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MICROPROBE ANALYSES OF RARE EARTH ELEMENT FRACTIONATION IN METEORITIC MINERALS

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Abstract

Two meteorites were analyzed by PIXE with the Los Alamos Nuclear Microprobe. The enstatite achondrite Peña Blanca Spring and the ordinary chondrite St. Severin were chosen as likely candidates for use in ^{244}Pu ($t_{1/2} = 82$ my) cosmochronology and geochronology. These applications require the meteoritic minerals to have unfractionated actinides and lanthanides relative to "cosmic" elemental abundance ratios. The PIXE analyses produced evidence of actinide-lanthanide fractionation in Peña Blanca Spring oldhamite (CaS) whereas the St. Severin phosphates, whitlockite and chlorapatite, do not exhibit this fractionation.

1. INTRODUCTION

A fissiogenic xenon component in meteorites, unlike any previously known xenon component was discovered in 1965 [1]. This suggested the presence of a, now extinct, spontaneously fissioning nuclide at some time prior to the formation of that meteorite and, by inference, prior to the formation of the solar system. It was soon proven that the fissioning transuranic isotope had

decayed in-situ [2] and that the xenon spectrum was that of ^{244}Pu ($t_{1/2} = 82$ my) [3]. Thus, the observed ^{244}Pu xenon could be given time significance, which is important for cosmochemistry and geochronology.

Cosmochemistry deals with the time scales of "galactic" events occurring prior to the formation of the solar system. Post-condensation time scales in the solar system are, therefore, geochronology. The time dependence of r-process nucleosynthesis is modelled by using the relative abundances of the r-process nuclides: $^{244}\text{Pu}/^{238}\text{U}/^{235}\text{U}/^{232}\text{Th}/^{129}\text{I}/^{127}\text{I}$ at the time of solar system isolation (see Ref. 4). Much effort has been expended in trying to determine the initial Pu/U of the solar system. Recently a consensus has been reached with $\text{Pu/U} = 0.005$ [5,6]. This yields time scales of a few hundred million years for the interval between r-process nucleosynthesis and solar system condensation [4]. (This picture has been considerably complicated by the possibility of several nucleosynthetic events, based on the discoveries of ^{26}Al ($t_{1/2} = 0.72$ my) [7], ^{107}Pd ($t_{1/2} = 6.5$ my) [8], and other "unknown nuclear" isotopic anomalies.)

Geochronology using ^{244}Pu has the potential for determining precise relative ages of early solar system materials. The calculated actinide production ratios are insensitive to reasonable variations in the assumed nucleosynthesis conditions [9]. Because ^{244}Pu is the longest lived Pu isotope, it was thought that the straightforward normalization of ^{244}Pu with another simultaneously produced actinide, such as U, could be used for ^{244}Pu chronologies. Prior to 1970, it was thought that little chemical fractionation of the actinides occurred, especially for chondritic meteorites, because chondrites, on a whole rock basis, show little fractionation among refractory lithophile elements. As discussed below, observational and experimental data proved that actinide chemical fractionation in meteorites had occurred.

Based on theoretical arguments, normalization of the Pu abundances to the light lanthanide Pr was proposed [10]. It was concluded that the solar system condensation sequence of the actinides would follow the order: Th-Pu-U as temperature decreased and that Th, trivalent Pu, and the light rare earth elements (LREE) would roughly co-condense [10]. This argument has been observationally substantiated. For example, the Pu/U ratio for the Ca-phosphate mineral whitlockite varies by a factor of three in chondrites [11] whereas the Pu/Nd ratio is nearly constant at 1.8×10^{-4} for several meteorites, as well as both the whitlockite and clinopyroxene in the igneous meteorite Angra dos Reis [5].

Experimental studies of actinide-actinide and actinide-lanthanide fractionation in synthetic meteorite systems have substantiated and extended the concept of Pu-LREE coherence. Whitlockite, apatite, and clinopyroxene were synthesized, during slow cooling, from anhydrous fO_2 -buffered silicate-phosphate melts. Under reducing fO_2 conditions similar to those present during meteorite formation, the experimentally determined partition coefficients demonstrate that the Pu is largely trivalent (like the LREE) whereas the Th and U are tetravalent [12] resulting in strong actinide-actinide fractionation. In the whitlockite-liquid system, $D_{Th}/D_U \sim 2$ and $D_{Pu}/D_U \sim 6$, where $D_x = (\text{conc. } X \text{ in whit.})/(\text{conc. } X \text{ in liquid})$ [13]. Since the ionic radius of trivalent Pu falls between Ce and Pr, it was not unexpected that the experimentally observed fractionation of Pu from Sm in the clinopyroxene-liquid system [14] fell on the REE clinopyroxene-liquid fractionation trend [15]. Furthermore, the experimentally measured partitioning behavior of Pu is intermediate between the LREE and Th-U so that if a meteoritic mineral has an unfractionated abundance of Ce/Nd/Th/U relative

