MIXING AND RE-SOLUTION PROCESSES AFFECTING EVAPORITE MINERAL DISTRIBUTIONS ON EARTH AND MARS

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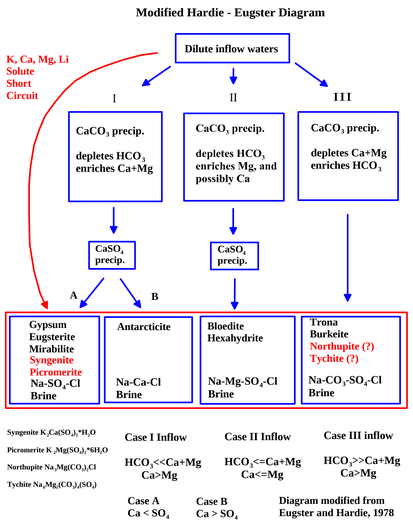
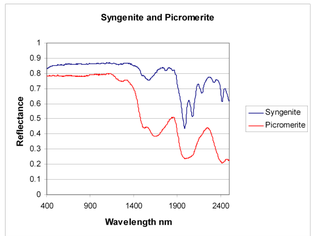
Introduction: Mineral assemblages produced by evaporation or freezing can only be predicted by chemical modeling if appropriate processes are taken into account. This paper describes several processes that can lead to more complex assemblages than those expected from simple fractional crystallization.

Dilute Inflow Additions to Brine

The well-known Hardie-Eugster diagram, shown below, illustrates how the development of distinct terrestrial brine chemical types is determined both by initial inflow water composition and the subsequent precipitation and fractionation of key mineral phases (chemical divides). On Earth, the final, highly "evolved", brine compositions always include a NaCl component; other chemical components differ between brine types and lead to a variety of characteristic mineral phases in efflorescent crusts developed from each brine type.





The H-E diagram is a powerful conceptual tool. However, it does not account for all of the mineralogical details seen in terrestrial evaporite deposits. One important process is the addition of dilute inflow waters to more concentrated brines, as often occurs from springs along playa margins or from ephemeral streamflow. In these cases, solutes that ordinarily are removed in the course of brine "evolution" can be added back to the brine--short-circuiting the normal H-E brine pathways. This can lead to the formation of peculiar, and often spectrally interesting minerals, such as syngenite (added Ca and K) and picromerite (added K and Mg). Many permutations of this process and its affects are likely to exist.

On Mars the solute composition of dilute waters is likely to be quite different from that of Earth. Short-circuiting of Martian brine pathways (such as those proposed by Tosca, 2005) would likely involve late additions of Fe and might lead to such minerals as Fe-chlorides and Fe-sulfates in evaporite crusts. Different Fe oxidation states may also come into play depending on the origins of dilute inflow waters.

Hydrothermal or Other Unusual Chemical Additions to Brine

Unusual chemical components, such as boron derived from deep-circulating hydrothermal waters, can impose additional chemical divides on the development of brines. Although relatively rare, such chemical processes can produce large mineral deposits, as seen in the case of borate mineral deposits on Earth.

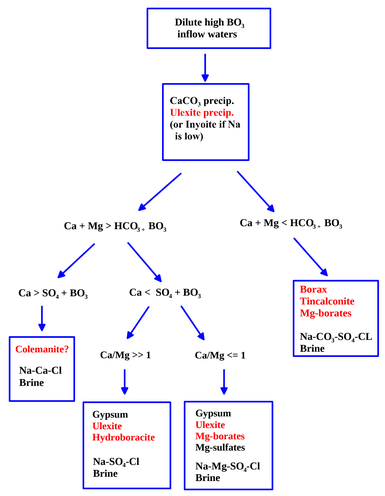
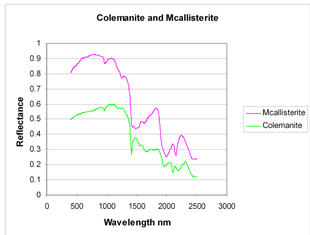


