

In Dodo-Goldilocks, several chunks of bright material 1.5 to 2 cm across were dislodged by the RA on sol 20 (17) and had disappeared by sol 24 without any obvious residue (fig. S8, A and B). This is expected for H<sub>2</sub>O ice. Over the next 2 months, the material in the trench sublimated by several mm (fig. S8C). Pore ice has been predicted by thermodynamical arguments (18), but the exposure of nearly pure ice usually requires a liquid phase or brine on Earth. If dominant in the region, this supports the Odyssey GRS conclusion that ice concentrations exceed pore ice (5, 19, 20).

Because attempts to collect and to deliver ice-cemented soil materials to the TEGA ovens were not successful, we sampled sublimated till material at the bottom of one trench (Snow White) on sol 63. A small, endothermic peak was observed (fig. S9) coincident with the melting of ice with an onset temperature at -2°C and a peak around 6°C. Evolved water was recorded by TEGA's mass spectrometer as the temperature increased from -20° to +35°C.

Integration of the endothermic peak provides an estimate of the enthalpy of 0.35 J, which corresponds to 1.0 mg of water ice. If we assume that the TEGA oven was full, this sample contained ~2% ice. Because this sample was a sublimated lag, this does not represent the ice concentration in the ice layer.

Early in the mission, the RA pointed its camera under the lander to assess the footpad stability and captured an image of the ice table excavated by the 12 thrusters (Fig. 3A and fig. S3). The curved shadow of the strut provides a means to estimate its depth as 5 cm. The strut to the left of the image shows a number of blobs that have been interpreted as liquid brine splashed onto the strut during the last few seconds of landing (21). Perchlorate brines can have eutectic temperatures as low as -70°C once the perchlorate concentration reaches 30 to 50%. The planetary distribution of brines is unknown, if they exist at all, but salts do tend to concentrate with the presence of small amounts of water.

Atmospheric water vapor was measured regularly by using the TECP (fig. S10). Water vapor partial pressure remained near 2 Pa throughout most days, dropping rapidly at 18. local true solar time (LTST) to a minimum of <0.05 at 1.5 LTST. Vapor pressure of 2 Pa is about that of saturation over ice at 210 K. The water vapor measurements and 2-m air temperatures suggest that the typical mid-sol relative humidity was ~5%. The air was close to saturation at night early in the mission and was saturated toward the end, as seen via ground fog and low clouds (22). Surface temperatures are expected to be colder than those measured at 2 m, and indeed frost formation was observed in the second half of the mission (Fig. 3B).

Water ice clouds were detected by the light detection and ranging (LIDAR) (23) instrument as layers of enhanced back scatter. Near summer solstice, the most prominent clouds were detected at heights above 10 km. As the season progressed and the polar atmosphere cooled, clouds formed

in the boundary layer in late summer [after solar longitude of Mars ( $L_s$ ) = 117°], and fall streaks are clearly seen in the LIDAR observations (22). Late at night water ice was observed to fall from the clouds at 4 km altitude, and ground fogs were seen in the lower ~700 m of atmosphere (22). This diurnal cycle deposited ice onto the surface at night, reducing the vapor pressure to low values (fig. S10), sublimated it in the morning, and redistributed it throughout the planetary boundary layer in the turbulent afternoon. Near midnight, ice clouds formed and precipitated a portion of the atmospheric H<sub>2</sub>O back to the surface in the early morning.

Orbital dynamics and particularly obliquity variations strongly influence the martian climate (24) and offer the possibility of liquid water in the recent past. As the obliquity exceeds 30°, the polar cap becomes warmer and increasingly unstable, releasing water vapor into the atmosphere. Models predict a wetter environment when the summer temperatures are able to exceed 0°C (25).

The pressure at the Phoenix landing site is always higher than the triple point pressure. Several lines of evidence support liquid films of water in the soil in the recent past: CaCO<sub>3</sub> identified by TEGA (13) likely forms in a wet environment, segregated ice (fig. S8, A to C) is a signature of frozen liquid water, soil is often cemented by wetted soils, and the likelihood of thicker snowfalls melting during the warmer days at high obliquity. This evidence for periodic liquid water in an alkaline environment with a sprinkling of various salts and a perchlorate energy source (15) implies that this region could have previously met the criteria for habitability during favorable Milankovich cycles.

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16. The longest wavelength filter available is at 1  $\mu$ m, and the trend was downward.
17. A martian solar day has a mean period of 24 hours 39 min 35.244 s and is referred to as a sol to distinguish this from a ~3% shorter solar day on Earth.
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26. We thank our project manager, B. Goldstein; the Jet Propulsion Laboratory team; and our aerospace partner, Lockheed Martin. The University of Arizona supported Phoenix throughout the mission. We appreciate the help of the orbiter teams, in particular, the THEMIS (Thermal Emission Imaging System) team [P. Christensen, principal investigator (PI)] and the HiRISE (High-Resolution Imaging Science Experiment) team (A. McEwen, PI). Funding for this research came from NASA and the Canadian Space Agency.

