Movement of Trace Elements during Residence in the Antarctic Ice: A Laboratory Simulation

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ABSTRACT

Thousands of meteorites have been found in Antarctica in recent years which represents a wealth of new material for meteorite research. While it has been recognized that meteorites returned from Antarctica have spent thousands of years buried in the ice and that this could have caused some weathering of the samples, only recently has serious attention been paid to the amount of weathering that may have occurred. From the early days of the Antarctic meteorite program, the curatorial process has given a simple weathering classification to recovered meteorites based primarily on visual observations. It was assumed that if a meteorite did not show obvious weathering, it must be relatively undisturbed chemically. However, recent work has determined that differences in the trace element distribution between Antarctic eucrites and non-Antarctic eucrites may be due to weathering during residence in the ice, and samples that demonstrate trace elements disturbances do not necessarily correspond to eucrites that appear badly weathered to the naked eye.

This study constitutes a preliminary test of the idea that long-term residence in the ice is the cause of the trace element disturbances observed in the eucrites. Samples of a non-Antarctic eucrite were leached in water at room temperature conditions. Liquid samples were analyzed for their rare earth element abundances using ion chromatography. The results for the short-term study showed little or no evidence of leaching having occurred. However, there were tantalizing hints that something may be happening.

The residual solid samples are currently being analyzed for the unleached trace metals using instrumental neutron activation analysis and should show evidence of disturbance if the chromatography clues were real. In addition, another set of samples continues to be intermittently sampled for later analysis.

The results should give us information about the movement of trace elements under our simulated conditions and allow us to make some tentative extrapolations to what we observe in actual Antarctic eucrite samples.

INTRODUCTION

In the past twenty years, a treasure trove of meteoritic material has become available with the discovery of thousands of meteorites in Antarctica. While it has been recognized that meteorites returned from Antarctica have spent thousands of years buried in the ice, and that this could have caused some alteration of the samples, only recently has serious attention been paid to weathering affects that may be present. Most of this work has concentrated upon the changes in mineralogy that result from weathering (Gooding, 1981; Velbel, 1988). The little work that has been directed toward changes in the overall chemistry of the meteorites were done on chondritic materials (Jovanovic and Reed, 1985).

Prior to 1969 about 2000 meteorites had been identified in the 250 years since meteorites were recognized to come from outside the Earth. Since 1969, approximately 12000 meteorite samples (many of which are paired samples of the same meteorite) have been recovered from the ice in Antarctica by teams of scientists sent from the US and Japan. Meteorites from Antarctica have extended the amount of material available on which to do meteorite research, as well as filled in gaps in existing suites of meteorites. In addition, new types of extraterrestrial material have been discovered, including meteorites that originate from a known source, such as the Moon.

Meteorites that are recovered from the ice have spent an average of about 230,000 years, but up to as long as 1,000,000, years immersed in the Antarctic icesheet (Schultz, 1990). Despite the low temperatures, it has come to be recognized that chemical reactions are occurring that alter the meteorites from their pristine state (Gooding, 1986). These meteorites must be carefully examined to look for the effects of weathering prior to using them in studies of their origin.

Studies of how materials weather in Antarctica were originally initiated to provide models for how materials may weather on Mars. These studies looked at basaltic weathering because it is proposed that the surface of Mars may be basaltic. Berkeley and Drake (1981) report in their study on an Antarctic Martian weathering analog that weathering in the Antarctic environment is extremely slow and inhibited by the lack of liquid water. In contrast, Conca and Wright (1987) found in laboratory simulations that etch pits and associated minerals observed in basaltic cobbles from Antarctica could form quickly during the short period of time when small amounts of liquid water were available during the austral summer.

The eucrite association (eucrites, howardites, diogenites and mesosiderites) represents an occurrence of planetary volcanism from the smaller bodies of the Solar System. This

meteorite association is studied to understand chemical and genetic relationships among the meteorite groups and to look at igneous processes that occurred 4.5 billion years ago in the Solar System.

