

ACIDIC BRINES IN DEEP ANTARCTIC ICE PROMOTE THE ENGLACIAL PRECIPITATION OF JAROSITE AND SUPPORT THE ICE WEATHERING MODEL FOR JAROSITE FORMATION ON MARS. G. Bacco^{1,2}, P.B. Niles³, B. Delmonte¹, G. Cibir⁴, E. di Stefano^{1,2}, D. Hampai⁵, L. Keller³, V. Maggi^{1,2}, A. Marcelli^{5,6}, J. Michalski⁷, C. Snead⁸ and M. Frezzotti⁹, ¹Department of Environmental and Earth Sciences, University of Milano-Bicocca, Milano, Italy (giovanni.baccolo@unimib.it); ²INFN section of Milano-Bicocca, Milano, Italy; ³NASA Johnson Space Center, Houston, TX 77058, USA (paul.b.niles@nasa.gov); ⁴Diamond Light Source, Harwell Science and Innovation Campus, Didcot OX11 0DE, UK; ⁵Laboratori Nazionali di Frascati, INFN, 00044 Frascati, Italy; ⁶Rome International Center for Materials Science - Superstripes, 00185 Rome, Italy; ⁷Department of Earth Sciences, University of Hong Kong, Hong Kong, Hong Kong; ⁸Jacobs, NASA Johnson Space Center, Houston, TX 77058, USA; ⁹Department of Science, University Roma Tre, Rome, Italy.

Introduction: Once believed stable and immobile from the geochemical point of view, Antarctic deep ice is now receiving growing consideration as a matrix capable of favoring complex reactions that involve the soluble and insoluble impurities trapped within the same ice.

One of the reactions that have been recognized to occur in deep ice is the precipitation of jarosite, a hydrated potassium-iron(III) sulphate [1].

The englacial precipitation of jarosite requires the weathering of iron-bearing minerals through interaction with acidic brines [2]. Our evidence shows that jarosite is the dominant iron-bearing mineral in the deepest part of the Talos Dome ice core (East Antarctica), suggesting that deep ice is a favorable environment for the occurrence of acidic brines. Moreover, this implies that deep Antarctic ice is a geochemically dynamic environment, capable of promoting the dissolution of some minerals and the precipitation of others [3].

But the implications are not limited to Antarctica or Earth. They extend to Mars where jarosite is a common mineral found in surficial layered sediments [4-6]. Since its early prediction on Mars [7], many models have been proposed to describe its genetic environment.

Among them, one has strong similarities with what we have observed in deep Antarctic ice: the ice weathering model [8]. According to it, Martian jarosite formed in past glacial epochs inside massive ice- and dust-rich deposits that were spread on the planet during high obliquity periods [9]. Weathering reactions occurred in depth of such deposits, thanks to the presence of acidic brines [10].

The englacial precipitation of jarosite in Antarctic ice resembles the scenario described by the ice-weathering model. This paradigm changes our interpretation of aqueous geochemistry on Mars. Ice could be much more important than previously thought.

A renewed interest in deep Antarctic ice: After ice coring projects carried out in the last decades, the consideration for deep Antarctic ice is growing again and future deep ice cores are expected in the near future. This is because scientists want to extend ice core-based climatic records to 1.5 million years before present [11]. This interest is paving the way for studies focused on englacial geochemical reactions [2].

The identification of jarosite in the Talos Dome ice core: We have analyzed 54 samples consisting of insoluble particles extracted from ice sections of the Talos Dome ice core, drilled at a peripheral ice dome of East Antarctica. Our results show that below 1000 m deep, jarosite appears as one of the main iron-bearing phases that define the mineral assemblage of the micrometric insoluble particles trapped into ice. Moving down along the core its concentration increases and in the last sections (between 1500 and 1620 m deep) it is the dominant Fe-mineral.

This is the first time that jarosite is observed in ice cores; our evidence suggests that it is not a mineral originally present in the dust deposited at the considered Antarctic site, but it is formed directly into the ice, as a consequence of englacial geochemical reactions. Along with the increase of jarosite we observe a decrease in ferrous minerals, such as hornblende, pyrite, muscovite, and a general increase in iron oxidation state. This agrees with the occurrence of acidic/oxidative weathering in deep ice; jarosite is a common product of such an alteration pathway [12].

