

LABORATORY TRACE ELEMENT PARTITIONING STUDIES RELEVANT TO ^{244}Pu -RARE EARTH CHRONOLOGY. J.H. Jones, R. Heuser, D.S. Burnett and G.J. Fine, Div. of Geol. & Plan. Sci., Calif. Inst. of Technology, Pasadena CA 91125

Because only one plutonium isotope survived the time interval between nucleosynthesis and meteorite formation, ^{244}Pu abundances in meteorites depend on both chemistry and time. Thus, a useful ^{244}Pu chronology requires that early solar system Pu chemistry be understood. Clinopyroxene and Ca-phosphate mineral separates from Angra dos Reis (AdoR) were found to have the same Pu/Nd ratio, whereas the Pu/U and Pu/Th ratios varied (1,2). The observed coherence of Pu with Nd rather than the other actinide elements undoubtedly reflects the presence of trivalent Pu as opposed to tetravalent U and Th (3,4,5) for the reducing conditions under which meteorites formed. We report laboratory crystal-liquid partitioning studies testing the degree of chemical coherence of Pu and a typical rare earth element (Sm).

Crystals of diopsidic clinopyroxene or Ca-phosphate were grown at 1 bar pressure from melts of $\sim\text{Ab}_{20}\text{An}_{20}\text{Di}_{60}\text{Ca}_3(\text{PO}_4)_2$ (4,5) in Pt capsules. Co-CoO buffers provide $f_{\text{O}_2} = 10^{-9}$ bar. ^{239}Pu and ^{151}Sm , present at trace levels, were analyzed by fission and beta track radiography (4,5). Clinopyroxene. Our techniques require large (>30-40 microns) crystals for quantitative analysis; consequently our standard thermal history has been single-stage linear cooling (few deg/hr) from about 10° above the liquidus to $\sim 60^\circ$ below ($\sim 1210^\circ\text{C}$ for cpx). Crystals do not re-equilibrate with the liquid at lower temperatures; however, valid D values are still obtained if crystal growth is slow enough for the liquid to remain homogeneous (i.e. equilibrium is maintained at the crystal-liquid interface). Nine crystals from 3 different single-stage runs give a well-defined Sm partition coefficient $D_{\text{Sm}}(\text{cpx}) = 0.352 \pm 0.018$. The 5% standard deviation of the data points is consistent with counting statistics (6). However, because experiments in graphite capsules showed a strong tendency to supercool (7), we adopted an alternate, "self-seeding, two-stage" thermal history designed to minimize supercooling and to check the D values from our standard thermal history. Samples were dropped from above the liquidus to $5-10^\circ$ below and held for ~ 15 hr. Tests confirmed (3 of 3 cases) that small crystals were produced in this way. Subsequent to the 15 hr. seeding period, slow cooling was initiated, ending at the same final temperature as our standard runs. The mean $D_{\text{Sm}}(\text{cpx})$ of 16 crystals from 3 two-stage runs is 0.325 which, although not largely different, is still $4 \sigma_{\text{mean}}$ lower than the result from the single-stage runs. This difference probably indicates supercooling in our single-stage experiments, but it cannot be concluded that the D values are higher because of kinetic disequilibrium due to too rapid crystal growth. This is because, in the presence of a seed, crystal growth occurs over a wider temperature interval, and the D_{Sm} from the two-stage runs may represent higher effective temperatures. This latter interpretation better explains the larger observed spread in D_{Sm} from the two stage runs (standard deviation=17%, over 4 times estimated counting statistics and twice the total range expected from fractional crystallization). However, one two-stage sample has inhomogeneous ($\sim 15\%$) glass Al concentrations and Al gradients in the glass at some crystal edges showing that even the presence of a seed crystal does not prevent local supercooling. Consequently, we believe the variations in $D_{\text{Sm}}(\text{cpx})$ represent both the temperature variation of D due to crystal nucleation and growth at different temperatures and some contribution from rapid crystal growth. The variations in $D_{\text{Sm}}(\text{cpx})$ correlate with $D_{\text{Al}}(\text{cpx})$ and $D_{\text{Pu}}(\text{cpx})$ (figures 1 and 2). In figure 1, the point marked with an arrow comes from a crystal showing strong Al zoning and, within positional uncertainties, could lie on the main trend; the anomalous point in the upper left does not

