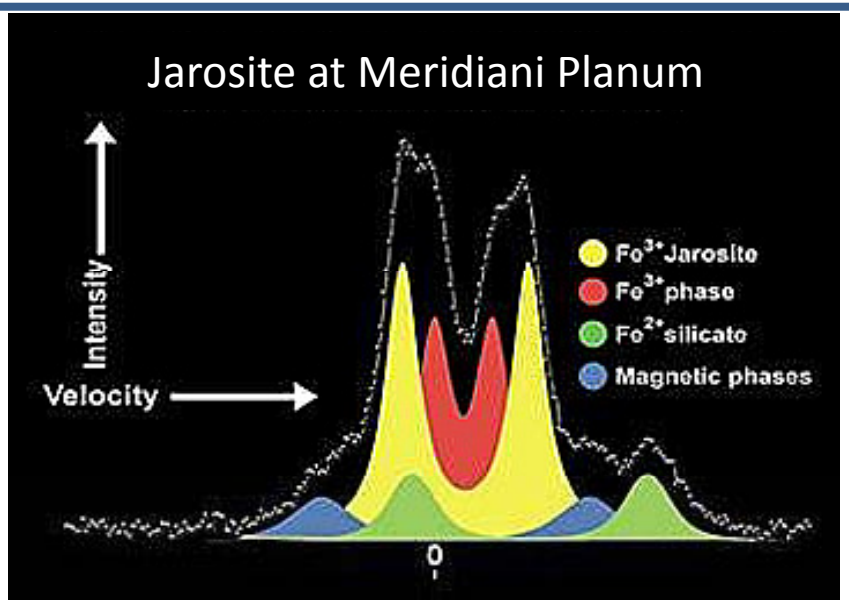
FE-SULFATES ON MARS:
Considerations for Martian Environmental Conditions, Mars Sample Return & Hazards

P. L. King[1,2], M. D. Lane[3], B. C. Hyde[2], M. D. Dyar[4], & J. L. Bishop[5]

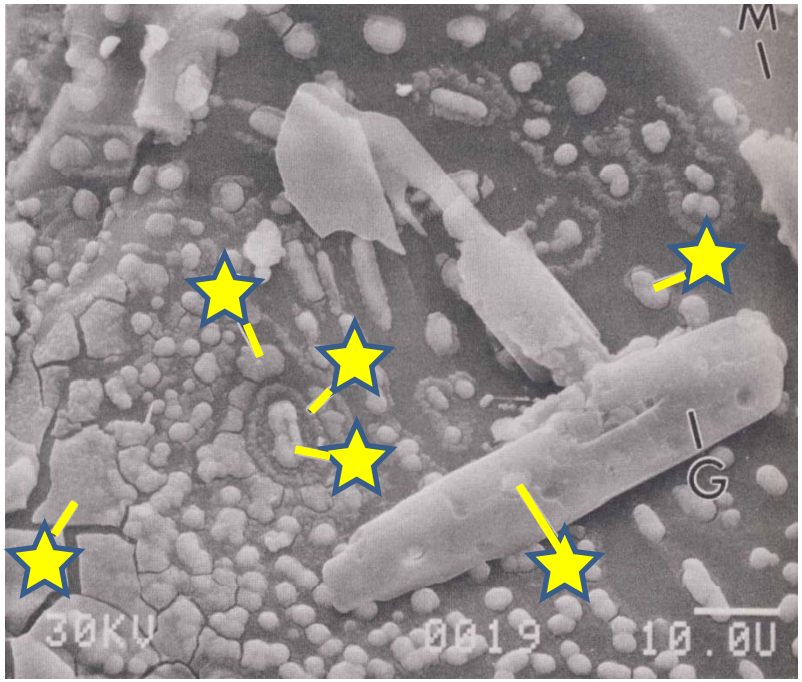
[1]Inst. Meteoritics, Univ. New Mexico, Albuquerque, NM USA
[2]Dept. Earth Science, Univ. Western Ontario, London, ON Canada
[3]Planetary Science Institute, Tucson, AZ USA
[4]Mount Holyoke College, South Hadley, MA USA
[5]SETI Institute/NASA-Ames Res. Cen., Mountain View, CA USA

Evidence for Fe-sulfates on Mars



Klingelhoefer et al. (2004)

Fe-sulfate (+/- K, P) in QUE94201



Wentworth & Gooding (1994)

- Fe-sulfates indicate (limited) water
- Sensitive to environmental conditions
- To preserve / unravel mineralogy during sample return we need to know how Fe-sulfates behave under different environmental conditions

