Noble gases in iddingsite from the Lafayette meteorite:
Evidence for liquid water on Mars in the last few hundred million years

T. D. SWINDLE1*, A. H. TREIMAN2, D. J. LINDSTROM2, M. K. BURKLAND1, B. A. COHEN1,
J. A. GRIER1, B. LI1 AND E. K. OLSON1

1Lunar and Planetary Laboratory, University of Arizona, 1629 East University Boulevard, Tucson, Arizona 85721-0092, USA
2Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, Texas 77058-1113, USA
3NASA/Johnson Space Center, Houston, Texas 77058-3696, USA
*Correspondence author's e-mail address: tswindle@u.arizona.edu

(Received 1998 June 8; accepted in revised form 1999 September 20)

Abstract—We analyzed noble gases from 18 samples of weathering products ("iddingsite") from the Lafayette meteorite. Potassium-argon ages of 12 samples range from near zero to 670 ± 91 Ma. These ages confirm the martian origin of the iddingsite, but it is not clear whether any or all of the ages represent iddingsite formation as opposed to later alteration or incorporation of martian atmospheric 40Ar. In any case, because iddingsite formation requires liquid water, this data requires the presence of liquid water near the surface of Mars at least as recently as 1300 Ma ago, and probably as recently as 650 Ma ago. Krypton and Xe analysis of a single 34 µg sample indicates the presence of fractionated martian atmosphere within the iddingsite. This also confirms the martian origin of the iddingsite. The mechanism of incorporation could either be through interaction with liquid water during iddingsite formation or a result of shock implantation of adsorbed atmospheric gas.

INTRODUCTION

The question of where and when there has been liquid water on Mars is one of the most fundamental problems concerning the red planet. Photogeological evidence suggests that there has been water flowing on the surface from time to time (Carr, 1996), and some interpretations suggest that there have been oceans on Mars on occasion (e.g., Parker et al., 1989, 1993; Baker et al., 1991), ideas that have only gained strength with the results of the Mars Global Surveyor mission (e.g., Head et al., 1998). However, absolute martian chronology is not well understood—there are two very different crater frequency vs. time relations that have been suggested (Tanaka et al., 1992). In other words, these studies can provide the "where" but are less useful at constraining the "when."

We have been studying liquid-water-derived weathering products in a martian meteorite in an attempt to determine absolute radiometric ages. Although we do not know where on Mars any of the martian meteorites come from, our studies can address the question of when liquid water was available.

Our samples are from the Lafayette meteorite (martian meteorites have been reviewed by McSween, 1985, 1994). Lafayette is one of three known nakhlites and has the highest abundance of hydrous weathering products (3%; Treiman et al., 1993) of any martian meteorite. We analyzed "iddingsite," a mixture of smectite clays, iron oxides, and ferricyanides. Gooding et al. (1991) and Treiman et al. (1993) studied the weathering products in nakhlites and concluded that the microstratigraphy indicates that the iddingsite formed on Mars.

The primary purpose of this study was to determine when the iddingsite formed, using variants of the K-Ar dating system. As long as the ages are greater than the terrestrial residence time of Lafayette (perhaps as much as 10,000 years (Jull et al., 1997), but certainly not more), this also serves as a confirmation that the iddingsite is preterrestrial (i.e., martian).

The Lafayette meteorite itself apparently formed ~1300 Ma ago, because 40Ar-39Ar, Rb-Sr, and Sm-Nd studies have all given the same age (Podosek, 1973; Shih et al., 1998). The simplest scenario would be that the iddingsite formed soon after the host rock formed, when the heat flow associated with the emplacement of the host rock could lead to the melting of ice and/or mobilization of water. However, our results suggest a more complicated (and more interesting) scenario.

We also tested a suggestion by Drake et al. (1994) that water-formed iddingsite might be the principal carrier of noble gases in nakhlites. Their motivation was a puzzling observation by Ott and Begemann (1985). On a plot of the isotopic ratio 129Xe/132Xe vs. 85Kr/132Xe (Fig. 1), many shergottite meteorites seem to plot along a mixing line between martian atmosphere (as measured in the impact glass in EET 79001) and the Chassigny meteorite. This could be plausibly interpreted as an indication that the meteorites originally contained Kr and Xe with elemental and isotopic compositions like that of Chassigny and then gained additional noble gases through a nonfractionating process, such as shock. However, the nakhlites all seem to plot off the line, in the direction of lower Kr/Xe ratios. In addition, Ott and Begemann (1986) observed that an HCI-etched sample of Nakhl plotted on the line and suggested that the carrier of the anomalous atmospheric-like component was olivine, the major phase dissolved. Drake et al. (1994) suggested that the carrier was the iddingsite, which would also have dissolved. Furthermore, they noted that elemental fractionation frequently occurs when noble gases are incorporated into water-borne rocks. Bogard and Garrison (1998) have confirmed Ott and Begemann's (1985) mixing line with many more samples of glass from shergottites and have stressed the similarity of the nakhlite elemental fractionation pattern to that of noble gases in water itself, rather than in sediments.

We used our largest sample (34 µg) for an analysis of Kr and Xe, primarily to test the suggestion of Drake et al. (1994) that the iddingsite could be the primary carrier of heavy noble gases in the nakhlites.

Preliminary results have been given by Swindle et al. (1995a, 1997), and Drake et al. (1994). Chemical instrumental neutron activation analyses (INAA) of most of the samples in the present study have been reported by Treiman and Lindstrom (1997).

PROCEDURES

A total of 25 samples of iddingsite were extracted from chips of Lafayette in two different sets (Treiman and Lindstrom, 1997).
Fig. 1. Ratio of $^{129}\text{Xe}/^{132}\text{Xe}$ or $^{84}\text{Kr}/^{132}\text{Xe}$ for some SNC meteorites. Most shergottite glasses, including all those of Bogard and Garrison (1998), fall along a mixing line between Chassigny (mantle?) and EETA79001.27 glass (atmosphere?). On the other hand, nakhlites all fall above the mixing line, which suggests a contribution from a fractionated martian atmosphere. Our iddingsite analysis plots just beyond the nakhlites, in agreement with the suggestion of Drake et al. (1994) that iddingsite is the principal carrier of the fractionated atmospheric component in nakhlites. Data from compilations in Drake et al. (1994) and Bogard and Garrison (1998).

