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# Glauconite Nucleation in Silica Tubular Microstructures from Low-Temperature Solution Experiments

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The origin of glauconites, has been the subject of many researches, mainly because of its importance in the interpretation of the sedimentary record. However, the precise conditions and mechanisms for crystallization are still intriguing and, in particular, data about the glauconitization kinetics are very scarce. As is known, glauconite is an authigenic dioctahedral layer-silicate, which naturally occurs, in marine sediments, mainly connected with microenvironments semi-isolated from seawater. The earlier hypothesis relates the glauconite formation to cationic diffusion processes taking place on the structure of pre-existing layer silicates. Nevertheless, further works, based on both, field evidences and improved analytical studies, clearly indicates that glauconites form in a much faster process, by direct precipitation from seawater, via nucleation and growth. In addition, the small single-crystal domains observed by HREM (Ireland et al., 1983) shown that nucleation must have been favoured relative to the growth, indicating a high supersaturation degree at the formation sites. In this work, the initial stages of the glauconite formation were, firstly, investigated by performing low-temperature syntheses experiments. Secondly, both, the structural and compositional characteristics of the obtained crystals, were compared with those of natural glauconites becoming from different source-areas and showing various crystallinity stages.

Synthetic samples were obtained from solutions by using a modified procedure of the method previously reported by (Harder, 1980). These experiments were performed at room temperature, under reducing conditions and basic pH-s (from 8 to 11). Soluble salts containing $Fe^{2+}$, $Mg^{2+}$, $K^{+}$, $Al^{3+}$ , were employed. In order to limit the extents of the $Fe^{2+}$, oxidation, solution of Na-dithionite in water were prepared at first. The addition of the remaining solutes was performed in a second step.

The following experimental set-up was applied: small amounts of ferrous crystals were seeded into the solution, so that silica microtubular structures, also known as "silica garden" were obtained (Collins et al., 1999). These structures are formed via polymerization of the amorphous silica at specific sites. Figure 1(a) and approach, in several aspects, the glauconite-forming microenvironments.

The growth of glauconitic minerals takes place in a second step by the selective nucleation at the sites provided by the porous silica matrix in the internal walls of the microtubules, Figure 1(b). No direct precipitation from the solution by three-dimensional nucleation was observed. This fact clearly indicates that the layer-silicate formation is connected with a heterogeneous nucleation process, related to the confined environments.

From the morphological point of view, the SEM micrographs of the resulting crystals, Figure 1(b) closely resemble the natural occurrence of glaucony from siliceous substrates (Odin, 1988). In addition, microanalysis performed at the level of a single crystal, by EDX, fits the glauconite stoichiometry, with low potassium content.

Further structural characterization was carried-out by HREM. Lattice fringes analysis shown the existence of single-crystal domains with sizes in the order of 15nm and d-spacing corresponding to (001) and (003) reflections of 2:1 layer silicates, in sharp contact with the amorphous silica host. Single domains, with kaolinite-like layers, were also observed.

The previous study suggests that a complex structural transformation take place just at the internal wall of the microtubules, leading the formation of layered Al-Fe-Mg-silicates. The obtained crystals have several ordering degrees as result of non-stoichiometric interface reactions, in a similar way to the "smectite" to "illite" transformation in natural systems.

Furthermore, the polymerization process heavily determines thermodynamical conditions inside the tubes. In particular a nearly neutral pH and the availability of silica monomers are expected to occur at the interface. These factors and the presence of reducing conditions seem to be determining conditions for glauconite formation.

As a consequence, in the spite of the limitations to describe natural processes by laboratory analogous, the previous results indicates that glauconitic minerals can be formed by direct crystal growth from the seawater following an heterogeneous nucleation step from porous hosts. This is consistent with the model proposed by (Odin, 1988) and suggest that a reconstructive structural process from pre-existing layer silicates is unlikely.

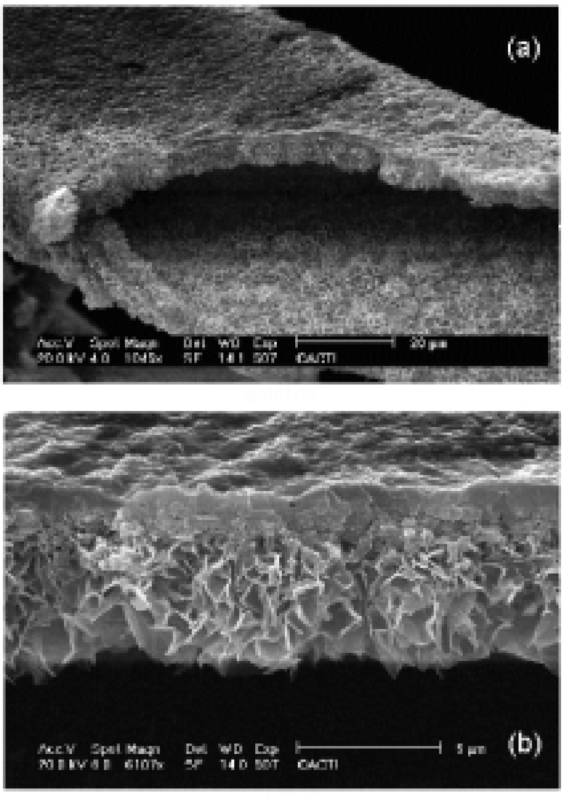

Figure 1: (a) SEM micrograph of silica tubular structures. (b)High magnification showing the glauconitic crystals grown inside.

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