

FROM SURFACE COMPLEXATION (ADSORPTION) TO SURFACE PRECIPITATION: A CASE STUDY

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Studies using surface analytical methods have shown that the adsorption of heavy metals on clay and oxide surfaces can result in the formation of multinuclear or polynuclear surface complexes (1, 2, 3). Such precipitates could significantly affect the bioavailability, mobility, and the fate of metals in soil and water environments.

In order to study the phenomena of surface precipitation pyrophyllite was chosen as a model clay mineral. Pyrophyllite has a negligible layer charge and the adsorption of metal ions on it can therefore be ascribed to edge surface sites only.

Nickel adsorption isotherms and pH-edges were performed. In the pH region above 7 Ni adsorption was linear over an expanded concentration range and the data did not exhibit any dependence on initial salt concentrations. One can speculate that the formation of multinuclear or polynuclear surface complexes is responsible for the observed adsorption behavior.

High-resolution transmission electron microscopy (HRTEM) and extended x-ray absorption fine structure (XAFS) spectroscopy were employed to find direct evidence for the presence of multinuclear Ni surface complexes. HRTEM images from Ni treated samples (pH = 7.5) reveal that discrete crystalline particles were formed on the pyrophyllite surface. XAFS spectra suggest the formation of mononuclear complexes at low surface coverage and the continuous formation of multinuclear surface complexes in addition to mononuclear complexes with increasing Ni sorption density. We observed the presence of multinuclear surface complexes at metal surface loadings far below a theoretical monolayer coverage and in a pH range well below the pH where the formation of metal hydroxide precipitates would be expected according to the thermodynamic solubility product. This observation suggests that the total coverage of surface sites is not responsible for the formation of multinuclear surface complexes and implies that the pyrophyllite surface promotes hydrolysis and multinuclear complex formation.

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"MALLEO ET MENTE ET CATINO": THE ROLE OF SYNTHESIS IN MINERALOGY, INCLUDING CLAYS

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It was N. L. Bowen who modified the motto of the Geological Society *Malleo et Mente* (with hammer and mind) in his Presidential Address to the Society, by adding "*et catino*" (and with a crucible). He referred of course to the field of experimental petrology as a key way to understand the earth.

The author will discuss the beginnings of systematic mineral synthesis as it started in the late forties, including, as it must, in any fundamental study, the phase equilibria involved. The synthesis of clay minerals and zeolites demanded the development of a new convenient "*crucible*"—hydrothermal apparatus—because they were hydrated or hydroxylated.

As in much of the materials science field, few scientists today appreciate the importance of low temperature synthesis. It is the only way to get hydroxylated phases and really ordered oxide phases. Moreover, with the contemporary interest in layered phases, intercalated, etc., even physicists and electrical engineers can become very interested in clays.

Besides discussing the "*pioneering*" years, the author will illustrate the power of new techniques such as acoustic wave stimulation, hydrothermal with an electrical field, microwave hydrothermal, etc., as new ways to affect the equilibrium on kinetics of such silicate reactions.