

Fig. 1. A two-box model showing the location of reducing (R) and oxidizing (O) conditions on Mars through time. Oxidizing conditions in stage I represent local O oases, which may have developed in small pools formed by precipitation or seepage. Oxidizing conditions in stage II represent buried O oases located where groundwater is enriched by volcanics from an evolved mantle. Based on Fig. 3 in [14].

the formation of putative glacial features in the southern highlands, and probably did not exist (see discussion in [19]). More realistic are the smaller, isolated lacustrine basins proposed for low-lying areas in the northern plains surrounded by outflow channels [20,21] and in the cratered highlands where numerous ancient valley networks terminate [22]. Such basins are supported by geomorphic evidence (e.g., possible wave-cut terraces [20,21]) and occur during the interval that other fluvial features were forming. In addition to these basins, smaller isolated pools may have developed in topographic depressions (e.g., impact craters) if precipitation occurred in the highlands as suggested in [3]. It is especially likely that these smaller pools allowed eroded materials to concentrate, raise the local pH, and induce the formation of carbonates. Such "oases" could be the most likely locations of carbonate deposits on Mars. Other oases may exist underground where oxidizing volcanic gases interact with groundwater to raise the pH, and may help explain the presence of carbonates in the SNC meteorites [23]. Based on this view and the terrestrial example [14], a "two-box" model for the oxidizing stages for Mars is proposed (Fig. 1).

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 AN ATTEMPT TO COMPREHEND MARTIAN WEATHERING CONDITIONS THROUGH THE ANALYSIS OF TERRESTRIAL PALAGONITE SAMPLES. C. Douglas¹, I. P. Wright¹, J. B. Bell², R. V. Morris³, D. C. Golden³, and C. T. Pillingier¹. ¹The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK, ²Mail Stop 245-3, NASA Ames Research Center, Moffett Field CA 94035-1000, USA, ³NASA Johnson Space Center, Houston TX 77058, USA.

Spectroscopic observations of the martian surface in the visible to near infrared (0.4–1.0 μm), coupled with measurements made by Viking, have shown that the surface is composed of a mixture of fine-grained weathered and nonweathered minerals. The majority of the weathered components are thought to be materials like smectite clays, scapolite, or palagonite [1]. Until materials are returned for analysis there are two possible ways of proceeding with an investigation of martian surface processes: (1) the study of weathering products in meteorites that have a martian origin (SNCs) and (2) the analysis of certain terrestrial weathering products as analogs to the material found in SNCs, or predicted to be present on the martian surface. Herein, we describe some preliminary measurements of the carbon chemistry of terrestrial palagonite samples that exhibit spectroscopic similarities with the martian surface [2–4]. The data should aid the understanding of weathering in SNCs and comparisons between terrestrial palagonites and the martian surface.

The SNC meteorites contain a variety of weathering products including carbonates, sulphates, and clays of martian and terrestrial origin [5–7]. The C chemistry of SNC meteorites has already been studied extensively so it would seem reasonable to characterize the nature of C in terrestrial palagonites with a view to comparing the data with the results from SNC meteorites [6]. Several mechanisms for the formation of palagonites (which are hydrated and devitrified basaltic glasses) have been proposed: (1) hydrothermal alteration (induced by volcanism, geothermal gradients, or impact), (2) subpermafrost magmatic intrusion, (3) subaerial intrusion above the permafrost layer, and (4) static gas-solid weathering [8].

As a preliminary investigation, two terrestrial palagonite samples have been analyzed for C stable isotopes by the use of stepped combustion and static mass spectrometry. One, PN-9, collected from Mauna Kea, is a palagonitic soil and has been studied extensively because its infrared absorption features closely resemble that of the martian surface [2.5.9]. The C released between room temperature

and 1200°C accounted for 2.2 wt% of the sample, far in excess of even the most C-rich SNCs; clearly care must be taken when using palagonites as analogs of martian weathering products. The isotopic release profile of PN-9 shows at least three distinct C components. The first is a heavy component, reaching a $\delta^{13}\text{C}$ of -9.5% , and released between room temperature and 200°C, accounting for 210 ± 10 ppm. This low-temperature C may be a loosely bound labile material or it may be adsorbed atmospheric CO_2 . Atmospheric CO_2 will be adsorbed more easily onto fine-grained material and so analysis of size separates may prove interesting. A second component is released between 300°C and 450°C, which reaches a $\delta^{13}\text{C}$ maximum of -21.4% ; this represents a lower limit to the actual isotopic composition of this component because of a concomitant release of third-component organic materials ($\delta^{13}\text{C} = -25\%$) over the temperature range 200°–600°C. Carbon components with a similar release temperature and isotopic composition have been observed in SNCs on previous occasions; e.g., LEW 88516, (sub-samples .8 and .13) have distinct C components of $\delta^{13}\text{C}$ of -19.5% and -21.6% respectively across the 250°–450°C temperature interval [10]. This possibly coincidental similarity between SNCs and palagonites deserves further study.