Samples ranged in size from 0.5 to 34 µg. Some were single pieces; others consisted of several pieces. We did three essentially different experiments, which will be discussed in turn.

With the exception of one sample used for analysis of Kr and Xe, all samples were irradiated at the University of Missouri Research Reactor in two irradiations. All packaging of samples for irradiation was done at Johnson Space Center (Treiman and Lindstrom, 1997).

In all cases, after the samples were sealed in the extraction line, the sample holder (either the laser port or the vial cracker) was heated with heating tape to 130–150 °C overnight before analyses began. In the case of the second set of irradiated samples, the temperature was ~150 °C. Although this was somewhat higher than we had intended, we will argue later that this should not have caused gas loss.

With the exception of the sealed irradiated vials (discussed below), all extractions were done with a Liconix 6W CW Ar ion laser. Samples were loaded into a sample holder with a quartz viewport, and then the laser beam, focused through optics from U.S. Optics, was fired at the sample. When too much power was applied too quickly, particularly if the beam was not focused on the center of the particle, we found that the samples tended to jump away. Therefore, we usually used a slightly defocused beam and ramped the power up slowly (over tens of seconds) until the sample began to melt.

During extraction, released gases were exposed to a hot SAES 101 getter. Gas was then expanded into a volume containing a cold getter and then into the mass spectrometer. The extraction step took a minimum of 7 min (2 min exposed to the cold getter), but sometimes required 10 to 15 min for samples where there were multiple particles in a vial.

All noble gas analyses were performed with the VG5400 noble gas mass spectrometer at the University of Arizona. Analyses were done by peak-jumping, and amounts and isotopic ratios extrapolated to the time of admission of the sample gas into the mass spectrometer.

We ran a variety of blanks before, between, and after sample runs, including "cold" blanks (where the laser was not fired), and blanks where the laser was fired at quartz vials or the walls of the sample chamber. Although it is possible that even the "hot" blanks may be underestimates of the true blank contribution (because the laser may couple differently to the sample), there was no evidence in the blank data for any isotopic composition other than terrestrial atmosphere, and most of our arguments would be insensitive to the addition of gas with that composition.

Krypton and Xenon—The largest single sample, a 34 µg single piece from the first extraction, was analyzed for Kr and Xe. The gas was removed before admitting it into the mass spectrometer, so we had two measurements, with both gases analyzed simultaneously in each measurement. The first split was only analyzed through five cycles (~10 min), which led to larger uncertainties. Running both gases simultaneously sacrifices some of the precision for Xe (because the pumpout/memory curve is not as well defined), but the sacrifice is not as large as it would be for two equally sized splits (to get both gases). Blanks were quite low (Table 1), and the blanks run before the sample were of atmospheric composition.

Argon-40—Argon-39 Experiments—For the first set of five samples analyzed for Ar, we tried to determine the age based on the amount of radiogenic 40Ar compared to the amount of reactor-produced 39Ar. Because the iddingsite consists in part of clays, which are notoriously susceptible to recoil loss of 39Ar (Turner and Cadogan, 1974; see Kapusta et al., 1997; Onstott et al., 1997; Dong et al., 1997 for recent discussions), we sealed each sample in a high-purity quartz vial, which had been evacuated by a mechanical pump to ~10^{-3} torr. The samples were left in the vials for INAA and then shipped to University of Arizona for noble gas analysis of both the gas that had been released into the vial (Villa et al., 1983) and the sample itself. An additional vial, with no sample in it, was sealed under the same conditions to serve as a control.

For the sealed irradiated vials, we designed a "vial cracker" that fit onto the spot where the laser port was normally attached. The vial cracker consisted of an all-metal cross, with a linear-motion feedthrough with a beveled tip. Once a vial was cracked, the gas

<table>
<thead>
<tr>
<th>Type</th>
<th>Laser?</th>
<th>Split</th>
<th>$^{84}\text{Kr}$</th>
<th>$^{86}\text{Kr}$</th>
<th>$^{129}\text{Xe}$</th>
<th>$^{132}\text{Xe}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>No</td>
<td>100%</td>
<td>3.7 ± 2.4</td>
<td>2.3 ± 0.9</td>
<td>1.7 ± 1.1</td>
<td>1.8 ± 0.9</td>
</tr>
<tr>
<td>Blank</td>
<td>Yes</td>
<td>100%</td>
<td>4.1 ± 1.4</td>
<td>0.8 ± 0.3</td>
<td>0.6 ± 0.1</td>
<td>0.5 ± 0.8</td>
</tr>
<tr>
<td>Sample</td>
<td>Yes</td>
<td>30%</td>
<td>12.6 ± 1.2</td>
<td>2.9 ± 1.1</td>
<td>2.8 ± 1.6</td>
<td>3.1 ± 1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70%</td>
<td>20.3 ± 2.4</td>
<td>8.0 ± 2.1</td>
<td>9.6 ± 1.0</td>
<td>4.8 ± 1.2</td>
</tr>
<tr>
<td>Blank</td>
<td>No</td>
<td>30%</td>
<td>1.9 ± 1.6</td>
<td>1.3 ± 0.7</td>
<td>1.0 ± 0.7</td>
<td>0.3 ± 0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70%</td>
<td>5.5 ± 2.7</td>
<td>3.6 ± 0.8</td>
<td>0.6 ± 0.8</td>
<td>0.1 ± 0.5</td>
</tr>
<tr>
<td>Blank</td>
<td>Yes</td>
<td>30%</td>
<td>2.8 ± 1.1</td>
<td>2.6 ± 0.9</td>
<td>0.5 ± 0.7</td>
<td>1.0 ± 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70%</td>
<td>3.7 ± 1.2</td>
<td>2.1 ± 0.8</td>
<td>1.2 ± 0.9</td>
<td>0.4 ± 1.3</td>
</tr>
</tbody>
</table>

