

EVIDENCE FOR CALCIUM CARBONATE AT THE PHOENIX LANDING SITE. W. V. Boynton¹, D. W. Ming², B. Sutter³, R. E. Arvidson⁴, J. Hoffman⁵, P.B. Niles², P. Smith¹ and the Phoenix Science Team

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Introduction: The Phoenix mission has recently finished its study of the north polar environment of Mars with the aim to help understand both the current climate and to put constraints on past climate. An important part of understanding the past climate is the study of secondary minerals, those formed by reaction with volatile compounds such as H₂O and CO₂. This work describes observations made by the Thermal and Evolved-Gas Analyzer (TEGA) on the Phoenix Lander related to carbonate minerals.

Carbonates are generally considered to be products of aqueous processes. A wet and warmer climate during the early history of Mars coupled with a much denser CO₂ atmosphere are ideal conditions for the aqueous alteration of basaltic materials and the subsequent formation of carbonates [1,2]. Carbonates (Mg- and Ca-rich) are predicted to be thermodynamically stable minerals in the present martian environment [3], however, there have been only a few indications of carbonates on the surface by a host of orbiting and landed missions to Mars. Carbonates (Mg-rich) have been suggested to be a component (2-5 wt %) of the martian global dust based upon orbital thermal emission spectroscopy [4]. The identifications, based on the presence of a 1480 cm⁻¹ absorption feature, are consistent with Mg-carbonates. A similar feature is observed in brighter, undisturbed soils by Mini-TESS on the Gusev plains [5]. Recently, Mg-rich carbonates have been identified in the Nili Fossae region by the CRISM instrument onboard the Mars Reconnaissance Orbiter [6]. Carbonates have also been confirmed as aqueous alteration phases in martian meteorites [7,8,9] so it is puzzling why there have not been more discoveries of carbonates by landers, rovers, and orbiters. Carbonates may hold important clues about the history of liquid water and aqueous processes on the surface of Mars.

Results: The TEGA instrument is a combination of a thermal analyzer (TA, a differential scanning calorimeter) and an evolved-gas analyzer (EGA, a magnetic sector mass spectrometer). The TA has 8 ovens, each of which can be used for only one sample. Soil samples are sealed in the oven and a programmed heating rate is applied, typically ranging from 5 K/min to 20 K/min. As the sample is heated, a flow of pure nitrogen is used as a carrier gas to bring any gases evolved from the sample to the EGA. If there is a phase transition, such as the decomposition of calcite, one sees an increase in the amount of power going to the oven due to the endothermic reaction, and a corre-

sponding increase in the CO₂ content in the carrier gas flow.

Figure 1 shows the result for the Wicked Witch sample, a sub-surface sample taken just above the ice layer in the Snow White trench [10]. A clear endothermic peak is seen between 680 °C and 810 °C. (The origin of the higher-temperature peak is unknown. It is thought to be due to a transition in the Ni oven body itself, since we see this transition even in an empty oven.) The most likely phase candidate for the 680 °C endothermic reaction is CaCO₃ (e.g., calcite, ikiate, aragonite). The onset temperature for this endothermic peak agrees well with the calcite decomposition onset temperature of 677 °C at 30 mbar pressure found by Sutter et al. [11].

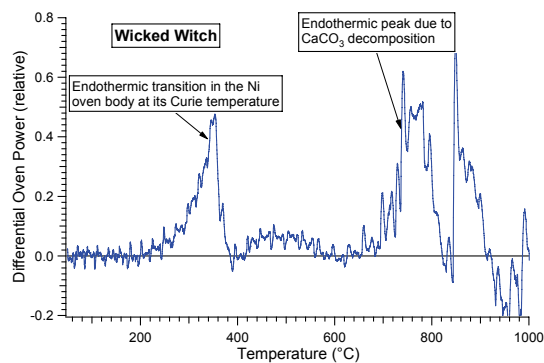


Figure 1. Differential oven power for the Wicked Witch sample. There is a clear endothermic transition with an onset around 680 °C due to CaCO₃.

