Jarosite in Antarctic deep ice supports the ice-weathering model for jarosite formation on Mars

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Jarosite on Earth

Jarosite is a potassium-iron(3+) hydrated sulphate, his formula his: $KFe_3(SO_4)_2(OH)_6$

This mineral is a typical low-temperature oxidation product which forms where there are available iron-bearing minerals, limited amounts of water, an acidic-oxidative environment.

Jarosite on Earth mostly occurs in three environments, they are (see Papike et al., 2006 for details):

- highly acidic and oxidizing surficial environments where jarosite precipitates as the result of pyrite-bearing ore deposits (**supergene jarosite**)
- near-surface playa settings in acid-saline lakes, where jarosite precipitates from aqueous sulfate derived from the oxidation of pyrite in groundwater, or of sulfate aerosols transported from seawater (**sedimentary jarosite**).
- hot springs (volcanic contexts) where the oxidation of H_2S in presence of water leads to jarosite precipitation (**steam-heated jarosite**).

Papike et al. (2006) Comparative planetary mineralogy: Implications of martian and terrestrial jarosite. A crystal chemical perspective. *Geochim. Cosmochim. Ac.* 70:1309-1321.

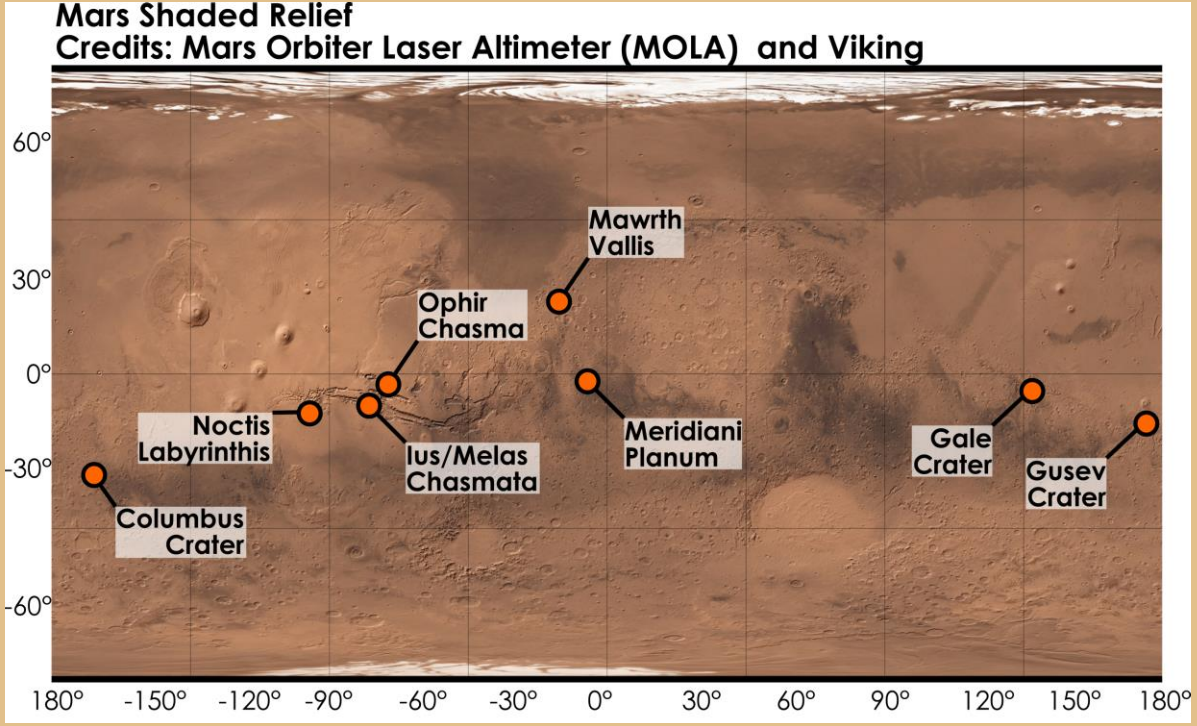
Jarosite on Mars

The history of Martian jarosite begins in 1987, when Roger Burns predicted its stability under Martian surficial conditions **[1]**. The first direct observation of jarosite on Mars dates back to 2004, when the Opportunity rover landed on Mars at Meridiani Planum and found abundant jarosite in the sedimentary rocks that were for this reason renamed after Dr. Burns **[2]**.

An artwork showing the Opportunity rover while inspecting the rocks of Burns' formation at Meridiani planum. Credits: NASA/JPL-Caltech/Cornell/ASU

Since then jarosite has been repeatadley identified on the Red Planet, both by the other rovers that reached the planet and by remote sensing data from orbiters.

What remains to understand is how jarosite formed in the geologic past of the planet and how it was preserved. The mineral is in fact stable only under particular conditions.



A map of Mars based on MOLA and Viking data [3] showing the sites where jarosite was identified. Credits: NASA & USGS *if I am missing something, please let me know!*

[1] Burns (1987) Ferric sulfates on Mars. *J. Geophys. Res.* 92:E570-E574.
[2] Klingelhöfer et al. (2004) Jarosite and Hematite at Meridiani Planum from Opportunity's Mössbauer Spectrometer. *Science* 306:1740-1745.