The present study will look specifically at eucrites to examine the chemical effects of weathering and to further ongoing studies of asteroidal differentiation and early Solar System history. Of the approximately 4300 meteorite samples which have been returned from Antarctica by US scientists, about 80 have been classified as basaltic achondrites (Score and Lindstrom, 1990). This includes 56 samples of eucrites which represent approximately 28 meteorites.

Eucrites are generally breccias with remnant igneous textures that resemble terrestrial basalts and are modelled in an analogous manner. They consist of calcium-poor pyroxenes and calcium-rich plagioclases, in roughly equal amounts. In addition, the eucrites contain accessory amounts of olivine, tridymite, quartz, cristobalite, chromite, magnetite, ilmenite and phosphates, such as apatite and whitlockite, as well as minor amounts of metal and troilite (Duke and Silver, 1967).

As eucrites are basalts, the results of weathering studies of terrestrial basalts in Antarctica should apply to how eucrites weather in the Antarctic environment. Prior work with the Antarctic eucrites has led to the definition of two groupings based on the abundances of the REE: those with normal REE patterns (similar to REE patterns observed for eucrite falls), and those with abnormal patterns, mostly apparent enrichments in Ce and Eu (Mittlefehldt and Lindstrom, 1991). This is an important observation. The REE are used extensively to model igneous materials and abnormal abundances due to causes other than igneous processes must be carefully examined.

Mittlefehldt and Lindstrom (1991) proposed that the abnormalities observed in some Antarctic eucrites are caused by terrestrial weathering that occurs in the Antarctic ice. The primary REE minerals in the eucrites are the calcium phosphates. The phosphates are readily susceptible to dissolution in slightly acidic solutions. It was proposed that the phosphates dissolved during the residence of the meteorite in Antarctica. When the phosphates dissolve and the weathering solutions are removed from the meteorite, they carry with them a large part of the REE budget of the meteorite. Because Eu has been preferentially crystallized in the plagioclase, which is much less susceptible to alteration, Eu is retained in the meteorite. It is proposed that the Ce anomaly arises because it is oxidized to the +4 state by the acidic conditions that leach the apatite. Ce^{+4} forms an insoluble Ce oxide which precipitates and remains behind in the meteorite. Therefore, the abnormalities are

not enrichments of Ce and Eu, but depletions of the other REE.

This doesn't appear to happen in all cases. There are Antarctic eucrites with normal REE patterns that fall within the range of patterns exhibited by non-Antarctic eucrites. However, the presence of the abnormal Antarctic eucrites presents problems for workers who model the origins and evolution of the eucrites using REE data. Using abnormal eucrites may lead to erroneous conclusions in models.

There are two schools of thought as to causes of differences in the chemistry between Antarctic and non-Antarctic meteorites. (1) Differences are pre-terrestrial and are indicative of a change in the population of meteoritic material over time. (2) Differences are due to weathering during residence in the ice. A workshop was recently held to look at differences between Antarctic and non-Antarctic meteorites in an attempt to resolve this issue (Koeberl and Cassidy, 1991).

This study arises out of concerns for observed abundances of trace elements in eucrites. Early observations of inconsistencies in REE abundances in eucrites were made in Yamato eucrites in connection with dating studies involving the Hf/Lu system (Shimizu, et al., 1982; Tatsumoto, et al., 1981). More recently, Mittlefehldt and Lindstrom (1991) made an extensive study of Antarctic eucrites and found the two distinct populations. Strait (1990) looked for correlations between chemistry and visual evidence of weathering and found none. These latest studies have led to the current study because of the facility with which liquid and solid samples can be analyzed using the complementary techniques of ion chromatography (IC) and instrumental neutron activation analysis (INAA). The possibility that leaching during residence in the ice could be the cause of these disturbances is being examined in a laboratory simulation.

