Chloride Deposits on Mars: Chlorine from the Sky, or Chlorine from the Rocks?

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THE UNIVERSITY OF CHICAGO

Department of the Geophysical Sciences

Overview/Problem

Chloride-rich deposits are abundant on the highlands of Mars

…But their origin is unconstrained

…Source of Cl? Environmental context?

Chloride deposits present on Mars

Geology, published online on 5 August 2015 as doi:10.1130/G36895.1

Late-stage formation of Martian chloride salts through ponding and evaporation

Brian M. Hynek[1,2], Mikki K. Osterloo[2], and Kathryn S. Kierein-Young[2]
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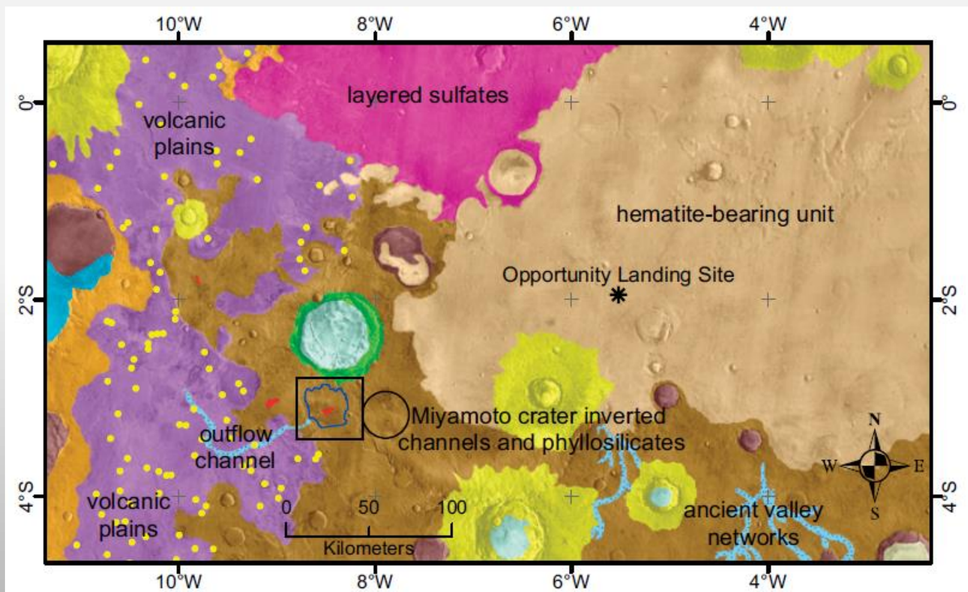
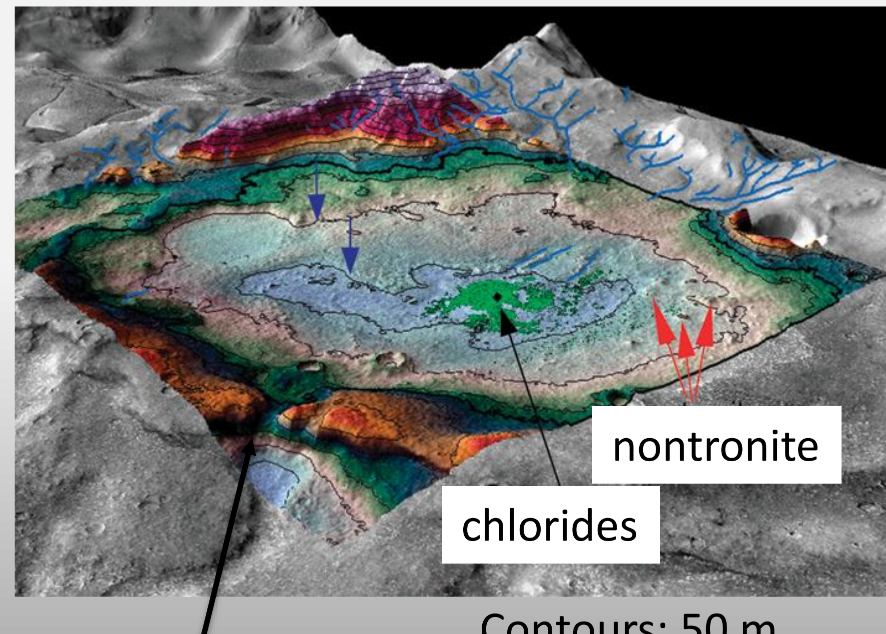
[2]Laboratory for Atmospheric and Space Physics, University of Colorado–Boulder, 3665 Discovery Drive, Boulder, Colorado 80303, USA





Hesperian: blue, purple, light brown
H-N: pink
Noachian: brown, orange

Outlet

Contours: 50 m
Width DTM: 26 km

Deposits can be quantified

1225 km^2 basin

Chloride deposit:

4 m max thickness

29.83 km^2

~ 0.12 km^3

~ 1.4×10^{11} kg NaCl

(assuming 45 % porosity)

Lake:

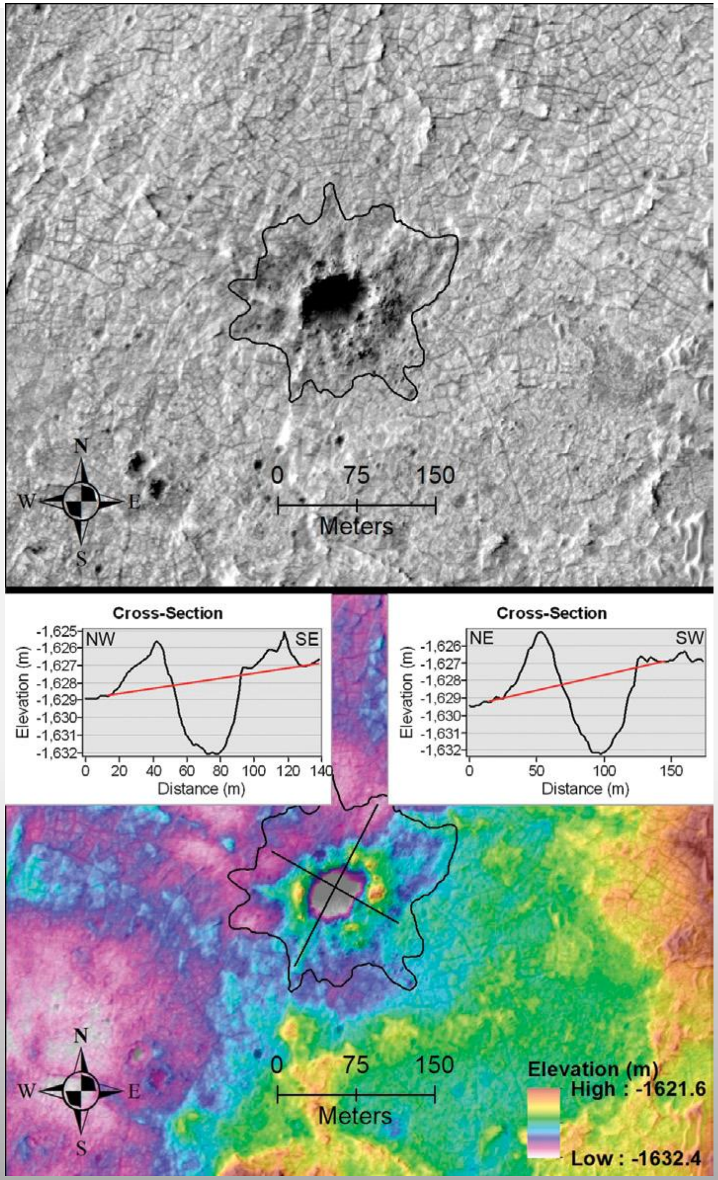
35.87 km^3

35.87×10^{12} kg H_2O

Salinity:

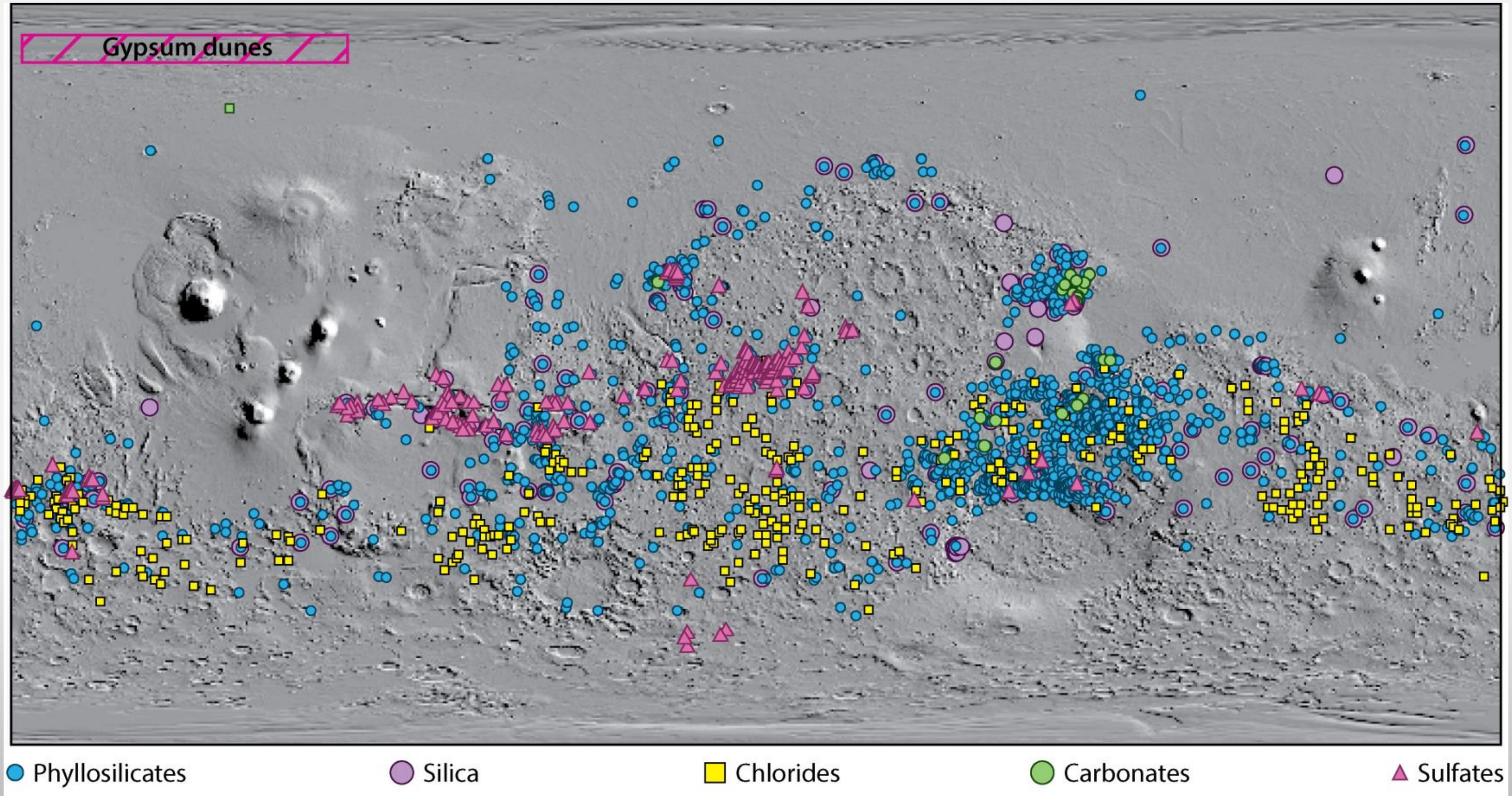
~ 4 g NaCl/kg H_2O

Hynek et al. (2015) *Geology*



Hynek et al. (2015)

Chlorides are widespread



Ehlmann BL, Edwards CS. 2014.
Annu. Rev. Earth Planet. Sci. 42:291–315

Where did the Cl come from?

A. Basaltic minerals (chlorapatite)
 ↳ Weathered/leached by water
  ↳ Discharged into lakes

B. Volcanic outgassing (HCl)
 ↳ Aerosols
  ↳ Dry deposition on surface (ClO_4^-?)
   ↳ "Washed" into lakes

Melwani Daswani & Kite, in prep.

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Cl abundance (e.g. Filiberto +, 2016, *M&PS*)

Martian breccia NWA 7034 (Santos +, 2015, *GCA*)

Fast apatite weathering (e.g. Hurowitz & McLennan, 2007, *EPSL*)

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Formation (e.g. Smith+, 2014, *Icarus*)

Phoenix WCL (Hecht +, 2009, *Science*)

Melwani Daswani & Kite, in prep.

Weathering basalt

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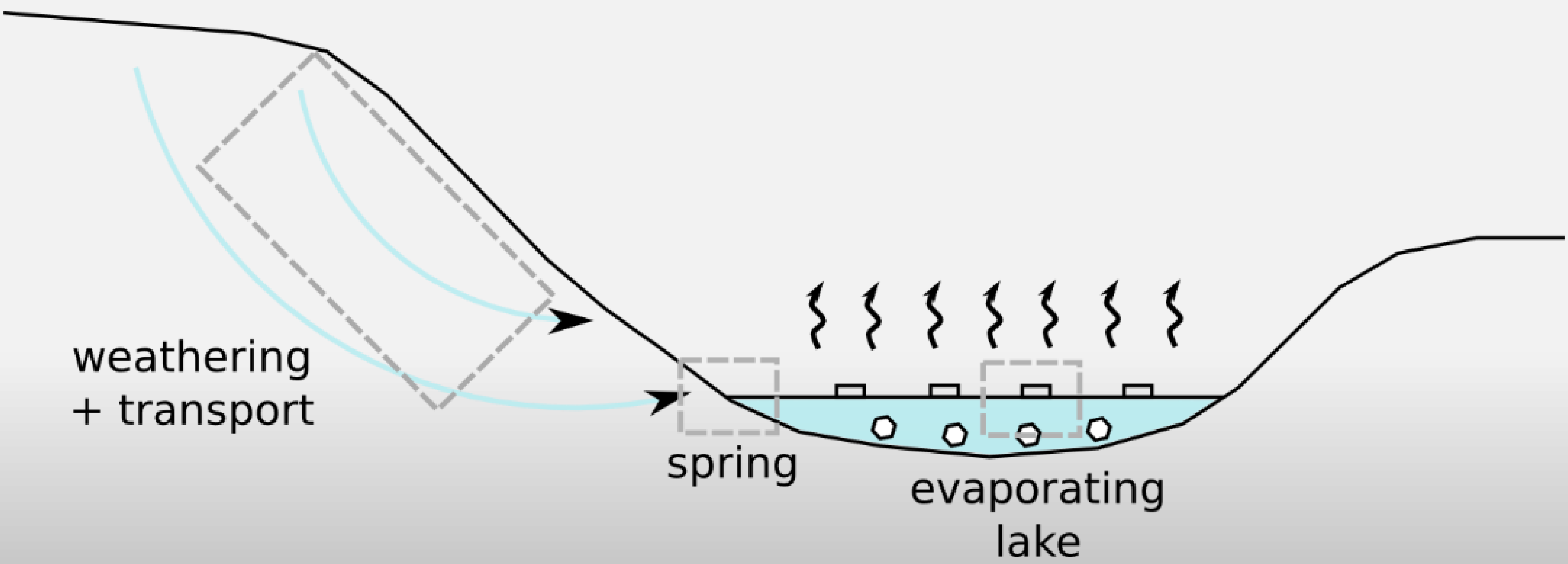
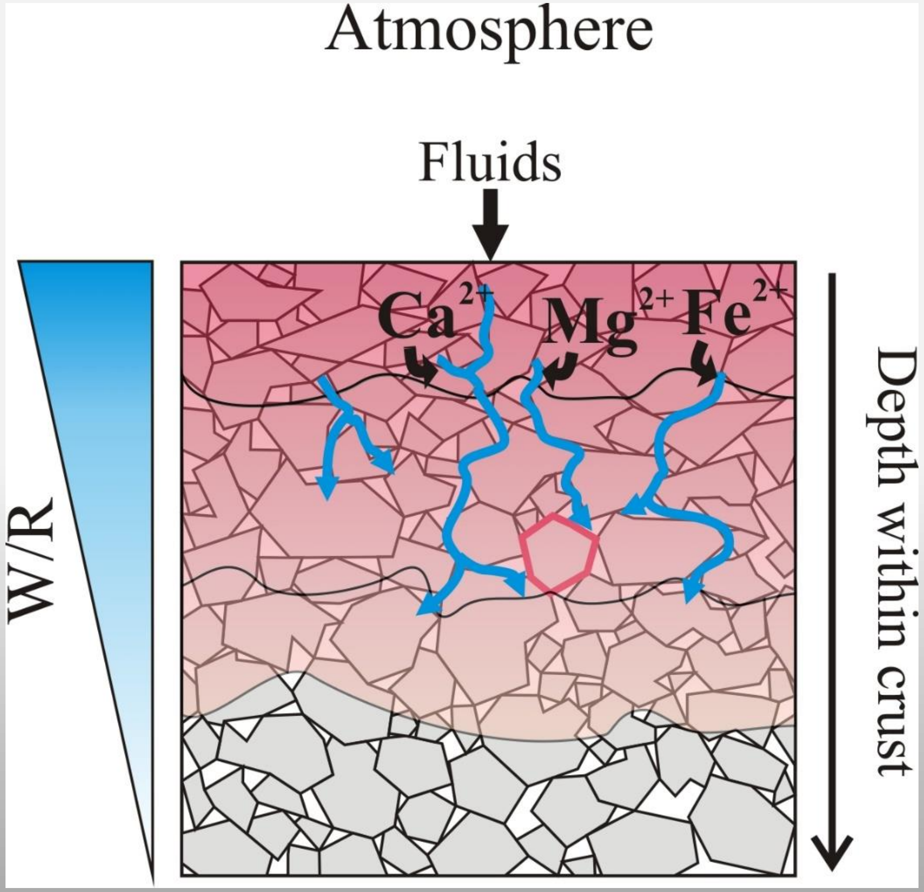


