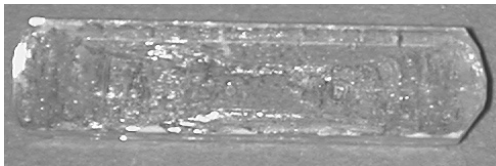


SALT-HYDRATE STABILITIES AND MARS SAMPLE RETURN MISSIONS

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epsomite



*low-pH₂O desiccation
(amorphous)*



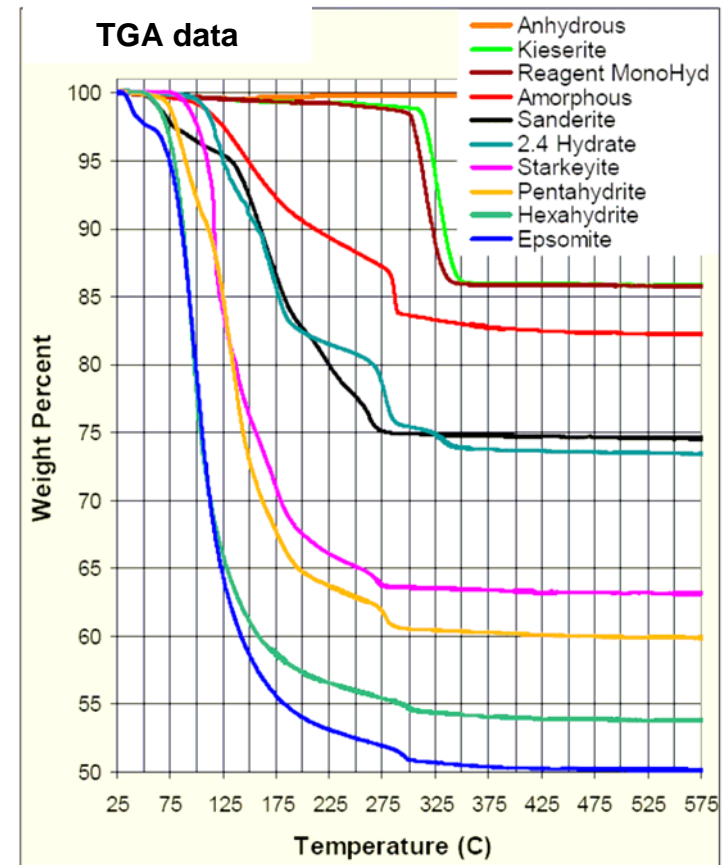
rehydrated epsomite

Case histories

- **Meteorites:** Epsomite in primitive CI1 chondrites has been cited as evidence of late-stage oxidation of the CI1 parent body but there is strong evidence that epsomite has formed in these meteorites after they were placed in humid terrestrial museums.
- **Lunar Samples:** Goethite (FeOOH) “rust” observed in Apollo 16 rocks stimulated great interest but was eventually found to have formed by hydration-oxidation of lawrencite (FeCl_2).

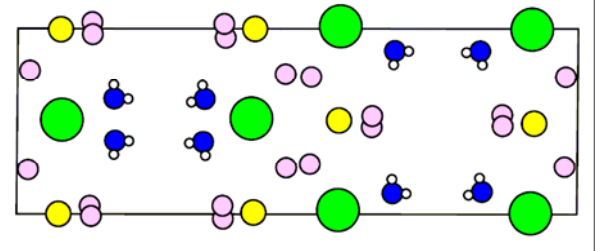
Mg-sulfates – Many variants, especially in cold, water-poor environments

<i>Formula</i>	<i>Mineral name</i>
MgSO_4 anhydrous	none (reagent)
$\text{MgSO}_4 \cdot 1\text{H}_2\text{O}$	kieserite
$\text{MgSO}_4 \cdot 1\text{H}_2\text{O}$ type 2	none (reagent)
$\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$	sanderite
$\text{MgSO}_4 \cdot 2.4\text{H}_2\text{O}$	none
$\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$	starkeyite
$\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$	pentahydrate
$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	hexahydrate
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	epsomite
$\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$	meridianiite
$\text{MgSO}_4 \cdot n\text{H}_2\text{O}$	amorphous (<i>n</i> variable)

