Search for past life on Mars: Physical and chemical characterization of minerals of biotic and abiotic origin: part 1 - Calcite

Fabien Stalport,1 Patrice Coll,1 Michel Cabane,2 Alain Person,3 Rafael Navarro González,1,4 Francois Raulin,1 Marie Jo Vaulay,5 Patrick Ausset,1 Chris P. McKay,6 Cyril Szopa,2 and John Zarnecki7

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[1] Several lines of evidence suggest that early Mars once had liquid water on its surface, a denser atmosphere and a mild climate. Similar environmental conditions led to the origin of life on the Earth more than 3.5 billion years ago; consequently, life might also have originated on Mars. The Viking landers searched for evidence of organic molecules on the surface of Mars, and found that the Martian soil is depleted in organics at ppb levels at the landing sites. We contend that inorganic compounds could give us interesting clues as to the existence of possible biological activity in future astrobiological missions to Mars. Consequently, we have investigated the physical and chemical properties of calcite, which could be expected on Mars because liquid water was certainly present on the surface of early Mars and carbon dioxide was abundant in its atmosphere. Calcite is interesting because on Earth this mineral is produced by abiotic processes as well as by biological activity. One may suppose that crystalline defects and trace element in the crystal lattice and the growth speed of biotic calcites must indicate a difference between them and pure abiotic calcites. We investigated twelve different terrestrial calcite samples from various origins: biotic, diageneric and abiotic. The minerals were studied by X-ray diffraction and electron scanning microscopy to determine their mineralogical and chemical composition, and differential thermal analysis coupled to thermogravimetric analysis (DTA-TG) to determine their thermal behavior. Our results show that the thermal degradation of abiotic calcite starts at a temperature at least 40°C higher than the degradation temperature of any biotic calcite investigated. Consequently, in the case of a Martian in-situ study or in a sample return mission, the analysis of Martian minerals by DTA-TG represents a promising approach to detect evidence of past biological activity on Mars.


1. Introduction

[2] Environmental conditions favorable for the emergence of life similar to that on Earth must have been present on Mars during the first hundred million years after its formation, or even more recently [Ori, 1999]. These conditions included a dense atmosphere [Pollack et al., 1987], liquid water on the surface and mild temperatures [Carr, 1986; Paige, 2005]. The first microorganisms may have been present on Earth under similar environmental conditions as early as 3.8 billion years ago [Schopf, 1993; Mojzsis et al., 1996]. Consequently, it is possible that life originated on Mars just as it originated on primitive Earth.

[3] The principal objective of the two landers of the Viking Mission was to search for evidence of biological activity in the top layers of the Martian soil. Different experiments for detecting present life were carried out, in particular in terms of organic molecule detection (For complete information, see Biemann et al. [1977], Owana and Berdahl [1977], Levin and Straat [1977], and Klein [1979]). No organic molecule was detected at the landing site; this put serious questions on the possibility of extant life on Mars. Moreover the results of the exobiological experiments of the two Viking landers suggested the presence of oxidants in the Martian soil (detected in the atmosphere [Encrenaz et al., 2004] and assumed to exist in the soil).

[4] Since Mars continues to be a relevant object of astrobiological interest, there are several space missions planned for the search of present and/or past life in the subsurface [Cabane et al., 2004]. Following the difficulty of detection of organic compounds on the surface of Mars, we propose to evaluate the potential of inorganic compounds as tracers of biological activity. In this paper we first focus on carbonates, the presence of which are suggested because of the past presence of liquid water and its atmosphere of CO₂ [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], and the analyses of several Martian meteorites pointed to their presence which could be of Martian origin [McKay et al., 1996]. The carbonates are interesting to study because on Earth they are produced by abiotic processes but also by...
2. Sample Description

[5] The present paper is devoted to a study of calcite, CaCO$_3$, a common mineral on Earth, that could be present on Mars if one assumes the transformation of gaseous CO$_2$ into solid carbonates. Calcite can be formed from three possible processes on Earth: a biotic process, a diageneric process and an abiotic process [Tucker and Wright, 1990]. Many living organisms, eukaryotes and prokaryotes, are able to biomineralize calcite by biologically induced or controlled mineralization. Carbonate rocks like limestones are mainly produced on the oceanic floor by precipitation of carbonates (mainly calcite) of only biotic origin. Calcite is also produced by purely chemical precipitation according to different processes (magmatism, dissolution and precipitation, metamorphism, hydrothermalism) which are completely independent of the presence of life. Finally, calcite is also the result of diagenesis. In this process biotic phases change by mechanisms of dissolution-recrystallization adapting to the new thermodynamic conditions of their new abiotic environment. Thus diageneric calcite structure will be a mixing between biotic and abiotic calcite structure.

