Rb-Sr FORMATION AGE OF ALH 84001 CARBONATES. L. E. Borg[1], L. E. Nyquist[1], C. -Y. Shih[2], H. Wiesmann[2], Y. Reese[2], and J. N. Connelly[3] [1]SN2/NASA Johnson Space Center, Houston TX 77058, [2]Code C23, Lockheed Martin, 2400 NASA Road 1, Houston TX 77258, [3]Dept. Geol. Sci., University of Texas Austin 78712.

Synopsis: Our preferred age for the formation of carbonates in the martian meteorite ALH84001 is 3.90±0.04 Ga for $\lambda(^{87}Rb)$ = 0.01402 Ga^{-1}, or 3.85±0.04 Ga for $\lambda(^{87}Rb)$ = 0.0142 Ga^{-1}. This age is determined by a three point Rb-Sr isochron defined by leachates of high-graded carbonate-rich material. Major cation and especially phosphorous analyses of the leachates permit contributions from igneous whitlockite to be recognized for low-acidity leachates, and the corresponding data are omitted from the isochron. Data for the two highest acidity leachates plot close to the preferred isochron, but are omitted because we believe they contain contributions leached from the pyroxene substrate on which most of the carbonates are found. Nevertheless, the isochron age for all five highest-acidity leachates is 3.94±0.04 Ga, and is within error of the age obtained for the more restricted data set. All leachates used to define the isochron have major cation compositions that are similar to those obtained by microprobe analyses of the carbonate rosettes and are consistent with progressive digestion of the carbonates according to their composition.

The age thus obtained for the carbonates is about 600 Ma younger than the crystallization age of ALH84001 determined by Sm-Nd analyses [1-2], but is within error limits of the age of impact metamorphism inferred from the Rb-Sr and Ar-Ar systematics of silicates which yield ages of 3.85±0.05 Ga [3] and 4.05-3.80 Ga [4] to 4.3-3.8 Ga [5], respectively. Similarities between the carbonate crystallization age and the age of impact metamorphism as determined by Ar-Ar and Rb-Sr, suggests that the carbonate formation is impact-related. Nevertheless, both high and low temperature scenarios for the origin of the carbonates are possible.

Introduction: The origin of carbonate minerals in ALH84001 has received much attention since [6] reported that the carbonates possibly contain evidence for martian microbial life. Several models have been proposed for the origin of the carbonates in ALH84001 including: (1) impact metasomatism [7], (2) impact melting of pre-existing carbonates [8], (3) evaporation of surficial fluids at low temperature [9-10], and (4) low temperature alteration by hydrothermal fluids [11]. The time of carbonate formation has important implications for Martian planetary evolution as well as its possible biological evolution. An old age would be consistent with a wetter, warmer early Mars and thus with models of carbonate formation involving aqueous activity. An intermediate age, combined with clear evidence of formation via aqueous processes, would gain special significance because it would extend the time period during which water might have been relatively abundant on the Martian surface and available to support life. Carbonate formation via impact metasomatism or other high temperature phenomena could be consistent with virtually any age, but also might be expected to be more prevalent at early times. We have approached the difficult problem of determining the age of ALH84001 carbonates by isotopic analyses of a programmed sequence of carbonate-rich leachates.

Procedure: A 1 gram sample of ALH84001 was gently crushed and sieved at 100-200 and 200-300 mesh. Grains containing carbonates were hand-picked so that carbonate abundances in the high-graded sample approached 10%. A series of progressively more reactive reagents were used to leach this high-graded sample; these reagents were predetermined by experimentation with terrestrial carbonates. Small aliquots of each leachate were analyzed for Ca, Mg, Fe, K, P, Sr, Nd, and Pb by isotope dilution and atomic absorption. The remaining aliquots were spiked for Rb-Sr, Sm-Nd, and U-Pb and put through standard cation chromatography separation procedures. We report results of the Rb-Sr analyses of the leachates, the other isotopic analyses are in progress.

Results: The major-element analyses of the leachates are presented in Figure 1. The first leachates have compositions that are unlike any of the carbonates analyzed in ALH84001 (e.g. [12]). S1 and S2 (the first and second leachates) contain no Fe or P and lie on the magnesite-calcite join. The leaching agents used for S1 and S2 were extremely weak and are likely to have primarily removed surface coatings. The S3 leachate has significantly higher abundances of Ca and P. Assuming Sr contents in ALH84001 whitlockite are similar to those estimated from whole rock leachates of the basaltic shergottite QUE94201 from [13], mass balance calculations based on P abundances suggest that roughly 5% of the Sr in this fraction is derived from whitlockite. The S4 leachate has a major element composition that is similar to the bulk carbonate composition estimated by [13], but also has a significant amount of P. The maximum Sr contribution from whitlockite to the S4 leachate can be calculated assuming that 100% of the Sr in the S3 leachate is derived from whitlockite. In this case ~30% of the Sr in the S4 leachate would be of igneous origin. This is obviously an extreme upper limit; mass balance calculations similar to those made for S3 suggest that S4 contains ~1% whitlockite-derived Sr. The S5-S8 leachates have no measurable P. That the leachates would become progressively more Mg-rich with increasing acidity of the leaching reagent was expected from experiments with terrestrial carbonates in which dissolution of calcite, then siderite, and then magnesite was observed.

