Implications from the Terrestrial Formation of Jarosite - Alunite Minerals for Weathering on Mars

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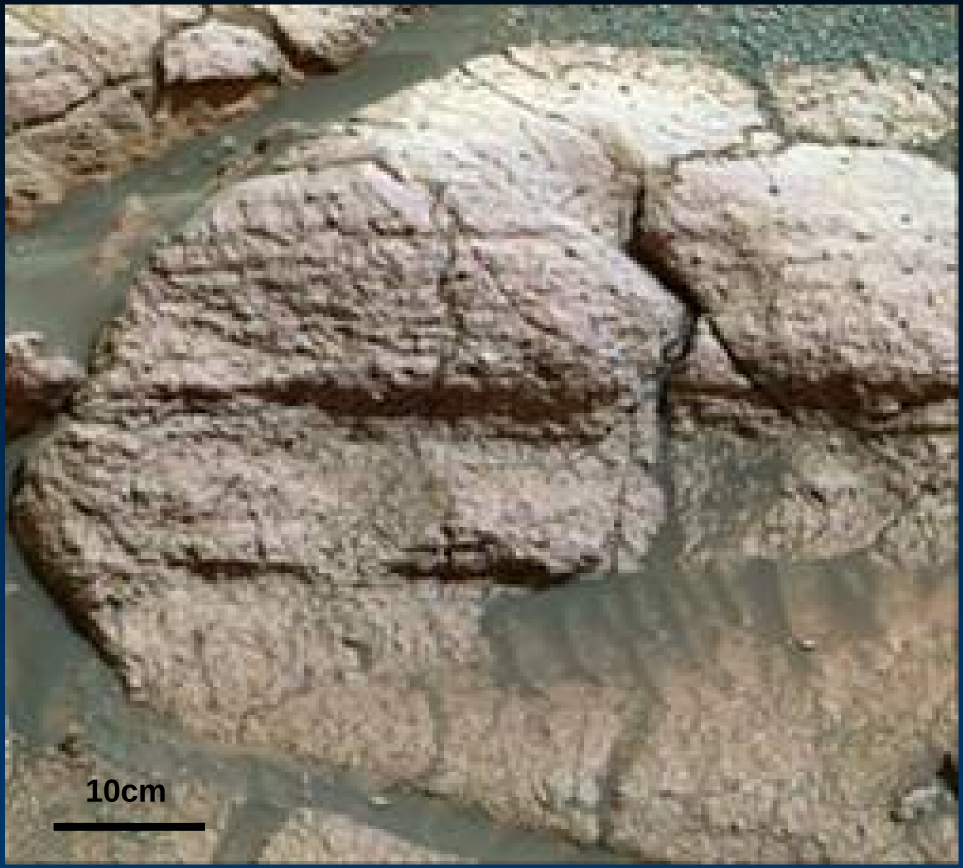


"El Capitan" at Meridiani Planum shows fine parallel lamination in its upper part. It also contains scattered sphere-shaped objects (ranging from 1 to 2 mm in size) rich in jarosite and hematite. (©*NASA/JPL/Cornell*).

Compositions of Rocks and Soils
Pathfinder Samples, Ares Vallis, July 1997

(after Economou et al., 2003)

	Rocks	Soils	Average Earth (Taylor, 1964)
No analyses	(5)	(6)	
SiO_2	49.7	41.6	51.3
Al_2O_3	11.5	10.2	16.6
Fe_2O_3	16.9	22.1	12.3
MnO	0.4	0.3	0.2
MgO	3.7	7.4	7.5
CaO	6.4	6.0	9.4
Na_2O	4.0	2.8	2.6
K_2O	0.9	0.6	1.0
TiO_2	0.6	0.8	1.5
Cr_2O_3	0.1	0.3	0.03
P_2O_5	0.5	0.8	0.3
SO_3	2.8	6.1	0.06
Cl	0.6	0.9	0.006
H_2O	1.9	–	
	100		

Opportunity Landing Area and Rover Path

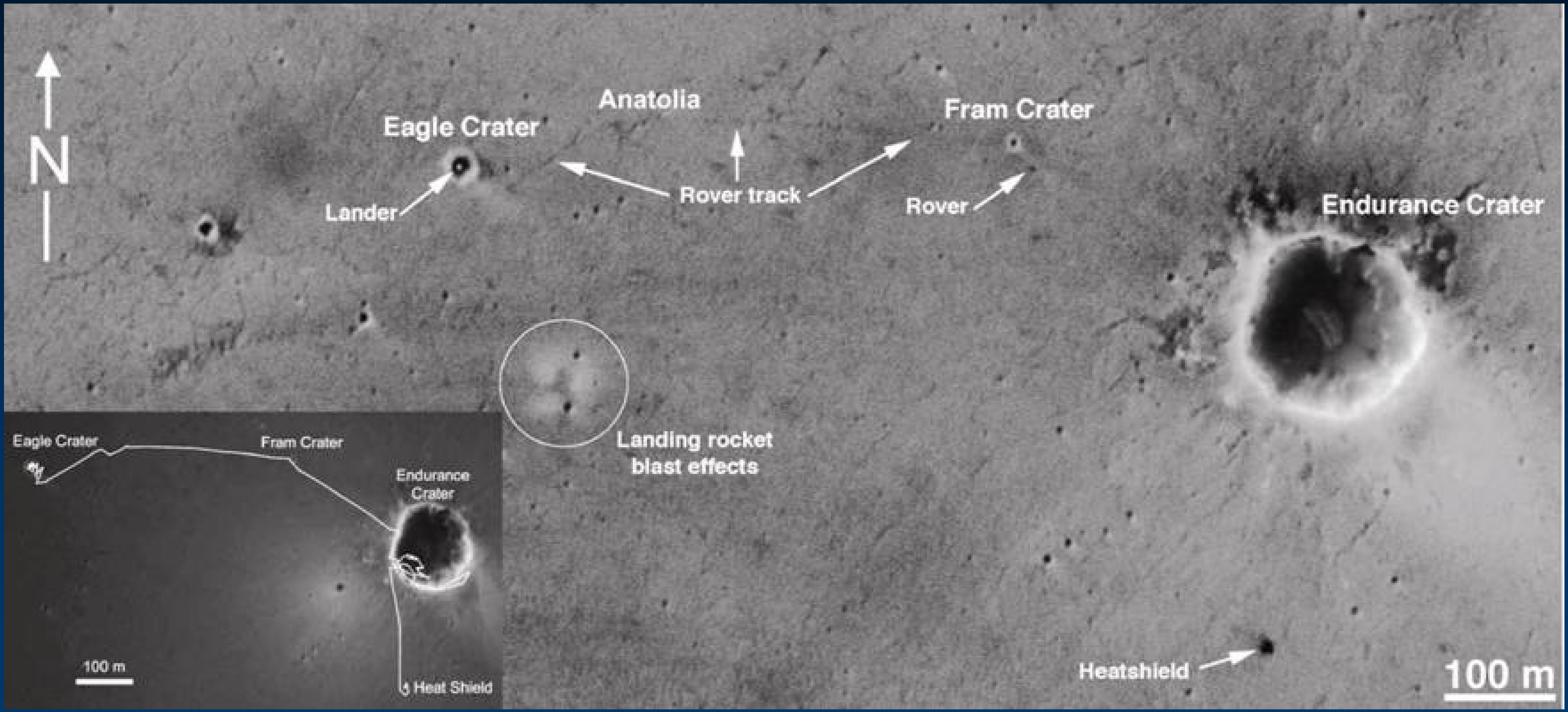
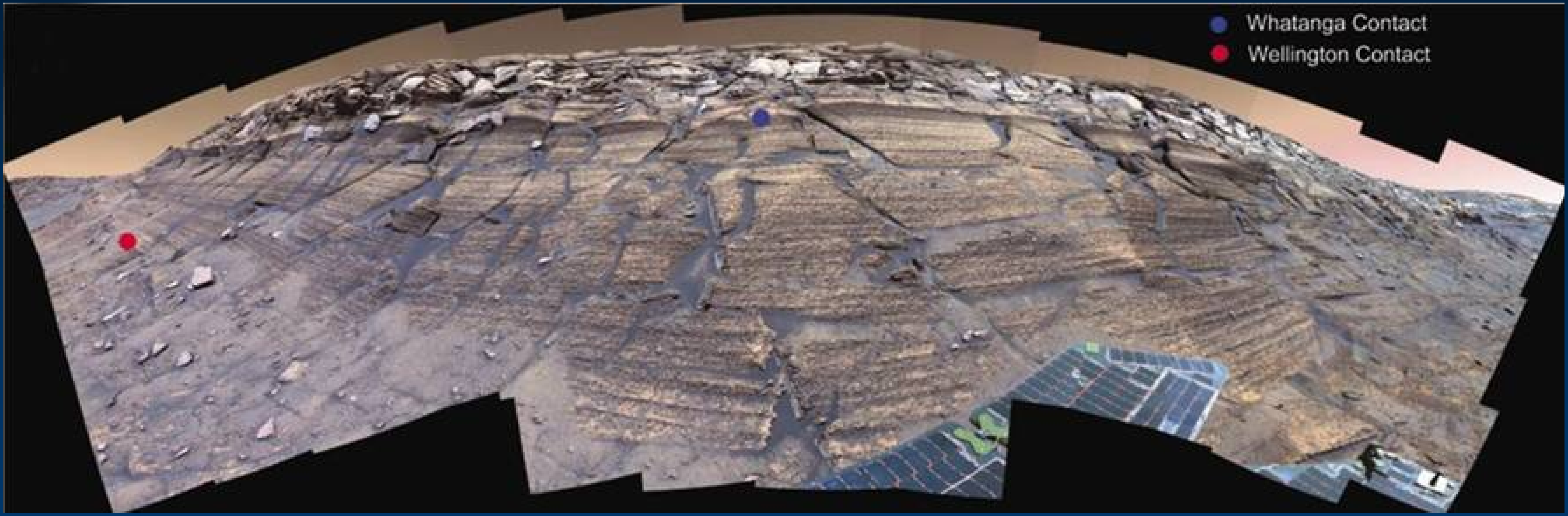


Image credit: NASA/JPL/MSSS

‘Burns’ formation at Burns cliff, SE rim Endurance crater



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‘Burns’ formation at Burns cliff, SE rim Endurance crater

