EXAMINATION OF EFFECTS OF SHOCK AND WEATHERING FOR THE ANTARCTIC L6 CHONDRITES, YAMATO-74190 AND ALLAN HILLS-769, BY THE Rb-Sr METHOD

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Abstract: Possible weathering effect on the Rb-Sr system has been examined for the Allan Hills-769 chondrite (L6) by leaching experiments. The results of measurement of leachability of K, Rb and Sr with 1 N-HCl in the weathered and fresh specimens of the meteorite which had no fusion crust suggest that the weathering effect in the antarctic ice was limited to the surface of the grains of meteorite regarding the Rb-Sr system.

The results of the Rb-Sr isotopic measurement of the Yamato-74190 chondrite (L6) suggest that moderate impact events were responsible for the observed Rb-Sr isotopic disturbance. Because majority of Rb-Sr data of the mineral separates are grossly correlated for ~4.5 b.y. isochron, the Rb-Sr system of this meteorite appears to have retained the nature of the early thermal metamorphism much better than the K-Ar system which shows youngest age of ~0.36 b.y. (KANEOKA *et al.*: Mem. Natl Inst. Polar Res., Spec. Issue, **12**, 186, 1979).

1. Introduction

Recent space explorations for the terrestrial planets suggest that impact cratering process is an important factor in the evolution of planetary surface. From examinations of meteoritic and lunar materials, it was also shown that most extraterrestrial materials had been subjected to repeated impacts since formation of the parent bodies 4.6 b.y. ago. Chemical and isotopic information recorded in these materials has been considered to provide us with invaluable knowledge for gaining access to the origin and evolution of the planetary materials.

In this context, the olivine hypersthene chondrites may be one of the typical meteoritic materials to understand chemical and isotopic characteristics for shock brecciation events. In order to clarify the impact evolution history of this meteorite group, we have undertaken a joint Rb-Sr and Sm-Nd isotopic study for the Antarctic L chondrite, Yamato-74190 (L6).

As demonstrated by the studies on the Pasamonte and Stannern achondrites (UNRUH *et al.*, 1977; LUGMAIR and SCHEININ, 1975), the parent-daughter isotopic systems of Rb-Sr and Sm-Nd are considered to be good indicators in finding out how severe the impacts were and when the intense thermal events took place.

In this work, we have performed a Rb-Sr systematics examination for well-recrystallized L6 chondrite (Yamato-74190) (KIMURA *et al.*, 1978; NAGAHARA, 1979).

Because the Antarctic meteorites are finds, and the meteorites must have been buried in the "ice chamber" of $\sim -10°C$ for $10^4 \sim 10^6$ years as inferred from the studies on cosmic ray-induced nuclides (NISHIIZUMI and HONDA, 1978; KIRSTEN *et al.*, 1978) and the ice-sheet dynamic theory (NAGATA, 1978), the possible terrestrial weathering effect on the Rb-Sr system would be a considerable factor to gain access to the preterrestrial natures of the isotopes.

To check such problems, we have performed leaching experiments of K, Rb and Sr in the specimens which appeared to have been exceedingly weathered, and compared the results with those for the Allan Hills-769 chondrite (L6).

2. Experimental

2.1. Sample preparation

The Yamato-74190 chondrite has been recovered as a single block ($\sim$3 kg) partially covered with fusion crust (YANAI, 1978). A piece ($\sim$4 g) of this meteorite was used for Rb-Sr analysis. It was washed with 1 N-HCl solution (15 s) and acetone, and then pulverized ($\leqq$200 mesh). The mineral separation was performed by the Franz isodynamic separator and with heavy liquid (bromoform, methylene iodide and acetone).

In order to reduce possible selective leaching of Rb and Sr from mineral grains, the heavy liquid treatment was done in a time as short as possible. In some cases, however, the heavier mineral fractions have been immersed in the heavy liquid for 30–60 min. All the specimens were washed with sub-boiled acetone before chemical decomposition. The mineral separation employed in this work is rather similar to those of MASON and GRAHAM (1970) and of ONUMA *et al.* (1974) except some modifications.