Fe^{3+}-salts at Gusev Crater

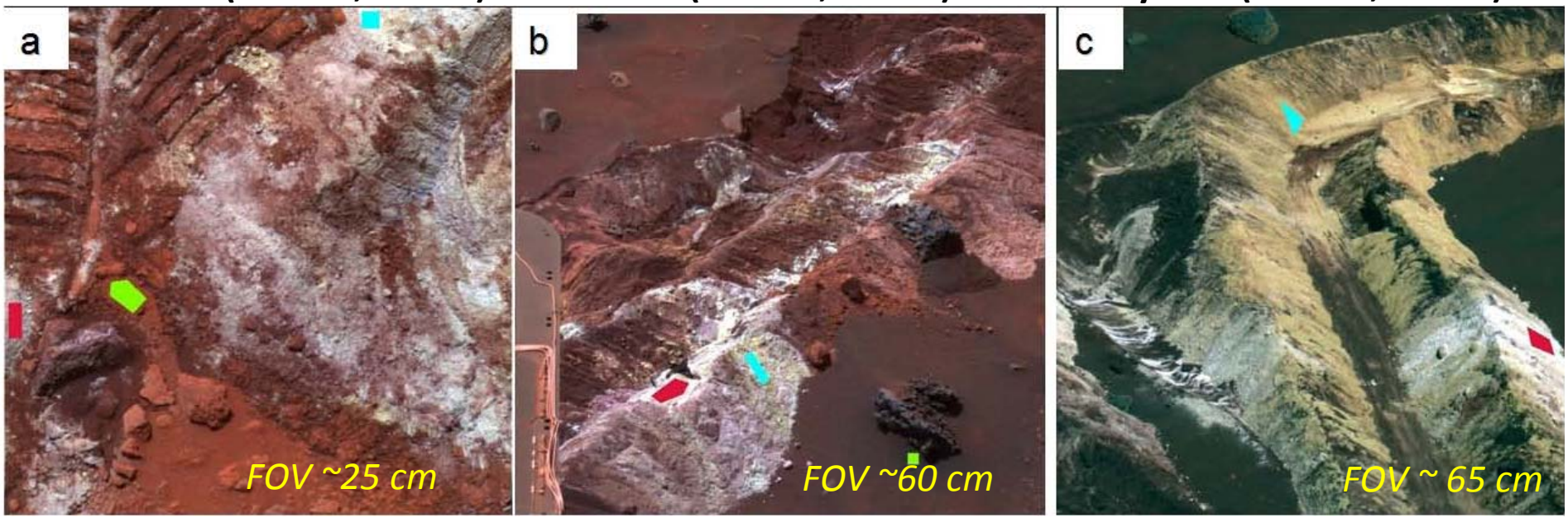
Variety of localities, Gusev Crater (Johnson et al., 2007)

1. Visible-near IR – spectral deconvolution

Paso Robles soil, Gusev Crater (Lane et al., 2008)

2. Visible-near IR spectral matching
3. Thermal IR spectral deconvolution
4. Mössbauer spectral matching
5. Constraints from APXS… v. low K & Na

Paso Robles (Sol 400, P2551) **Arad (Sol 721, P2538)** **Tyrone (Sol 790, P2531)**



False-color images from Gusev Crater (blue=432 nm, green=535 nm, red=754 nm) Johnson et al. (2007)

Summary of proposed Fe^{3+} sulfates at Gusev Crater

Fe-sulfates identified with ≥ 4 methods

Ferricopiapite	$Fe^{3+}_{4.6}(SO_4)_6(OH)_2 \cdot 20H_2O$	**
(Para)coquimbite	$Fe^{3+}_2(SO_4)_3 \cdot 9H_2O$	
Fibroferrite	$Fe^{3+}SO_4(OH) \cdot 5H_2O$	

Fe-sulfates identified with ≥ 3 methods

Parabutlerite	$Fe^{3+}(SO_4)(OH) \cdot 2H_2O$
Rhomboclase	$(H_3O)Fe^{3+}(SO_4)_2 \cdot 3H_2O$

Fe-sulfates identified with ≥ 1 method

H_3O^+ jarosite	$H_3O^+Fe^{3+}_6(SO_4)_4(OH)_{12}$
Bilinite	$Fe^{2+}Fe^{3+}_2(SO_4)_4 \cdot 22H_2O$
Butlerite	$Fe^{3+}(SO_4)(OH) \cdot 2H_2O$
Metahohmannite	$Fe^{3+}_2(SO_4)2O \cdot 4H_2O$

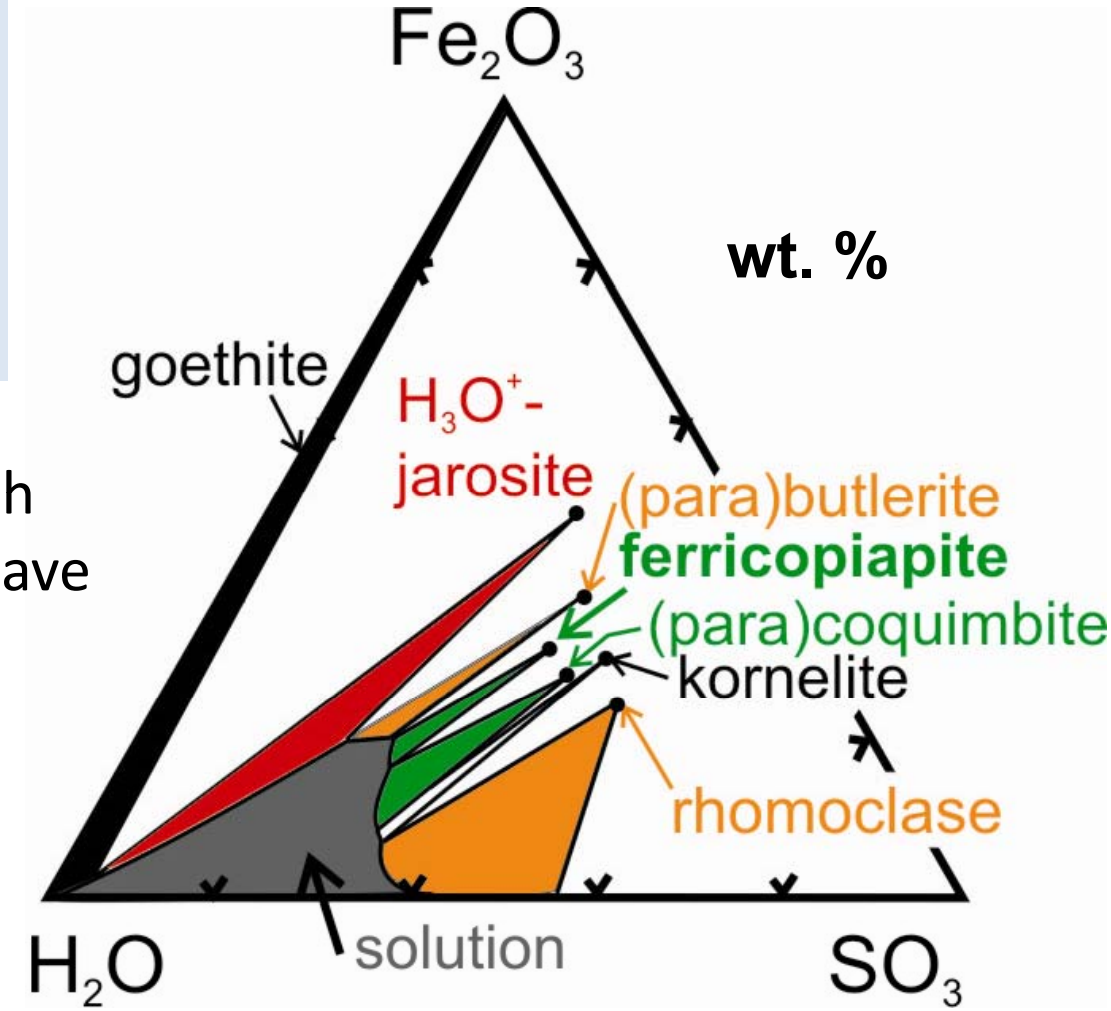
Bulk chemistry of the precipitating solution