[6] Several samples were investigated (Table 1). They were selected among fossil or contemporary specimen, collected around the world, composed mostly of calcite. They were grouped in three families, according to their mode of formation. These are (i) biotic calcites, divided into two subgroups, modern biotic calcites (MBC) and fossil biotic calcites (FBC); (ii) diageneric calcites (DC) and (iii) abiotic calcites (AC).

3. Sample Preparation

[7] The minerals were ground in an agate mortar (size grains <50µm). The chemical composition of the mortar was selected to avoid any contamination of the sample. Before the crushing of each sample, mortars were cleaned with nitric acid in distilled water to dissolve possible grains of previous samples, also to avoid any contamination.

4. Experimentation

[8] Three different analyses were carried out in all samples:

[9] i- X-ray diffraction to determine the mineralogical composition of the samples. The measurements were achieved with a SIEMENS diffractometer (Cu Kα)

[10] ii- Electron scanning microscopy to estimate the chemical elemental composition of calcite minerals. The measurements were achieved with a JEOL microscope (type JSM-6031-F)

[11] iii- Differential thermal analysis coupled with a thermogravimetric analysis (DTA-TG) to compare thermal degradations of the samples of biotic origin and abiotic origin. Samples were heated in a DTA-TG SETARAM 92-10. The samples are deposited in an alumina crucible (Al$_2$O$_3$) which is thermally inert: no transition phase nor loss of mass. The inert reference is alumina (alumina powder (Al$_2$O$_3$)). The mass deposited in the crucible is 20 to 40 mg. The conditions of heating are 20ºC per minute from ambient (~25ºC) to 1000ºC under one bar of an inert atmosphere of N$_2$ circulating at the rate of 1 liter per minute to evacuate formed gases (e.g. CO$_2$) and to avoid their accumulation. The sample mass losses are measured with a microbalance.

5. Results and Discussion

[12] The samples were first analyzed with X-ray diffraction. The results are presented in Table 1. They are mainly composed of calcite with traces (a few percent) of parasitic...
minerals (quartz, feldspars). These low level "pollutants" have no major influence on the performed thermal analysis.

[13] The results of electron scanning microscopy are presented in Table 1. It can be seen that the calcites of abiotic origin are pure, whereas most of the biotic calcites have magnesium in their crystalline structure. Biotic calcites have in their crystal lattice a higher number of trace elements and imperfections compared to abiotic calcites. These defects are due to the growth speed of the biotic calcite grains and the imperfections are due to substitutions of calcium atoms by other chemical elements (magnesium in this case). These defects and imperfections increase the calcite crystal entropy and structurally weaken the calcite [Astilleros et al., 2002].

[14] Differential thermal analysis is based on sample heating. Thermogravimetry (TG) provides Quantification of the sample mass loss and comparison of thermal degradations of the biotic samples with their abiotic equivalents. If a biotic sample mineral has more trace elements and imperfections in its crystal lattice it is more fragile structurally, and should then be thermally degraded at temperatures lower than an abiotic mineral.

[15] In theory, calcite mass losses begin at temperatures between 700°C and 950°C. They are caused by the decomposition of the calcite which releases CO₂ under its gaseous state and forms calcium oxide CaO. When the temperature of 1000°C is reached at the end of the analyses, the reaction is total and the theoretical mass loss by-production of CO₂ for a pure calcite is approximately 44%. This endothermic reaction can be described as following [L’vov et al., 2002].

$$\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$$

[16] The data showing the mass loss of the sample (emission of gaseous CO₂) during the temperature increase is shown in Figure 1, where mass loss (as a percentage) is plotted as a function of temperature.

[17] Two domains are clearly highlighted according to the origin of the sample. The first one corresponds to the biotic calcite domain, both fossil and current, and the second one to the abiotic calcite domain (respectively displayed in green and red in Figure 1). These domains have been bordered by oblique parallel lines (roughly parallel to the average maximum mass variation). The two domains defined by these lines are the biotic, lower temperature, and abiotic, higher temperature. The temperature difference obtained between the two parallel lines is approximately 45°C, indicating a quite clear separation of the areas. We also observe that the mass losses of the diagenetic calcites occupies the space between these two domains, which corresponds exactly to the definition of diagenetization, namely they are intermediate between biotic calcites and abiotic calcites. Moreover, it can be observed that the diagenetic calcites are closer to the abiotic domain, whereas the diagenetic calcites which preserved a part of their biotic signature are closer to the biotic domain border.

