Mars Sample Return: Which Samples and Why

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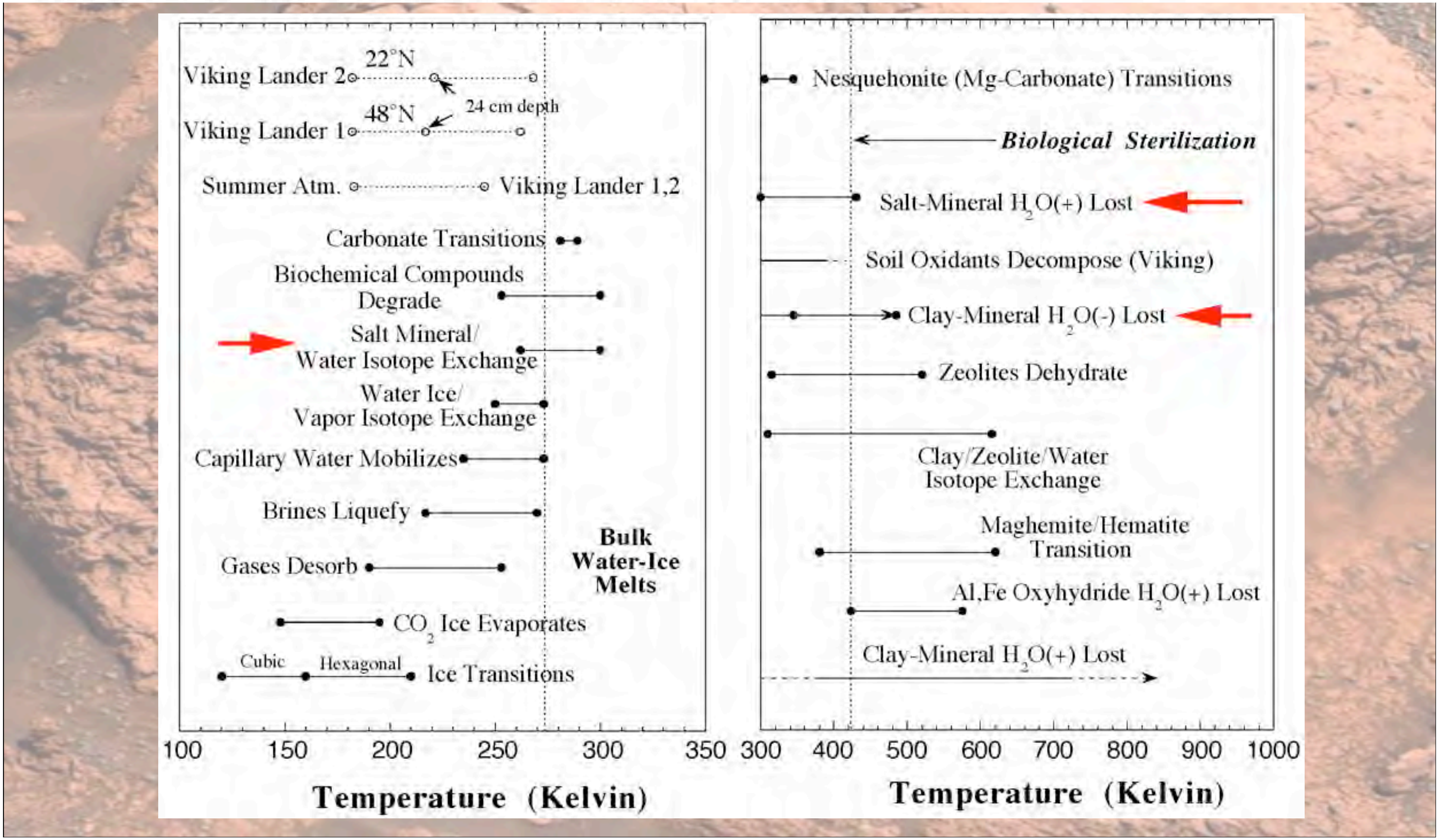
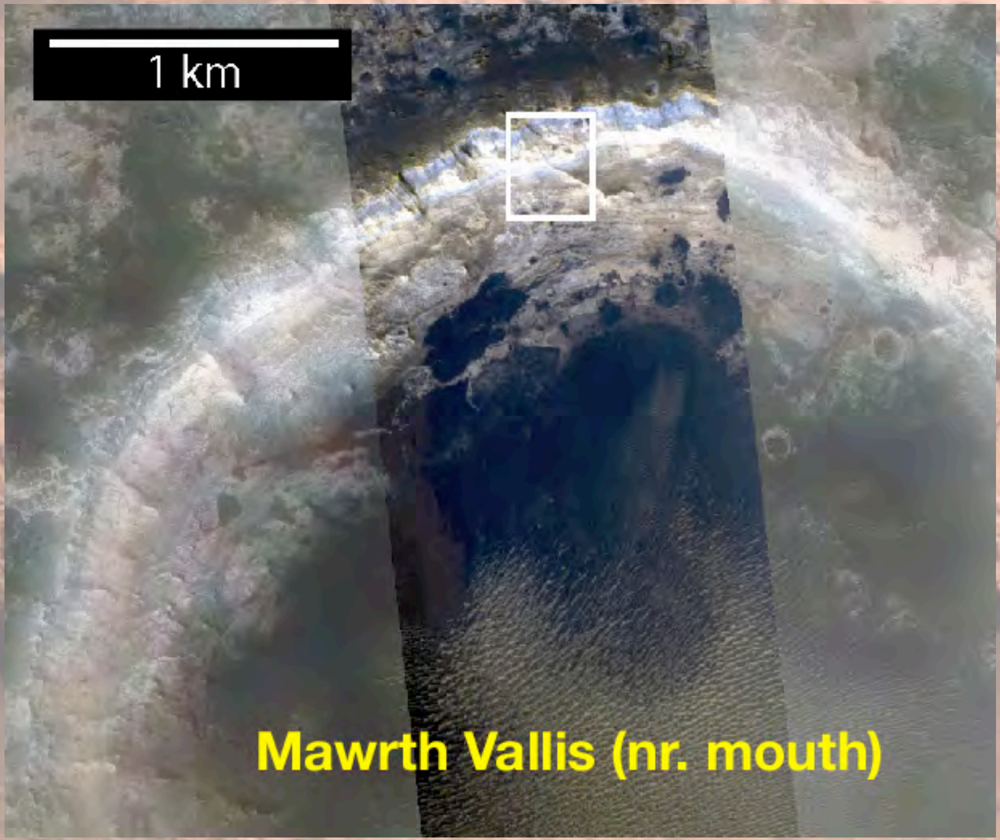
Issues involved in a Martian sample return: Integrity preservation and the Curation and Analysis Planning Team for Extraterrestrial Materials (CAPTEM) position



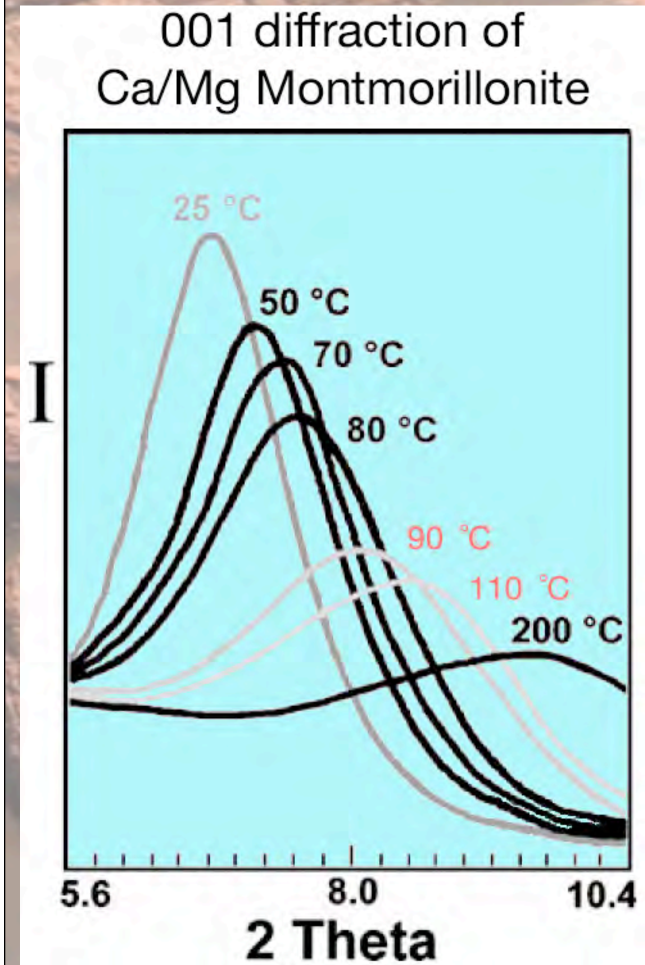
Clay Minerals

CRISM and HiRISE have shown the presence of phyllosilicates on the surface of Mars.