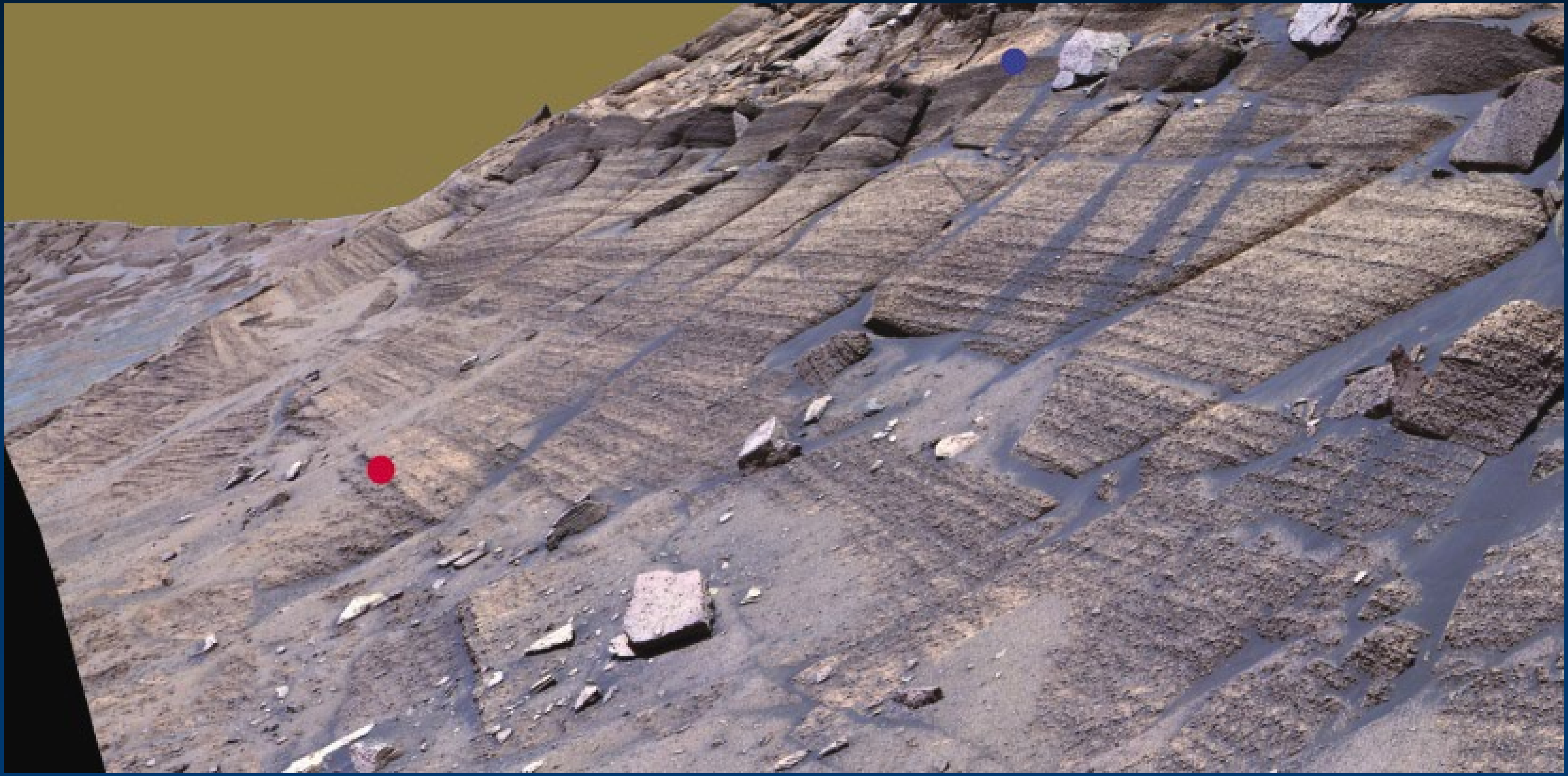
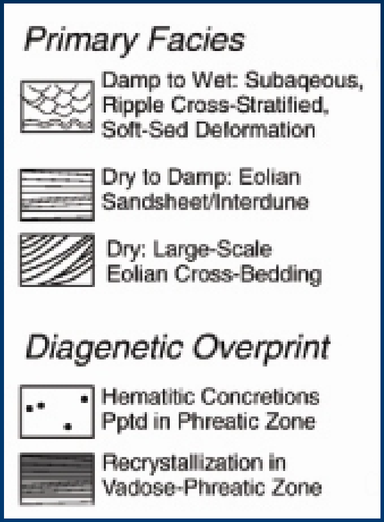
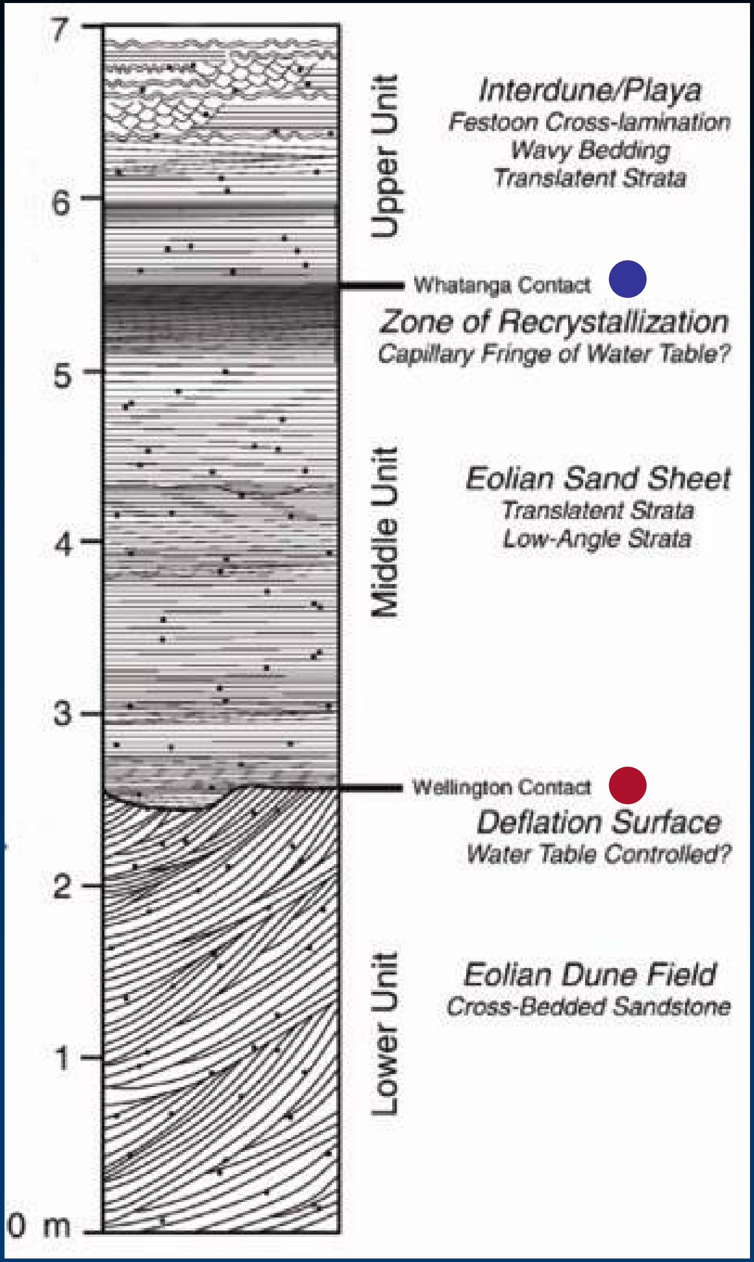


Image credit: NASA/JPL/MSSS

Stratigraphy of ‘Burns’ formation





(after Grotzinger et al., 2005)

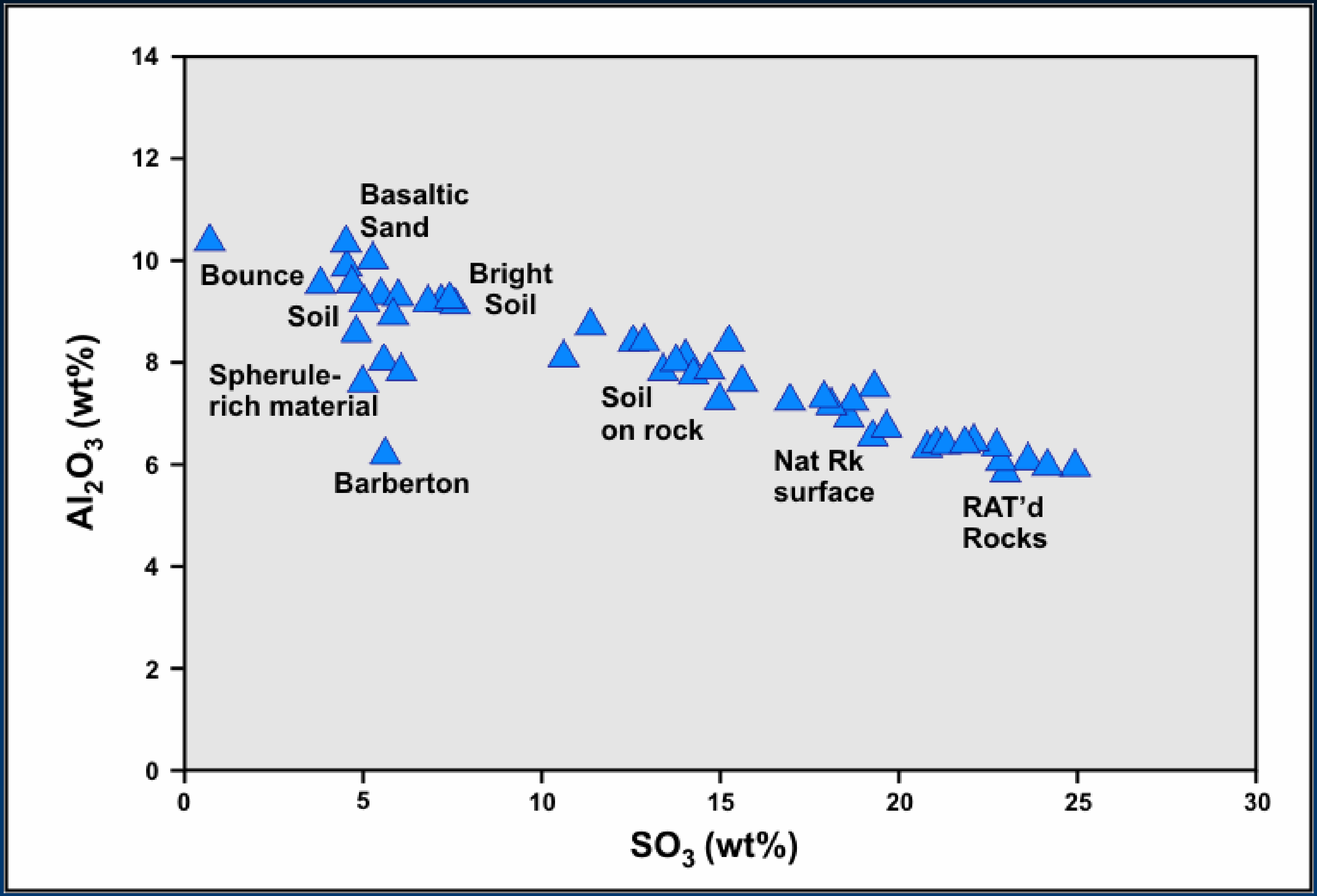
Average Mineralogy (vol %), Eagle crater

Mini TES (Miniature Thermal Emission Spectroscopy)

	Average (13)	Range
Sulfate	25	10 - 35
Hematite	24	0 - 45
Sheet silicates (e.g. micas/clay)	3	0 - 20
Glass	15	5 - 25
Oxide/hydroxide	6	0 - 20
Feldspar	12	0 - 45
Olivine	9	0 - 20
Pyroxene	6	0 - 15