Solutions in equilibrium with ferricopiapite-coquimbite have

wt% Fe_2O_3 : H_2O : SO_3 =

8-20 : 52-60 : 25-32

Mol% Fe / SO_4 ~ 0.5



Modified from Merwin & Posnjak (1937)

Forming Fe-S-O-H phases

Addition of H_2SO_4 to basalt via volcanic/hydrothermal SO_2

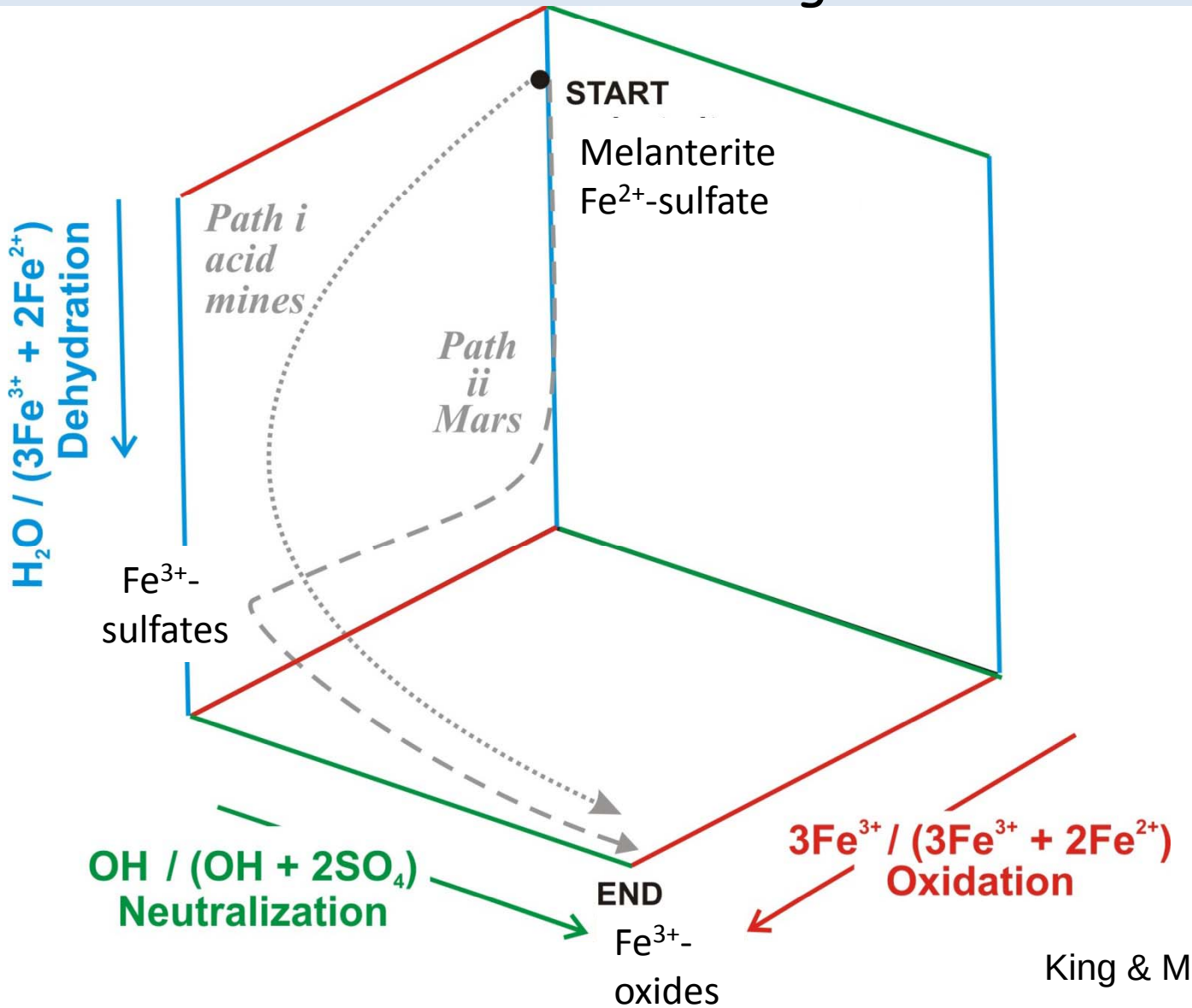
Oxidation & hydration of Fe sulfides to produce Fe^{2+} & SO_4^{2-}/HSO_4^-

Fe^{2+}-sulfates e.g. melanterite

Summarized in King & McSween (2005)

