Exploring Mars at the Nanoscale: Applications of transmission electron microscopy and atom probe tomography in planetary exploration

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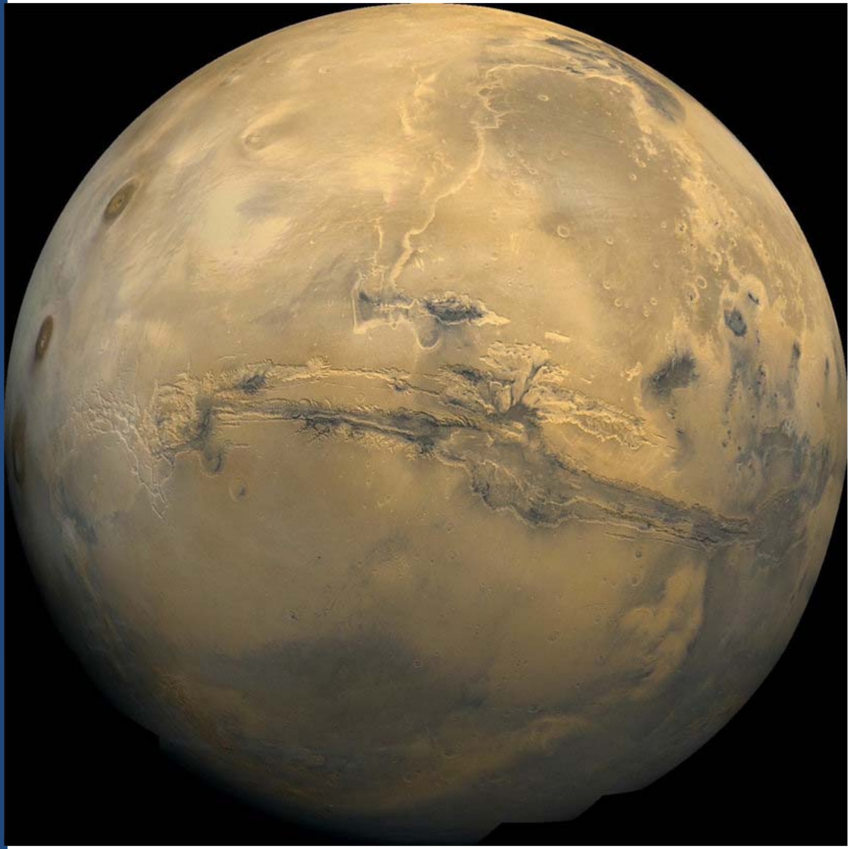
Science & Technology Facilities Council
Microscopy Australia
Oxford Materials
ammrf Australian Microscopy & Microanalysis Research Facility
Kelvin Nanocharacterisation Centre

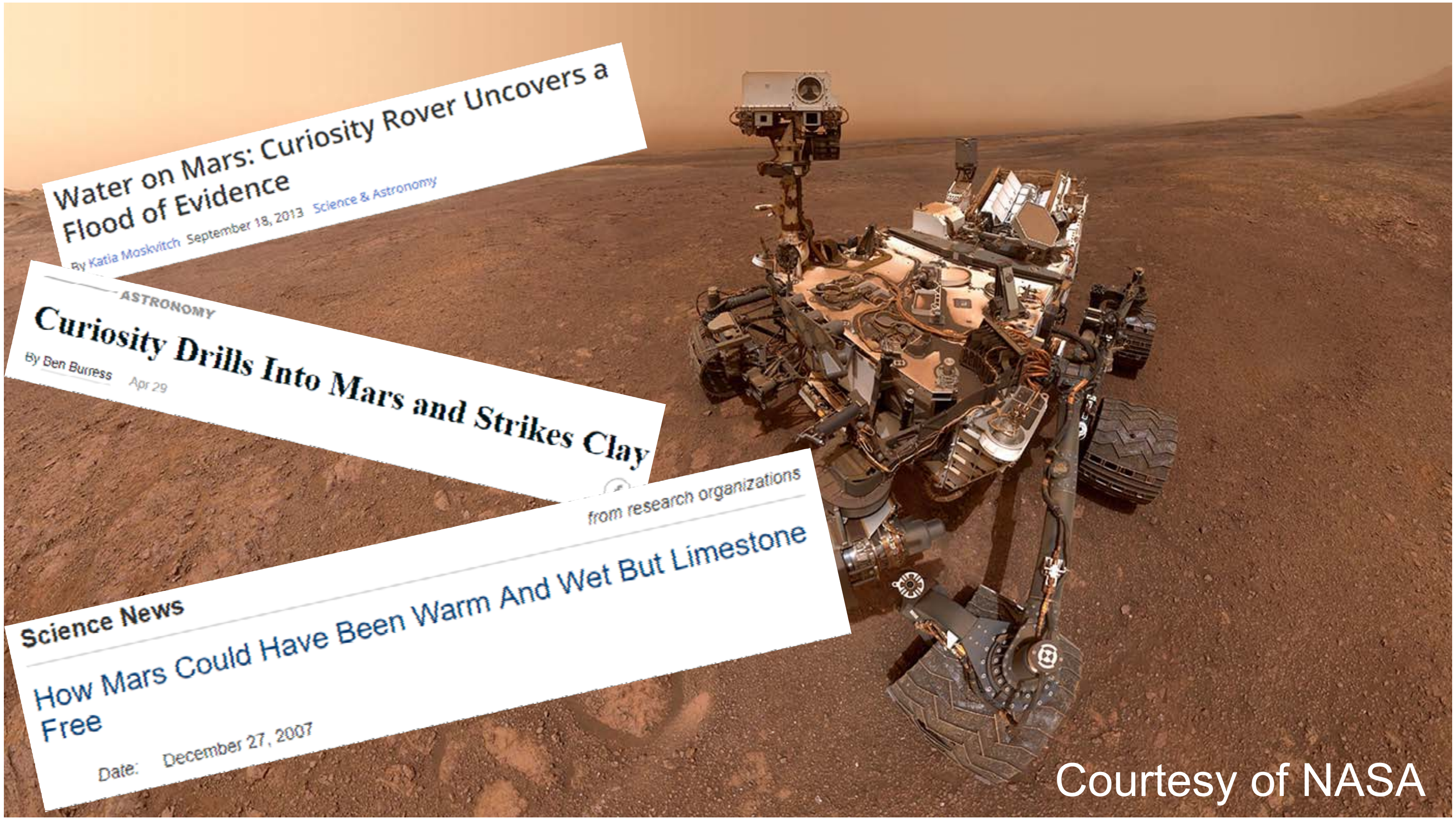
Mars-water and habitability



Courtesy of NASA

- Remote sensing indicates large fluvial systems were once active on the Martian Surface.
- Modern Mars is too cold for liquid water to be present at the surface.
- Could liquid water persist somewhere on Mars
- Martian meteorites provide a physical sample of the Mars' crust.

Evidence of Water on Mars : Curiosity



Courtesy of NASA

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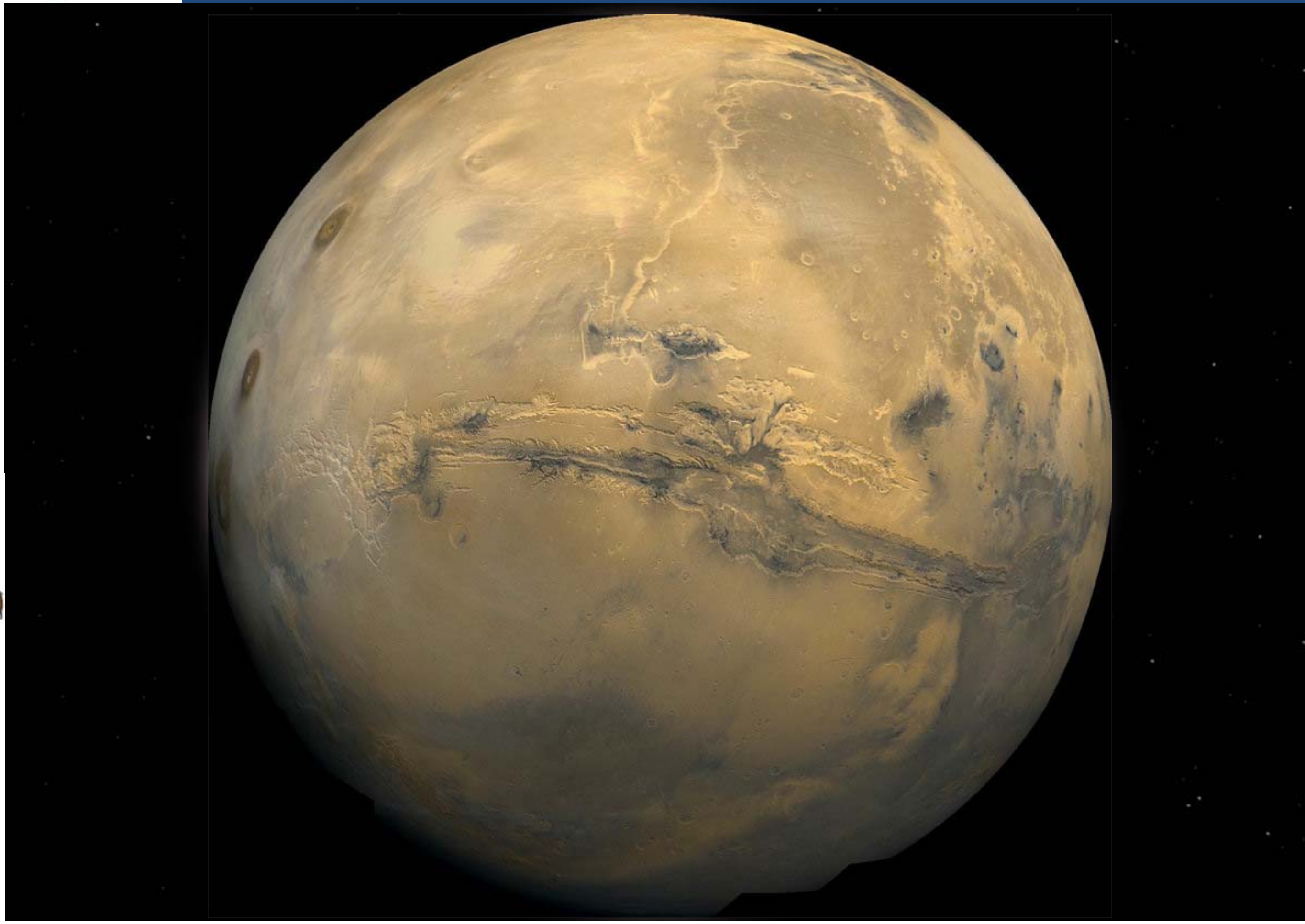
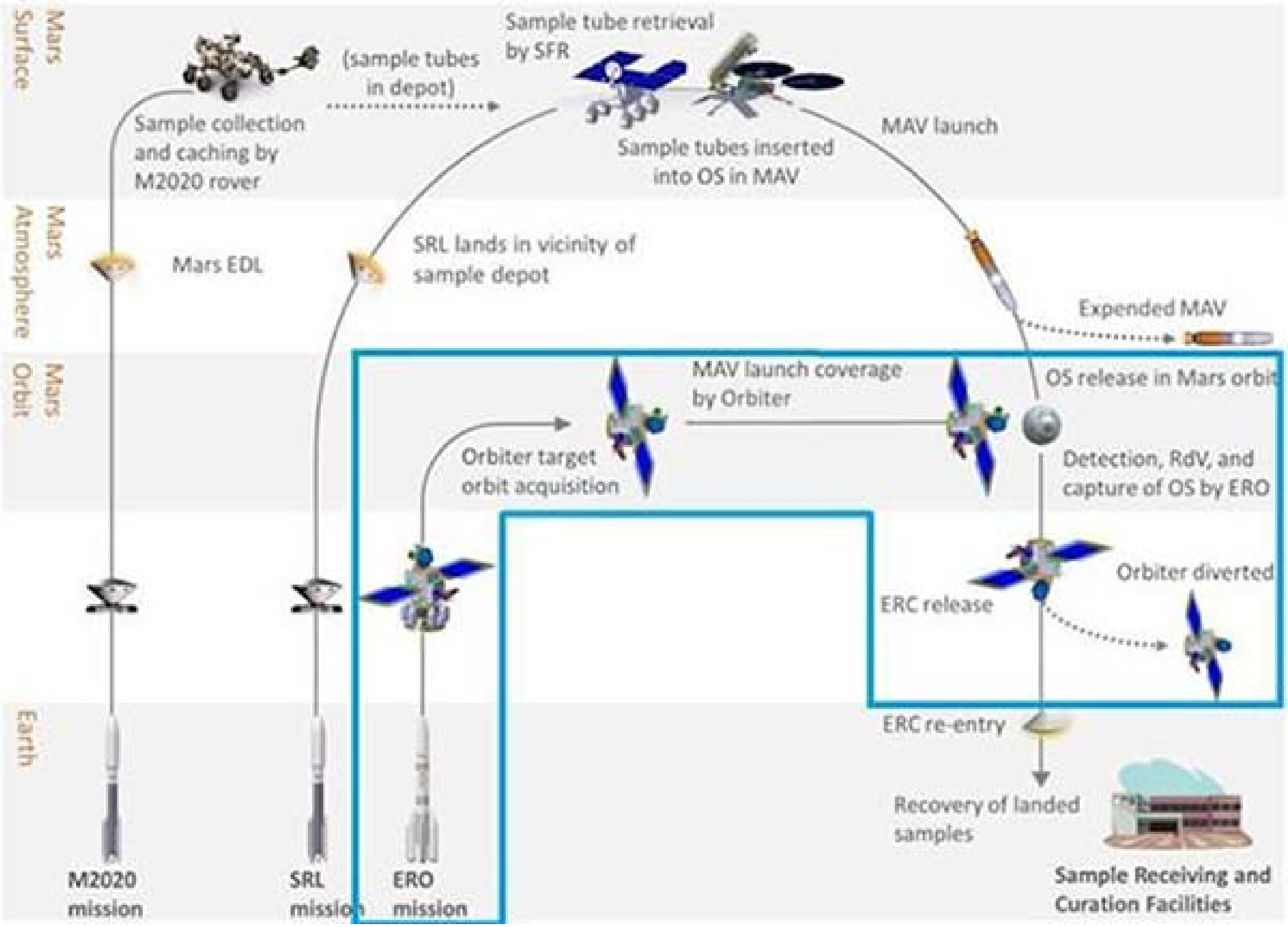
RIP Oppy

Martian Oceans?



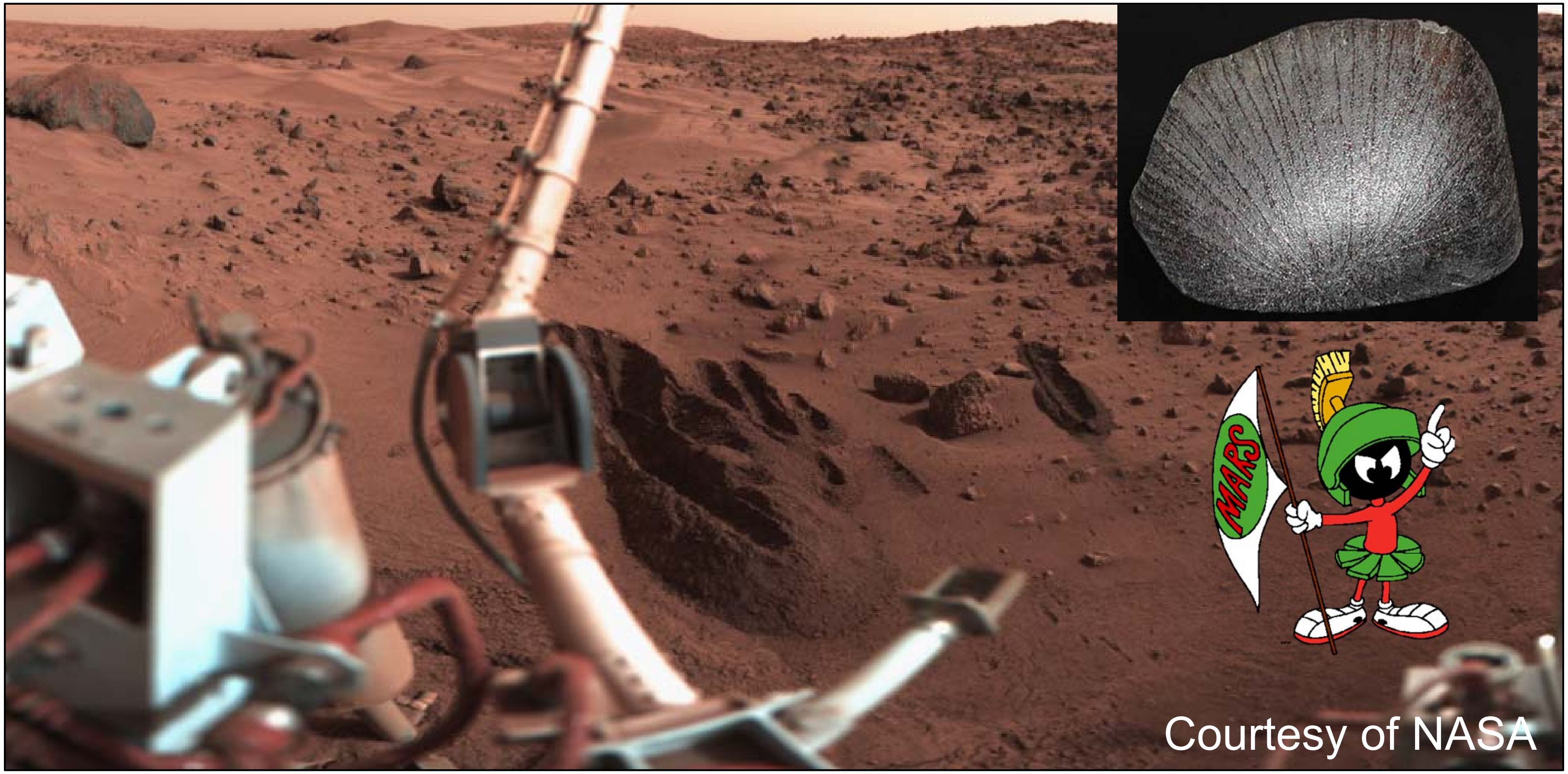
Courtesy of NASA

Mars Sample Return



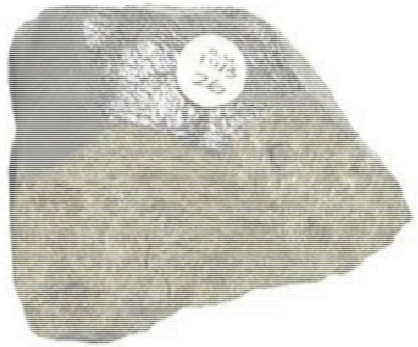
- Several missions in one
- Return ~1kg of Mars
- Must maximise research output from small sample volumes

Viking 1: Landed on Mars, 20 July 1976



Lafayette
0.4 wt. % water

Nakhla
0.1 wt.% water



Nakhla

Nakhla 31°19′ N., 30°21′ E.