Thermochemical modeling method



- CHIM-XPT code (Reed, 1998)
- Debye-Hückel theory
- Soltherm thermodynamic database (mostly derived from Holland & Powell 2011 and ASU GEOPIG SUPCRT database)

Allows computations of:

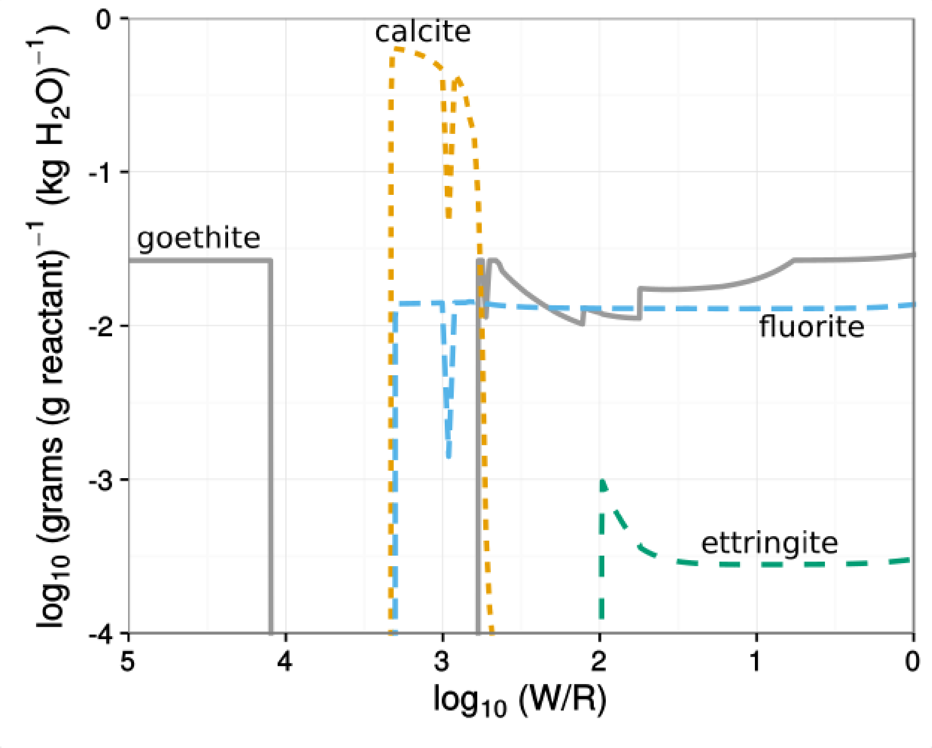
- mineral stabilities and precipitation
- aqueous speciation
- mineral-gas-liquid equilibria
- enthalpies, P-T, pH, Eh

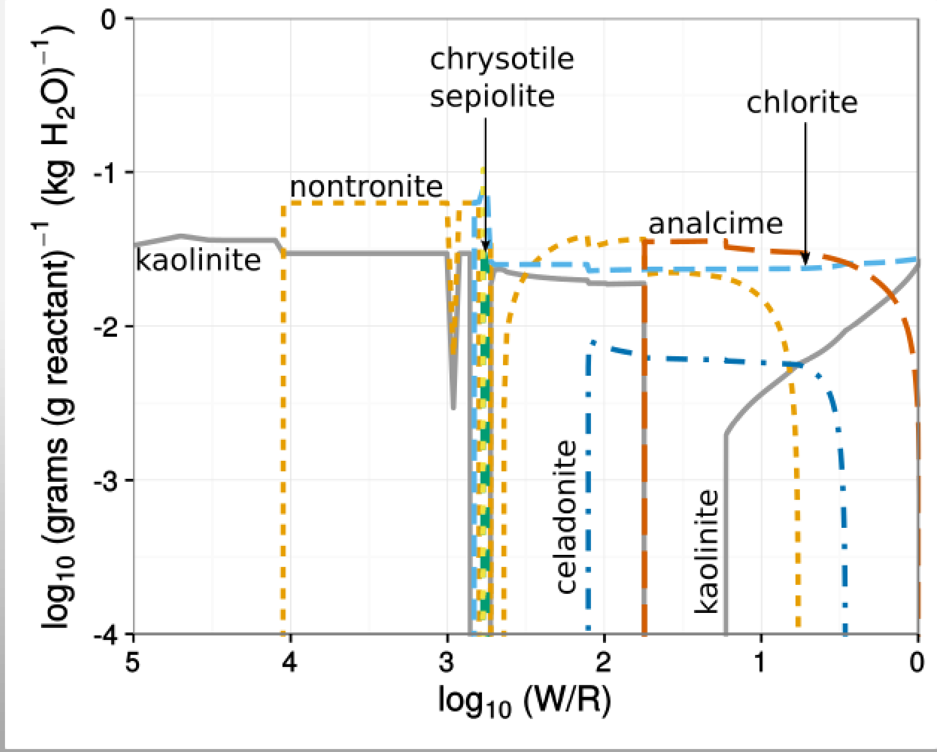
Result: minerals formed by weathering

Incongruent dissolution, no apatite re-precipitation allowed

60 mbar initial pCO_2
0.01 °C

Melwani Daswani & Kite, in prep.