How Martian jarosite formed?

Thanks to the well-defined conditions leading to its precipitation and conservation, jarosite is a valuable probe to infer about Martian conditions.

To form jarosite requires: (1) a low water/rock ratio (and low water activity); (2) an acidic/oxidative environment (pH<4); (3) presence of Fe-bearing minerals **[1]**. If pH is too high or water is too abundant, jarosite is not stable and easily converts to more stable Fe-mineral phases, such as goethite and hematite **[2]**.

Lake Tyrell (Australia) is an endorheic lake where jarosite precipitates because of high evaporation rates and acidic groundwater upwelling [5]. This is a good analogue for the playa hypothesis to explain jarosite formation.

The most accepted model to explain the presence of jarosite on Mars relies on the *playa hypothesis*. In accordance to it jarosite precipitated in settings similar to Earth playas (see the side picture) because of the interaction between acidic groundwater and altered basalts **[3,4]**.

This model has its limits. It doesn't account for the fact that the interaction between acidic fluids and massive basaltic rocks buffers pH consuming acidity **[6]**. Moreover, we don't have evidence of closed basins which favoured the concentration and upwelling of the huge quantity of groundwater needed to explain the formation of Meridiani Planum jarosite-reach sediments **[7]**.

Additional hypotheses have been drawn and involve the interaction between acidic volcanic emissions, water and weathered rocks (resembling terrestrial steam-heated jarosite), a fluvial origin or a meteorite impact **[8]**.

[1] Papike et al. (2006) Comparative planetary mineralogy: Implications of martian and terrestrial jarosite. A crystal chemical perspective. *Geochim. Cosmochim. Ac.* 70:1309-1321.
[2] Elwood-Madden et al. (2009) How long was Meridiani Planum wet? Applying a jarosite stopwatch to determine the duration of aqueous diagenesis. *Geology* 37:635-638.
[3] McLennan et al. (2005) Provenance and diagenesis of the evaporite-bearing Burns formation, Meridiani Planum, Mars. *Earth and Planet. Sci. Lett.* 240:95-121.
[4] Arvidson et al. (2006) Nature and origin of the hematite-bearing plains of Terra Meridiani based on analyses of orbital and Mars Exploration rover data sets. *J. Geophys. Res.* 111:E12S08.
[5] Long et al. (1992) Formation of alunite, jarosite and hydrous iron oxides in a hypersaline system: Lake Tyrrell, Victoria, Australia. *Chemical Geology* 96:183-202.
[6] Zolotov & Mironenko (2007) Timing of acid weathering on Mars: A kinetic-thermodynamic assessment. J. Geophys. Res. 112:E07006.
[7] Hynek & Phillips (2008) The stratigraphy of Meridiani Planum, Mars, and implications for the layereddeposits' origin. *Earth and Planet. Sci. Lett.* 274:214-220.
[8] Hynek et al. (2019) Sulfur Cycling and Mass Balance at Meridiani, Mars. *Geophys. Res. Lett.* 46:11728-11737.

Jarosite and ice: a complicated story

Additional settings were jarosite has been rarely identified on Earth are ice- and cold-related. Jarosite is in fact a typical constituent of rock varnishes found on the surface of Antarctic nunataks **[1]** and it is also common in meteorites found at Antarctic blue ice fields **[2]**.

Jarosite has also been identified as the result of acidic weathering in peri-glacial environments **[3,4]**, supporting the original hypothesis of Burns that jarosite could be a common weathering product under cold-wet conditions **[5]**.

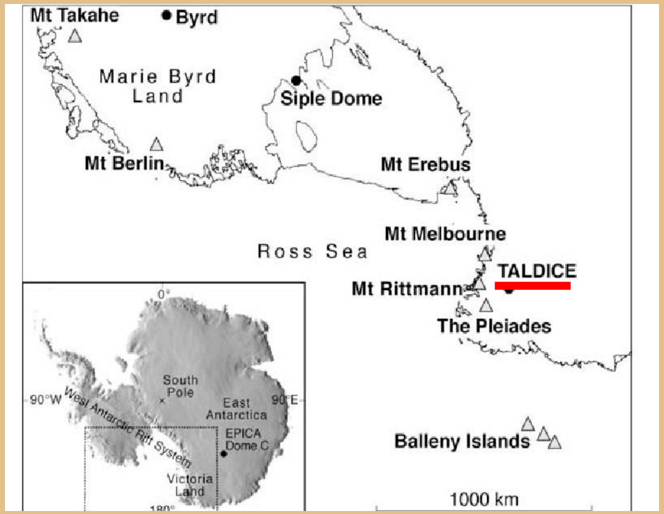
Also on Mars the formation of jarosite has been related to ice-related settings. Niles & Michalski developed a model (the ice-weathering model) to explain its formation inside ancient massive dust-rich ice deposits that were present on Mars during past glacial periods **[6]**. Jarosite would have been produced inside ancient ice deposits, where dust and acidic volcanic species reacted with each other. Because of climate changes, ice sublimated and the sublimation residue rich in jarosite was re-worked by aeolian processes, producing the layered formations observed at many sites on Mars.

