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SOLUTIONS TO PROBLEMS OF WEATHERING IN ANTARCTIC EUCRITES

Final Report

NASA/ASEE Summer Faculty Fellowship Program--1990

Johnson Space Center

A065 9909

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Division:	Solar System Exploration
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Date Submitted:	August 10, 1990
Contract Number:	NGT-44-005-803

ABSTRACT

The number of samples available for studies of asteroidal differentiation and early Solar System history has been dramatically increased with the discovery of meteorites in Antarctica. However, it has been recently shown that significant differences in minor and trace element abundances between Antarctic and non-Antarctic eucrites are probably due to weathering (Mittlefehldt and Lindstrom, 1990). This alteration is thought to occur in interstitial material leaving primary silicate phases intact and suitable for petrologic modelling.

This study performed neutron activation analysis for major and trace elements on a suite of eucrites from both Antarctic and non-antarctic sources. The chemistry was examined to see if there was an easy way to distinguish Antarctic eucrites that had been disturbed in their trace element systematics from those that had normal abundances relative to non-Antarctic eucrites. There was no simple correlation found, and identifying the disturbed meteorites still remains a problem.

In addition, a set of mineral separates from an eucrite studied that had been studied earlier were analyzed. The separates were acid-washed to remove any interstitial material or contamination before they were analyzed. The results showed no abnormalities in the chemistry and provides a possible way to use Antarctic eucrites that have been disturbed in modelling of the eucrite parent body.

INTRODUCTION

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 processes that occurred 4.5 billion years ago in the Solar System.

The eucrites are pyroxene-plagioclase achondrites, the diogenites are hypersthene achondrites, the howardites are polymict breccias of eucritic and diogenitic material and the mesosiderites are stony irons with silicates of a composition similar to the eucrites. A spectrum of chemical and mineralogical compositions tie together the eucrites, howardites and diogenites (Figure 1). At one time all four classes of meteorites were considered to come from one parent body, possibly even the Moon (Duke and Silver, 1967). The return of lunar samples eliminated the Moon as a parent body, and recent work on chemistry and mineralogy of the mesosiderites has shown that while they may form in a similar process to the howardite-eucrite-diogenite grouping, they come from a separate parent body (Mittlefehldt, 1990).

This study will look specifically at the eucrites to examine the chemical effects of weathering and to further ongoing studies of asteroidal differentiation and early Solar System history. Eucrites have textures that resemble terrestrial basalts and are modelled in an analogous manner. They consist of calcium-poor pyroxenes and calcium-rich plagioclases, with the pyroxene generally dominant over plagioclase. 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).

The eucrites can be divided into several classes based on structural and chemical composition. Structurally, the meteorites are divided into monomict and polymict brecciated meteorites. Classically, eucrites were monomict and howardites were polymict. The new influx of meteorites from Antarctica has necessitated the addition of a mineralogical-chemical criteria which adds a group called polymict eucrites. These have a polymict structure, but eucritic compositions (Delaney, et al., 1983). The polymict eucrites contain clasts that represent a wide range of igneous lithologies, including eucrites, two-pyroxene mafic rocks, pigeonite cumulate eucrites, alkali-enriched mafic rocks, diogenites, fayalite rich clasts and feldspar cumulate eucrites. (Delaney, et al., 1984).

There are two models for the formation of the eucrites. Both models depend upon different interpretations of the same set of samples and analyses. Mason (1962) proposed that the eucrites formed by the complete melting of an asteroid and that the meteorites might be related as successive members of a fractional crystallization sequence from a melt of approximately chondritic composition. The eucrites were derived from a thin surface crust, while the core consisted of pallasitic material (another type of stony-iron meteorite) surrounded by a diogenitic mantle (Mason, 1967). Stolper (1977) proposed partial melting of the eucrite parent body in successive stages that produced the different types of basaltic achondrites. The different groupings of meteorites were produced when melting occurred in the source region from which earlier melts had been removed.

In 1969 a important event happened in the world of meteoritics: meteorites were discovered in abundance on the ice in Antarctica. Prior to this about 2000 meteorites had been identified in the 250 years since meteorites were recognized to have come from outside the Earth. Since 1969, approximately 12000 meteorite samples have been recovered from the ice in Antarctica by teams of scientists sent from the US and Japan. Samples from Antarctica are individual rocks that have been picked up from the ice. Some of these were members of the same meteorite that shattered before or upon impact with the ice. Chemical and petrographic analysis allows these to be paired. This means that the number of samples from Antarctica is much larger actual number of meteorites represented.