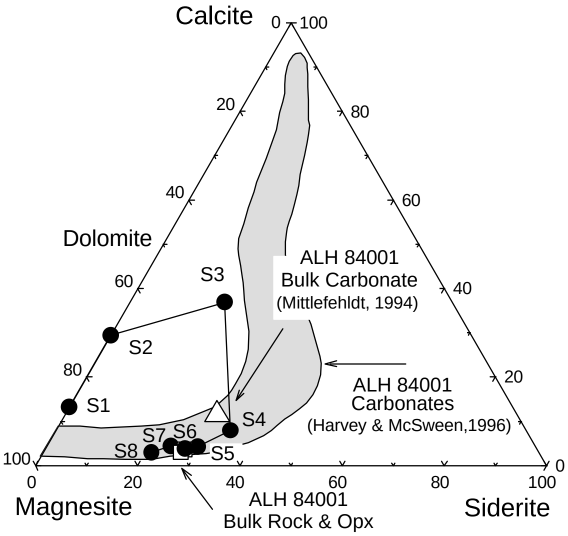

Figure 1. Ternary diagram illustrating compositions of leachates from ALH84001. Note compositional similarities between carbonate compositions (shaded area) from [7] and S4-S8 leachates. Also note compositional differences between the carbonate compositions and S1-S3 leachates.

A Rb-Sr isochron diagram of our leachate data is presented in Figure 2. The age of 3.90±0.04 Ga is defined by our best leachates (S4-S6). Blank contributions to Sr in all of the leachates was less than 0.2%, with the exception of S8 (2.5%), which contained less than 1 ng of Sr. S4 lies on the isochron, suggesting that the whitlockite contribution to its Rb-Sr systematics was indeed small. Those leachates having compositions unlike the carbonates (S1-S2), a high P/Sr ratio (S3), or a very low abundance of Sr (S8) lie off the best isochron. The S7 and S8 leachates appear to lie on a mixing line between the S6 leachate and our previous pyroxene analyses [1], suggesting that they contain a contribution from pyroxene leached by the strong reagents used. Furthermore, visual examination of a control suite of carbonates indicated that all were dissolved by the 6th step. The calculated age range for two (S4,S5; 3.89 Ga), three (S4-S6; 3.90±0.04 Ga), four (S4-S7; 3.93±0.04 Ga), or five (S4-S8; 3.94±0.04 Ga) data points is ~3.9-4.0 Ga. Our preferred age of 3.90±0.04 Ga is that determined by S4-S6.

Discussion: The age of carbonate formation in ALH84001 is substantially younger than the crystallization age of 4.50±0.13 Ga derived from Sm-Nd analyses of silicates and phosphates [1-2], but is similar to the age of impact metamorphism determined by Ar-Ar and Rb-Sr analyses of silicate phases [3-4]. This suggests a relationship between the impact event and carbonate formation. Scenarios involving direct formation of the carbonates via impact metasomatism [6] or impact melting of pre-existing carbonates [8] are clearly compatible with our data. However, another possibility is that ice buried beneath the Martian surface was melted by heat from the impact to produce water that percolated into the newly formed basin and precipitated the carbonates, consistent with the models of [8-9]. Alternatively, if Mars were warmer and wetter ~3.9 Ga ago, a crater lake may have persisted for a time interval that was short compared to the uncertainties of the radiometric ages. Thus, the carbonates could have been precipitated at relatively low temperatures and still have crystallization ages that are indistinguishable from the age of impact metamorphism.

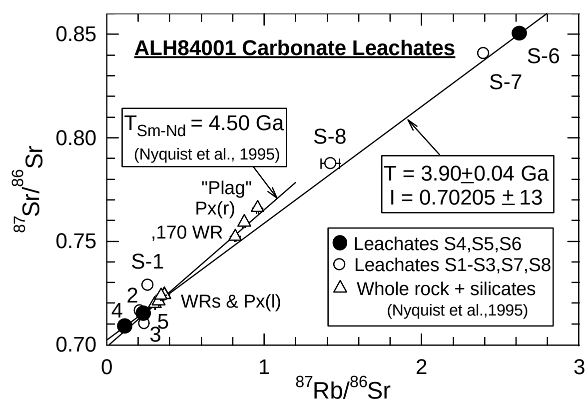

Figure 2. Rb-Sr isochron plot of leachates from ALH84001. Our preferred age of 3.90±0.04 Ga is defined by S4-S6; leachates S4-S8 define an age of 3.94±0.04 Ga. Leachates used to define the isochrons have major cation compositions similar to those of the carbonates (see Fig. 1).

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