EXPERIMENTAL

In an attempt to understand apparent deviations in the trace element abundances of Antarctic eucrites we will be leaching non-Antarctic eucrites under conditions that we hope will promote the dissolution of phosphate minerals that are the primary REE carriers in the eucrites. At this point we have no intention of simulating actual Antarctic conditions. The chemistry of Antarctic ice will be used to establish the chemical environment of the study.

Studies of hydrothermal weathering of basalts at mid-ocean ridges conditions (high pressure and temperature in seawater(Seyfried and Mottl, 1982) were used to establish preliminary experimental conditions for this study.

Studies of weathering processes need to look at material that is known have been collected shortly after its fall to

earth (falls). The environmental conditions these meteorites have experienced is well documented. The record of available falls was examined and samples were chosen that represented extremes in a range of REE chemistries and were available in abundance. Four meteorites were initially selected. This preliminary study was done only using Stannern because of its availability.

Sample Preparation

A 6.5 g sample of Stannern was inspected and obvious altered portions were removed. In particular, the material along cracks that could provide entry for water into the stone was removed. The sample was split, and processed into a variety of sample forms: powdered, whole rock chips and a basaltic clast. Meteorites in the Antarctic environment would be present as whole rocks, however, to speed up any potential leaching of the phosphates, we have chosen to analyze powdered samples as well as small, whole chips.

The samples were prepared in the clean room facility of the INAA lab at Johnson Space Center. A comparison blank was prepared using crushed suprasil glass. In addition, plain water was subjected to the same conditions to control for possible contamination from outside sources, such as sample handling. The samples prepared are summarized in Table 1. Sample material not used in the leaching study was saved for later analysis by INAA and SEM.

Low density polyethylene (LDPE) bottles were used for the leach runs and for storage of the samples taken for IC analysis. LDPE plastic was chosen because it is low in potential trace element contamination. All bottles were cleaned by immersion for 2 days in hot 6 M HNO_3, rinsed in triply distilled water and allowed to air dry.

Antarctic ice is apparently relatively clean, with levels of major elements (Na, K, Ca, Fe, Mg, etc.), on the order of 10^{-9} to 10^{-12} g/g ((Boutron, 1980; Miklishanskiy, et al., 1980), so distilled water was used as the Antarctic melt water simulant. The water in contact with the eucrites in the Antarctic environment would have been weakly acidic due to equilibration with CO_2, NO_x, and SO_x present in the Antarctic atmosphere (Jovanovic and Reed, 1985). It is thought the slightly acidic conditions would oxidize sulfides in the eucrite to sulfuric acid, providing localized strongly acidic conditions. Therefore, water used for the experiment was allowed to equilibrate with the atmosphere for several days. The pH was determined to be ~5 (slightly acidic) at the time the study was commenced.

Approximately one gram samples of Stannern were placed in 60-mL LDPE screw cap bottles. About 50 mL of the equilibrated triply distilled water was added to each bottle.

TABLE 1. - STANNERN SAMPLE SUMMARY

Number	Weight (g)	Sample	Study Time
1	1.19636	Glass	30 Day
2	1.23035	Glass	Long-term
3	1.26042	Glass	Long-term/Unsampled
4	–	Water	30 Day
5	–	Water	Long-term
6	–	Water	Long-term/Unsampled
7	0.85012	Powder	30 Day
8	1.13482	Powder	Long-term
9	0.89999	Powder	Long-term/Unsampled
10	0.33566	Basalt Clast	Long-term
11	0.92267	Chip	30 Day
12	0.88286	Chip	Long-term

TABLE 2. - SAMPLE SCHEDULE TIMES IN HOURS AFTER START

Number	A	B	C	D	E	F
1	1	24	96	260	526	1007
2	96	1007				
3						
4	1	24	96	260	526	1007
5	96	1007				
6						
7	1	24	96	260	526	1007
8	96	1007				
9						
10	96	1007				
11	1	24	96	260	526	1007
12	96	1007				

The bottle was tightly closed and allowed to sit at room temperature for a period of time. Two run-time intervals were established: 30 days, to allow for some immediate summertime results; and an as yet undefined longer time period - on the order of 3 months to a year or more. The length of time for the long-term study has been extended indefinitely on the basis of the preliminary results from the 30-day study.