[18] For a more precise determination of the temperature difference between the two domains, mass loss data are represented, as a function of the temperature T, as the first derivative of the mass (dML/dT) (Figure 2). Hence the maximum of each derivative curve represents the inflection point of the original curve, i.e. the temperature at which the mass loss rate is most significant. We can then simply use these particular points to delineate the different domains. The temperature difference between biotic and abiotic domains is about 40°C. Again, most of the diagenetic calcites are found in the space between these two domains (Figure 2).

[19] Biotic calcites are structurally more fragile than abiotic calcites due to trace element (magnesium), crystal
defects (sample MBC1 of biotic origin is a pure calcite consequently its mass loss is due principally to crystal defect) and speed growth. Finally two diagenetic calcite samples are old biotic calcite deposits and their respective mass losses are located at the border of the biotic domain. This means that these samples preserved their biotic signature in spite of the circulation of fluids specific to terrestrial conditions, which erase these biotic signatures by diagenesis. This result is encouraging for a possible preservation of mineral biotic calcite structures at Mars for billion years, as there are probably no fluid circulations on Mars because of the low atmospheric pressure and minimal liquid water activity.

6. Conclusion

[20] The principal aim of these experiments on carbonates was to propose an effective technique of analysis in the characterization of samples of abiotic origin and possibly biotic origin on Mars and a simple technique of analysis for future space missions.

[21] The technique of thermal analysis allows us to observe a clear difference between carbonate samples of biotic and abiotic origin. This work shows that the thermal degradation of abiotic calcite occurs at a temperature at least 40°C higher than the degradation of any biotic calcite. The knowledge of the above biotic and abiotic limits can be used to define the ‘degree of biomineralization’ of a given sample, from highly diagenitized to fully biotic minerals. It is easy to understand that the defects due to the fast growth of the biotic carbonates, the substitution of calcium atoms by other elements during this growth, increase their fragility, hence their sensibility to thermal stresses. Consequently, in the case of a Martian in-situ or sample return experiments, the techniques of thermal analyses DTA-TG represent a promising approach to detect evidence of past biological activity on Mars.

[22] Future studies will focus on carbonates linked to primitive living organisms. These will include stromatolites and microbialites, bacterial carbonate deposits that are the oldest fossils of biological activity traces known on the Earth. The second point will be the addition of more carbonate references like aragonite. One extension of this work will be to study other biomineralisation such as nitrates, sulphates, phosphate, silica.

[23] A persistent question however concerns the preservation of biotic carbonates on Mars. Could biotic structures of primitive organisms on Martian subsoil have been preserved? Carbonates formed by an organism through biologically induced or controlled mineralization have in general a good potential of fossilization compared to organic matter. Organic matter is 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 sediment into sedimentary rock will produce a rock containing the deposits of fossil biotic carbonates which keep their original mineralogical composition. The crystalline structure of biotic carbonate (macro and microstructure) is very well preserved, thus there is conservation of this biotic signature [Tucker and Wright, 1990]. However, the conservation of this original mineralogy is often temporary: the fluid circulations (rain, water) in the rock partially or entirely dissolve biotic carbonates when they emerge. Vacuums are filled by secondary precipitation of another mineral (abiotic calcite, silica . . .). These fluid circulations are common in the terrestrial subsoil but on Mars there are no fluid circulations able to dissolve Martian subsoil biotic structures since the loss of the atmosphere and liquid state water more 3 billion years ago [Martineau and Pollard, 2003]. Thus hypothetical biotic structures may be preserved on Mars even now, and their presence may be deduced using simple techniques such as DTA-TG, by measuring the temperatures at which they break down, delivering gaseous CO2 under endothermic reactions.

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P. Ausset, P. Coll, R. N. González, F. Raulin, and F. Stalport, Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Université Paris XII, Paris VII, F-94010 Créteil, France. (stalport@lisa.univ-paris12.fr)


C. P. McKay, Space Science Division, MS 245-3, NASA Ames Research Center, Moffett Field, CA 94035-1000, USA.

A. Person, Laboratoire de Géologie Sédimentaire, Université Paris VI, 4 Place Jussieu, F-75005 Paris, France.

M. J. Vaulay, Interfaces, Traitements, Organisation et Dynamique des Systèmes (ITODYS), Université Paris VII, F-75005 Paris, France.

J. Zanecki, Planetary and Space Sciences Research Institute, Open University, Milton Keynes, MK15 0BT, UK.