From Loizeau et al. (2008) LPSC 39, Abstract # 1586
(mosaic of HiRISE image PSP_004052_2045)

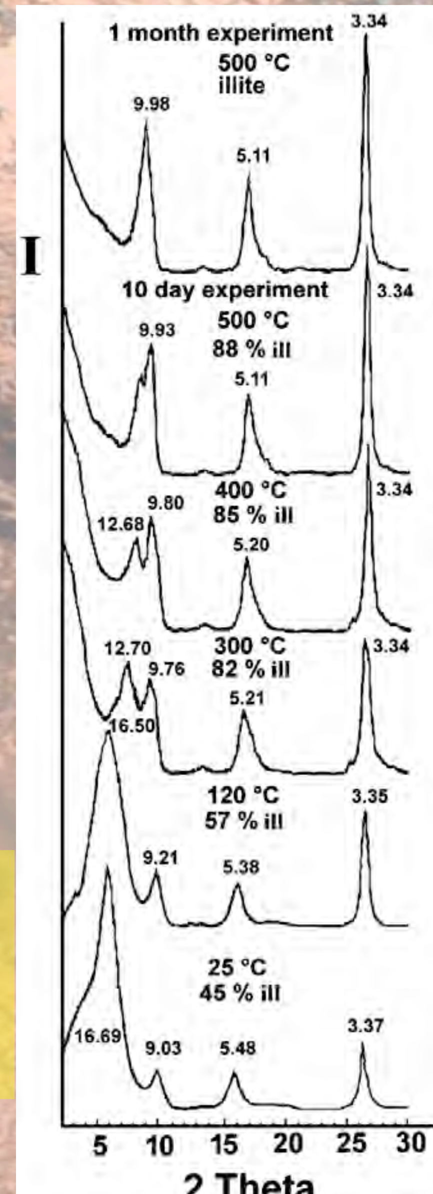
Heating of Clay Minerals



Temperature experiments using Montmorillonite. From Kolarikova et al. (2005) *App*. *Clay Sci*. 29.

Changes in profile intensity with increasing temperature.

Degree of illitization is directly proportional to increasing temperature.



Heating of Clay Minerals

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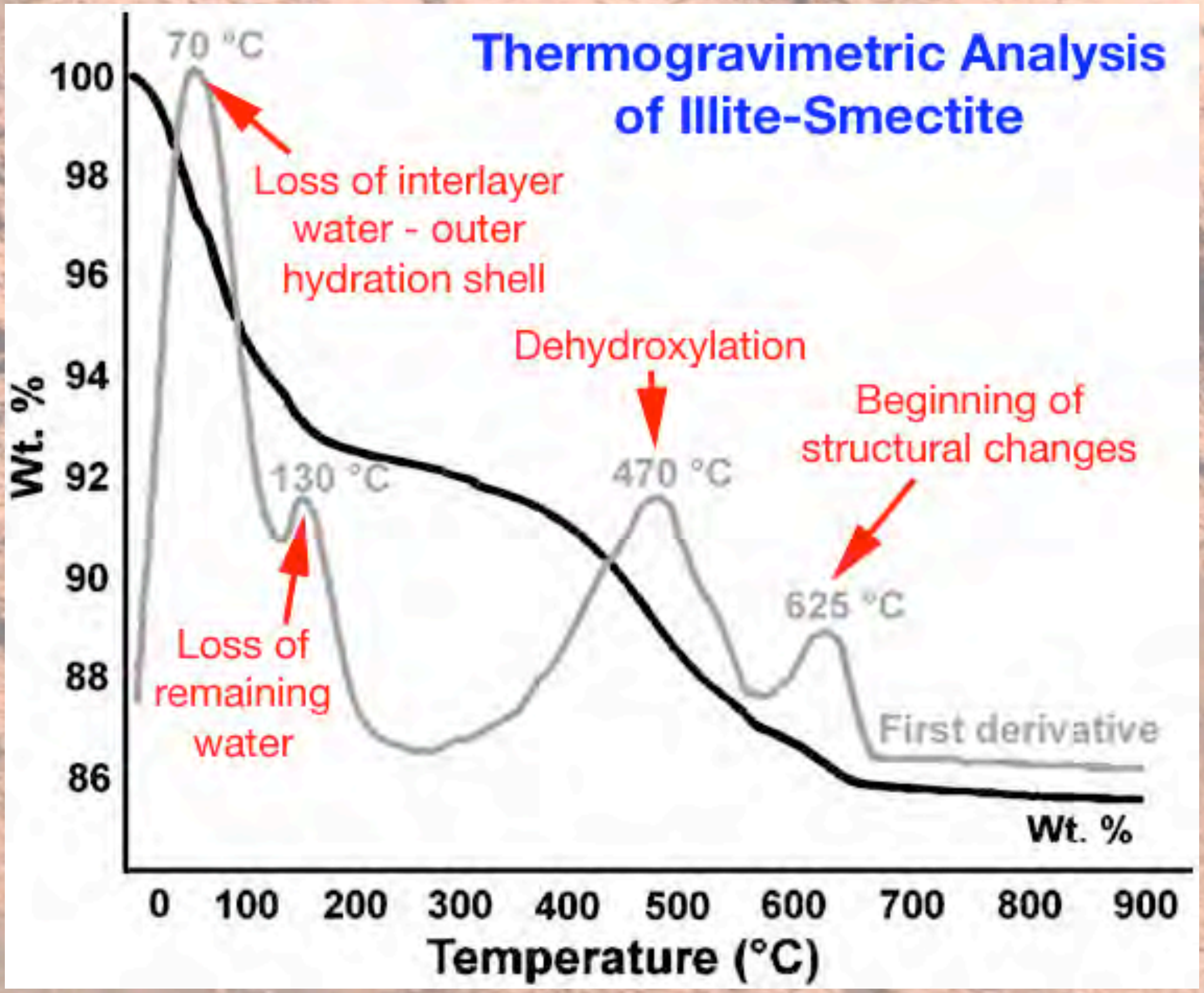
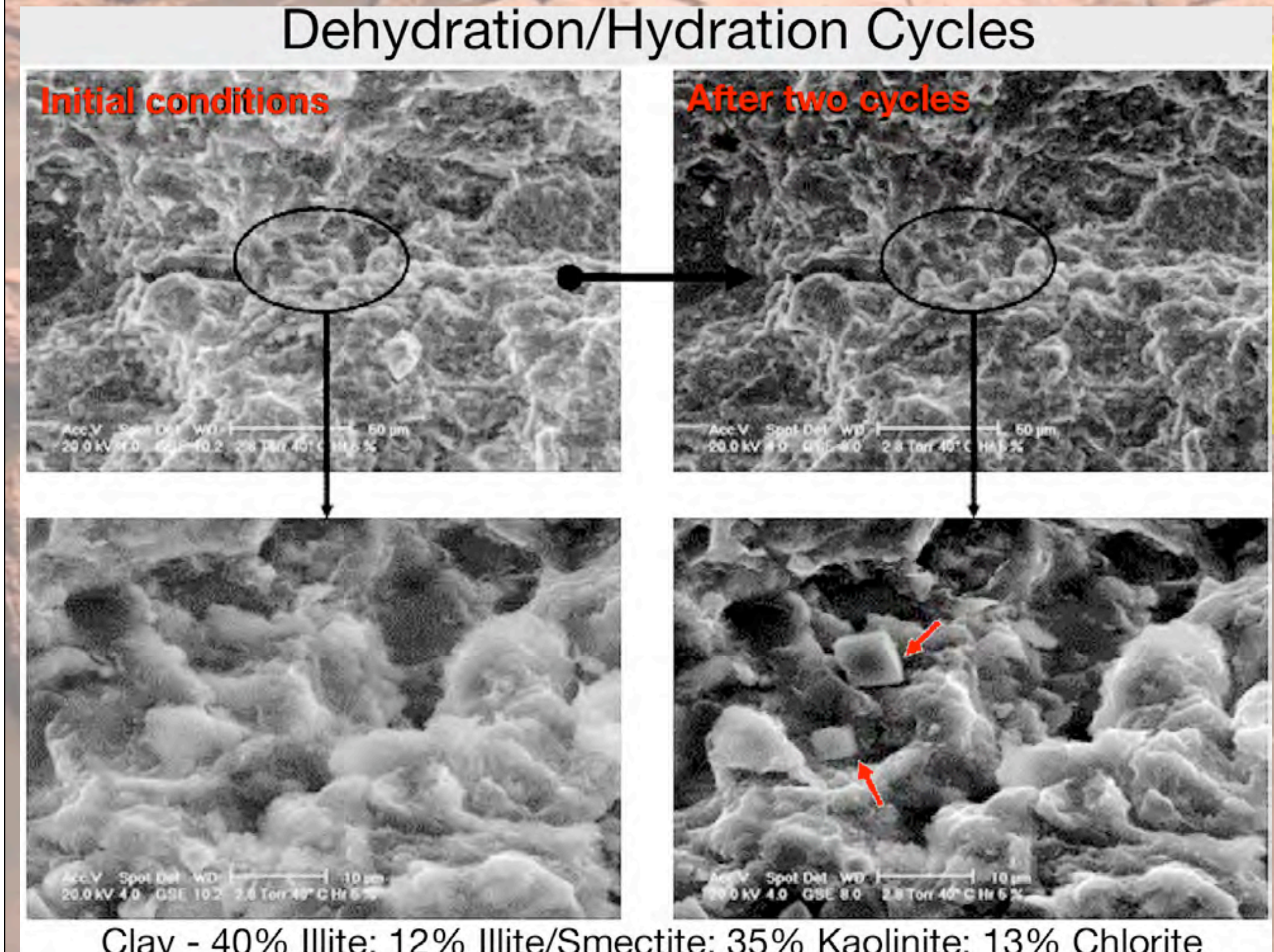