Abu Hommos, Alexandria, Egypt

Fell 1911, June 28, 0900 hrs

Synonym(s): *Abdel Malek, El Nakhla el Baharia*

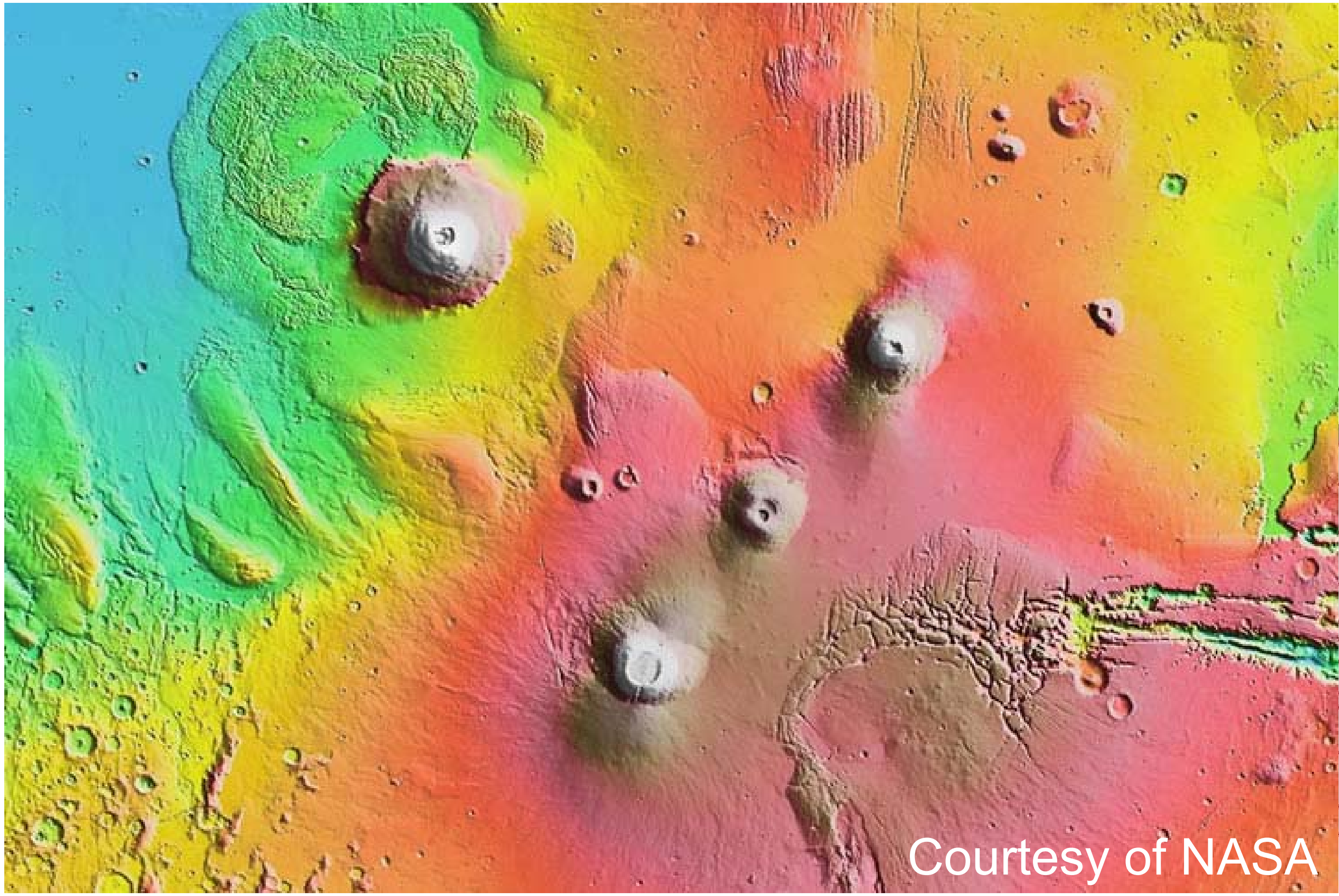
Stone. Achondrite, Ca-rich. Nakhlite (ACANOM).

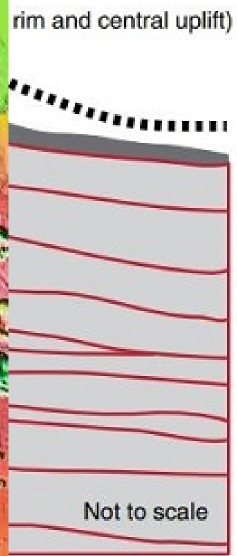
About 40 stones, of total weight about 40kg, and varying in weight from 1813g to 20g fell, after appearance of cloud and detonations, W.F. Hume, Cairo Scientific Journal, 1911, **5** (59), p.212. Mentioned, J. Ball, Geol. Reports, Surv. Dept. (Egypt), Cairo, 1912 (25). One of the stones killed a dog. Description and analysis, G.T. Prior, Min. Mag., 1912, **16**, p.274. Consists mainly of a green diopside with some highly ferriferous olivine and a little feldspar. New analysis, 16.16 % total iron, T.S. McCarthy et al., Meteoritics, 1974, **9**, p.215. Ar-Ar age, 1300 m.y., F.A. Podosek and J.C. Huneke, Geochimica et Cosmochimica Acta, 1973, **37**, p.667. Rb-Sr

Nakhla

0.1 wt.% water

Nakhlite Meteorites history: Formation

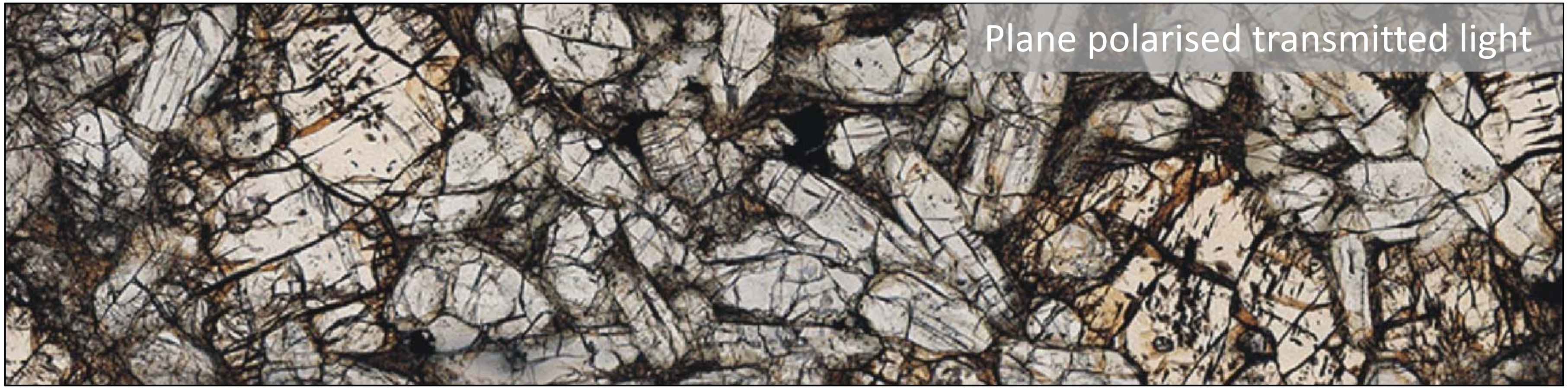


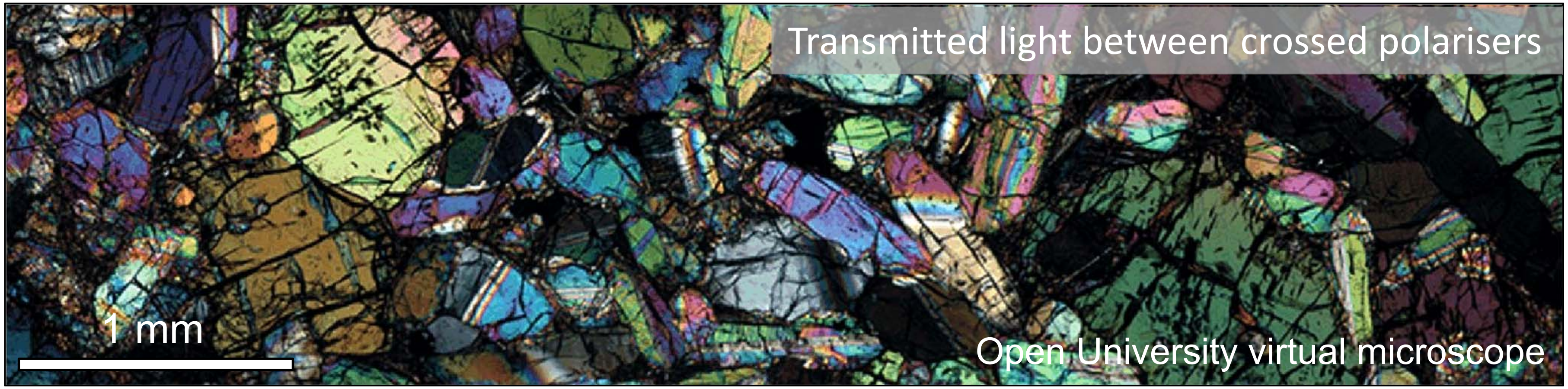


Nakhlite Meteorites history: Formation

- 1400-1300 million year old volcanic rocks.
- Made mainly of the Mg-Fe-(Ca) silicate minerals augite and olivine.

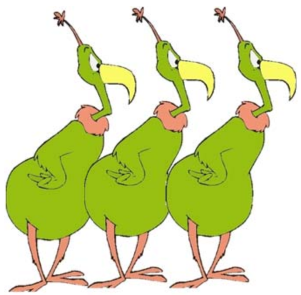
Nakhlite meteorite in thin section

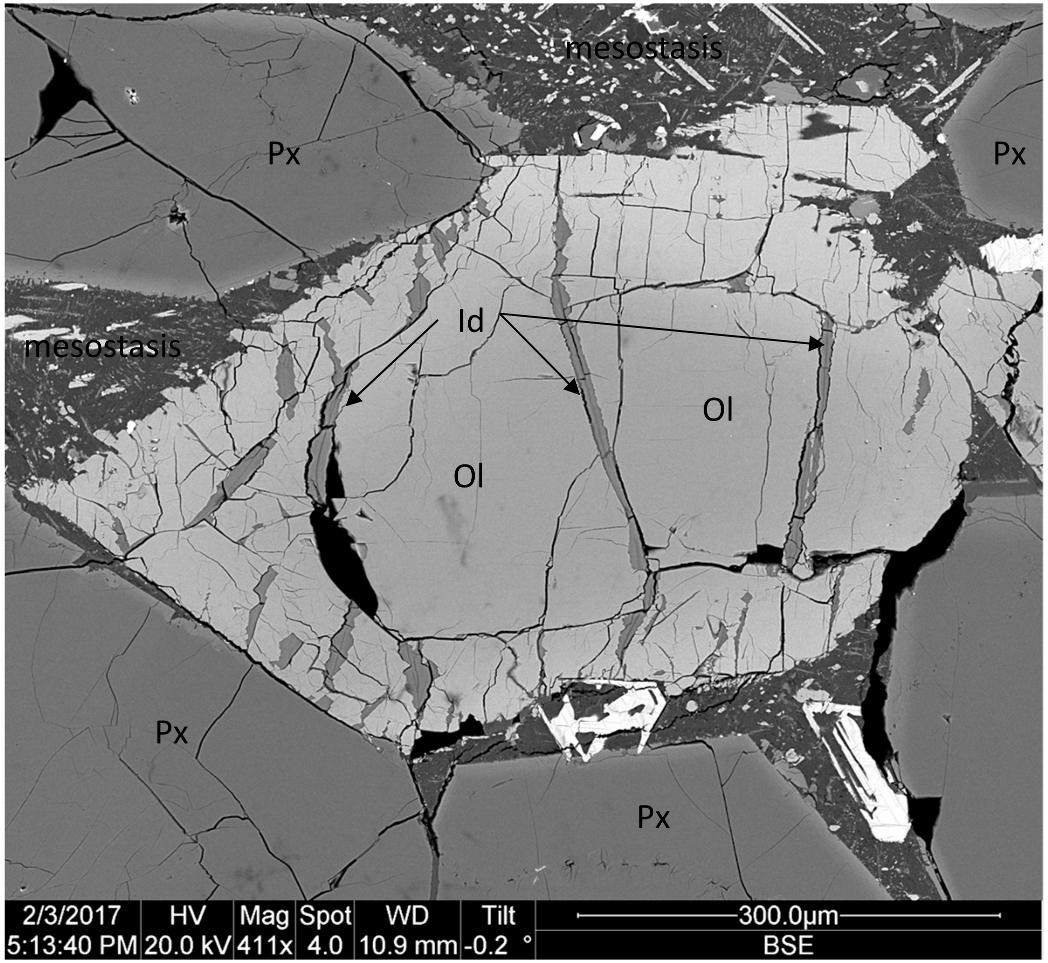




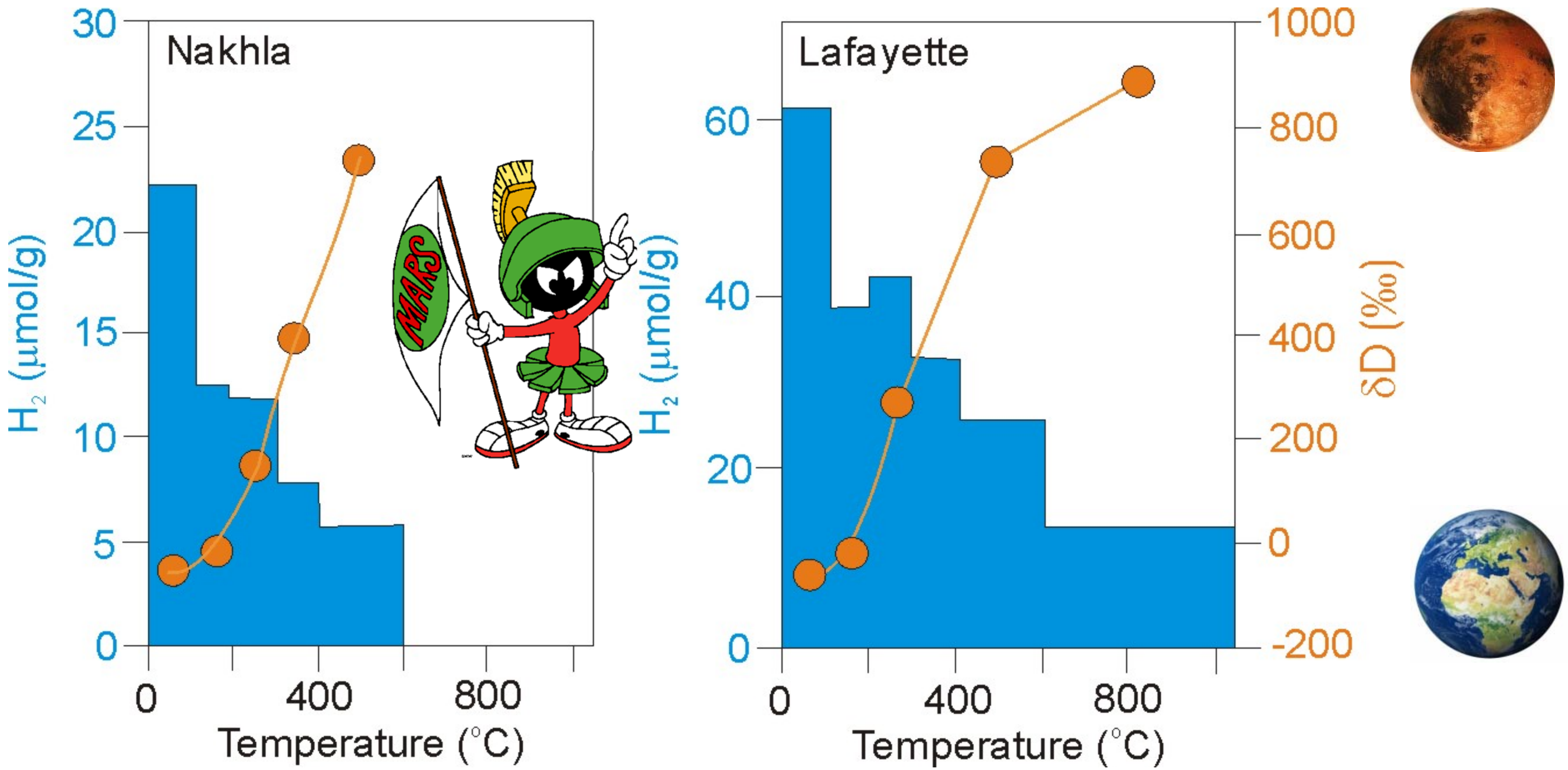
Nakhlite meteorites history: evidence of water