The Allan Hills-769 chondrite showed a weathering trend from the brown-colored surface to a dark-colored inside of the specimen which had no fusion crust. However, the several cm inner part of the specimen appeared fresh. A typically weathered outer part and an apparently fresh inner part (see visualized picture in Fig. 1) were leached with 1 N-HCl solution successively for 0.5 to 5 min in a vessel with ultrasonic agitation, and K, Rb and Sr contents in the leached fractions and in the residues were measured.

2.2. Chemical procedure

All the reagents used in the chemical processes were purified by four-fold sub-boiling of commercial special grade reagents. The sample decompositions were made with a teflon bomb. The blank analyses for each reagent and for total chemical process are given in Table 1. Total blank effect on sample analysis was found to be

Table 1. Blank analysis for Rb and Sr during the course of this work.

Reagent	Rb (ng)	Sr (ng)
HF (1 m*l*)	0.14	0.20
$HClO_4$ (0.5 m*l*)	0.014	0.04
6N-HCl (10 m*l*)	0.05	0.23
Total reagents	0.19	0.47
Total chemistry	0.44	1.40

usually less than 1%, but the corresponding effect in the analysis of Rb in the smaller sample was relatively large (2–3%).

Because the variation of the Sr isotopic ratio of the samples analyzed here is relatively similar to that of average crustal material, blank contribution to Sr isotopic measurement is believed to be negligible.

The total errors in concentration measurements were estimated from blank variations and uncertainties in mass spectrometry.

2.3. *Mass spectrometry*

The Rb-Sr isotopic and K concentration measurements were performed using the MS-05RB mass spectrometer at Kobe University. The precision of the Sr isotopic measurements has been checked by a well-documented terrestrial rock and the E&A Sr standard during the course of this work. Mass spectrometry of Sr was similar to that of NAKAMURA *et al.* (1976).

Our typical precision of the $^{87}Sr/^{86}Sr$ ratio was found to be 2–3 digits at the fourth place, which is one order of magnitude worse than current precise measurements.

Table 2. Results of Sr isotopic measurements for the E&A standard (200 ng).

Date	$^{87}Sr/^{86}Sr$ ($\pm$2 sigma mean)
79- 4-3	0.7073±0.0003
79-12-20	0.7081±0.0002
79-12-24	0.7078±0.0002
80- 1- 6	0.7072±0.0003
80- 1-13	0.7084±0.0007
80- 1-21	0.7077±0.0005
80- 3- 8	0.7080±0.0004
80- 3-28	0.7081±0.0003
80- 4- 7	0.7084±0.0002
80- 4-26	0.7092±0.0002
Mean	0.7080±0.0004
(Recommend	0.7080)

However, precision in the present work is considered to be still allowable in evaluation of younger Rb-Sr ages and/or late Rb-Sr isotopic disturbances typically found for the L chondrites.

As shown in Table 2, the obtained $^{87}Sr/^{86}Sr$ ratio of the E&A standard is 0.7080 $\pm$0.0004 (2 sigma mean), which is in agreement with the recommended value.

3. Results and Discussion

3.1. Weathering effect for the Antarctic meteorite

In order to find the weathering effect on easily soluble elements of K, Rb and Sr in the outer part of the grains, acid leaching experiment was performed with a considerably weathered grain and a non-weathered one. The results are given in Table 3 and Fig. 1. To compare the relative leachabilities of these elements with 1 N-HCl solution, the elemental ratio for each fraction was compared. From Table 3, it was found that compared to the fresh sample, K, Rb and Sr in the weathered grain were more easily leachable in the experiment of 0.5 min leaching. In the case of the weathered sample, the amounts of leached fractions for Rb and Sr were lessened with time, but K was leached rather constantly with time.

Table 3. Results of successive leaching experiments with 1 N-HCl for the weathered outer part and for the fresh inner part of the Allan Hills-769 chondrite.