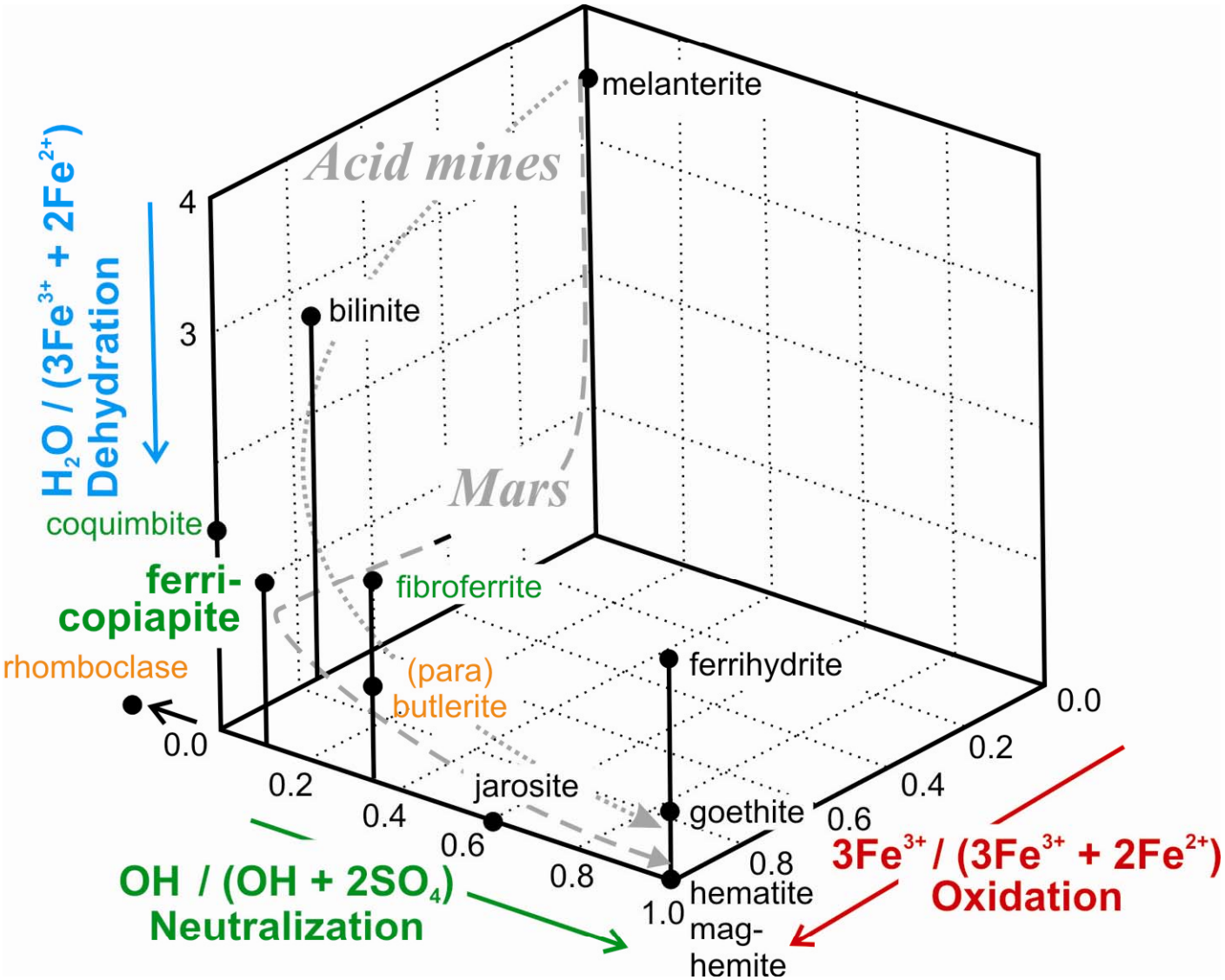
Forming Fe-S-O-H phases

note- not like Ca- or Mg-sulfates



Modified after
King & McSween (2005)