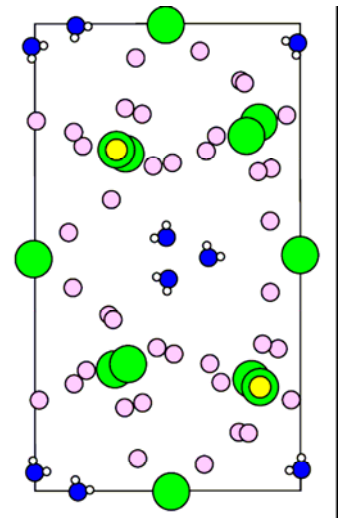


Ca sulfate forms:

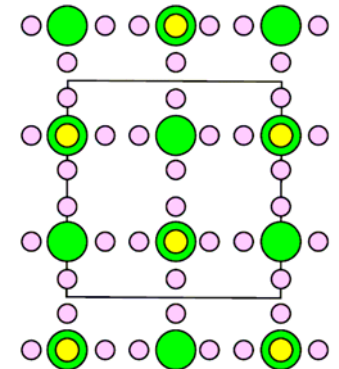
Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$



Bassanite $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$



Anhydrite CaSO_4

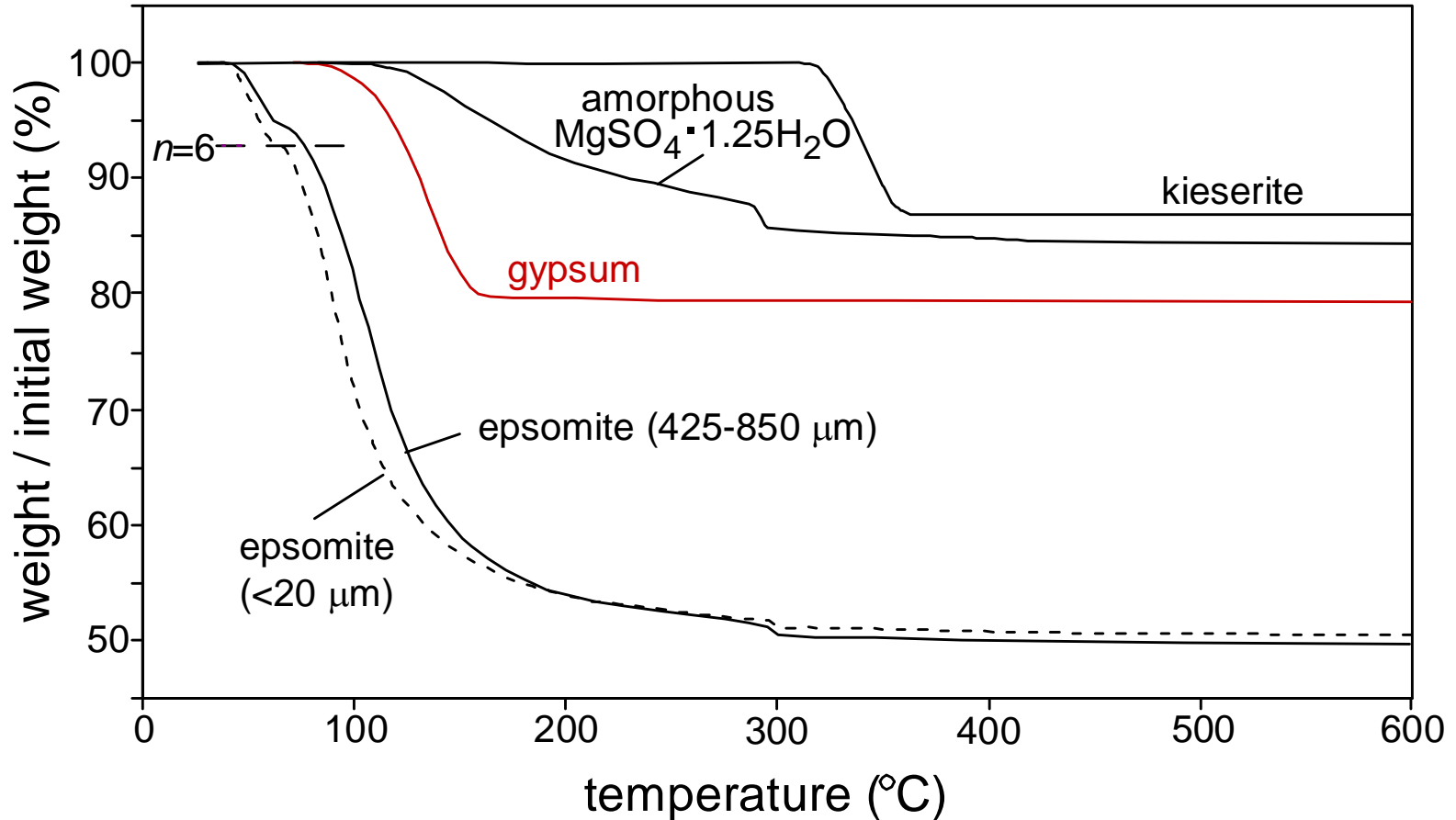


Legend for the crystal structure diagrams:

- Green circle: Ca
- Yellow circle: S
- Pink circle: O
- Blue circle with two white dots: H₂O