All amounts given in counts per second, extrapolated to the time gas was admitted to the mass spectrometer. All uncertainties in this and all tables and figures are 1σ. Blank- and sensitivity-corrected results: $[^{132}\text{Xe}]$: $8 \times 10^{-11}$ cm$^3$ STP/g, $^{129}\text{Xe}/^{132}\text{Xe}$: 2.04 ± 0.28, $^{84}\text{Kr}/^{132}\text{Xe}$: 6 ± 3.
was exposed to the hot getter for 5 min and the cold getter for 2 min. After a vial was cracked and the gas within it analyzed, the cracked vial was removed from the vial cracker and loaded into the laser port. After all vials had been cracked, the laser port was loaded onto the extraction line, and the Ar remaining in the samples was analyzed using laser extraction.

For the vials, blanks were negligible compared to the residual atmospheric Ar in the vials and so are not discussed further. Blanks for the laser extractions were variable in amount, but the isotopic compositions could consistently be represented as mixtures of a Cl-derived component ($^{35}$Cl, $^{37}$Cl, $^{37}$Cl, $^{38}$Cl), atmospheric Ar, and a slight hydrocarbon signal at mass 39. The component that varied the most was the amount of atmospheric Ar, and the factor exerting the most influence on the amount of atmospheric Ar was the length of time the sample gas spent in the extraction line. Four of the five Ar samples in the first set yielded $^{40}$Ar/$^{36}$Ar ratios within 1σ of terrestrial atmosphere (and the fifth was only 3σ higher), even after correcting for nominal "average" blanks (Table 2). Furthermore, in several cases, the particles fragmented during the vial cracking and/or loading and unloading of the vials, so we were unable to quantitatively degas the sample, although we tried to degas the largest pieces, which should contain most of the mass. This, coupled with the degradation of the INAA experiment by trace contaminants in the vials (which weighed a factor of 10^4 more than the samples they contained), convinced us that we needed to redesign the experiment for the second set of samples.

Potassium-Argon Experiments—One of our primary goals in the K-Ar set of experiments was to improve the INAA portion of the experiment. The INAA data has been discussed in Treiman and Lindstrom (1997). In the first experiment, we found that K values determined via INAA (K was one of the few elements that could be reliably determined) agreed with the amounts of K we determined from the combination of the vials and the laser extractions, for those samples for which we believed we had had quantitative degassing. Therefore, for the second set of experiments, samples were removed from the irradiated vials and placed in unirradiated vials for gamma-ray counting before shipping to Arizona. We then used the INAA values for K and did not analyze the $^{39}$Ar released during the irradiation. Masses were computed from INAA data by assuming that the samples contained 29.0 wt% FeO (Treiman and Lindstrom, 1997). Although this procedure replaces the cracking of the vial with an extra sample-handling step, the sample-handling step comes prior to the INAA, so any sample loss is irrelevant. Furthermore, we found that the samples were more likely to be intact (either because very small pieces were lost or because of elimination of the rather violent vial-cracking step), making us more confident that we were achieving quantitative outgassing.

We also ran a more systematic set of blanks. Although most of the blanks were of 5 min duration, we also ran blanks of 10, 12, and 15 min duration. Over the course of the week in which all the samples were analyzed, the blanks of a given duration were consistent with one another to within ±10% (Table 3), so we used the average values (or interpolations, for intermediate times). The "cold" blanks were no different than any of those involving the laser (as long as they involved comparable lengths of time in the extraction line), so we believe there was no significant contribution to the blank from material heated by the laser.

For the Kr/Xe experiment and the $^{40}$Ar/$^{39}$Ar experiment, spectrometer sensitivities were calculated based on analysis of calibrated amounts of air. For the second set of experiments, Ar sensitivities were calculated based on analyses of 20 samples of the GA1550 and MMib-1 Ar standards (McDougall and Harrison, 1988), which were consistent with one another to within 10% (1σ).

**RESULTS**

Krypton and Xenon

Krypton and Xe results, along with the average of blanks run immediately before and after the sample, are given in Table 1. Note that the sample gas was split before admittance to the mass spectrometer, as was the gas for the two blanks run after the sample.

The crucial result is that the $^{129}$Xe/$^{132}$Xe ratio was higher than terrestrial. Because it was only by ~3σ, several aspects of data reduction were done in a variety of ways to ensure that the higher $^{129}$Xe/$^{132}$Xe ratio was not an artifact of the data reduction procedure. Values listed in Table 1 were determined by extrapolating plots of counts/second vs. time, to the time the gas was admitted to the mass spectrometer. Note that the $^{129}$Xe/$^{132}$Xe ratio of the first split of the sample gas is atmospheric, within 1σ. However, it is also within 2σ of the ratio for the more precisely measured second split, and an inspection of the data showed that if the final cycle is omitted, the data for the first split are consistent with those of the second split to within 1σ. The data for the second split give $^{129}$Xe/$^{132}$Xe < 1.6, even if up to three data points from either the beginning or end of the analysis are omitted.

For the "blank-corrected" values given at the bottom of Table 1, the isotopic ratios were calculated from plots of isotopic ratio vs. time. A blank consisting of the average of the two blanks run before the sample was then subtracted. Note that because those blanks were actually slightly higher than the blanks run after the sample, this may be a slight overcorrection, but averaging in more of the blanks would not change any of the conclusions.

**Argon-40—Argon-39 Experiment (Including Sealed Vials)**

Our primary intent with the sealed vials was to determine whether any significant fraction of the $^{39}$Ar was lost by recoil.

