

LABORATORY PARTITIONING STUDIES TESTING THE VALIDITY OF  $^{244}\text{Pu}$ -RARE EARTH CHRONOLOGY. T.M. Benjamin, J.H. Jones and D.S. Burnett, Div. of Geol. & Planet. Sci.; Calif. Inst. of Tech.; Pasadena, Calif. 91125

It is well-established that age differences between most meteorites are, at best, barely resolvable with traditional geochronological techniques based on the decay of long-lived ( $\approx 10^9$  yr) nuclei. However, relative age measurements with much higher time resolution are possible utilizing measurements of the decay products of short lived ( $\approx 10^8$  yr) nuclei (1). The nuclei  $^{129}\text{I}$  and  $^{244}\text{Pu}$  are potentially most useful for this purpose because the decay products (Xe isotopes) are clearly recognized in a wide variety of meteorites. Relative ages from both  $^{129}\text{I}$  and  $^{244}\text{Pu}$  are potentially complementary but may not be internally consistent at present (2). We are attempting to understand the chemical fractionations of Pu relative to other actinide and lanthanide elements because only  $^{244}\text{Pu}$  was present in meteorites, and relative ages between two meteorites must be calculated by assuming that differences in the ratio of  $^{244}\text{Pu}$  to some other nuclide, e.g.  $^{238}\text{U}$ , reflect only the decay of  $^{244}\text{Pu}$  and not chemical fractionation. Several studies (3,4,5) show that significant fractionations of Pu, U and Th can occur; however actinide and lanthanide data on mineral separates from the Angra dos Reis achondrite (5,6) and from an Allende coarse-grained white inclusion (7) indicated that the ratio Pu/Nd might be relatively invariant. Boynton (8) proposed that the coherence of Pu and light rare earths could be explained if Pu were trivalent under meteoritic redox conditions. The importance of trivalent Pu and similar partitioning properties of Pu and light rare earths are supported by our previous experimental studies (4). Our present studies are focussed on a direct comparison of Pu and light rare earth (specifically Sm) partitioning on the same synthetic crystal-melt systems.

A starting composition of 25% Ab-25% An-50% Di (molar), to which about 7ppm  $^{239}\text{Pu}$  and 50ppm  $^{151}\text{Sm}$  ( $^{151}\text{Sm}/\text{Total Sm}=0.97$ ) were added, has diopsidic clinopyroxene as the liquidus phase. A second composition, made by adding 25%  $\text{Ca}_3(\text{PO}_4)_2$  by weight to the above, has  $\text{Ca}_3(\text{PO}_4)_2$  as the liquidus phase. Pu and Sm crystal-liquid partition coefficients (D) can be measured for the same crystal by fission track and  $^{151}\text{Sm}$  beta radiography, respectively. Crystals were grown at 1 atmosphere and  $f\text{O}_2=10^{-9}$  or air by slow cooling from initial temperatures of (1276, 1330°C) to (1210, 1250°C) for (clinopyroxene,  $\text{Ca}_3(\text{PO}_4)_2$ ) using cooling rates of 1.5-10 deg/hr. Microprobe analyses of the synthesis products show ~10% crystallization. Pu radiography is described in (4). Beta radiography (9) was done by microprobe counting of Ag L-alpha X-rays (10) on nuclear emulsions (Ilford K5, 25 micron) exposed to polished sections of our synthesis products (15kV; 5 nAmp current; semiconductor detector). Although most background appears to arise from brehmstrahlung on the organic constituents of the emulsion, interpolated manual background corrections (20 to 50%) were made for each spectrum to allow for possible Ag brehmstrahlung contributions. A small (<5%) correction is made for  $^{239}\text{Pu}$  alpha background. For our 30 micron spot size and counting times (50 sec), volatilization of the emulsion organic constituents is not significant ( $\approx 1\%$  increase in Ag counting rate). Exposure times are chosen to give Ag counting rates in a range ( $\approx 15\%$  Ag metal counting rates) where rates and  $^{151}\text{Sm}$  content were shown to be proportional. Emulsion "fading" during exposure (loss of Ag) was found to be ~6%/day and thus negligible for our total exposure times ( $\approx 6$  hr). Multiple exposures for different times on the same slide are used to measure D values differing greatly from 1. We have occasionally observed "radiationless" developing (i.e. Ag formed by chemical or physical mechanisms) which only occurs over regions of the emulsion exposed to our samples. Control of the clamping pressure during exposure of the sample to emulsion appears to alleviate this effect, but it is a poten-

