



Role of Organic Acids in Bioformation of Kaolinite: Results of Laboratory Experiments

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Clay minerals and other solid silica phases have a broad distribution in the geological record and greatly affect fundamental physicochemical properties of sedimentary rocks, including porosity. An increasing number of studies suggests that microbial activity and microbially produced organic acids might play an important role in authigenic clay mineral formation, at low temperatures and under neutral pH conditions. In particular, early laboratory experiments (Linares and Huertas, 1971) reported the precipitation of kaolinite in solutions of SiO_2 and Al_2O_3 with different molar ratios $\text{SiO}_2/\text{Al}_2\text{O}_3$, together with fulvic acid (a non-characterized mixture of many different acids containing carboxyl and phenolate groups) that was extracted from peat soil. Despite many attempts, these experiments could not be reproduced until recently. Fiore et al. (2011) hypothesized that the non-sterile fulvic acid might have contained microbes that participated in the formation of kaolinite. Using solutions saturated with Si and Al and containing oxalate and/or mixed microbial culture extracted from peat-moss soil, they performed incubation experiments, which produced kaolinite exclusively in solutions containing oxalate and microbes.

We proposed to test the role of specific organic acids for kaolinite formation, conducting laboratory experiments at 25°C , with solutions of sodium silicate, aluminum chloride and various organic compounds (i.e. EDTA, citric acid, succinic acid and oxalic acid). Specific organic acids may stabilize aluminum in octahedral coordination positions, which is crucial for the initial nucleation step. In our experiments, a poorly crystalline mineral that is possibly a kaolinite precursor formed exclusively in the presence of succinic acid. In experiments with other organic compounds, no incorporation of Al was observed, and amorphous silica was the only precipitated phase. In natural environments, succinic acid is produced by a large variety of microbes as an intermediate product of the tricarboxylic acid cycle. Our results demonstrate, for the first time, that the formation of a specific clay mineral (proto-kaolinite) occurs in the presence of a specific organic compound (succinic acid). This implies that microbial species capable of excreting succinate among their EPS may promote authigenic kaolinite formation at low temperature and neutral pH. This biological degradation process might play a crucial role for the formation of authigenic kaolinite, which is a widespread clay mineral in sedimentary environments.

Fiore, S., Dumontet, S., Huertas, F.J., and Pasquale, V., 2011. Bacteria-induced crystallization of kaolinite. *Applied Clay Science*, 53:566-571.

Linares, J., and Huertas, F., 1971. Kaolinite: Synthesis at room temperature. *Science* 171: 896-897.