^{39}Ar-^{40}Ar AGE OF ALH84001.

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Background: Martian meteorite ALH84001 currently presents the only opportunity to directly study material that dates from the earliest history of Mars. Among the SNC meteorites, the nakhlites and Chassigny give radiometric ages of ~1.3 Ga, and several shergottites give radiometric ages much younger than this (1). Only ALH84001 gives Rb-Sr and Sm-Nd isochron ages near 4.6 Ga, which implies that it initially formed very early in Martian history (2). A somewhat younger age of 3.92 Ga has been reported for ALH84001 using the ^{39}Ar-^{40}Ar isotopic chronometer (3, 4). The feldspar in ALH84001 has been shock melted, and Scott et al (5) suggest that "plagioclase, silica, and the carbonate in ALH84001 were probably all melted and partly mobilized during a single shock event of ~50 GPa that also formed the brecciated zones". Experiments with eucrites and other shocked meteorites suggest that it is possible to reset the K-Ar chronometer without resetting the Rb-Sr or Sm-Nd chronometers (6). Thus, precise definition of the ^{39}Ar-^{40}Ar age of ALH84001 is of importance because it defines the time of plagioclase melting by shock impact on Mars and may define the carbonate formation time as well.

New ^{39}Ar-^{40}Ar Results: We made high precision ^{39}Ar-^{40}Ar measurements of a 90 mg whole rock sample of ALH84001 (Fig. 1; "rectangles" are ages, continuous line is K/Ca). Our results are generally similar to Ar-Ar results previously reported (3, 4), and we concur with these authors' conclusion that the ^{39}Ar-^{40}Ar age of this meteorite is much older than the determined isotopic chronologies of other martian meteorites. However, the Ar release profile of ALH84001 is complex, and the meteorite contains trapped Ar, which necessitates an uncertain correction to the radiogenic ^{40}Ar and thus to the derived age. With these considerations, we believe that the time of the shock event that melted feldspar in ALH84001 is poorly constrained within the time period of ~3.8-4.3 Ga, but we suggest that the actual time may be ~4.2 Ga. These conclusions differ from those of (3, 4).

Simple Age Interpretation: Fig. 1 indicates that Ar is released from two different phases, one with K/Ca ratios of ~0.18-0.12 (plagioclase) and one with ratios of <0.02 (pyroxene). The sudden decrease in ages over ~78-93% of the ^{39}Ar release coincides with the onset of Ar degassing from pyroxene and is strongly suggestive of gain of ^{39}Ar by recoil redistribution during the neutron irradiation, a phenomenon commonly observed. This redistributed ^{39}Ar most likely derived from grain surfaces of feldspar, as the recoil distance of ^{39}Ar is only ~0.16 μm. An expected higher apparent age in the early extractions due to recoil loss of ^{39}Ar is masked by recent diffusive loss of radiogenic Ar from grain surfaces. The slightly lower K/Ca ratios in the early extractions may reflect terrestrial weathering, but the sharply lower ratio at ~10% ^{39}Ar release is probably due to carbonate decomposition. The sharp increase in ages for the last two extractions (5.3-5.8 Ga at >98% ^{39}Ar release) is not likely due to system blanks nor to ^{39}Ar recoil. The reasonable assumption is that the ages at <12% ^{39}Ar release and ~78-92% ^{39}Ar release have been modified by ^{39}Ar recoil redistribution and that the apparent "plateau" age of 4.29 ±0.06 Ga (~12-78% ^{39}Ar) is a measure of the degassing age. This approach differs, however, from that of (3, 4), who implicitly assume that the recoil ^{39}Ar derives from the interior of the high-K grains and prefer to sum all of the Ar-Ar ages above ~12% ^{39}Ar release to derive a somewhat lower age of ~4.13 Ga. These ages, however, do not consider the effects of trapped Ar in ALH84001 and thus may be only upper limits to the shock degassing time, as we next discuss.

Derivation of Cosmogenic and Trapped Ar: Ar isotopes in irradiated ALH84001 have several sources. Part of the ^{36}Ar and ^{38}Ar are produced from cosmic rays and correlate in their release with ^{37}Ar, which is produced in the reactor from Ca, the major target for production of cosmogenic ^{36,38}Ar. At low and intermediate extraction temperatures, ^{38}Ar produced in the reactor from ^{37}Cl complicates the interpretation of ^{38}Ar components. However, for the last three extractions, which released relatively large amounts of ^{36,38}Ar, the ^{36}Ar/^{38}Ar ratio is constant at 0.65, which is the expected value for pure cosmogenic Ar. For these same extractions, the ^{36}Ar/^{37}Ar ratio is nearly constant at 1.2 x10^{-3}, but it is considerably higher at lower extraction temperatures due to the presence of trapped Ar components. Thus, we used the concentration of ^{37}Ar released at each temperature and the ^{36}Ar/^{37}Ar ratio of 1.26 x10^{-3} to correct the total ^{36}Ar for cosmogenic ^{36}Ar (3.6 x10^{-9} cm^3/g). The remaining ^{36}Ar (3.8 x10^{-9} cm^3/g) is assumed to be a trapped component, either terrestrial or Martian in origin, and presumably includes some amount of ^{40}Ar.