Sample	Leaching time (min)	K	Rb	Sr	K/Rb	Rb/Sr	K/Sr
		(ng)					
Leached							
(Weathered outside)	0.5	978	6.47	74.5	151	0.087	13.1
	2	952	4.80	71.6	205	0.067	13.3
	5	1060	3.33	16.7	318	0.199	63.5
(Fresher inside)	0.5	450	2.68	14.2	168	0.189	31.6
Residue	(Weight in mg)	(ppm)					
(Weathered)	298	875	2.89	10.8	303	0.268	81.0
(Fresher)	98	832	2.77	10.3	300	0.269	80.8

Although the relative leachabilities of K and Rb to Sr or of K to Rb are not considered to be so simple, it is worth pointing out that the general trend of these elemental ratios for the leached fractions approaches to those for the residue with time.

Concentrations of K, Rb and Sr in the residue obtained after five minutes leaching of the weathered grain are rather similar to those of the non-weathered sample, and the agreement of the relevant ratios of both samples is noteworthy. The obtained K, Rb and Sr concentrations in the both samples appear to be generally lower than in the average L chondrites (GOPALAN and WETHERILL, 1968; MINSTER and ALLEGRE, 1979b) but still within the usual variations found for this meteorite group.

In Fig. 1, the relative variations of the Rb/Sr ratio of the weathered sample to that of the fresher sample are plotted against leaching time. In this diagram, the relative values are recalculated to the bulk grain which was successively treated; the values for the bulk grain are evaluated from summation for residue and individual leached fractions. As found for the leached fractions, the Rb/Sr ratio for bulk weathered sample is getting closer to that of the fresh sample with leaching time. Thus, it is suggested that weathering effects on Rb and Sr appear to be limited to the surface of the grain. At the same time, an additional emphasis may be placed on that the Rb/Sr variation for the weathered grain is as low as 4%.

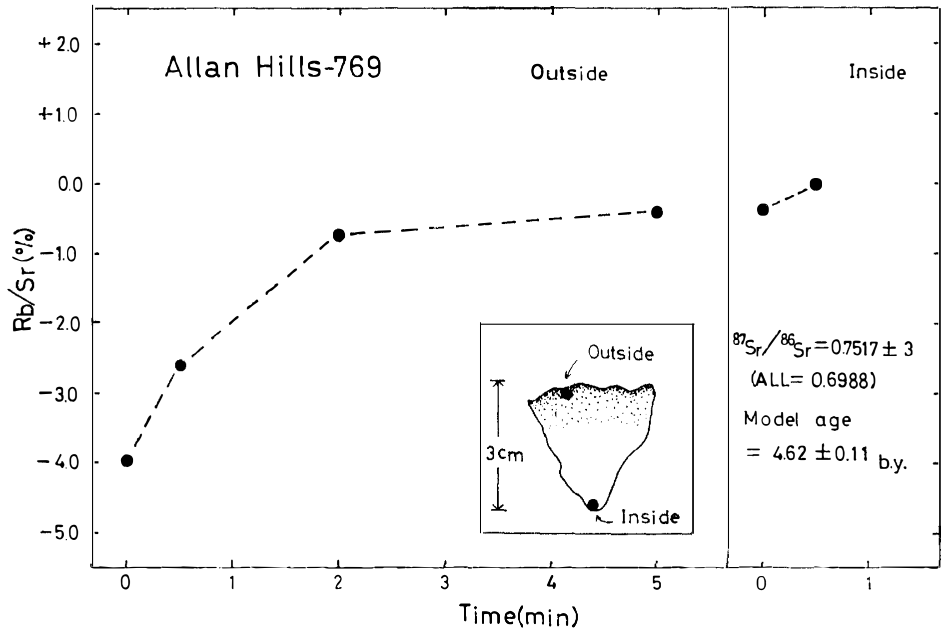

Fig. 1. Relative variation of the Rb/Sr ratio in the residue with time of leaching by the 1 N-HCl solution. The Rb/Sr ratio of the weathered specimen is approaching to that of the fresh sample with leaching.

From the above observations, it is suggested that K and Rb had been more lost than Sr from the surface of the grains by weathering for hundreds of thousands of years while buried in the Antarctic ice, but the inside of the grains seems to be retaining its preterrestrial nature in terms of Rb and Sr.

The present results are considered to be parallel with the observation of preterrestrial amino acids in the Antarctic C2 carbonaceous chondrite (CRONIN *et al.*, 1979).

