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 $\delta^{13}C$ 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 $\delta^{13}C$ 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 ($\delta^{13}C = –25‰$) 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 $\delta^{13}C$ 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 4× 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 $\delta^{13}C$ 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 $\delta^{13}C$.

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 montmorillinite 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.

References: [1] Banin A. (1992) Mars (H. H. Keiffer et al., eds.), 594–625, Univ. of Arizona. [2] Adams J. B. et al. (1986) JGR, 91, 8098–8112. [3] Bell J. F. et al. (1990) JGR, 95, 14447–14461. [4] Morris R. V. et al. (1990) JGR, 95, 14427–14434. [5] Gooding J. L. et al. (1992) Icarus, 99, 28–41. [6] Wright I. P. et al. (1988) GCA, 52, 917–924. [7] Gooding J. L. et al. (1988) GCA, 52, 909–915. [8] Bell J. F. et al. (1993) JGR, 98, 3373–3385. [9] Golden D. C. et al. (1993) JGR, 98, 3401–3411. [10] Wright I. P. et al. (1993) LPS XXIV, 1541–1542.

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 photo-chemical escape fluxes are so large at the present that the isotope ratio measured by Viking (about 1.62× 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 photodisso-ciation 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

$$N_2^+ + O \rightarrow NO^+ + N \tag{1}$$

and

$$O^{++} + N_2 \rightarrow N^+ + N + O^+ \tag{2}$$
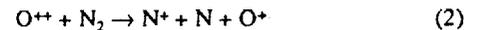
are thus changed slightly at earlier times compared to models in which the O mixing ratio is assumed to be proportional only to the CO_2 mixing ratio.

The role of dissociative recombination of N_2^+

$$N_2^+ + e \rightarrow N + N \tag{3}$$

is important because it involves an inherent fractionation mecha-nism 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 approxi-mation 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 fraction-ation due to dissociative recombination are slightly reduced at earlier times. Another possibility that we will explore for reducing

the fractionation in dissociative recombination is to incorporate the higher electron temperatures that have been indicated by a recent analysis of Viking RPA data [5]. Higher electron temperatures provide more energy for the ^{15}N atoms released in dissociative recombination of $^{15}N/^{14}N$ at the exobase, and thus the escaping fraction is larger than that computed by Wallis [6]. Luhmann et al. [7] have computed the sputtering rates of atmospheric O and C by O^+ ions picked up by the solar wind. The addition of sputtering as a loss process for N_2 greatly exacerbates the problem with overfractionation of $^{15}N/^{14}N$ [8]. We find that even a dense, early atmosphere cannot inhibit the enormous escape rates and subsequent fractionation implied by the Luhmann et al. fluxes.

References: [1] Fox J. L. and Dalgarno A. (1983) *JGR, 88,* 9027. [2] Fox J. L. (1993) *JGR, 98,* 3297. [3] Zahnle K. J. and Walker J. C. G. (1982) *Rev. Geophys., 20,* 280. [4] Bougher S. W. et al. (1990) *JGR, 95,* 14811. [5] Hanson W. B. and Mantas G. P. (1988) *JGR, 93,* 7538. [6] Wallis M. K. (1978) *Planet. Space Sci., 26,* 949. [7] Luhmann J. G. et al. (1992) *GRL, 19,* 2151. [8] Jakosky B. M. et al. (1993) In preparation.

$S_{11}-91$ $/1/3S.$ **N94-21670** ^{2}

FLUVIAL VALLEYS IN THE HEAVILY CRATERED TERRAINS OF MARS: EVIDENCE FOR PALEOCLIMATIC CHANGE?
V. C. Gulick and V. R. Baker, Department of Geosciences and the Lunar and Planetary Laboratory, University of Arizona, Tucson AZ 85721, USA.

