

Search for past life on Mars: Physical and chemical characterization of minerals of biotic and abiotic origin:

2. Aragonite

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[1] One of the major objectives of the future Martian surface probes will be to reveal a past or present biological activity. We propose that biominerals could have recorded such an activity at Mars, and thus could be interesting targets for these missions. Therefore, we try to find a method capable to discriminate biominerals from their geochemical counterparts. With this aim, various terrestrial aragonites of biotic and abiotic origins were studied as reference minerals, because they could have also been produced at Mars. Their thermal properties were studied with differential thermal analysis, and then compared. The results show that biotic aragonites thermally decompose at temperatures at least 20°C lower than the temperatures of decomposition of abiotic aragonites. Therefore, the temperatures of thermal degradation of such biominerals could be a relevant parameter to find a past biological activity at Mars, and differential thermal analysis could be useful for situ astrobiological exploration of Mars.
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1. Introduction

[2] The primary objective of the NASA twin rovers, Spirit and Opportunity, operating on the surface of Mars since 2004, was to demonstrate the presence of liquid water in the past. At the same time, the ESA Mars Express probe orbited Mars with the same goal. Mineralogical data recovered from these missions brought evidences that the martian environment was moister during the first hundred millions years following its formation [Bibring *et al.*, 2006]: sulphates, formation of which completely

depends on the presence of liquid water, were detected both by the rovers [Squyres *et al.*, 2004; Christensen *et al.*, 2004; Klingelhöfer *et al.*, 2004] and Mars Express [Gendrin *et al.*, 2005; Bibring *et al.*, 2005]; Mars Express also detected clays deposits [Poulet *et al.*, 2005], i.e. hydrated silicates which are produced by the alteration of mafic or ultramafic rocks in the presence of perennial liquid water [Bibring *et al.*, 2006]. During this period, Mars was profusely bombarded by bodies coming from the interplanetary medium, i.e. meteorites, micrometeorites and comets [Brack, 1998; Botta and Bada, 2002], which are known or suspected to contain organic molecules of prebiotic interest (e.g. amino acids, PAHs...). Finally, the Martian atmosphere must have been denser to keep water liquid. For these reasons, Mars should have been particularly hospitable to the emergence of a kind of biological activity, for a period when life arose on the Earth [Allwood *et al.*, 2006].

[3] If we suppose that life emerged at Mars, fossil records of its activity could have survived during several billions years, up to today. The more common materials known to be produced by living organisms are organic molecules. However, if we except methane possibly detected in the atmosphere [Formisano *et al.*, 2004], no organic molecule was yet detected at Mars, even with in situ analysis [Biemann *et al.*, 1977]. Also, even if it is expected that future space probes could detect organics on the martian surface, it cannot be excluded that the absence of detection of organic molecules could result from their destruction induced by the harsh surface conditions [Oro and Holzer, 1979; Stoker and Bullock, 1997; ten Kate *et al.*, 2006].

[4] In that case, we can assume that traces of a biological activity could have been more efficiently preserved in the form of inorganic materials. Indeed, terrestrial living organisms are able to produce mineral matrices in a process called “biomineralization” [Lowenstam, 1981; Mann, 1983, 2001]. There are two biomineralization processes: (1) biologically induced mineralization (mainly produced by prokaryotic microorganisms). Inorganic minerals are deposited by adventitious precipitation, which occurs from secondary interactions between various metabolic processes and the surrounding environment. The synthesized minerals have no interest for the organism; and (2) biologically controlled mineralization (mainly produced by eukaryotic micro and macroorganisms): the organism uses cellular activities to direct the nucleation, growth, morphology and final location of the mineral that is deposited [Lowenstam, 1981; Mann, 1983; Weiner and Dove, 2003]. It is a highly regulated process that produces

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Table 1. List of the Studied Samples and Their Origin, Chemical Composition, and Mineral Composition^a