#### Supporting Online Material

www.sciencemag.org/cgi/content/full/325/5936/58/DC1  
Materials and Methods  
Figs. S1 to S10  
References

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## Evidence for Calcium Carbonate at the Mars Phoenix Landing Site

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Carbonates are generally products of aqueous processes and may hold important clues about the history of liquid water on the surface of Mars. Calcium carbonate (approximately 3 to 5 weight percent) has been identified in the soils around the Phoenix landing site by scanning calorimetry showing an endothermic transition beginning around 725°C accompanied by evolution of carbon dioxide and by the ability of the soil to buffer pH against acid addition. Based on empirical kinetics, the amount of calcium carbonate is most consistent with formation in the past by the interaction of atmospheric carbon dioxide with liquid water films on particle surfaces.

**T**he key to understanding Mars' past climate is the study of secondary minerals that have formed by reaction with volatile

compounds such as H<sub>2</sub>O and CO<sub>2</sub>. A wet and warmer climate during the early history of Mars, coupled with a much denser CO<sub>2</sub> atmosphere,



rium calculations based on the measured ion concentrations in solution and the quantity of acid added show that the amount of calcium carbonate needed to neutralize the acid is 0.3% by weight. Lacking a full titration of the amount of carbonate, this quantity is only a lower limit to the concentration of calcium carbonate in the soil. Two other samples, both subsurface samples from the Sorceress location (similar to Wicked Witch), were shown also to contain  $\geq 0.3\%$  of calcium carbonate by weight. The WCL results

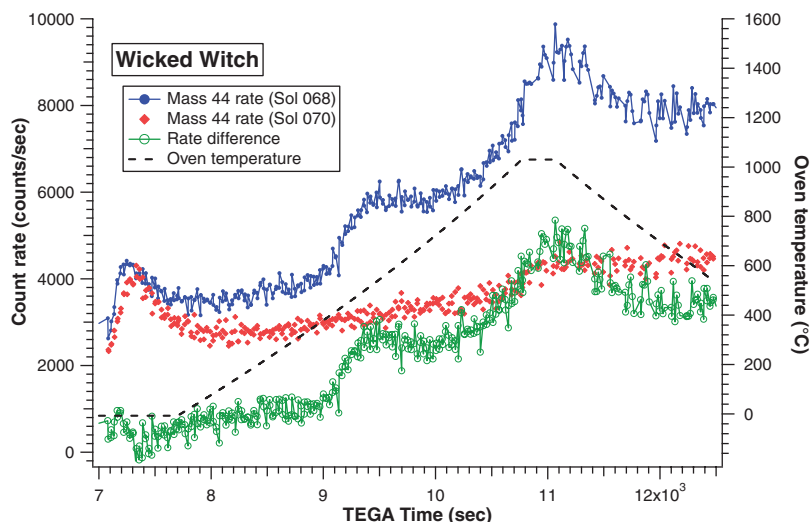
are entirely consistent with the TEGA calorimetry and evolved-gas data, which strongly suggest the presence of calcium carbonate in the soils around the Phoenix landing site.

Low-temperature carbonate dissolution and precipitation are among the most important pedogenic processes in terrestrial semiarid to arid soils (22). Carbonates precipitate as coatings on soil particles and in soil pores that can result in cementation of particles. Calcium carbonate generally precipitates by reaction of  $\text{CO}_2$ -charged

