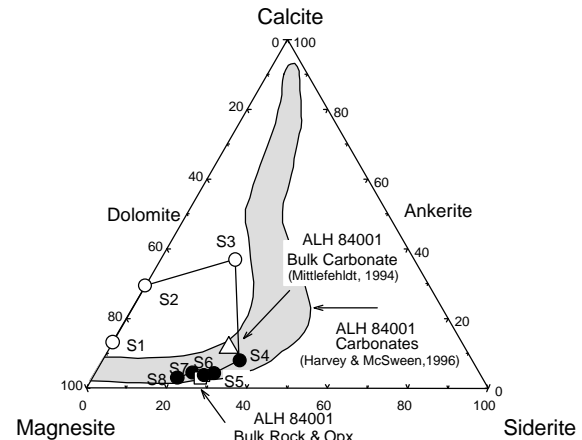


**Pb-Pb AGE OF THE CARBONATES IN THE MARTIAN METEORITE ALH84001.** L. E. Borg<sup>1</sup>, J. N. Connelly<sup>2</sup>, L. E. Nyquist<sup>1</sup>, and C. -Y. Shih<sup>3</sup> <sup>1</sup>SN2/NASA Johnson Space Center Houston, TX 77058, <sup>2</sup>Department of Geological Sciences, The University of Texas, Austin TX 78713, <sup>3</sup>Code C23, Lockheed Martin, 2400 NASA Road 1, Houston, TX 77258.

**Introduction:** The origin of the carbonates in ALH84001 has received considerable attention since [1] reported that they contain possible evidence for Martian microbial life. The potential for the existence of life in the carbonates is dependent on their mechanism of formation, which in turn can be constrained by their age. A variety of mechanisms for carbonate production have been proposed including: (1) impact driven metasomatism [2], (2) impact melting of pre-existing carbonates [3], (3) evaporation of surficial fluids [4-5], and (4) precipitation from hydrothermal fluids [6]. An old age is consistent with formation in relatively wet and warm conditions present on early Mars and thus with models of carbonate formation involving aqueous activity. However, if the carbonates are produced by impact metasomatism, the carbonate formation age would also be expected to be old and furthermore to be concordant with the Ar outgassing age of ~4.0 Ga [7-8]. A young age would be more consistent with carbonate formation by either a small impact (that did not reset the Ar isotopic systematics of ALH84001) or with hydrothermal activity associated with recent volcanism.

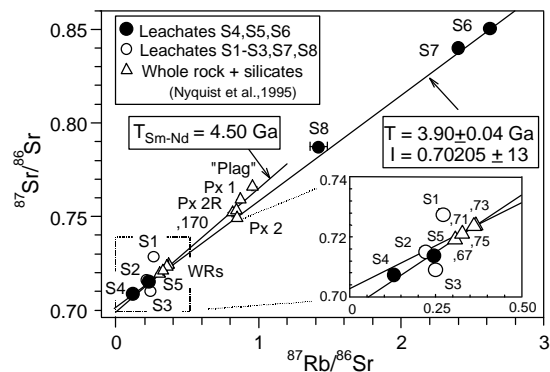
The age of the carbonates has been previously reported to be  $1.39 \pm 0.10$  Ga [9] and  $3.90 \pm 0.04$  Ga [10]. The younger age is based on Rb-Sr analysis of shocked-melted feldspathic glass and carbonate, and the assumption that these two phases are in isotopic equilibrium. Equilibrium between feldspathic glass and carbonate is supported by textural observations that the carbonates selectively replace the glass [e.g.11]. However, the carbonates are Fe and Mg-rich [e.g.12], so that most of their major cations must be derived from a source other than plagioclase glass [Fig. 1]. As a result, isotopic equilibrium between carbonate and glass is not assured. Our older age of  $3.90 \pm 0.04$  Ga was determined through Rb-Sr analysis of several leachates containing dissolved carbonate from ALH84001 [Fig.2]. Although the leachates have major element compositions similar to the carbonates and the Rb-Sr isochron is defined by 3-5 data points we have sought to confirm the Rb-Sr age through Pb-Pb analysis of the same leachate fractions.

