand-picked individual grains, representing the whole density range, have been determined by LA-ICP-MS.

Results

Two effects influence trace element behaviour during glauconitization: changes in crystal structure/chemistry and geochemical conditions prevailing on the sea bottom. Crystal chemical changes are reflected e.g. in the behaviour of Sr and Ba, the amounts of wich decrease parallel to Ca (smectite), while Rb increases parallel to K (mica).

Concerning REE behaviour, the two autochtonous populations of mixed volcanic and biogenic substrates exhibited depletion during evolution. The third one, showing no direct evidence of source material, exhibited enrichment. Possible causes and the effect of substrates are discussed in detail.

4.2.P16

Thermodynamics of the heterogeneous equilibria in the unsaturated zone of soils

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In most of studies devoted to reactive transport modelling, integrating the kinetics of mineral-solutions reactions, thermodynamic data established for water saturated systems are directly applied to the unsaturated zone (UZ) ([1]; and ref. therein). [2] introduced simple corrections of the thermodynamic constants by extrapolating them at negative pressure to discuss the geochemical route of petrogenetic assemblages in UZ. This pressure consideration derives from the capillary nature of UZ water, which can sustain high tension in fine pores under arid and semi-arid climates. A theoretical approach of the negative pressure water has been largely discussed these latter years (e.g. [3]), as its general consequences on solid/solutions equilibria.

However, the complexity of these geochemical UZ systems is not at all limited to pay attention to the capillary state of liquid water. In the usual way to calculate thermodynamic constants, the pressure inside the system is supposed to be the same for all components. One crucial question arises: what are the pressure of gases and/or minerals in equilibrium with water inside UZ pores ([4])?

To make the calculations in such a frame easier and more efficient for further investigations, a thermodynamic computer package has been developed [5] which implements all the aspects currently under examination. Preliminary applications of this approach to the reactivity of mineral and gas phases in soil aqueous solutions and mass transfer of pollutants through the UZ allow prominent thermodynamic interpretations of some field or experimental observations (e.g. [6], [7]). Applications of this new approach to the problems of soil salinisation or transfer of pollutants may improve our knowledge of the reactivity inside the UZ and its effective role in the specific transfer rate of metals and organic pollutants towards rivers and aquifers.

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