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

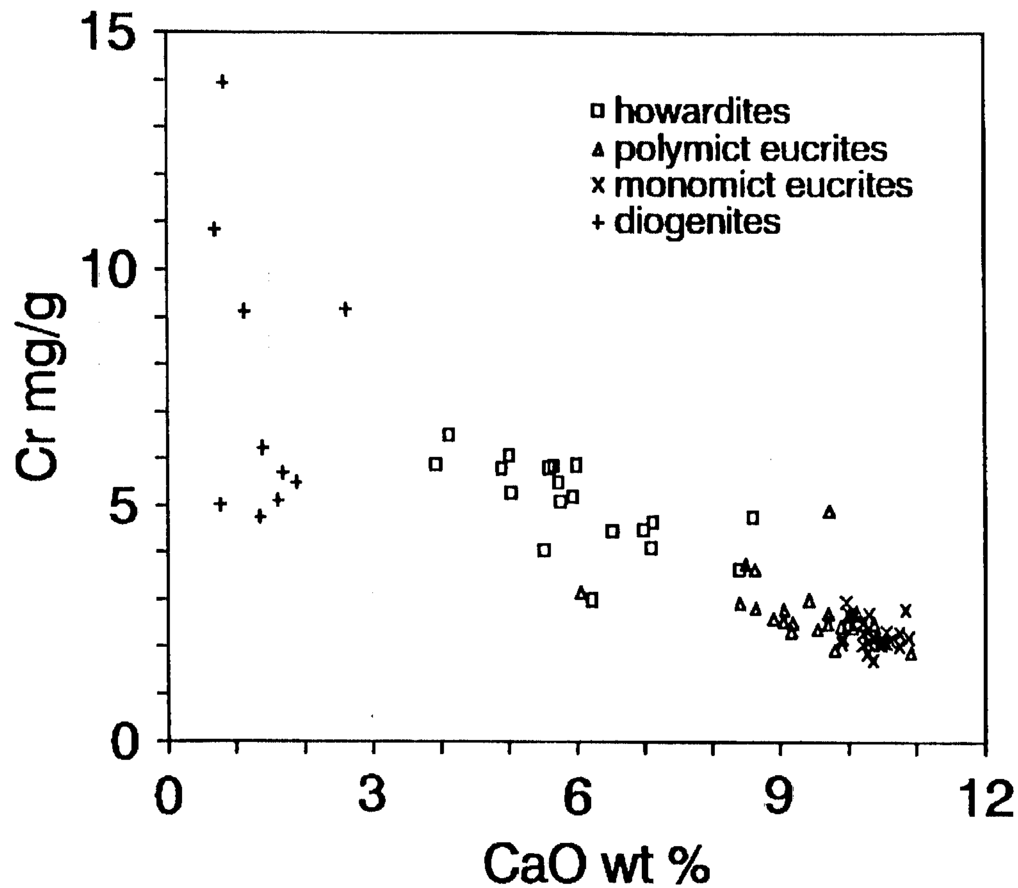

Figure 1. The chemical relationship between the types of basaltic achondrites is demonstrated. Note the close overlap of the monomict and polymict eucrites.

extraterrestrial material have been discovered, including meteorites that originate from a known source - the Moon.

About 4300 meteorite samples have been returned from Antarctica by US scientists, of which ~80 have been classified as basaltic achondrites (Score and Lindstrom, 1990). This includes 56 samples of eucrites which represent approximately 28 meteorites, as well as 17 howardite samples and 8 diogenite samples.

Meteorites are traditionally divided into two types - falls and finds. "Falls" are meteorites that have been recovered from observed meteorite falls. Therefore their residence time upon the earth is well documented. Finds are stones that have been found and subsequently recognized as meteoritic. Their residence time upon the earth is unknown, although there are ways that this can be approximated (Schultz, 1990). Most prior meteorite work has been done on material from falls. This reduces the chance that observations are the result of interactions that occurred upon the earth rather than the processes that are of interest - those that occurred during the formation and evolution of the solar system.

With the wealth of material coming from Antarctica, this strategy has changed. Meteorites that are recovered from the ice have spent from an average of about 230,000 years 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, 1990). These meteorites must be carefully examined to look for the effects of weathering prior to using them in any studies of their origin.