Clay Minerals

Hydration/Dehydration Cycling



An aggregation/ desegregation of small particles is seen after repeated wetting and drying.

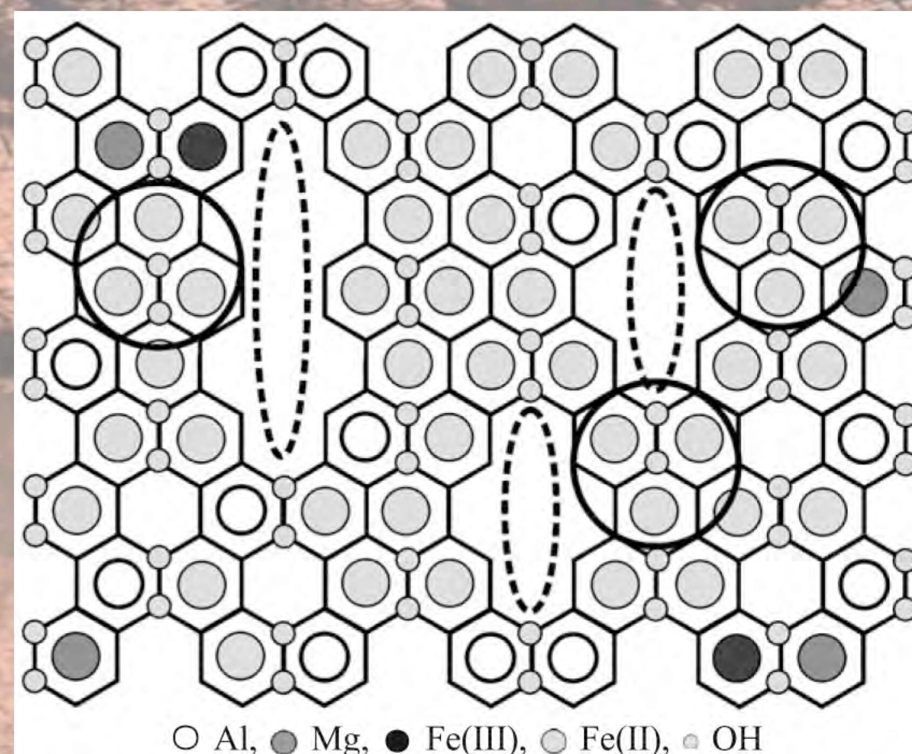
Montes et al. (2004) App. Clay Sci. 25.

Clay Minerals

Reduction of Fe^{3+}

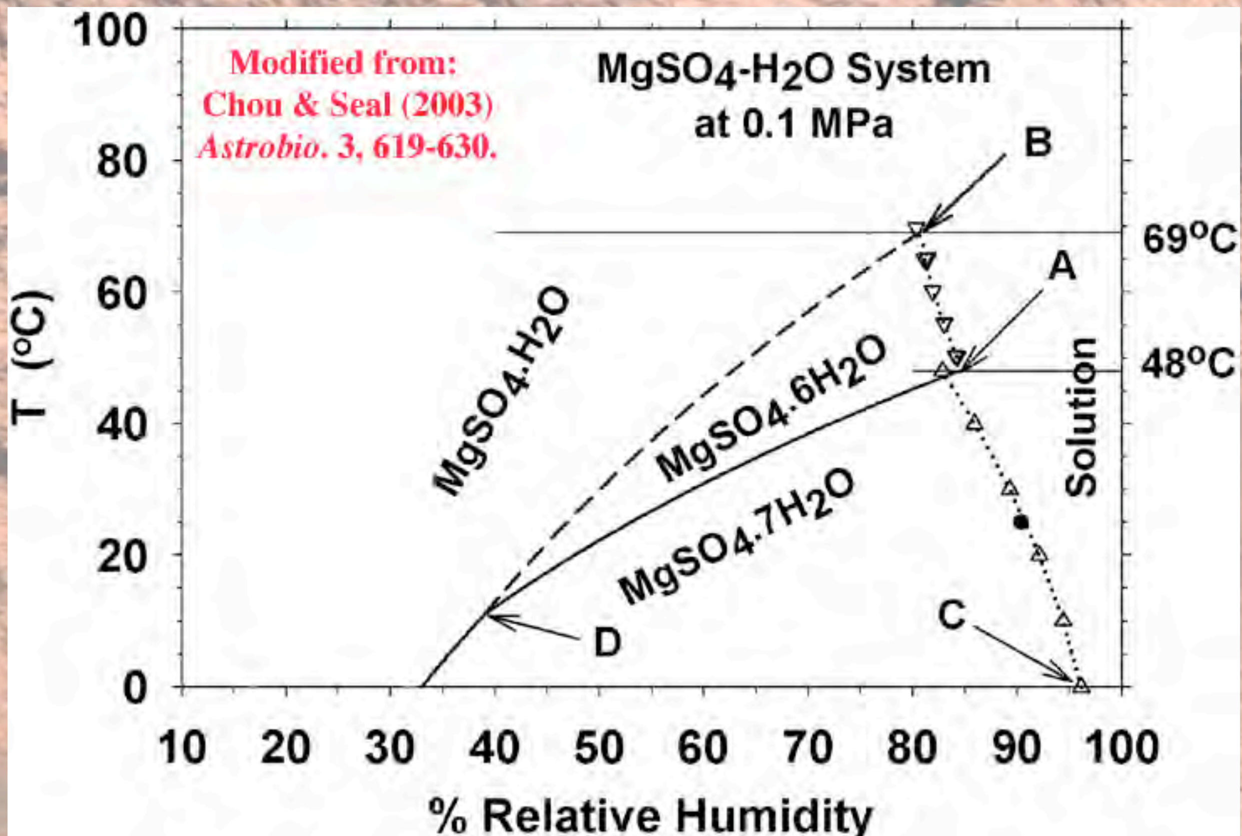
Reduction of Fe^{3+} to Fe^{2+} in clays can produce structural vacancies and a reduction in the amount of structural OH.