Code	Samples Origin	Location	Age	X-Ray Results	SEM Results
AI1	Microbialite	Trona Pinnacles California, USA	subactual	Aragonite, calcite	C, O, Ca
AI2	Bacterial deposit	Mauritania	current	Aragonite, calcite	C, O, Ca, Sr
AI3	Microbialite	Sicilia	subactual	Aragonite	C, O, Ca
AI4	Microbialite	France	current	Aragonite	C, O, Ca, Sr
AC1	Otolith	Mauritania	current	Aragonite	C, O, Ca
AC2	Nautile	New Caledonia	current	Aragonite	C, O, Ca
AC3	Coral	Tahiti	current	Aragonite	C, O, Ca
AC4	Coral	Tuamotou	current	Aragonite	C, O, Ca
AC5	Coral	La Réunion	current	Aragonite	C, O, Ca
AC6	Coral	France	current	Aragonite	C, O, Ca
ACF1	Gastropod fossilized	Chile	10 MY	Aragonite	C, O, Ca
ACF2	Brachiopod fossilized	Chile	10 MY	Aragonite	C, O, Ca
ACF3	Lamellibranche fossilized	France	200 MY	Aragonite, calcite	C, O, Ca
AA1	Aragonite crystal	Morocco	-	Aragonite	C, O, Ca
AA2	Aragonite crystal	Morocco	-	Aragonite	C, O, Ca
AA3	Aragonite crystal	Tunisia	-	Aragonite	C, O, Ca
AA4	Aragonite crystal	France	-	Aragonite	C, O, Ca
AA5	Aragonite crystal	France	-	Aragonite	C, O, Ca
AA6	Aragonite crystal	Spain	-	Aragonite	C, O, Ca

^aThe samples labelled with “AI” are current biotic aragonites produced by prokaryotes, and by mineralization biologically induced. The samples labelled with “AC” are current biotic aragonites produced by eukaryotes, and by mineralization biologically controlled. The samples labelled with “ACF” are fossilized biotic aragonites produced by eukaryotes and by mineralization biologically controlled. The samples labelled with “AA” are abiotic aragonites formed by abiotic processes. Results of the X-ray diffraction analyses confirmed the mineralogical composition of the samples: they are composed of aragonite with a few traces of calcite. Their chemical composition is dominated by carbon, oxygen and calcium. A few biologically induced aragonites include strontium in their crystal lattice.

materials (such as bones, shells and teethes) which have specific biological functions and structures.

[5] Biominerals and their abiotic counterparts have the same chemical and mineralogical composition. However their different processes of formation influence the crystal lattice and the presence of minor/trace elements [Weiner and Dove, 2003], thus inducing differences between these minerals. Therefore, we assume that these differences could be sufficient to discriminate between biotic and abiotic minerals, notably from their thermal resistance.

[6] Among minerals produced by living organisms, we chose to focus on calcium carbonates because: (1) their possible presence on the Mars surface is suggested by the past presence of liquid water and its CO₂ atmosphere [Owen, 1992]. Even if no large carbonate deposit has been detected yet, carbonates were found to be part of the Martian dust material [Bandfield et al., 2003], the analyses of several Martian meteorites pointed to their presence, suggesting they could be of Martian origin [Gooding, 1992; McKay et al., 1996; Bridges et al., 2001], and some geomorphological structures (such as karsts) of the Mars surface could be attributed to carbonate deposits [Bérczi, 2005]. (2) Six types of calcium carbonates (i.e. calcite, aragonite, vaterite, calcium carbonate monohydrate, calcium carbonate hexahydrate, and amorphous calcium carbonate) are produced by living organisms [Weiner and Dove, 2003].

[7] We started our study with calcite [Stalport et al., 2005] and showed that it is possible to discriminate between the biotic calcites and the abiotic ones by measuring their temperature of thermal degradation. We then continued the study with aragonite. In the frame of the search for life at Mars, we compared the thermal resistance of aragonite minerals of biotic and abiotic origins, to determine if results

similar to those obtained with calcite can be obtained with aragonite.