- Nakhlite meteorites from Mars contain precious samples of the planet's water;
- Evidence for recent ~633 Ma aqueous activity
- The heat source for these fluids is unknown





Demonstrating a Martian provenance for the water

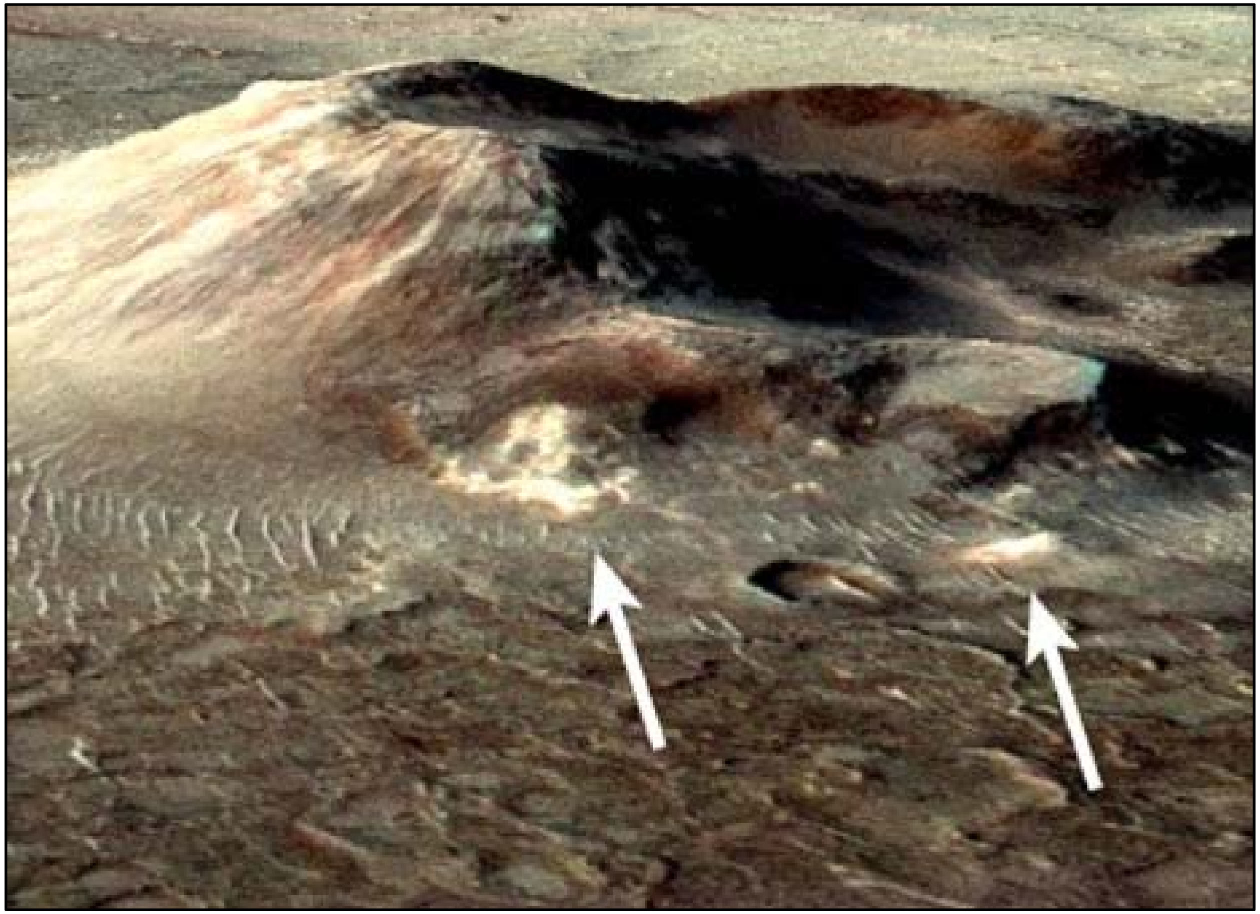


Driver/heat source for fluids

Volcanism

Impact

Silica hot springs on Mars

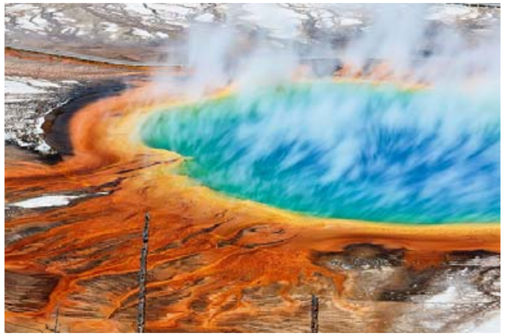


- Nili Patera caldera in Syrtis Major hosts deposits of hydrated silica that are spatially related to volcanic cones (Skok *et al.*, 2010).

Nakhlite meteorites history: Impact-ejection

~1-20 million years

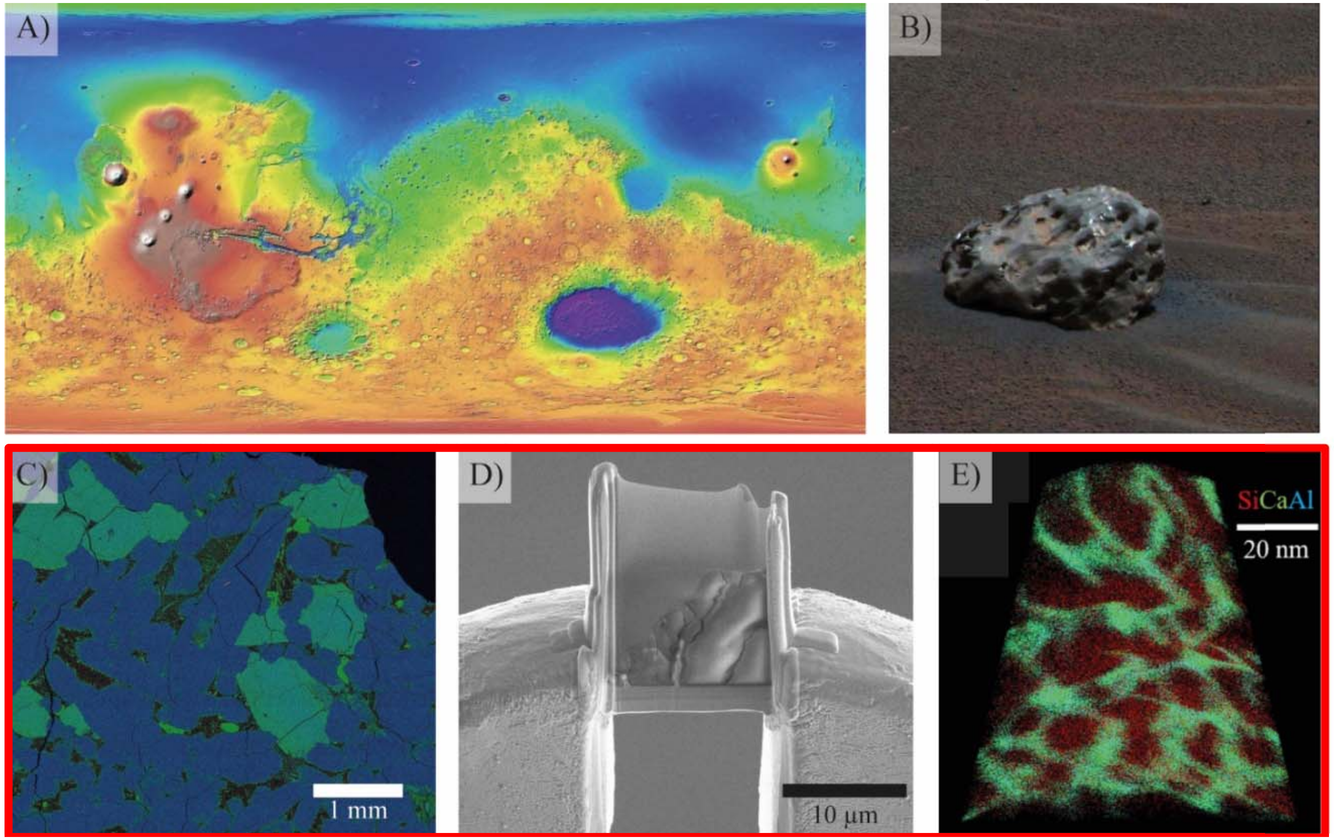
Nakhlite timeline



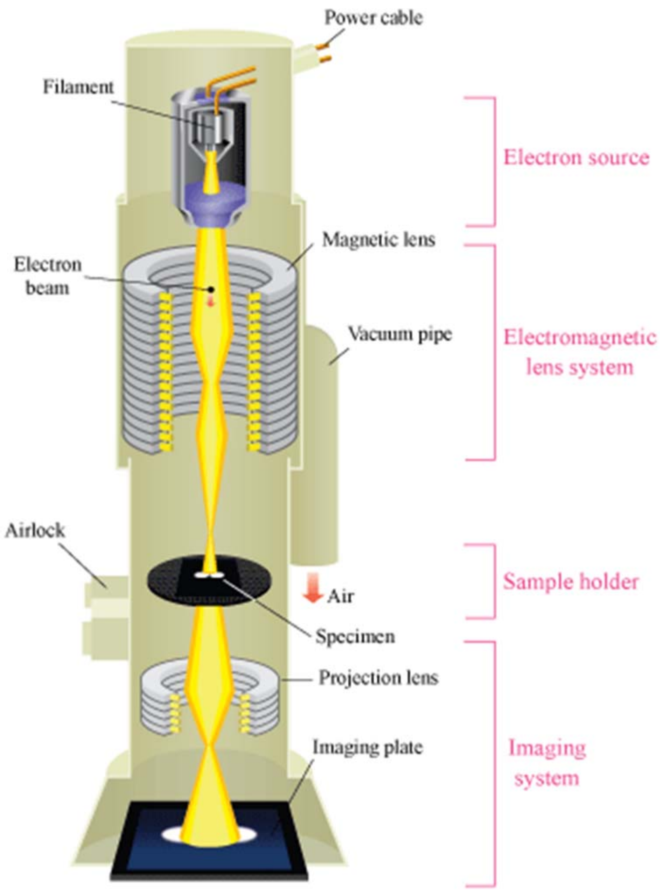
1.4-1.3 0.633 0.011 0

Billion Years

Correlative Study

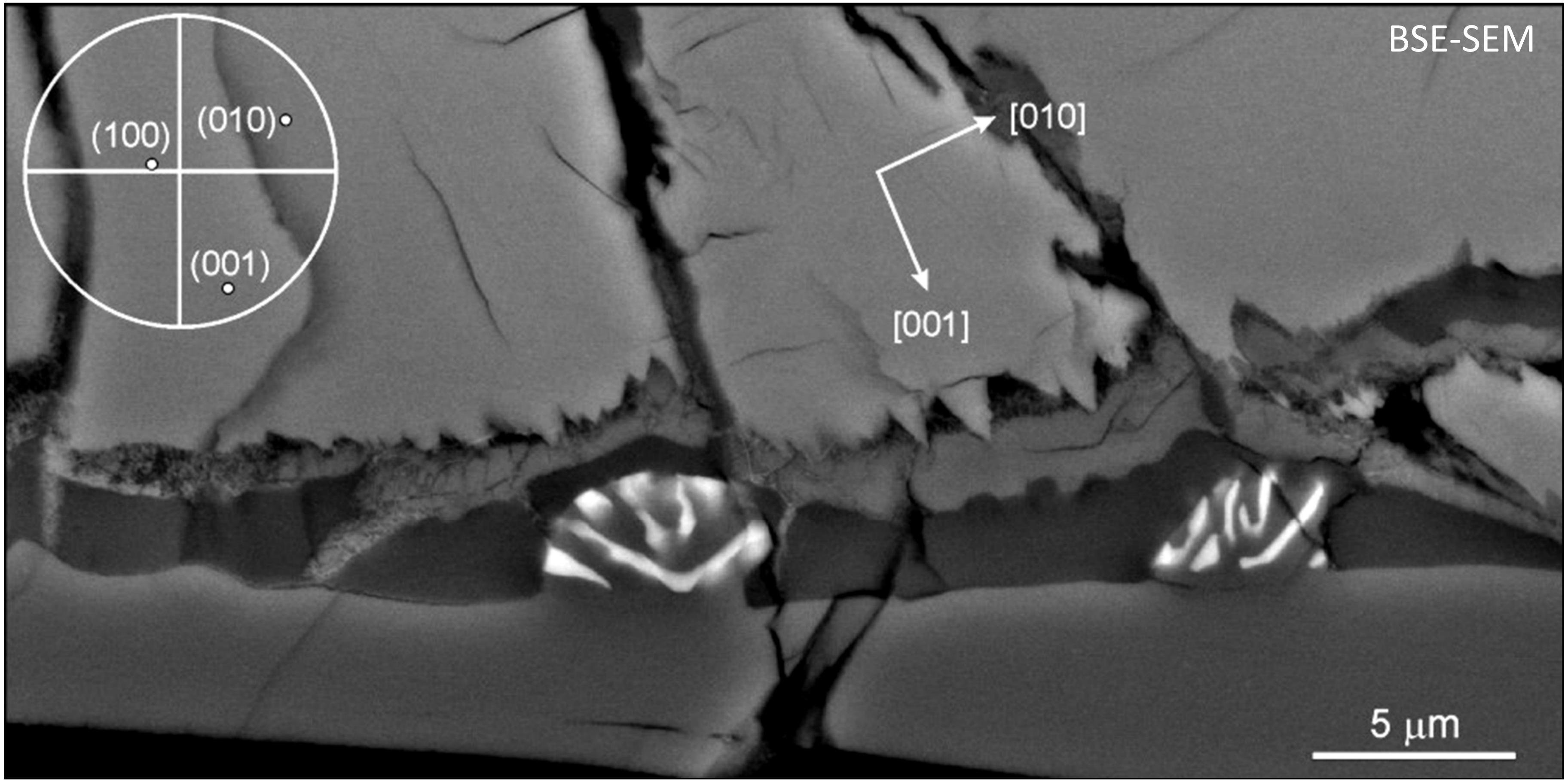


Transmission electron microscopy



- JEOL ARM200F. Nominal spot size in STEM mode 0.2 nm.
- EELS using a Gatan GIF Quantum ER spectrometer;
- EDX using a Bruker SDDEDX spectrometer.

SEM: Water-rich ‘iddingsite’ veins within olivine



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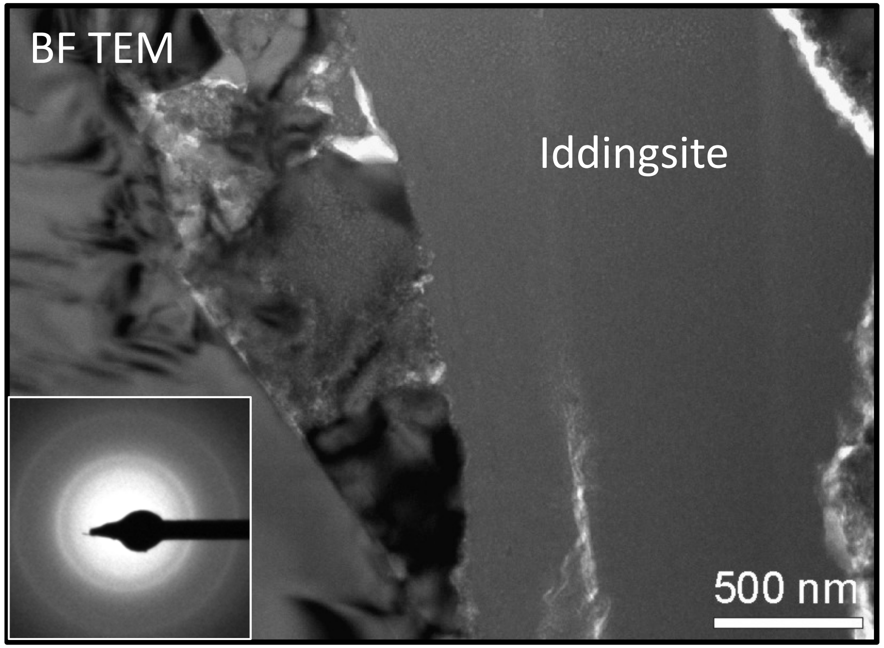
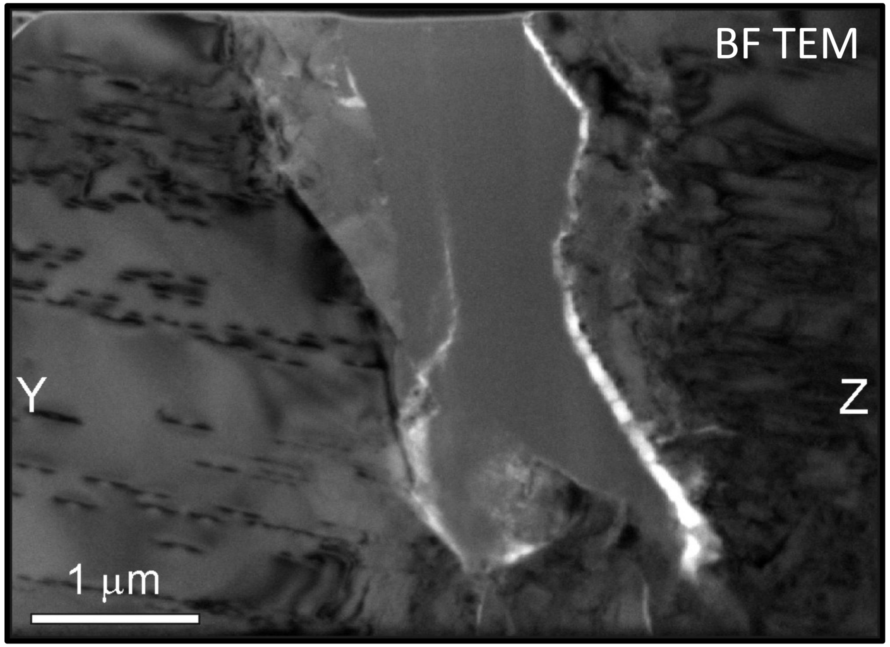
What is the ‘iddingsite’ made from?