Komadel et al. (2006)
App. Clay Sci. 34.



$MgSO_4.nH_2O$

Epsomite	$MgSO_4.7H_2O$	Starkeyite	$MgSO_4.4H_2O$
Hexahydrite	$MgSO_4.6H_2O$	Sanderite	$MgSO_4.2H_2O$
Pentahydrite	$MgSO_4.5H_2O$	Kieserite	$MgSO_4.H_2O$

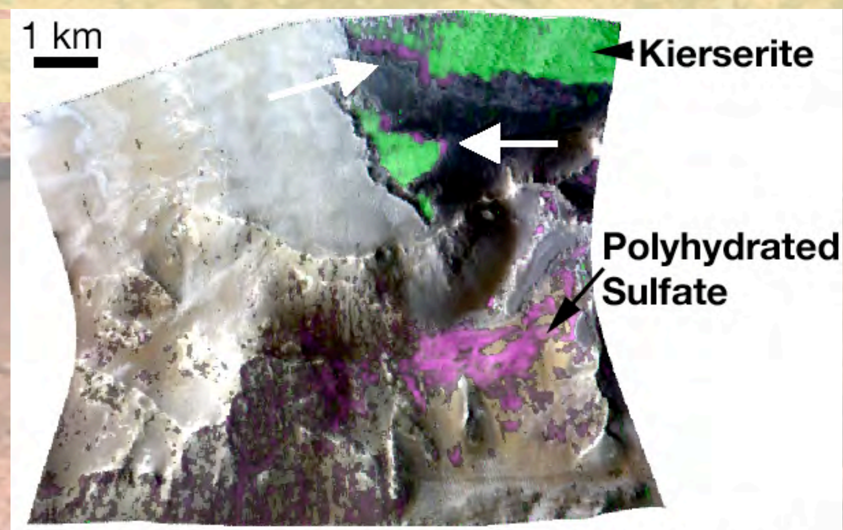


Vaniman et al. (2004) Magnesium Sulphate Salts and the History of Water on Mars. *Nature* **431**, 663-665.

"Because phases in the $MgSO_4.nH_2O$ system are sensitive to temperature and humidity, they can reveal much about the history of water on Mars. However, their ease of transformation implies that salt hydrates collected on Mars will not be returned to Earth unmodified, and that accurate *in situ* analysis is imperative."

See also Wang et al. (2005, 2006), LPSC 36/37.

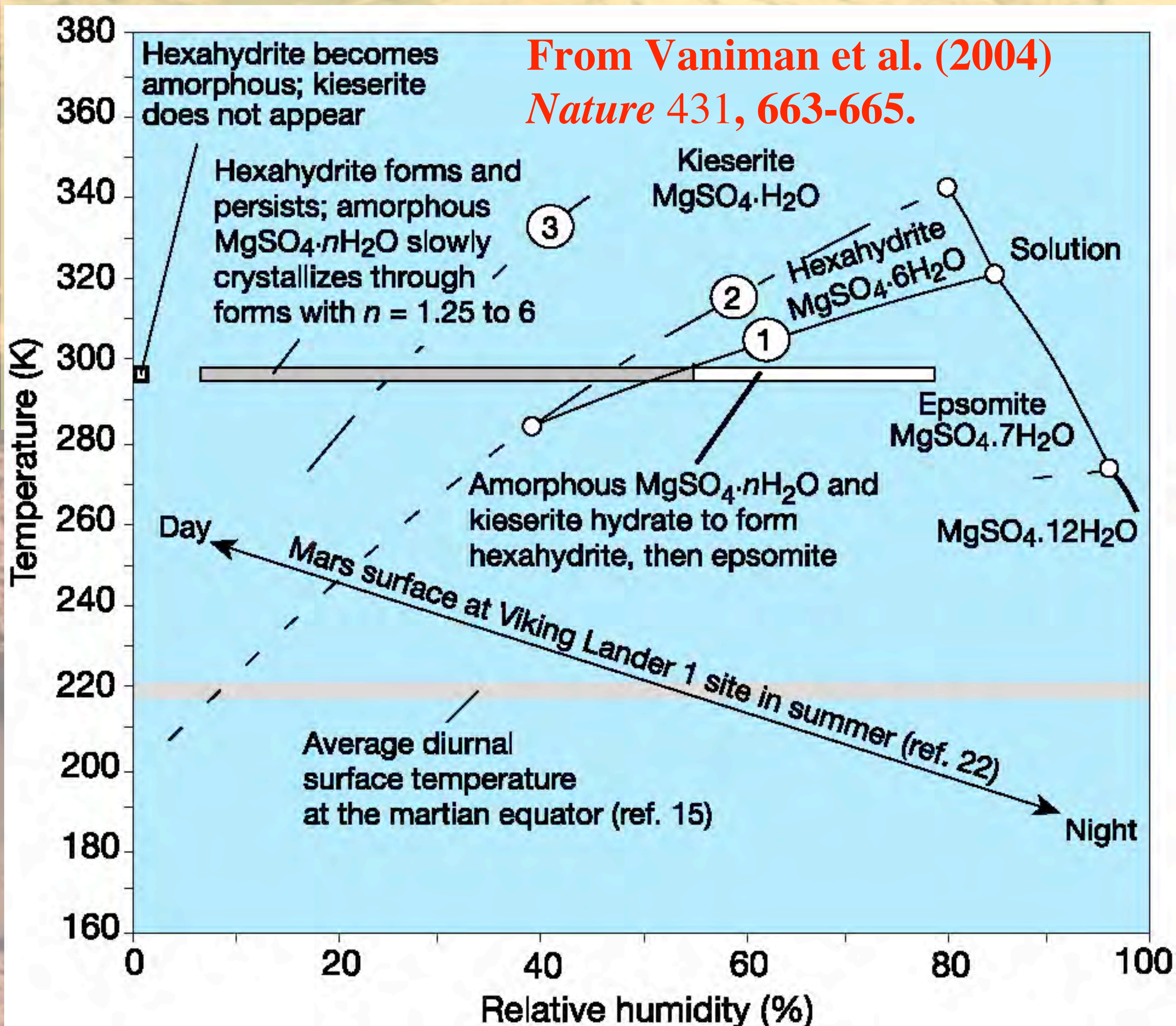
Presence of Kieserite on Mars (e.g., Roach et al., 2008, LPSC 39, Abstract # 1823. CRISM target FRT0000510D).



Tithonium Chasma Interior Layered Deposit

$MgSO_4.nH_2O$

Curves 1 and 2 from the experiments of Chou & Seal (2003, *Astrobiology* **3**, 619-630); Curve 3 is the Hexahydrite-Kieserite transition based on thermodynamic data.

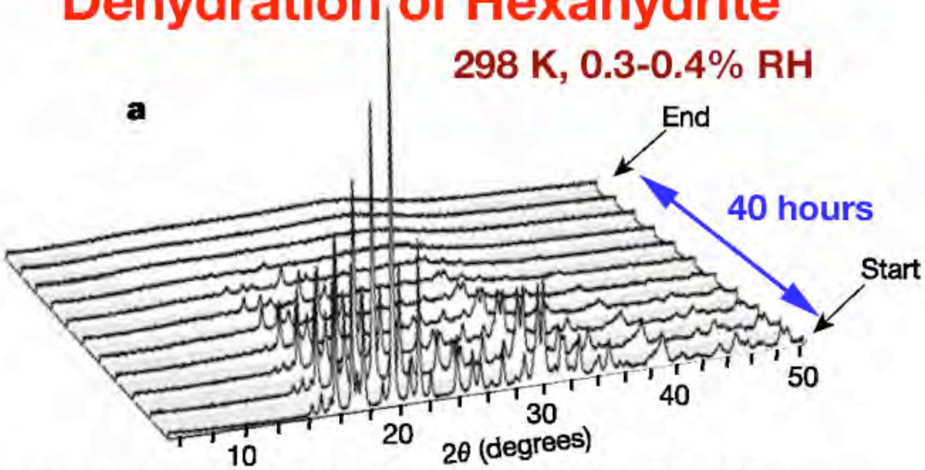


Estimating the stability of Hexahydrite on Mars depends upon the extrapolation of Curves 2 & 3.

