Cryosalt Formation in Clay Aggregates

MERVE YEŞILBAŞ[1,*] AND JEAN-FRANÇOIS BOILY[1]

[1]Department of Chemistry, Umeå University, SE-901 87, Umeå, Sweden (*merve.yesilbas@umu.se)

Hydrohalite ($NaCl \cdot 2H_2O$) is a cryogenic salt that precipitates out of salt-bearing waters upon freezing. Its natural occurrences include sediments of saline lakes, polar seawaters, the Earth's atmosphere and potentially planet Mars. The geological record even abounds in cases where cryogenic salts have clearly formed, only to have effloresced to their dehydrated counterparts over time. In some of these settings, (nano)confinement by mineral particles in porous media or particle aggregates could stabilize cryogenic salts.

In this study clay minerals were investigated for their ability at preserving hydrohalite under cryogenic conditions. Clays are of especial interest because they are the second major components of tropospheric mineral aerosols, and because they can stabilize thin water and ice films [1,2].

Fourier Transform Infrared (FTIR) Spectroscopy measurements of Na- and Ca-montmorillonites reacted with aqueous solutions of 0-5 M NaCl at 25 °C were used to identify conditions leading to (meta)stable forms of hydrohalite upon freezing to -10 °C. The signature FTIR spectral profile of hydrohalite (stretching ν_{OH} ~ 3245-3265, 3408, 3462, 3555 cm^{-1}, and bending δ_{OH}~ 1614 and 1641 cm^{-1}) was used as a sensitive indicator to its formation, while the silicate component of the clays (stretching $\nu_{Si\text{-}O}$ ~ 1000 cm^{-1}) was used as a proxy for delamination.

Measurements revealed that Ca-montmorillonite does not stabilize hydrohalite because it cannot delaminate. On the other hand, rapid (~ 20 min) freezing of delaminated Na-montmorillonite particle aggregates exposed to solutions exceeding 0.1 M NaCl stabilize hydrohalite for at least 30-100 min. Although high salt concentrations promote restacking of montmorillonite layers the relative speed of freezing effectively outcompetes this process. From these results we expect that the stability of (ephemeral) forms of clay-hosted hydrohalite could be altered under dynamic conditions involving strong influx of salts (*e.g.* as atmospheric aerosols) *vs.* freshwater, or strong temperature gradients, for example as experienced by atmospheric mineral particles.

[1] Yeşilbaş, M. and Boily, J.-F. (2016), *Scientific Reports*. **6**, 32136.
[2] Yeşilbaş, M. and Boily, J.-F. (2016), *J. Phys. Chem. Lett*. **7**, 2849-2855.