Fe^{3+}-sulfates via dehydration-oxidation-neutralization

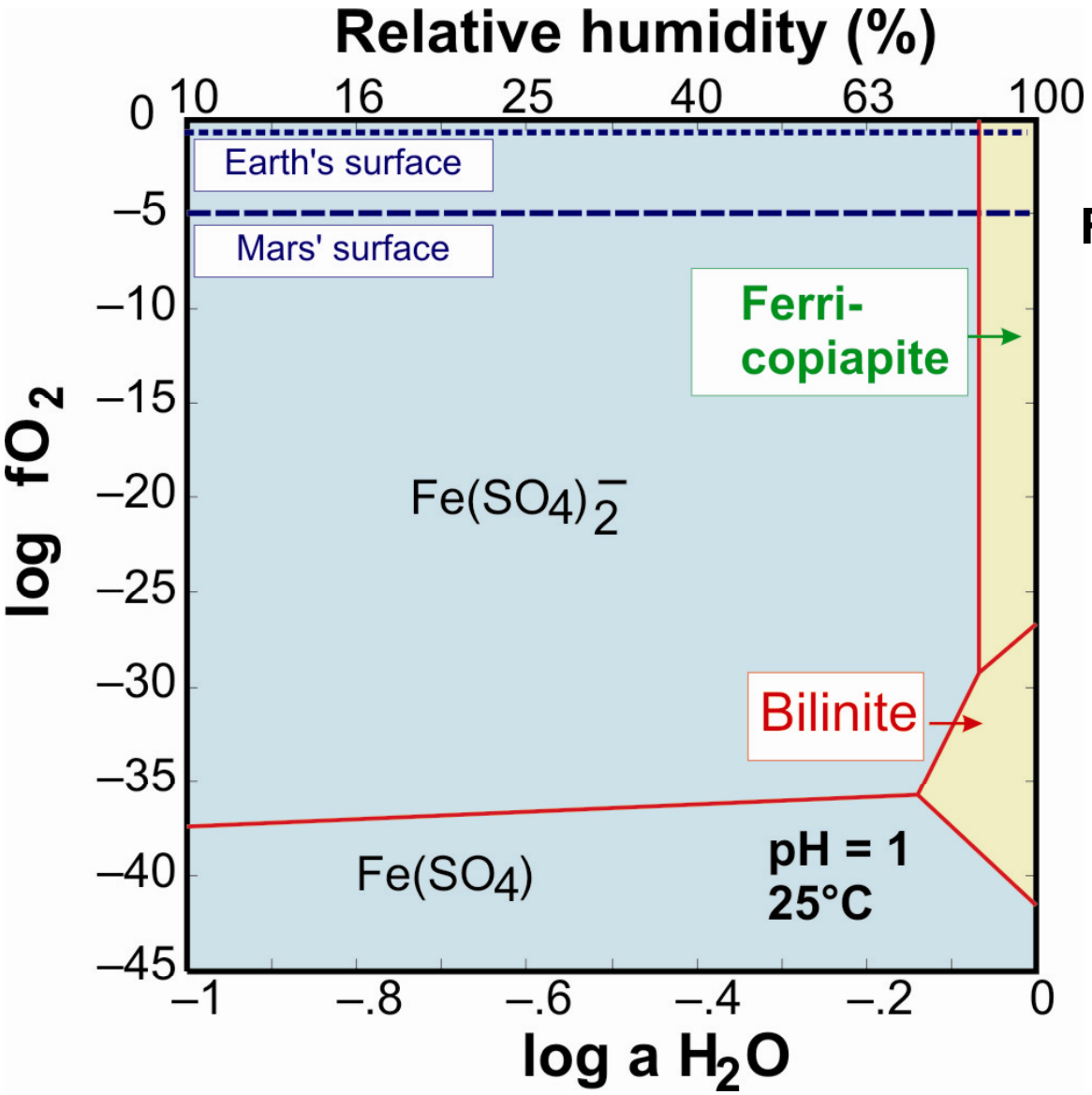


Modified after King & McSween (2005)

Thermodynamic modeling

- Thermodynamic database & compositions chosen have strong influence on results
- We used
  - Marion et al. (2008) + Bethke & Yeakel (2007) 39 minerals & species, plus
  - aFe=0.3, $a$$HSO_4^-$=$a$$SO_4^{2-}$=0.08 based on Paso Robles soils
  - Fe-S-O aqueous species *not* suppressed