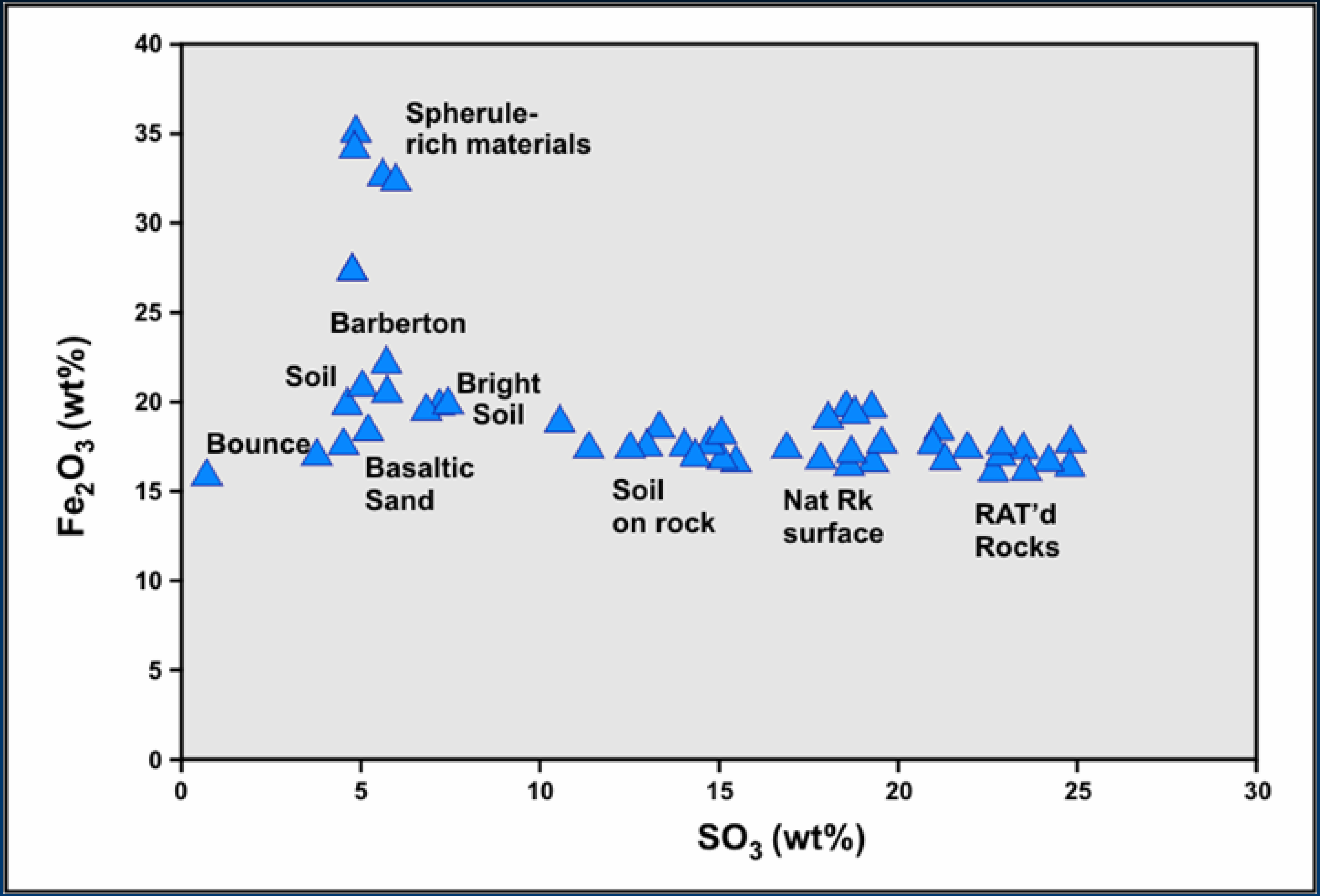
(after Christiansen et al., 2004)

Meridiani Materials APXS (Alpha Particle X-ray Spectroscopy)



(after Jolliff et al., 2006)

Meridiani Materials APXS
(Alpha Particle X-ray Spectroscopy)



(after Jolliff et al., 2006)

Features of Martian Materials

- High SO_3 content (present as Ca - and Mg - sulfates + jarosite)
- High Cl and Br content
- Features in ‘Burns’ formation imply reworked sand and evaporative minerals derived from an evaporative basin (interdune depression or playa lake)

Jarosite – Alunite Minerals

$AB_3\ (XO_4)_2\ (OH)_6$

A = K, Pb, Ca, Na, H_3O^+, NH_4^+, Sr, REE

B = Fe, Al, (Cu, Zn)

XO_4 = SO_4^{2-}, PO_4^{3-}, AsO_4^{3-}

OH sites can contain halides

Common members of the Jarosite – Alunite family

Alunite	$K\ Al_3(SO_4)_2(OH)_6$
Jarosite	$K\ Fe_3(SO_4)_2(OH)_6$
Natroalunite	$Na\ Al_3(SO_4)_2(OH)_6$
Natrojarosite	$Na\ Fe_3(SO_4)_2(OH)_6$
Hinsdalite	$Pb\ Al_3(PO_4)(SO_4)(OH)_6$
Plumbogummite	$Pb\ Al_3H(PO_4)_2(OH)_6$

Features of Martian Materials

- Acidic – pH ~ 2 - jarosite
- Oxidizing – Fe^{3+}
- Sulfate rich environment

Jarosite – Alunite Formation on Earth

- in the supergene zone of many ore deposits
- in weathering profiles unrelated to mineralization, particularly in micaceous, sulfide-bearing sediments
- as an authigenic component of Quaternary salt-lake sediments in Australia or as an authigenic precipitate from acid crater-lake waters
- as products of sulfate aeolinites in the playa-dune system of White Sands, New Mexico

Jarosite – Alunite Formation on Earth

- as diagenetic component of Tertiary to Quaternary sediments in South Australia.
- as evaporite crusts precipitated from acid sulfate and iron-rich waters of Rio Tinto, Southern Spain.
- in acid sulfate soils occurs where pyrite in previously saturated soils is exposed to oxygen

Locations and Distribution of Jarosite from Different Geological and Climatic Settings throughout Australia

Supergene Jarosite Formation

$$FeS_2 + \tfrac{7}{2}O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

Pyrite

$$2\ Fe^{2+} + 1\tfrac{1}{2}\ O_2 \longrightarrow Fe^{3+} + H_2O$$

$$4KAlSi_3O_8 + 22H_2O \longrightarrow 4K^+ + 4OH^- + Al_4Si_4(OH)_8 + 8H_4SiO_4$$