Two-milliliter samples were removed at regular intervals from designated bottles and placed in 5-mL sample vials. A total of six samples were removed for each run. The sample was preserved with the addition of ~ two drops of ultra-pure HNO_3 per 2 mL sample. Finally, the vial was sealed with wax to allow for transportation to Michigan with minimal sample loss. A schedule for the samples already collected is shown in Table 2.

At the end of the study, the remaining liquid was decanted from the solid and transferred to a sample bottle and preserved as before. The solid was carefully dried, and a portion removed for neutron activation analysis. The remainder was saved for later work.

The liquid samples were returned to Alma College for analysis. The REE were determined using ion chromatography. Transition metals (Fe, Cu, Co, Mn, Pb, Ni, Zn, etc.) will be analyzed later, and the solid samples are in the process of being analyzed by INAA at JSC. Neutron activation analysis is being run on leached and unleached glass as a background monitor, leached and unleached powders and the leached chips. A portion of the remaining solid will be made into grain mounts at a future date and examined by SEM for mineral weathering products.

Analysis

The REE in the leach samples were analyzed by ion chromatography. A Dionex 4500i gradient pump system with a post column reactor and UV/Visible detector was used for the analysis The chromatographic output was analyzed by a Spectra Physics 4400 integrator.

The method used to separate the various RE elements is based upon their relative attraction for a resin based ion exchange column and an organic chelating agent. This analysis used a gradient analysis from 80% 100 mM oxalic acid and 20% water to 26% 100 mM oxalic acid/23% 100 mM diglycolic acid/51% water over 8 minutes and then isocratic at the latter composition for another 12 minutes. Post column reaction with 4-(2-pyridylazo)resorcinol was used with photometric detection at 520 nm. The eluants were prepared from Fluka puriss quality reagents and 18 MΩ water. All

samples and reagents were filtered through a 0.45 μm filter before analysis.

A typical run showing the separation of 13 REE in a standard solution is shown in Figure 1. The retention times are reproducible between runs on any one day and are predictably reproduced from day to day. The concentrations for the standard on the calibrated system were within ±5% of the true value, with the exception of La, which was 40% low. Er, Yb and Lu are observable as peaks in the chromatogram, but are not processed by the integrator.

Figure 2 shows a typical calibration of the standard used to calibrate the system. This shows that the system is capable of reproducing concentrations from run to run, and demonstrates that the detection limit for the system is well below the 10 ppm level of the standard. The calibration is done with a standard prepared by dilution from 1000 ppm atomic absorption lanthanide standards (Aldrich Chemical).to 10 ppm levels.

Sample chromatograms for two of the samples are shown in Figure 3. All of the samples exhibited basically the same pattern, showing no real evidence of leaching having occurred. The samples show no presence of the REE in any sample other than a possible La peak (a retention time of 4-5 minutes) and possibly something in the range of Pr or Nd (a retention time of 6-8 minutes). Most samples that show the possible La peak. The peak is occasionally ₋85%, and usually ₋95% of the retention time for La. Only 12A, 7C and 7D show the peak in the 6-8 minute range, and the retention time varies from 6.45 to 8.73, with 7D having an additional peak at 5.26 minutes.

One note about the above possibilities is the problems with reproducibility in the system when only one or two of the lanthanides are present. Several of the elements must be present for the column interactions to work properly. Therefore, no definite conclusions can be made about what was observed in these runs. At best, it can only be said that the lanthanides did not leach to any detectable amount in thirty days.

The solid samples remaining from the 30-day run (1, 4, 7, and 11) have been decanted from the liquid, dried and prepared for INAA. The first count set has been completed and seems to confirm the results from the IC: no depletion in the REE was observed. However, one sample showed a discolored area which may be the result of alteration due to the presence of the water. The sample will be examined in the SEM to determine this possibility.