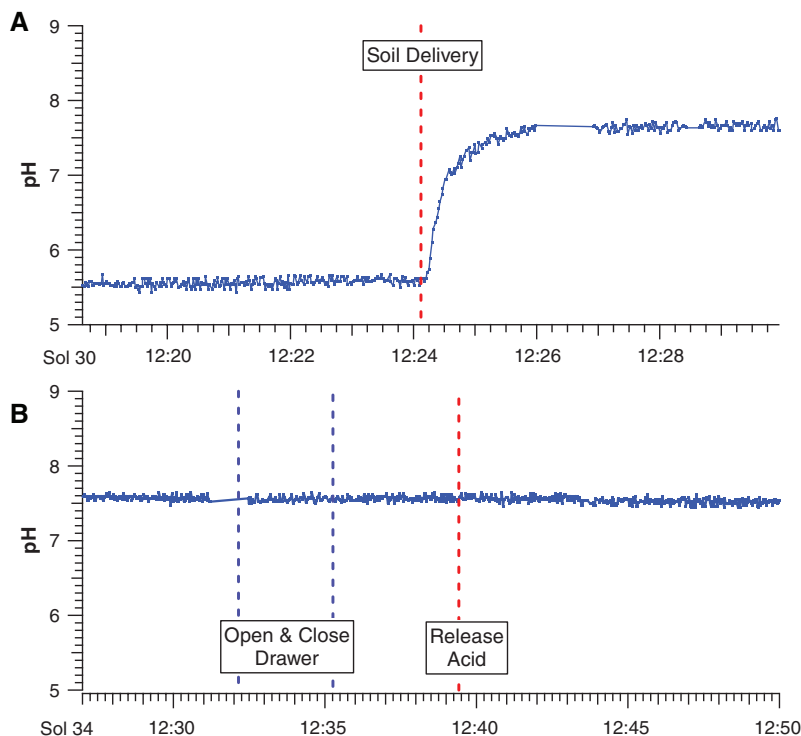
water with  $\text{Ca}^{2+}$  released by dissolution of parent materials. Soils at the Phoenix landing site are in physical proximity to an ice-cemented soil layer several cm under the surface and are covered with a surface frost during the winter. These water reservoirs suggest the diffusion of water vapor through the soils (23) and the possibility of films of unfrozen water on particle surfaces. The latter can weather basaltic minerals and mobilize ions (24, 25). Given that atmospheric  $\text{CO}_2$  would dissolve in these thin films, calcium carbonate would precipitate if the water film becomes supersaturated. 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 periods of high obliquity (26). Another possibility for the formation of calcium carbonate is by hydrothermal aqueous alteration associated with an impact event or other thermal source (e.g., volcanic). An impact event into a volatile-rich target (i.e., ice and ice-cemented sediments) would rapidly melt and/or vaporize the ice, resulting in localized hydrothermal conditions. The Phoenix landing site lies on the ejecta of the Heimdall crater, which is located 20 km away. Consequently, calcium carbonate formed in the subsurface may have been transported to the Phoenix site by the excavation of subsurface material during the impact event that formed Heimdall. In this case, calcium carbonate has persisted in the soil since the impact event,  $\sim 0.5$  billion years ago (27).

There are nonaqueous processes that can form carbonates, but the reaction rates appear to be far too small to account for the amount of calcium carbonate that we find (28). The presence of several percent by mass of calcium carbonate in the soil at the Phoenix site is of the expected magnitude if there has been periodically wet or damp martian soil in the geologic past, but it is difficult to produce under current martian conditions. This inference applies even if the calcium carbonate has been transported to the Phoenix site by wind, because the calcium carbonate would still have formed in damp or wet soil elsewhere on Mars. Two possible objections are (i) that the carbonate might be magmatic (e.g., carbonatites) and (ii) that the soil particles might have an abnormally large specific surface area, which would make a larger mass fraction of dry carbonate formation more feasible. There is, however, no evidence to support either objection. For the latter, preliminary analysis of microscopic imagery (29) indicates a modest specific surface area. Consequently, the simplest explanation is that the amount of carbonate provides geochemical evidence of past liquid water.

The presence of calcium carbonate in the soil has implications for our understanding of Mars. Calcium carbonate buffers an alkaline pH, which is similar to that of many habitable environments, notably terrestrial seawater. Another implication of the presence of calcium carbonate is that various ions may be adsorbed at exposed  $\text{Ca}^{2+}$  lat-



**Fig. 2.** Plot of Mass 44 ( $\text{CO}_2$ ) count rate and temperature versus run time. The first peak is atmospheric  $\text{CO}_2$  that diffuses into the oven and plumbs overnight; the second may be due to carbonates with a low decomposition temperature (e.g.,  $\text{FeCO}_3$  or  $\text{MgCO}_3$ ). The high temperature peak is due to decomposition of  $\text{CaCO}_3$ .



**Fig. 3.** Plot of pH versus local Mars time (A) upon soil delivery and (B) upon addition of 2-nitrobenzoic acid.

tice sites of calcium carbonate and affect Mars' soil geochemistry, and calcium carbonate can cement small soil grains and change the physical properties of the surface of Mars.