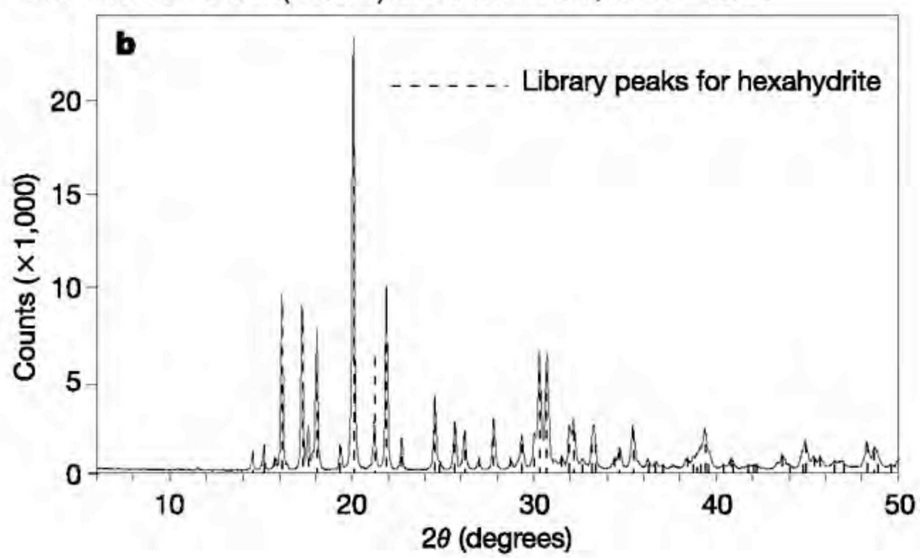
$MgSO_4.nH_2O$

Dehydration of Hexahydrite

298 K, 0.3-0.4% RH

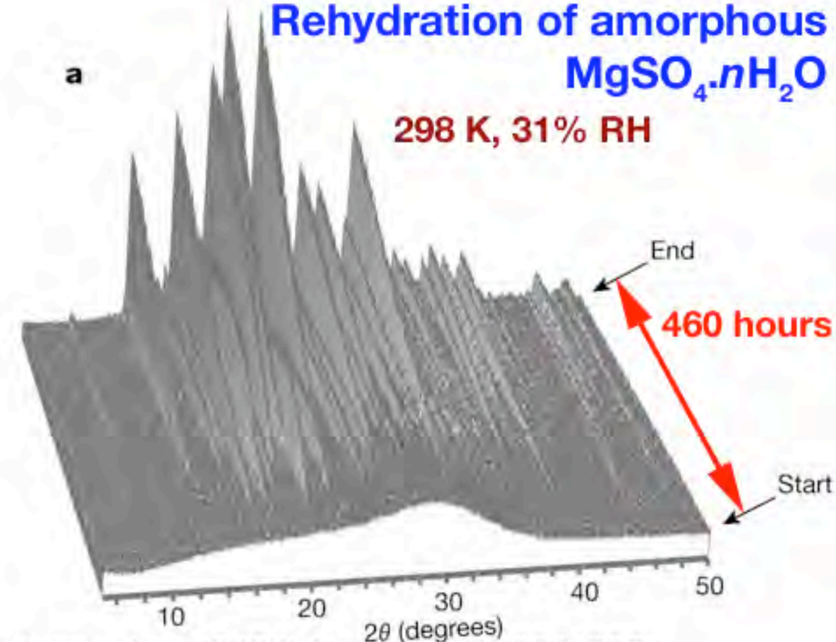


Vaniman et al. (2004) Nature 431, 663-665.

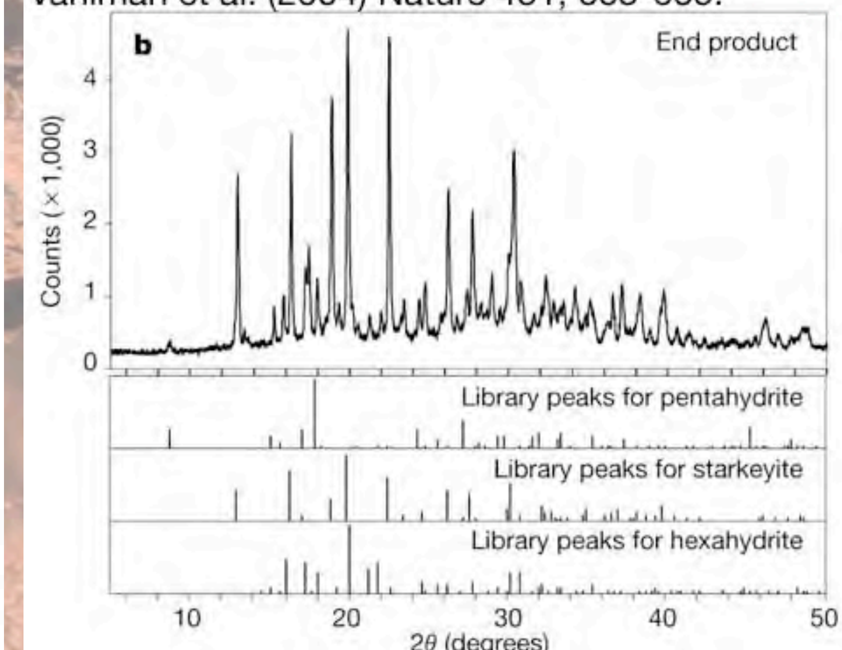


Rehydration of amorphous $MgSO_4.nH_2O$

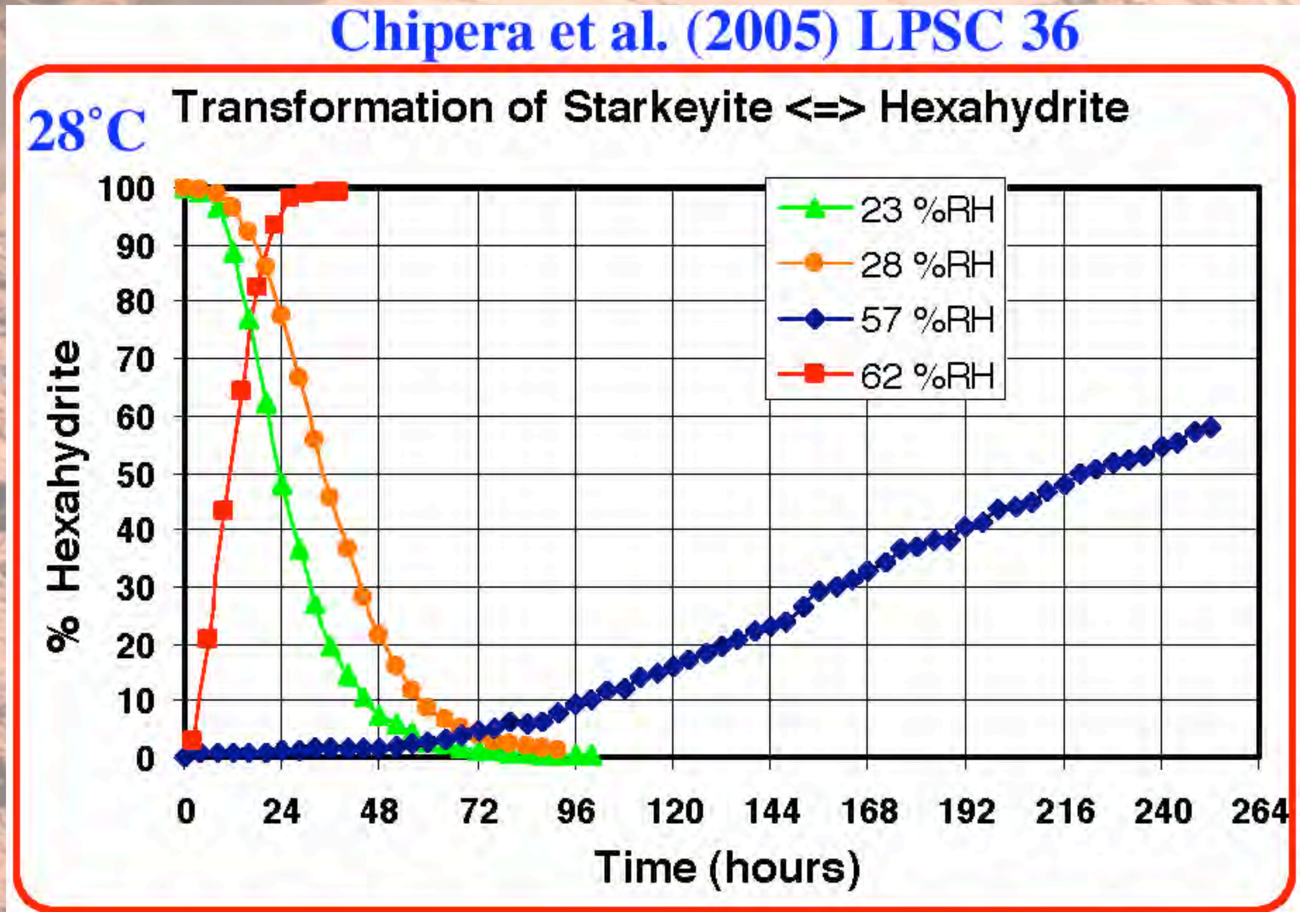
298 K, 31% RH



Vaniman et al. (2004) Nature 431, 663-665.