Standard
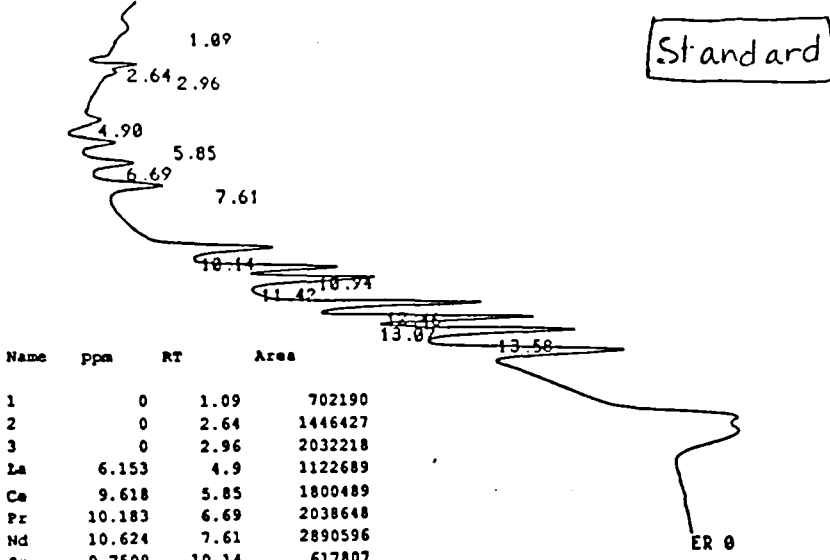
Name	ppm	RT	Area
1	0	1.09	702190
2	0	2.64	1446427
3	0	2.96	2032218
La	6.153	4.9	1122689
Ce	9.618	5.85	1800489
Pr	10.183	6.69	2038648
Nd	10.624	7.61	2890596
Sm	9.7509	10.14	617807
Eu	10.524	10.94	4598184
Gd	10.254	11.42	5620331
Tb	10.635	12.46	5553819
Dy	10.079	13.07	5884729
Ho	10.455	13.58	6969844
Er		(14.3)	
Yb		(16.9)	
Lu		(17.57	

Figure 1.- A typical run of the standard showing the appearance of the 10 ppm standard. Retention times in parentheses are manually calculated. The peaks before ~5 minutes are injection peaks, an artifact of the sample injection. The curve in the baseline is due to the gradient analysis. (RT = retention time in minutes)

Calibration
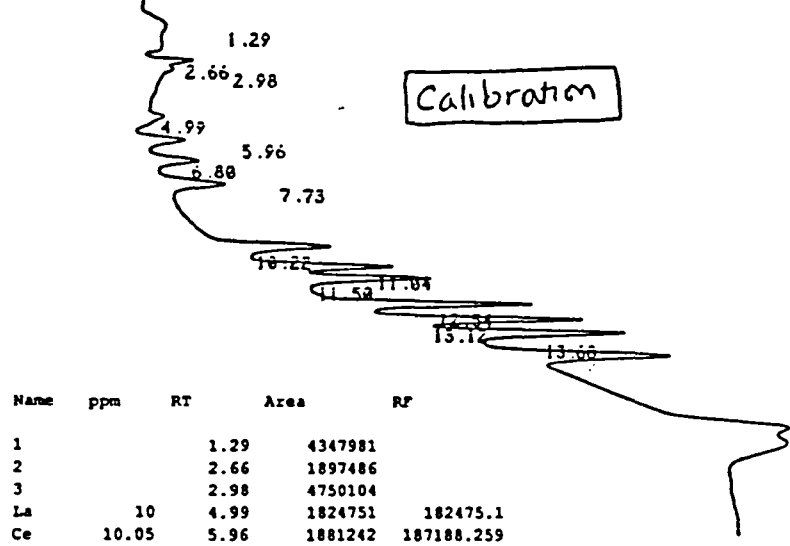
Name	ppm	RT	Area	RF
1		1.29	4347981	
2		2.66	1897486	
3		2.98	4750104	
La	10	4.99	1824751	182475.1
Ce	10.05	5.96	1881242	187188.259
Pr	10.03	6.8	2007972	200196.61
Nd	10.1	7.73	2748236	272102.574
Sm	9.95	10.22	630424	63359.196
Eu	10.15	11.04	4434829	436928.966
Gd	10.1	11.5	5535761	548095.149
Tb	10.1	12.54	5274236	522201.584
Dy	9.9	13.12	5780496	583888.485
Ho	10.05	13.68	6699779	666644.677
Er	10.05	(14.0)		
Yb	10.2	(16.7)		
Lu	10	(17.4)		