2015		
	Amorphous gel	Changela & Bridges
2005		
	Smectite, hematite, goethite, quartz, cristobalite, tridymite, amorphous silica	Thomas-Keptra *et al.*
1995		
	Fe-saponite, hematite, two-ring ferrihydrite Smectite	Treiman & Gooding Gooding *et al.*
1985		
1975	Fine-grained/colloidal material	Ashworth & Hutchison

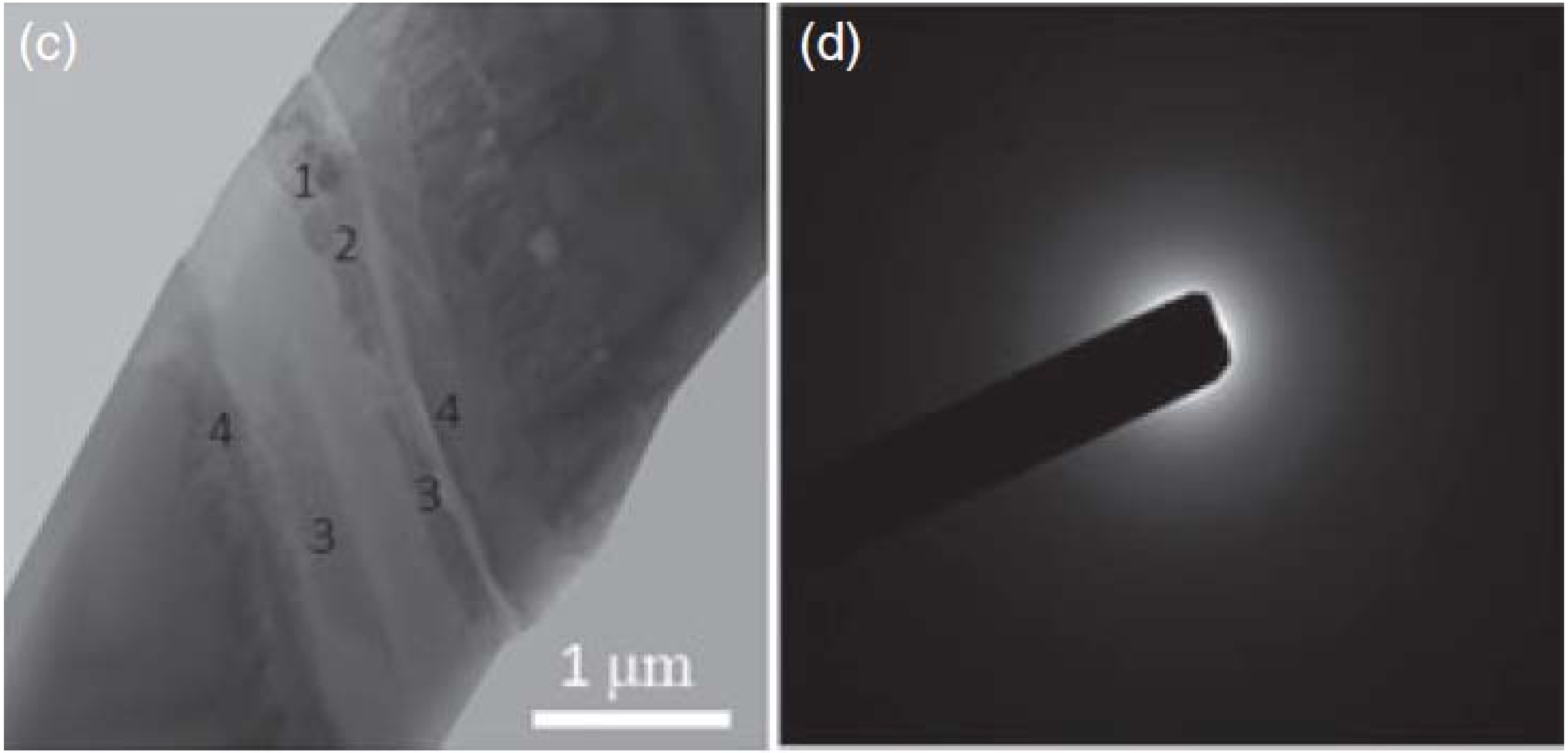
TEM: Initial vein characterisation



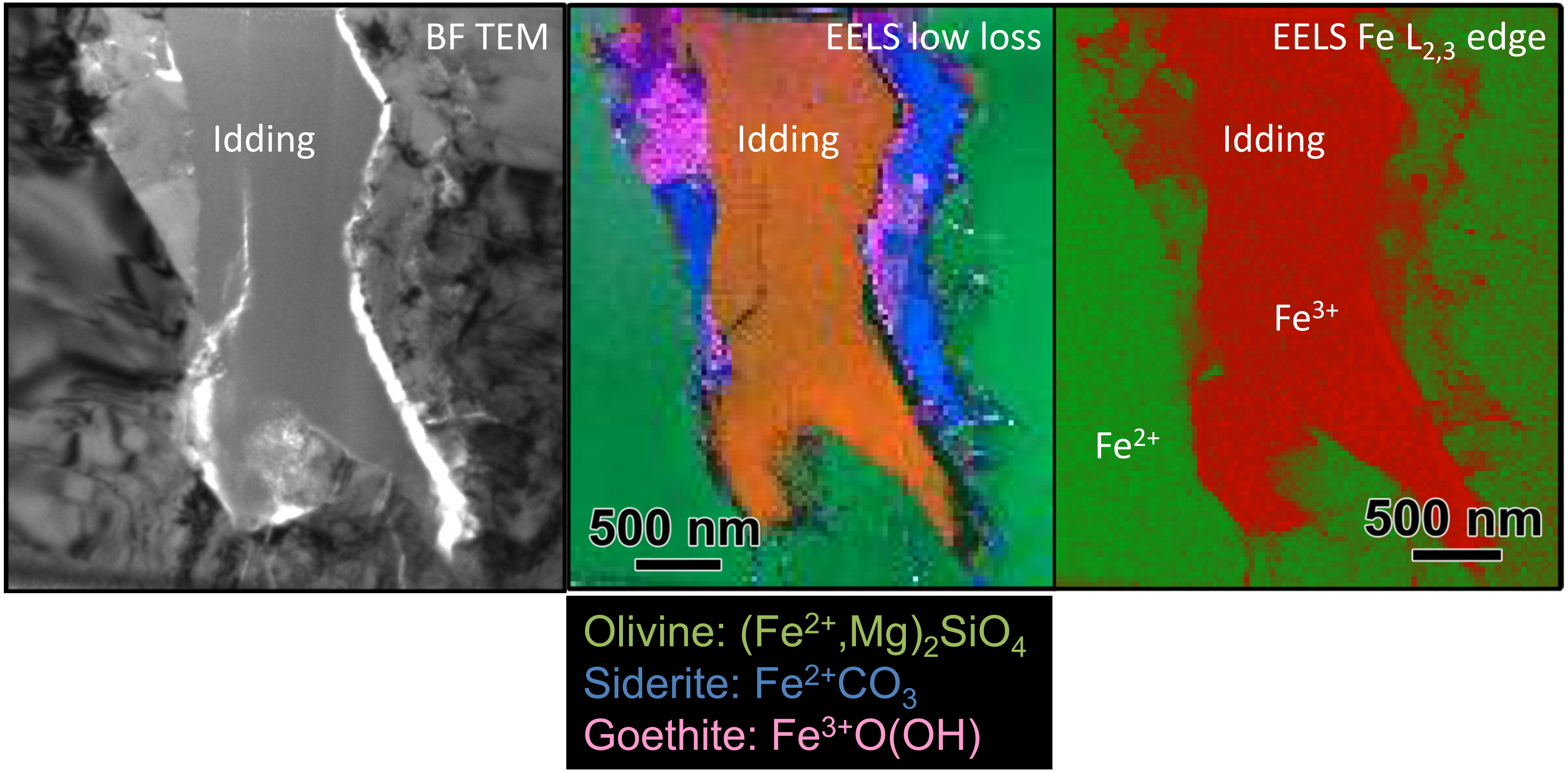


- Foils made by FIB, then Ar ion milled to ~50 nm.
- Iddingsite is featureless in BF TEM and nanocrystalline.

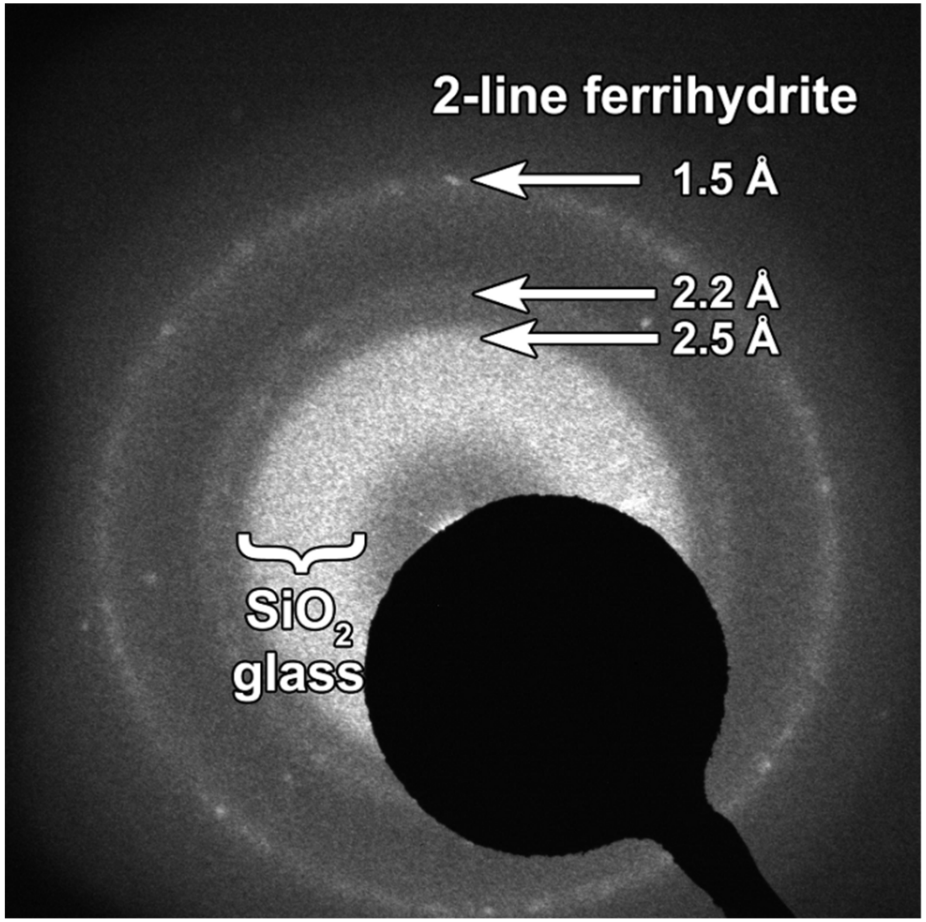
“Amorphous gel” of Changela and Bridges



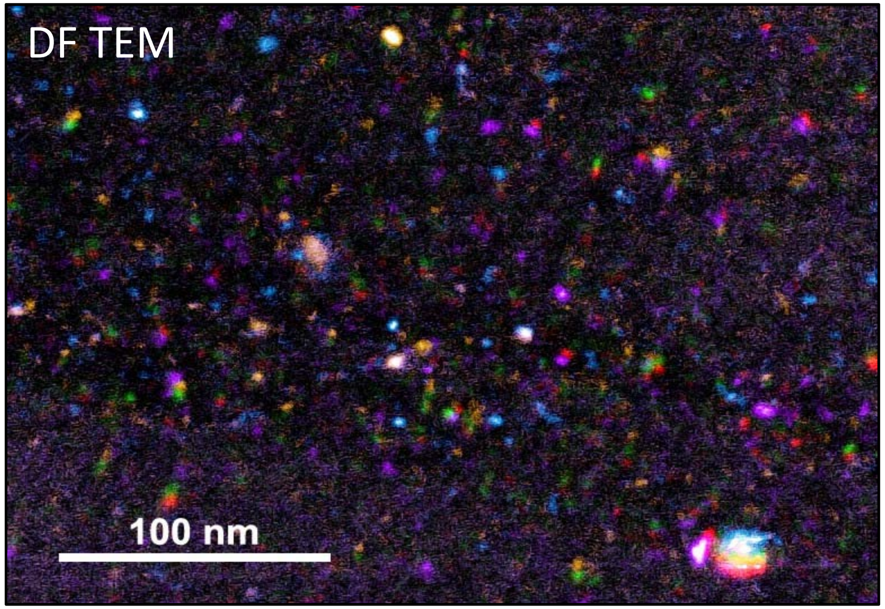
TEM : Vein phase identification using EELS



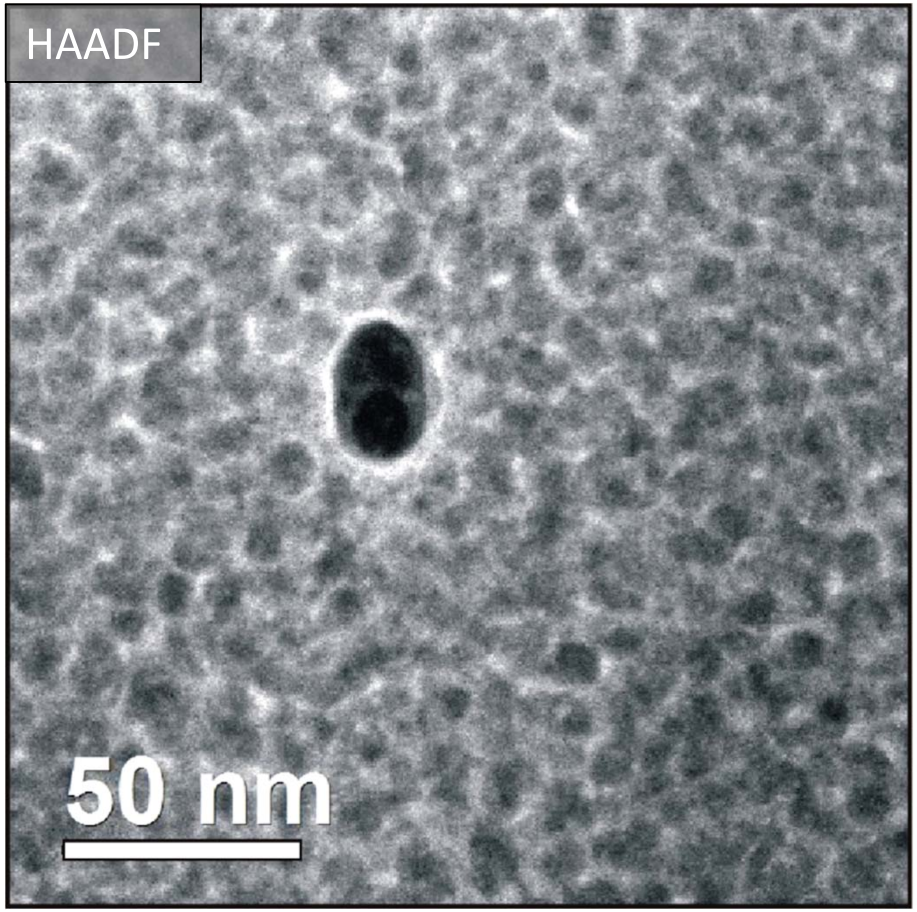
TEM : Water-bearing constituents of iddingsite

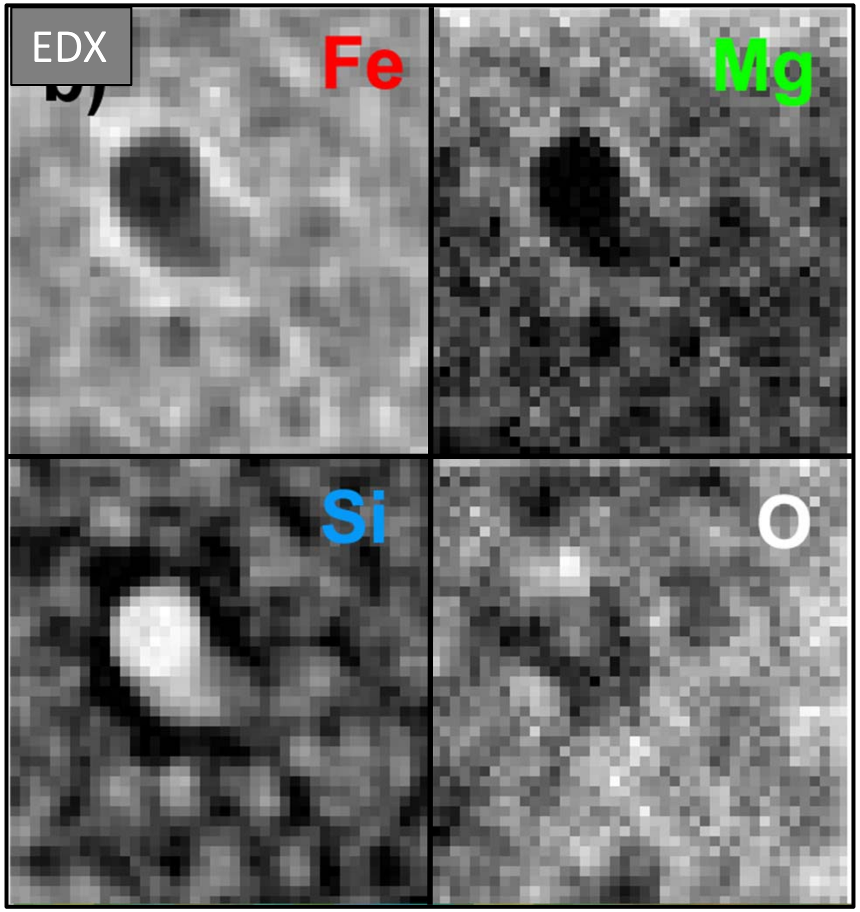


- SAED and dark-field TEM reveals nanocrystals of ferrihydrite: $Fe^{3+}_{8.2}O_{8.5}(OH)_{7.4} + 3H_2O$.

