THE CRYSTAL CHEMICAL EVOLUTION OF GLAUCONITES

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This is the first comprehensive report on the study of three glauconite populations from the Upper Oligocene sandstones of the Eger Formation, North Hungary. Two samples originate from Nyárjas summit (Novaj, samples #Ny1 and #Ny3) and the third sample comes from the type section of the Eger Formation (Eger, Wind brick yard, sample #EWT).

The samples have been treated with dilute (5%) acetic acid to remove carbonates, the detrital and glauconitic grains have been separated upon grain size, magnetic susceptibility (0.5, 0.6, 0.7 and 0.8 A) and density (2.33–2.83 g/cm^3 density range, step size 0.05 g/cm^3). The final separation step was hand-picking under the stereomicroscope. The glauconite populations were characterised by powder XRD, FTIR, main (WDX, EDX, ICP-OES) and trace (LA-ICP-MS) element chemistry.

Although originating from the same formation, the three samples exhibited significantly different characteristics. Sample #Ny1 represents a complete evolution series from the lowest to the highest densities, while #EWT is a highly evolved population of mainly high density grains and #Ny3 is a less evolved population with the dominance of low density fractions.

The substrates of the glauconitic grains differ, too: the substrate in #EWT is volcanic debris only, while in the other two samples both volcanic debris and biogenic grain (foraminifera tests, faecal pellets, echinoderm fragments and snails) substrates are present. Glauconites of #EWT are allochthonous while those of the two other samples are autochthonous.

The smectite-mica structural evolution (see e.g. Wiewióra and Lacka, 1985) is detectable on the powder XRD patterns of all the three samples; however, each population is characterised by a specific and constant d_{060} value (1.515, 1.517 and 1.521 Å for #EWT, #Ny1 and #Ny3, respectively).

As confirmed by main element chemistry, the populations basically preserve their tetrahedral trivalent cation proportion. As expected, the d_{060} value relates to the tetrahedral cation proportion: the higher the trivalent cation substitution, the higher is the d_{060} (0.20–0.25 p.f.u. for #EWT, 0.40–0.45 p.f.u. for #Ny1 and 0.50–0.60 p.f.u. for #Ny3, respectively; formula unit is always calculated for 11 O atoms). Concerning octahedral occupancy, samples #Ny3 and #Ny1 decrease from 2.2 to 2.0 p.f.u., while #EWT decreases from 2.1 to 2.0 p.f.u. The different evolutionary stage is reflected in the different interlayer charge ranges:

0.45–0.90 p.f.u. for #Ny1, 0.50–0.85 p.f.u. for #Ny3 and 0.50–0.90 p.f.u. for #EWT. The reworked and diagenetically altered nature of #EWT is reflected in the main chemistry: data are a little scattered and increasing density fractions are not strictly following the expected chemical evolution trend.

The REE content of glauconite is dependent on the substrate type but also on diagenetic processes: #Ny1 and #Ny3 reveal decreasing REE content with increasing evolutionary stage while #EWT has an increasing REE content due to the postgenetic precipitation of REE-Ca phosphates (with the dominance of Ce). Within a given density fraction, usually faecal pellets have the highest, echinoderm test fragments the lowest REE-content (analytical error due to high porosity cannot be entirely excluded), while other biogenic grains and rock fragments have overlapping values within the two extremes. Glauconites exhibit negative Ce and Eu anomaly (normalised to PAAS), except for #EWT, which has positive Ce anomaly due to the above mentioned phosphate precipitation.

Based on the clear, from diagenesis undisturbed example of #Ny1, both the structural and crystal chemical evolution steps of glauconitisation were recorded. The gradual incorporation of K, Fe^{2+} and Fe^{3+} into the structure parallel to the release of Al (for a comprehensive overview see Odin and Fullagar, 1988) have been confirmed by bulk chemistry. Due to the chemically stable tetrahedral sheet, the increase in the interlayer charge is compensated by the decrease of the cationic charge of the octahedral sheet. Three substitutions take place in the octahedral sheet: (1) Al => Fe^{3+}, (2) Al => Fe^{2+}, (3) Al => □ (vacancy). The second substitution process decreases only the octahedral cation charge, while the third one decreases both the octahedral occupancy and the octahedral cation charge. The latter two substitutions are equally significant in compensating the increase in the interlayer charge.

References

ODIN G. S., FULLAGAR, P. D. (1988): Developments in Sedimentology, 45, 295–332.
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