2. Samples Description and Preparation

[8] The biotic samples analyzed have been produced either by prokaryotes (biologically induced mineralization producing minerals such as microbialites and bacterial deposits), or by eukaryotes, (biologically controlled mineralization producing minerals such as shells, corals and otoliths). All the studied samples and their characteristics are presented in the Table 1. Among the samples, a few ones have been produced several millions years ago, whereas the others are rather current samples, thus allowing to see the potential effect of aging on the measurements. We compared the properties of these biotic aragonites with those of abiotic ones (crystals).

[9] Each sample was ground in an agate mortar (SiO₂). The obtained powder was then sieved with stainless steel sieves. The size fraction used in this study was composed of particles with diameters in the 63–100 μm range. The mortar and sieves were cleaned with nitric acid (HNO₃) before the preparation of each sample, in order to dissolve possible particles of aragonite remaining from previous samples preparation, in order to prevent any contamination between the different samples studied.

3. Experimentation

[10] Three different analyzes were carried out for the studied samples:

[11] (1) X-ray diffraction to determine the mineralogical composition of the samples. The measurements were achieved with a SIEMENS diffractometer (Cu Kα). The wavelength of the line is 1.5418 Å. All the samples were

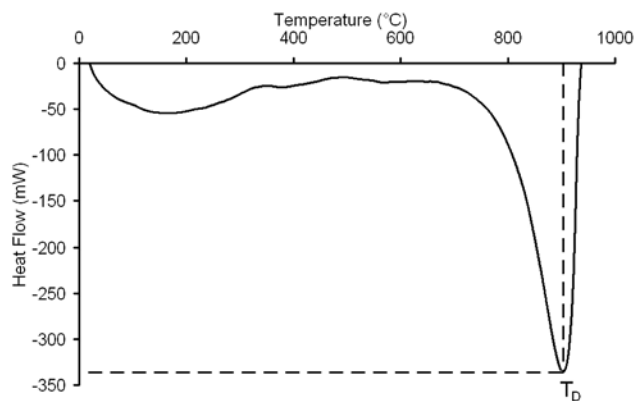


Figure 1. Illustration of thermal exchanges of aragonite measured as a function of the temperature by differential thermal analysis (here for a biotic aragonite AC4). The heat induces a transformation of the aragonite, by endothermic decomposition, into gaseous CO_2 and solid calcium oxide CaO . We observe the maximum for energy absorption for a given temperature that we define as the “temperature of thermal decomposition (TD)” of the studied aragonites.

studied for 2θ diffraction angles ranging from 3° to 72° . Measurements were done by steps of 0.01° , and they lasted 4 seconds for each step. The scattered X-rays are detected with a silicon crystal doped with lithium. Each sample was flattened on a plate as a disc of 1 cm diameter and 0.5 mm thickness.

[12] (2) Scanning Electron Microscope (SEM) to estimate the chemical elemental composition of aragonite minerals. Measurements were achieved with a JEOL microscope (type JSM-6031-F). For the measurements, electrons are emitted from a tungsten cathode. The electrons beam produced has energy of 100 keV. The mass of material used was approximately 1mg for each sample. The studied powders were coated with a platinum film in order to avoid their destruction by the electrons beam.

[13] (3) Differential Thermal Analysis (DTA) to compare the thermal degradation of the studied samples. The measurements were done with a DTA-TG SETARAM 92-10 instrument. The samples were put in an alumina crucible (Al_2O_3) which is thermally inert. The inert reference was also alumina powder. The mass of sample put in the crucible was 30.5 ± 0.5 mg. The conditions of heating were $20^\circ\text{C}/\text{min}$, from the ambient to 1000°C , under 1 bar of an inert atmosphere of N_2 flowing at the rate of $1 \text{ L}\cdot\text{min}^{-1}$. This gas flow is used to remove the gaseous molecules which evolve from the sample (e.g. CO_2).