The problem is that despite that jarosite on Earth has frequently been found in cold settings, so far its production inside ice has never been reported, weakening the ice-weathering model. *But things are changing…*

[1] Giorgetti & Baroni (2007) High-resolution analysis of silica and sulphate-rich rock varnishes from Victoria Land (Antarctica). *Eur. J. Mineral.* 19:381-389; [2] Hallis (2013) Alteration assemblages in the Miller Range and Elephant Moraine regions of Antarctica: comparisons between terrestrial igneous rocks and Martian meteorites. *Meteorit. Planet. Sci.* 48:165-179; [3] Lacelle & Léveillé (2010) Acid drainage generation and associated Ca–Fe–SO4 minerals in a periglacial environment, Eagle Plains, Northern Yukon, Canada: A potential analogue for low-temperature sulfate formation on Mars. *Planet. Sp. Expl.* 58:509-521; [4] Battler et al. (2013) Characterization of the acidic cold seep emplaced jarositic Golden Deposit,NWT, Canada, as an analogue for jarosite deposition on Mars. *Icarus* 224:382-398; [5] Burns (1987) Ferric sulfates on Mars. *J. Geophys. Res.* 92:E570-E574; [6] Niles & Michalski (2009) Meridiani Planum sediments on Mars formed through weathering in massive ice deposits. *Nat. Geosci.* 2:215-220.

Iron-mineralogy in the Talos Dome ice core (East Antarctica)

The study presented here is based on the analysis of ice core samples from the Talos Dome ice core (TD).



This is a 1620 long ice core retrieved from a peripheral site of East Antarctica, not far from the Ross Sea and from local ice-free sites present in the Transantarctic Mountains sector of Victoria Land which emit local mineral dust.

The core has actually been dated until 1440 m, with an ice age of approximately 150k yr before present (BP) **[1,2]** but studies are on course to extend its dating which probably reaches much older periods (3-400k BP).

This study was born from our aim to characterize the deepest and less investigated part of the core, focusing on the iron mineralogy of dust.

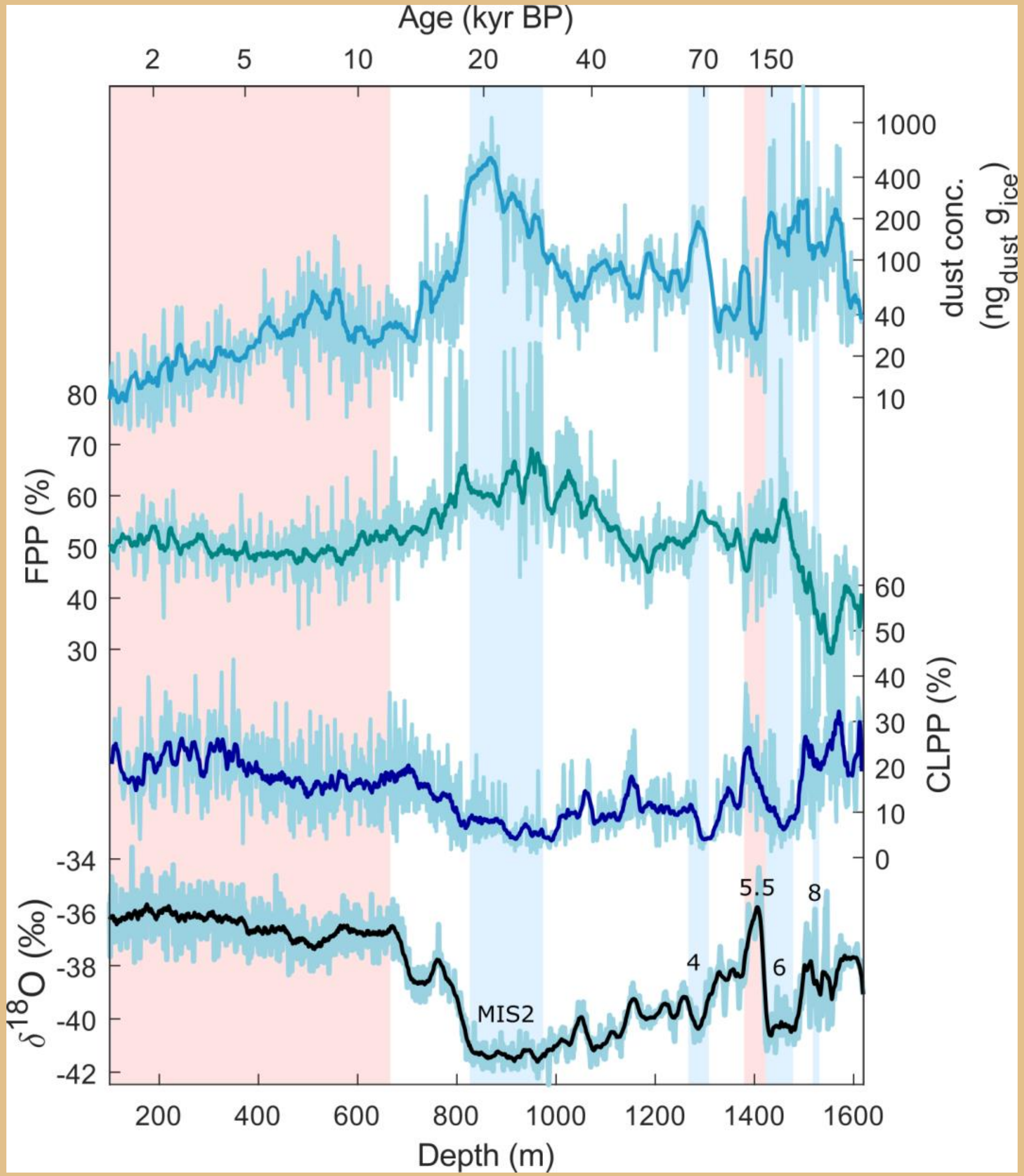
[1] Veres et al. (2012) The Antarctic ice core chronology (AICC2012): an optimized multi-parameter and multi-site dating approach for the last 120 thousand years. *Clim. Past* 9:1733-1748.
[2] Bazin et al. (2012) An optimized multi-proxy, multi-site Antarctic ice and gas orbital chronology (AICC2012): 120–800 ka. *Clim. Past* 9:1715-1731.