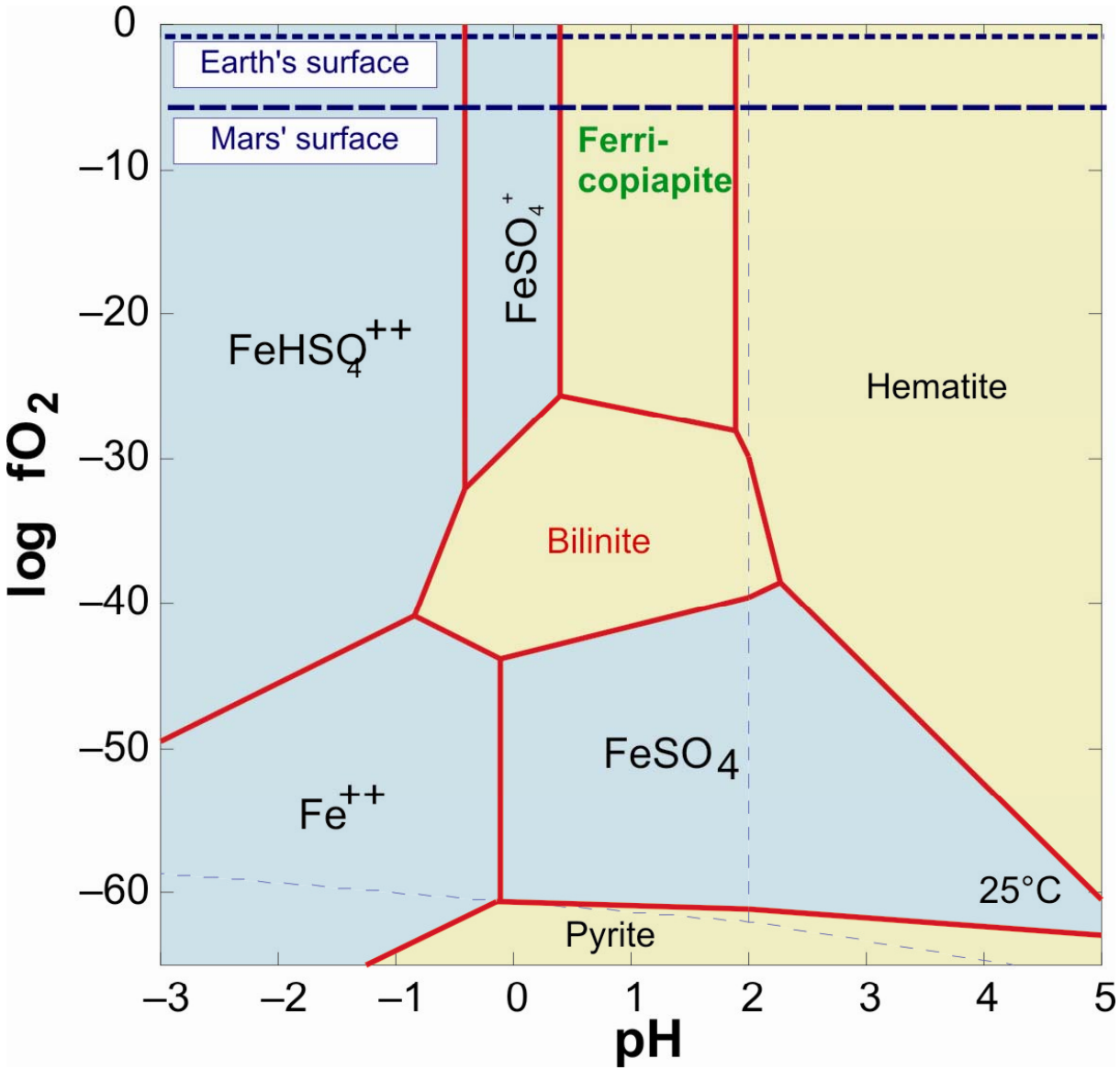
Oxidation-dehydration diagram, pH = 1



Ferricopiapite - with $20H_2O$

- only stable at high *loga*H_2O
- fO_2 has a minor effect on its stability

Oxidation-neutralization diagram, $\log aH_2O=0$



Ferricopiapite

- pH ~ 0.5 to 2

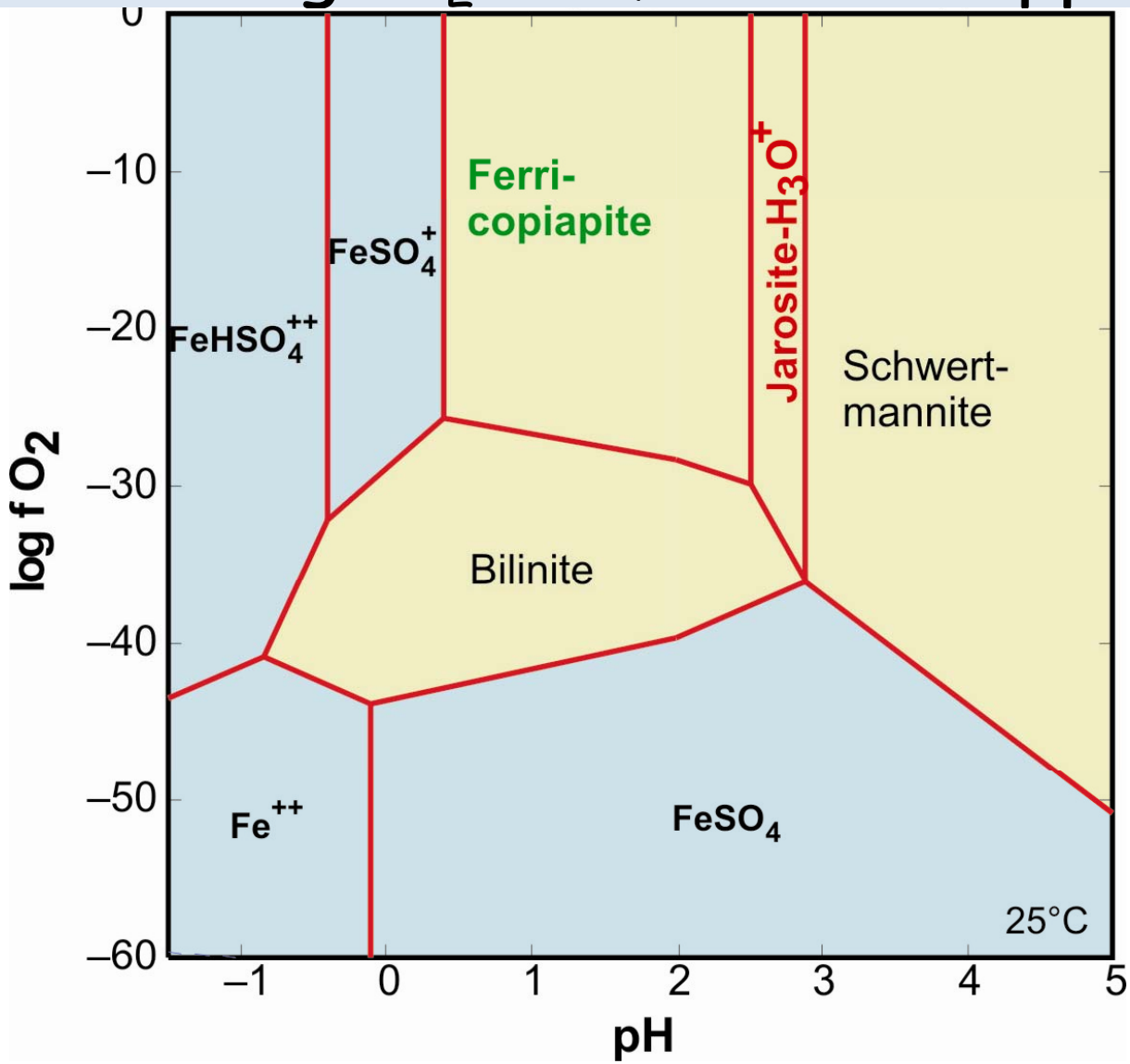
If HSO_4^- or SO_4^{2-} increased:

S-mineral fields extend to lower pH

+ Melanterite

+ Rhomboclase

Oxidation-neutralization diagram
$\log aH_2O=0$, oxides suppressed



Ferricopiapite

- pH ~ 0.5 to 2.5

SUITES of minerals help us to better determine environmental conditions

Addition of K & P stabilizes K-jarosite & strengite

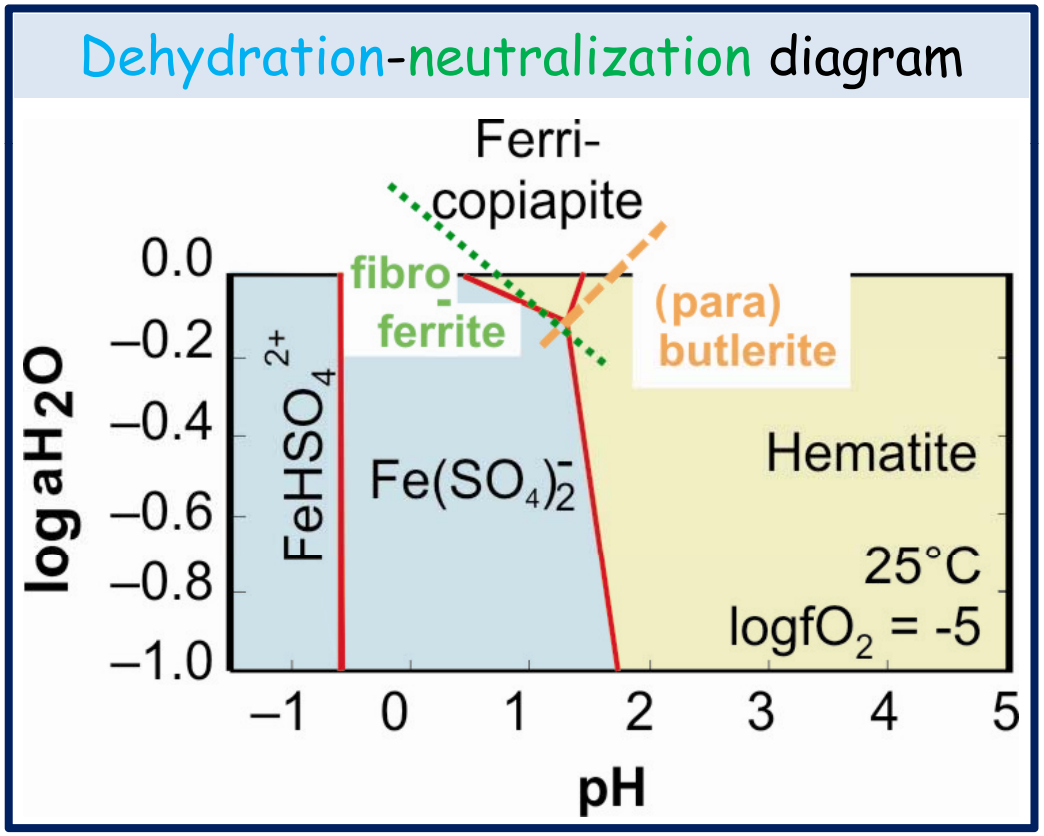
Summary of Fe^{3+}-sulfate stability with Paso Robles composition solutions

Ferricopiapite
pH<2.5, RH>~90%, $logfO_2$>-30

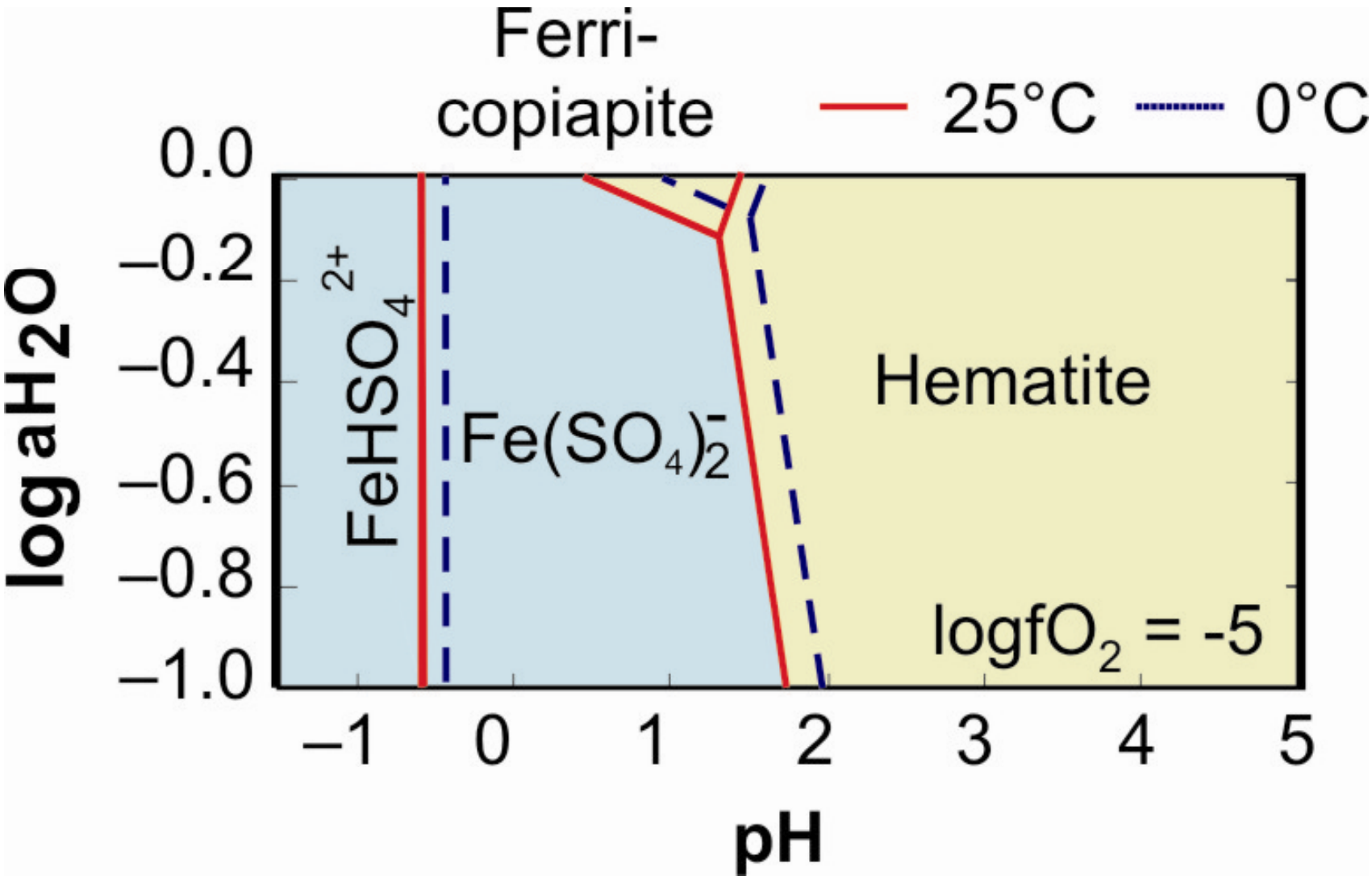
(Para)coquimbite
difficult to form

Fibroferrite & (para)butlerite
no thermodynamic data,
we know $logaH_2O$/pH ,
but we don't know the
lines' intercepts