## Pu-Rare earth partitioning

T.M. Benjamin

tially serious source of error. For this reason and also as a test of equilibrium partitioning (4), we have gone to considerable lengths to demonstrate reproducibility of our results and to estimate our statistical errors independent of the scatter in the results. Statistical errors in the Ag X-ray counting rates are not given by the number of observed counts but instead by fluctuations in the number of beta tracks in the area analyzed by the microprobe beam. Based on the measured spread in a large number (42) of analyses of an exposure of a homogeneous  $^{151}\text{Sm}$  glass, we expect repeated analyses of a sample having a counting rate,  $R$  (expressed in % of Ag metal counting rate), with a beam spot of diameter,  $d$  (in microns), to show a standard deviation (in %) given by  $2.2 \times 10^4 / (R^{1/2} d^2)$ . To be acceptable, the scatter in the observed data must be compatible with this error estimate.

Figure 1 shows a point by point display of our  $D_{\text{Sm}}(\text{cpx})$  data with horizontal rows of points representing independent analyses of a given grain. The data represent both different points on a grain from a single exposure and the analysis of the same point on different emulsion slides. Results for different synthesis runs are also distinguished. The expected standard deviation calculated from the above equation is shown at the top of the figure and does a reasonably good job of describing the observed scatter. Consequently our  $D_{\text{Sm}}(\text{cpx})$  data appear quite reproducible, corresponding to a value of  $0.35 \pm 0.02$ . Correction for zoning (4) would increase this to about 0.36. Our  $D_{\text{Sm}}(\text{cpx})$ , at trace concentration levels, are slightly higher than 0.26 and 0.32 reported by Grutzeck et al. (11) for similar compositions using percent levels of  $\text{Sm}_2\text{O}_3$ . The differences are in the same sense, but smaller, than the "Henry's Law" deviations reported by Mysen (12) for Sm in orthopyroxene. However, our results are preliminary.

The Ag counting rates for  $\text{Ca}_3(\text{PO}_4)_2$  crystals from 3 different synthesis runs show standard deviations ranging from 10 to 19%, consistently higher than the predicted 9%, although counting rates for co-existing glass were compatible with the expected range for only statistical errors. Also, the average values for the runs:  $7.2 \pm 0.5$ ,  $9.8 \pm 1.0$  and  $6.2 \pm 0.5$  do not agree well. Consequently, our  $D_{\text{Sm}}(\text{Ca}_3(\text{PO}_4)_2)$  are not well determined at present. Nevertheless strong Sm partitioning into  $\text{Ca}_3(\text{PO}_4)_2$  is indicated with a measured  $D \sim 8 \pm 2$  which, when corrected for zoning (4) will reduce to about 6. This result is somewhat higher than the  $D_{\text{Gd}}$  of about 3.5 measured for a diopside- $\text{Ca}_3(\text{PO}_4)_2$  composition by Green et al. (13) using percent levels of  $\text{Gd}_2\text{O}_3$ .

In our previous study of actinide partitioning (4) we found  $D_{\text{Pu}}(\text{Ca}_3(\text{PO}_4)_2) = 3.4$  for  $f_{\text{O}_2} = 10^{-9}$  and  $D_{\text{Pu}}(\text{Ca}_3(\text{PO}_4)_2) = 0.5$  in air, reflecting the importance of trivalent Pu under more reducing conditions. The  $D_{\text{Pu}}(\text{Ca}_3(\text{PO}_4)_2)$  in our recent samples have not been particularly reproducible, but show values intermediate between 0.5 and 4, suggesting that we have not been achieving redox equilibrium in our recent runs. This interpretation can be checked in future work, but there was no evidence for this effect in the original results. Consequently,  $D_{\text{Pu}}(\text{Ca}_3\text{PO}_4) = 3.4$  should still be a good value for reducing conditions. Although possibly also affected by redox equilibration problems, our best estimate of  $D_{\text{Pu}}(\text{cpx})$  is 0.15 for  $f_{\text{O}_2} = 10^{-9}$  and  $(P, T) = (1 \text{ atm}, 1276^\circ\text{C})$ . This is 3 times higher than the 0.05 result in (4), reflecting primarily the absence of  $\text{P}_2\text{O}_5$  in our present pyroxene synthesis runs. A similar, but larger (x10), reduction in  $D(\text{cpx})$  for U and Th in  $\text{P}_2\text{O}_5$ -rich melts was observed previously (4).