Materials and methods

We analysed sections of the Talos Dome with the following techniques:

- **Coulter counter**: insoluble particle concentration and grain size (University of Milano-Bicocca)
- **X-ray fluorescence**: major element composition of insoluble dust extracted from the ice (Diamond synchrotron)
- **X-ray absorption spectroscopy**: iron mineralogy and oxidation (Diamond synchrotron)
- **Scanning electron microscopy coupled with EDX**: morphology and elemental mapping of single dust grains
- **Transmission electron microscopy with EDX**: diffraction and stoichiometric elemental composition

Dust Concentration and Grain Size



TD dust records shows typical features observed in other Antarctic ice cores:

- High dust concentration during full glacial periods (MIS2, MIS4, MIS6)
- Fine dust deposited during glacial periods, confirming its remote source (South America)
- Low concentration during interglacials and stadial periods (Holocene, MIS3, MIS5.5)
- Strong anti-correlation with isotopic signals, suggesting a coupling between the atmospheric dust cycle and climate

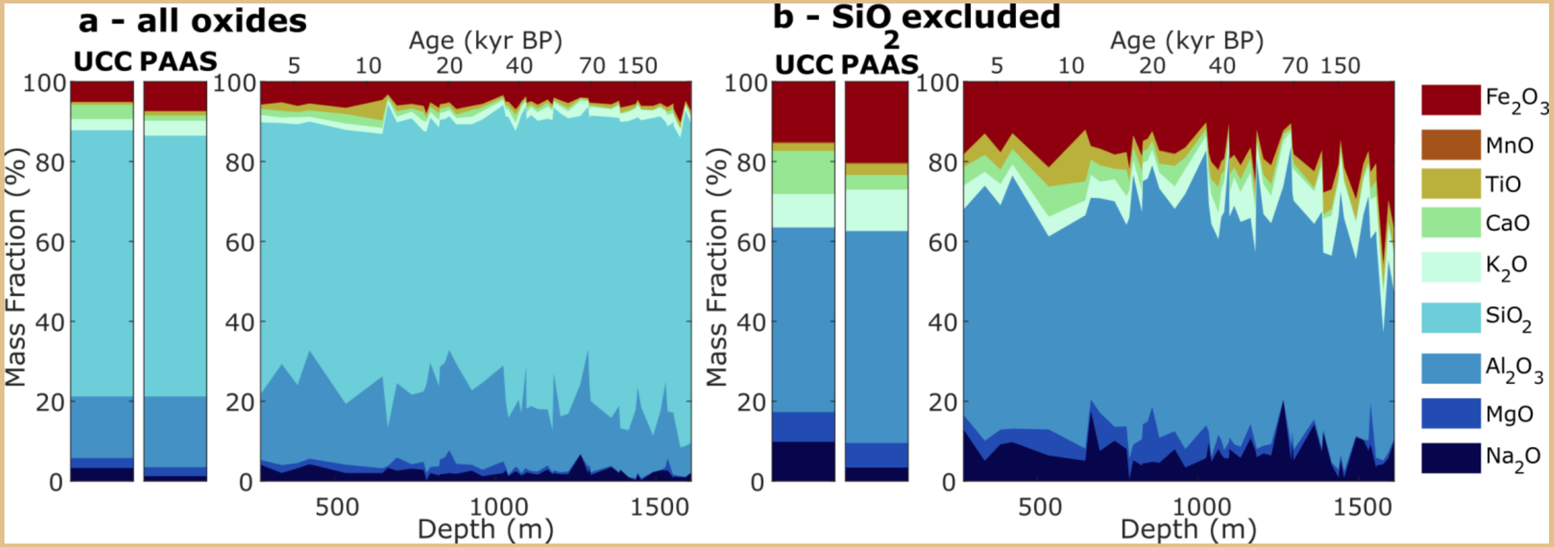
But some anomalies are also found:

- Very coarse particles during interglacials, related to local dust sources
- Grain size anomalies in the deepest sections (below 1400 m deep), compatible with aggregation processes (decrease of FPP and increase of CLPP, see figure caption)