Deep ice as a geochemical reactor: To address deep englacial reactions it is necessary to consider the complex dynamics affecting deep ice. The latter is subject to several physico/chemical transformations driven by thermodynamics. Deep ancient ice recrystallizes, progressively increasing the average size of ice crystals [13]. During this process the impurities not compatible with the ice molecular lattice are expelled and accumulated at grain junctions or within intra-grain micro-inclusions [14].

The accumulation of impurities in confined environments determines a local lowering of the pressure melting point, allowing for the occurrence of limited amounts of liquid water. High solute concentrations, liquid waters, confined environments: these are the ingredients for brines and depict a highly reactive environment. The pH of such brines is low because of the concentration of atmospheric acidic species, such as sulfuric and nitric acids, which are highly incompatible with the ice lattice and are rapidly remobilized and concentrated [15-17].

This scenario is confirmed by the same observation of englacial precipitation of jarosite since it requires a

low pH, a limited activity of liquid water and Fe-minerals [12].

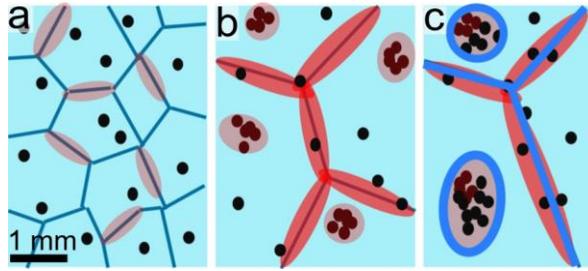


Figure 1 A model of deep ice metamorphism and acidic brines development. a) surficial ice: ice grains are millimetric, only highly incompatible atmospheric acids are accumulated at junctions. b) moderately deep ice (500-1000 m deep): grains increase their size, insoluble impurities aggregate within intra-grain micro-inclusions and acids are strongly segregated at junctions and inclusions. c) deep ice (>1000 m deep): grains are centimetric, both soluble and insoluble impurities are concentrated in small-scale acidic environments where because of high solute concentration, films of liquid water exist, favoring englacial reactions, such as jarosite precipitation.

Paleoclimatic implications: Traditionally mineral dust is considered a stable proxy in deep ice and its records have been used to synchronize and compare deep ice cores when other proxies were deteriorated. With this study we show that dust is also affected by such alterations.

To correctly interpret future deep ice core records, it will be essential to address englacial geochemical reactions, so as to disentangle the original climatic signals embedded into ice, from the ones depending on successive transformations.

Antarctic implications: From the geochemical point of view ice is not considered to be an important factor. Attention has already been given to the subglacial environment [19], but not the englacial one because it is considered stable and not favorable for reactions. Our results show that this is not true, and we need to change our perception of deep ice. From an immobile matrix to an environment whose characteristics can promote complex reactions still largely unknown.

The Antarctic significance of this study could extend to other contexts than deep ice cores. For example, the investigation of weathering processes affecting meteorites collected at the surface of blue ice areas [20]. They are traditionally interpreted as processes that occurred once meteorites were exposed to the atmosphere, but it is likely that they partly took place while meteorites were buried deep into ice.

Brines across the solar system: Our work demonstrates the power of large ice deposits as generators of brines on Earth. There is no reason that

this process should be limited to Earth, and we expect that we should find evidence for brines associated with large ice deposits all across the solar system. As observed in Earth's polar areas, the metamorphism of deep ice leads to the formation of small scale environments where acidic fluids interact with concentrated impurities. On bodies such as Mars, Earth, or elsewhere, the isolation from the planetary crust also prevents the moderation of pH and maintains acidic conditions consistent with jarosite formation.

Our study also demonstrates that brines are reactive even at cryogenic temperatures which could also have broad implications across the solar system. The finding of jarosite in deep ice certainly supports the ice weathering model proposed for Mars and suggests that ice could have been an important player not only with respect to Martian surficial morphology, but also its geochemistry.

Methods: insoluble impurities have been extracted from ice sections through the filtration of meltwater in a clean room. Impurities were retained on polycarbonate filters and inspected through SEM-EDX for morphology and elemental composition and through X-ray synchrotron absorption spectroscopy to determine the mineralogy and oxidation state of iron present in the insoluble particles. Further confirmation about the presence of jarosite came from XRD microscopy. Full details are found in Bacco et al. [1].

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