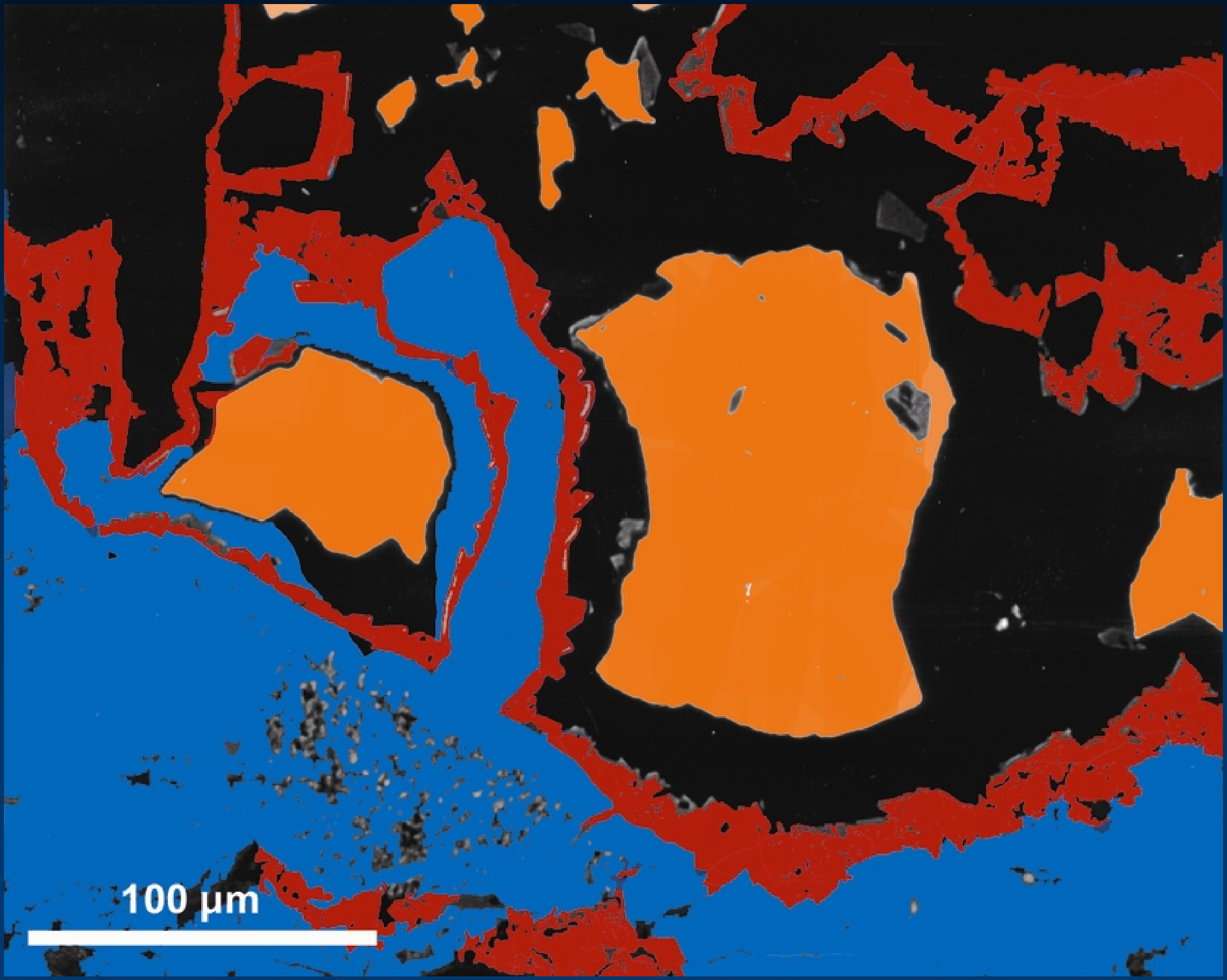
Feldspar

Kaolinite

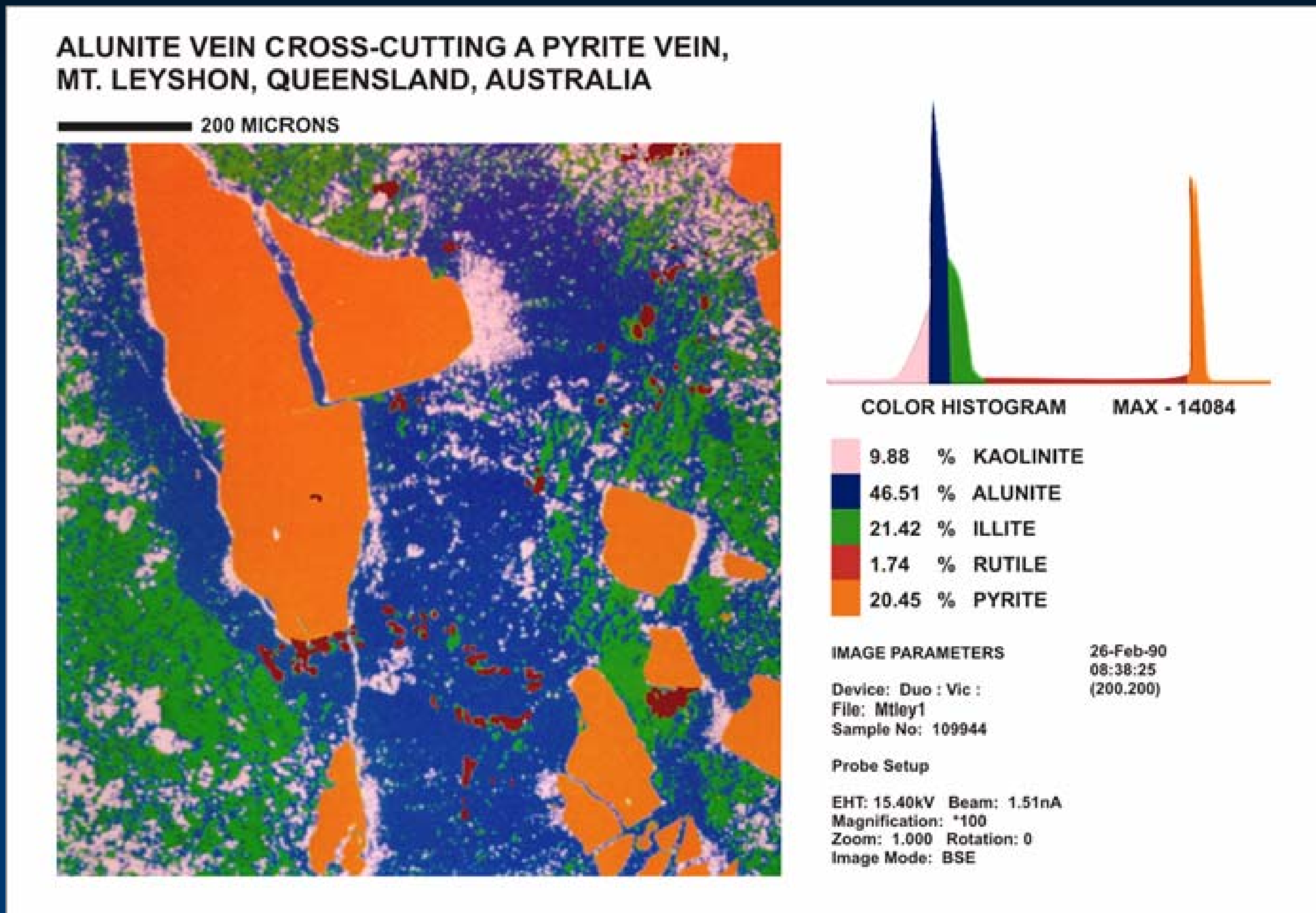
$$3Fe^{3+} + K^+ + 2SO_4^{2-} + 6OH^- \longrightarrow K\ Fe_3(SO_4)_2(OH)_6$$

Jarosite Vein (yellow) within the Weathering Profile at the Mt Leyshon Gold Mine, Queensland

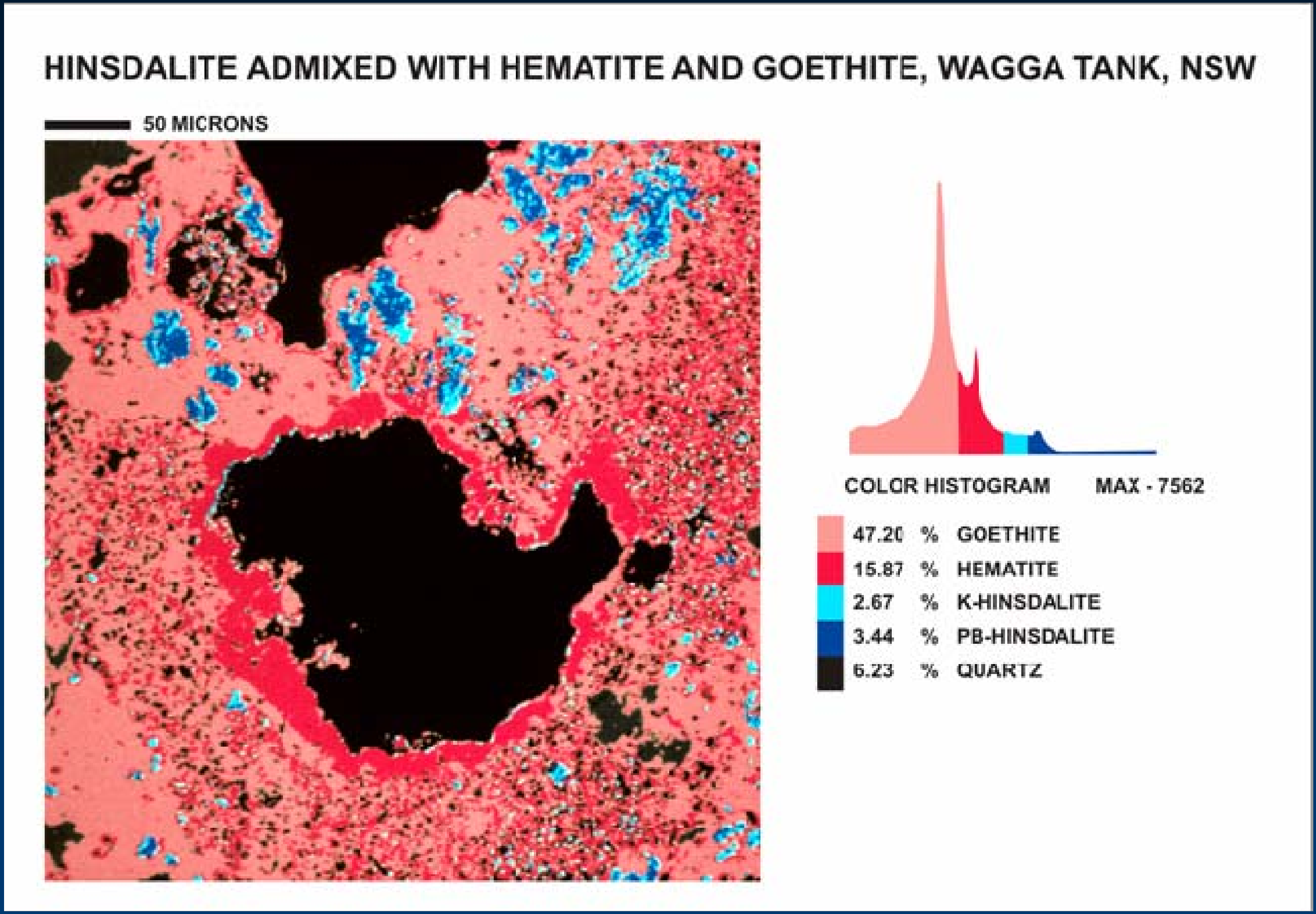
Pyrite, Jarosite and Alunite at Mt Leyshon showing Pyrite (orange) oxidising to Jarosite (red) and Alunite (blue)



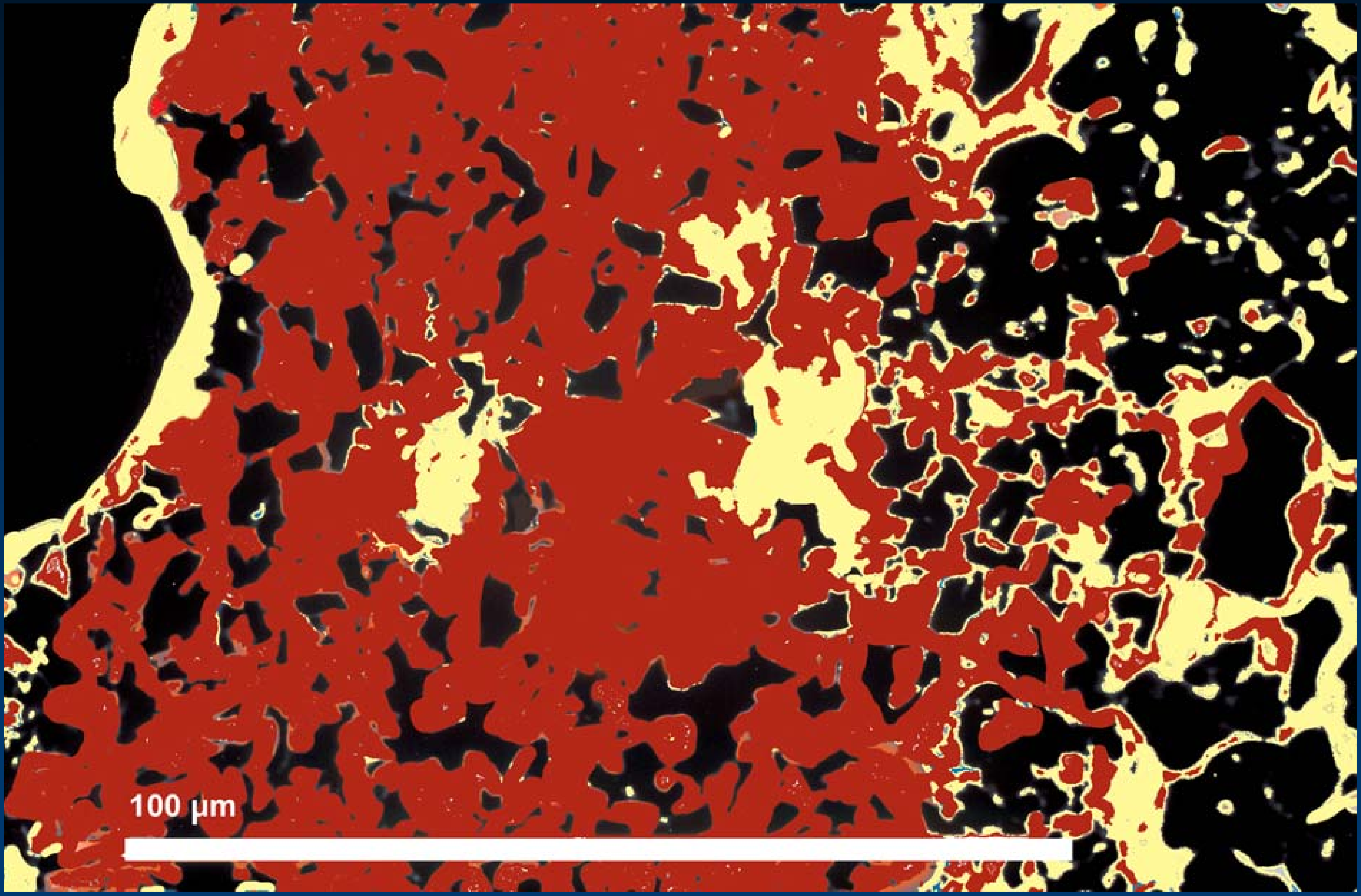
Alunite (blue) from Weathering of Pyrite, intimately associated with Kaolinite and Rutile, Mt Leyshon