Rhomboclase
forms at more acidic,
S-rich conditions



Temperature effects on a dehydration-neutralization diagram



Recommendations for Fe-sulfate return

Sample Containment

- Fe^{2+}-(Fe^{3+})-sulfates: fO_2 variations important
- Fe^{3+} sulfates - fO_2 variations not v. important
- Relative humidity: seal samples in containers on Mars
  (know moles of O_2 + aH_2O, calculate volume of martian air needed to keep minerals stable using PV = nRT). Understand that changes may occur, but know how to account for it.
- Temperature dependence of reactions: limited C_P data- need more
- Sulfates may get "sticky" or "clump", form acids, or Fe-oxides/hydroxides/oxyhydroxides
- Engineering & cost concerns aside:
  - Put samples in separate containers
  - Use acid-resistant materials
  - Use lids & insulation
  - Enclose a T-RH-P data logger

To maximize information from returned Fe-sulfates we need to

Understand Environmental Conditions

- Need to be able to characterization small Fe-sulfates, so we can determine environmental conditions
- Understand reaction kinetics of small particles (with high surface/volume)
- Have more thermodynamic data for Fe^{3+}-sulfate & phosphate phases & possible gels/deliquescence products
- Understand that disequilibrium may have occurred

Unravel Habitability

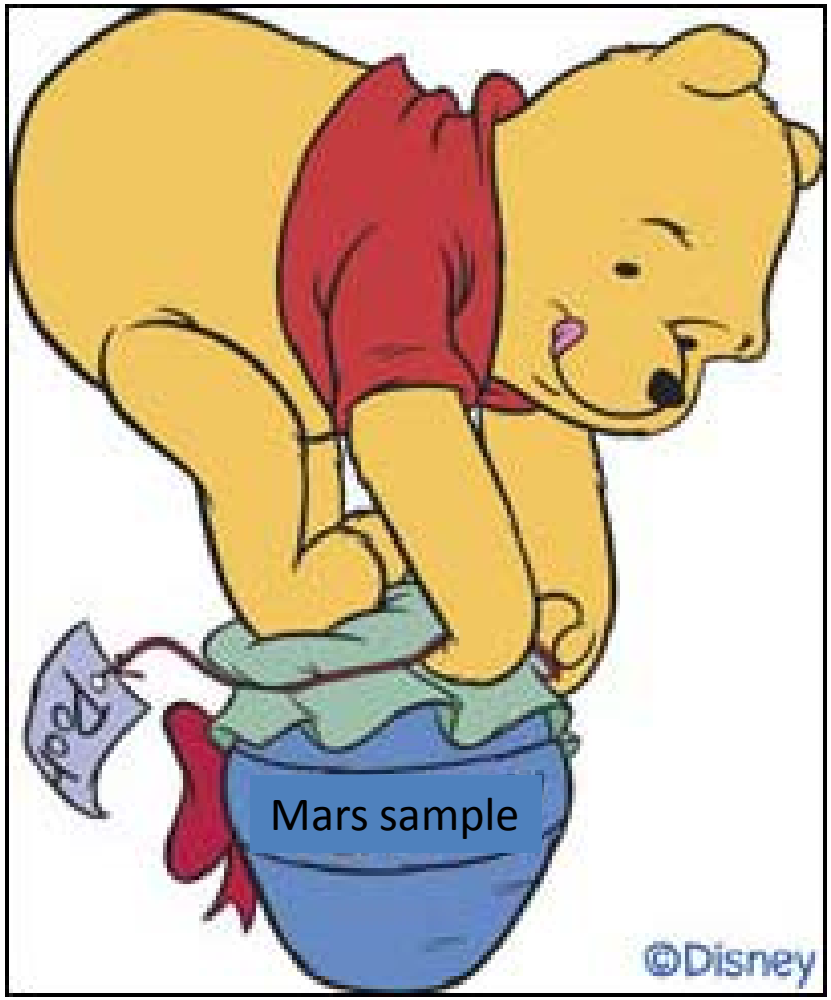
- Need to know effects of solution bulk composition, pH, fO_2 & aH_2O on life
- Understand radiation shielding properties of Fe-sulfates in protecting any life

Summary

- Thermodynamic models are useful for constraining environmental conditions & optimal conditions for sample return, especially if suites of Fe-sulfate minerals are identified
- Ferricopiapite, if present, occurs at

  pH<2.5, RH>~90%,

  $\log fO_2 > -30$



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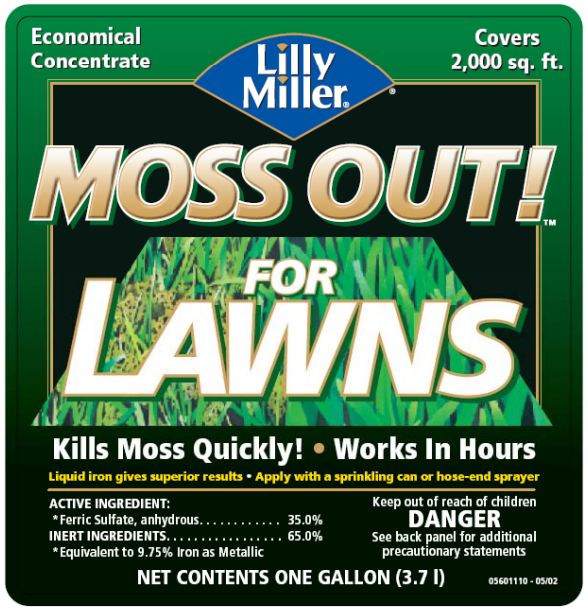
Fe-sulfate hazards

Fe^{2+}-sulfates
-not very toxic

Fe^{3+}-sulfates - toxic



- Overall, likely insufficient volume to be extremely hazardous (see abstract)
- Acid Fe-sulfates may produce irritation if ingested, inhaled or touched

$Fe^{3+}(H_2SO_4)(OH)(SO_4).3H_2O \rightarrow$

rhomboclase

$H^+ + 2SO_4^{2-} + Fe^{3+} + 4H_2O$

acid