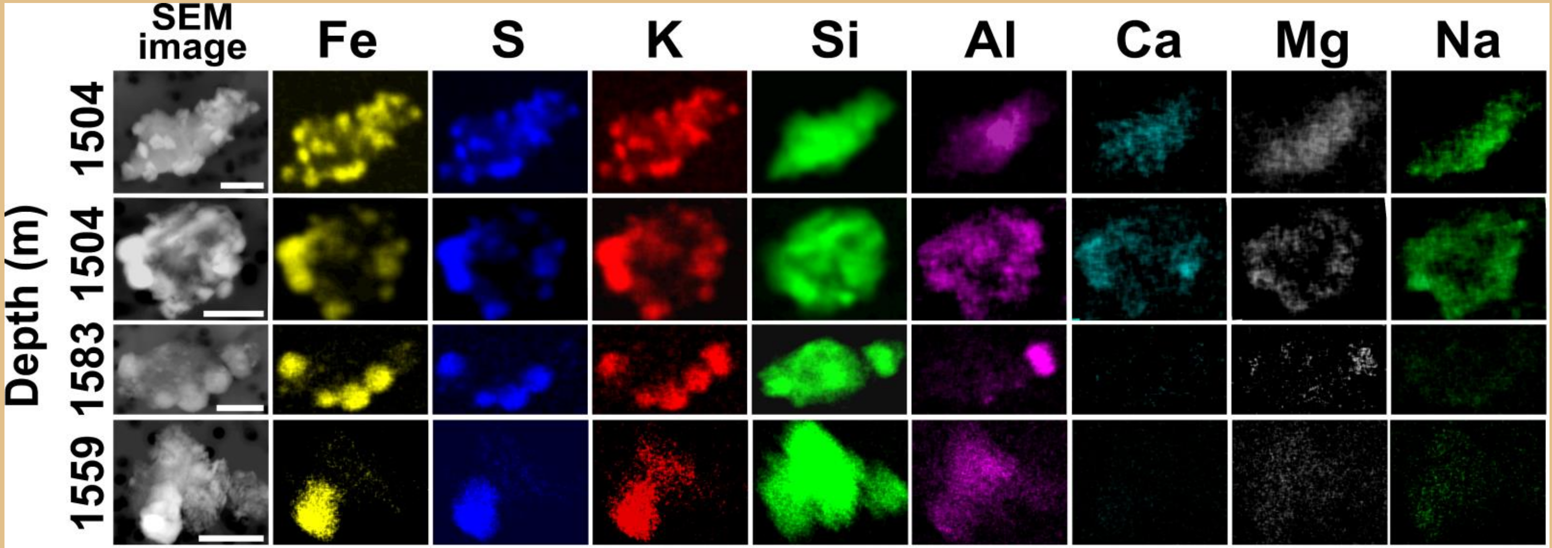
TD dust records. From the top to the bottom: dust concentration; Fine Particle Percentage (representing the relative contribution of fine (<2µm) particles); Coarse Local Particle Percentage (represeting the relative amount of coarse (5-10µm) particles; isotopic composition of ice (Stenni et al., 2010). ***Unpublished, work in preparation***

[1] Stenni et al., (2010) Expression of the bipolar see-saw in Antarctic climate records during the last deglaciation. *Nat. Geosci.* 4:46-49.

Elemental composition of dust



Major element composition (from synchrotron XRF) of dust particles from the TD core. ***Unpublished, work in preparation***



Elemental maps of dust particles from the TD ice core (data from SEM-EDX). From Baccolo et al., 2021.

Major element composition and elemental mapping of micrometric insoluble impurities present inside TD revealed that:

- The composition of impurities in the upper sections of the core are well-compatible with the Upper Continental Crust average composition (UCC)
- In the lower sections of the core some mobile and soluble elements are depleted (Ca, Mg, Na), suggesting that some leaching processes are active in deep ice
- The composition of the particles from the deepest ice (below 1400 m deep) mostly consist in Fe, K and S, reflecting the composition of jarosite.
- Jarosite presence has also been confirmed by TEM-diffraction and stoichiometric analyses (see Baccolo et al., 2021)

Baccolo et al. (2021) Jarosite formation in deep Antarctic ice provides a window into acidic, water-limited weathering on Mars. *Nat. Comm.* 12:436.

