CAN CARBONATES BE DATED USING K-AR TECHNIQUES?

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Abstract: To determine the feasibility of using the potassium-argon system to date carbonates, we analyzed several carbonates, using an electron microprobe and noble gas mass spectrometer. Although this study analyzed only a limited range of carbonates, the early results are not promising. Electron microprobe analysis gave K_20 results of <0.01 wt% except for one analysis of a sample with an inclusion. Mass spectrometer analysis of fresh water bivalves (50-75Ma old) gave predominantly atmospheric $^{40}Ar/^{36}Ar$ ratios with 3 σ upper limits of 10ppm and 50ppm of potassium. A 946Ma old ankerite sample from a pegmatitic vein outgassed large amounts of Ar which corresponded to 1.5 wt % potassium. It is believed this was due to K-rich inclusions which may or may not be of the same age as the carbonate.

Introduction: When Allan Hills 84001 was first discovered to be a Martian meteorite [1] one of the distinct things about it was the abundance of carbonates. Early attempts to determine the age of Allan Hills 84001 carbonates [2, 3] were inconclusive [4]. Dating the carbonate formation would provide important clues to the history of Mars. We were unaware of any previous attempts to date carbonates using noble gas methods so a feasibility study was undertaken using terrestrial carbonates. The goal of this experiment was to use noble gas analyses to look for radiogenic argon and electron microprobe analyses to look for potassium. The ultimate goal was to develop methods of dating the carbonates in Allan Hills 84001, with possible terrestrial applications as well.

Experimental: We obtained four terrestrial carbonates with ages, dated by other methods, of 54.4Ma, 66Ma, 75Ma and 946Ma. The three younger carbonates, 31-91, 20-92, 18-93, are all fresh-water bivalve shells (*Unionidae*). They are pure aragonite and therefore have not been altered. 31-91 is early Eocene from the Bighorn Basin, north of Cody Wyoming, with an age of 54.4 Ma (meter level 1760m in Fig. 6 of [5]). 20-92 is Maastrichtian, just below the K-T boundary from north of Jordan, Montana, with an age of 66 Ma (from section B on p. 295 of [6]). 18-93 is Campanian, Dinosaur Park formation, extreme south-east corner of Alberta with an age of approximately 75 Ma (from 36 m in Fig. A5, ref [7]). The older carbonate, N6 from Richmond mine [8], is from a pegmatitic, ankerite-dominant, vein associated with the Coeur d'Alene Mineralization. The old Richmond Mine is about 14 miles SE of Mullan Idaho, 5 miles SW of Saltese, ID and about 1/2 mile west of Silver Lake, ID. The age of this sample is 946±7 Ma .

Samples were step heated in a VG 5400 mass spectrometer to search for radiogenic ^{40}Ar. Electron microprobe analyses were performed on polished sections to determine the abundance and distribution of potassium. The electron microprobe was a Cameca SX-50 with a detection limit of ~0.01 wt.% K_2O [4].

Results: Electron microprobe analyses showed that the carbonates contained very little potassium (see table 1). The younger carbonates were pure calcium carbonate consistent with aragonite and had less than 0.01 wt % K_2O. The N6 carbonate also showed less than 0.01 wt % K_2O except for one analysis, a K-rich silicate inclusion, which is probably orthoclase. The grain also has a rim of Ca-carbonate. The ratio of Mg/Fe=4 corresponds to an ankerite composition [9].

Two younger carbonates, 31-91 and 20-92, released $6.3x10^{-8}$ and $2.3x10^{-7}$ cm^3STP/gm of ^{40}Ar (see table 2), but the argon was predominantly atmospheric. Blank corrected $^{40}Ar/^{36}Ar$ ratios in general were air or below. For both samples the average $^{40}Ar/^{36}Ar$ ratios are slightly below 295, which could be a result of under-correction for ^{36}Ar. Due to high pressures resulting from CO_2 release, an increase in hydrogen pressures could increase $H^{35}Cl$ and give ^{36}Ar numbers that are too high. Three sigma corresponds to 10 ppm and 50ppm, respectively, of potassium. In the absence of evidence for radiogenic $^{40}Ar^*$, we consider these upper limits.

The older carbonate, N6, outgassed a large amount of ^{40}Ar, $7.3x10^{-5}$ cm^3STP/gm. This corresponds to 1.56 wt % of potassium based upon an age of 946Ma. This was significantly more than was expected. If the K-rich inclusion is orthoclase, then it will have about 16 wt% K_2O, which indicates the orthoclase is approximately 10 wt% of the noble gas sample. Some inclusions could be seen under microscope, but 10 wt% seems high. It is possible that the inclusions are heterogeneously distributed and were internal to the noble gas sample. It is also possible that the inclusions are older than the 946Ma used for data analysis with a corresponding increase in the ^{40}Ar.

Table 1: Electron probe data on carbonates			
Sample	20-92	18-93	N6
Age	66Ma	75Ma	946Ma
MgO	0.00	<.01	16.98
Na_2O	0.22	0.25	0.02
CaO	53.60	53.38	28.99
FeO	0.02	0.02	6.92
SrO	0.00	0.00	0.00
Al_2O_3	0.18	0.08	0.24
K_20	<.01	<.01	<.01
MnO	0.12	0.06	0.16
SiO_2	<.01	<.01	<.01
SO_2	0.05	0.05	<.01
TiO_2	0.07	0.10	0.07
P_2O_5	0.03	0.02	0.02
CO_2	42.72	42.42	46.04
Total	97.00	96.37	99.43

Table 2: Noble gas data on carbonates			
Sample	31-91	20-92	N6
Age	54.4Ma	66Ma	946Ma
^{40}Ar cm^3STP/gm	$6.3x10^{-8}$	$2.3x10^{-7}$	$7.3x10^{-5}$
$^{40}Ar/^{36}Ar$	284	290	25000
[K]*	<10ppm	<50ppm	1.56wt%

* Based on age and amount of radiogenic ^{40}Ar*

Conclusions:

- The two fresh water bivalves analyzed with the mass spectrometer contained little or no potassium with 3 σ upper limits of 10ppm and 50ppm. Biogenic carbonates might be expected to be of high purity. There was insufficient potassium to allow age determinations by potassium-argon dating.
- The vein carbonate has potassium in amounts large enough to allow potassium-argon dating, but the potassium primarily comes from inclusions, which may or may not be of the same age as the carbonates of interest.
- Although a limited range of carbonates has been analyzed the early results are not promising. The original goal of dating Allan Hills 84001 carbonates is no longer critical since less ambiguous (although still preliminary) results have been obtained by other methods [10].

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