

CALCIUM ISOTOPE DISEQUILIBRIUM IN ALLENDE INCLUSION HN-3.

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As part of our ongoing effort to study the influence of physico-chemical processes in the interstellar medium (or the early solar system) on the survival of nucleosynthetic effects and the resulting relative magnitudes of isotope anomalies in different elements we discuss results on three selected samples.

The type B1 Allende inclusion HN-3 was discovered by H. Nagasawa and described by Nagahara et al. (1987). Mayeda et al. (1986) found a systematic difference between the melilite and anorthite oxygen isotope compositions of this and two other type B1 inclusions. These differences, however, are too large to be explained by simple isotope equilibration between the mineral phases and the ambient gas. In addition, the tie lines in a three isotope oxygen plot between the two mineral phases do not have the required slope of 1/2. Rather, these data suggest that variable oxygen exchange of mineral phases with reservoirs of different isotope composition has occurred. Their Si isotope data might also reflect disequilibrium. Nakamura and Nagasawa (1987) measured REE abundances in HN-3 melilite, fassaite and anorthite and found positive Yb anomalies in, at least, anorthite and melilite. These anomalies increase with decreasing REE concentrations in the order (fassaite) < melilite < anorthite. On the basis of these observations Nagahara et al. (1987) proposed that HN-3 crystallized from incompletely molten material of both interstellar and solar system provenance.

Because of the remarkable findings briefly described above, we undertook an extensive study of the isotope compositions of other elements. Here we will concentrate on the isotope composition of Ca in the three primary Ca bearing mineral phases. It was expected that the non-linear ⁴⁸Ca effects, if present, among the co-existing phases would be of the same magnitude for the following reasons: a) Al-Mg data from single crystal B1 anorthites all define "isochrons" with slope 5×10^{-5} whereas Al-Mg data from B2 anorthites do not (Hutcheon, 1982) and b) petrologic and petrographic observations suggest that type B1 CAIs crystallized from material containing a smaller proportion of relict grains than B2 CAIs (Stolper, 1982 and Wark and Lovering, 1982). These Mg-Al observations argue for equilibrated isotope behavior within type B1 CAIs, in contrast to what could be expected for type B2 CAIs. However, these observations are not inconsistent with ⁴⁸Ca effects of different magnitudes residing in co-existing mineral phases of a type B1 CAI, since they are from anorthite, a mineral with a low crystallization temperature relative to spinel and melilite.

The Ca isotope compositions were measured in HN-3 melilite, anorthite and fassaite separates (prepared by H. Nagasawa) performing four to seven repeat measurements for each Ca fraction. Calcium was normalized to ⁴⁰Ca and fractionation corrected to ⁴⁴Ca/⁴⁰Ca = 0.0217. No non-linear isotope effects were resolved on any isotopes other than ⁴⁸Ca. The data for ⁴⁸Ca are given in Table 1 and are expressed in relative deviations from normal ⁴⁸Ca/⁴⁰Ca in parts in 10⁴ (ε units). Surprisingly, a clear difference can be resolved between melilite and fassaite. Melilite has the largest ⁴⁸Ca effect of 6.5 ± 0.8 ε units while fassaite has the smallest with 4.0 ± 0.8 ε units. The ⁴⁸Ca effect of anorthite of 5.6 ± 1.0 ε units is intermediate and cannot be clearly resolved from melilite and only marginally from that in fassaite.

What are the possible explanations for this roughly 2 ε unit range in ⁴⁸Ca effects? 1) The primary minerals, melilite, fassaite and anorthite do not contain stoichiometric potassium. However, it is known that alkali elements entered CAIs during open system alteration. Melilite alters most easily among these phases and therefore would be expected to contain more potassium than the other two minerals. Potassium rich material could be elevated in ⁴⁰Ca due to decay of ⁴⁰K. Since Ca isotope ratios are normalized to ⁴⁰Ca, an enrichment in ⁴⁰Ca could cause an

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apparent enrichment of almost equal relative magnitude in ^{48}Ca due to fractionation correction to $^{44}\text{Ca}/^{40}\text{Ca}$. In order to check this possibility we renormalized all raw data to $^{42}\text{Ca}/^{44}\text{Ca}$. In this case ^{40}Ca is a free parameter and radiogenic contributions or deficiencies would be observed as deviations from normal $^{40}\text{Ca}/^{44}\text{Ca}$. No variations outside error in ^{40}Ca were observed for these samples and the possibility of the variation of ^{48}Ca due to an artifact can be excluded.

2) Material with a lower ^{48}Ca excess could have entered the CAI after melilite and anorthite crystallization had commenced but before fassaite crystallization. This would be consistent with the decrease of the ^{48}Ca effects with decreasing crystallization temperatures of melilite (1400°C), anorthite (1260°C) and fassaite (1230°C). However these experimentally determined anorthite and fassaite temperatures differ only by 30°C (Stolper, 1982). 3) Post formation preferential Ca isotope exchange of fassaite (and possibly anorthite) relative to melilite with less anomalous or normal Ca cannot be excluded. Experimental determinations of Ca self diffusion coefficients in melilite, fassaite and anorthite will place constraints on detailed exchange models. It is unlikely that the amount of exchange is related to the Ca contents of the minerals since the Ca contents of the minerals decrease in the order melilite (~42 % CaO), fassaite ~25 % CaO) and anorthite (~20 % CaO).

More tenable explanations include: 4) Melilite and anorthite could contain relict grains or grains with ^{48}Ca effects larger than that of the bulk inclusion. 5) Some melilite and anorthite grains themselves could be relict with larger ^{48}Ca effects. Melilite is the highest temperature Ca bearing phase in the type B1 crystallization sequence (Stolper, 1982).

The Ti isotope composition has been measured only in fassaite: the $11.5 \pm \epsilon$ unit excess for ^{50}Ti is unremarkable and within the range of values we observed for the coarse grained F-series inclusions (Prombo and Lugmair, 1987).

Table 1
 ^{48}Ca Effects in HN-3 Separated Minerals (ϵ units)

Melilite	Anorthite	Fassaite
7.9 ± 1.2	4.8 ± 1.4	3.9 ± 1.5
4.8 ± 1.8	5.8 ± 1.6	4.2 ± 1.8
6.5 ± 1.6	7.2 ± 1.7	2.6 ± 1.7
5.4 ± 2.0	5.3 ± 1.3	5.7 ± 2.3
6.2 ± 1.3		5.0 ± 1.9
6.4 ± 1.4		3.4 ± 2.0
6.4 ± 2.1		
Wt. Mean 6.5 ± 0.8	5.6 ± 1.0	4.0 ± 0.8

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