The model age of the fresh specimen of Allan Hills-769 calculated from the

Allende initial $^{87}Sr/^{86}Sr$ ratio of 0.6988 (GRAY *et al.*, 1973) is 4.62±0.11 b.y. Therefore, the Rb-Sr system in the whole rock appeared to be normal. Hence, it is considered that the effect of leaching in the Antarctic ice or of loss of Rb by late impacts in the preterrestrial history of this meteorite may not be so significant, although redistribution of Rb and Sr among mineral grains is not clear from the present results.

In the beginning, we have expected much more significant weathering damage for the Rb-Sr system in the sample. However, our results are found to be unexpected ones, though the present experiments are quite limited to only one and small piece of a chondrite. Nevertheless, if similar weathering features of the meteorites were established for the Antarctic meteorites by future works, the meteorites buried in the Antarctic "Icebox" will be considered as a potential plentiful source of well-frozen meteorites.

3.2. *Rb-Sr systematics of Yamato-74190*

The results of Rb-Sr measurements for the whole rock and mineral separates are shown in Table 4 and Fig. 2. Although the mineral separation may not be complete enough, the spread of Rb and Sr concentrations among the separated fractions are relatively large as expected from the chemical features of minerals but the spread of the $^{87}Rb/^{86}Sr$ ratio is rather small (Fig. 2). However, the variation of the $^{87}Sr/^{86}Sr$ ratio for the fractions appeared to be still enough to evaluate a late impact age if the Rb-Sr system had been completely reset by the event. As shown in Fig. 2, however, the data points were scattered and could not define an age.

Table 4. Results of Rb-Sr analysis for Yamato-74190 chondrite.

Sample	Weight (mg)	Rb (ppm)	Sr (ppm)	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$
$2.6<d<2.7$ g/cm³	15	14.0	87.4	0.433	0.7300±3**
$2.7<d<2.8$ g/cm³	14	12.0	78.6	0.443	0.7287±2
$d<2.8$ g/cm³	14	13.8	81.5	0.492	0.7280±3
$3.1<d<3.2$ g/cm³	15	3.31	28.3	0.351	0.7199±2
$3.2<d<3.3$ g/cm³	21	2.62	21.7	0.349	0.7234±2
$d<3.3$ g/cm³	14	7.89	58.5	0.391	0.7256±3
$d<2.8$ g/cm³ (−1.2A)	6.6	10.7	76.7	0.394	0.7241±3
$d>3.3$ g/cm³ (+0.5A)	280	0.303	1.91	0.464	0.7368±3
Magnetic (−0.5A*)	24	4.69	33.8	0.404	0.7275±2
Non-magnetic (+0.5A*)	302	1.66	10.8	0.450	0.7303±2
Whole rock (WR)	56	1.79	11.0	0.472	0.7296±3

* The samples, +0.5A and −0.5A, show the magnetic and non-magnetic fractions separated at the current of 0.5 ampere of the Franz isodynamic separater.