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**TABLE 2. Argon-40—Argon-39 results.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (µg)</th>
<th>Vial $^{40}$Ar (10^-6 cm^3/g)</th>
<th>Vial $^{39}$Ar (10^-6 cm^3/g)</th>
<th>Laser extraction $^{40}$Ar (10^-6 cm^3/g)</th>
<th>Laser extraction $^{39}$Ar (10^-6 cm^3/g)</th>
<th>Laser extraction $^{40}$Ar/$^{39}$Ar (10^-6 cm^3/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 1A</td>
<td>8</td>
<td>5.4</td>
<td>1.5</td>
<td>300.0 ± 2.3</td>
<td>5.0</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>10.4</td>
<td>23</td>
<td>2.8</td>
<td>298.5 ± 5.2</td>
<td>11.2</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>10.8</td>
<td>13.2</td>
<td>3.4</td>
<td>299.0 ± 1.8</td>
<td>23.7</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>10.8</td>
<td>2.3</td>
<td>4.2</td>
<td>299.9 ± 1.8</td>
<td>33.0</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>10.5</td>
<td>4.7</td>
<td>3.2</td>
<td>299.1 ± 1.0</td>
<td>15.1</td>
<td>6.8</td>
</tr>
<tr>
<td>Blank</td>
<td></td>
<td>9.5</td>
<td>-1</td>
<td>302.3 ± 1.1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Blank tube released <2% as much $^{39}$Ar as smallest amount from a sample via cracking of a vial.*
Unfortunately, the answer turned out to be yes. The results from the vials are given in Table 2, along with the results of the subsequent laser extractions of the samples. All of the sample vials contained measurable $^{39}$Ar. Furthermore, the empty vials contained no more than 2% as much $^{39}$Ar as the smallest amount from a sample vial, so there is no indication that the $^{39}$Ar comes from anything other than the sample. The quantity of $^{39}$Ar in the vial is often comparable to that remaining in the sample (Table 2).

The $^{40}$Ar/$^{36}$Ar ratios of the gas released by cracking the vials is (within errors) the same for all vials, $\pm 10^{-3}$ torr. The fact that the ratio is slightly higher than that of air (295.5) could reflect isotope fractionation during the pumping process, with the lighter isotope ($^{36}$Ar) preferentially pumped away.

Only one of the laser extractions gave a $^{40}$Ar/$^{36}$Ar ratio above atmospheric (after blank correction), leading us to believe that our samples had adsorbed substantial amounts of terrestrial Ar. That sample gave an age of approximately 280 ± 70 Ma, based on the gas extracted with the laser. Taking a 3σ upper limit to the amount of radiogenic $^{40}$Ar in the vial, we get an upper limit to the age of $\sim 750$ Ma.

**Potassium-Argon Experiment**

In the K-Ar experiment, which involved more samples, better-designed handling, and more careful monitoring of blanks, we were able to detect radiogenic $^{40}$Ar for most samples (Table 4). Apparent ages, calculated by combining the noble gas determination of the amount of $^{40}$Ar with the INAA determination of the amount of K, range from $\sim 0$ to 670 ± 91 Ma for sample 11C. Sample 11C is the only sample with an apparent age $\geq 450$ Ma. The implications of the ages, and possible complications in calculating the ages, will be discussed below.

We find no correlation of apparent ages with chemistry (Treiman and Lindstrom, 1997), although 11C, the sample with the oldest apparent age, is the highest in Cr and Zn and lowest in Co and Hg. It is also low in K (Fig. 2), but it is not simply the low-K measurement that generates the older age, because 11C also has the highest amount of radiogenic $^{40}$Ar (Table 4).

**DISCUSSION**

**Krypton and Xenon**

The elemental and isotopic ratios of our direct measurement of the Lafayette iddingsite are consistent with the Drake et al. (1994) hypothesis. The data fall in the region with the bulk nakhlites (Fig. 1) and do have enhanced amounts of Kr and, especially, Xe, relative to the bulk rock. However, subsequent experiments on Nakhl by Gilmour et al. (1999) seem to indicate that iddingsite is not the dominant carrier of elementally fractionated martian atmosphere in the nakhlites.

Gilmour et al. (1999) analyzed Xe (only) in mineral separates from Nakhl and used the $^{129}$Xe/$^{132}$Xe ratio to track the atmospheric component. They found that olivine and pyroxene have concentrations of atmospheric Xe comparable to the whole rock and that mesostasis is enriched in atmospheric Xe. Their mass balance calculations suggest that roughly half the atmospheric Xe is in the mesostasis, with no need for a significant contribution from iddingsite (although we note that iddingsite can be concentrated in areas of mesostasis). Furthermore, they suggest that the susceptibility of the atmospheric component to etching (Ott et al., 1988) is the result of the Xe residing close to grain surfaces. Gilmour et al. (1999) favor incorporation of gas-rich martian soil into the melt that formed the nakhlites. In their model, the soil would be gas-rich because of adsorption onto clay minerals.

The mass balance for our iddingsite measurement is marginally consistent with either the Drake et al. (1994) hypothesis or with Gilmour et al.'s (1999) work. The iddingsite contains 8 × 10$^{-11}$ cm$^3$.