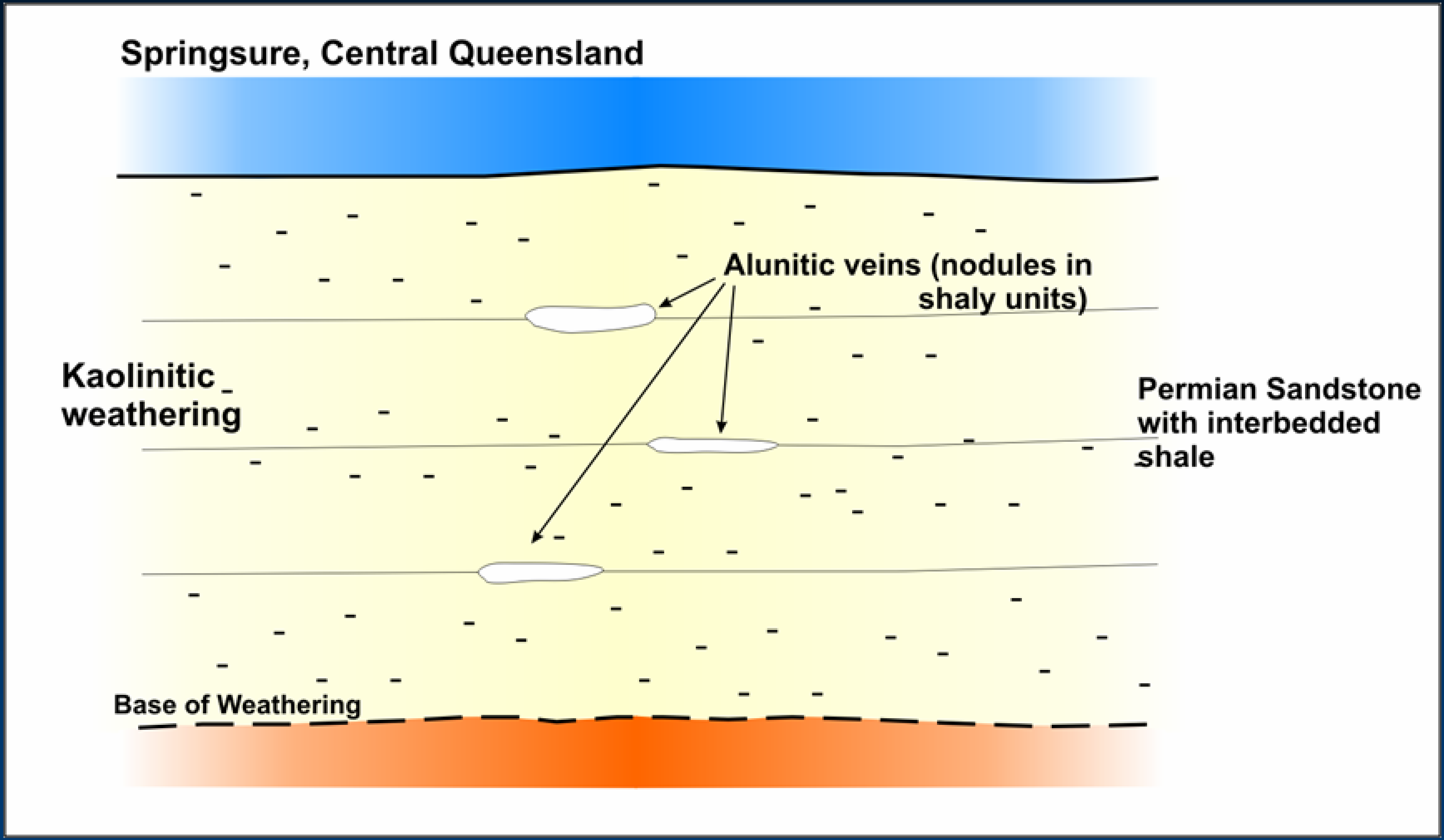
Pb and K rich Hinsdalite (blue) from Wagga Tank, NSW, intimately associated with Goethite (pink) and Hematite (red). The Hinsdalite shows compositional variations at the micron scale.



Plumbojarosite (red) intimately associated with Goethite (cream), Currawang, NSW.

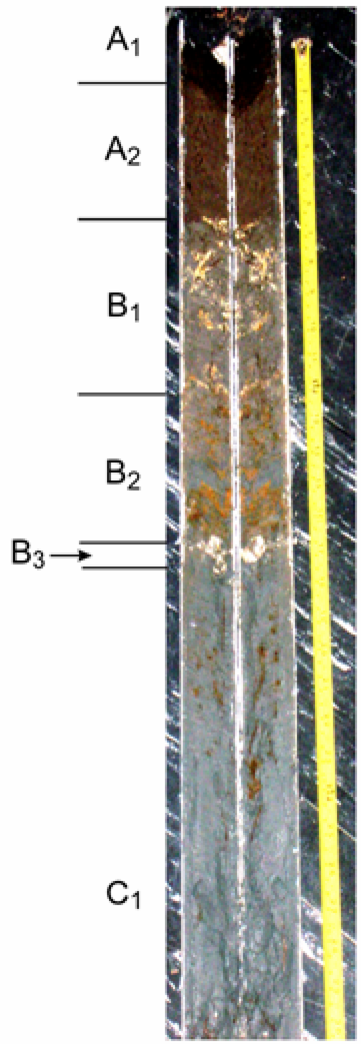


Jarosite / Alunite from Non – Mineralized Weathering Profiles



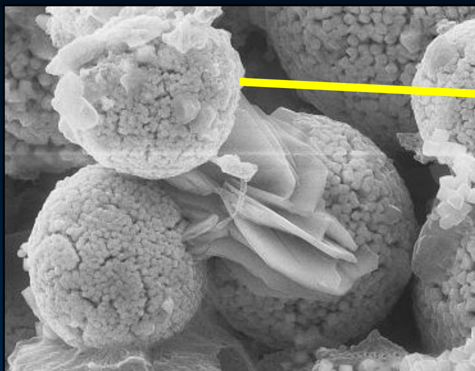
Jarosite from Acid Sulfate Soils

1.5m Vertical Profile, Mays Swamp, Kempsey area, NSW
(after Isaacson et al., 2006)



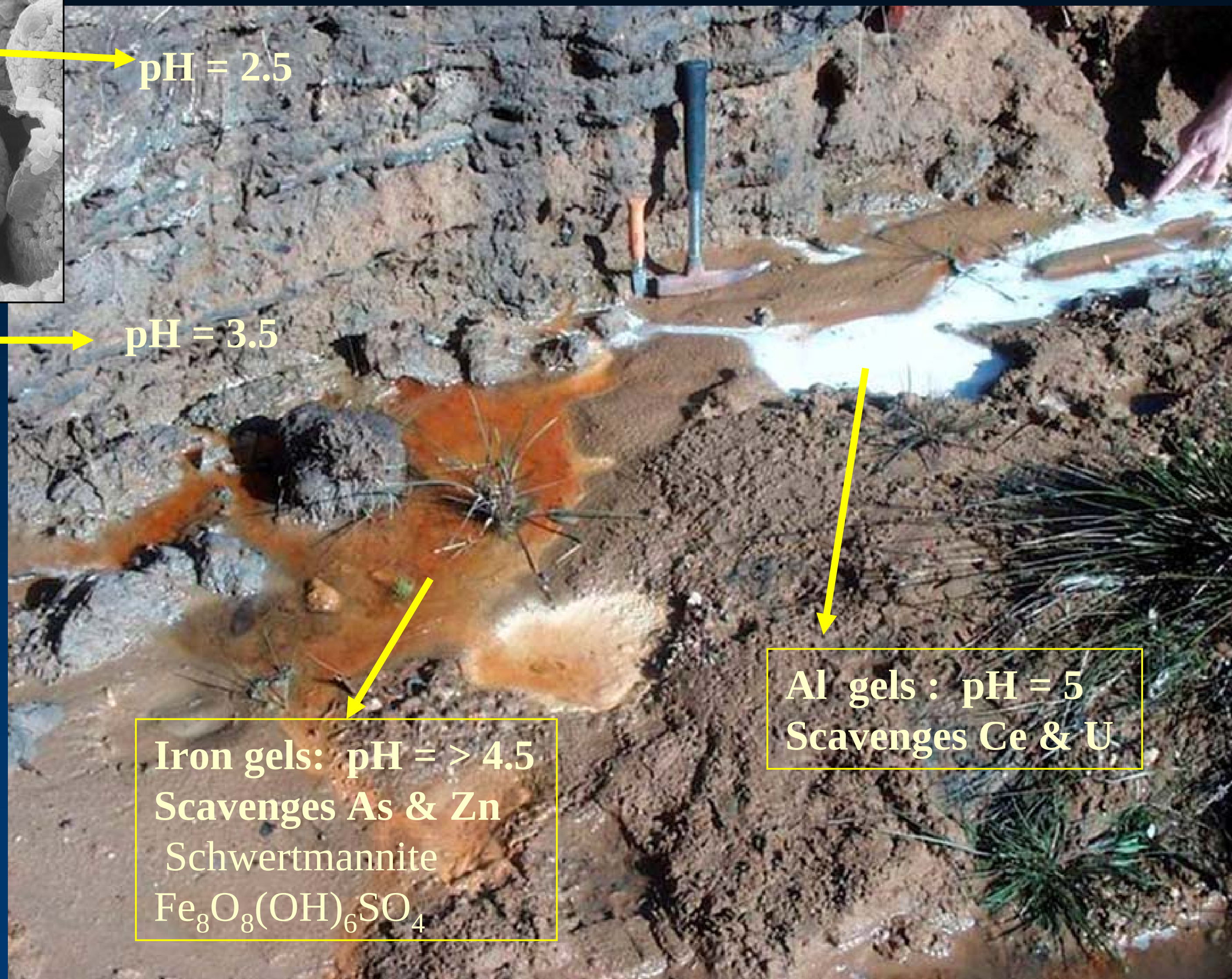
Horizon ID	Description
A_1	Black, rich in organic matter, peat like sediment
A_2	Lighter brown, alluvial like sediment, organic matter in the form of root cavities present
Oxidised B_1	Grey thick, estuarine sediment interlaid with prevalent yellow **jarosite** crystalline mottles associated with root cavities
Oxidised B_2	Grey thick, estuarine sediment interlaid with prevalent red/brown **jarosite/goethite** crystalline mottles associated with root cavities. Crystals up to 1cm prevalent
Transition B_3	Shell layer with thick grey estuarine sediment occurring between shell fragments. **Gypsum** immediately above shells
Reduced C_1	Blue/Grey thick estuarine sediment, red/brown goethite/hematite mottles occurring around limited root cavities

Jarosite from Acid Sulfate Soils
Mt Torrens, SA (after Fitzpatrick et al., 2003)