$MgSO_4.nH_2O$



Temperature, time, and relative humidity have significant affects on the "*n*" of $MgSO_4.nH_2O$.

$Fe^{2+}SO_4.nH_2O$

Brown et al. (2008) LPSC 39, Abstract # 1008.

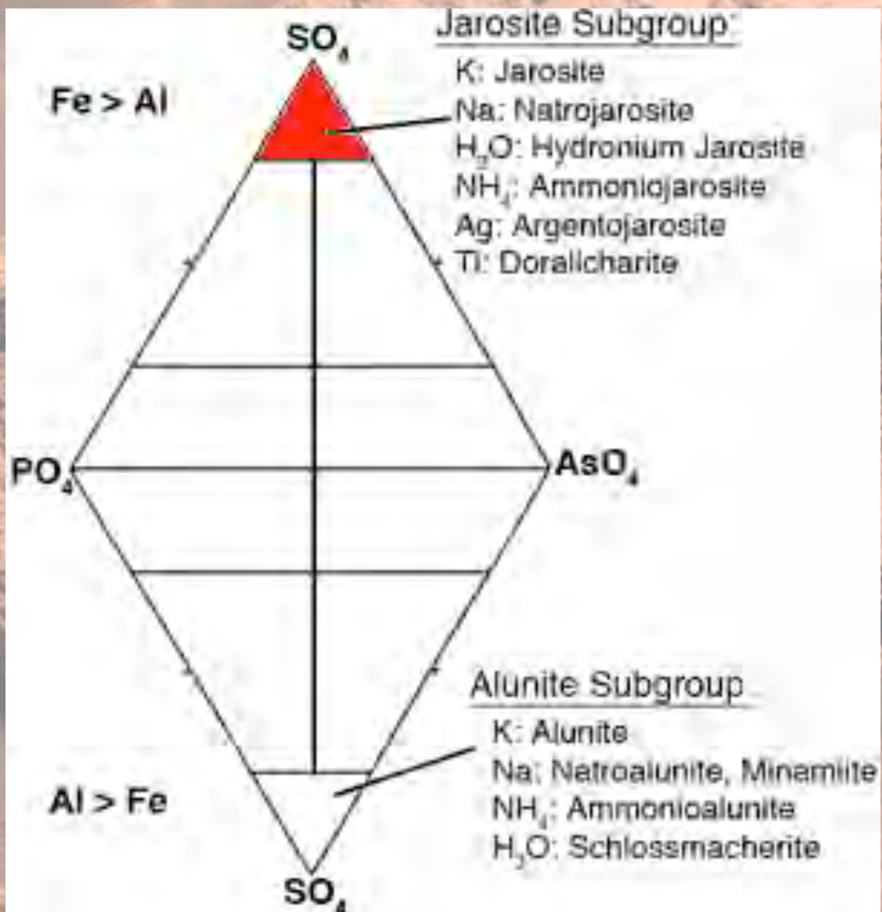
Melanterite	$Fe^{2+}SO_4.7H_2O$
Rozentite	$Fe^{2+}SO_4.5H_2O$
Szomolonokite	$Fe^{2+}SO_4.4H_2O$
Halotrichite	$Fe^{2+}Al_2SO_4.22H_2O$
Römerite	$Fe^{2+}{}_3(SO_4)_4.14H_2O$

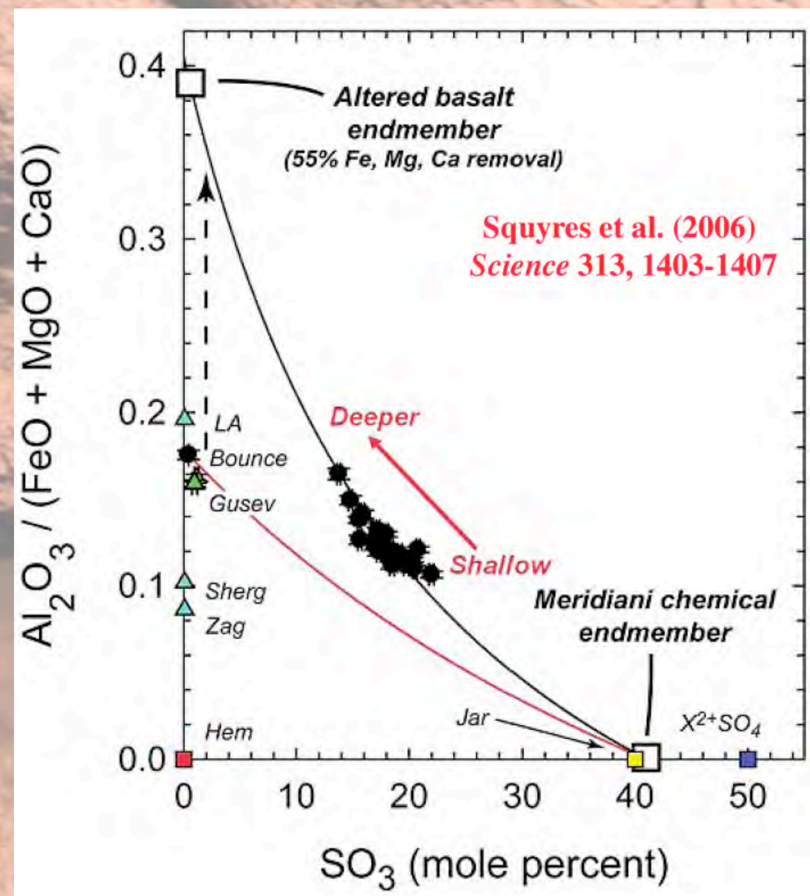
1) Melanterite is stable only under ambient conditions and breaks down to an amorphous form in a vacuum;
2) Rozenite breaks down to an amorphous phase when heated under vacuum above 70°C;
3) Römerite breaks down to an amorphous phase above 50°C;
4) Halotrichite breaks down to an amorphous phase when heated above 40-50°C;
5) Szomolonokite is stable in vacuo under heating to 300°C.

Jarosite: $(K,Na,H_3O)(Al,Fe^{3+})_3(SO_4)_2(OH,H_2O)_6$

Dutirzac & Jambor (2000) *Rev. Min. Geochem. 40*, 405-452.

Al:Fe^{3+} ratio determines whether minerals are in the jarosite or alunite families.