Result: evolution of the fluid composition

Incongruent dissolution, no apatite re-precipitation allowed

60 mbar initial pCO_2

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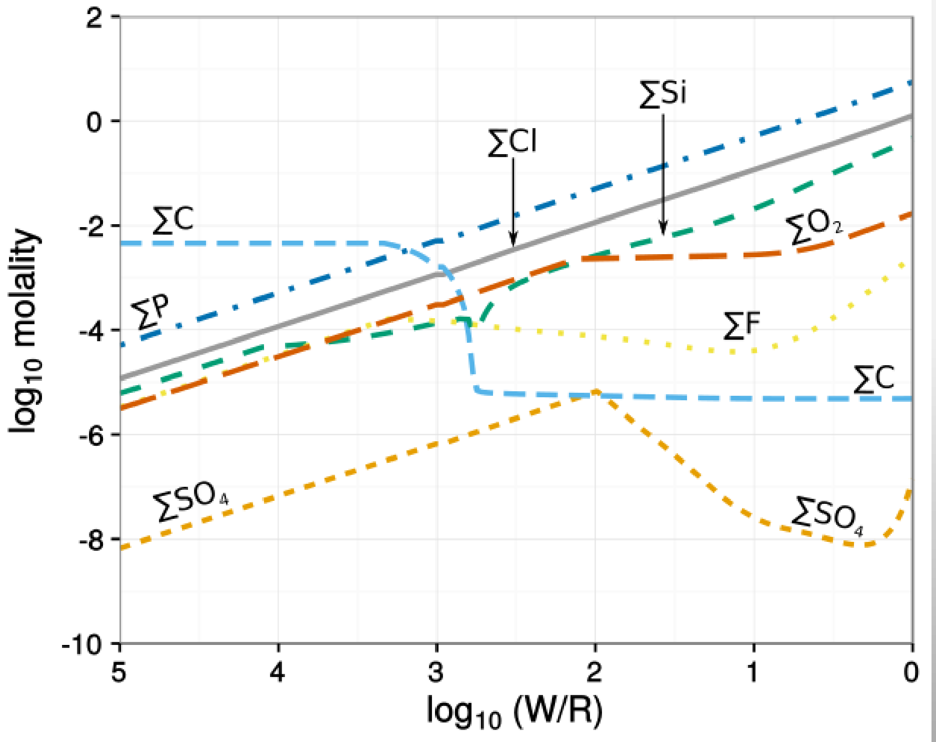
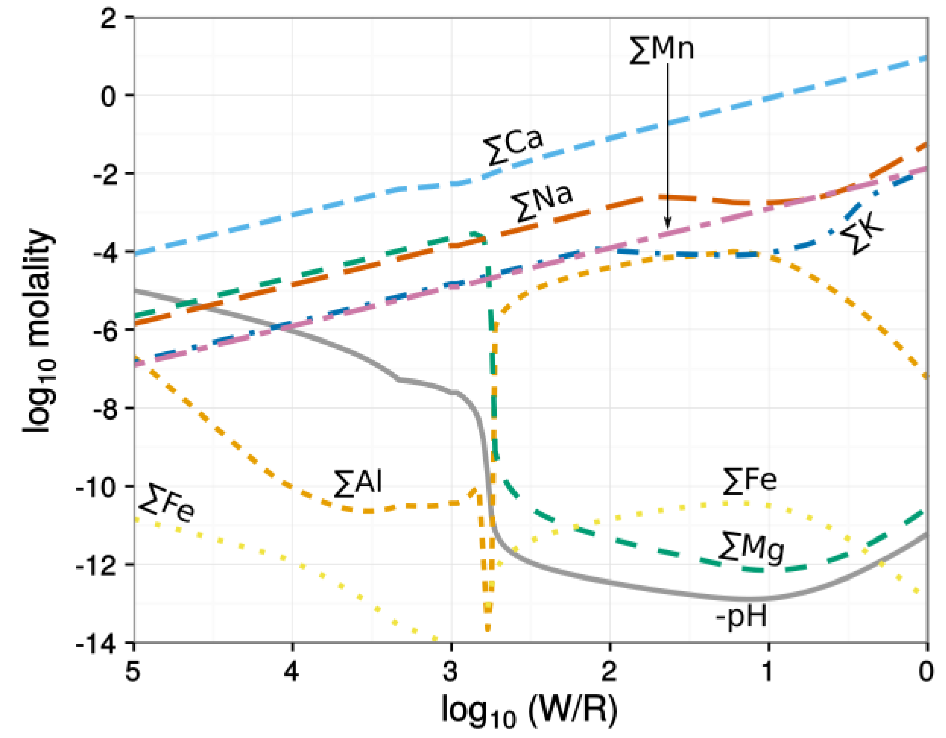




Quantifying H_2O and Cl required

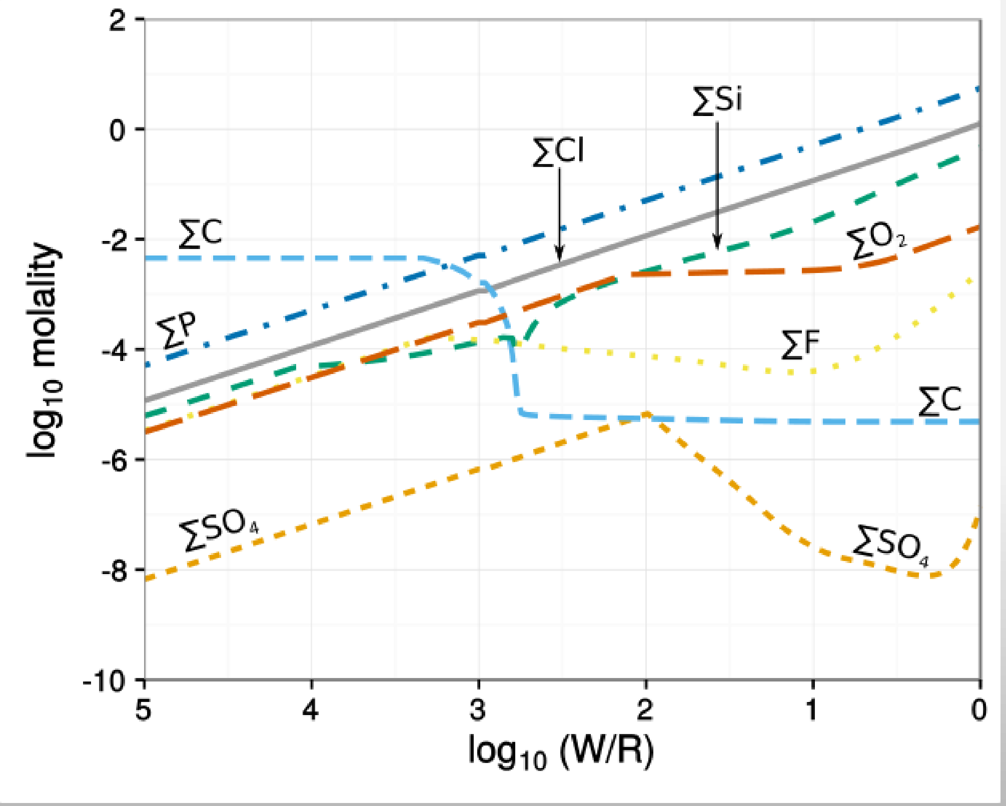
At W/R = 1

Melwani Daswani & Kite, in prep.

$\sum Cl = 1.26$ mol/kg H_2O

$= 4.48 \times 10^{-2}$ kg Cl/ kg H_2O

Assuming all Cl in solution precipitates as NaCl in the basin (~36 km^3) we were looking at previously (0.12 km^3 salt, 45 % porosity): 8.6×10^{10} kg Cl:



1.9×10^{12} kg H_2O required
$= 1.9 \times 10^{9}$ m^3 H_2O
≈ 0.05 times the volume of the basin

(≈ 1.6 m H_2O across basin)

Enough Cl from volcanic outgassing?

Estimated (e.g. Craddock & Greeley, 2009, *Icarus*)

Volcanic outgassing (HCl)

↳ Aerosols

Formation (e.g. Smith+, 2014, *Icarus*)

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Table 1
Extrusive volumes (10^6 km^3) of martian volcanic material with time[a].

Epoch	Extruded volume	Mass[b] (10^{22} g)
Late Amazonian	2.11	0.7
Middle Amazonian	8.49	2.8
Early Amazonian	15.76	5.2
Late Hesperian	15.63	5.16
Early Hesperian	17.65	5.82
Late Noachian	7.77	2.56
Middle Noachian	1.39	0.46
Early Noachian	?	?
Total	68.8	22.7

[a] Data from Greeley and Schneid (1991).
[b] Assumes a density of 3.3 g/cm^3.

Table 3
Mass (10^{18} g) of martian volcanic gases released through time.

Epoch	Constituents
	HCl
Late Amazonian	0.06
Middle Amazonian	0.22
Early Amazonian	0.42
Late Hesperian	0.41
Early Hesperian	0.47
Late Noachian	0.2
Middle Noachian	0.04
Early Noachian	?
Total	1.82

Adapted from Craddock & Greeley (2009)

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Volcanic outgassing (HCl)

