NANO CONFINED WATER IN CLAY MINERALS

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Kaolin- and smectite-group minerals are among the most abundant and industrially important minerals on Earth. Halloysite, a naturally occurring hydrated polymorph of kaolinite, is emerging as an attractive material for use in a variety of industrial applications, which take advantage of the distinct nano-tubular morphology of this mineral as a reinforcing material in polymer nanocomposites, as well as a vehicle for the controlled release of drugs or enzyme immobilization. Smectites are ubiquitous in nature possessing an intrinsically expansive and reactive surface.

From the perspective of surface chemistry, a unique attribute of hydrated halloysite is the presence of a confined monolayer of water between the siloxane and hydroxylated surfaces. Additionally, halloysite is typically characterized by a tubular or spheroidal meso-structure, leading to further organization of water molecules at the particle scale. Finally, the presence of some "free" water is apparently necessary to maintain the system fully hydrated. Similarly, water sorbed to smectites is also nanoconfined but distinct from that of halloysite because of the influence of interlayer cations.

While water plays a critical role in controlling the structure of halloysite and smectite, surprisingly, relatively little is known about the chemical and physical properties of water associated with these two types of clay minerals.

The study presents an integrated experimental study of water on samples of halloysite and smectite. For halloysite, samples were kept fully hydrated since collection, and samples prepared in the laboratory at different water contents. A novel application of low temperature differential scanning calorimetry is presented to identify and probe the nature of the three different populations of water molecules. In the fully hydrated halloysite, the calorimetry results show anomalies in the freezing and melting peaks with distinct peaks reflecting freezing of the bulk water and the capillary water confined inside the nano-tubular pores; the latter freezing process is observed to occur at temperatures as low as -37°C; upon re-heating two melting events are also observed, albeit in a much narrower temperature range. Air drying leads to the deintercalation of water but similar calorimetric curves are observed after rehydration of the clay. In all samples, a significant amount of water – as large as 16% w/w - is found not to freeze.

The calorimetric data are supported by: low temperature (~ 20 K) FTIR spectroscopy which shows clear changes that occur upon freezing in the vibrational bands of the water and of the clay itself; ATR-FTIR spectroscopy to study the nature of water in halloysite and smectite; and XRD for monitoring the loss of the interlayer water.

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