have a reproducible D_{Sm} and a reanalysis (plotted at same D_{Al}) was much lower. The correlations of D_{Sm} and D_{Pu} (fig. 2, open symbols) are such that D_{Sm}/D_{Pu} stays constant at 1.9. This constancy would not be expected for kinetic disequilibrium, and the range in D is 2-3 times larger than can be explained entirely by fractional crystallization. The correlations in figs. 1 and 2 probably reflect primarily the temperature dependence of D_{Pu} and D_{Sm} with some contribution from fractional crystallization and kinetic disequilibrium. The data provide a well defined $D_{Sm}/D_{Pu}=1.9\pm 0.1$ with the lower D values being our best estimate for equilibrium values at $\sim 1250^\circ\text{C}$. Correcting for fractional crystallization would give $D_{Sm}=0.31$ and $D_{Pu}=0.17$. Using $D_{Nd}/D_{Sm}=0.78$ (8), we obtain $D_{Pu}/D_{Nd}=0.68$. Effect of melt composition (phosphorus) on cpx partitioning. Our absolute D values apply only to the compositions and temperatures of our experiments; however, in many applications the relative D values for Pu and RE are more important. These will be less variable, but it is still important to test experimentally the constancy of D_{Pu}/D_{Sm} . Addition of P causes an order of magnitude decrease to $D(\text{cpx})$ for U and Th (4,5) and also has the advantage that the system composition can be changed without appreciable effect on the crystal composition. The liquidus temperatures of the P-free and P-bearing systems do not differ appreciably and cpx remains the liquidus phase. The results for the P-bearing samples (dark symbols on figure 2) also show a correlation between D_{Sm} and D_{Pu} but, because D_{Pu} is lowered more than D_{Sm} , $D_{Sm}/D_{Pu}=2.6$ compared to 1.9 for the P-free systems. This could be due to: [1] an appreciable fraction of Pu^{+4} in the $f_{O_2}=10^{-9}$ experiments; [2] a change in the $\text{Pu}^{+3}/\text{Pu}^{+4}$ ratio with composition; [3] melt complexing effects which recognize differences between trivalent actinides and rare-earths; [4] a change in the rare earth (and Pu^{+3}) partition coefficient pattern with composition. Alternative [1] is unlikely in view of the experiments discussed below. Alternative [4] is possible because, although cpx partition coefficient patterns for rare earths are similar, the relative D values are not constant based on phenocryst-matrix measurements (9). Experiments are in progress to obtain D_{Ce} and D_{Yb} for our P-rich composition. $D_{Pu}(\text{cpx})$ for very reducing conditions. Our previous work has shown that there are large increases in D_{Pu} between $f_{O_2}=0.2$ and 10^{-9} bar (1250°C), which can be ascribed to the importance of Pu^{+3} at the lower f_{O_2} ; however, partitioning data give no direct, quantitative information on $\text{Pu}^{+3}/\text{Pu}^{+4}$. Furthermore, the applicability of our data to meteorites and lunar samples is compromised if significant Pu^{+4} remains, because these materials formed under more reducing conditions. Experiments were carried out with the P-free composition in graphite crucibles in evacuated SiO_2 glass ($f_{O_2}<10^{-17}$ bar), but, to avoid supercooling problems with graphite (7), seed crystals of natural diopside were added. Large (>100 micron) crystals were obtained, both planar overgrowths and independent nucleation from the seeds. Four crystals from 2 runs give $D_{Pu}=0.15-0.20$, in good agreement with the range for P-free samples on fig. 2 although 1 anomalous crystal gives 0.11. Thus, there is no change in D_{Pu} from $f_{O_2}=10^{-9}$ to $f_{O_2}<10^{-17}$ bar, almost certainly indicating that Pu was mostly trivalent for our 10^{-9} bar experiments. Within the errors, 10-20% Pu could still be present at $f_{O_2}=10^{-9}$ bar; but it appears impossible that D for Pu^{+3} and Nd could be equal for our experiments. Ca-phosphate partitioning. D_{Sm} and D_{Pu} for Ca-phosphate (whitlockite) are plotted on figure 3. Unlike the $D(\text{cpx})$ data, the variations for both elements fall within the range possible for fractional crystallization, as shown by the dashed curve. Only data from single-stage cooling histories are shown, because of difficulties in buffering for the longer two-stage runs. Fractional crystallization (zoning)