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, and those with abnormal patterns, mostly apparent enrichments in Ce and Eu (Mittlefehldt and Lindstrom, 1990). 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 examined.

The REE are incompatible in most minerals that crystallize in a melt. They tend to act as a group and not be fractionated from one another easily. There are slight differences in their size, however, and this leads to variable incorporation into mineral phases and consequent known fractionations. The fractionations are smooth functions of atomic number. An analysis of the REE contents of a suite of related geologic materials provides evidence for the geochemical history of these samples. The only common exception to the smooth fractionation is Eu because under certain oxidizing-reducing (redox) conditions, the element will exist in the +2 oxidation state rather than the more normal +3 state exhibited by the other REE when the conditions are reducing enough. In the +2 state, it has a different ionic radius, and is incorporated into different mineral phases than the other REE.

In all cases, the REE are considered incompatible, and do not readily enter into the crystallizing minerals until the late stages when they are higher in abundance in the melt. As the melt continues to crystallize, the solids will be progressively more concentrated in REE as the REE are concentrated in the melt. Therefore, early and late materials from a single melt body can be determined by their REE abundances. The size of the Eu anomaly gives clues as to how much plagioclase has been previously crystallized from the melt.

Abnormalities in the REE pattern, one or more elements breaking the smooth pattern, are not readily explained in igneous materials. In chondritic materials, which are presumed to condense from the solar nebula, abnormalities are sometimes observed which can be attributed to localized redox conditions in the solar nebula. In an achondritic material, however, these abnormalities will have been reset by melting and recrystallization.

It has recently been proposed (Mittlefehldt and Lindstrom, 1990) 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 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 these abnormal Antarctic eucrites presents problems for workers who model the origins and evolution of the eucrites using REE data. Using abnormal eucrites will lead to erroneous results in models. This study had a two-fold purpose: first to enable abnormal eucrites to be readily recognized and second to look at ways to use abnormal eucrites in petrogenetic models.

SAMPLES

In the first case a suite of eucrites from a variety of locales was analyzed. Included in the set were five non-Antarctic meteorites to enable comparisons to be made with stones that have not undergone Antarctic exposure. All five non-Antarctic meteorites were falls. Antarctic meteorites were sampled in a variety of ways. Several groupings of clast and matrix samples were taken, as well as a paired interior/exterior samples. This latter was done with the assumption that weathering is more extensive on the exposed outer surface of a rock than in the enclosed interior of a rock. The latter assumption is not always true, as cracks and fissures in the stone allow water to enter the supposedly pristine interior of the rock. Care must be taken to examine all samples for evidence of weathering, regardless of whether it is an interior or an exterior sample. The easiest indication of weathering is ferrous rust, which can result from the oxidation of metal and troilite in the sample. Unfortunately, in the case of eucrites, these minerals are rare and the ubiquitous weathering is the alteration of silicates to produce a sialic rust (Gooding, 1990), which does not have the characteristic "rusty" color of weathered iron.

The second part of the study attempted to find a way to use the abnormal Antarctic eucrites. An abnormal sample, LEW85300,57, examined in an earlier study (Mittlefehdlt and Lindstrom, 1990) was utilized. The sample was separated into its constituent minerals. If the weathering truly affected primarily the phosphates, the primary pyroxene and plagioclase should be minimally affected. Minerals separates were performed in two different ways: magnetic separation and heavy liquid density separations.

The separates were washed with a series of different acids to remove phosphates, cerium oxide, and other interstitial material from the pyroxene and plagioclase. This should remove the phases that caused the abnormal REE patterns in the whole rocks.

EXPERIMENTAL

All samples were described, obvious weathered material was removed (this was primarily rusty appearing material), the samples crushed in a diatomite mortar and pestle and packaged in silica tubes for irradiation. In addition to the meteorite samples, four standard samples were included to determine concentrations, as well as three standard materials included as system monitors. Irradiation was performed at the University of Missouri Research Reactor at a thermal neutron flux of ~5 x 1013 n-cm-2-sec-1. The samples were counted three times in the JSC neutron activation facility to obtain data on a number of nuclides with varying half-lives. The spectra were processed in an updated version of the TEABAGS program (Lindstrom and Korotev, 1982) and further processed using undocumented software to perform various corrections and determine concentrations. The final results are available from the author at the listed address.