**Methods:** A 1 gram chip of ALH84001,170 was gently crushed and sieved at 150  $\mu$ m. Composite grains containing carbonate minerals were hand-picked, yielding a mineral separate that was ~90% orthopyroxene and ~10% carbonate; i.e. a sample in which carbonate was high-graded by a factor of 10 or more. This high-graded fraction was then leached in a series of progressively stronger reagents. The leaching procedure was derived from experiments conducted on mixtures of terrestrial calcite, magnesite, siderite, and synthetic whitlockite. The goal of the leaching procedure was to: (1) separate soluble carbonates from insoluble silicates, (2) separate the most easily soluble igneous components, such as whitlockite, from secondary carbonate components, and (3) separate carbonate components of various compositions. Splits from each ALH84001 leachate were analyzed for Ca, Mg, Fe (by isotope dilution) and P (by colorimetry). The results are presented in Fig. [1]. Rb-Sr and U-Pb were separated from



**Figure 1.** Ternary diagram illustrating the compositions of ALH84001 leachates.

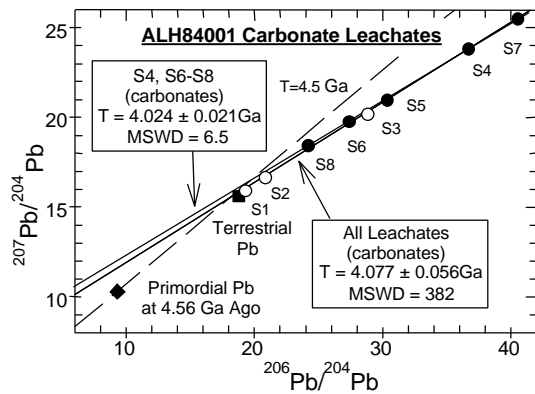
the remaining leachate fractions using standard cation chromatographic techniques and analyzed by thermal ionization mass spectrometry at the Johnson Space Center and The University of Texas at Austin, respectively. Laboratory Pb blank contributions are estimated to range from 0.1% to 3.8% and are less than 1.5% for all leachates except S1 and S8.



**Figure 2.** Rb-Sr isochron of ALH84001 from [10]. Leachates S4-S6 define an age of  $3.90 \pm 0.04$  Ga, whereas leachates S4-S8 define an age of  $3.94 \pm 0.04$  Ga.

**Results:** The Pb-Pb isochron is presented in Fig. 3. The  $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$  isochron defines an age of  $4.024 \pm 0.021$  Ga using the S4, S6-S8 leachates. An age of  $4.077 \pm 0.056$  Ga is defined on the same isochron diagram using all of the leachates. Although the age calculated using just the S4, S6-S8 leachates are similar to those calculated using all of the leachates, the goodness of isochron fit as measured by the MSWD varies significantly. For example, an MSWD of 6.5 is calculated from the S4, S6-S8 leachates, whereas an MSWD of 382 is calculated from all of the leachates. This suggests that the data for the S1-S3, and S5 leachates are not within analytical uncertainty of the isochron. The S1-S3 leachates

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**Figure 3.** Pb-Pb isochron of ALH84001 leachates.

seem to fall off both the best Pb-Pb isochron [Fig. 3] and the Rb-Sr isochron [Fig. 2]. The isotopic composition of average terrestrial Pb is also plotted on Fig. 3. It is apparent that the S1-S3 and S5 leachates all fall towards terrestrial Pb to the right of the isochron defined by the remaining samples. It is therefore likely that these fractions contain a significant component of terrestrial Pb. Terrestrial Pb contamination could have occurred during residence of the meteorite in Antarctica or during sample preparation and chemical separation in the laboratory. The concentration of Pb was measured in all leaching reagents and isotopic tracers and found to contribute <2 pg Pb to individual leachates. Chemical separation blanks are routinely measured to be ~1 pg of Pb. Blank corrections of 3 pg were made to all of the leachates in order to account for the laboratory contribution of terrestrial Pb in the leachates. It is therefore likely that the terrestrial Pb observed in the S1-S3 and S5 leachates is derived from residence in Antarctica.