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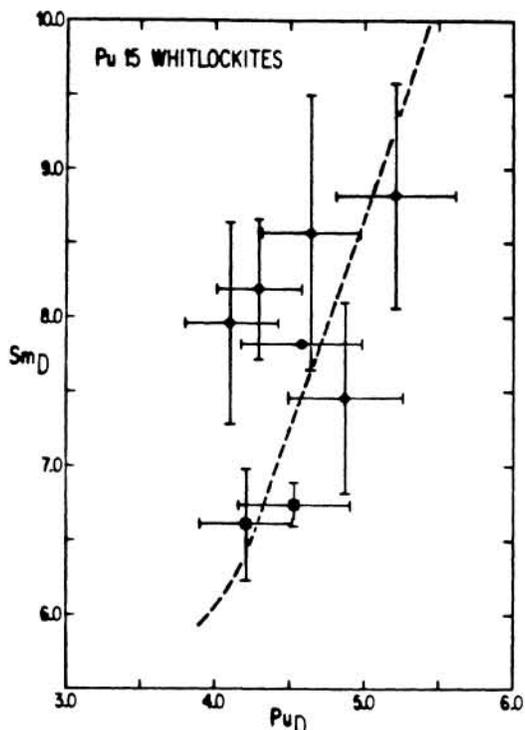


Figure 3.

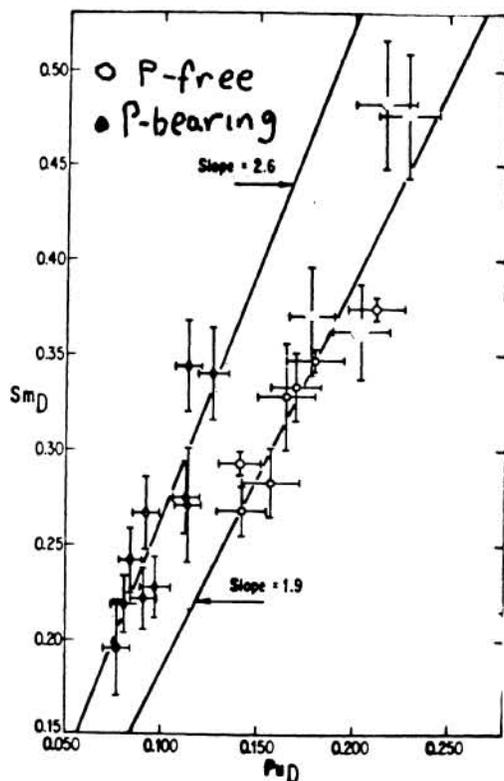


Figure 2.

corrections are large since both D's are much greater than 1. Our best estimates are $D_{Pu}(Ca-phos)=4$ and $D_{Sm}(Ca-phos)=6$.

Discussion. The present results are consistent with the conclusions drawn in our previous LSC abstracts, based on less complete data. To the extent that the D values are not equal, our results do not support the concept of Pu-Nd chronology. However, because the D values are small, many petrogenetic processes would leave Pu and Nd approximately unfractionated. Moreover, because we have shown that D_{Pu}/D_{Sm} varies significantly with changes in bulk composition, D_{Pu}/D_{Nd} may be closer to 1 for other compositions. In terms of ionic radius, Pu^{+3} lies between Ce and Pr and, within errors, $D_{Ce}=D_{Pu}$ for cpx. Thus a Pu/Ce chronology has advantages, but use of Pu/Nd is attractive in terms of chronological studies involving several parent-daughter systems. We are cautiously optimistic about the prospects of Pu-RE relative meteorite ages, e.g. on achondritic clasts. At present, however, such measurements (on whole rock samples) require additional chemical data; light RE, U and Th abundances, for proper interpretation (4,5).

References: (1) Wasserburg et al., *Ear. Planet. Sci. Lett.* **35**, 294, 1977 (2) Lugmair and Marti, *ibid*, **35**, 273, 1977 (3) Boynton, *ibid*, **40**, 63, 1978 (4) Benjamin et al., 9th LSC Proc., 1393, 1978 (5) Benjamin et al., *Geochim. Cosmochim.* **44**, 1251, 1980 (6) Jones and Burnett, *in press*, *Nucl. Inst., Meth.*, 1981 (7) Jones and Burnett, 11th LSC Proc., 1980 (8) Grutzeck et al., *Geophys. Res. Lett.* **1**, 273, 1974 (9) Schnetzler and Philpotts, *Geochim. Cosmochim.* **34**, 331, 1970.