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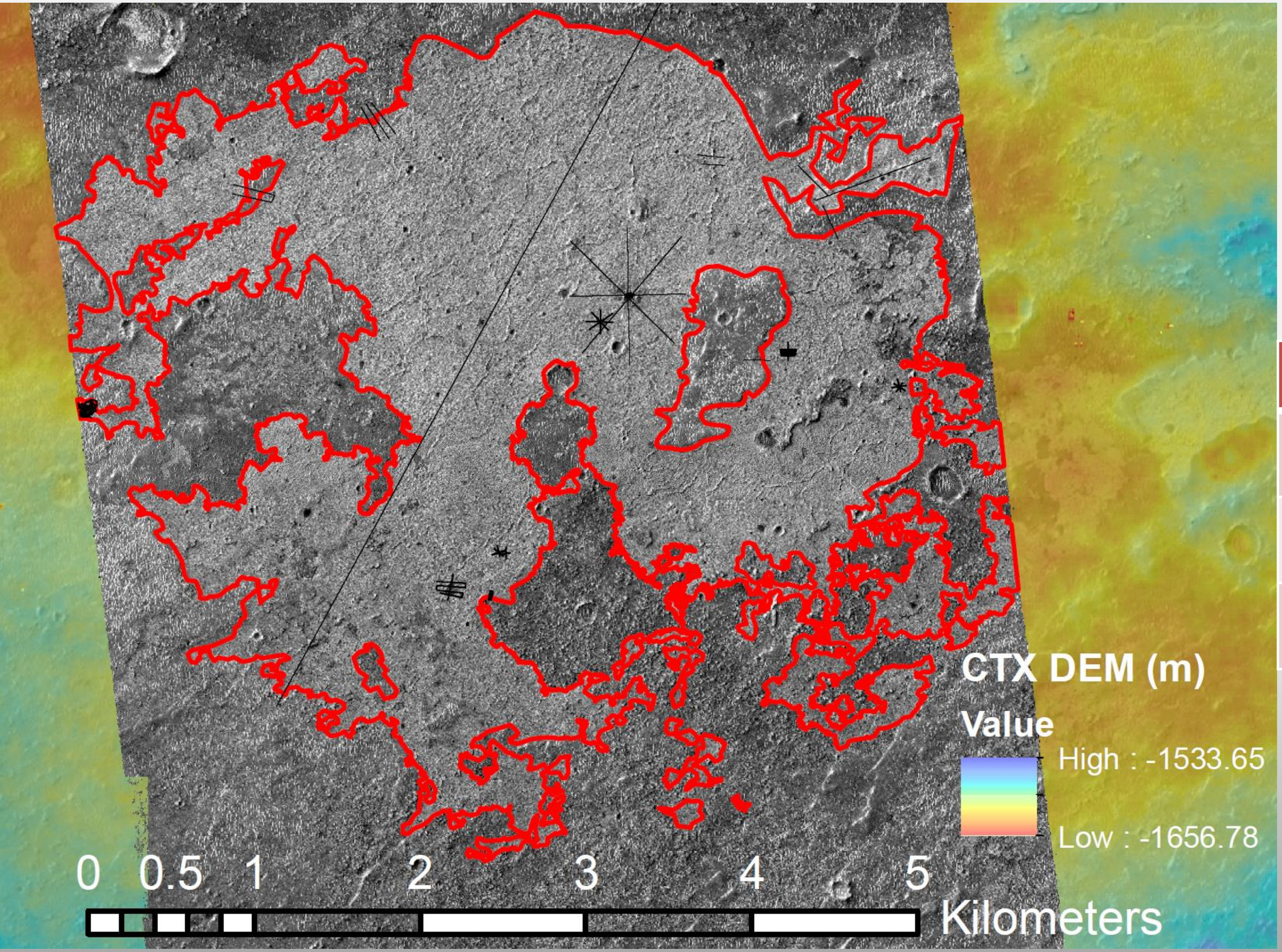
≈ 3.3 kg m^{-2} globally

Adapted from Craddock & Greeley (2009)

Detailed mapping to improve mass balance constraints



Melwani Daswani & Kite, in prep.

Chloride deposit:
Thickness: ~1.5 m
Volume: ~2.15 × 10^7 m^3

	NaCl (kg)	Cl (kg)
10% NaCl	4.7×10^9	2.8×10^9
25% NaCl	1.2×10^{10}	7.1×10^9
Hynek et al., 2015	1.4×10^{11}	8.5×10^{10}

HiRISE image 25cm/pixel

Cl masses are somewhat different for other deposits

	Near Miyamoto Crater (this study)	Near Miyamoto Crater (Hynek et al. 2015)	Terra Sirenum (this study)	West of Knobel Crater (this study)
Mean deposit thickness (m)	1.5	4	2.6	8.0
Basin area (m^2)	8.4×10^8	1.2×10^9	3.5×10^9	3.5×10^9
Deposit volume (m^3)	2.2×10^7	1.2×10^8	5.8×10^7	4.2×10^6
10 % NaCl mass (Cl kg/m^2)	3.4	12.8	2.2	0.2
25 % NaCl mass (Cl kg/m^2)	8.5	32	5.5	0.4

Summary/conclusions

Origin of the Cl

Near-subsurface basalt weathering

+ Can "hide" sulfates in subsurface
+ Can make clay minerals prior to chlorides
+ Mass balance consistent

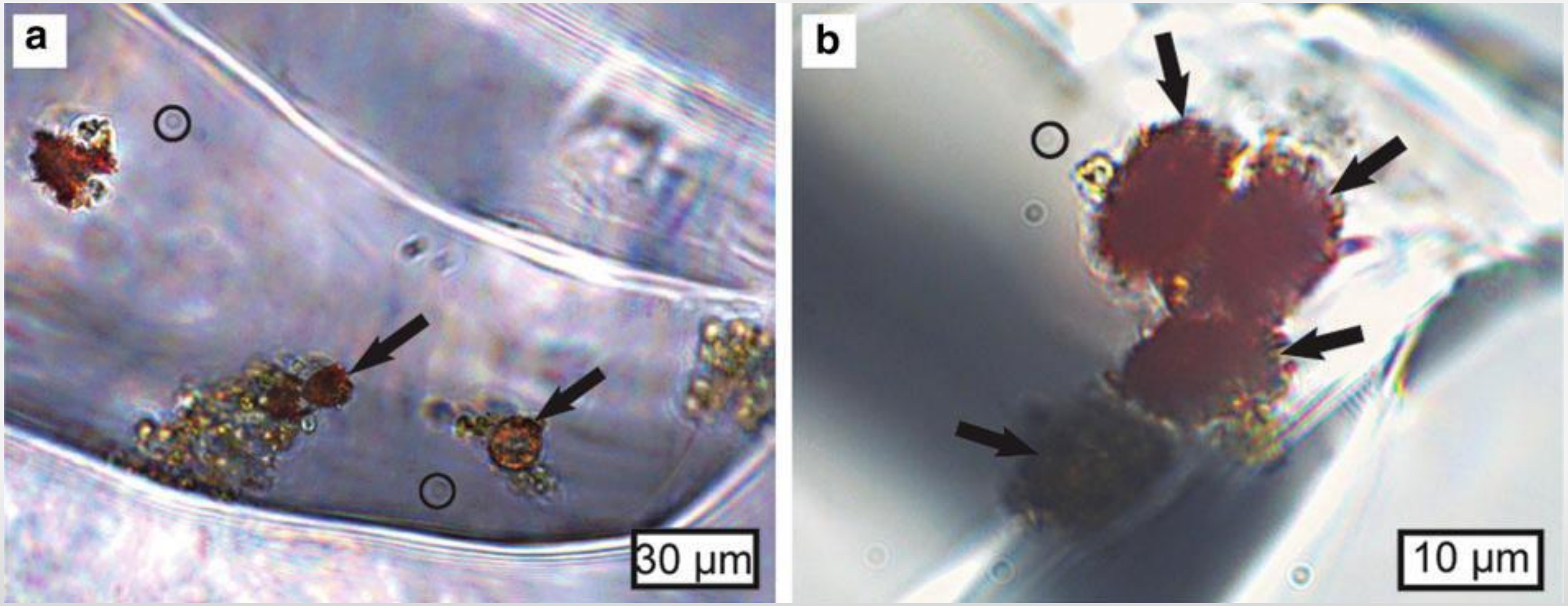
- Requires > 1 season of T above freezing

Volcanic Cl phases

+ Cl-phases detected on the surface, probably volcanogenic
+ Mass balance consistent
+ Does not require subsurface fluids
+ Consistent with inverted channels

- Sulfur is transported to lake

Fluid inclusions in chlorides can preserve DNA, microorganisms.