RESULTS

The results were examined in a variety of ways. Antarctic samples were compared to the non-Antarctic meteorites analyzed, clasts were compared to matrix and interior samples were compared to exterior samples. Observations of the sample sets are summarized below and followed by a discussion of the entire suite of samples.

LEW88005 - Three splits of this sample were analyzed, two clasts (,13 and ,16) and one matrix (,22) sample. Split ,16 showed little weathering, while split ,13 had obvious weathering, mostly non-ferrous. The matrix had slight amounts of weathering. The two clasts were different in their chemistries, especially when compared to the matrix. ,16 tended to track the matrix more closely than did the more obviously weathered ,13. All of the splits exhibited Ce anomalies; the two clast samples exhibited Eu anomalies, but the matrix sample did not.Barium was enriched in the clast relative to the matrix, and Cr and Co depleted; in all cases variations in split ,16 were more pronounced than split ,13. Split ,13 was depleted in the REE relative to the matrix, while split ,16 was not.

EET87542 - Three splits were also analyzed from EET87542. The two matrix (,11 and ,16) samples and one clast (,16) sample were all remarkably consistent in their chemistries. The only exceptions were U, which was enhanced and K and Na which were slightly depleted in the clast relative to the matrix. None of the samples exhibited Ce anomalies. All of the samples were described as having small rusty patches pervasive over the surface, larger patches of which were removed.

HOW88401 - Five samples were taken from HOW88401, both clast - matrix pairs and an interior - exterior pair. Splits ,13 and ,15 were compared as an interior/exterior pair, while clasts splits ,9 ,13 and ,21 were compared to matrix split ,25. This meteorite showed more variety in its chemistry than the other clast - matrix pairings. There was a wide spread of REE abundances, as well as a variety of patterns. Splits ,13 and ,25 showed the Ce anomaly indicative of abnormal eucrites. With the exception of split ,15, the exterior sample, none of the samples were originally described as having any obvious weathering. Split ,21 is depleted in all of the measured elements relative to the matrix. Split ,9 was enriched in all elements except Fe, Sc, Cr, Co and Eu, which are the same as the matrix. Split ,13 was depleted in all elements relative to the matrix except Ca, Fe, Sc, Cr and Co. Split ,13 had a large piece of chromite, which is shown by its enriched Cr. The matrix pattern was flat at 7 times the cosmic abundance of the REE with no Eu anomaly, but a positive Ce anomaly.

The interior/exterior comparison leads to some interesting observations. First, the interior is depleted in all elements relative to the exterior except for Fe, Cr and Sc. Fe and Cr are enriched in the interior, while Sc is not changed. The REE in the exterior sample are the most enriched of all the splits from this sample, has no Ce anomaly, but does have a pronounced negative Eu anomaly.

Other Eucrites - Of the remaining five samples, three exhibited Ce anomalies and two did not. One of the latter samples (EET85548,12) is apparently a plagioclase cumulate with low REE abundances. The Ce abundance was below the detection limit, so it was not possible to tell if there was a Ce anomaly. This sample was observed to have slight weathering. Of the other four samples, two were described as having little to no weathering (LEW85353,6 and EET87520,14), while the other two exhibited mild weathering (LEW87026,11 and RKPA80204,16). The samples were all whole rock, and the abundances of elements other than the REE tended to fall within ranges established by non-Antarctic eucrites with the exception of EET85548,12 the plagioclase cumulate.

LEW85300,57 - In this study only mineral separates were analyzed of LEW85300,57. In a prior study (Mittlefehldt and Lindstrom, 1990), a suite of whole rock samples from the LEW8530x suite were analyzed. The ,57 split exhibited extensively disturbed REE systematics. It was chosen for this study because of this. Four mineral separates were analyzed, of which data was obtained for three. The two pyroxene samples were almost identical, except for Eu, which was more depleted in the heavy density pyroxene separate ($3.55 < d < 3.7$) than in the pyroxene obtained by magnetic separation. The pattern obtained was a typical pyroxene pattern with depleted LREE relative to HREE and a negative Eu anomaly. The plagioclase pattern obtained from the magnetic separation was also a typical pattern for plagioclase: LREE enriched and a strong positive Eu anomaly. None of these samples exhibited a Ce anomaly.

DISCUSSION

In general, the Antarctic meteorites fall in the same range of abundances that the non-Antarctic eucrites do. The exceptions were generally readily explained, such as being extensively weathered (HOW88401,15) or a different lithology (the cumulate eucrite EET87548,12).