** The uncertainties indicate 2 sigma mean and correspond to the last digit.

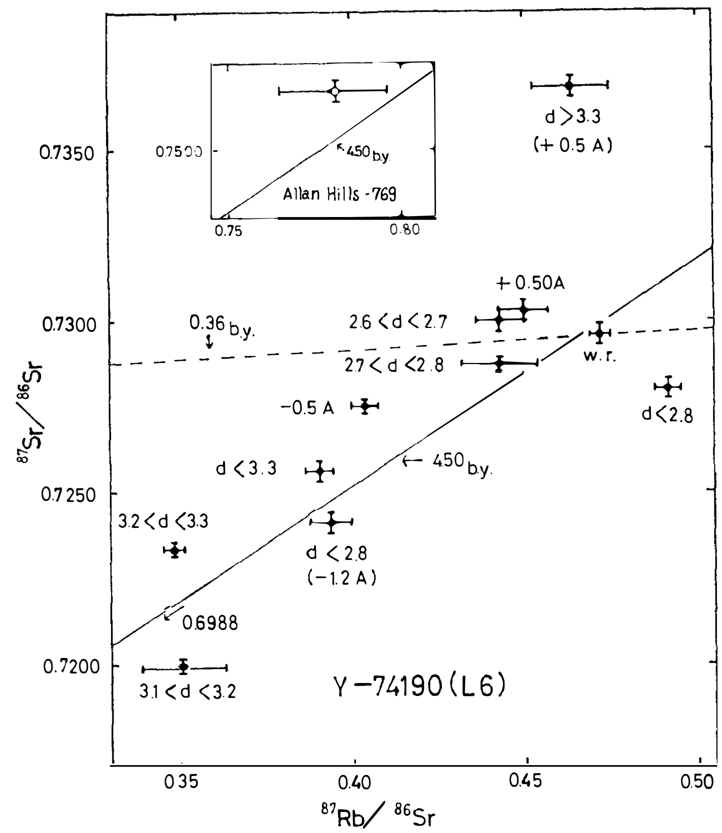

Fig. 2. Rb-Sr evolution diagram for Yamato-74190 chondrite (L6). Most data points are scattered from a possible "initial isochron" and deviate from the 0.36 b.y. line which is calculated from the ^{40}Ar-^{39}Ar age. The data point distribution suggests that moderate late impacts were responsible for the partial Rb loss and redistributions of Rb and Sr among mineral grains in the meteorite.

Similar results on equilibriated L chondrites were reported by GOPALAN and WETHERILL (1971).

The model age of the whole rock was calculated to be 4.45 ± 0.10 b.y. using the Allende initial $^{87}Sr/^{86}Sr$ ratio. Thus, the whole rock data is almost plotted on the "initial isochron" (MINSTER and ALLEGRE, 1979a). However, the majority of the data points deviate from the reference line to the left side.

From the mineralogical examinations (KIMURA *et al.*, 1978; NAGAHARA, 1979) and our leaching experiments for the Allan Hills-769 chondrite, and in view of our experimental uncertainties (including possible selective leaching of Rb to Sr in heavy liquid treatment), the observed data point dispersion in the diagram may not be considered as a result of experimental artifact nor of weathering in the Antarctic ice, but may be ascribed to a preterrestrial nature of the meteorite.

Therefore, the data point distribution suggests that the Rb-Sr system of the meteorite was disturbed by later impacts which lead to loss of Rb and to redistribution of Rb and Sr among mineral grains like the case of the K-Ar system (KANEOKA *et al.*, 1979; KAMAGUCHI and OKANO, 1979).

It is interesting to compare the observed Rb-Sr feature with the ^{40}Ar-^{39}Ar age of the meteorite, because the ^{39}Ar* release pattern apparently suggests significantly younger events (KANEOKA *et al.*, 1979). For comparison, the reference line which is calculated for the whole rock Rb-Sr data using the ^{40}Ar/^{39}Ar age of 360 m.y. is shown in the dotted line in Fig. 2. As demonstrated by KANEOKA *et al.* (1979), any ^{39}Ar* retentive fraction of the meteorite does not appear to exceed 1.5 b.y., although the majority ($\sim$90%) of ^{39}Ar* fractions suggests the apparent age of 300 to 500 m.y. Nevertheless, as seen in Fig. 2, the Rb-Sr system does not suggest such specific young ages, even though the system might have been more or less influenced by younger events.

In spite of the marked perturbation of the Rb-Sr system, some data points appear to indicate a gross correlation between the ^{87}Rb/^{86}Sr ratio and the ^{87}Sr/^{86}Sr ratio. For example, it was tried to calculate a possible age defined by the data points excepting three extremely deviated points. The regression line for the eight data points yields the slope which corresponds to 4.2 ± 0.5 b.y. This age may not represent an age of any significance. However, it is considered that the presently observed distribution of Rb-Sr data points may reflect almost uniform extents of Rb/Sr resetting effect without seriously affecting a possible isochron which corresponds to the typical thermal metamorphism age of 4.45 b.y. (MINSTER and ALLEGRE, 1979a).

From the comparison of the Rb-Sr results with those of the K-Ar system, it is suggested that the Rb-Sr system of this meteorite was much less susceptible to late impact events than the K-Ar system, and that the events responsible for the Rb-Sr isotopic disturbance may not have been so intensive as has been suggested from petrological textures of the meteorite.

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