Photomicrographs of single-celled algae and prokaryotes in fluid inclusions in halite from Qaidam Basin (Wang et al. 2016, *Astrobiology*)

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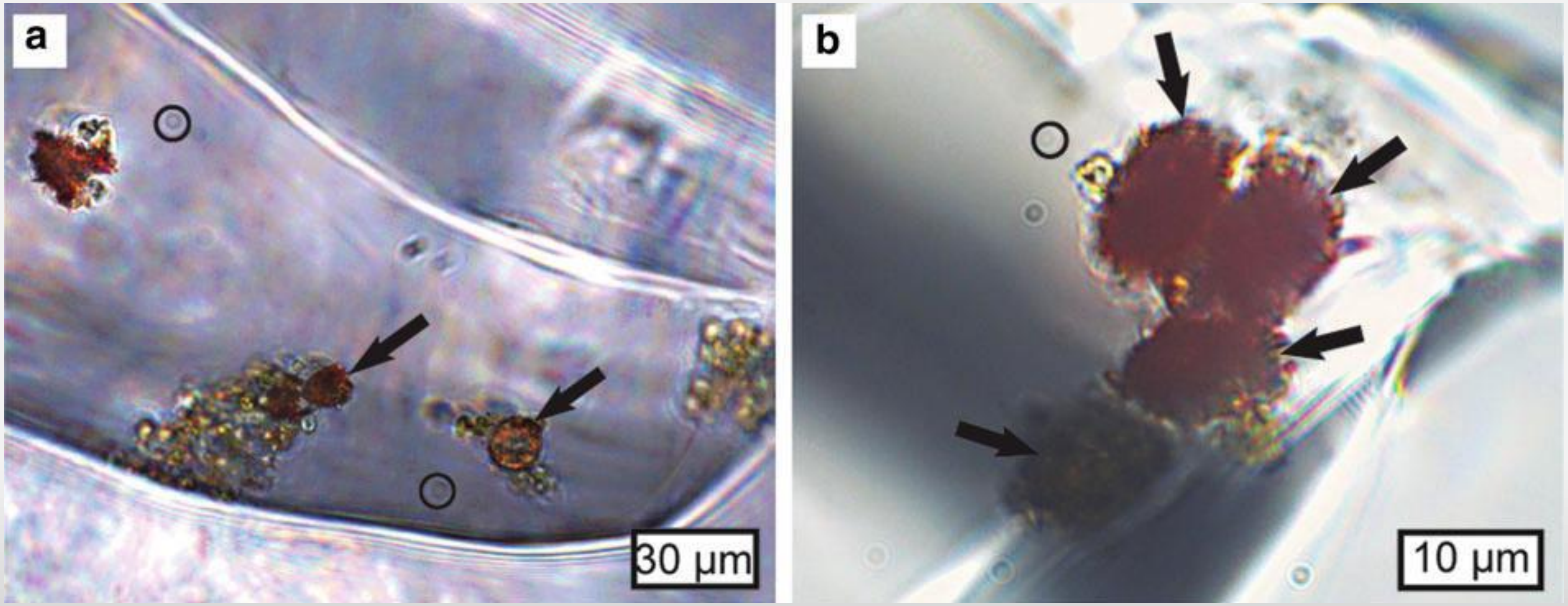


Photomicrographs of single-celled algae and prokaryotes in fluid inclusions in halite from Qaidam Basin (Wang et al. 2016, *Astrobiology*)

Possible shielding from GCR damage?

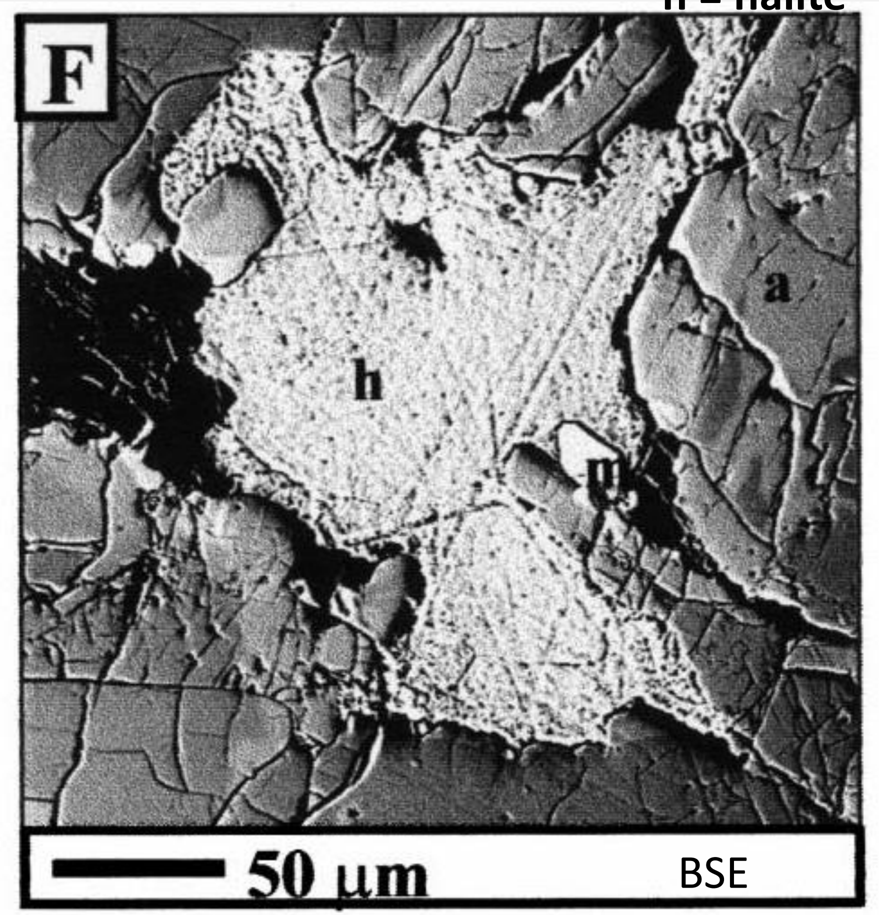
We have already sampled martian chlorides

Group	Crystallization age	Secondary minerals
Nakhlites	~ 1.3 Ga	siderite gypsum anhydrite halite goethite smectite SiO_2
Shergottites	165 – 475 Ma	gypsum halite phyllosilicates carbonates (ambiguous origin)

Nakhla

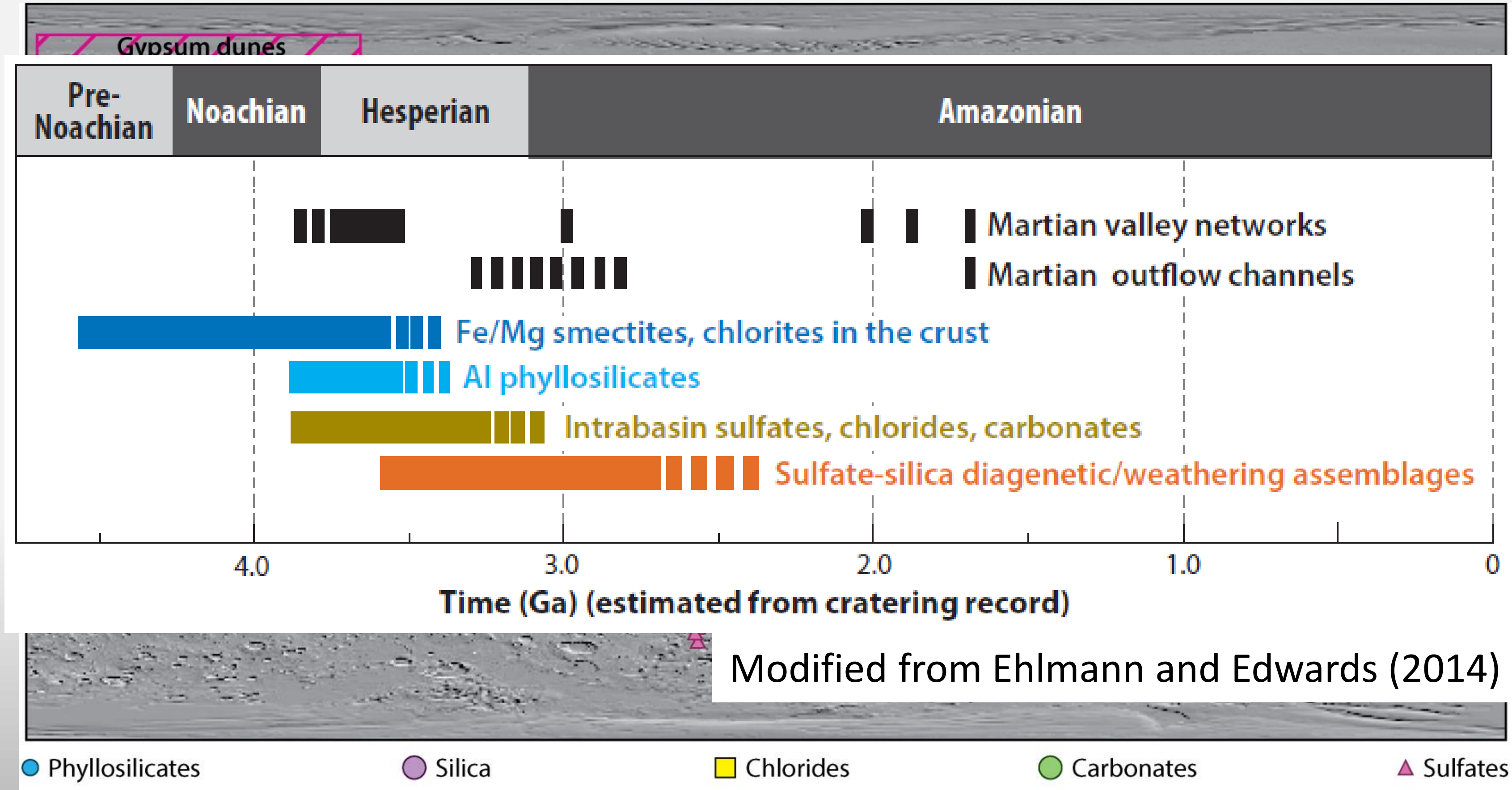
a = augite

h = halite



Bridges et al. (2001), *Space Sci. Rev.*.; Bridges and Grady (2000), *Earth Planet. Sci. Lett.*