The other palagonite sample analyzed (PH-1) was collected from the Puu Huluhulu cinder cone on Mauna Kea, immediately adjacent to an intruded lava slab [8]. It consists of a thermally altered palagonite tephra containing small amounts of hematite formed from the recrystallization of Fe material during the emplacement of the slab. Hematite is thought to be present on the surface of Mars in small quantities and so PH-1, which contains crystalline hematite, is in better agreement with the martian spectral observations [8]. Analysis of PH-1 showed it to contain 4x less C (0.6 wt%) than PN-9. The lower C content may result from volatile loss during emplacement of the lava slab, or alternatively the high C content of PN-9 may result from the input of organics during soil formation. Analysis of PH-1 showed the presence of a C component below 300°C with a $\delta^{13}\text{C}$ of at least -23.5% . It is possible that this may be a mixture of components: the remains of a small amount of the low-temperature heavy component released in PN-9 and organics of lower $\delta^{13}\text{C}$.

At present the study of the low-temperature C components in the palagonites is at an early stage. However, further analyses together with studies of smectite and montmorillonite clays may help to clarify the situation. A complete understanding of the low-temperature weathering products produced on Earth will ultimately help constrain the operation of atmospheric and liquid phase reactions occurring on Mars. A major problem for the interpretation of data from SNC meteorites is in distinguishing terrestrial and preterrestrial weathering products. It is hoped that this particular study will help solve some of the difficulties.

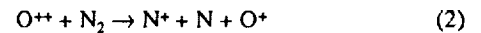
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REQUIREMENTS FOR THE EARLY ATMOSPHERE OF MARS FROM NITROGEN ISOTOPE RATIOS. J. L. Fox, Institute for Terrestrial and Planetary Atmospheres, State University of New York at Stony Brook, Stony Brook NY 11794, USA.

The N escape models of Fox and Dalgarno [1] and Fox [2] required the presence of a dense, early CO_2 atmosphere to inhibit fractionation of the N isotopes ^{15}N and ^{14}N . The computed photochemical escape fluxes are so large at the present that the isotope ratio measured by Viking (about 1.62x terrestrial) can be produced in about 1.5 b.y. We have refined this model in several ways. It has been updated to incorporate the variation of the escape fluxes with increases in the solar fluxes at earlier times according to the model of Zahnle and Walker [3]. As expected, this exacerbates the problem with overfractionation, but not greatly. Most of the escape and fractionation of the N occurs in the last 1.5 b.y., when the solar flux was only slightly different from the present. The dense early atmosphere must persist only a bit longer in order to reproduce the measured isotope ratio. We have also modified the model to take into account changes in the O mixing ratio with time in the past, assuming that the O abundance is proportional to the square root of the solar flux. Although the production rate of O from photodissociation of CO_2 scales as the solar flux, the strength of the winds and other mixing processes also increases with the solar flux [4], resulting in possibly more effective transport of O to the lower atmosphere where it is destroyed by catalytic and three-body recombination mechanisms. The escape fluxes due to the ion-neutral reactions



and



are thus changed slightly at earlier times compared to models in which the O mixing ratio is assumed to be proportional only to the CO_2 mixing ratio.

The role of dissociative recombination of N_2^+



is important because it involves an inherent fractionation mechanism in addition to that produced by diffusive separation between the homopause and the exobase. Previously we have assumed that the rate of dissociative recombination at earlier times scales as the mixing ratio of N_2 at the exobase. Although this is a good approximation for small mixing ratios of N_2 , it is an overestimate for large mixing ratios. Ion-neutral chemistry tends to transform ions whose parent neutrals have high ionization potentials, such as N_2^+ , into ions whose parents have lower ionization potentials. The ratio of exobase densities of N_2^+ to those of other ions are thus smaller than the ratio of the production rates. For example, we have found that if the mixing ratio of N_2 is 0.75 at the homopause, it is about 0.95 at the exobase, but N_2^+ constitutes only half the total ion density at the exobase. Thus the dissociative recombination rate and the fractionation due to dissociative recombination are slightly reduced at earlier times. Another possibility that we will explore for reducing