

### The Fe-Mg-saponite solid solution series – a hydrothermal synthesis study

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Although the boundary conditions of saponite formation are generally considered to be well known, significant gaps in knowledge still persist how the solution chemistry, temperature and reaction time influence the mineralogy, crystallinity, stability and chemical composition of ferrous saponite.

We synthesized ferrous saponite and Mg-saponite in Teflon-lined, stainless steel autoclaves within two to seven days at temperatures of 60 °C, 120 °C and 180 °C, alkaline pH, reducing conditions and initial solutions with distinct molar Si:Fe:Mg ratios of 4:0:2, 4:1:1, 4:1.5:0.5, 4:1.75:0.25, and 4:1.82:0.18. X-ray diffraction, high-resolution transmission electron microscopy as well as infrared spectroscopic and thermo-analytical analysis of the received precipitates confirmed the nature of the clay minerals to be trioctahedral ferrous saponite, with small admixtures of co-precipitated brucite, opal-CT, 2-line ferrihydrite, and nontronite as the probable alteration product of ferrous saponite. The compositions of the synthetic saponites were highly variable,  $(\text{Na}_{0,44-0,59}\text{K}_{0,00-0,05}\text{Ca}_{0,00-0,02})(\text{Fe}^{2+}_{0,37-2,41}\text{Mg}_{0,24-2,44}\text{Fe}^{3+}_{0,00-0,28})_{\Sigma=2,65-2,85}[(\text{Fe}^{3+}_{0,00-0,37}\text{Si}_{3,63-4,00})\text{O}_{10}](\text{OH})_2$ , but in accordance with naturally occurring trioctahedral Fe and Mg end members, except for the Al content. This suggests the existence of a complete solid solution series of Fe-Mg-saponites (Baldermann et al., in press).

Based on the experimental solution data and solid phase compositions a conceptual reaction sequence for the formation of ferrous saponite was developed. At  $\text{pH} \geq 10.4$ , brucite-type octahedral sheets were formed, which served as a template for subsequent condensation of dissolved Si-O tetrahedrons. Incorporation of Fe(II) in the octahedral template sheets via isomorphic substitution is suggested to stabilize the saponite structure, explaining (i) the abundance of saponite enriched in <sup>56</sup>Fe(II) at elevated Fe supply and (ii) the effect of structural Fe on controlling the net formation rates of ferrous saponite.

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