to CI carbonaceous chondrites that mineral can be inferred to have solar system, unfractionated, Pu/Nd and Pu/U [12, 16].

This relationship yields a measure of Pu fractionation or the lack of fractionation in a particular meteorite sample. Even with known partition coefficients, all inter-elemental fractionation corrections are model dependent. The best way to utilize ^{244}Pu abundances for cosmo- and geochronology is to find chemically unfractionated samples. The experimentally determined bracketing of Pu by the LREE and Th-U in chemical fractionation is used in this approach. The U abundance is determined by thermal-induced fission track radiography and the LREE by PIXE. Electron microprobes do not have adequate sensitivity for the LREE in the chosen meteoritic minerals [17]. The data presented here for Peña Blanca Spring and St. Severin represent the initial efforts to use the Los Alamos Nuclear Microprobe [18] to address the problem of LREE (and therefore, Pu) fractionation in meteoritic minerals.

2. EXPERIMENTAL

The following observations were used to conclude that the enstatite chondrites might be good candidates for Pu chronology as well as providing the initial Pu/U value in the solar system [17].

- 1) The mineral oldhamite (CaS) is the primary host of Th and U in well equilibrated enstatite (E6) chondrites.
- 2) The oldhamite and the bulk enstatite chondrites have unfractionated, cosmic, Th/U values.
- 3) The oldhamite was enriched in U.
- 4) Excess fossil fission tracks, attributed to ^{244}Pu in the oldhamite, were found in Khairpur (E6).
- 5) The water soluble phases in Abee (E4), which include oldhamite, were enriched in the REE [19].

Two large oldhamite grains from the enstatite achondrite, Peña Blanca Spring, containing extreme U enrichment, 1920 ± 100 ppm, were chosen for our LREE analysis. The oldhamite experiments used 1-2 nA of 2.0 MeV protons focussed into a 20 μm spot with a total integrated charge of $6-12 \times 10^{-6}$ Coulomb. The samples were mounted 45° from the beam axis. The proton-induced X-rays were detected, at 90° from the beam axis, by a Si(Li) detector (180 eV FWHM, Mn K α) using a 38 μm Al absorber. An electronic pulse pile-up rejector was used, deadtimes were typically <5%.

Recent data on whitlockite and apatite from equilibrated ordinary chondrites suggest a major Pu-REE fractionation between these phosphate minerals. Measurements of apat/whit for Pu ~ 5 [20] and for Nd ~ 0.77 [21] were reported. These results yield an apat/whit fractionation of Pu/Nd of ~ 6.5 . The St. Severin (LL6) ordinary chondrite was chosen for LREE analysis of the phosphates because these phosphate minerals have been thoroughly discussed and characterized [21].

The St. Severin sample analysis geometry is identical to that used for data acquisition for the Peña Blanca Spring oldhamite. Two whitlockite and two chlorapatite grains were analyzed using 2.0 MeV protons focussed to a 15 μm spot. A total integrated charge of 20×10^{-6} Coulomb was accumulated in approximately 1 hour for each analysis, deadtimes were <5%.

3. DISCUSSION

The data for the two meteorites are given in Table 1 and figs. 1-5. Concentrations were estimated from comparison with a reference glass synthesized from 25% Durango apatite [23] and synthetic diopside with an absorption correction of 30% for the CaS to compensate for the difference in matrix absorption of the X-rays. Detailed quantitative spectra deconvolution [24] has not yet

been applied to these data. Although the counting statistics yield errors of only 4 to 12%, the tabulated error estimates reflect, primarily, the uncertainty in the LREE abundances in the Durango apatite reference. New instrumental neutron activation analyses of the Durango apatite, in conjunction with the quantitative spectra deconvolution, will significantly reduce these errors. Even at this stage of analysis we are able to productively address the problems posed: U-REE fractionation in Peña Blanca Spring oldhamite and Pu-REE fractionation between chlorapatite and whitlockite in St. Severin.