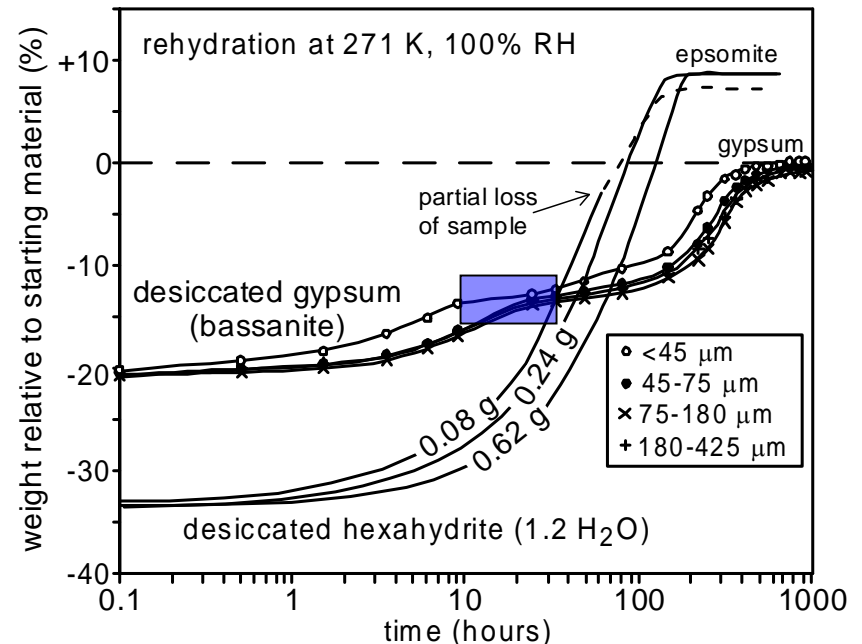
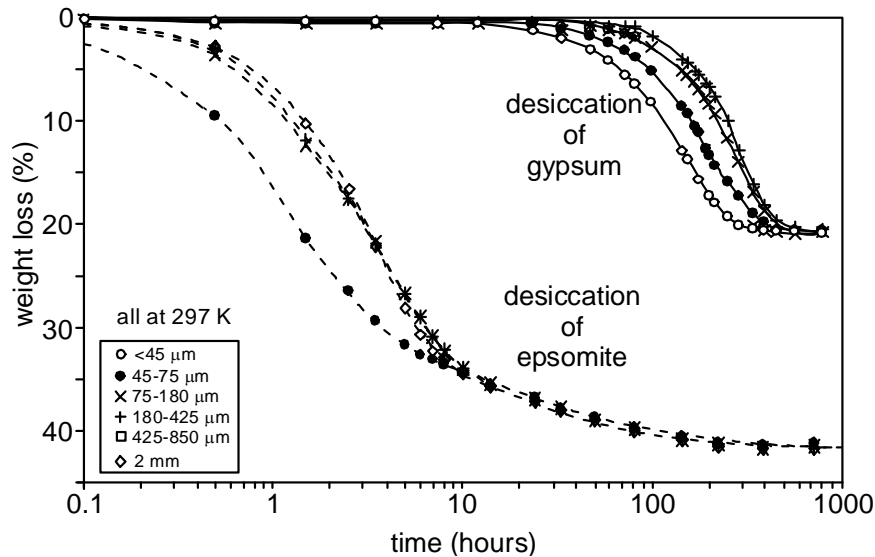
Crystallographic axes:

Gypsum is *relatively* resistant to dehydration



Ca-sulfates lag behind Mg-sulfates in most transformations

Dehydration, and rehydration from vapor, in the gypsum-bassanite-anhydrite system are relatively sluggish at low temperatures. The Mg-sulfates are *generally* more susceptible to water loss or gain.