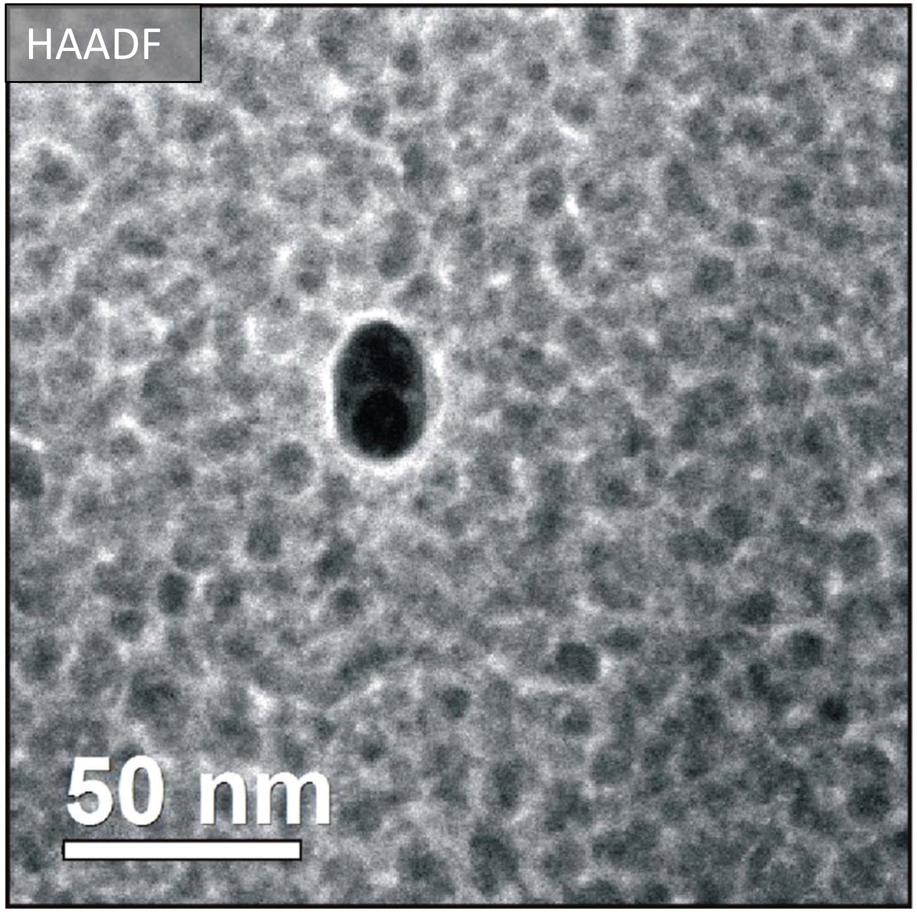


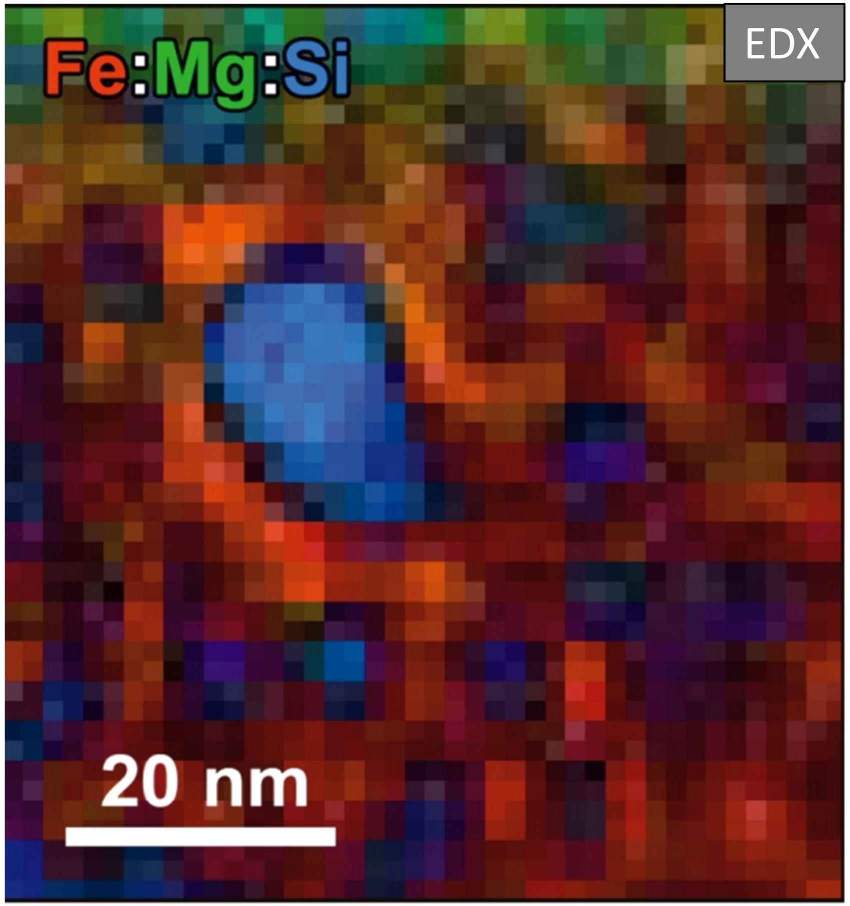
TEM : Water-bearing constituents of iddingsite





TEM : Water-bearing constituents of iddingsite



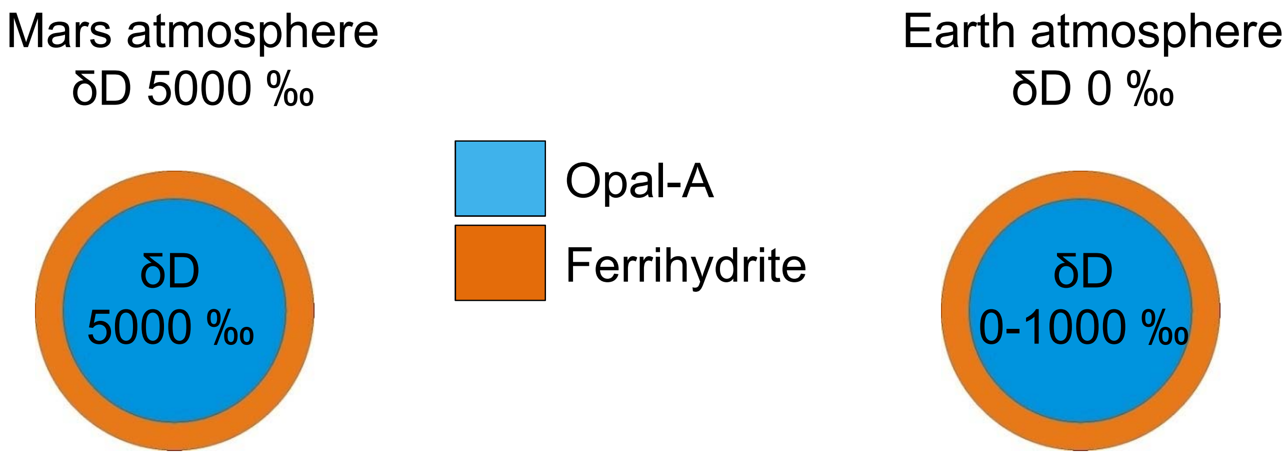


TEM : The carriers of water identified

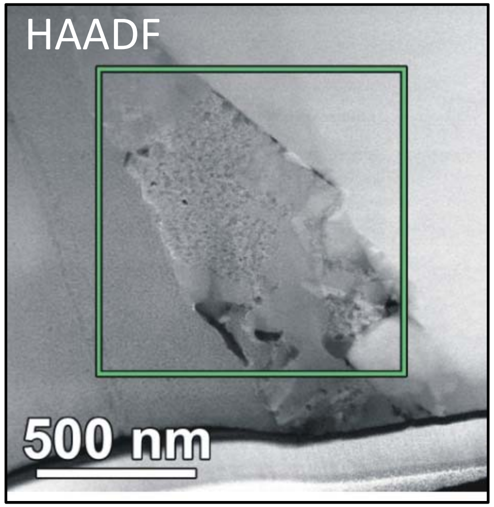
- Nanoparticles of opal-A — Amorphous $SiO_2.nH_2O$
- Shells of ferrihydrite — $Fe^{3+}_{8.2}O_{8.5}(OH)_{7.4} + 3H_2O$
- Shells also host nontronite? — $(Ca,Mg,Na)_{0.3}Fe^{3+}_2(Si,Al)_4O_{10}(OH)_2.nH_2O$

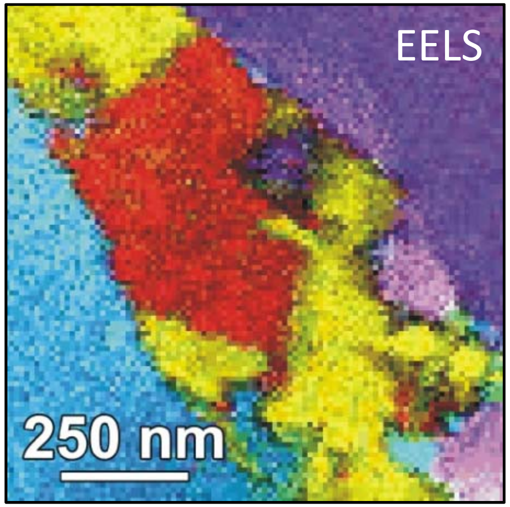
Addition & exchange of water/OH whilst on Earth

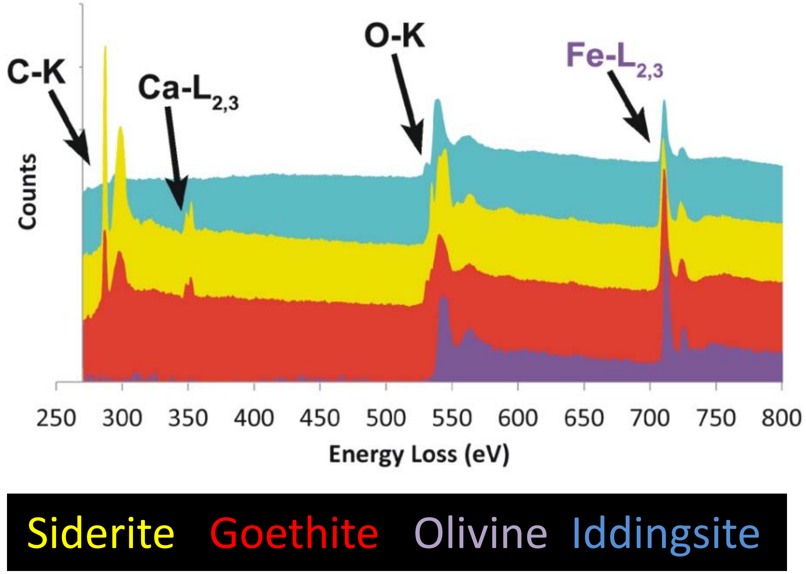
- δD of opal is lower than the present-day Martian atmosphere due to exchange of H whilst on Earth;
  - The nanoparticles have a reactive surface area of 250 m^2/g. Industrial catalysts = 1-1000 m^2/g.

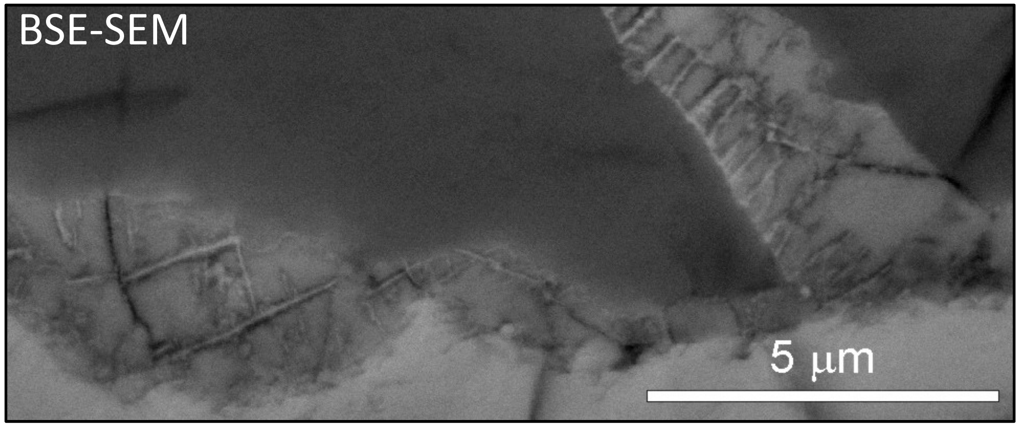


Addition & exchange of water/OH whilst on Earth









- Goethite formed by oxidation of siderite. Maybe after fall of the meteorite.

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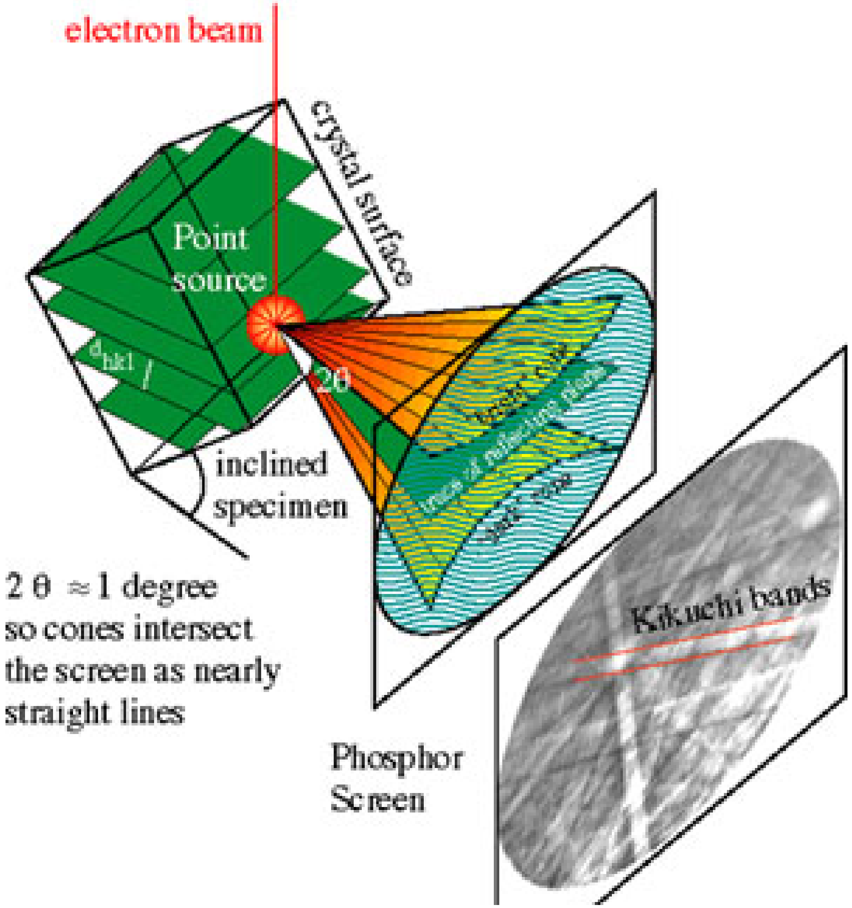
Electron backscatter diffraction