The suite of samples as a whole was examined to determine if there was a simple way to distinguish abnormal from normal Antarctic eucrites. Abnormal eucrites have been defined as samples which have more than a 10% fractionation of La from Ce. Seven of the sixteen samples exhibited Ce anomalies, however only two of them show greater than 20% fractionation. This data set, therefore is not a particularly good one for looking at differentiating normal from abnormal eucrites (Figure 2).

Easy, obvious ways of differentiating the two groups are not particularly useful. Weathering, identified by naked eye or using a binocular microscope, whether ferrous or sialic, shows no apparent correlation between the amount of weathering observed on the meteorite and the presence of a Ce anomaly. Of the seven samples which had a Ce anomaly, four of them had no obvious weathering. The most heavily weathered sample, the exterior one, had no Ce anomaly.

Even when this data set is combined with earlier data collected to look at the Ce anomaly problem, no simple result comes out that unequivocably sets apart the abnormal eucrites. Previous work has shown that chondrite normalized Ce/La and Eu/Sm deviate from a chondritic ratio of one more extensively in the Antarctic meteorites. This is not clearly demonstrated in this limited data set, but the one sample in which Eu/Sm deviates from chondritic is one of the abnormal samples. The other samples fall within a typical range as established by non-Antarctic eucrites. It was attempted to use Hf, another incompatible element in the same fashion, but similar results were obtained (Figure 3).

The interior - exterior pair in this study showed depletions for all elements except iron and chromium in the interior of the sample relative to the exterior (Figure 4). Apparently the materials being removed contain Ca, Na, and most of the trace elements. This would correspond to phosphates and other interstitial material. Pyroxene, which contains most of the iron, and chromite, which contains the chromium, are less susceptible to weathering and are not removed.

Leached materials appear to be removed from the interior and deposited on the outside of HOW88401. However, this is not always the case. Other samples from the prior study show variable results for interior/exterior couples. The materials leached from the interior are sometimes deposited on the exterior of the sample, but in other cases, are completely removed from the sample. It would be interesting to analyze the ice in contact with an abnormal eucrite and see if the leached elements end up in the ice.

Finally, the attempt to see if abnormal eucrites potentially could be used for geochemical modelling seems to have been successful. The mineral separates from LEW85300,57, a decidedly disturbed eucrite, show normal REE patterns with no evidence of the disturbance present in the whole rock. Comparisons between the results obtained in this study and earlier studies on mineral separates from non-Antarctic eucrites show good agreement (Duke and Silver, 1967; Schnetzler and Philpotts, 1969).

According to our results, the Ce anomaly does arise in the interstitial material as hypothesized (Mittlefehldt and Lindstrom, 1990) and not in the major minerals. This result does not agree with an earlier study by Heavilon and Crozaz, 1990 using in situ secondary ion mass spectrometry. They looked