Whether the formation of the martian valley networks provides unequivocal evidence for drastically different climatic conditions remains debatable. Recent theoretical climate modeling precludes the existence of a temperate climate early in Mars' geological history [1]. An alternative hypothesis [2] suggests that Mars had a globally higher heat flow early in its geological history, bringing water tables to within 350 m of the surface. While a globally higher heat flow would initiate groundwater circulation at depth, the valley networks probably required water tables to be even closer to the surface. Additionally, we have previously reported that the clustered distribution of the valley networks within terrain types, particularly in the heavily cratered highlands [3], suggests regional hydrological processes were important. In this abstract, we summarize the case for localized hydrothermal systems and present estimates of both erosion volumes and of the implied water volumes for several martian valley systems.

Sustained groundwater outflow requires that hydraulic gradients be maintained. On Earth, rainfall or melting snow or ice eventually infiltrate into the subsurface and maintain these gradients. Thus on Earth, groundwater outflow and surface runoff are intimately connected and such a connection is reflected in the formation of fluvial systems. In locations where sapping valleys do form they are associated with runoff-dominated systems, regardless of lithologic or climatic conditions [3].

On Mars, however, it is not clear how hydraulic gradients were maintained, particularly in the southern highlands, where most fluvial valleys exhibit a sapping morphology. In these regions, sapping valleys generally do not form together with runoff valleys, but instead form as isolated systems. Thus, groundwater outflow does not seem closely linked to an atmospheric hydrological cycle. In the heavily cratered terrains, evidence for fluvial erosion is found

on the ejecta blankets of impact craters, on some volcanos, and in intercrater plains regions. Many valleys in the intercrater plains are associated with dark units that have been interpreted as igneous sill intrusions [4]. An asymmetric distribution of valleys around impact craters is common on Mars, unlike drainages situated around terrestrial impact craters that tend to be more uniformly distributed. While most martian valley networks are attributed to formation by groundwater outflow processes [5–7], the distribution of these networks is unlike that formed by terrestrial sapping valleys.

Lacking an atmospheric hydrologic cycle, subsurface energy sources must maintain hydraulic gradients. Two possibilities are a global, uniformly higher heat flow and localized energy sources, such as magmatic intrusions. Although a global, higher heat flow would produce vertical temperature gradients, it would not produce anomalously large, localized horizontal temperature gradients in the groundwater by itself. Such gradients are necessary to produce lateral flow and recharge of aquifers. However, the addition of vigorous, localized hydrothermal circulation to a uniformly higher heat flow overcomes this problem. Such systems would naturally be associated with igneous intrusions, volcano formation, and large impact craters, all of which are locales for valley formation on Mars, particularly in the heavily cratered terrains. Depending on the volume of the associated magmatic intrusion, martian hydrothermal systems can circulate groundwater into the surface environment for several million years; such systems are thus able to maintain hydraulic gradients sufficient for valley formation. Rather than replenishing groundwater through rainfall and infiltration, our numerical modeling demonstrates that a martian hydrothermal system replenishes itself by continually drawing in colder, denser groundwater radially from more distant parts of the aquifer. The total quantity of groundwater that passes through the modeled hydrothermal system over its lifetime is comparable to that needed to form a single outflow channel. Hence, subsurface aquifers of the required magnitude to form fluvial valleys must have existed on Mars.

The clustered distribution or localization of sapping valleys on Mars and their isolation from runoff valleys strongly suggests localized, subsurface sources of water. In short, a rainfall genesis should produce associated runoff valleys and a more uniform distribution of fluvial valleys within a given terrain type or surface
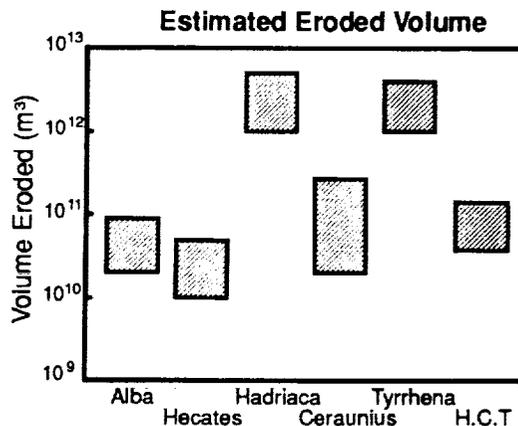

Fig. 1.