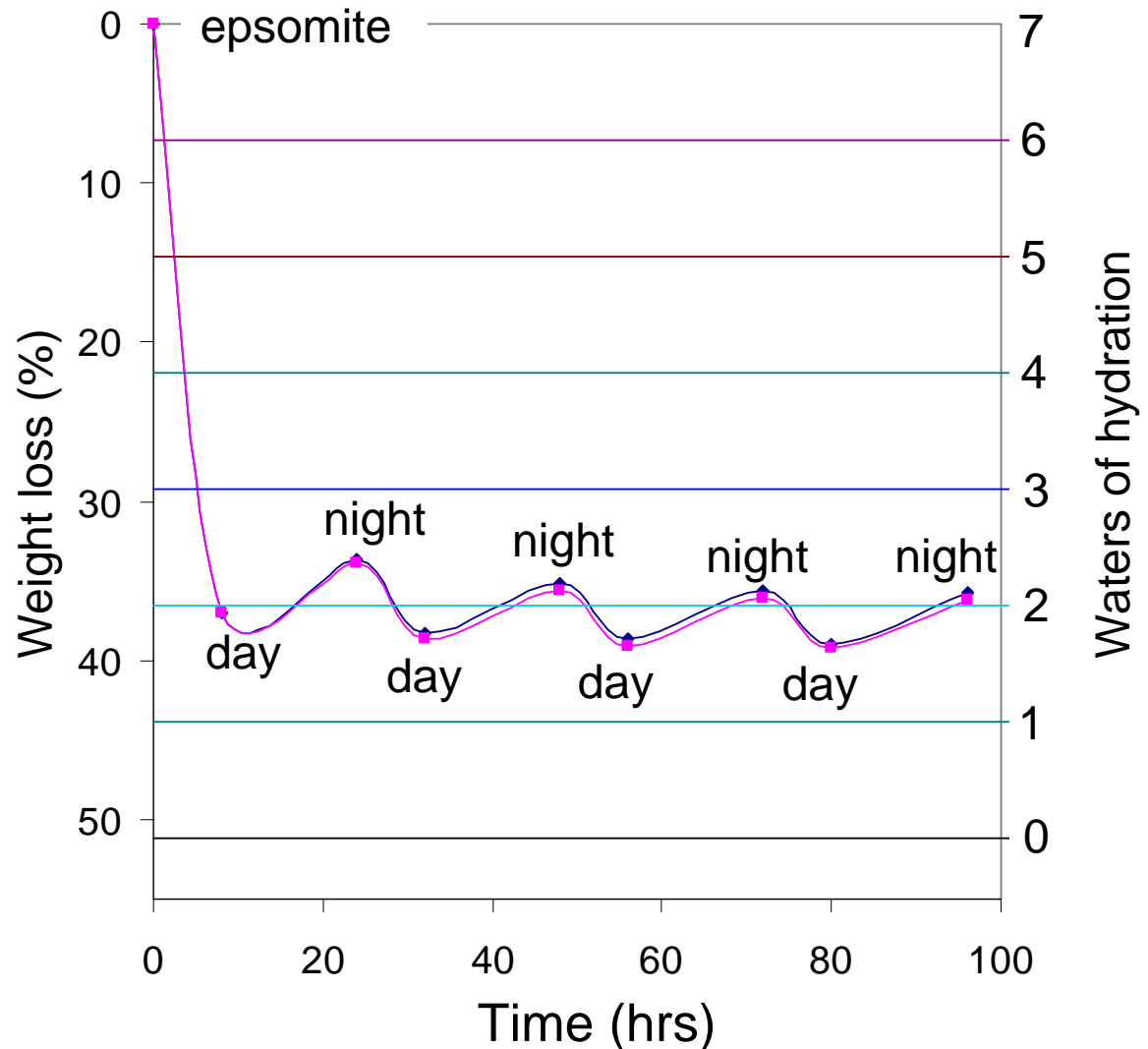


Bassanite with $n \sim 0.8$

An example of sampling on Mars - Excavation of epsomite

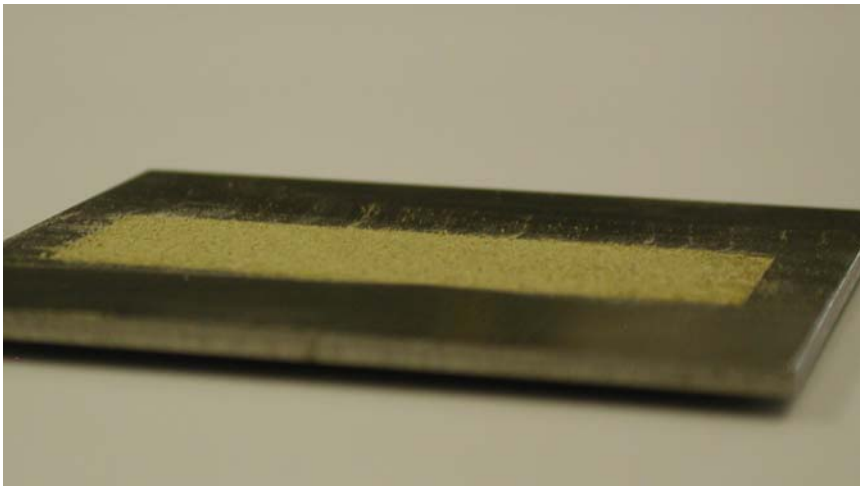
Day: 8 hrs at
297 K, $p_{\text{H}_2\text{O}}$
 ~ 0.8 Pa

Night: 16 hrs
at 243 K, $p_{\text{H}_2\text{O}}$
 ~ 38 Pa (over
water ice; at
210 K would be
 ~ 1 Pa)