A plot of ^{36}Ar/^{40}Ar ratios versus ^{39}Ar-^{40}Ar ages (Fig. 2) gives some insight into the nature of the trapped ^{36}Ar/^{40}Ar ratio in ALH84001. Open symbols represent the plateau extractions; solid symbols labeled with temperatures are all other extractions. Except for the 1200-1550^{0}C extractions, uncertainties in ^{36}Ar/^{40}Ar are smaller than the symbol. The two arrows indicate expected mixing trends between a sample with an Ar-Ar age of 4.0 Ga and either trapped terrestrial air or Martian atmosphere. The lower temperature extractions (300-450^{0}C) plot at lower ages because of recent diffusive loss of Ar (see Fig. 1). They do not define the nature of the trapped component, which at these lower temperatures was likely adsorbed terrestrial air. The 900-1075^{0}C extractions plot at slightly lower ages because of ^{39}Ar recoil (Fig. 1), but they also released significant trapped ^{36}Ar. For the 900-1075^{0}C extractions, this trapped ^{36}Ar could reasonably be terrestrial, but could not be Martian atmosphere, as this would require absurdly large ages in order for these data to plot on the 4.0 Ga/Martian mixing line. Because the 900-1075^{0}C extractions represent early release of Ar from orthopyroxene, the presence of larger amounts of terrestrial Ar (compared to temperatures of ~500-850^{0}C) might represent weathered surfaces of pyroxene grains. The 1300^0 and 1550^{0}C extractions appear to suggest a trapped Martian component, but uncertainties in these data are larger. These and other extractions may also contain relic radiogenic ^{40}Ar (without ^{36}Ar) not entirely degassed by the shock event.

Effects of Trapped Ar on Age: Knowing the ^{40}Ar/^{36}Ar ratio of the trapped component in ALH84001 is critical, as the trapped ^{40}Ar must be subtracted from the total ^{40}Ar in order to derive a corrected ^{39}Ar-^{40}Ar age. If we correct the ^{40}Ar data in Fig. 1 using the reasonable assumption that all trapped ^{36}Ar is terrestrial air with ^{40}Ar/^{36}Ar =295, the ^{39}Ar-^{40}Ar age of the "plateau" decreases from 4.29 ±0.06 Ga to 4.18 ±0.12 Ga and the age summed over ~12-100% ^{39}Ar release decreases from 4.19 Ga to 3.87 Ga. The larger decrease for the ~12-100% age is caused by larger amounts of trapped ^{36}Ar residing in those same extractions that exhibit the greatest ^{39}Ar recoil effect (~78-93% ^{39}Ar release). If instead, we assume that the trapped Ar has a ^{40}Ar/^{36}Ar ratio of 2400 characteristic of the Martian atmosphere, the trapped ^{40}Ar is larger than the total ^{40}Ar for many temperature extractions and the ages become negative. This fact and Fig. 1 indicate that little, if any of the trapped ^{36}Ar in our sample of ALH84001 derived from the Martian atmosphere. Even with a correction for Martian atmospheric, however, a quasi-plateau remains in the ^{39}Ar-^{40}Ar age spectrum, and two extractions of this "plateau" give the same age of 3.81 Ga. This is an absolute minimum for the shock degassing time of ALH84001. Further, all of the trapped Ar in ALH84001 need not be terrestrial or Martian atmosphere. Some Martian meteorites contain a trapped ^{36}Ar component deriving from the Martian mantle and having an unknown ^{40}Ar/^{36}Ar ratio (7). If this mantle ^{40}Ar/^{36}Ar ratio is less than the terrestrial value of 295, the corrections to the ages shown in Fig. 1 would be less and the "plateau" age could lie in the range of 4.18-4.29 Ga. Thus, we conclude that the limiting range in Ar-Ar ages for ALH84001 is 3.8-4.3 Ga, with a fair probability of the age being ~4.2 Ga.

References: (1) H. McSween, *Meteoritics 29*, 757, 1994; (2) L. Nyquist et al., *LPS XXVI*, 1065, 1995; (3) R. Ash et al., *Nature 380*, 57, 1996; (4) G. Turner et al., *GCA 61*, 1997; (5) E. Scott et al., *LPS XXVII*, 1997; (6) D. Bogard, *Meteoritics 30*, 244, 1995; (7) D. Bogard, *JGR-Planets 102*, 1653, 1997.