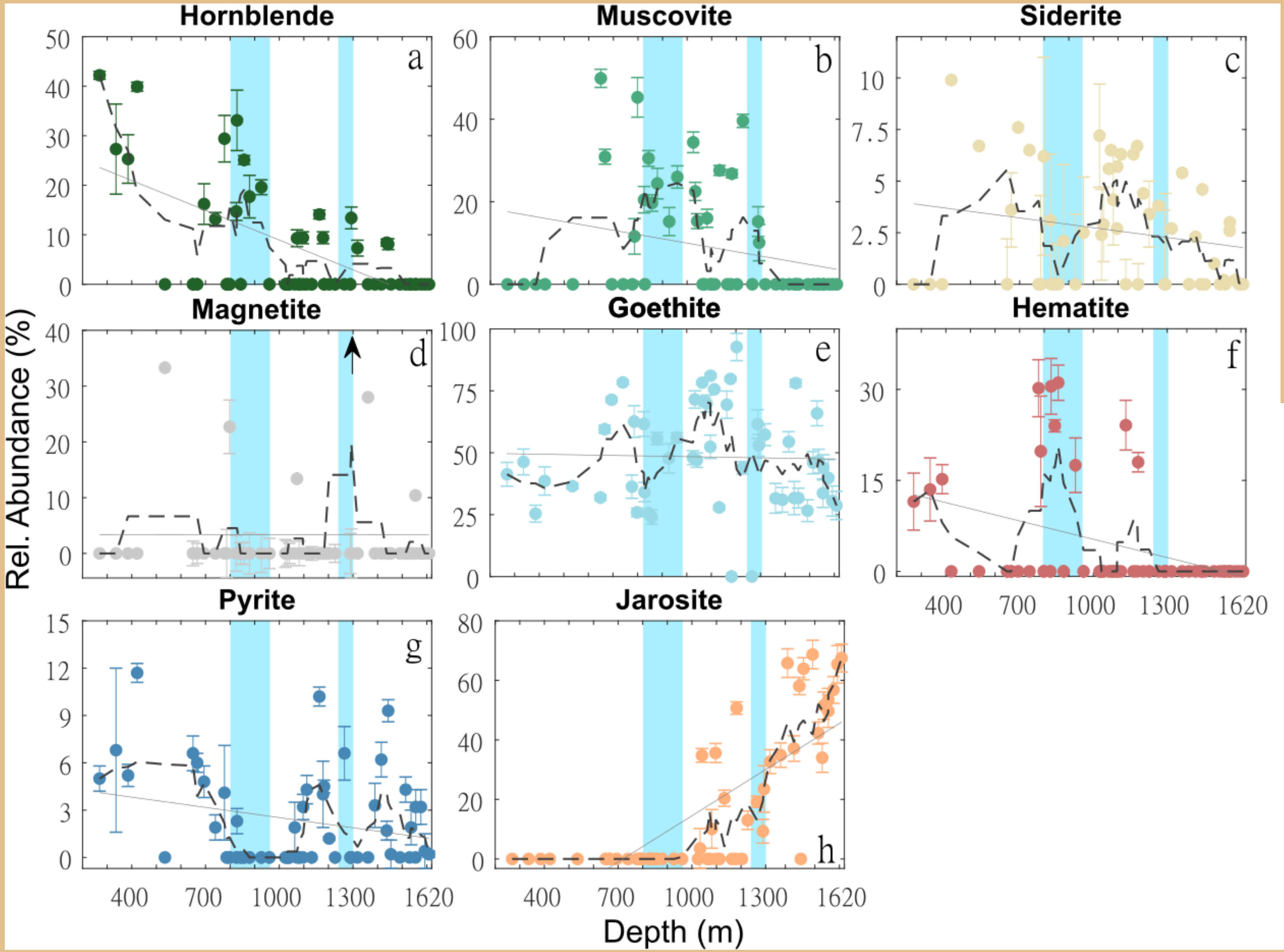
Mineralogy

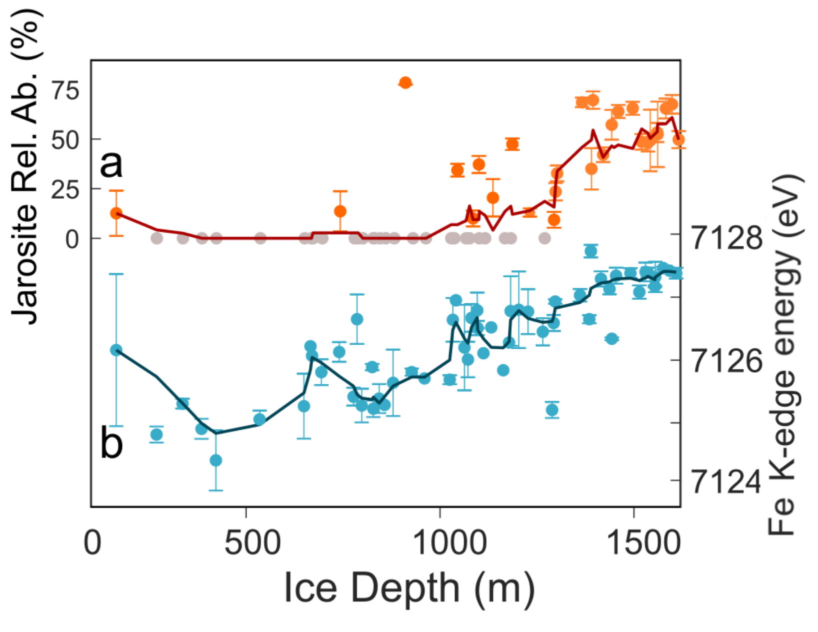
Through synchrotron XAS analyses it was possible to investigate the oxidation state of iron in TD dust and its mineralogy.

The oxidation presents a clear trend from a mix of Fe^{2+} and Fe^{3+} in the first 1000 m of the core, toward a completely oxidized state in deep ice (Baccolo et al., 2021).

The mineral assemblage changes with depth. Jarosite increases and becomes the dominant mineral below 1500 m, others decrease (hornblende, muscovite, siderite, pyrite, hematite) and others are stable (magnetite, goethite).