The presence of Antarctic Pb in the S1-S3 leachates is not unexpected given the relative weakness of these leaching reagents and the profusion of Pb contamination in some Antarctic meteorites [13]. Explaining terrestrial Pb contamination in S5 is more difficult because S4 lies on the Pb-Pb isochron. The S4 leachate may lie on the isochron because the large amount of carbonate dissolved in this fraction dominates the Pb isotopic composition of the leachate. In contrast, the S5 leachate contains a much smaller amount of carbonate, and is thus more susceptible to Pb contamination. Leachates S7 and S8 were obtained with the strongest reagents and also appear to lie on the 4.02 Ga isochron indicating that most of the terrestrial components have been leached from the sample by this stage. This suggests that a minimal amount of Pb was leached from the silicates by these strong reagents.

The Pb-Pb age is in good agreement with our previous Rb-Sr age [10]. However the ages are not concordant and differ by about 60 Ma. This discrepancy is difficult to explain since both the Pb-Pb and Rb-Sr isochrons appear to be very robust. One possibility is that the blank contributions are slightly different than what we measured in the laboratory and that either the Rb-Sr or Pb-Pb age needs to be adjusted slightly. Nevertheless, the overall agreement between the two systems is remarkable given the fact that we are analyzing leachates and not physical mineral fractions. Our preferred formation age of the carbonates is around 3.95 Ga.

**Age constraints on carbonate formation:** The crystallization age of the meteorite has been interpreted to be  $4.50 \pm 0.13$  Ga [14] making the carbonate about 500 to 600 Ma younger than the silicates. The clearly resolved difference between the age of silicate crystallization and carbonate precipitation is consistent with formation of the carbonate by a secondary alteration process around 3.95 Ga. During the period in which the carbonates formed, Mars is argued to have been both relatively wet and warm [e.g. 15]. The primary evidence for these conditions on Mars at this time comes from the presence of valley networks, arguably of fluvial origin, on ancient Noachian age terrain. The end of the Noachian has been estimated to have occurred at 3.5 to 3.8 Ga, based on various cratering models [16-17]. Thus, the carbonates pre-date estimates of the time of transition from relatively warm and wet to cold and dry surface conditions by 100 to 400 Ma. Since liquid water is a prerequisite for life as we know it, the likely presence of water on the Martian surface at the time of carbonate formation is consistent with the hypothesis that relicts of ancient life are preserved in the carbonates of ALH84001.

The Ar-Ar ages determined on ALH84001 whole rocks (3.80-4.05 Ga [7] to 4.0-4.3 Ga [8]) are within error of the Rb-Sr and Pb-Pb ages of the carbonates. These observations are consistent with models of carbonate formation by impact processes [e.g. 2-3]. It is important to point out, however, that there is a significant amount of time represented in the analytical uncertainties of the Ar-Ar, Pb-Pb, and Rb-Sr ages. Thus, the carbonate formation age and the age of the impact event might be indistinguishable by the various dating techniques and yet be separated by a large amount of time.

The apparent concordance between the Ar-Ar age of the bulk meteorite and the Rb-Sr and Pb-Pb ages of the carbonates is suggestive of a relationship between impact processes and carbonate formation. A direct causal relationship between impact and carbonate formation would not support the hypothesis that life existed in Martian water and was entrained in carbonate precipitated at low temperature. However, carbonate precipitation at low temperature might be indirectly impact-related. For example, an impact could shock the host rock resetting the Ar-Ar age, melting near surface ice, and/or creating a basin to collect water for the precipitation of the carbonates. Impact release of water from the frozen subsurface could also facilitate rock/water interactions producing a fluid that contained high concentrations of Ca, Fe, and Mg with which to form the carbonates.

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