

SUBSTITUTION PROCESSES DURING GLAUCONITISATION

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By differentiating between glauconitic grains of different evolutionary stages within the same population we may get a deeper insight into the glauconitisation process. Previous studies dealt mainly with the highly evolved glauconitic grains (density around 2.8 g/cm^3), which, due to the late evolutionary stage, often camouflaged the steps of glauconitisation.

By studying also the low-density glauconitic grains (starting from $\geq 2.83 \text{ g/cm}^3$ down to $\leq 2.33 \text{ g/cm}^3$ with density steps of 0.05 g/cm^3) the glauconitisation process (see also Weiszburg and Tóth, 2004) can be traced back to the starting material. For this purpose, glauconite populations from sandstones of the Upper Oligocene Eger Formation (Hungary) have been studied in detail. The substrates for glauconitisation were volcanic debris (tuff fragments) and biogenic grains (foraminifera tests and test fragments, echinoderm test fragments, snails and faecal pellets). Selected grains have been studied by scanning electron microscopy (SEM equipped with energy dispersive spectrometer) and electron probe microanalysis (EPMA).

The first step of glauconite formation is the primary precipitation of an iron-rich dioctahedral layer silicate of a layer charge around 0.5–0.6 that still contains relatively high amounts of Al (up to 10–12 wt% Al_2O_3). We suppose that volcanic material contribution (e.g. tuff, volcanic debris) plays an important role in the formation of that iron-rich smectite precursor. Two major processes yield these smectites: (1) primary precipitation in semi-confined voids, e.g. foraminifera chambers and other fossil casts, voids of echinoderm test fragments, pores of volcanic tuff/glass and (2) primary precipitation as substitution of the carbonate test material, the (often glassy) matrix of volcanic debris and the chemically less resistant mineral grains within the hosting rock fragments (pseudomorph formation). Smectitic material precipitating in voids is porous at the beginning, and often contains detrital grains up to a size of $40 \mu\text{m}$. Smectite formed by substitution is, on the other hand, more compact, of low porosity, and usually does not contain detrital grains. In the case of the carbonate test material substitution, the process seems to progress from the inside, from the already smectitic test-filling material towards the outer surface of the carbonate test.

The main mass of nascent glauconite (i.e. iron-rich smectite precursor) is produced by primary precipitation in

voids and substitution of the matrix of volcanic debris. Larger mineral inclusions (up to few tens of micrometres) within glauconitic grains may survive long: unaltered micas and feldspars have been observed to approx. 2.53 g/cm^3 density. A great part of detrital grain inclusions, however, slowly undergoes substitution: this process has been observed at feldspars, chain and layer silicates. The rest of the detrital grains (more resistant minerals like quartz or TiO_2 polymorphs) are supposed to get expelled from the glauconitic grains during the glauconitisation process. Detrital grains are already rare above 2.58 g/cm^3 density. It should be noted that beside chemical resistance, crystal size is of primary importance in determining whether a mineral undergoes glauconitisation or not: unaltered amphibole, muscovite and feldspar crystals are present in the sandstone from the lowest studied grain size fraction on ($63\text{--}125 \mu\text{m}$; feldspar is present even in the clay fraction). This size effect might be coupled by the fact that crystals already in the size range of the glauconite grains can hardly get into a semi-confined environment that favours glauconitisation.

The second phase of glauconitisation is a chemical evolution (for details see also Weiszburg and Tóth, 2004) affecting the void-filling and substituting smectitic materials similarly, so in the final stage there is no real difference between the two initial types. The iron-rich dioctahedral (octahedral occupancy 2.1–2.2) smectite precursor becomes denser and gradually turns into an iron-rich clear dioctahedral (octahedral occupancy around 2.0) mica. This well-known process involves the incorporation of K and Fe (both Fe^{2+} and Fe^{3+}) into the structure parallel to the release of Al.

The described processes result in homogeneous, low-porosity grains at the end of glauconitisation, sometimes even the substrate type is difficult to recognise.

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References

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