Chlorides are widespread



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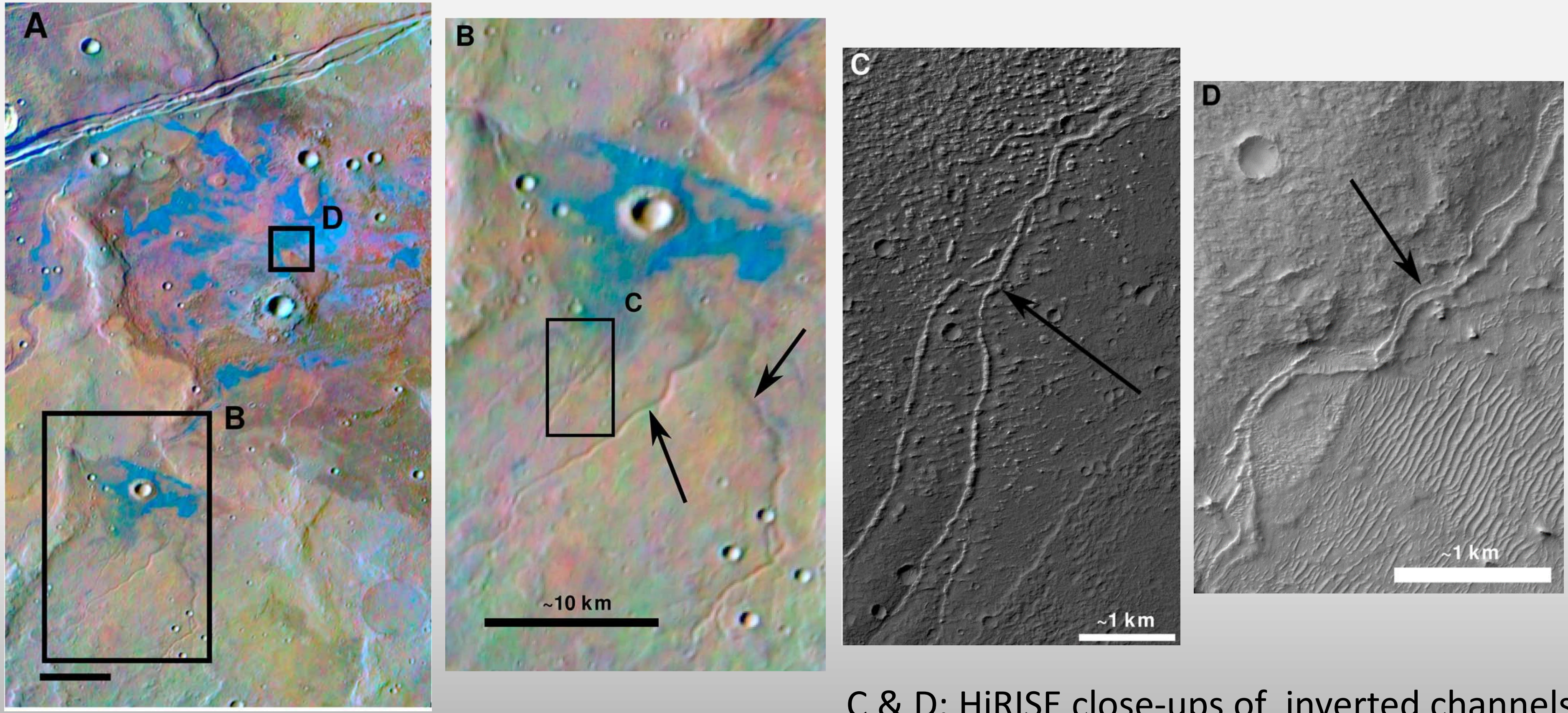
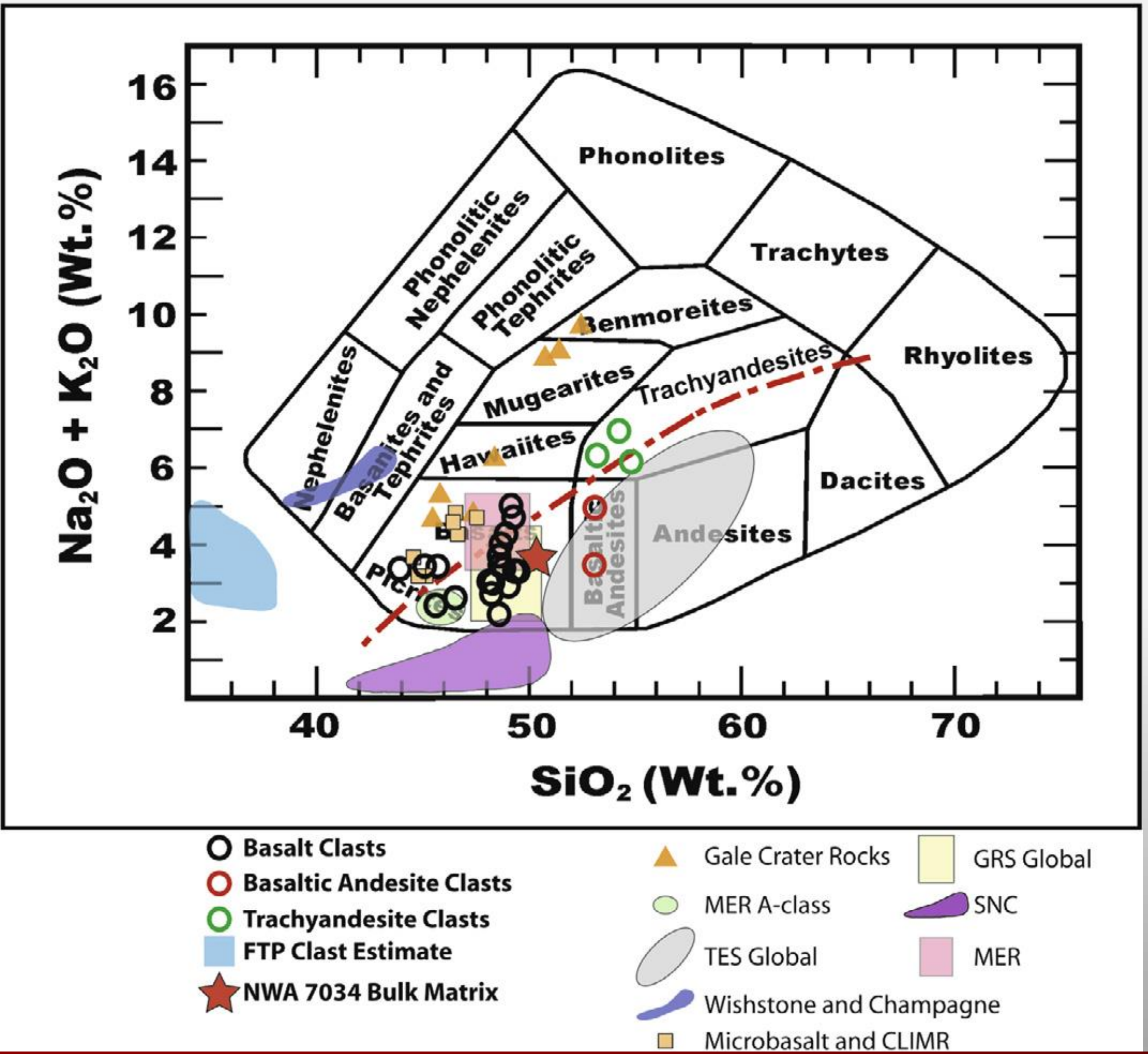