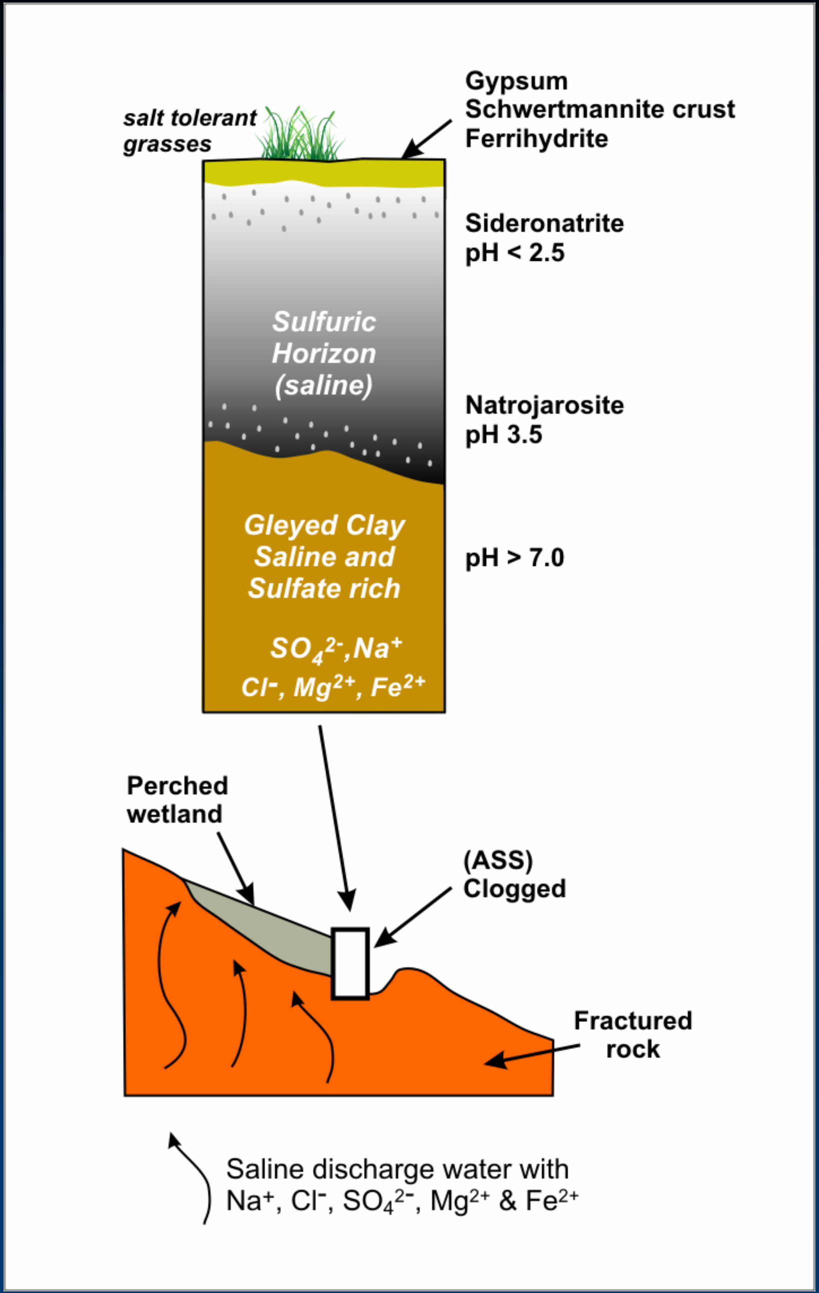


Natrojarosite

- Extreme acidity
- Extreme salinity

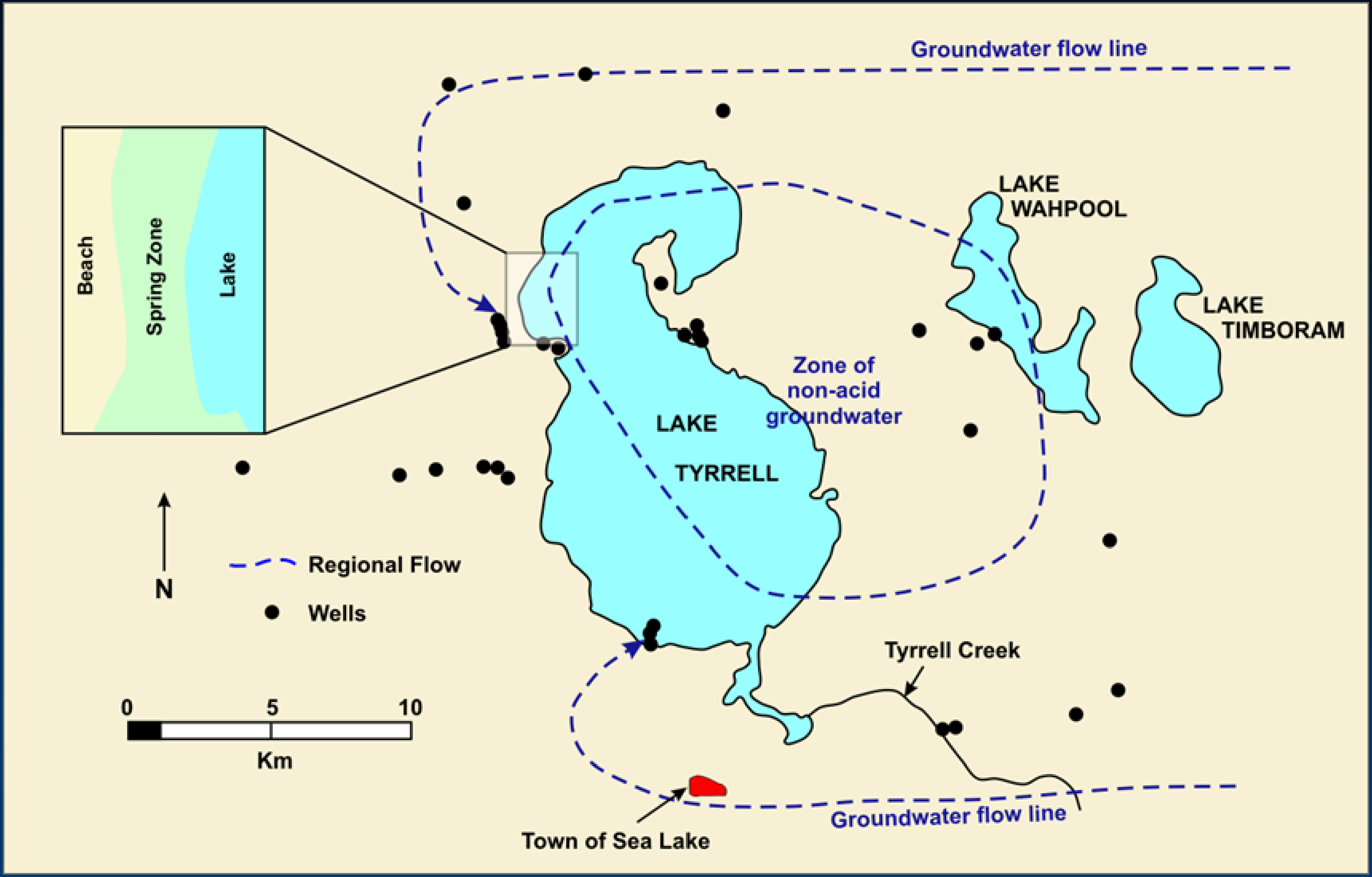


Jarosite in Acid – Sulfate Soils



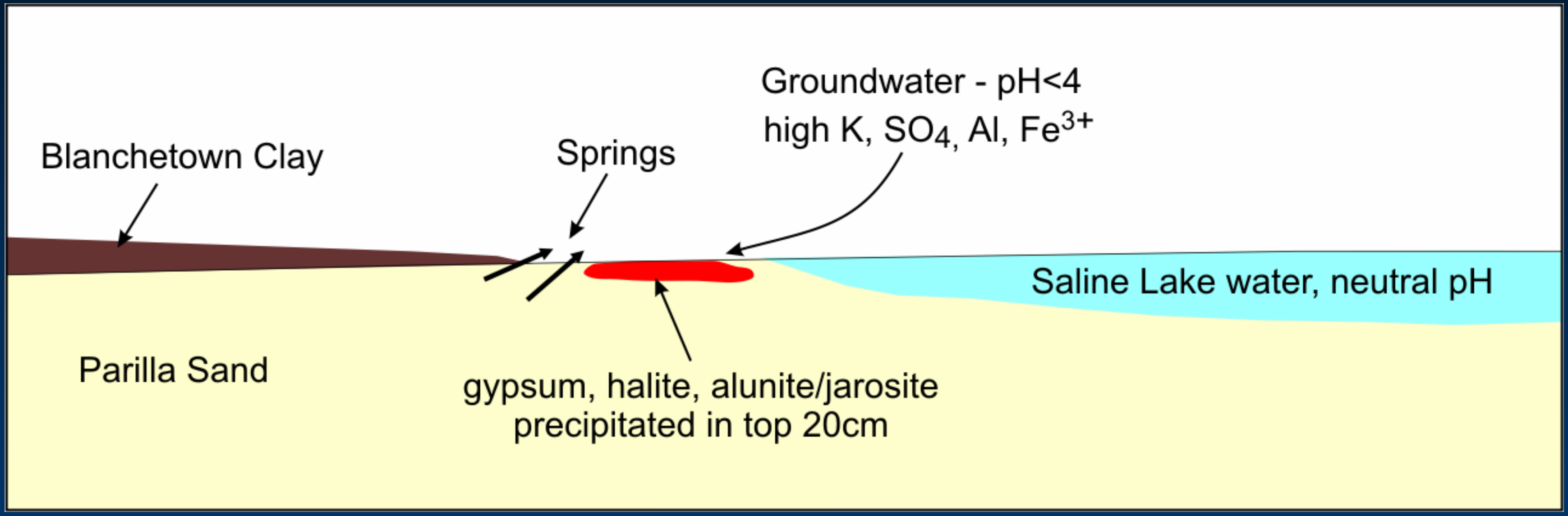
(after Fitzpatrick et al., 2000)

Jarosite Associated with Playa Lakes



Lake Tyrrell, Victoria (after Long et al., 1992)