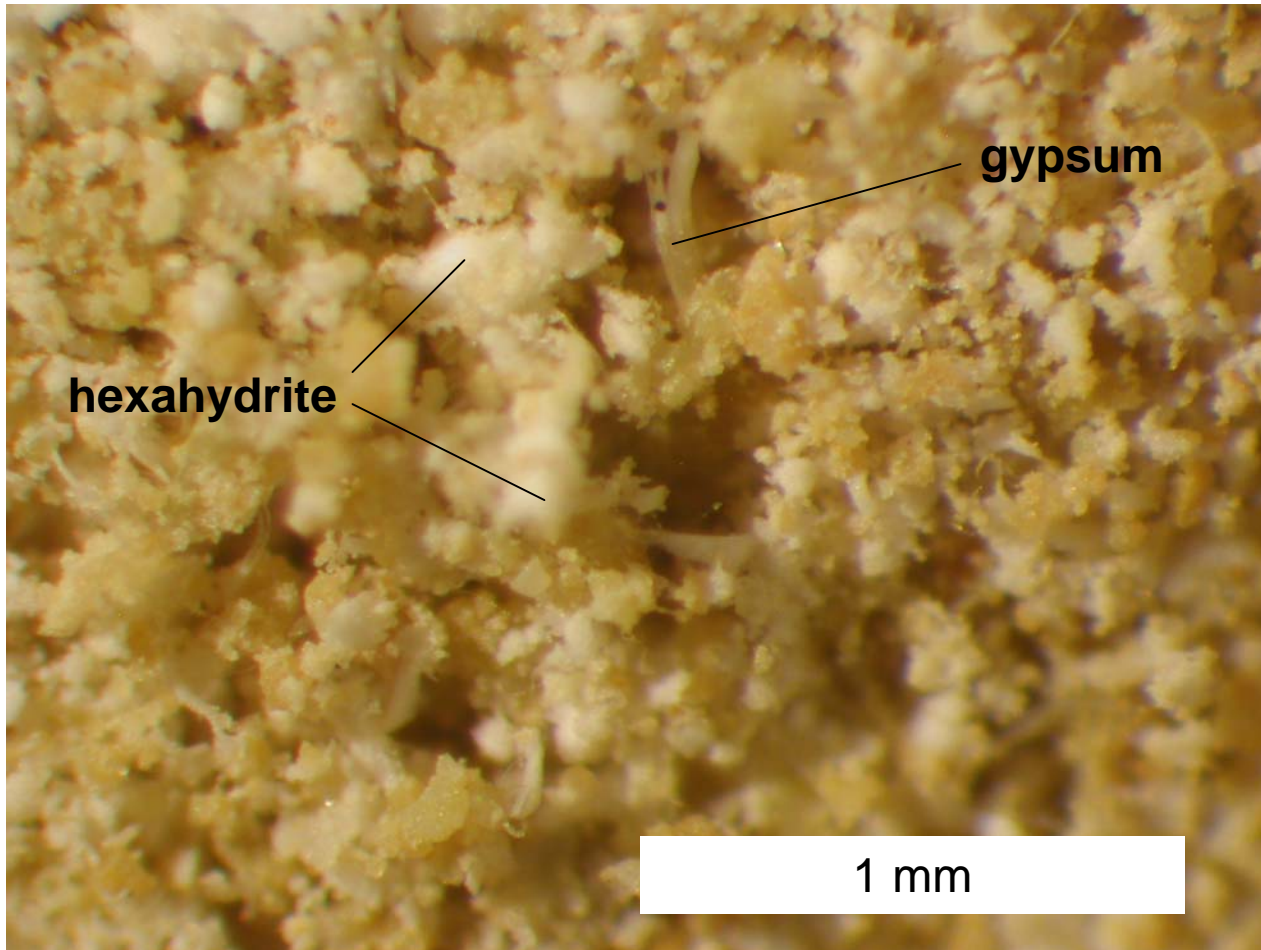


An example of mixed reactive phases – Smectite plus an Mg-sulfate salt precipitate . . .

Mixture of nontronite and MgSO_4 brine, evacuated to 1 torr in 5 cm x 5 cm sample mount and allowed to rehydrate at 31% RH, 298 K



. . . producing a new phase.



Ferric sulfates

Some are aggressive in acid attack. Those with independent H₂O molecules in their structure do not dehydrate and rehydrate reversibly.

Copiapite [Fe₅(SO₄)₆(OH)₂•20H₂O] – experience with CheMin4 at Rio Tinto;
may subject Mylar to acid attack