Figure 2.- A typical calibration run. The response factor (RF) is calculated by the integrator and used to calculate the concentration.

CHANNEL A   INJECT 11/01/91 12:27:02   STORED TO BIN # 53
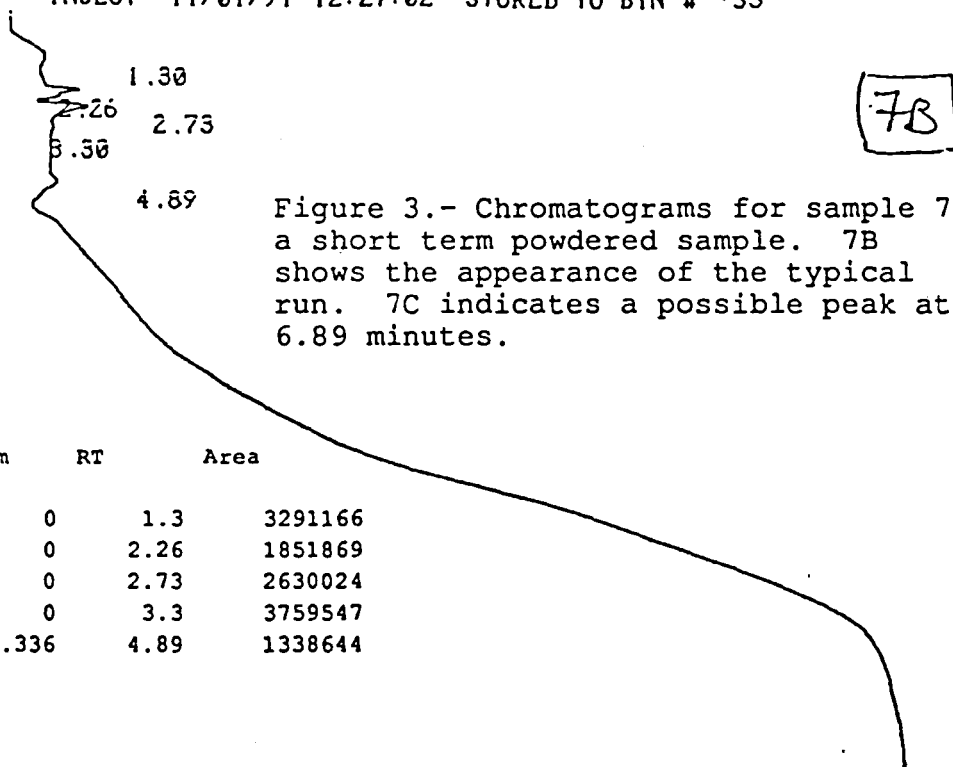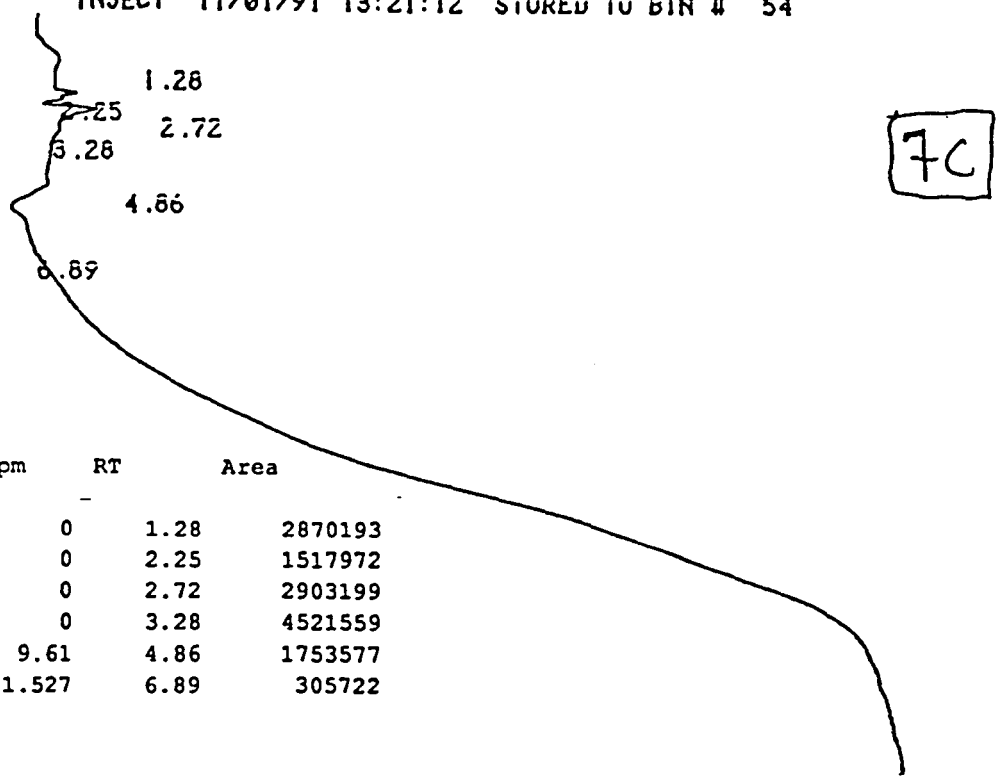
1.30
2.26   2.73
3.30