Diagram from Crowley, 1996



Some key borate minerals

- Colemanite $Ca_2B_6O_{11}*5H_2O$
- Ulexite $NaCaB_5O_6(OH)_6*5H_2O$
- Borax $Na_2B_4O_5(OH)_4*8H_2O$
- Tincalconite $Na_2B_4O_5(OH)_4*3H_2O$
- Hydroboracite $CaMgB_6O_8(OH)_6*3H_2O$
- Pinnoite $MgB_2O_4*3H_2O$
- Rivadavite $Na_4MgB_{24}O_{40}*22H_2O$
- Mcallisterite $Mg_2B_{12}O_{14}(OH)_{12}*9H_2O$

Are there Martian analogs to this process--perhaps involving Fe-borates? Such minerals are extremely rare on Earth, and their spectral properties are essentially unknown.

Conclusions: Mixing and re-solution processes can have important effects on terrestrial evaporite mineralogy. New spectral information from CRISM and follow-on missions may afford insights into the operation of such processes on Mars.

References:

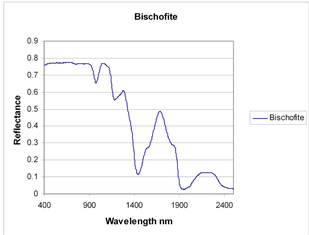
Bibring, J. P. et al., 2005, Science, 307, p. 1576-1581.
Crowley, J. K., 1996, Economic Geology, 91, p. 622-635.
Eugster, H. P. and Hardie, L. A., 1978, in Lakes--Chem., Geol., Phys., Springer-Verlag, p. 238-293.
Tosca, N. J. and McLennan, S. M., 2006, EPSL, 241, p. 21-31.

Efflorescent Crust Recycling/Zone Refining

$MgCl_2 \geq MgSO_4 \geq NaCl \geq Na_2SO_4 >$ Borates

$CaCl_2$ NaF Na_2CO_3

KCl K_2SO_4



Dilute inflow in the form of precipitation or other intermittent water sources can partially dissolve pre-existing evaporite deposits and crusts. On Earth the presence of abundant highly soluble halite in many evaporites, quickly increases the inflow solute concentrations, lowering the activity of water. This tends to stabilize certain chemical components in solid phases, notably, Na-carbonates, Na-sulfates, and various borates, while leaching other components into the brine. In the recycling order shown above, components to the right of NaCl are mainly preserved in solid phases, whereas those to the left are leached into the 'bitterns". Nearly pure crusts of Na-(Ca)-borates and/or trona are produced by this process in some terrestrial playa settings. The bitterns are composed of components that are very soluble and in some cases extremely hygroscopic.

Chemical modeling based on Mars-like inflow water chemistry suggests some ways in which this process might operate on Martian evaporites:

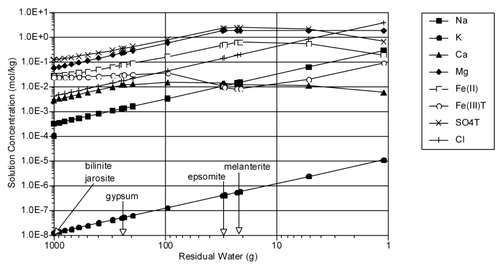
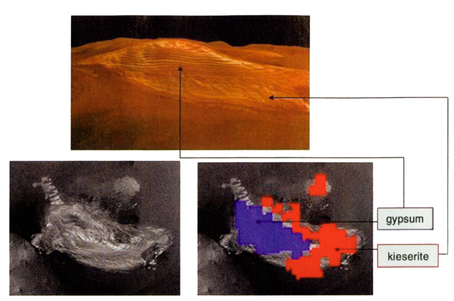


Figure 1 . The change in ion concentrations as a hypothetical martian brine evaporates at 0°C with pH = 2.0. Arrows show where specific minerals start to precipitate. Hematite, goethite, and lepidocrocite were excluded from the mineral database in this simulation.



After Bibring et al., 2005

The abundance of $MgSO_4$ component coupled with colder temperatures suggests that all components to the right of $MgSO_4$ would be stable and this is consistent with modeling (Fig. 1). The final bitterns contain abundant $MgCl_2$ component, which might form minerals such as bischofite. The bitterns have other interesting properties--contact between the bitterns and hydrous minerals can cause dehydration reactions, for example altering epsomite to kieserite.