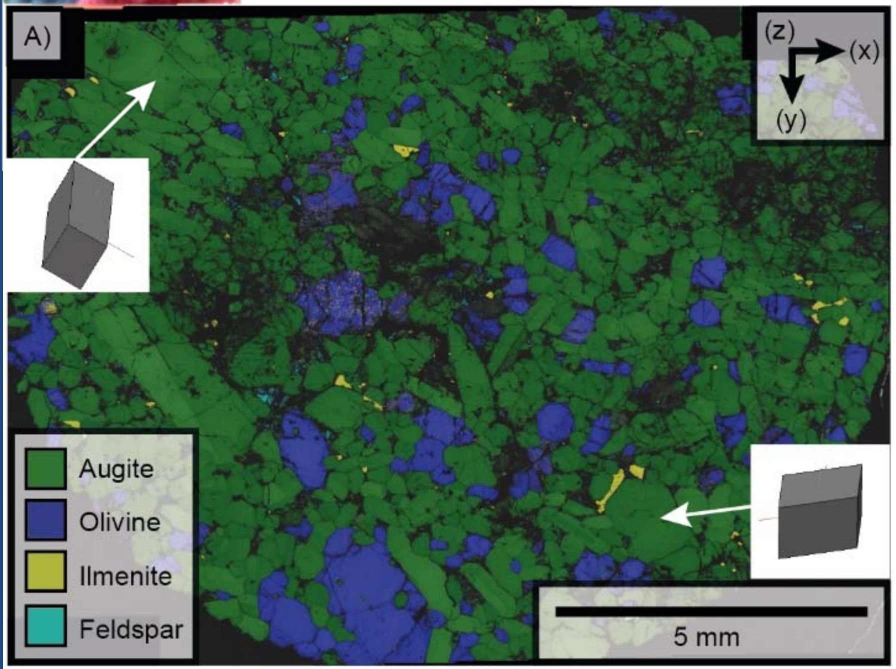


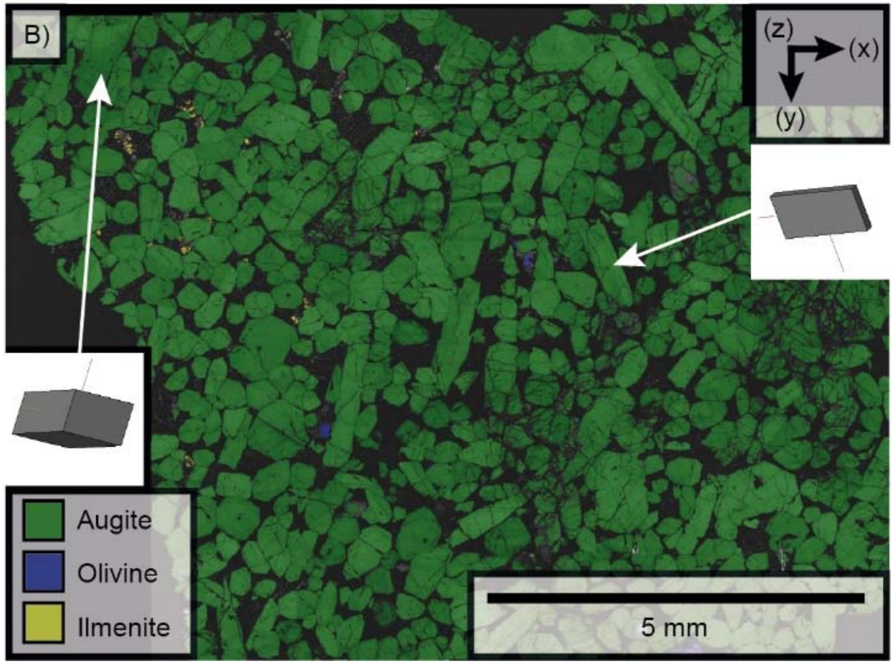
http://www.gm.univ-montp2.fr/spip.php?article104&lang=fr

- Rapid crystallographic mapping
- Max spatial resolution ~80 nm
- Max angular resolution ~0.1°
- Mineralogy
- Crystallinity
- Crystal orientation
- Internal deformation
- Grain shape
- Zeiss Sigma VP – Oxford Instruments

Lafayette

MIL 03346

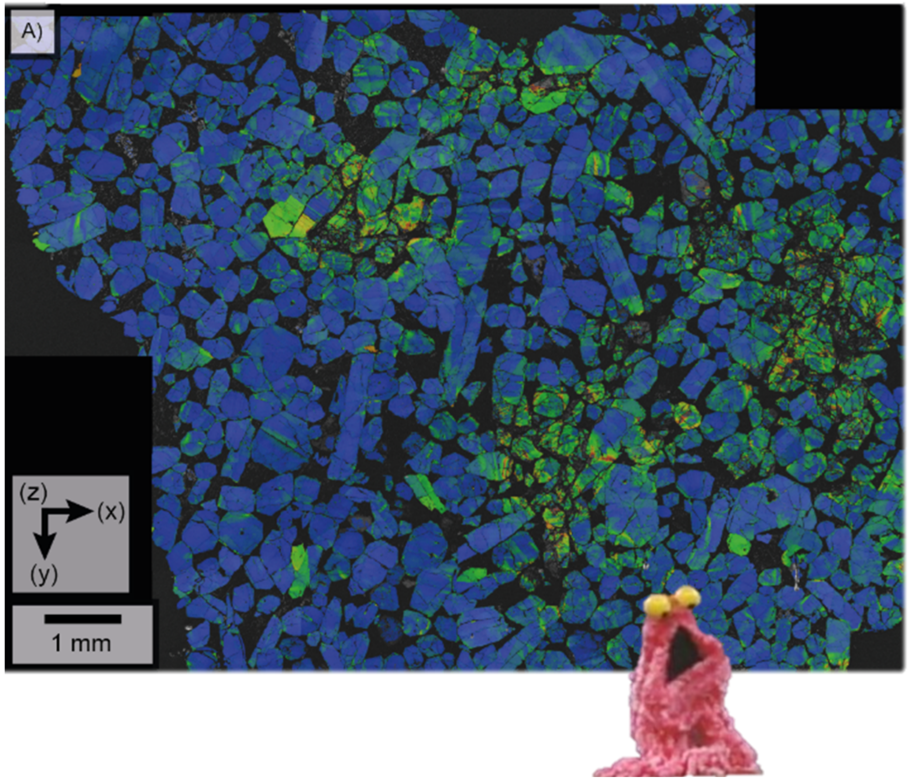


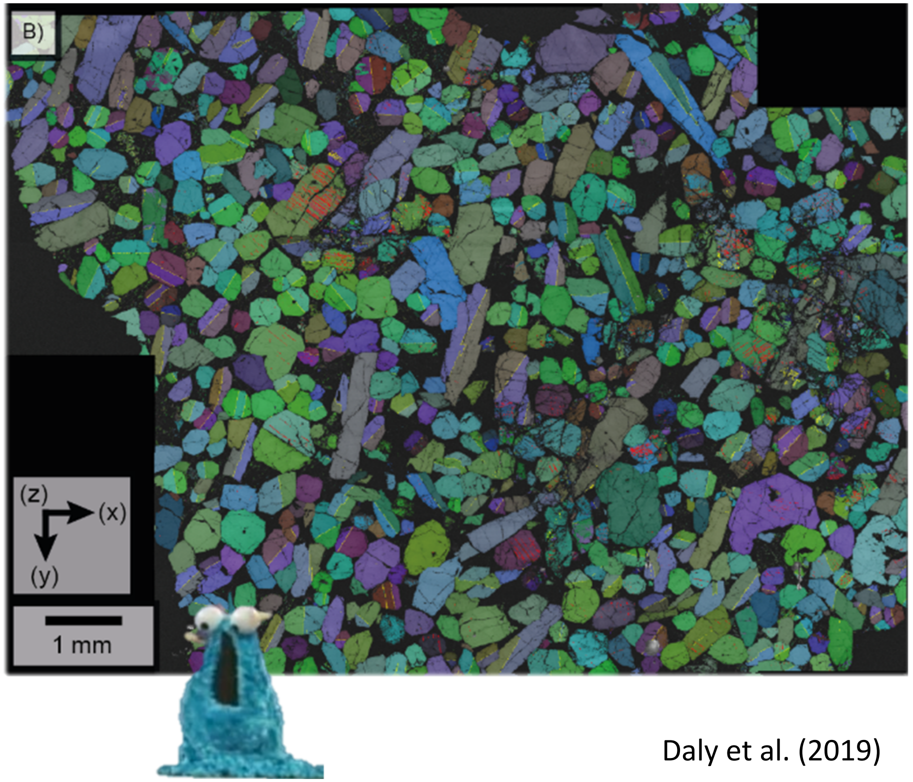


Daly et al. (2019)

EBSD : Deformation associated with shock twinning

MIL 03346

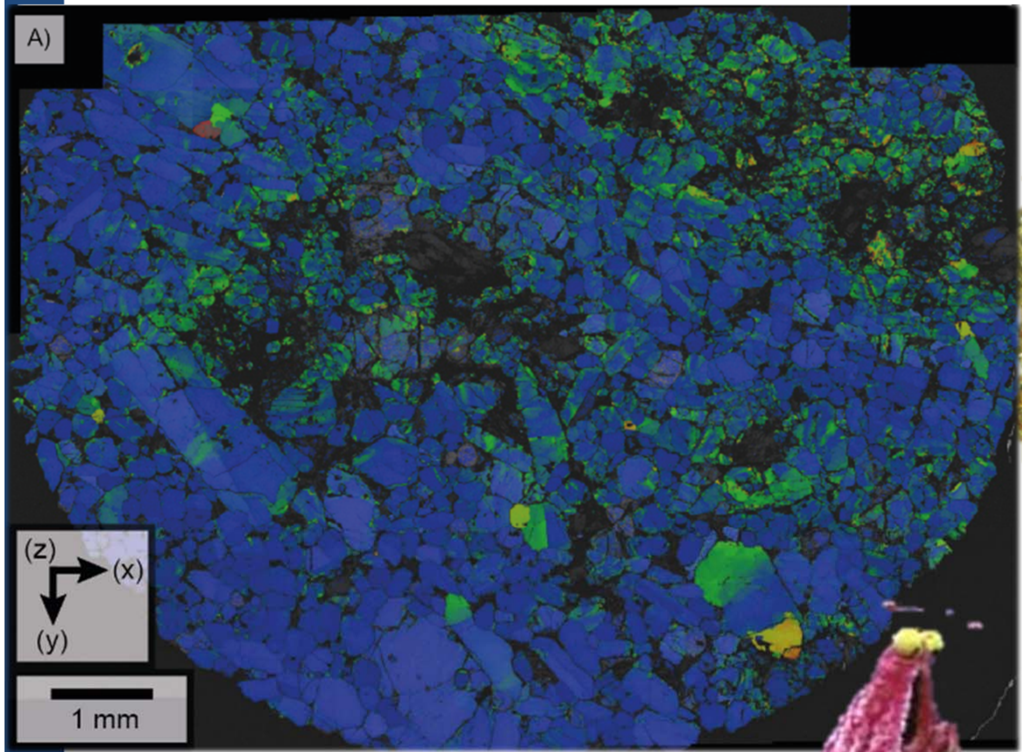


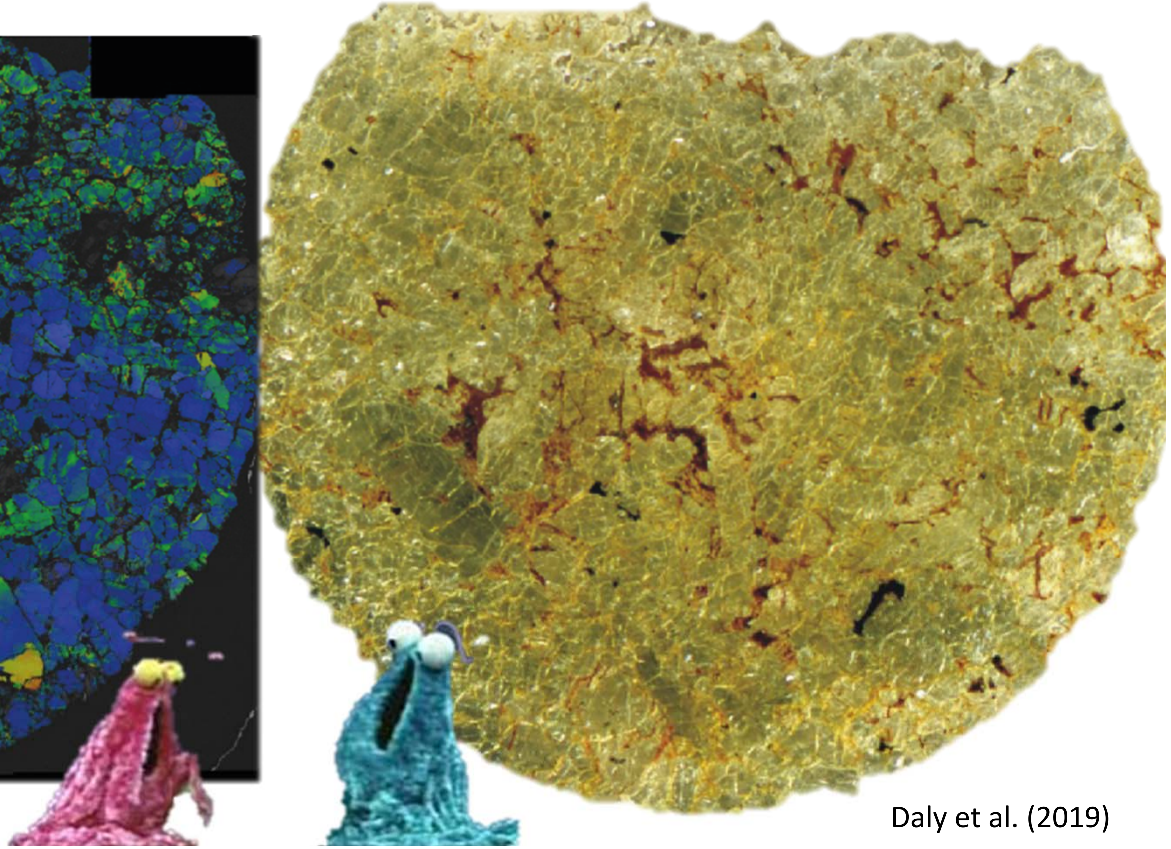


Daly et al. (2019)

EBSD: Deformation associated with aqueous alteration

Lafayette





Daly et al. (2019)

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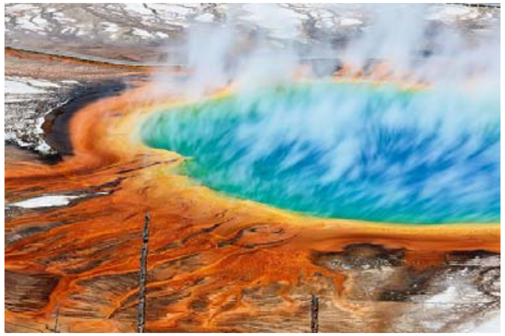
Nakhlite timeline



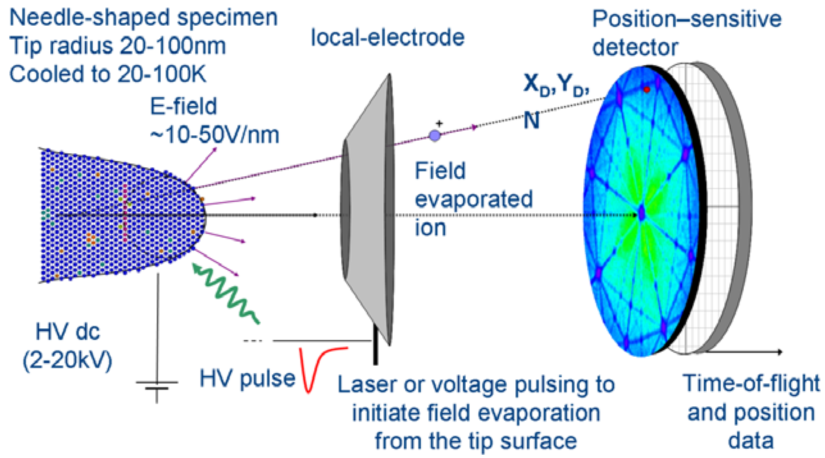
1.4-1.3 — 0.633 — 0.011 — 0

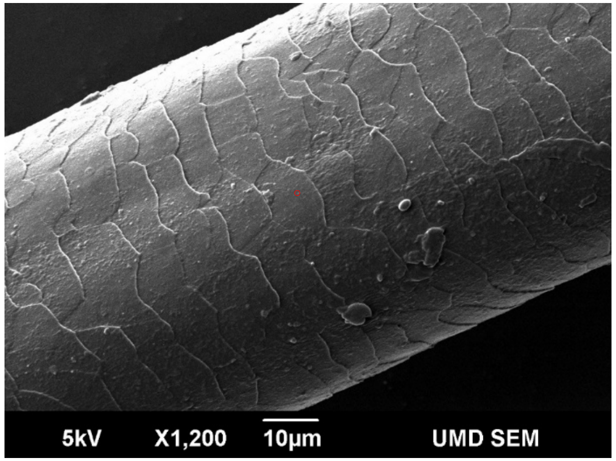
Billion Years

APT : searching for robust water reservoirs

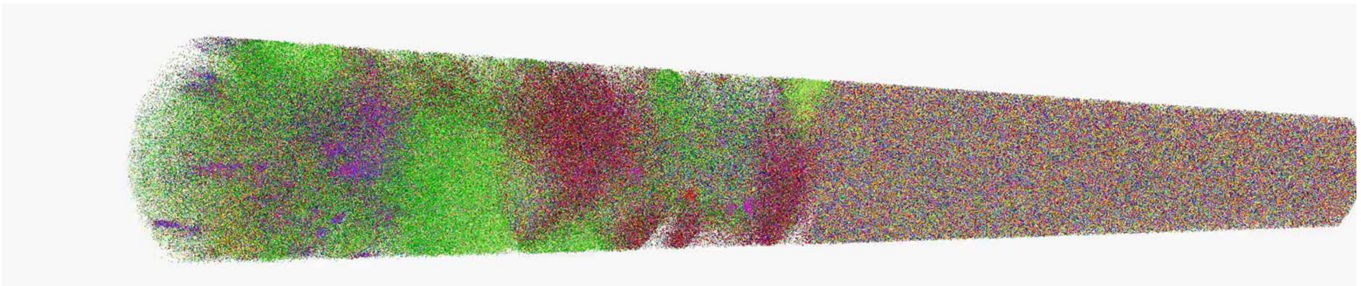
- LEAP 5000XHR Atom Probe, University of Oxford.
- Detection limits ~1 atomic ppm
- 100% ionisation - Whole periodic table
- Molecular species including OH and H_2O
- Mass spectrum and 3D atomic positions reconstructed using the IVAS software.