Confirming the assignment of the endothermic transition to CaCO₃ is the associated release of CO₂ (figure 2). Here one can see two releases of CO₂, one at high temperature and another at a lower temperature. The high temperature release is due to the decomposition of CaCO₃, but the low temperature release is not so clear. It could be from Mg or Fe carbonates, which decompose over this temperature range, from organic compounds oxidized by other materials in the soil, or from adsorbed CO₂, e.g., CO₂ adsorbed in the channel and cages of zeolites.

At this time we are not able to rigorously quantify the amount of carbonate, but it is on the order of 1% to 5% of the soil. We see differences in the carbonate amount in the different soil samples, but again it will take more work to be sure we understand the full extent of the differences.

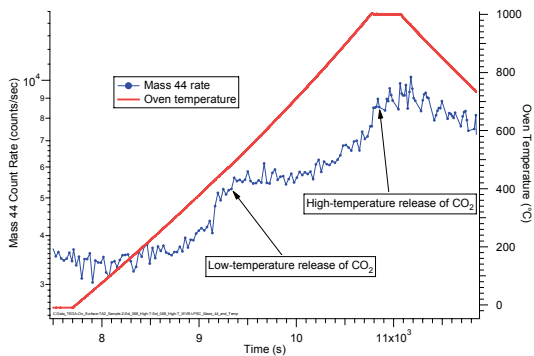


Figure 2. Plot of mass 44 (CO_2) and temperature vs. time for Wicked Witch. Two distinct releases of CO_2 are observed.

Source of the carbonates: The discovery of soil carbonate at the Phoenix landing site does not define where or when the carbonates formed. However, carbonates generally form by aqueous processes and the discovery addresses the Mars Phoenix mission science objective to study the history of water at the landing site.

Low temperature carbonate dissolution and precipitation are among the most important soil forming processes in terrestrial semiarid to arid soils [12]. Generally carbonates form in soils by reaction of CO_2 -charged water with Ca^{2+} released by dissolution of parent materials. Soils at the Phoenix landing site are in direct contact with several water-bearing reservoirs: an ice-cemented soil layer several cm under the surface, the atmosphere, and a surface frost layer during winter. These reservoirs suggest the diffusion of water vapor through the soils [13] and the possibility of films of unfrozen water on particle surfaces which could leach calcium and other cations from basaltic grains. Atmospheric CO_2 will dissolve in these films of unfrozen water enabling calcium carbonate to precipitate once the water film becomes supersaturated with respect to calcite. These precipitation events may be facilitated by the evaporation of the thin films during diurnal or seasonal cycles, and may be much more frequent during high obliquity events [14].

Another possibility for the source of carbonates in the Phoenix soils is a non-aqueous process outlined by Booth and Kieffer [15]. Carbonate forms in this process through the heterogeneous reaction of atmospheric CO_2 with particle surfaces. This reaction depends upon molecular collision of gaseous CO_2 with a surface and is affected by p_{CO_2} , temperature, particle surface area, the chemistry of the surface, and possibly the photochemistry of the environment. It can happen on the planetary surface or on the surface of dust grains suspended in the atmosphere.

Carbonates may have instead been inherited in Phoenix soils from an external source. For example, the Phoenix

landing site lies on the ejecta blanket of Heimdall crater. Carbonates may have formed in the subsurface and were transported to the Phoenix site by the excavation of subsurface material during the impact event that formed Heimdall crater, in which case the carbonate has persisted in the soil since the impact event.

Finally, the carbonates may have formed elsewhere on Mars and were transported to the Phoenix landing site by eolian processes. Banfield et al. [4] have suggested that the global Mars dust has 3-5 wt. % carbonate, although the thermal emission spectra suggested Mg-carbonates as the best fit to the data. It is not clear however, if the origin of the carbonate in the dust is due the eolian redistribution of carbonates formed by aqueous processes at the surface or from a carbonate-bearing source rock that may have formed by subsurface aqueous processes. The recent discovery of a Mg-rich carbonate deposit in the Nili Fossae region may be a source material for the carbonate in the Martian dust [6].

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