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CARBONATES, SURFATES, PHOSPHATES, NITRATES, AND ORGANIC MATERIALS: THEIR ASSOCIATION IN A MARTIAN METEORITE.

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The debate concerning the evolution of CO_2 on Mars continues. It would appear that in order to explain the valley networks and other relict fluvial landforms it is necessary to accept that liquid water was once present at the surface of Mars. This in turn requires, at some point in the planet's history, a higher surface temperature than exists today, a proposition explained traditionally by an early dense CO_2 atmosphere [e.g., 1]. However, there are a number of problems with this notion: for instance, CO_2 alone is not an efficient greenhouse gas because of its tendency to form clouds [2]. Moreover, if there was an early dense CO_2 atmosphere, it is necessary to explain where the elemental constituents now reside. There are two possibilities for the latter, namely loss to outer space of atmospheric CO_2 or the formation of vast carbonate deposits. While some models of atmospheric loss predict that up to 0.4 bar of CO_2 could be removed from the martian surface [3], this is still not enough to account for the original atmospheric inventory, usually considered to have been in the range of 1–5 bar. Thus, most models of the evolution of the martian surface require removal of CO_2 from the atmosphere and into carbonate deposits. However, as yet, the evidence for the existence of carbonates on Mars is fairly scant [e.g., 4]. This is an issue that would have been resolved by results obtained from Mars Observer.

While the existence of carbonates on Mars remains unsubstantiated, their presence in meteorites from Mars is undisputed. Furthermore, their origin as low-temperature secondary minerals, introduced at some point after the rock fabric of the meteorite had crystallized and cooled, has been demonstrated by isotopic measurements [5,6] and petrographic descriptions [7]. That the carbonate minerals are not simply weathering products produced on Earth has been demonstrated in one case by ^{14}C measurements, which show that there has not been an input of modern terrestrial C to the sample [8]. However, measurements from another sample show the presence of the ^{14}C isotope, interpreted as resulting from terrestrial contamination [9]. These results are somewhat unexpected since the $^{12}C/^{13}C$ and $^{16}O/^{18}O$ ratios of the carbonate minerals from the two different samples are similar [5,10]. At this point the exact significance of the ^{14}C data is unclear, but it would seem that in any particular sample there may be a few components containing ^{14}C that have been added from the terrestrial environment in addition to preterrestrial (i.e., martian) carbonates, characterized by the absence of ^{14}C. The presence of terrestrial contaminants in any meteorite sample is to be expected [5,11]; what is important is the use of analytical protocols that can effectively identify the components of interest. It is with challenges of this nature in mind that work continues with the study of weathering components in martian meteorites.

A particularly interesting sample is EET A79001, a meteorite collected from Antarctica. While rocks that experience Antarctic conditions may suffer from the effects of terrestrial inorganic weathering processes (e.g., the build-up on the outer surfaces of magnesium carbonate and bicarbonates, and hydrated magnesium and calcium sulfates), they are relatively free of organic contamination. Thus, it is interesting to note the association, deep within the meteorite, of carbonate minerals and organic compounds [12]. The carbonates are Mg-bearing and also contain P, i.e., there could be magnesium phosphates present [7]. Calcium sulfate, possibly gypsum, is also present [7], and there is also some tenuous evidence for the presence of nitrates [5,13]. On the basis of N isotope measurements it is clear that the nitrates could not have formed by a mechanism that utilized martian atmospheric N as a source material [5,13].

Because of the potential ramifications for martian surface evolution of the coexisting salts and organic compounds in EET A79001, it was perhaps inevitable that a further study of Antarctic weathering processes was necessary in order to constrain the possible extent of such effects. In this regard it is worth noting that EET A79001 has a weathering category "A" (i.e., only minor effects) and a fracturing category "A" (i.e., minor cracks). Since the meteorite is a single stone of mass 7.9 kg, measuring about 20 cm across, it is clear that samples from the center of the specimen ought to be predominantly free of the effects of terrestrial weathering. In contrast, a recently discovered martian meteorite from Antarctica, LEW 88516 (weathering A/B; fracturing A), weighs only 13.2 g and is less than 2 cm in size. Since the terrestrial ages of both Antarctic meteorites are similar, i.e., <50,000 yr, [14,15] it may be anticipated that the effects of weathering in LEW 88516 would be more severe than in EET A79001. However, LEW 88516 was found to contain the lowest C content of any of the nine known martian meteorites [16], even when material was taken specifically from the surface layers for analysis. This tends to support the notion that terrestrial weathering processes are not necessarily responsible for the components observed in EET A79001. A further consideration here arises from O isotope measurements of water released by heating, which, at face value, seem to demonstrate that EET A79001 has been affected to some degree by terrestrial weathering [17]. However, since it is now considered that the O isotope data should be treated with caution [8], their true significance, for the time being, remains poorly established.