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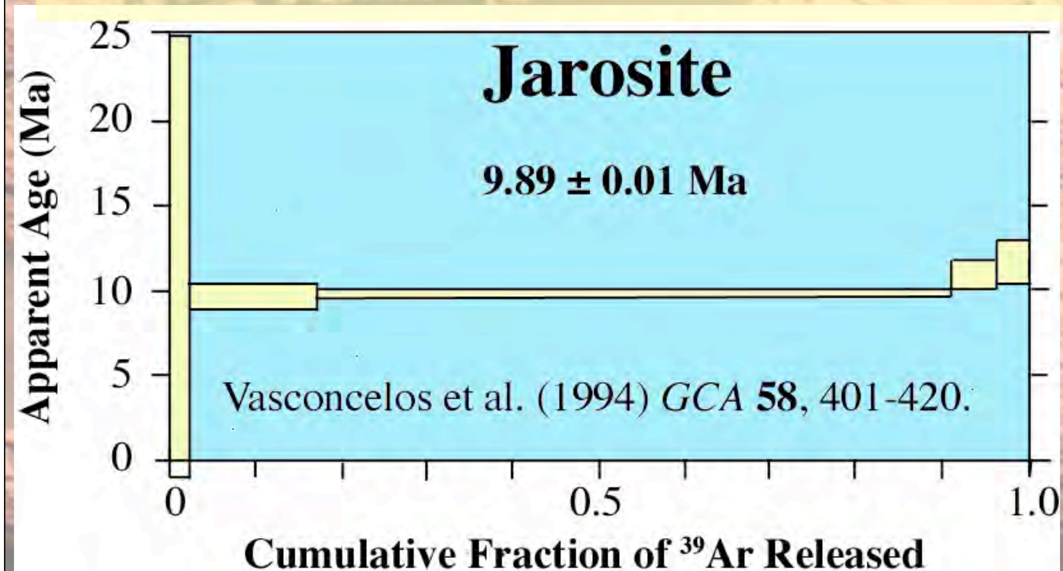
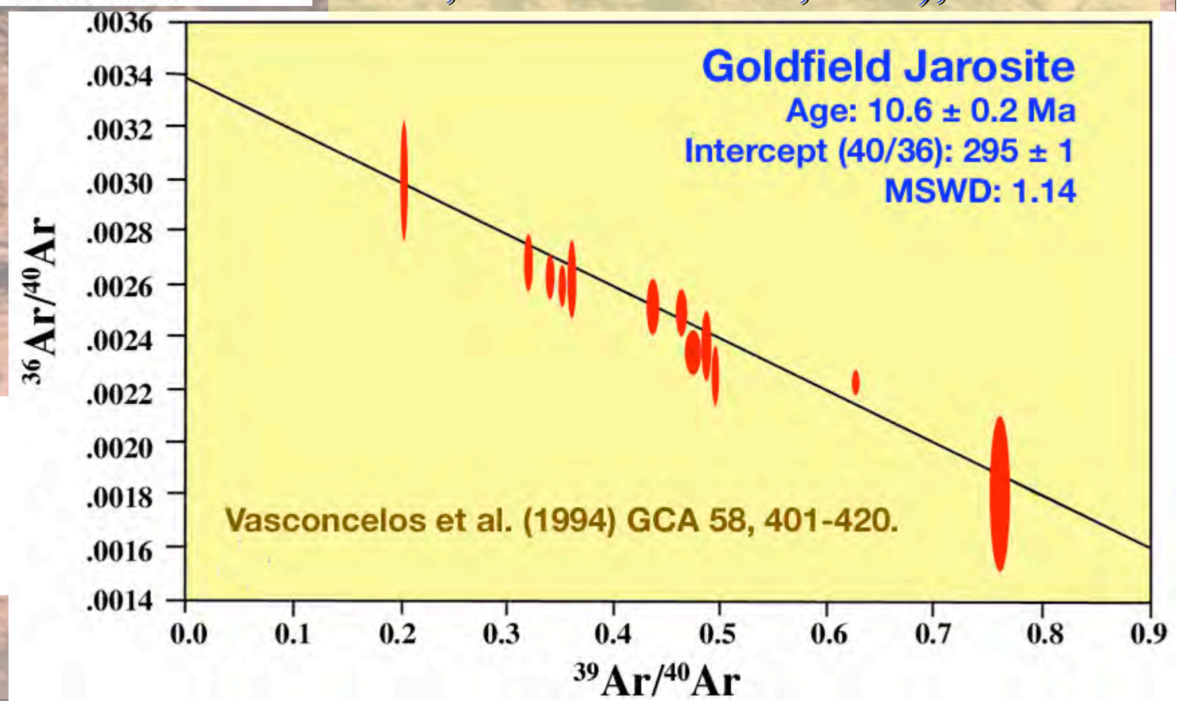


Jarosite/Alunite can be used to obtain age data using argon methods Vasconcelos et al. (1994) *GCA* **58**, 401-420; Papike et al. (2006) *GCA* **70**, 1309-1321); Landis & Rye (Mars Sulfate Wksp, 2006; Chem. Geol. 215, 2005);

Little to no Ar loss at 90˚C for 12-14 hours.

Ar diffusion: 8.2^{-22} cm sec^{-1} (in Alunite).



Gypsum $CaSO_4.2H_2O$

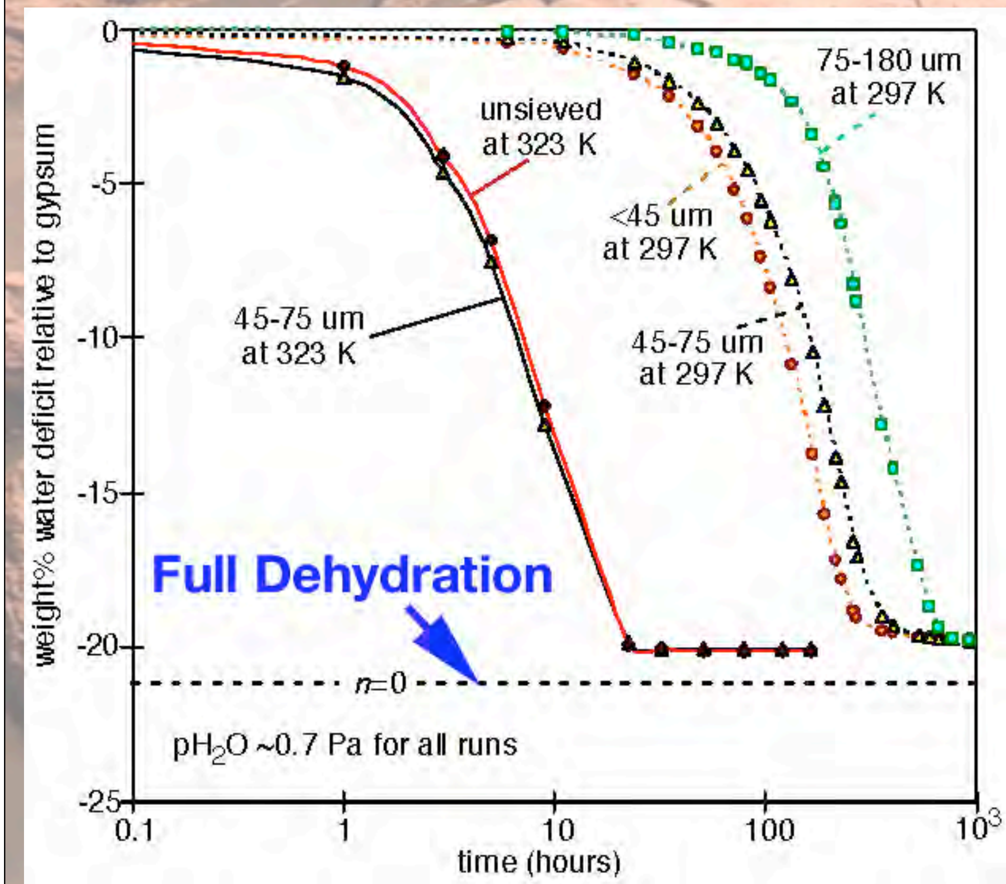
$CaSO_4.2H_2O$ --> $CaSO_4.0.5H_2O + 1.5H_2O$
Gypsum Bassanite

Irreversible: 370 ± 5 K

$CaSO_4.0.5H_2O$ --> $CaSO_4 + 0.5H_2O$
Bassanite Anhydrite

>633 K

$CaSO_4.2H_2O$ --> $CaSO_4.0.5H_2O + 1.5H_2O$
Gypsum Bassanite



White Sands Gypsum

Vaniman et al. (2008)
LPSC 39, Abstract # 1816:

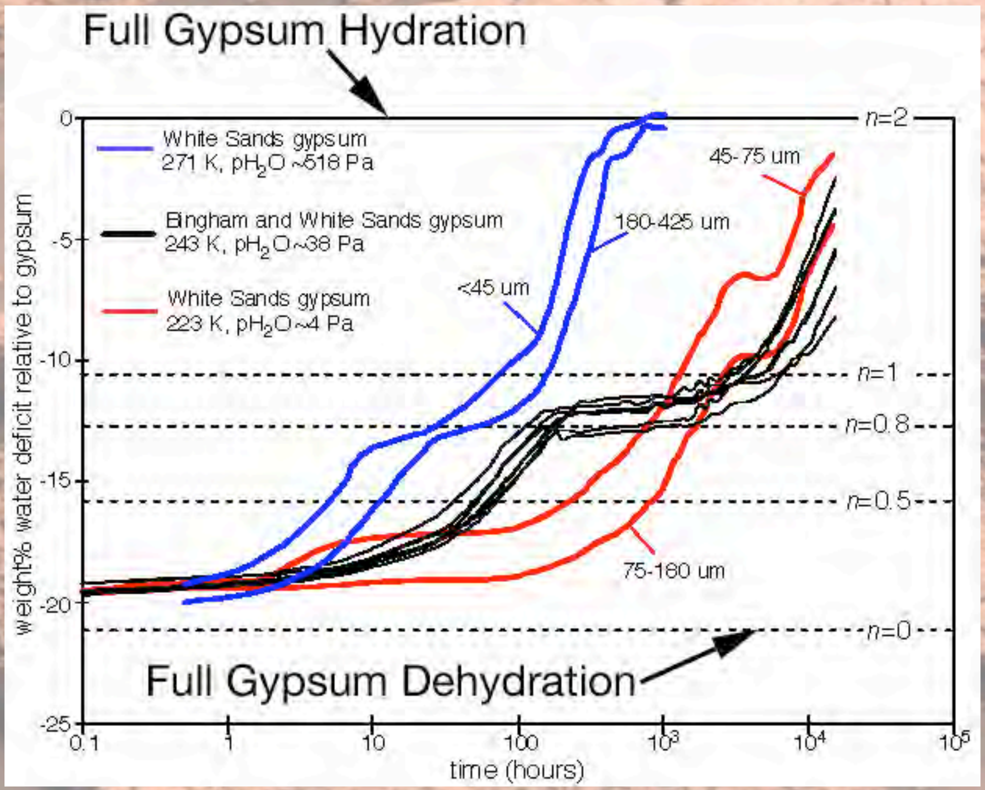
"….at Mars-like pH_2O, a very warm surface (24˚C) will require several hours to initiate desiccation and well over 100 hours to reach terminal low H_2O content in a Bassanite form."

"….. we still consider it unlikely that surface-exposed gypsum would be desiccated to bassanite forms by such a mechanism."

This dehydration could be facilitated by volcanism, impact, or burial.

$CaSO_4.0.5H_2O + 1.5H_2O$ --> $CaSO_4.2H_2O$

Bassanite **Gypsum**



Vaniman et al. (2008) LPSC 39, Abstract # 1816:
"…. relatively aggressive first-stage rehydration of dehydrated Bassanite forms, even at temperatures as low as 223 K if in vapor communication with H_2O ice."

Implications: Dehydration of other phases could promote rehydration of Bassanite in the sample capsule. Results in $CaSO_4$ with variable water contents (and isotopic compositions).

Sample Return Challenges

Materials: desirements in Neal (2000) JGR 105.

It is important that flight spares be created of all components that contact the samples and that these spares be stored for subsequent analysis to document homogeneity and purity.

Sample container should be sealed with Mars atmosphere and maintained at that pressure.

Sterilization: high-dose gamma radiation should be further explored (cf. Allen, 1999, JGR 104).

Long-term curation: ≤240 K in an inert atmosphere and sterile environment.

Sample Container Recommendation: isolate sample types in Teflon-cushioned compartments to reduce abrasion.

Sample Return Strategy

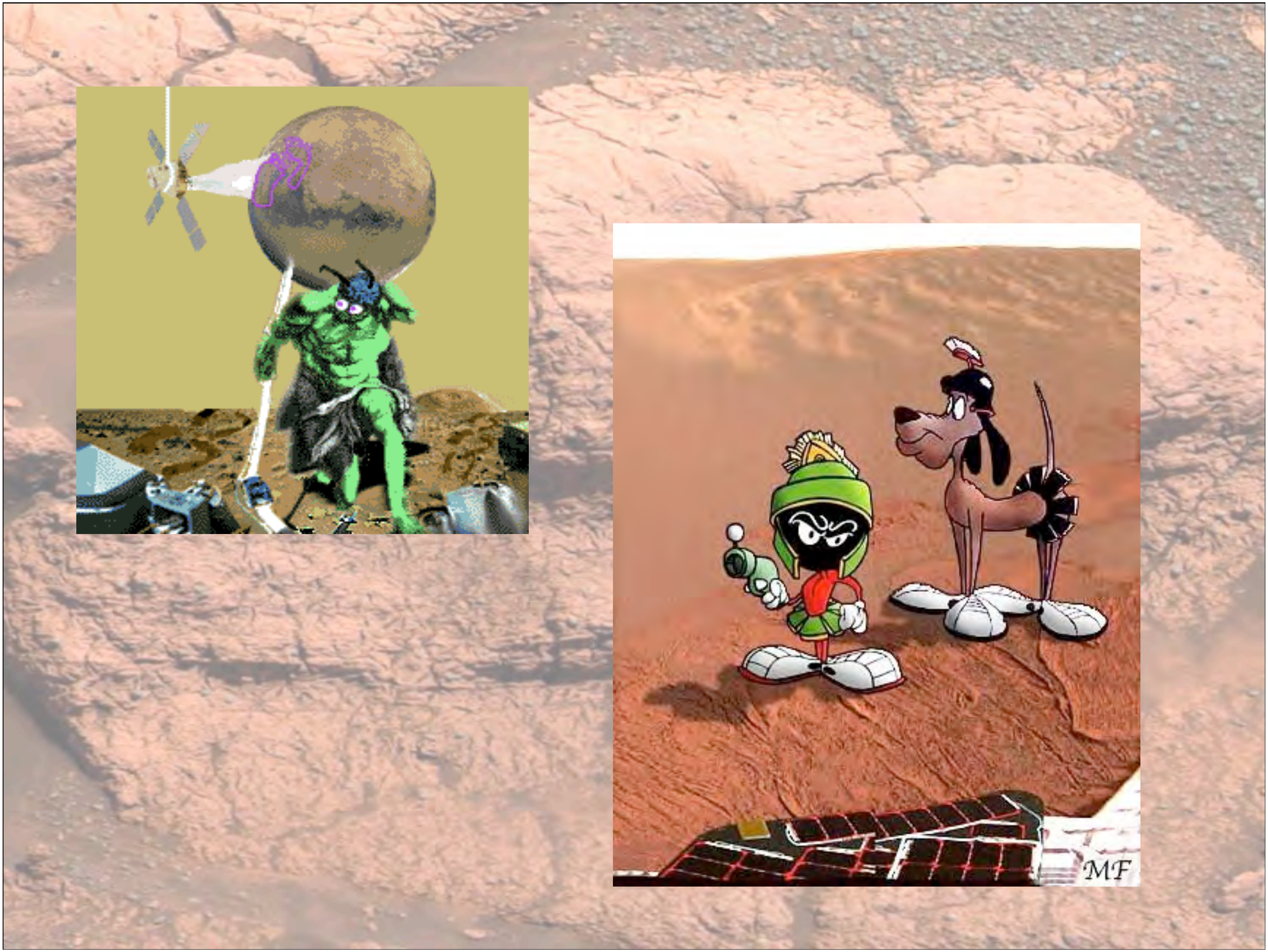
Initial sample return should return samples that will be the most stable in the varying conditions that they will experience not only during return to Earth, but also during their curation.

Such materials would be volcanic in nature, although sedimentary samples containing Jarosite could also be included.

The samples would need to be well documented on the surface but this does not mean that every piece of analytical equipment be taken to Mars in order to do this (e.g., context from pictorial documentation, RAT, Raman, APXS, organic C).

Without strict (and expensive!) environmental control, returning samples to address MEPAG Goals 1 (Life) and 2 (Past Climate) will probably yield at least *some* ambiguous results.

Therefore, for the first sample return, concentrate on samples to address MEPAG Goal 3 - Surface and Interior Evolution.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