Table 1 summarizes our best estimates of actinide and Sm partition coefficients at  $f_{\text{O}_2} = 10^{-9}$  based on the results of (4) and the present study. Possible effects of variations in  $(P, T)$  between our 1 atmosphere and 20Kbar experiments have been neglected. Using the  $D_{\text{Sm}}/D_{\text{Nd}}$  from (11) and assuming  $D_{\text{Sm}} = D_{\text{Nd}}$  for  $\text{Ca}_3(\text{PO}_4)_2$ , we infer  $D_{\text{Pu}}/D_{\text{Nd}} = 0.53$  and 0.48 for clinopyroxene and whitlockite respectively. Although our results suggest Pr or Ce might be a better refer-

## Pu-Rare earth partitioning

T.M. Benjamin

ence element for  $^{244}\text{Pu}$  chronology, in practice, the differences in D values we have measured would result in relatively little fractionation for many plausible igneous fractionation processes (see (4) for some specific models). Thus our present results support the proposed use of  $^{244}\text{Pu}/\text{Nd}$  for early solar system chronology. From Pu/Nd chronology it thus appears, surprisingly, that the age differences between the formation of Allende coarse-grained inclusions and the highly-evolved igneous cumulate, Angra dos Reis was less than 25 m.y., in agreement with model age differences from initial  $^{87}\text{Sr}/^{86}\text{Sr}$  (3,5).

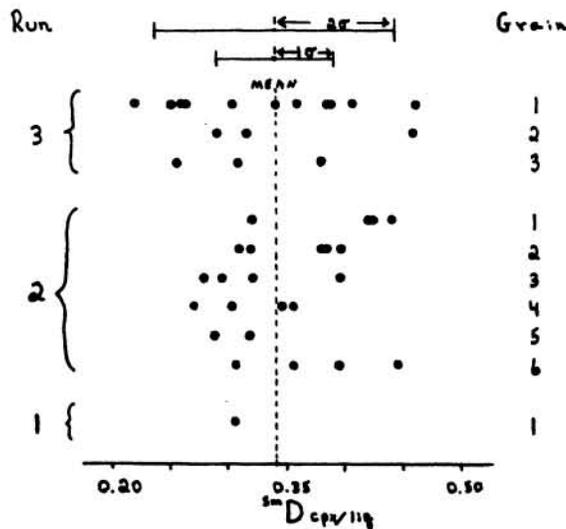


Fig. 1. Individual analyses of  $D_{\text{Sm}}(\text{cpx})$  show a spread consistent with independently calculated error estimates ( $\sigma = 0.05$ , see text,  $\sigma_{\text{mean}} = 0.02$ ).

D.H., Ringwood, A.E., Ware, N.G. Hibberson, W.O., Major, A. and Kiss, E. (1971) Proc. 2nd L.S.C., vol. 1, 601-615.

- References. (1) Wetherill, G.W. (1975) Ann. Rev. Nuc. Sci. 25, 283. (2) Gray, C.M., Papanastassiou, D.A. and Wasserburg, G.J. (1973) Icarus 20, 213-239. (3) Crozaz, G. (1974) E.P.S.L. 23, 164-169. (4) Benjamin, T.M., Heuser, W.R. and Burnett, D.S. (In press, 9th L.P.S.C. Proc.); also subm. to Geochim. Cosmochim. (5) Wasserburg, G.J., Tera, F., Papanastassiou, D.A. and Huneke, J.C. (1977) E.P.S.L. 35, 294-316. (6) Lugmair, G.W. and Marti, K. (1977) E.P.S.L. 35, 273-284. (7) Marti, K. Lugmair, G.W. and Scheinin, N.G. (1977) Lunar Sci. VIII, 619-621. (8) Boynton, W.V. (1978) E.P.S.L. 40, 63-70. (9) Mysen, B.O. and Seitz, M.G. (1975) J. G.R. 80, 2627-2635. (10) Holloway, J.R. and Drake, M.J. (1977) Geochim. Cosmochim. 41, 1395-1397. (11) Grutzeck, M., Kridelbaugh, S. and Weill, D. (1974) Geophy. Res. Lett. 1, 273-275. (12) Mysen, B.O. (1978) Geochim. Cosmochim. 42, 871-886. (13) Green,

Table 1. Best values for actinide-Sm crystal-liquid partition coefficients

	Th	U	Pu	Sm	
D(cpx)	0.03	0.02	0.15	0.36	(25%Ab+25%An+50%D1) = H
D(cpx)	0.002	0.002	0.05	-	85%H+15%Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>
D(Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> )	1.2	0.52	3.4	6	75%H+25%Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>