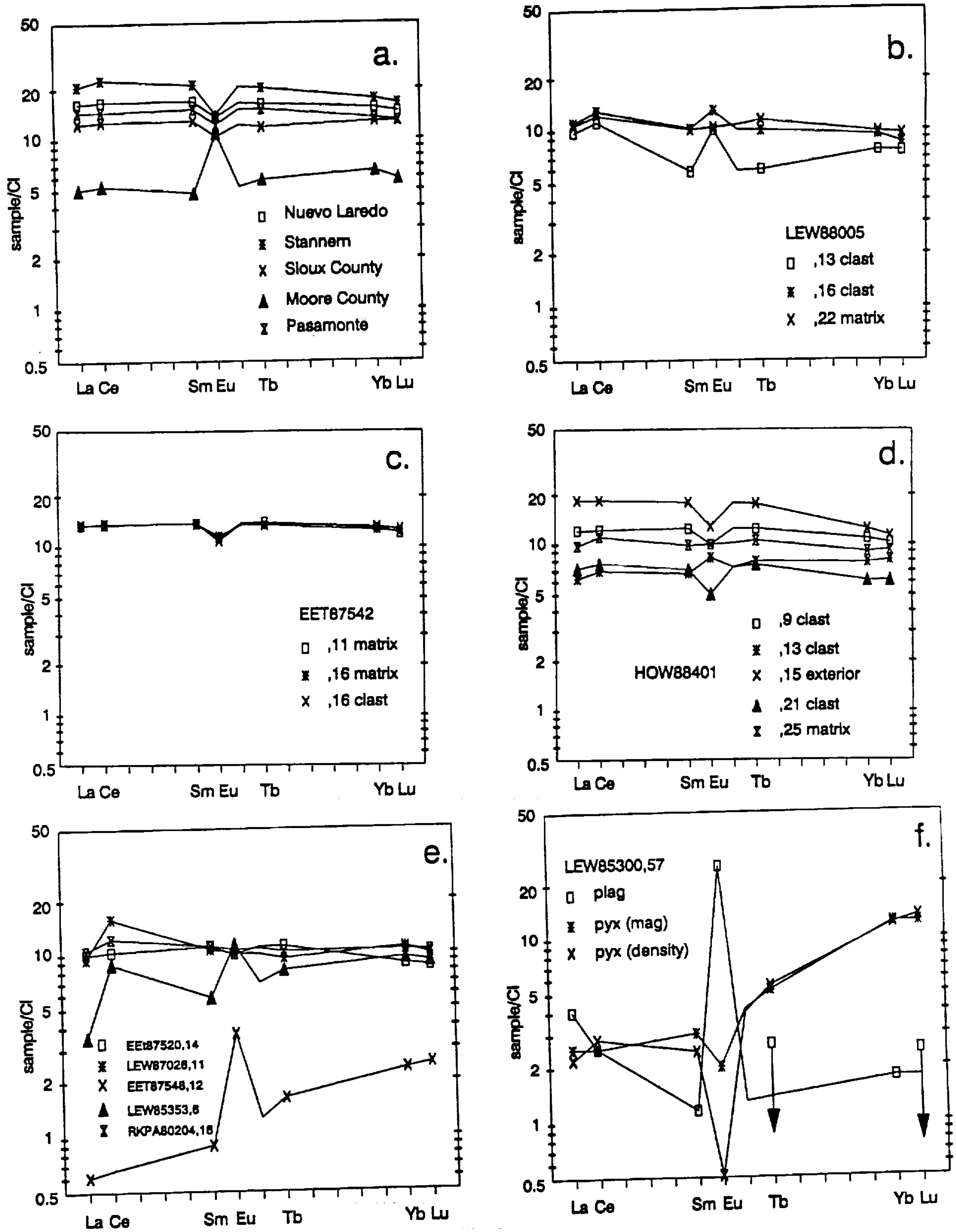

Figure 2.- The REE patterns for the eucrites analyzed in this study.
a) The non-Antarctic eucrites, b) LEW88005, c) EET87542, d) HOW88401,
e) a set of whole rock samples, f) mineral separates.