Atom Probe Tomography





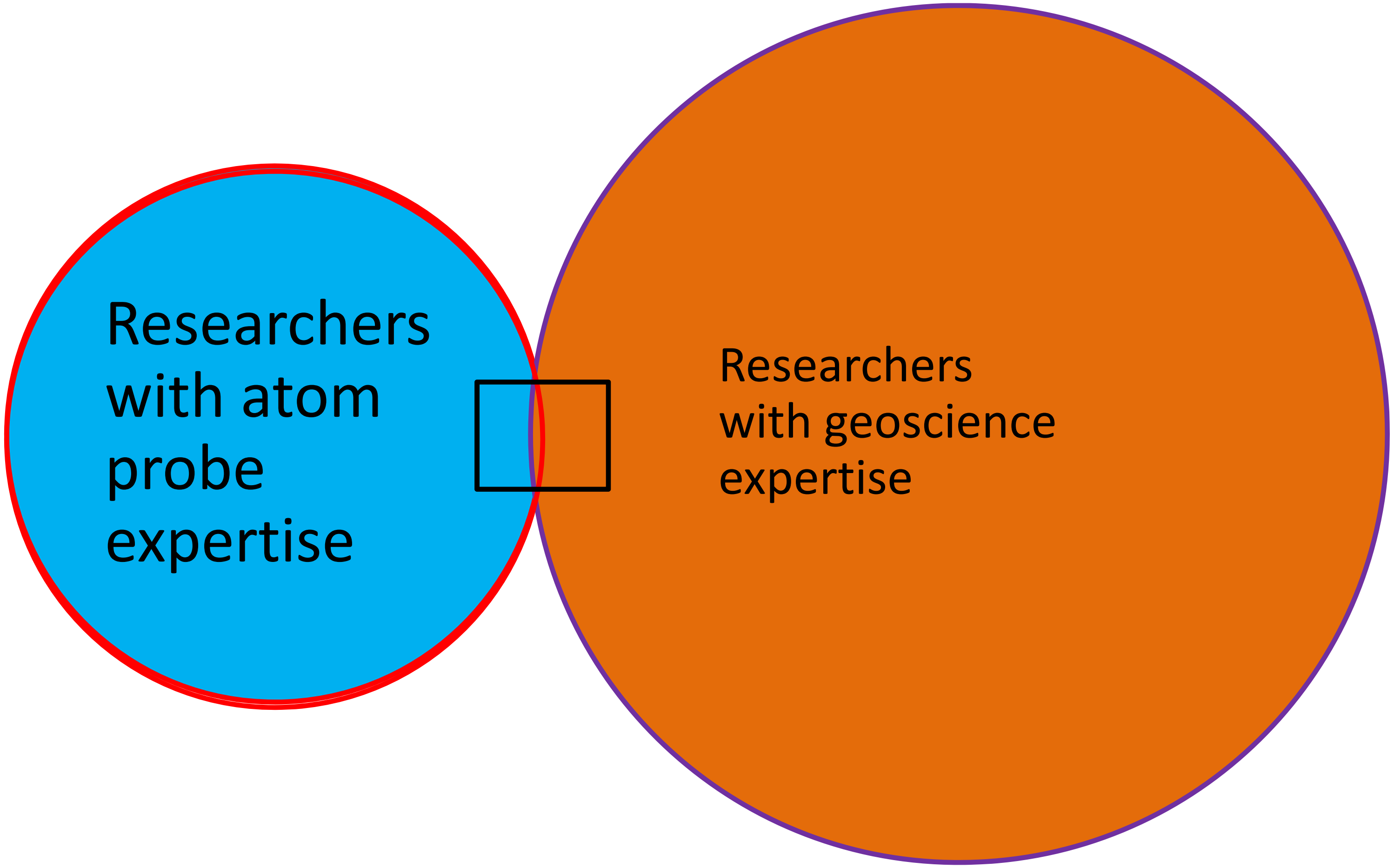
Gault et al. 2012



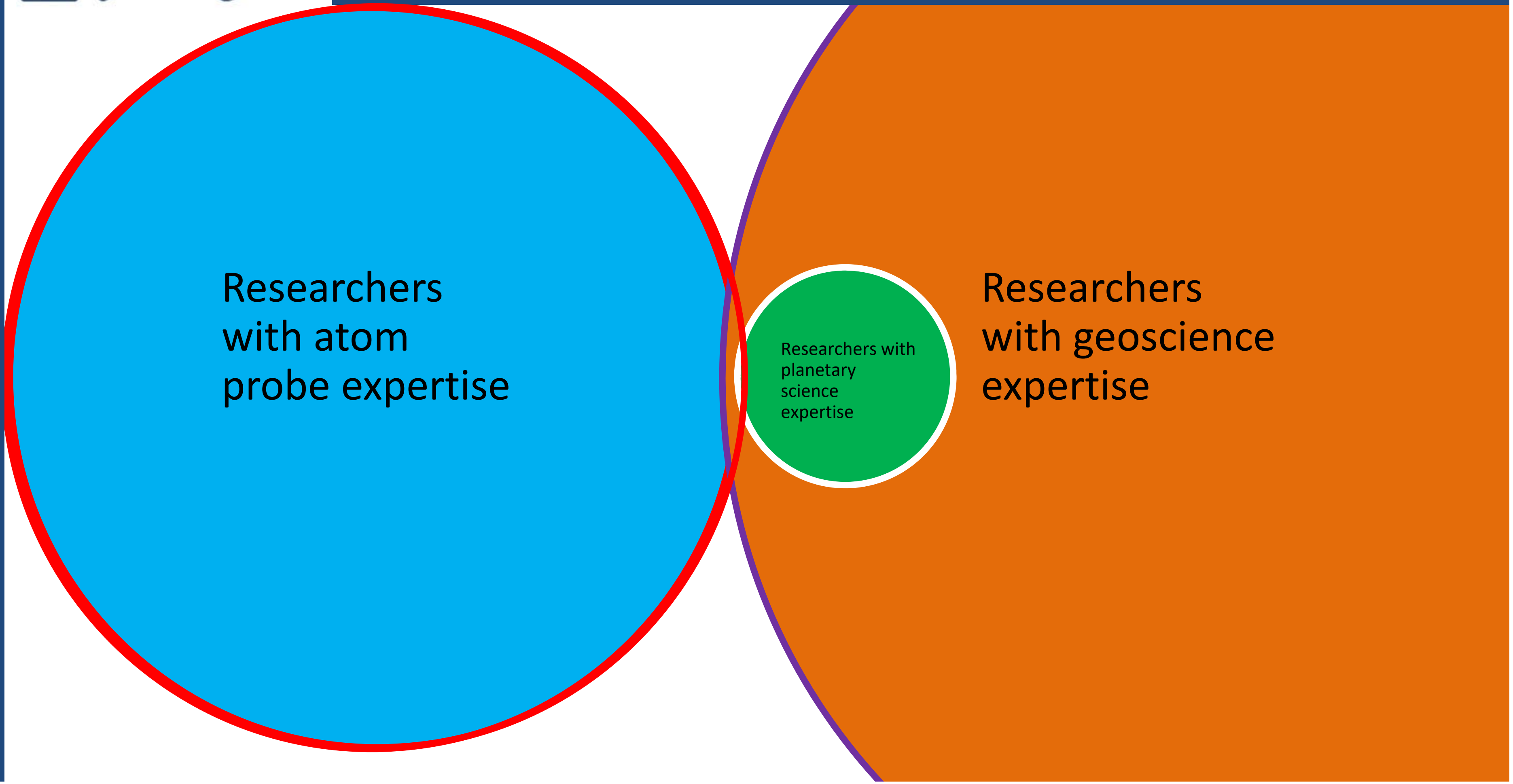
3D, Geochemistry, Isotopes

University of Glasgow

Atom probe in Geoscience

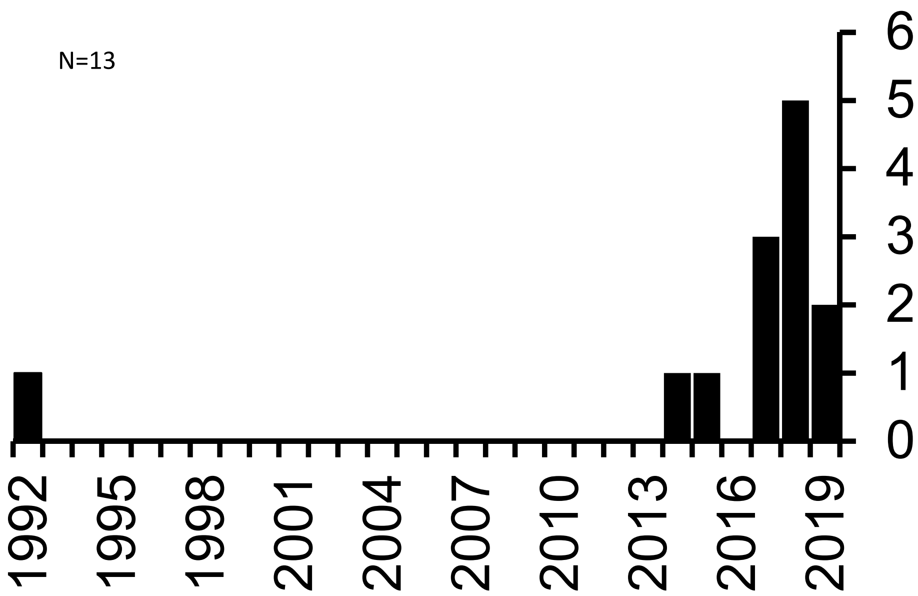


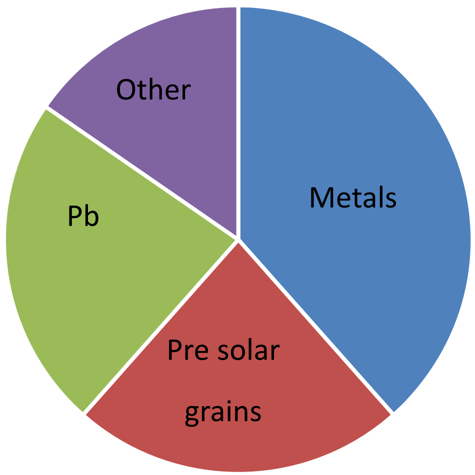
Atom Probe in Planetary Science



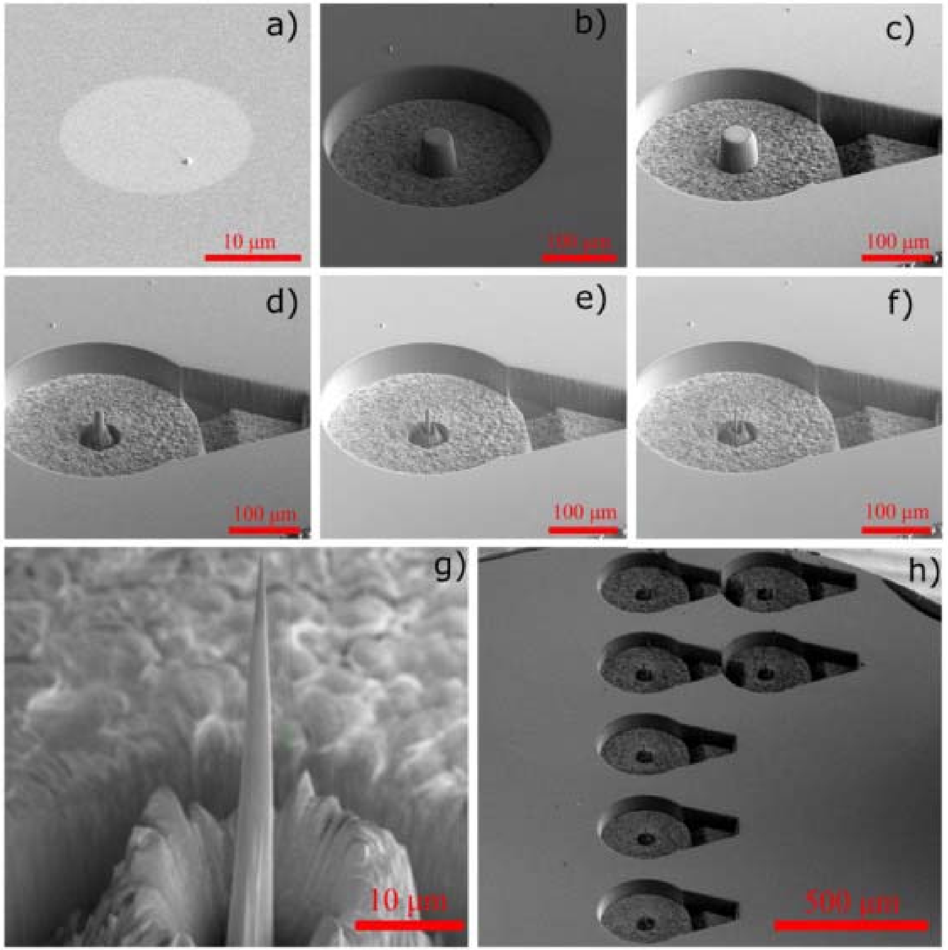
Atom probe Planetary Science publications

N=13





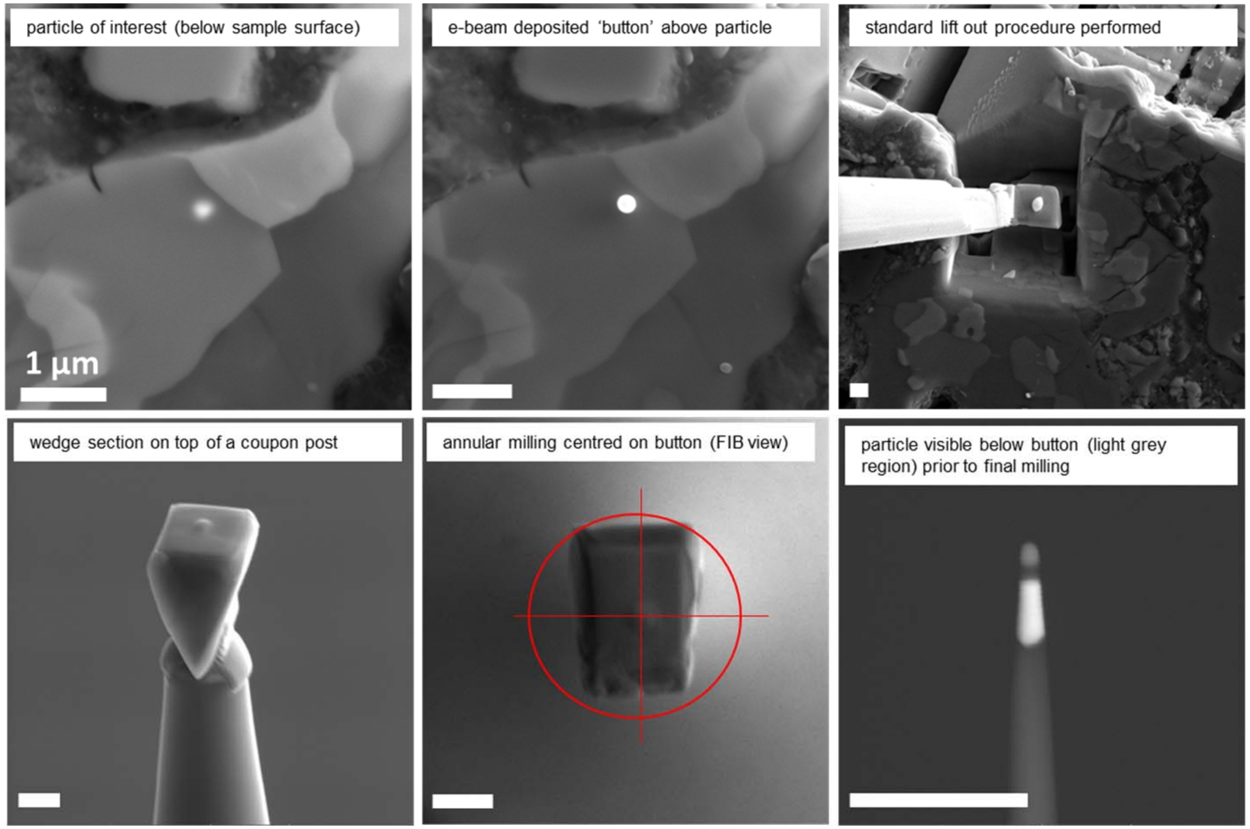
Site specific: Focused ion beam sample preparation