The two Peña Blanca Spring oldhamite grains have similar Ce and Nd concentrations that are consistent with a chondritic ratio [25] (Table 1). The elements Y, Sr, and Se show a factor of two difference between the two grains.

An oldhamite spectrum is plotted in fig. 1. The ordinate is given as square root of counts which results in all the plotted $\pm 1\sigma$ error bars being the same height. The tops of the major peaks, Ca and Mn, are truncated in order to accentuate the trace element peaks. The abscissa is in channel number (20 eV/ch). The peaks, from low to high X-ray energy, correspond to: Al, Y + Ca (escape), Ca, Ce, Nd, Mn, Fe, Fe, Cu, Ga, unassigned, As, Se, Se, Sr, and Y (the S is critically absorbed by the Al filter). Even with the large uncertainty in the REE concentrations, the observed REE enrichment is between a factor of 50 and 100. The U enrichment, over chondritic, is ~200 [17]. Further analysis will strengthen the conclusion that there appears to be at least a factor of two U-REE fractionation. Peña Blanca Spring oldhamite is therefore a poor candidate for Pu chronology. The smaller oldhamite grains in the enstatite chondrites may have less U-REE fractionation and are a high priority for future analysis.

Six spectra of St. Severin whitlockites were taken, all in good agreement. Fig. 2 is an energy vs square root of counts plot. The peaks

correspond to: Mg, Al, Y + Ca (escape), Ca (escape), Ca, La + Fe (escape), Ce, Nd, Mn, Fe, Fe, Ni, unassigned, Sr, and Y (the P is critically absorbed by the Al filter). The LREE, Ce and Nd, and the REE analog, Y, are in unfractionated proportions. Fig. 3 is an expanded portion of fig. 2 (see [24] for how these spectra will be treated quantitatively) with labels for the La, Ce, Nd, and Mn peaks.

The St. Severin chlorapatites are distinctly different from the whitlockites. In fig. 4 the peaks correspond to: Al, Y + Ca (escape), Ca (escape), Ca (trun), Cr, Mn, Fe, Fe, Ni, unassigned, Sr, and Y. Even in the expanded LREE region (fig. 5), little if any Ce and Nd are present. Estimated upper limits for Ce and Nd are given in Table 1. The Y concentration is down about a factor of eight relative to the whitlockite.

From these data we conclude that whitlockite and apatite do not have similar LREE enrichments, in contrast to previously published data [21]. In fact, if Y is accepted as a reliable REE analog, the LREE fractionation between whitlockite and chlorapatite is roughly equivalent to that found for Pu [20]. This indicates that ordinary chondrite phosphates may be viable mineral phases for Pu-Nd chronology.

4. CONCLUSION

The PIXE work at Los Alamos can yield significant results for the problems of Pu cosmo- and geochronology. Quantitative data reduction [24] will markedly strengthen our conclusions: Peña Blanca Spring oldhamite has a U-REE fractionation of a factor of two and is unsuitable whereas St. Severin phosphates appear unfractionated and merit further study.

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FIGURE CAPTIONS

- Fig. 1 Peña Blanca Spring Oldhamite, energy vs square root of counts. The REE are small peaks located in the "valley" just above channel 192.
- Fig. 2 St. Severin Whitlockite, energy vs square root of counts. The REE are small peaks located in the "valley" just above channel 192.
- Fig. 3 Expansion of the LREE region of fig. 2 showing the positions of La, Ce, Nd, and Mn. Compare with fig. 5.
- Fig. 4 St. Severin Chlorapatite, energy vs square root of counts, the REE region is located in the "valley" just above channel 192.
- Fig. 5 Expansion of the LREE region of fig. 4 showing Cr and Mn and the near absence of the LREE. Compare with fig. 3.

Fig 1

Fig 2

Fig 3

Fig 4

Fig 5

TABLE I

(all concentrations in ppm)

	Peña Blanca Spring	St. Severin		Cosmic
	Oldhamite	Whitlockite	Chlorapatite	[25]
Ce	~30	150 ± 50	< 50	0.616
Nd	~20	90 ± 40	< 30	0.457
Y	195 ± 35 , 390 ± 75	300 ± 50	40 ± 20	1.50
Sr	55 ± 15 , 80 ± 20	15 ± 10		7.91
Sc	30 ± 10 , 75 ± 25			18.2