Iron-mineralogy of dust from the TD ice core. ***Unpublished, work in preparation***





Jarosite abundance (a) and Fe oxidation trend (b) inferred from XAS spectra. From Baccolo et al., 2021.

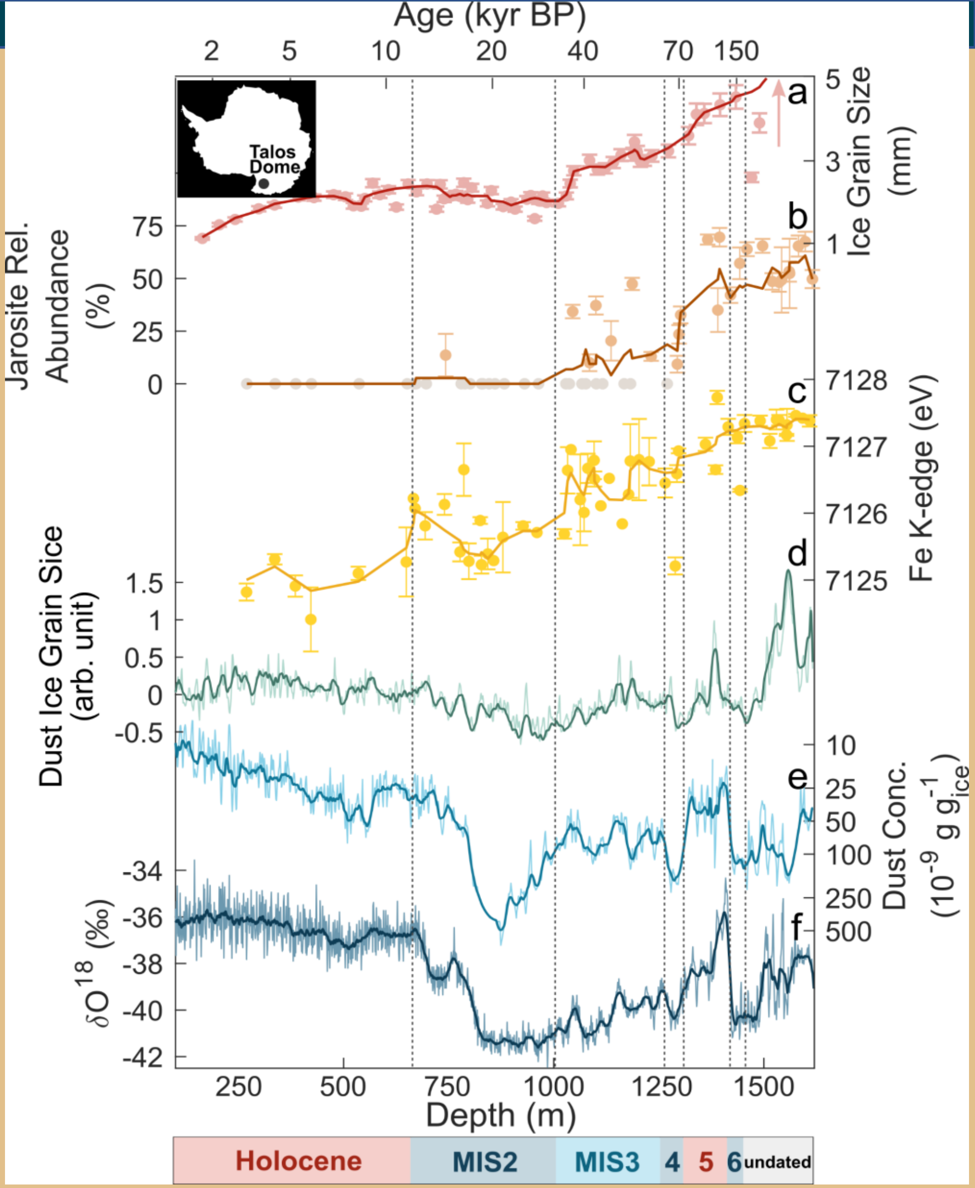
Englacial reactions, why and how?

In deep ice at TD we see:

- Anomalies in the grain size of dust (coarse particles)
- A depletion of some mobile and soluble elements
- The increasing occurrence of jarosite
- The decrease of other minerals (mostly ferrous)
- An evident oxidation trend of Fe

We explain this evidences as follows:

- Deep ice is subject to metamorphism (ice re-crystallization) leading to the accumulation of impurities in isolated environments
- The accumulation of impurities lowers the ice pressure-melting point allowing for the occurrence of tiny amounts of liquid water
- This favours the occurrence of englacial geochemical reactions (precipitation of jarosite, dissolution of pyrite and hornblende)
- Such reactions suggest that deep ice promotes acidic-oxidative weathering, likely related to the concentration of acidic atmospheric species



From the top to the bottom. a) size of ice crystals at TD [1]; b) jarosite abundance; c) iron oxidation; d) dust size anomalies; e) dust concentration; f) stable isotopes of ice [2]. From Baccolo et al. 2021 [3].