Fibroferrite [Fe(SO₄)(OH)•5H₂O] – experience suggests that fibroferrite
may become gelatinous on desiccation cycling

Coquimbite [Fe₂(SO₄)₃•9H₂O] – dehydrates reversibly at 25°C in vacuum;
irreversible dehydration to amorphous product at higher temperatures

Kornelite [Fe₂(SO₄)₃•7H₂O] – dehydrates reversibly at 25°C in vacuum;
irreversible dehydration to amorphous product at higher temperatures

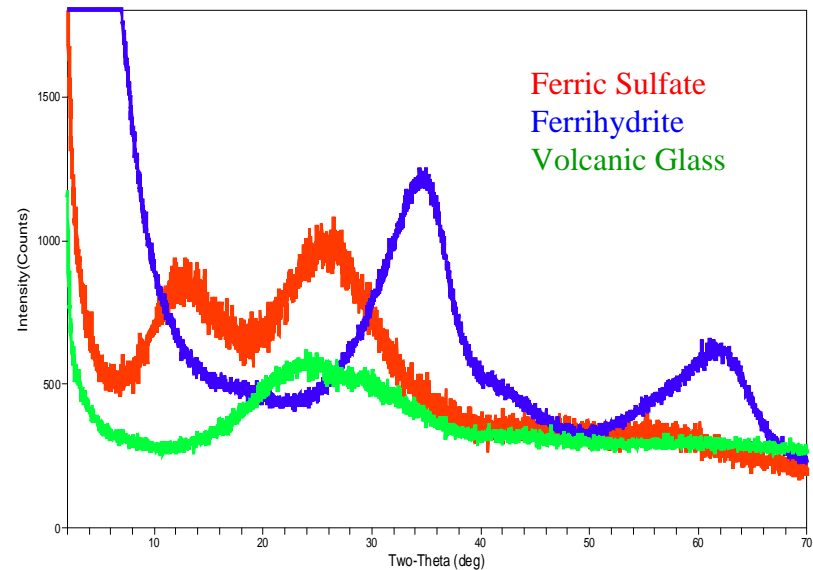
Botryogen [MgFe(SO₄)₂(OH)•7H₂O] – degrades irreversibly above 25°C
(accelerated at 50-75°C); forms a ceramic-like crust on heating

Others are more durable.

