

The influence of the cation vacancies on the minerals formation processes

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There were studied the pyrrhotine samples by using X- ray after being synthesized and kept in the atmosphere at a temperature of 20°C for 29 years (Table 1).

The composition	Percentage		
	Vacancies in the cell 1C	Goethite	
		In X-ray grams	As calculated
Fe _{0.870} S	26	0.8	0.55
Fe _{0.865} S	27	1.25	1.13
Fe _{0.860} S	28	1.88	1.68
Fe _{0.855} S	29	1.91	2.26
Fe _{0.850} S	30	3.15	2.84
Fe _{0.845} S	31	3.38	3.40
Fe _{0.840} S	32	4.93	4.00

Table 1: The parameters of some studied samples.

In the vacuum the pyrrhotines containing an excess of sulphur, turned into a stable state. As a result, there was formed the pyrrhotine having the composition Fe₇S₈ and the pyrite. But in the atmosphere there was formed Fe₇S₈ and goethite.

As it is seen from the table, the raised content of sulphur relative to the stable Fe₇S₈, leads to the increase in the cation vacancies concentration. Part of the ferric ions close to these vacancies, will be in non-equilibrium state. The substitution of the surface vacancies by the water molecules, leads to the goethite formation. The calculated contents of the goethite in terms of ferric ions in non-equilibrium positions as well as experimentally observed goethite content on the X-ray photograph are in good correspondence.

Thus, the non-equilibrium ferric ions and the adsorbed water form the goethite whose percentage corresponds to the vacancies contents.

Nanosized aluminosilicates (allophane): Formation mechanisms and sorption capacities

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Introduction

Imogolite and allophane are two naturally occurring nanostructured aluminosilicates. There is a growing interest for these materials since they are likely to play a significant role in the carbon storage in soils as well as in the mobility of trace metals in the environment. Imogolite and allophane, because of their nanostructured nature, are also excellent candidates for industrial applications (adsorbents for e.g. remediation processes, catalysis...) since they can be easily obtained by coprecipitation of aqueous aluminum and silicon. The structure of the tubular imogolite is known whereas allophane is less well characterized. However, nucleation and growth mechanisms of these phases are only partially elucidated at best. In the present work, we focused on allophane because of its higher sorption capacities as well as the higher yield of the synthesis compared to imogolite.

Results

We examined a series of systems at various hydrolysis ratios R (= [OH]/[Al]) and thus pH values, before and after the heating step in the synthesis protocol. The recovered solids were analyzed by a combination of techniques: X-ray diffraction, electron microscopy, FT InfraRed spectroscopy and solid-state NMR, viz. "standard" one dimensional MAS experiments for Al-27 and Si-29, as well as two dimensional MQMAS Al-27 spectra. With increasing R, the expected Q⁰-3Al signature became predominant within the end-product. In the allophane precursors (i.e. before heating) Al is present only as octahedral species (MQMAS NMR shows unreacted monomers and edge sharing Al octahedra). Upon heating, a sizable amount of tetrahedral Al is formed along with low quantities of Al in a presumably highly distorted octahedral or even Al(V) coordination. Consequences in terms of metal sorption (Ni, Cu...) have been investigated.