Jarosite Associated with Playa Lakes

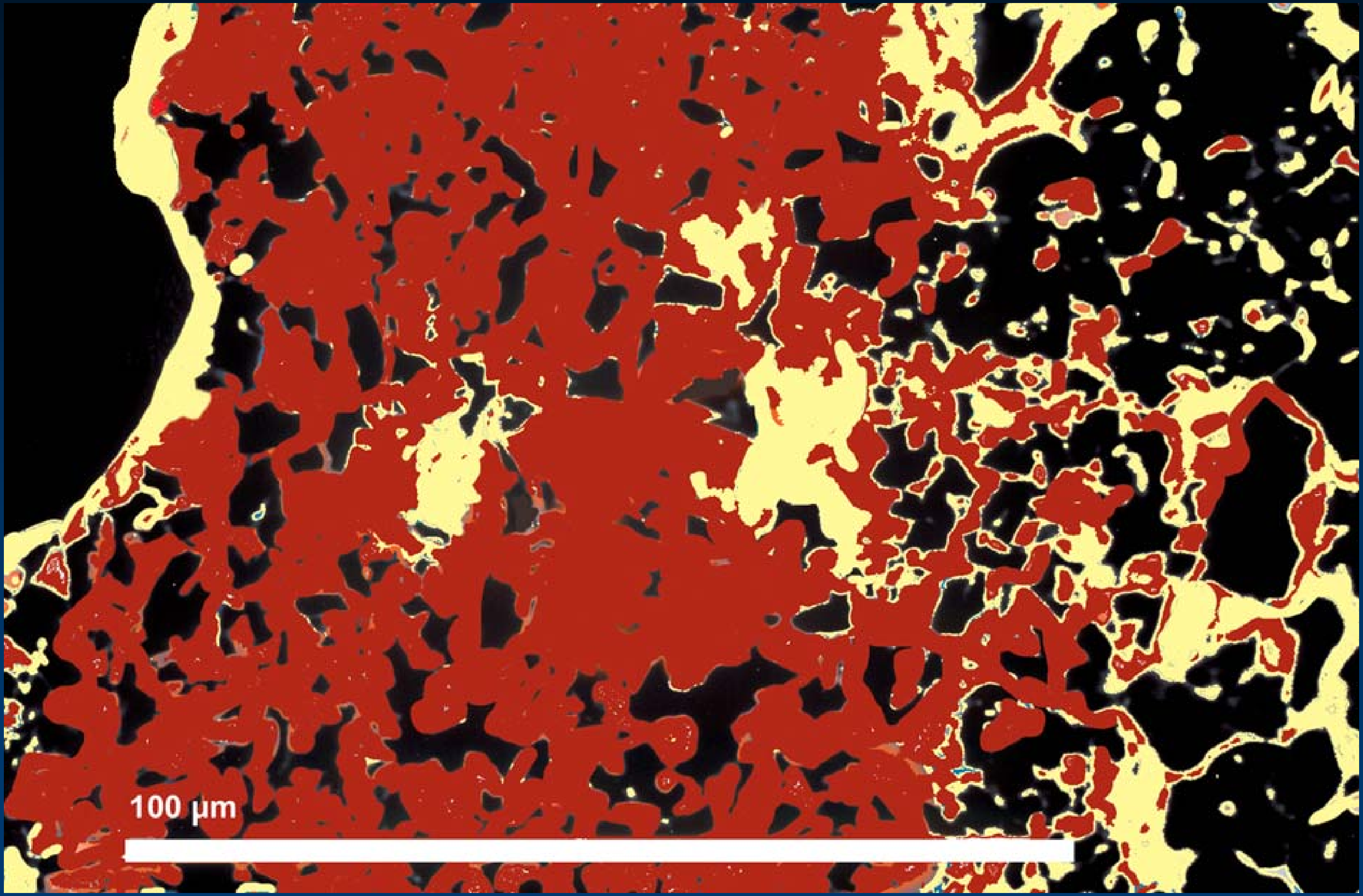


Lake Tyrrell, Victoria **(after Long et al., 1992)**

Implications of Martian Jarosite Occurrences

- **Fe Oxides (goethite) occur intimately with jarosite – Gusev crater**

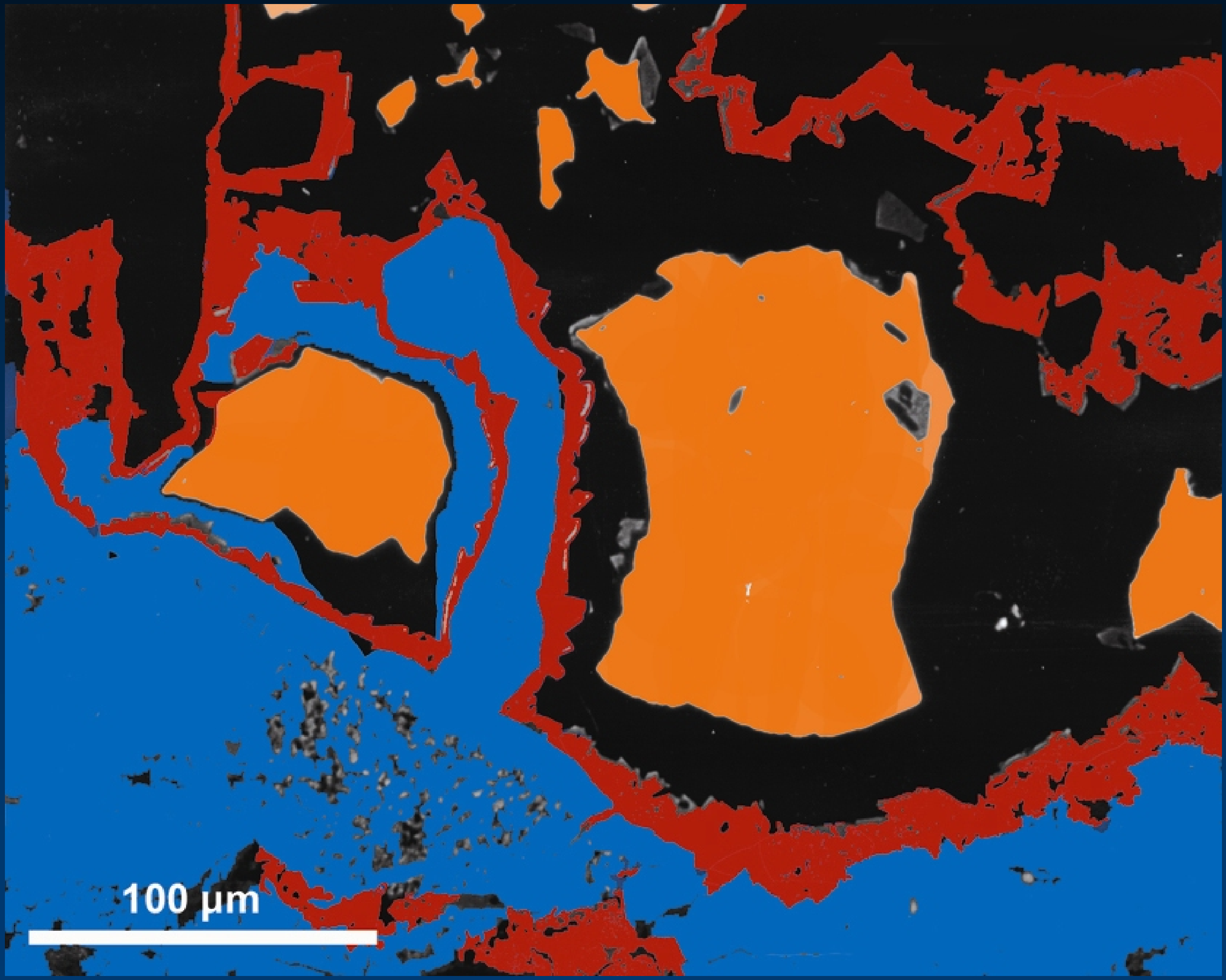
Plumbojarosite (red) intimately associated with Goethite (cream), Currawang, NSW.



Implications of Martian Jarosite Occurrences

- Fe Oxides (goethite) occur intimately with jarosite – Gusev crater
- Studies (~1930) suggest that goethite forms first
- Our studies imply that jarosite may form directly from pyrite

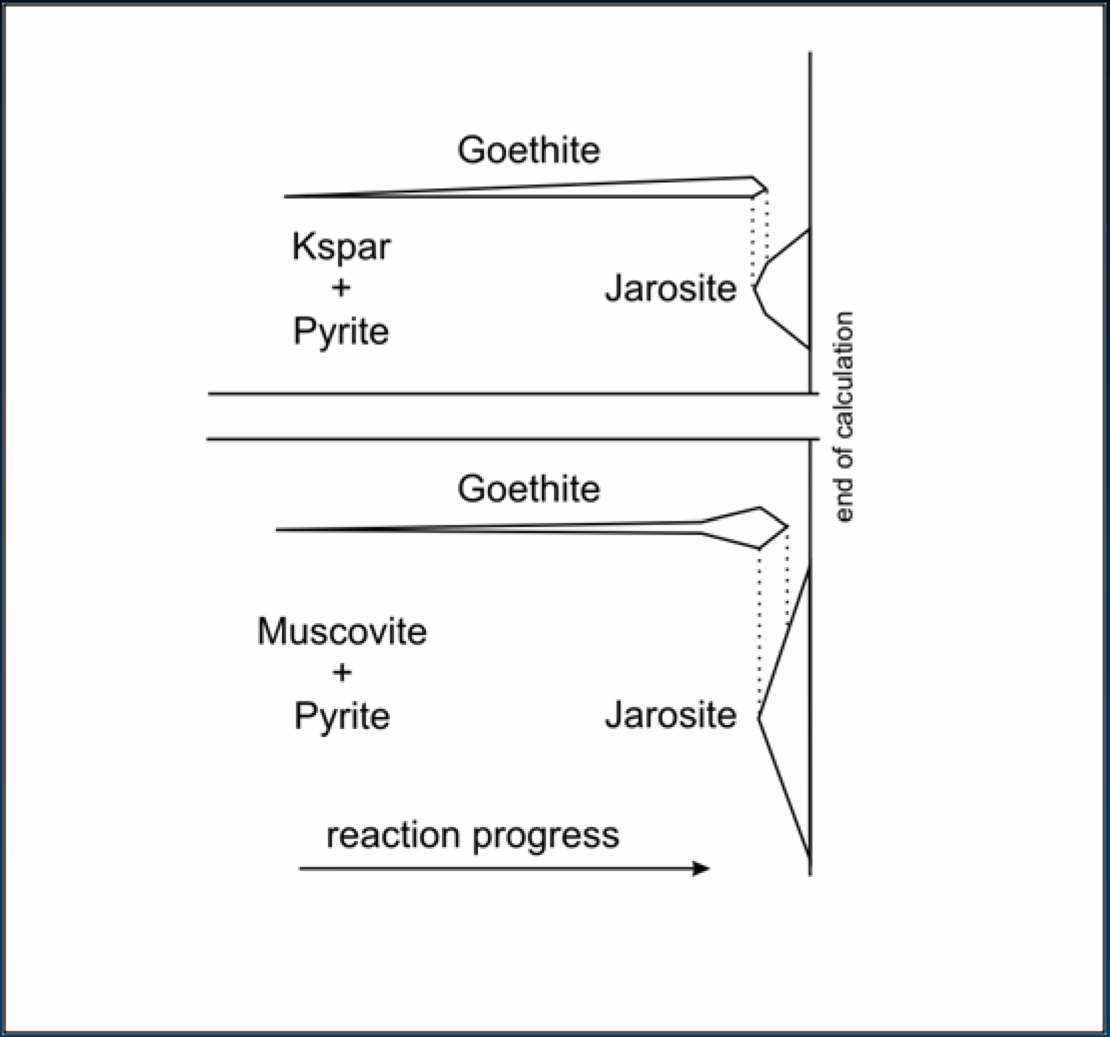
Pyrite, Jarosite and Alunite at Mt Leyshon showing Pyrite (orange) oxidising to Jarosite (red) and Alunite (blue)



Implications of Martian Jarosite Occurrences

- Fe Oxides (goethite) occur intimately with jarosite – Gusev crater
- Studies (~1930) suggest that goethite forms first
- Our studies imply that jarosite may form directly from pyrite
- Thermodynamic studies show amounts of goethite formed during weathering relative to jarosite, is affected by the original rock