[1] Montagnat et al. (2012) Measurements and numerical simulation of fabric evolution along the Talos Dome ice core, Antarctica. *Earth Planet. Sci. Lett.* 357–358:168–178.
[2] Stenni et al., (2010) Expression of the bipolar see-saw in Antarctic climate records during the last deglaciation. *Nat. Geosci.* 4:46-49.
[3] Baccolo et al. (2021) Jarosite formation in deep Antarctic ice provides a window into acidic, water-limited weathering on Mars. *Nat. Comm.* 12:436.

Implications

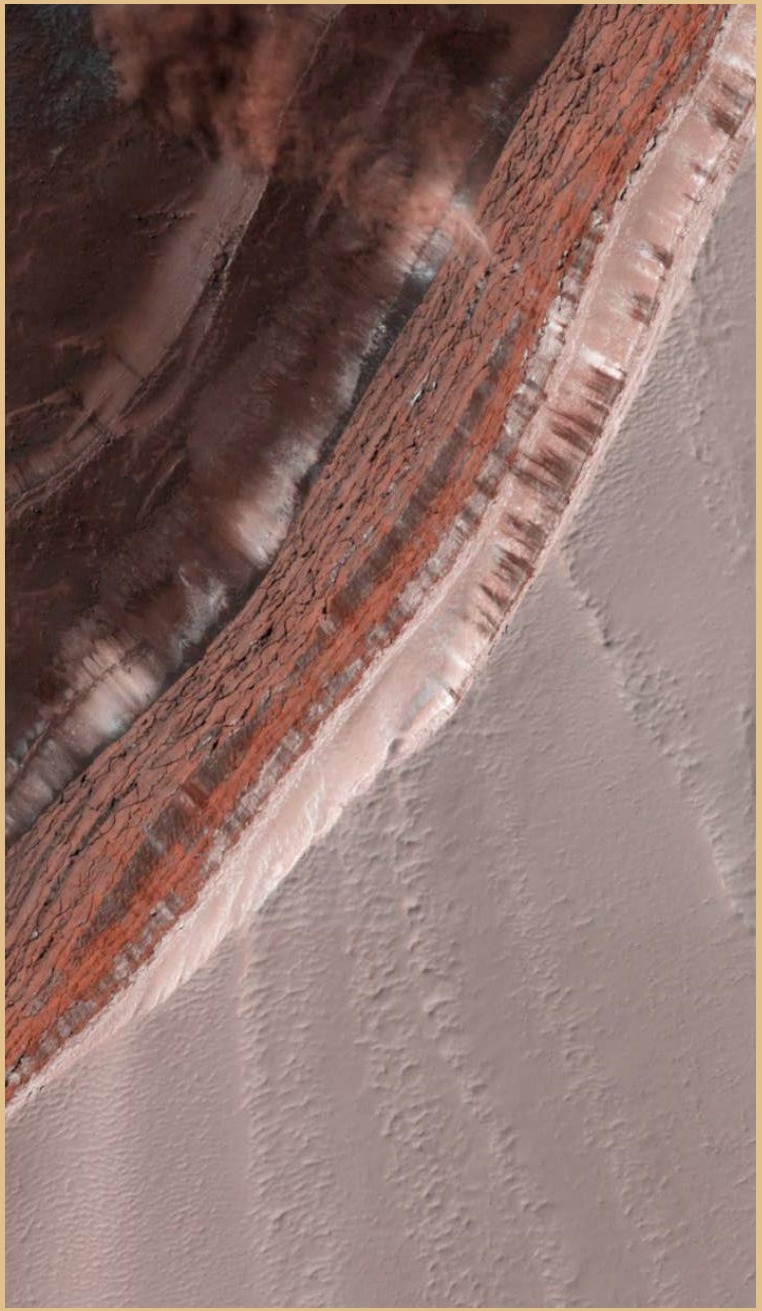
The present study has important implications with respect to both Antarctica and Mars and opens the way for future studies aimed at the comparison between Antarctic englacial processes and Martian geochemistry.

Antarctica:

- The englacial precipitation of jarosite in TD and the concurrent dissolution of other minerals tells us that deep ice is an active matrix, where complex geochemical processes take place
- The precipitation of jarosite is a strong evidence that the metamorphism of deep ice leads to the occurrence of limited amount of liquid water (it is needed for jarosite formation)
- This study could help to interpret the weathering of meteorites and nunataks which underwent prolonged ice-burial.

Mars:

- This study confirms that the englacial precipitation of jarosite is a viable geochemical path, supporting the ice-weathering model
- This gives credit to the fact that past glaciers could have had an important role in shaping not only the surficial morphology of wide sectors of Mars (well known), but also its geochemistry, providing an explanation to explain the wide occurrence of layered sediments rich in sulphates on Mars.
- Further studies are needed to assess if the processes described by the ice-weathering model are currently active in high-latitude Martian regions.



The cliff exposed at the margin of the Martian northern polar cap. The deepest exposed layers, also called *Basal Unit*, consist in a mixture of dust and water-ice that could have formed during sublimation episodes that affected polar deposits in the geologic past of Mars. This is an ideal setting for the precipitation of ice-related jarosite on the Red Planet. Credit: NASA/JPL-Caltech/University of Arizona

Thanks for your interest!