**Table 4. Potassium-argon results.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass ($^{40}$Ar/$^{36}$Ar)*</th>
<th>Potential spallation contributions</th>
<th>$^{36}$Ar as martian</th>
<th>$^{36}$Ar as terrestrial</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
<td>$^{36}$Ar/mass $^1$</td>
<td>$^{36}$Ar/mass $^2$</td>
<td>$^{36}$Ar/mass $^3$</td>
</tr>
<tr>
<td>9A</td>
<td>19.1 289 ± 59</td>
<td>6.9 ± 0.5</td>
<td>0.0 ± 0.1</td>
<td>0.6 &lt;20</td>
</tr>
<tr>
<td>9B</td>
<td>19.1 701 ± 105</td>
<td>8.5 ± 0.6</td>
<td>0.4 ± 0.1</td>
<td>0.7 464 ± 34</td>
</tr>
<tr>
<td>9C</td>
<td>10.6 634 ± 65</td>
<td>6.7 ± 0.8</td>
<td>0.2 ± 0.3</td>
<td>0.6 656 ± 42</td>
</tr>
<tr>
<td>9D</td>
<td>4.4 373 ± 37</td>
<td>1.4 ± 0.6</td>
<td>2.4 ± 0.4</td>
<td>0.1 1110 ± 100</td>
</tr>
<tr>
<td>9E</td>
<td>2.7 397 ± 49</td>
<td>0.0 ± 0.0</td>
<td>2.4 ± 0.0</td>
<td>&lt;0.5 1340 ± 140</td>
</tr>
<tr>
<td>9F</td>
<td>2.1 293 ± 51</td>
<td>0.0 ± 0.1</td>
<td>3.9 ± 0.6</td>
<td>&lt;0.2 910 ± 130</td>
</tr>
<tr>
<td>9G</td>
<td>1.3 467 ± 135</td>
<td>4.2 ± 0.9</td>
<td>0.1 ± 1.7</td>
<td>0.4 590 ± 210</td>
</tr>
<tr>
<td>9H</td>
<td>2.2 455 ± 82</td>
<td>0.0 ± 0.2</td>
<td>0.0 ± 1.1</td>
<td>&lt;0.4 910 ± 210</td>
</tr>
<tr>
<td>9K</td>
<td>1.3 330 ± 66</td>
<td>5.3 ± 1.4</td>
<td>1.5 ± 1.1</td>
<td>0.4 1340 ± 270</td>
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<tr>
<td>11A</td>
<td>7.5 356 ± 46</td>
<td>1.2 ± 0.5</td>
<td>0.3 ± 0.3</td>
<td>0.1 246 ± 65</td>
</tr>
<tr>
<td>11B</td>
<td>1.6 741 ± 131</td>
<td>5.1 ± 1.1</td>
<td>2.0 ± 0.8</td>
<td>0.4 430 ± 190</td>
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<tr>
<td>11C</td>
<td>6.4 466 ± 23</td>
<td>1.2 ± 0.6</td>
<td>0.2 ± 0.4</td>
<td>0.1 1020 ± 110</td>
</tr>
</tbody>
</table>

Masses in μg, noble gas amounts in 10$^{-8}$ cm$^3$ STP/g, elemental abundances in wt%, ages in Ma; uncertainties are 1σ.

*Measured ratio, corrected only for H$^{13}$C.

1Measured amount, corrected for blank.

2Calculated amount, based on amount of CaO.

3Radiogenic Ar, assuming all $^{36}$Ar not attributable to spallation is terrestrial or martian (see text). Where the lower limit to the atmospheric $^{36}$Ar is ≤0, the 1σ upper limit on the measured $^{40}$Ar is used as the upper limit to radiogenic $^{40}$Ar.

4Upper limits are 2σ; ages listed as zero are cases where the amount of radiogenic $^{40}$Ar is <0 at the 2σ level, under the assumptions used.
from the ancient martian meteorite Allan Hills (ALH) 84001 also plots with the nakhlites (Swindle et al., 1995b; Miura et al., 1995; Eugster, 1994; Murty and Mohapatra, 1997; Mathew et al., 1997), but ALH 84001 does not contain iddingsite; and the only plausible secondary alteration product, the carbonates, are apparently not the main carrier of the atmospheric noble gases (Gilmour et al., 1998), so some other process must be capable of producing this effect in martian rocks. Second, in step-heating experiments on bulk nakhlites (Ott, 1988; Swindle et al., 1987, 1989), the high $^{129}\text{Xe}/^{132}\text{Xe}$ ratios are in high-temperature extractions ($>800$ °C), and the mesosostasis may be more likely to be that retentive than the iddingsite.

In addition, although the amount of Kr and Xe in iddingsite may be too low for iddingsite to be the dominant carrier, it may be uncomfortably high to attribute to incorporation from water. As Drake et al. (1994) discuss, if the correction is made for the difference in Xe partial pressure between the terrestrial and martian atmospheres, the amount required in iddingsite is comparable to some of the highest amounts measured in terrestrial sediments (Ozima and Podosek, 1983), and these have tended to be exceptional, C-rich sediments.

An alternative, related to the suggestion of Gilmour et al. (1999), is that the iddingsite directly incorporated the noble gases from the martian atmosphere by adsorption. Given the Henry constants typical of plausible analog materials quoted by Ozima and Podosek (1983) (e.g., $38$ cm$^3$ STP/g-bar for Xe for Wyoming montmorillonite at $-77$ °C, Kr lower by about a factor of $5$), and the abundance of Xe in the martian atmosphere (from $4 \times 10^{-8}$ to $4 \times 10^{-9}$ of the total atoms are $^{129}$Xe; according to the various tabulations of Pepe and Carr, 1992), a martian clay could incorporate on the order of $10^{-10}$ to $10^{-9}$ cm$^3$ STP/g of $^{129}$Xe, with the observed elemental fractionation, at that temperature. The Henry constant is sensitively dependent on temperature (Podosek et al., 1981), so there could be a factor of $10$ to $100$ less gas trapped, if trapping occurred at temperatures $50$ to $100$ °C higher. Even so, the amount of gas trapped could be enough to provide much, if not most, of the gas in the iddingsite. Of course, adsorption is a reversible process, so any gas adsorbed at low temperatures on Mars would be expected to escape at the higher temperatures of Earth's surface (and certainly at the temperatures to which samples are typically preheated in terrestrial laboratories), unless there is some process acting to implant the gas more firmly. Gilmour et al. (1998) have suggested that shock has done just that to explain the trapped martian atmospheric noble gases in ALH 84001. We think it possible that the same process has act on Lafayette iddingsite and Nakhlah mesostasis, explaining both the results of this experiment and those of Gilmour et al. (1999).