4.89

7B

Figure 3.- Chromatograms for sample 7, a short term powdered sample. 7B shows the appearance of the typical run. 7C indicates a possible peak at 6.89 minutes.

Name	ppm	RT	Area
1	0	1.3	3291166
2	0	2.26	1851869
3	0	2.73	2630024
4	0	3.3	3759547
La	7.336	4.89	1338644

CHANNEL A   INJECT 11/01/91 13:21:12   STORED TO BIN # 54

1.28
2.25   2.72
3.28

4.86

6.89

7C

Name	ppm	RT	Area
1	0	1.28	2870193
2	0	2.25	1517972
3	0	2.72	2903199
4	0	3.28	4521559
La	9.61	4.86	1753577
Pr	1.527	6.89	305722

CONCLUSION

From this study we hoped to see a movement of the REE out of the solid into the liquid. Ce and Eu should have stayed behind, as observed in the disturbed eucrites previously studied (Strait, 1991; Mittlefehldt and Lindstrom, 1991). This was not observed in the leach results or the initial the INAA analysis.

The long term sample runs are still being leached, and the runs will be concluded six to nine months from now. The long term leach may produce concentrations of REE high enough in the leach to be observable by IC, or enough depletion in REE in the solid to be observable by INAA.

This study will continue with the analysis of the samples still being leached. In the future, further work could involve changing the chemical environment of the system by varying the pH and oxidation levels of the water, the temperature of the reaction, the water to rock ratio, and the water chemistry.

Because we are working in a very liquid environment and not Gooding's "hydrocryogenic" Antarctic environment (Gooding, 1986) , what we see does not reproduce what happens in Antarctica, but this study will still give us useful new information about the movement of REE and other trace elements during the weathering process.

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