Jarosite [KFe₃(SO₄)₂(OH)₆] – stable to 300°C and 20 mtorr, powder is
unchanged

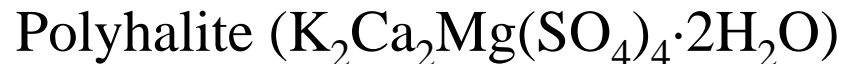
Fe-sulfates: A worst case?

- Ferric sulfates are highly soluble and readily deliquesce.
- Under cold conditions at high RH, where Mg- and Ca-sulfates with excess H₂O would form crystalline hydrates, ferric sulfates do not solidify but form a viscous, amorphous syrup with a double-humped radial distribution function in XRD.
- In a complex mixture with, e.g., Fe oxyhydroxide and reactive glass (impact or volcanic), what product would be received on Earth?



Mixed-cation sulfates may be present – and durable *by themselves*

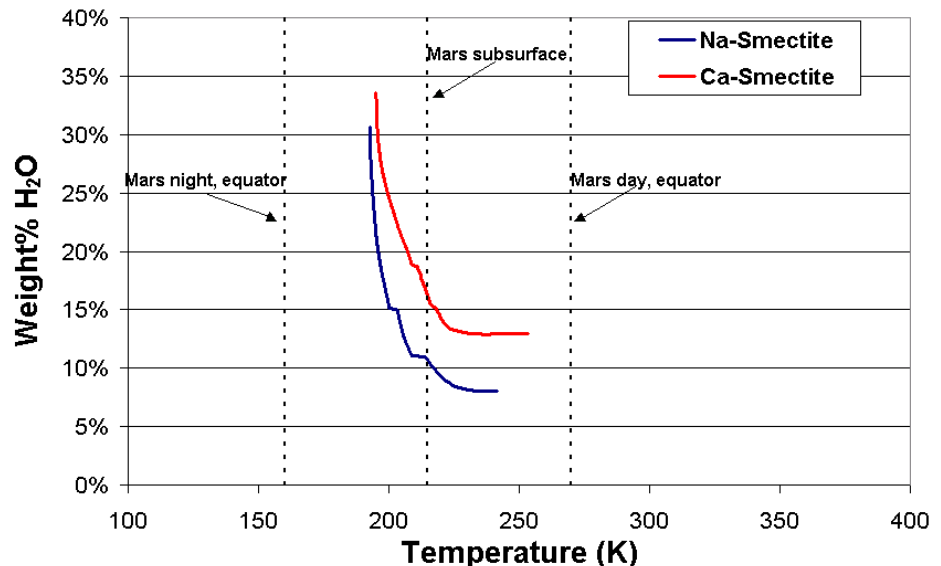
Experiments with the mixed-cation sulfates such as:



show that all are likely stable at Mars surface conditions.

But: Would they survive if collected along with H_2O ice or a hydrated smectite?

Water Content of Clay in the Martian Environment



Other salt hydrates

APXS data leave little doubt that halides are present.
Chloride hydrates could include:

Antarcticite ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$)

Bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)

Tachyhydrite ($\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$)

All have limited stability

Implications for Mars sample return

- *Start easy, with equatorial sample return*
 - Absence of persistent ground ice is likely to preclude presence of highly hydrated (and highly unstable) salts.
- *Analyze in situ*
 - Baseline mineralogy, composition, and fabric against which later observations on Earth can be compared. This is recognized by MEPAG in recommendations allowing for a sample analysis system of ~50 kg on the lander or rover.
- *Plan ahead for on-planet sample holding*
 - Heat of an equatorial summer plus heat produced by the RTG on the 2009 MSL rover can raise the sample cache to 50 °C.

Implications for Mars sample return (cont.)

- *Store separately*

- Separate containerization of each collected sample can minimize possible reactions (*e.g.*, loss of interlayer H₂O from smectite leading to chloride salt deliquescence).

- *Keep cool*

- Designs to keep temperature as low as possible should be considered. **Alternatives to sterilization by heating should also be considered.**

Implications for Mars sample return (concluded)

- *Process in an appropriate environment*
 - Examine a chilled split for physical alteration (deliquescence, solution, etc.) and get a baseline as-received mineral analysis before other splits are processed and allocated.
- *Analyze with vigilance*
 - Analytical results that produce unexpected evidence of H₂O exchange between minerals, suspicious mineral morphologies, and dissolution/precipitation features should be scrutinized to determine whether such features may be artifacts.