A & B: THEMIS radiance DCS (8/7/5) mosaics

C & D: HiRISE close-ups of inverted channels

Osterloo et al. (2010) *J. Geophys. Res.*

Finding a representative basalt composition



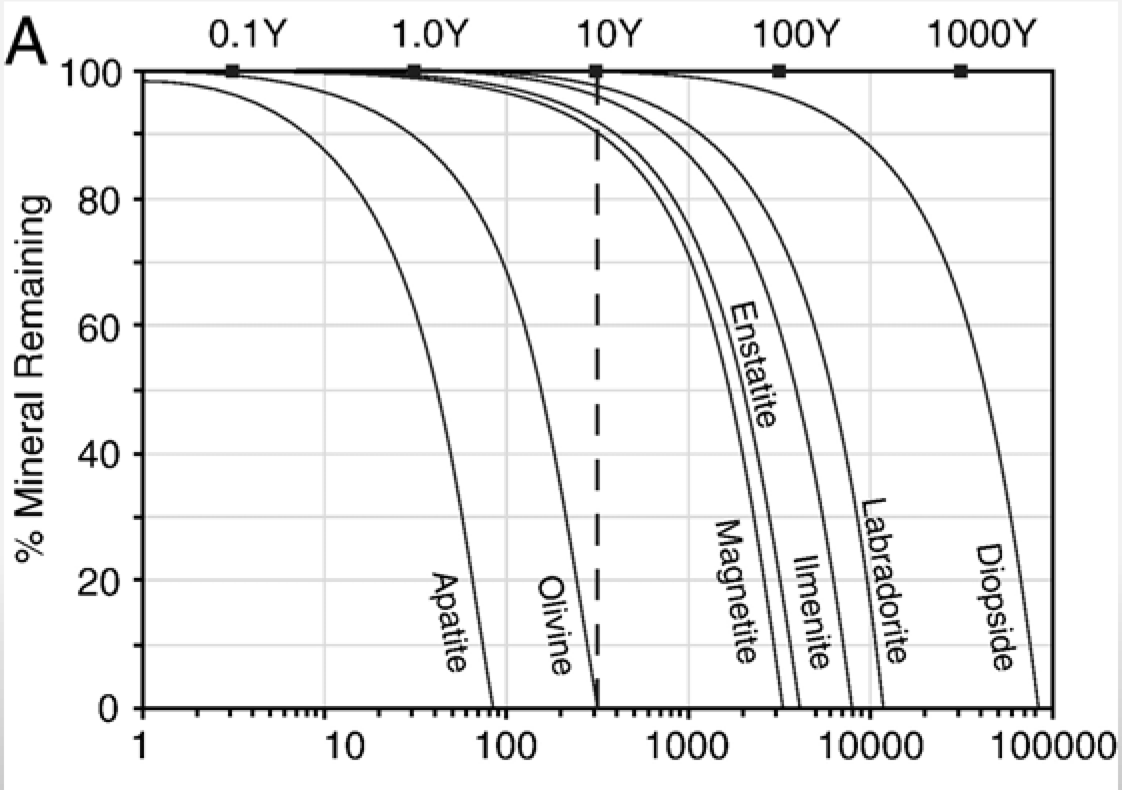
NWA 7034 basalt clasts

Mineral	Mode Vol. %	Norm. wt. %
Plag.	50	45.8
K-felds	2	1.8
Low Ca pyx	20	24.1
High Ca pyx	10	12.1
Apatite	5	6.0
Magnetite	3	5.4
Ilmenite	1	4.6

Apatite contains ~ 4.6 wt. % Cl

Santos et al. (2015), *Geochim. Cosmochim. Acta 157*, 56 – 85.

Minerals weather at different rates



Water/Rock

From Hurowitz and McLennan (2007), *Earth Planet. Sci. Lett., 260*, 432 – 443.

Adjusted reactant rock composition for 90 wt. % apatite
(Melwani Daswani & Kite, in prep.)

Mineral	Wt .%
Plagioclase	4.9
K-Felds	0.2
Low Ca pyx	2.6
High Ca pyx	1.3
Apatite	90.0
Magnetite	0.6
Ilmenite	0.5
Pyrite*	0.004*

*Added and adjusted from Wittmann et al., 2015 *M&PS 50*, 326 – 352.

Quantifying H_2O and Cl required

At W/R = 100

Melwani Daswani & Kite, in prep.

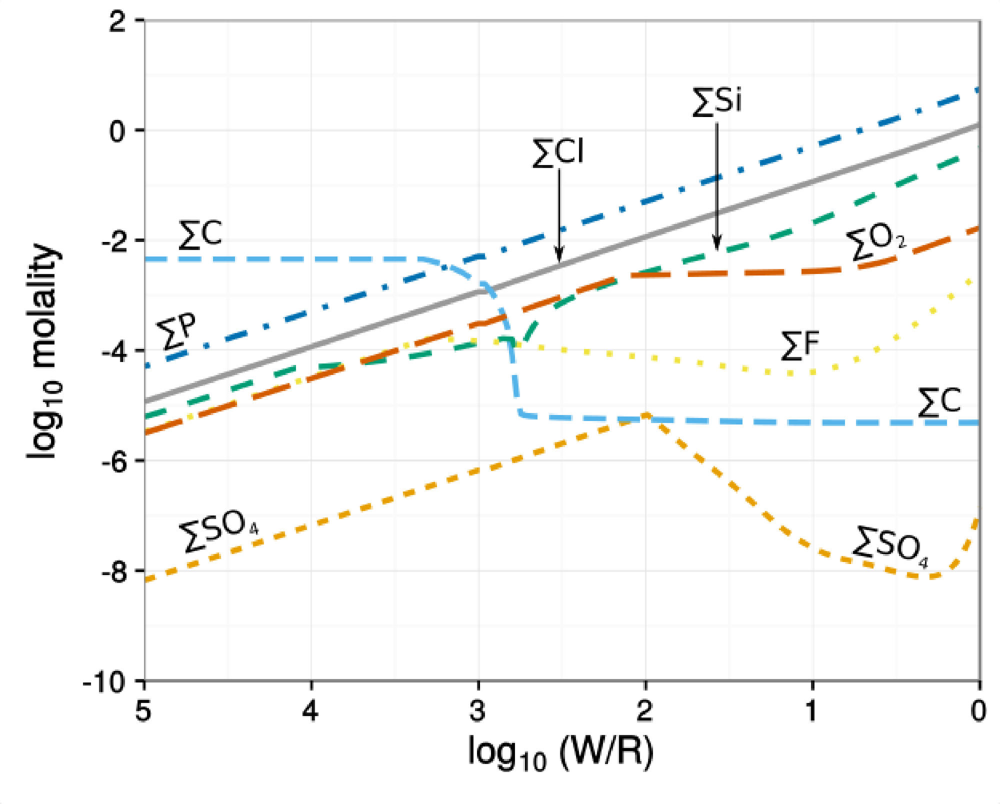
$\sum Cl = 1.15 \times 10^{-2}$ mol/kg H_2O

$= 4.1 \times 10^{-4}$ kg Cl/ kg H_2O

Assuming all Cl in solution precipitates as NaCl in the basin (~36 km^3) we were looking at previously (0.12 km^3 salt, 45 % porosity): 8.6×10^{10} kg Cl:

2.1×10^{14} kg H_2O required
$= 2.1 \times 10^{11}$ m^3 H_2O
≈ 5.9 times the volume of the basin

(≈ 172 m H_2O across basin)



What was the time scale of the event?

We know the mass of the chloride deposit (~ 1.4×10^{11} kg)
and the surface area of the basin (~ 1.2×10^{9} m^2) (Hynek et al., 2015)

Assumptions:

- Chlorides are NaCl
- Porosity of the deposit is 45 %
- Diffusivity (K) of the basin rock = 7×10^{-7} m^2 s^{-1} (typical for silicates)

We calculate ~ 2.5×10^{4} kg rock/m^2 (i.e. ~ 14.9 m depth) weathering

$$L = 2.32\sqrt{K\,\tau}$$

$\tau \approx 6 \times 10^{7}$ s ≈ 1 Mars year

Melwani Daswani & Kite, in prep.

Where did the Cl come from?

C. Other sources?

Meteoritic? Cometary?
Ancient reworked deposits?

Melwani Daswani & Kite, in prep.