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- The onset temperature for this endothermic peak is similar to the calcite decomposition onset temperature of 738°C measured in the TEGA engineering qualification model (17). Other carbonates have decomposition temperatures that are lower than that of calcite.
- In a calibration run on the TEGA engineering qualification model with a known amount of calcite, we found the heat of transition to be 2550 J/g, which implies 2.4 mg of CaCO<sub>3</sub> in the Wicked Witch sample.
- Estimation of the concentration of calcium carbonate in the sample is uncertain because the mass of sample in the oven is not tightly constrained. We estimate that this error is on the order of ± 25%.
- The cause of this delay will be explored in planned laboratory experiments in the future. The plumbing temperatures are heated to greater than 35°C, so one would not expect CO<sub>2</sub> to condense out on any plumbing surfaces. The sol 70 run shows that this effect is not due to a background signal.
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- A previous experiment suggested that carbonate could form in relatively dry Mars-like conditions as submicrometer coatings on soil particles (5). However, the results from this study cannot be extrapolated over time because the experiments did not proceed beyond a monolayer of carbonate. A more comprehensive experimental study under Mars-like conditions showed that, in a given time span, carbonate forms on the surface of basaltic particles in an amount that increases with the thickness of films of water around the particles (30, 31). Growth of more than a monolayer of carbonate occurs with logarithmic reaction kinetics. For damp or wet conditions (meaning 0.1 to 0.5 g H<sub>2</sub>O per g soil, equivalent to 10<sup>2</sup> to 10<sup>3</sup> monolayers of water), the number of CO<sub>2</sub>-reacted monolayers of substrate, *L*, per particle is found empirically to follow the relationship (30, 32)  $L(t) = D \log_{10}(1 + t/t_0)$  (Eq. 1). Here, the constant of proportionality *D* is ~1 monolayer CO<sub>2</sub>/log<sub>10</sub>t for powdered basalt, while *t*<sub>0</sub>, which represents a time scale for CO<sub>2</sub> adsorption or dissolution in H<sub>2</sub>O, is ~10<sup>-2</sup> to 10<sup>-3</sup> days. Because the Phoenix site contains material that was likely ejected from the nearby Heimdall crater up to 0.6 billion years ago (27), or 2.2 × 10<sup>11</sup> (Earth) days ago, the number of monolayers reacting with CO<sub>2</sub> can be calculated from Eq. 1 as ~13 to 14. By stoichiometry, 1 mol of CO<sub>2</sub> generates 1 mol of carbonate, so it follows that the mass fraction, *F*, of carbonate produced under these “damp” or “wet” soil conditions would be  $F = M \times [(L A_s/A)/N_A]$  (Eq. 2), where *M* is the molar mass of carbonate (100 g/mol for CaCO<sub>3</sub>), *A*<sub>s</sub> is the specific surface area of the particles,  $A = 2 \times 10^{-19} \text{ m}^{-2} \text{ molecule}^{-1}$  is the area taken up by a CO<sub>2</sub> molecule in reaction with the surface (32), and *N*<sub>A</sub> is Avogadro's number. Basalt glasses pulverized to 0.1 to 1 micrometer size have *A*<sub>s</sub> ~1 to 10 m<sup>2</sup>/g (33), whereas 17 m<sup>2</sup>/g was estimated for Viking lander 1 soil (34). Substituting numerical values into Eq. 2 gives a carbonate mass fraction up to 20 wt % for continuously “wet” conditions. In contrast, under persistently dry or vapor conditions (meaning zero to a few monolayers of H<sub>2</sub>O), the fraction of carbonate produced is smaller because the kinetic coefficient *D* is smaller. *D* was measured up to 0.07 monolayers CO<sub>2</sub>/log<sub>10</sub>t at 6.6 mbar and -15°C (24), giving up to 0.8 wt % in Eq. 2. Other values of *D* for dry or vapor conditions ranged from ~0.01 to 0.2, but high values occurred only at higher CO<sub>2</sub> pressures, up to 995 mbar (32).
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## Detection of Perchlorate and the Soluble Chemistry of Martian Soil at the Phoenix Lander Site

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The Wet Chemistry Laboratory on the Phoenix Mars Lander performed aqueous chemical analyses of martian soil from the polygon-patterned northern plains of the Vastitas Borealis. The solutions contained ~10 mM of dissolved salts with 0.4 to 0.6% perchlorate (ClO<sub>4</sub>) by mass leached from each sample. The remaining anions included small concentrations of chloride, bicarbonate, and possibly sulfate. Cations were dominated by Mg<sup>2+</sup> and Na<sup>+</sup>, with small contributions from K<sup>+</sup> and Ca<sup>2+</sup>. A moderately alkaline pH of 7.7 ± 0.5 was measured, consistent with a carbonate-buffered solution. Samples analyzed from the surface and the excavated boundary of the ~5-centimeter-deep ice table showed no significant difference in soluble chemistry.

The elemental composition of the martian surface has been measured in situ by the two Viking landers (1), the Mars Path-

finder lander (2), and the two Mars Exploration Rovers, Spirit and Opportunity (3, 4) with the use of x-ray fluorescence spectrometry. Elemental

analysis does not, however, predict the solution chemistry of the soil (5), which is important because it is the soluble constituents that are of primary importance to biological activity, prebiotic organic synthesis, and the thermophysical properties of any liquid solution. The only prior aqueous experiments were by the Viking missions in 1976, but these focused on specific protocols

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