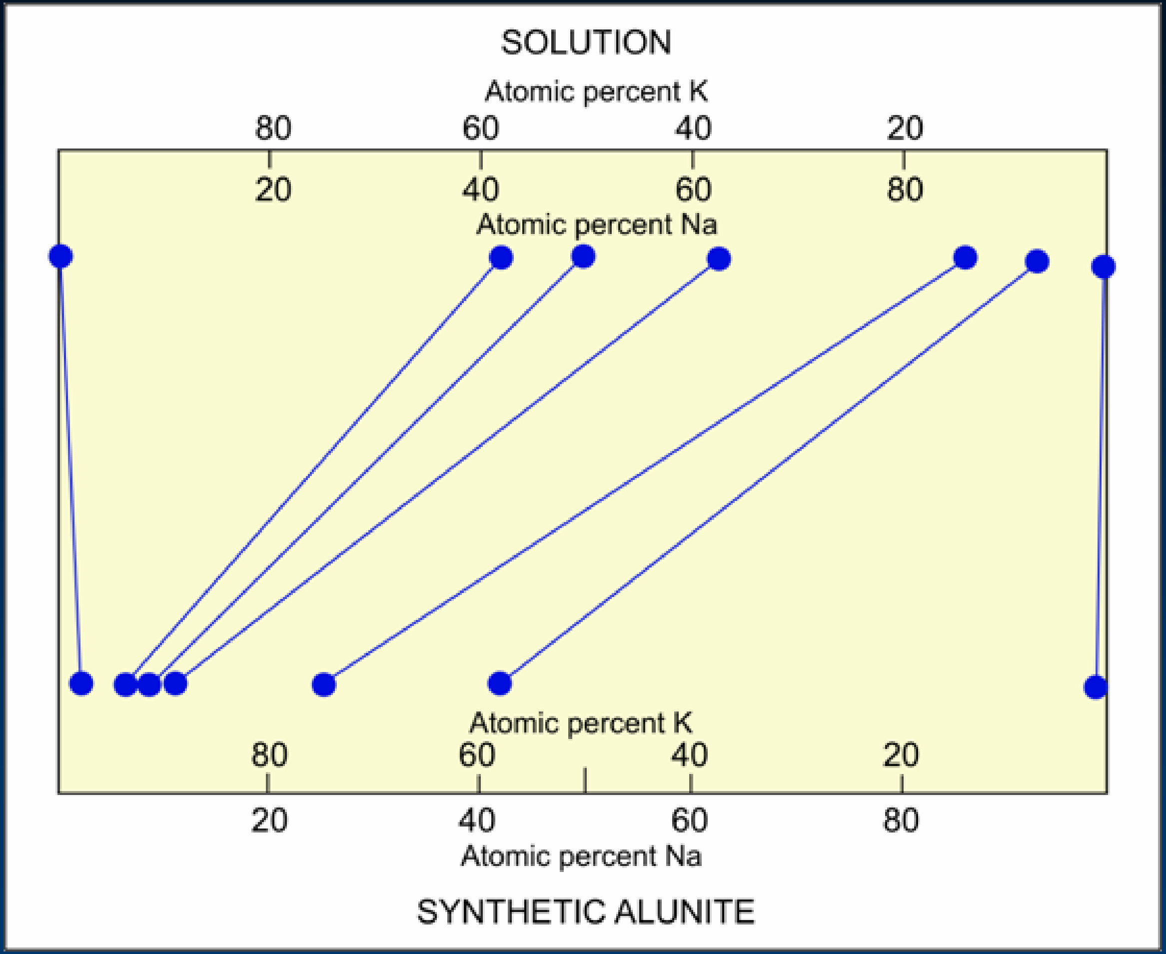
Thermodynamic studies of Jarosite Formation



Calculated paragenesis showing relative masses of minerals formed during the reaction of meteoric water with pyrite and K-feldspar or muscovite (after Bladh, 1982)

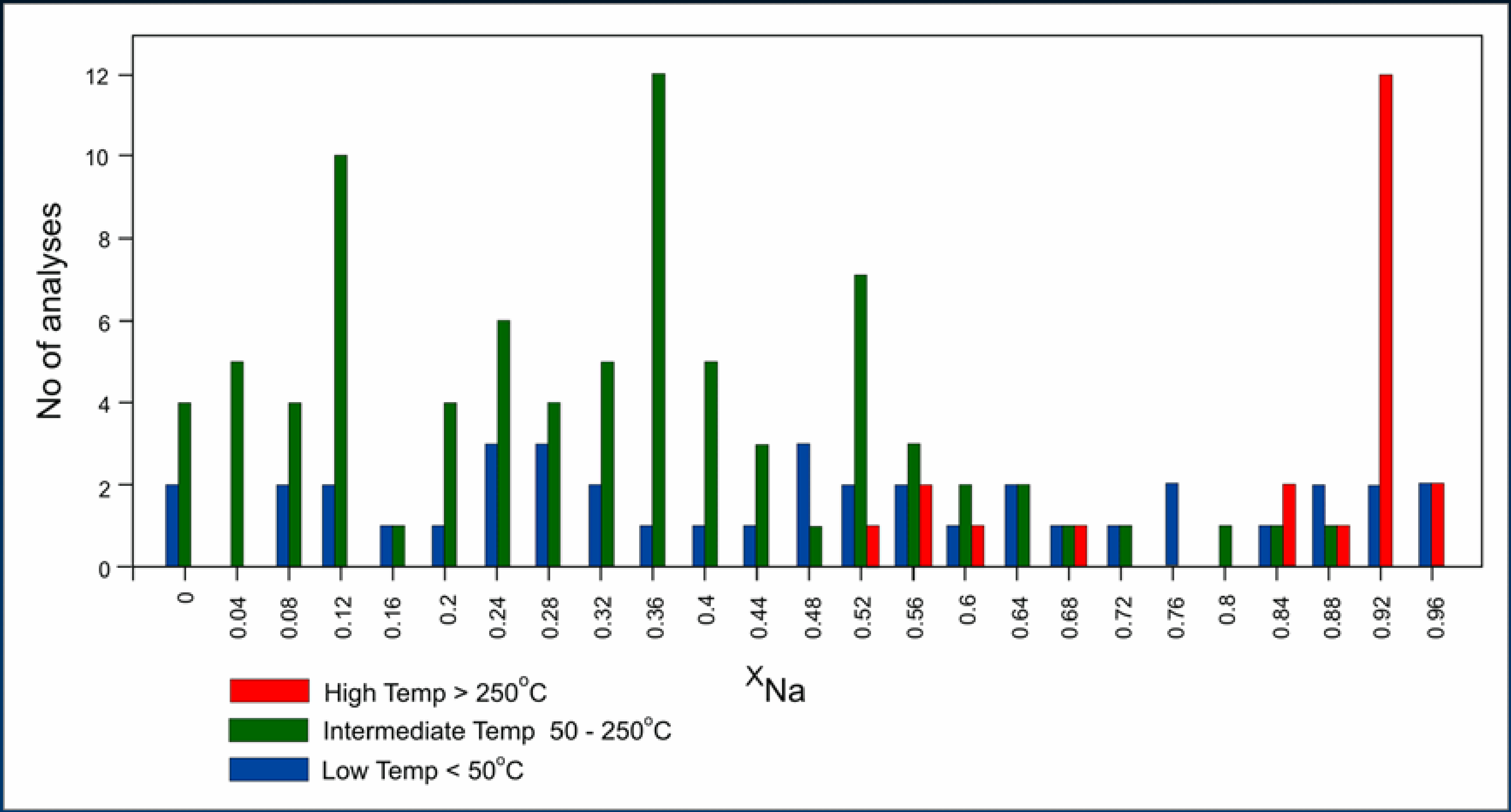
Experimental Studies of Alunite Formation
1 – Fluid Composition

K – rich alunites preferred



Relative atomic percentages of potassium and sodium in synthetic alunite and in solution prior to the precipitation of alunite (after Parker, 1962)

Experimental Studies of Alunite Formation
2 – Temperature



Compositional data on natural alunites (after Stoffregen and Cygan, 1990)

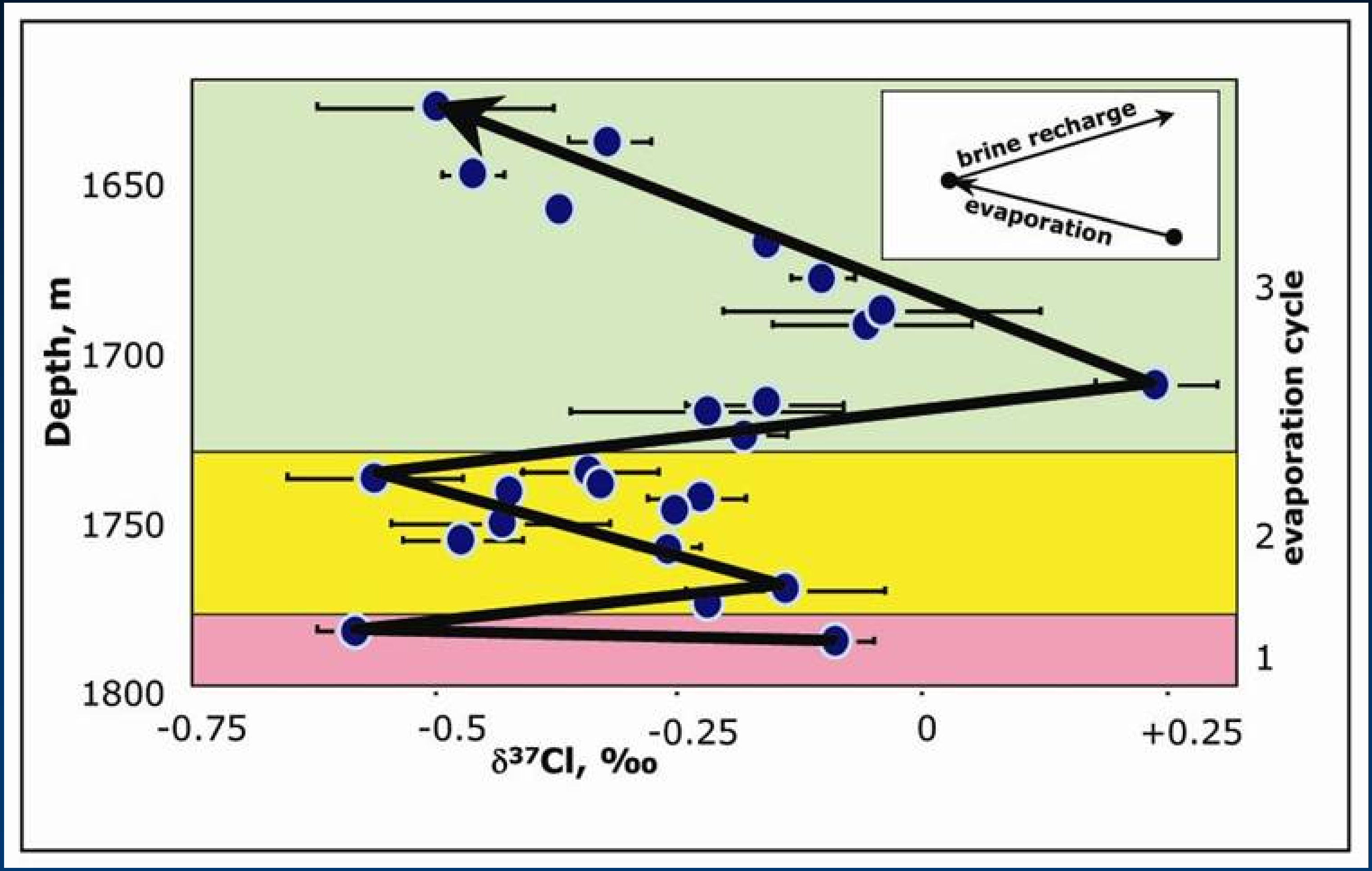
Jarosite – Alunite Minerals

$A\ B_3\ (XO_4)_2(OH)_6$

A	B	OH
NH_4^+	Fe^{3+}	OH^-
H_3O^+	Al^{3+}	Cl^-
Na^+		Br^-
K^+		

What ions are actually in Martian Jarosite ?

Chlorine Isotope Profile in a succession of Evaporite Beds



Jarosite – Alunite Minerals on Earth

- Jarosite-alunite minerals commonly found intimately associated with goethite
- Jarosite-alunite minerals form under acidic conditions and commonly under saline conditions → gypsum + halite
- Na-rich alunite favoured by higher temperature
- Na-rich alunite needs extremely Na rich fluid to form from solution
- More analog, experimental thermodynamic studies needed

Jarosite – Alunite Minerals on Mars

Questions to be answered by retrieval missions:

- Composition in A sites (Na^+, K^+, NH_4^+, H_3O^+). What does this tell us about the composition of the fluid from which it formed ?
- Composition in B sites. Does this provide information about the fluid/rock interaction ?
- Composition in (OH) sites. Are halides incorporated ? If so, can they indicate about evaporation/recharge ?
- O, H, S, Cl isotopes can be useful in defining formation conditions

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