4. Results

[14] From X-rays diffraction measurements, it was shown that the studied samples are essentially composed of aragonite, with a few traces of parasitic minerals (e.g. calcite). The content of calcite observed is too low to influence the thermal degradation of the samples. As a consequence, the obtained results are intrinsic to the studied aragonites (presented in Table 1). The X-rays diffractogram obtained with biotic and abiotic aragonites are slightly different. The observed differences could be explained by the presence of

a larger amount of structural defects in the crystal lattice of the biominerals; compared with abiotic aragonites.

[15] SEM measurements show that each sample includes carbon, oxygen and calcium elements. This result was expected as the chemical formula of aragonite is CaCO_3 . However, we noticed that a few aragonites formed from biologically induced mineralization include a few traces of strontium ($<5\%$). In some biological cases, strontium substitutes calcium in the crystal lattice of aragonite. The presence of strontium in the crystal lattice of biological induced aragonites could distort the crystal lattice. Hence, the entropy and the stabilization energy of aragonite increase and its thermal resistance could decrease [De Yoreo and Vekilov, 2003].

[16] Thermal analyses are based on the heating of the samples from the ambient temperature up to 1000°C . During this heating, aragonite reaches temperatures at which it decomposes into gaseous CO_2 and solid calcium oxide (CaO), which is an endothermic reaction. At 1000°C , this reaction is completed. During the heating of the samples, we obtained a series of data related to the thermal exchanges of aragonites, measured with DTA (Figure 1). These series of data allow us to compare the thermal degradation behaviour of abiotic aragonites with that of biotic aragonites. This behaviour depends on the thermal resistance of the aragonite crystal studied. The parameter selected to compare the different samples is the temperature of thermal decomposition (Figure 1).

[17] DTA measurements enable to discriminate two distinct classes of aragonites (Figure 2): (1) a first class of aragonites which have temperatures of thermal degradation lower than 883°C . This class includes all the studied biotic aragonites, meaning both current and ancient aragonites, formed by biologically induced or controlled processes. We can then discriminate between the aragonites formed by prokaryotes, which have temperatures of thermal degradation lower than 873°C , and the current biotic aragonites formed by eukaryotes, which have temperatures of thermal degradation lower than 881°C . These results therefore show that aragonites produced by prokaryotes are more fragile than those produced by eukaryotes. This seems consistent with the fact that prokaryotes use biologically induced mineralization, which produce poor crystalline aragonites, whereas eukaryotes use biologically controlled mineralization, which produce relatively quite pure crystalline aragonites; (2) the second class of aragonites includes all the abiotic aragonites studied, which have temperatures of thermal decomposition upper than 903°C .

[18] These results thus show that a significant difference exists between the temperatures of thermal decomposition of abiotic aragonites, and those of biotic aragonites. The biotic aragonite samples decompose at lower temperatures (at least 20°C lower) comparatively with the abiotic aragonite samples. This difference of temperature is increased to at least 30°C between these abiotic aragonites and biotic aragonites formed by prokaryotes. This result is the most interesting one because if life appeared at Mars, it was more probably in a primitive form, like prokaryotes, because of the probably short duration of the favourable period for life to emerge [Bibring et al., 2006].

[19] Hence the study of the thermal degradation of aragonite permits to unambiguously discriminate between