There is another effect that could contribute to the amount of noble gases, and the elemental fractionation seen, in the nakhlites and ALH 84001. Musselwhite and Lunine (1995) suggested that the martian polar caps could include noble gases in clathrates. They find that, depending on the assumptions used, up to $99\%$ of the Kr and Xe could be sequestered in clathrates and that Xe would be preferentially incorporated. If the bulk of the martian Xe is currently in polar clathrates, then the amount of Xe in the atmosphere (and the Xe/Kr ratio) could be significantly higher if the polar caps were melted. Hence, postulating that the Lafayette iddingsite acquired its gas during a time when less Xe was stored in the polar caps could help explain both the absolute amount of heavy noble gases and the elemental fractionation. A time-varying Xe abundance in the atmosphere could also explain why ALH 84001 plots with the nakhlites, if the atmosphere was also warmer when the
gases were implanted into ALH 84001 (perhaps during its ejection event 16 Ma ago (Eugster, 1994; Swindle et al., 1995b; Miura et al., 1995); although several workers have argued for incorporation of atmospheric gas into ALH 84001 several billion years ago (Grady et al., 1998; Murty and Mohapatra, 1997; Gilmour et al., 1998)). It is tempting to extend this idea to suggest that both the presence of liquid water in the nakhlites and an increased Xe abundance are related to a globally warmer episode. However, the lack of low-temperature aqueous alteration products in ALH 84001, a more heavily fractured rock than the nakhlites, is problematic. In addition, Gilmour et al. (1999) have argued that the abundances might still not be high enough to account for the gas in the nakhlites, at least if the incorporation mechanism was directly into a melt. An atmosphere with more, and elementally fractionated, Kr and Xe would still require a process (such as adsorption or incorporation from liquid water) to put the gas into the rocks, but the process need not be as efficient.

**Argon Experiments**

In the first 40Ar/36Ar set of experiments, only one of the samples had a 40Ar/36Ar ratio distinct from terrestrial atmosphere. In the second K-Ar set of experiments, nine of the samples have 40Ar/36Ar ratios at least 1σ greater than the terrestrial atmospheric value.

The strongest conclusion that can be reached is that the iddingsite samples are indeed preterrestrial, confirming the microstratigraphic arguments of Gooding et al. (1991) and Teirman et al. (1993).

**Source of Argon-36**—Slightly more than half (7 of 12) of the samples have non-zero amounts of 36Ar after correction for blanks. There are three other possible sources of the 36Ar: terrestrial atmosphere, martian atmosphere, and cosmic-ray spallation. Because these sources have very different 40Ar/36Ar ratios (Table 5), there are some cases where the age that we calculate could be dramatically different, depending on the source of the 36Ar. In principle, we might be able to distinguish based on the 38Ar/36Ar ratios, because these also differ (Table 5). But because our samples have all been irradiated, the 36Ar is predominantly derived from neutron-capture on 37Cl.

There are only two samples where spallation-produced (cosmogenic) 36Ar could be important. We can calculate how much cosmogenic 36Ar should be present, using the Ca contents of the samples (Teirman and Lindstrom, 1997) and the known cosmic-ray exposure age of 11 Ma (e.g., Bogard et al., 1984). Cosmogenic 36Ar is produced at a rate of about 1 x 10^-8 cm^2 STP/Ma/g of Ca (Freundel et al., 1986; Hohenberg et al., 1978). We find that only for samples 9B and 9C is the amount of spallation expected >50% of the uncertainty in the amount of 36Ar, so in most cases it is negligible. For those two samples, however, the predicted amount of cosmogenic 36Ar is slightly greater than the blank-corrected amount of 36Ar we measured (though by <2σ). Hence, for those two samples, we assumed that all the 36Ar is from spallation and have made no further corrections to the 40Ar.

**Table 5. Argon Compositions.**

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>36Ar/36Ar</th>
<th>40Ar/36Ar</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrestrial</td>
<td>0.188</td>
<td>295.5</td>
<td>1</td>
</tr>
<tr>
<td>Mars atmosphere</td>
<td>0.28-0.33</td>
<td>1900</td>
<td>2</td>
</tr>
<tr>
<td>Spallation</td>
<td>1.5</td>
<td>&lt;1</td>
<td>3</td>
</tr>
</tbody>
</table>

References: (1) Ozima and Podosek (1983); (2) Bogard (1997); Bogard and Garrison (1998); (3) Hohenberg et al. (1978).

Another possible source of 36Ar is martian atmosphere. After all, we have shown that there does appear to be martian atmospheric Kr and Xe trapped in the iddingsite. The ratio of 36Ar to 132Xe in the martian atmosphere is now estimated to be ~825 (Bogard and Garrison, 1998), a factor of several higher than suggested by the Viking measurements (e.g., Pepin and Carr, 1992). However, because the Xe/Kr ratio in the iddingsite appears to be fractionated relative to the martian atmosphere by a factor of 3–9, we would expect the Xe/Ar ratio to be fractionated to an even greater extent. For terrestrial sediments that have acquired atmospheric noble gases, the Ar/Kr fractionation is often comparable to the Kr/Xe fractionation (e.g., Table 8.1 of Ozima and Podosek, 1983); so the overall fractionation of the Ar/Xe ratio should be roughly 100. Because there is roughly 8 x 10^-11 cm^3 STP/g of 132Xe, that would mean that we would expect roughly 0.65–6.5 x 10^-9 cm^3 STP/g of 36Ar. Even the upper limit is smaller than the uncertainty in the measured amount of 36Ar for most samples. However, because the 40Ar/36Ar ratio of the martian atmosphere is ~1600 (Garrison and Bogard, 1998), this could account for 1.2–12 x 10^-6 cm^3 STP/g of 40Ar; so it could be the source of much, if not all of the 36Ar in many samples, although there are some samples (9B and 9C) where ages of several hundred million years would still be required.