So how do we explain the association of carbonates, sulfates, phosphates, nitrates, and organic materials in EET A79001? It has to be accepted that some of the inorganic minerals could have formed by terrestrial weathering processes. However, it is known for certain that martian meteorites, including EET A79001, contain preterrestrial weathering products [e.g., 7]. Furthermore, the associated organic compounds are present in higher abundances (i.e., by about 2 orders of magnitude) than can reasonably be expected for any contamination episode or handling procedures [12]. It would appear, therefore, that the coexistence of inorganic weathering products and organic materials in EET A79001 was established on Mars. In order to explain this phenomenon, perhaps attention should be turned to recent work that advocates an early CH_4/CO_2 greenhouse on Mars [18], since this might ultimately lead to the formation of nonvolatile surface reservoirs of reduced and oxidized forms of C. An additional consideration, which could be pursued through chemical evolution modeling studies, infrared measurements of the

martian surface, or further analyses of martian meteorites, is that there exist on Mars large deposits of oxalate minerals, such as $CaC_2O_4.H_2O$, $CaC_2O_4. 2H_2O$, $MgC_2O_4.2H_2O$, etc. On Earth these minerals fall at the very interface of inorganic and organic chemistry, being formed predominantly by biological processes. That they can form by purely inorganic reactions is demonstrated, however, by their presence in primitive carbonaceous chondrites [19]. If oxalates are present on Mars, this might explain the removal of CO_2 from the atmosphere without the formation of observable carbonate deposits.

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SIMULTANEOUS LABORATORY MEASUREMENTS OF CO_2 AND H_2O ADSORPTION ON PALAGONITE: IMPLICATIONS FOR THE MARTIAN CLIMATE AND VOLATILE RESERVOIR.

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We are measuring the simultaneous adsorption of H_2O and CO_2 on palagonite materials in order to improve the formulation of climate models for Mars. We report on the initial co-adsorption data. Models of the martian climate and volatile inventory indicate that the regolith serves as one of the primary reservoirs of outgassed volatiles and that it exchanges H_2O and CO_2 with the atmosphere in response to changes in insolation associated with astronomical cycles. Physical adsorbate must exist on the surfaces of the cold particulates that constitute the regolith, and the size of that reservoir can be assessed through laboratory measurements of adsorption on terrestrial analogs. Many studies of the independent adsorption of H_2O and CO_2 on Mars analogs have been made and appear in the literature [1–5]. Empirical expressions that relate the adsorptive coverage of each gas to the temperature of the soil and partial pressure have been derived based on the laboratory data. Numerical models incorporate these adsorption isotherms into climatic models, which predict how the adsorptive coverage of the regolith, and hence the pressure of each gas in the atmosphere will vary as the planet moves through its orbit [e.g., 6]. These models suggest that the regolith holds several tens to hundreds of millibars of CO_2 and that during periods of high obliquity warming of the high-latitude regolith will result in desorption of the CO_2, and a consequent increase in atmospheric pressure. At lower obliquities, the caps cool, and the equator warms, forcing the desorption of several tens of millibars of CO_2, which is trapped into quasipermanent CO_2 caps.
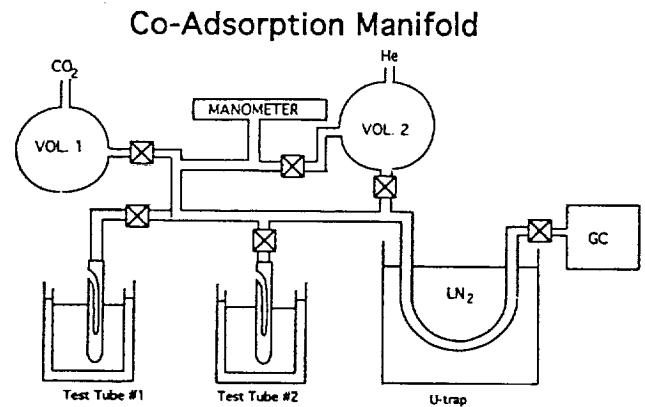
Co-Adsorption Manifold

Fig. 1.

There are a number of uncertainties in these models. Extrapolating the martian orbit more than several 10^4 yr in either direction is difficult because of the chaotic nature of the martian orbit [7]. The extent of the regolith is unclear particularly with respect to the specific surface area of regolith materials that is in diffusive contact with the atmosphere. Finally, the adsorptive behavior of H_2O and CO_2 has always been assumed to be independent. Yet there are data that suggest that near room temperature, there is adsorptive competition between H_2O and CO_2 [8], and H_2O actively displaces CO_2 from the adsorbed state. If that is the case on Mars, then current models of the CO_2 inventory overestimate its size, and climate models must account for new estimates of the inventory size and the effects of H_2O on CO_2 exchange. We have therefore undertaken laboratory measurement of the adsorptive competition between H_2O and CO_2 at conditions appropriate to the martian regolith in order to eliminate this uncertainty in the climate models.

The experimental apparatus is shown schematically in Fig. 1. The manifold and sample are baked out overnight and we then fill volume 2 to a known pressure with He and expand into the sample to estimate the dead volume in the system. The sample is cryogenically cooled to a preselected temperature, T_1. Doubly distilled water in test tube #2 is cryogenically cooled to temperature T_2. We maintain $T_2 > T_1$ in order to keep the relative humidity in the soil chamber well below unity. T_1 and T_2 are constantly monitored. To acquire a data point, we fill volume 1 with a known pressure of CO_2 and
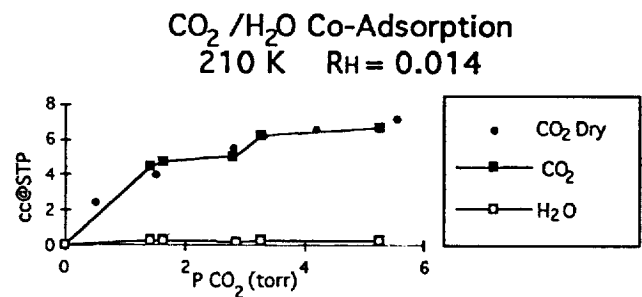
CO_2 / H_2O Co-Adsorption
210 K   RH = 0.014

Fig. 2.