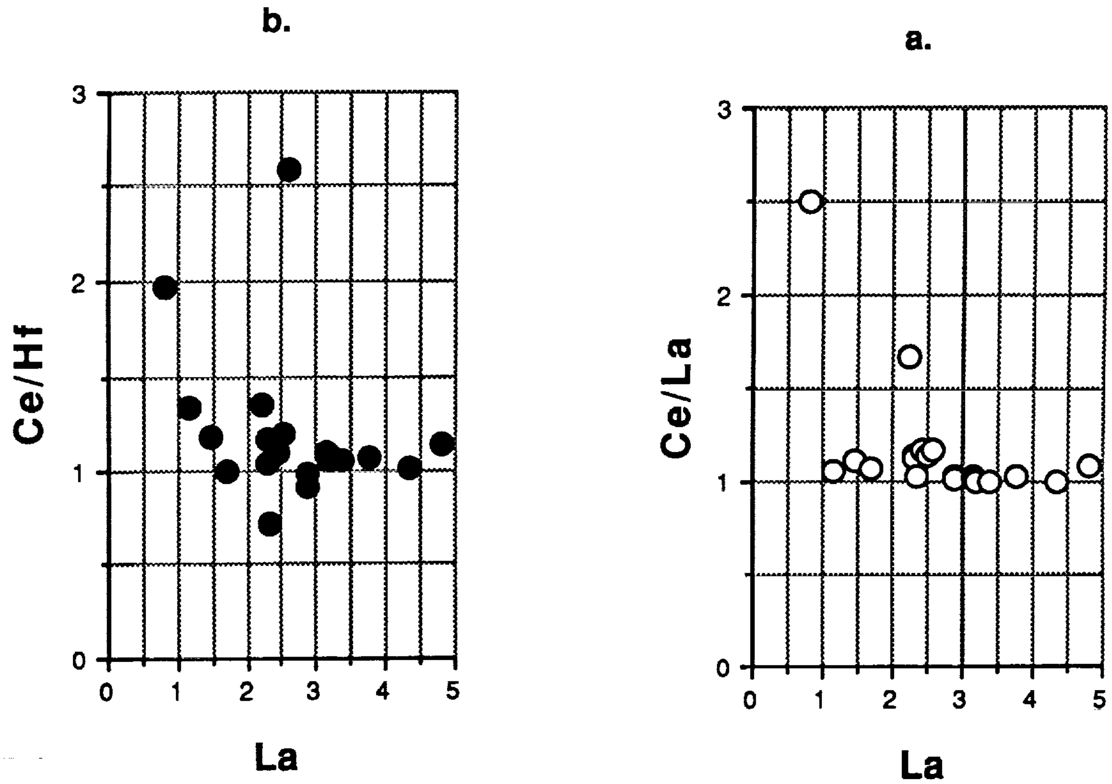

Figure 3.- Ratios of trace elements used to demonstrate differences between Antarctic and non-Antarctic meteorites. a. Ce/La b. Ce/Hf.

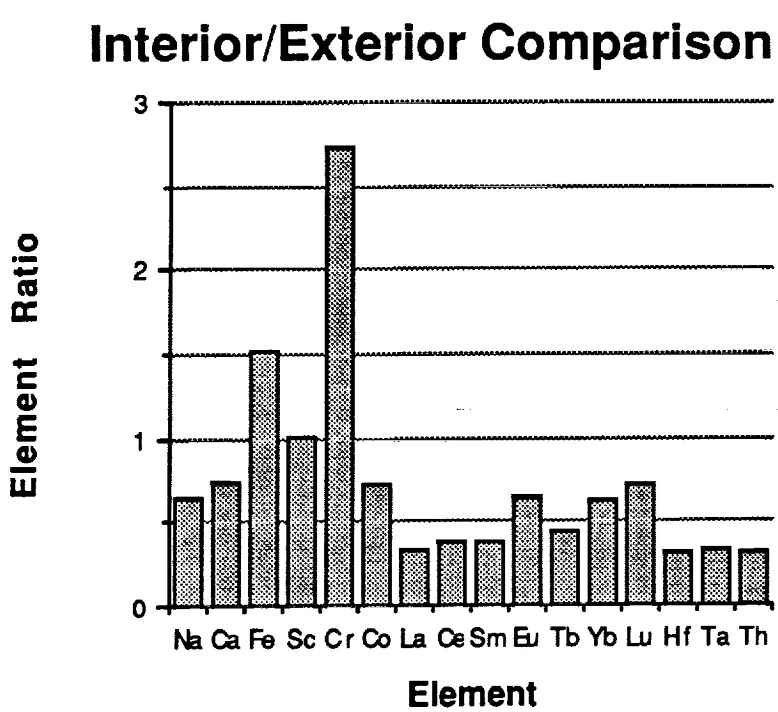

Figure 4.- Demonstration of the migration of elements between the interior and exterior of HOW88401.

at thin sections of the same meteorite, LEW85300, and found Ce anomalies present in pyroxene. Both positive and negative Ce anomalies were present, including adjacent spots with opposite anomalies or even no anomaly. The anomaly was randomly distributed. If this is real, the small scale variations in individual grains may be averaged out by the larger amounts of material analyzed using instrumental neutron activation analysis, as in this study. Or, the variable results may be due to interstitial material smeared on the surface of the thin section during preparation. In our study we removed these types of potential contaminants with the acid leaches. Further work needs to be done to resolve this problem.

Potentially, however, it appears that if a sample could be readily identified as abnormal, it could still be used for doing geochemical modelling if care is taken in handling the materials, i.e., using minerals separates.

CONCLUSION

In conclusion, this study did not establish an easy way to distinguish abnormal from normal Antarctic eucrites. However, if the sample is identified as abnormal, it can be used for modelling if mineral separates of the pyroxenes and plagioclases are used rather than whole rock data. This will require extra work on the part of the investigator, but will allow meteorites from Antarctica to be used in investigations of the evolution of the Solar System.

ACKNOWLEDGEMENT

I would like to acknowledge and thank David W. Mittlefehldt of Lockheed ESC for his help and support in this project. He re-introduced me to the neutron activation lab, and he provided access to his vast knowledge of the eucrites and other basaltic achondrites.

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