In Table 4, we have tabulated apparent ages based on the two end-member assumptions that all of the 36Ar is either martian or terrestrial. Although we suspect that the latter is closer to the truth, our conclusions are not sensitive to the choice.

Even if we do not know the exact source of the 36Ar (if the samples were all a mixture of K-derived 40Ar with a component with a uniform 40Ar/36Ar ratio), we would expect a plot such as Fig. 3 to give us a straight line, with the intercept giving the 40Ar/36Ar ratio and the slope giving the 40Ar/K ratio. There is clearly no linear relationship between the two variables.

**Fig. 3. Ratio of 40Ar/36Ar vs. K/36Ar for K-Ar samples (Table 4).** The data have been corrected only for HCl in case the atmospheric portion of the blanks misrepresents actual sample gas (in many samples, there is no 36Ar remaining after the blank correction). If all samples were the same age but contained a common 40Ar/36Ar component, a correlation might be expected, but clearly there is none. This could represent multiple ages, variable loss of radiogenic 40Ar, variable mixing of martian atmospheric 40Ar and blank-dominated 36Ar, or some combination of the three.
correlation. However, if the $^{36}\text{Ar}$ is dominated by blank (which it almost certainly is) and the $^{40}\text{Ar}$ by martian atmosphere, we would not expect a correlation either.  

Interpretation of Ages—We derive apparent ages ranging from near 0 to $\sim 650$ Ma (Table 4, Fig. 2). Taken at face value, this suggests formation or alteration of iddingsite did not occur at a single time for all samples.

The only other chronological information on iddingsite comes from a Rb-Sr study of Shih et al. (1998), who noted that a tie-line between the leachates of two iddingsite separates corresponded to an age of $679 \pm 66$ Ma (2o), remarkably close to the oldest K-Ar age observed here. Because the Rb-Sr system would be expected to be more stable in thermal events, this suggests that the age of $\sim 650$ Ma may represent the formation of the iddingsite, with the younger K-Ar ages representing one or more events more recently. In a transmission electron microscope (TEM) study of Lafayette iddingsite, Vicenzi and Heaney (1999) suggested sequential formation of phases within the iddingsite, with the K-rich material forming last, which is consistent with the apparent young ages. Shih et al. (1999) suggested that disturbed Rb-Sr systematics in the nakhlite Governor Valdares could be the result of iddingsite that formed more recently than $\sim 1300$ Ma ago. Although this is consistent with iddingsite formation 650 Ma ago, they were unable to put an exact date on that event or to demonstrate that it was indeed iddingsite that caused the disturbance.

Because we might expect the heat flow on Mars to be steadily declining, it might be more likely for the liquid water required for iddingsite formation to have been present at, or shortly after, the formation of the rock itself 1300 Ma ago. However, we have no evidence of any iddingsite formation or alteration for the first 650 Ma of the rock’s residence on Mars (from its time of formation 1300 Ma ago until 650 Ma ago). One possibility is that all of the samples have experienced partial loss of radiogenic $^{40}\text{Ar}$, either on Mars or during the experiment.  

Loss on Mars is possible, though by no means inevitable. Fine-grained clay samples on Earth have retained radiogenic Ar for as much as 450 Ma (Dong et al., 1997). Although clays are more susceptible to Ar loss than many other minerals, the fact that Mars is colder than Earth should reduce that Ar loss to some extent. Loss of Ar on Mars would seem to be ruled out by the lack of evidence for substantial Ar loss in the $^{40}\text{Ar}$-$^{39}\text{Ar}$ apparent age spectrum of a whole-rock sample of Lafayette—Podosek (1973) measured apparent ages of 0 ± 200 and 1200 ± 100 Ma in the first 1.6% and next 9.7% of the gas released, respectively, compared to an age of 1330 ± 30 Ma for the remainder of the extractions. However, this raises an interesting question. Podosek (1973) measured $<0.1$ wt% K in his sample. If iddingsite typically contains about 0.5–1.0 wt% K (Table 4) and Lafayette is 3% iddingsite, then the iddingsite should contribute about 0.015–0.03 wt% K to the whole rock, which would be about 15–30% of the total K measured by Podosek (1973); so there should be evidence for the lower iddingsite ages in the age spectrum, unless Podosek’s sample contained <3% iddingsite. One of us (A. H. T.) has looked at many thin sections of Lafayette, and the iddingsite is heterogeneously distributed. For example, a typical thin section might be iddingsite-free in 80% of the thin section but have as much as 10% iddingsite in the remaining areas. Whether or not such heterogeneity extends to the 100 mg scale (the size of the sample used by Podosek, 1973, is unknown), but heterogeneity is a reasonable possibility.  

Loss of radiogenic $^{40}\text{Ar}$ could have occurred in at least two stages of the experiment, during the irradiation and during the preheating after loading the samples into the extraction line. Although this can not be ruled out, we believe this is also unlikely. One of us (D. J. L.) has had experience with microgram-sized clay samples for which TEM evidence suggested peak temperatures during irradiation <150 °C. Furthermore, the fact that the $^{40}\text{Ar}$/$^{36}\text{Ar}$ ratio of the gas released from all the vials is virtually identical (and plausibly just residual atmosphere) suggests that the samples experienced little Ar loss during the irradiation. For example, sample 10.4 released the most radiogenic Ar in the laser extraction. The vial containing sample 10.4 released gas with a $^{40}\text{Ar}$/$^{36}\text{Ar}$ ratio of 928 ± 5.2, which is indistinguishable from either terrestrial atmosphere (929.5) or the average $^{40}\text{Ar}$/$^{36}\text{Ar}$ value of the other vials (903.5 ± 0.7). A 3σ upper limit to the amount of radiogenic $^{40}\text{Ar}$ in the vial still produces an apparent age of only $\sim 750$ Ma. Loss during the preheating of the samples after loading them onto the extraction line is also possible; but if the samples did not degas during the irradiation, we would not expect them to degas overnight at 150 °C. Furthermore, the irradiation and sample preparation of Podosek (1973) would seem to have been at least as susceptible to loss during the experiment.