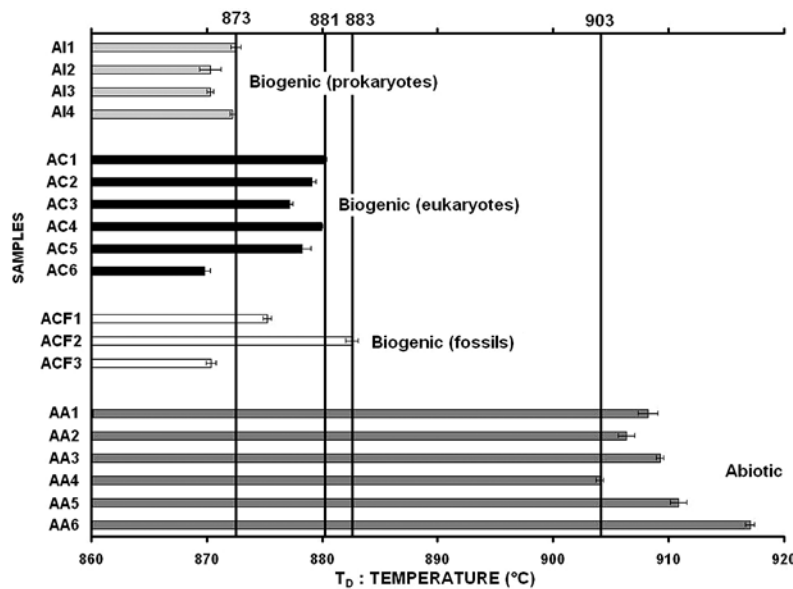


Figure 2. Temperatures of thermal decomposition of the studied aragonite samples. The difference between the temperatures of thermal decomposition of the biotic aragonites, current and fossil (produced by prokaryotes and eukaryotes) and the abiotic ones is approximately 20°C (materialized by black vertical lines). This difference of temperature is increased to 30°C when considering the abiotic aragonites and the biotic aragonites produced by prokaryotes.

biotic and abiotic aragonites, by using their temperatures of thermal decomposition. The observed differences are explained by the presence of a higher number of minor elements (e.g. strontium) and structural defaults in the crystal lattice of biotic aragonites, when compared with abiotic aragonites. These imperfections are induced by the growth speed of the biotic aragonite grains, which is faster than the growth speed of abiotic aragonites [De Yoreo and Vekilov, 2003].

5. Conclusion

[20] Our first work dealt with the calcite biomineralization. The obtained results with DTA permitted to separate calcite minerals formed under purely abiotic conditions from those formed by living organisms, including both eukaryotes and prokaryotes [Stalport et al., 2005]. Following these promising results, we studied aragonite because calcite and aragonite represent the essential of the terrestrial carbonated biomineralizations [Mann, 1983]. Once more, the DTA analyses are shown to be efficient to separate aragonite minerals formed under purely abiotic conditions from those formed by living organisms.

[21] Beyond the discrimination between biotic and abiotic calcites/aragonites, the DTA-TG analysis permits to unambiguously identify bacterial deposits of carbonates, and abiotic carbonated formations. The study of carbonates therefore represents an interesting approach in the framework of the search for life at Mars: (1) if life appeared at Mars, primitive organisms could have formed carbonated biomineralizations; (2) these bacterial deposits could have been preserved for billions years on the Mars surface. Indeed biotic crystalline structures are preserved from the dissolution in the absence of fluid circulations - it seems to be the case at Mars - and can conserve their mineralogical structure and chemical composition. Carbonates formed by

a living organism through biologically induced or controlled mineralization have, in general, a good potential of fossilization compared with organic material. Indeed, organic material can be potentially very quickly degraded by predation, putrefaction, and/or oxidation, whereas biotic carbonates precipitate, accumulate and form a sedimentary layer. Burial and diagenesis then will transform this layer into a carbonated sedimentary rock [Tucker and Wright, 1990]. The transformation of sediments into sedimentary rock will produce a rock containing deposits of fossil biotic carbonates which keep their original mineralogical composition. Then, the crystalline structure of biotic carbonates (macro and microstructure) is very well preserved, and the biotic signature is conserved [Tucker and Wright, 1990]. Thus hypothetical biotic structures may be preserved at Mars up to today, and their presence may be detected using techniques such as DTA, by measuring their decomposition temperatures, delivering gaseous CO₂ through endothermic reactions.

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