Satellite dish method

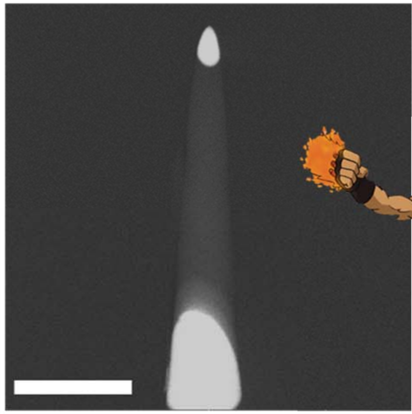
Halpin et al., 2019

Site specific: Focused ion beam sample preparation



Button method

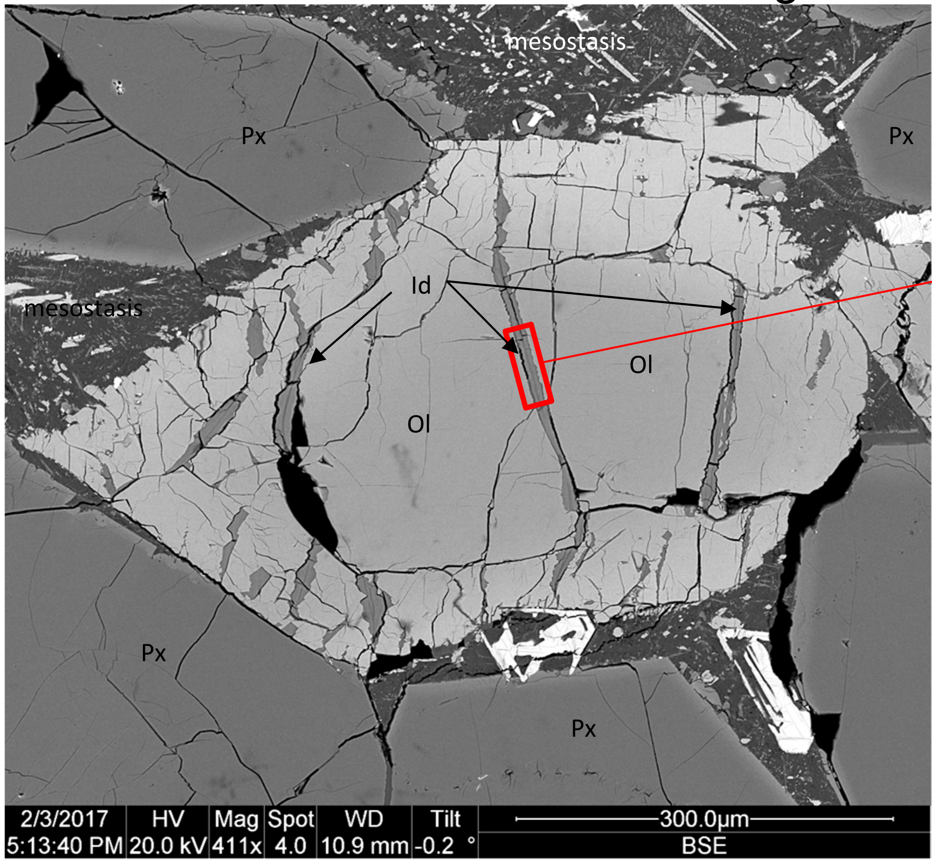
Particle successfully located at tip of APT needle

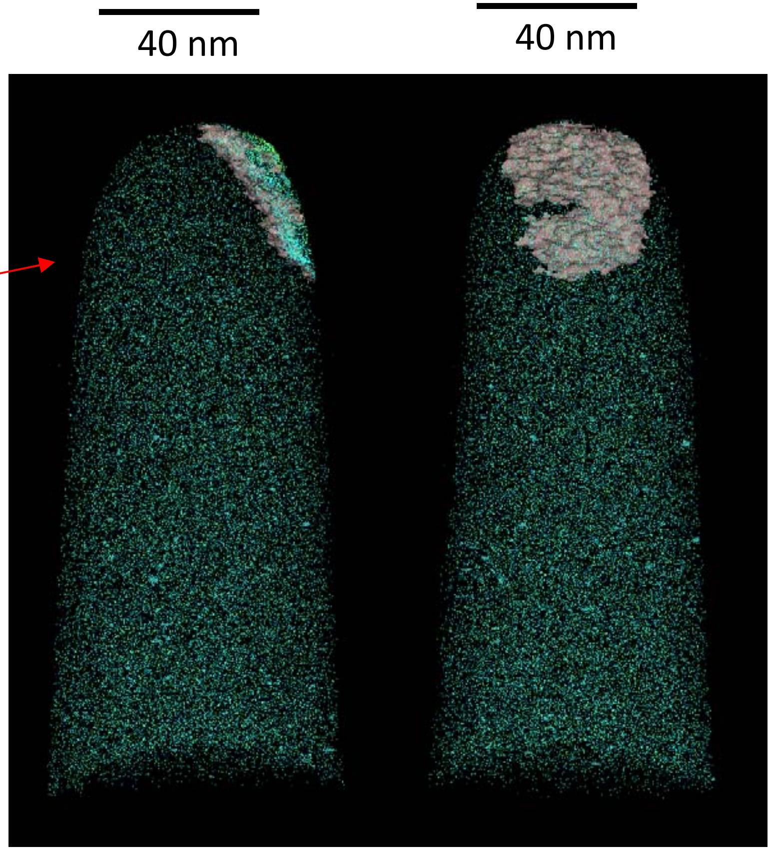


Rickard et al., (in review)

APT : searching for robust water reservoirs

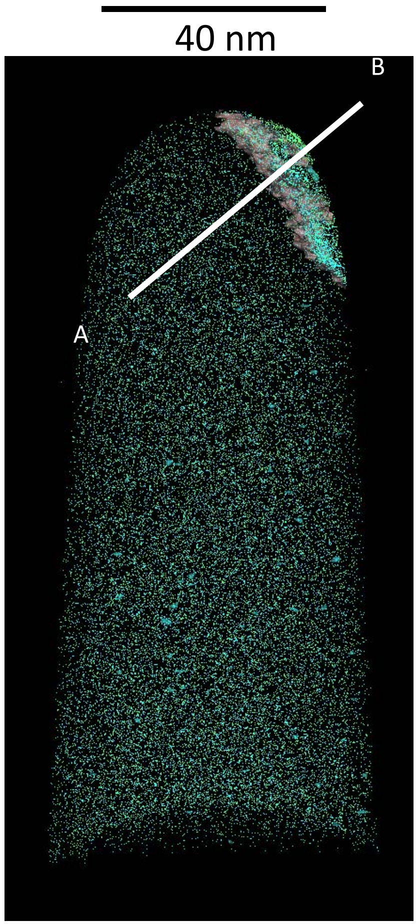
NWA 817 – Olivine/iddingsite interface

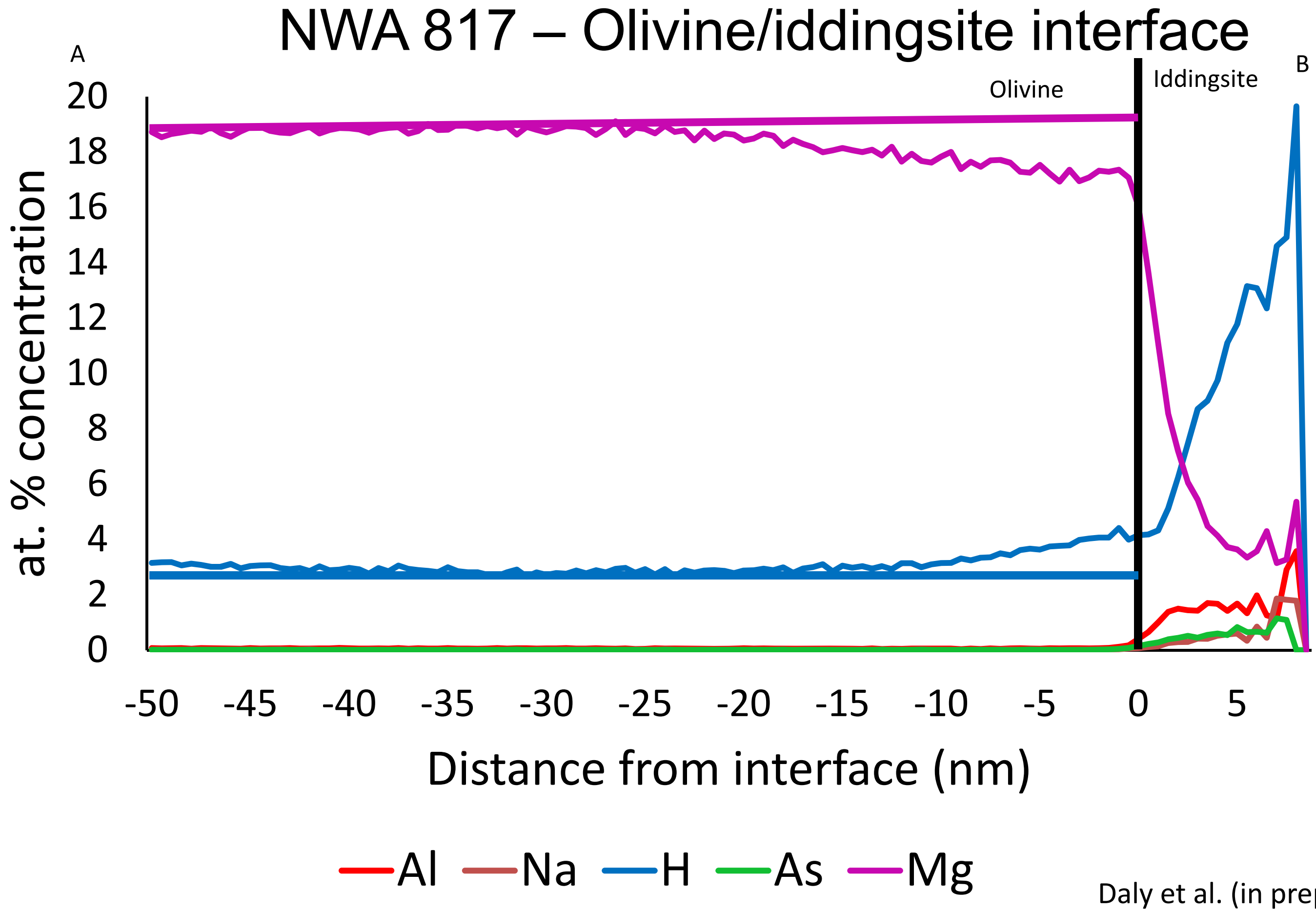




Daly et al. (in prep)

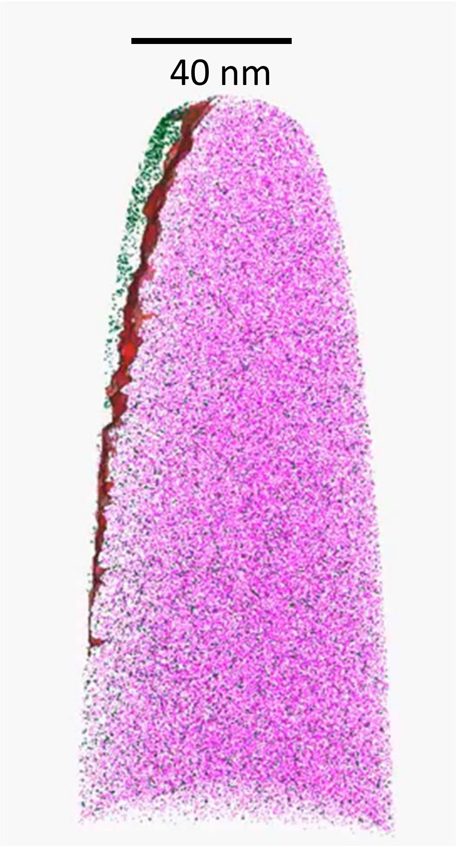
APT : searching for robust water reservoirs



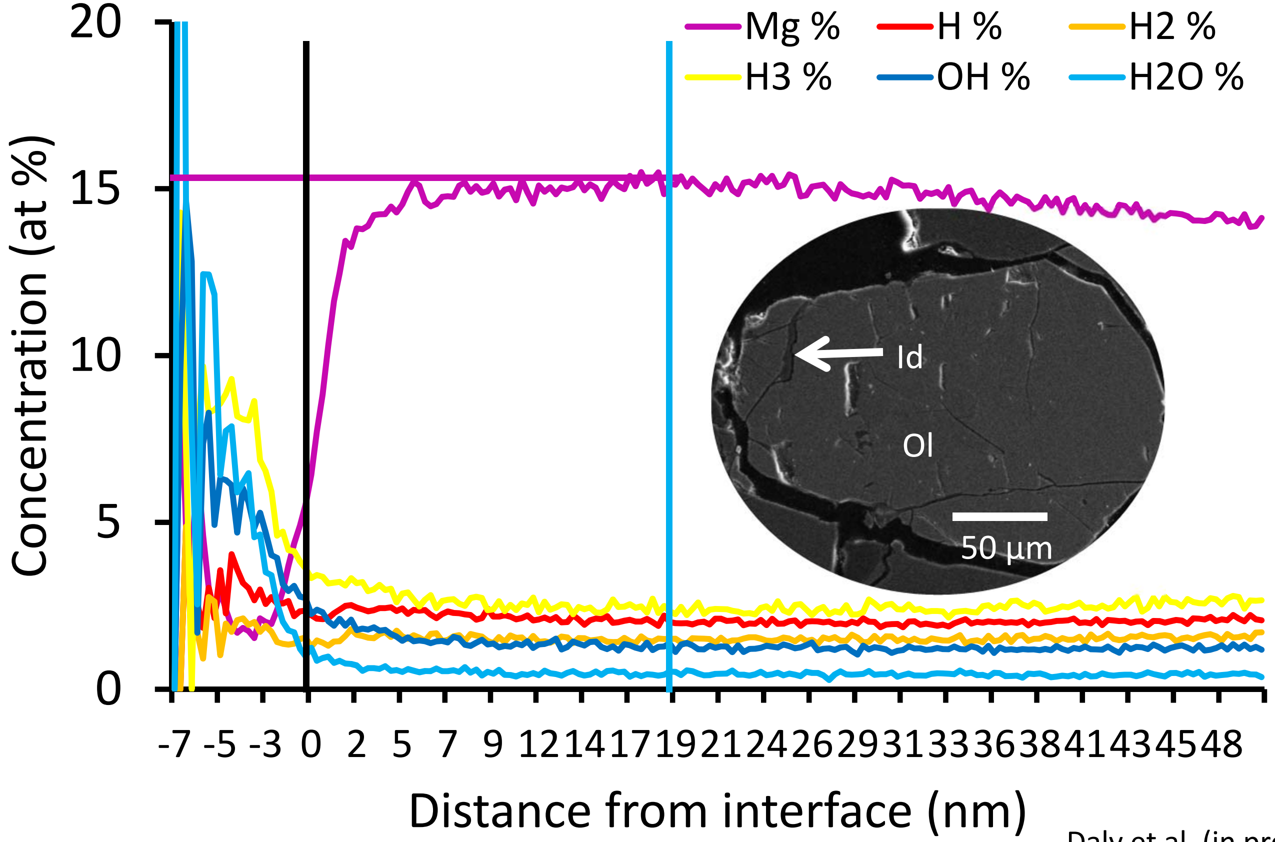


Daly et al. (in prep)

APT : searching for robust water reservoirs



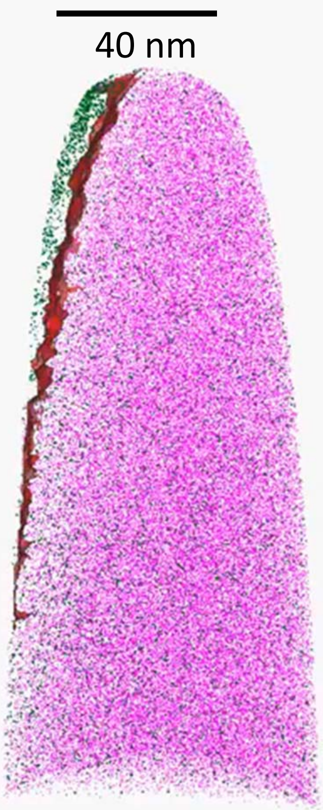
Lafayette Olivine/iddingsite interface



Daly et al. (in prep)

University of Glasgow

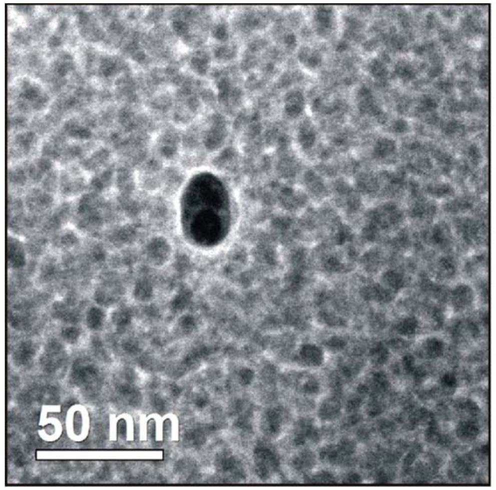
APT : implications for water reservoirs



Mg F interface

- Water is locked into the reaction rim in the olivine at the olivine-iddingsite interface.
- Water rock reaction occurs through cation exchange not dissolution-reprecipitation
- δD of this water exchanges less readily with the terrestrial atmosphere
  - Could provide a more robust Martian δD measurement to determine the provenance of the water
    - Meteoric vs crustal vs magmatic vs impact

Conclusions & outlook



- A impact event preceded and may have driven fluids on Mars ~633 Ma
- Water is hosted in opal-A ('fire opal'), and olivine-iddingsite reaction rims.
- The nanoparticles, and possibly also siderite have been altered by the Earth's atmosphere.
    - But olivine rims may be resistant.
- Returning samples for analysis by techniques including EBSD/TEM/APT is essential.

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