The other possible scenario for partial loss of radiogenic Ar is during passage through the terrestrial atmosphere. Samples LA8 and LA11 (the parents of samples with numbers beginning with "8" or "11") had no visible fusion crust. Samples from LA10 were taken at least 1 mm from fusion crust; and although LA9 did have fusion crust on it, the samples were taken >1 mm away from the fusion crust. Because all the samples started out as crumbs of 2–3 mm, it remains possible (but unlikely) that all could have been affected by Ar loss during atmospheric entry.

Thus, except for the lack of evidence for low-temperature Ar loss in the whole-rock sample of Podosek (1973), we see no evidence that iddingsite formation was really 1300 Ma ago.

The fact that we get a similar wide range of ages from crumbs LA9 and LA11, which are all iddingsite fragments taken within a few millimeters of one another, may or may not be consistent with varying ages of formation, but it is certainly consistent with varying losses of radiogenic Ar from different types of clay. Some of the clay fraction is fairly coarse and well-crystalline (Fig. 1e, d of Treiman et al., 1993), where clay grains are up to 3–5 or even 10 μm across. However, other areas have very fine-grained clays, within grain sizes of 0.1 or even 0.01 μm (e.g., Figs. 1f and 2a, respectively, of Treiman et al., 1993). Vicenzi and Eiler (1998), using focused ion beam secondary ion mass spectrometry (SIMS), found intricate banding of K content in a region filled with ultra fine-grained phyllosilicate, as well as enrichment in coarser-grained clays oriented perpendicular to banding, and suggested that differential Ar retentivity in the two phases could be the source of the variations in K-Ar we observe. We did not characterize the grain size of the individual fractions studied in the present work.

There were certainly events that led to high temperatures on Mars more recently than 650 Ma ago. For example, although there is controversy surrounding the age of the shergottites (see review by McSween, 1994), they are certainly <650 Ma old. There is also photogeological evidence for very young lava flows on Mars, perhaps <100 Ma old (Hartmann et al., 1999), based on Mars Global Surveyor imaging. Although there is no evidence that the nakhlites have been affected by post-formational heating, there was thermal activity going on on Mars in the last 100–200 Ma, so young
Implications for Martian Hydrology—At whatever time the iddingsite formed, this means that there was liquid water available that recently. Because the nakhlites probably formed within a few hundred meters of the surface (Treiman, 1986; Friedman et al., 1998, 1999), that means there was water that close to the surface when the iddingsite formed. In addition, if the iddingsite trapped atmospheric gases (with or without an intermediate step involving water), then the iddingsite must have formed close enough to the surface that either it or the water that formed it was in contact with the atmosphere, again suggesting that the water was relatively near the surface.

If the iddingsite formed 1300 Ma ago, the water could simply be permafrost that was melted during the magmatic episode that formed the nakhlites. This implies that there is permafrost wherever the nakhlites formed, which is consistent with theories that have a substantial fraction of Mars' water sequestered in permafrost (Clifford, 1993). If, instead, it is water liberated during a later magmatic episode or during a later impact, this implies that liquid water may occasionally be available.

Because most of the photogeologic evidence for liquid water on Mars apparently predates 1300 Ma (Carr, 1996), these results might suggest that even more liquid water might have been available to alter rocks 4 Ga ago. However, there are few signs of low-temperature aqueous alteration in ALH 84001, with the possible (and still controversial) exception of the carbonates. This suggests that some regions have remained dry for long periods of time. For example, the highlands may have remained drier because the depth to permafrost or aquifers was greater (Clifford, 1993).

SUMMARY AND CONCLUSIONS

Our strongest conclusion is that the iddingsite in Lafayette formed on Mars, in agreement with the microstratigraphic arguments of Gooding et al. (1991) and Treiman et al. (1993). A preterrestrial origin of the iddingsite is required both by the many non-zero K-Ar ages and by the presence of Xe that is isotopically distinct from any terrestrial Xe. The Xe is accompanied by Kr, but the Kr and Xe have been fractionated if they are derived from the present martian atmosphere. This is presumably the result of either incorporation via interaction with liquid water (Drake et al., 1994; Bogard and Garrison, 1998) or by adsorption from the martian atmosphere, perhaps accompanied by shock (see also Gilmour et al., 1998, 1999). Although the iddingsite is enriched in Kr and Xe compared to whole-rock analyses, it is not clear whether iddingsite is the dominant carrier of the atmospheric-derived gas (Drake et al., 1994) or merely a minor carrier (Gilmour et al., 1999).

Our 40Ar-39Ar experiment was disappointing, in that it mostly served to confirm that the iddingsite, which contains fine-grained clays, is susceptible to recoil loss of 39Ar during irradiation. Only one sample of five gave a clear signal of radiogenic or extraterrestrial 40Ar, and that was only by 3σ.

Potassium-argon ages of the second set of samples were more successful, ranging from near 0 to 670 ± 91 Ma. It is not clear whether any or all of the ages represent iddingsite formation, as opposed to later alteration. The fact that a Rb-Sr experiment (Shih et al., 1998) gave an apparent age for iddingsite of 679 ± 66 Ma (2σ) suggests that perhaps formation of iddingsite occurred (or began) ~650 Ma ago and that some samples either formed, or were thermally altered, later. The ages could be even younger than 650 Ma, if the samples have incorporated martian atmospheric 40Ar.

This means that liquid water was certainly present on Mars in the last 1300 Ma (the formation age of Lafayette), and probably within the last 650 Ma.

Acknowledgments—This manuscript was improved substantively as the result of thorough and constructive reviews by J. Gilmour and U. Ott. We also thank S. Baldwin, D. Bogard, M. Drake, and D. Krige for helpful conversations, and Associate Editor L. Schultz for his efforts in handling this paper. This work was supported by NASA grants NAGS-4767, NAGS-8270, and RTOP 344-31-10-17.

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