Rare earth distributions in mineral separates in HN3-1 in which anorthite has been shown to have a third 0 isotopic component(1) have been determined by using precise mass-spectrometric isotope dilution technique to study equilibrium-disequilibrium relations among coexisting minerals in HN3-1.

Ca-Al-rich inclusions(CAI) in the Allende meteorite show heterogeneous distribution of 0 isotopes among coexisting minerals(2), while they show distribution of REE, which is explained as a result of partitioning within the individual CAI under equilibrium(3,4,5). This coexisting equilibrium-disequilibrium distributions of REE and 0 isotopes can be explained only by a diffusion process which redistributed either 0 isotopes or REE in a heating event after the formation of the CAI(6,5). Clayton et al(7) suggested that CAI were formed originally with 160-enriched 0 distributed homogeneously but 0 isotopes in melilite were later replaced by those in the surrounding gas with normal isotope ratios by heating, due to a seemingly faster diffusion rate of 0 in melilite, which is later confirmed by Hayashi and Muehlenbacks(8).

Recently, however, Clayton et al(1) found that anorthite in CAI contain a third independent component of 0 isotopes. Thus, the diffusion process suggested by Clayton et al(7) is not sufficient enough to explain the 0 isotope distribution in CAI without, at least, adding another process to explain the presence of the third 0 isotopic component in anorthite.

Results of REE, Sr, and Ba analyses are plotted in Fig.1 in terms of the chondrite-normalized scale. The general trend of REE patterns for the mineral separates shows characteristics which are expected for these minerals in equilibrium, i.e., relative enrichment of light REE and positive Eu anomalies in melilite and anorthite and relative depletion of light REE and a negative Eu anomaly in fassaite, as in the case of other CAI(3,4,5), however, Yb shows distinct positive anomaly in melilite and anorthite.

If melilite crystallized from a melt with the bulk chemical composition of CAI before pyroxene as shown by the melting experiment(9), the REE pattern expected for pyroxene is depleted in La and Ce compared with Nd and Sm, and thus does not agree with the observed REE pattern for the melilite separate (Fig.2). The observed REE pattern can be explained by crystallization of melilite after or simultaneous with pyroxene, since pyroxene strongly exclude La and Ce to produce relative enrichment of La and Ce over Nd and Sm in melilite. If melilite crystallized before pyroxene as expected by experimental crystallization sequence, an alternative solution may be that residual liquid rich in light REE left after crystallization of pyroxene has incorporated in the melilite crystals in a secondary metamorphic or melting event.

Yb anomalies observed for melilite and anorthite REE patterns are another problem for a liquid crystallization model. If the observed Yb anomalies are due to the presence of a Yb anomaly in the original liquid from which all the minerals crystallized, pyroxene, as well as melilite and anorthite, must have a Yb anomaly of the same size. Another possibility is that Yb was present in part as Yb2+ and Yb3+ was preferentially taken by melilite and anorthite and produced positive Yb anomalies. Since Yb2+, if existed, would have occupied Ca site much more easily than smaller Yb3+ and would produced positive Yb anomalies in melilite and anorthite REE patterns. However, this is unlikely, because Yb2+/Yb3+ ratios in the solids under the nebular condition are expected to be very low, say, the order of 10-4(10). In addition Yb2+/Yb3+ ratio calculated from Eu2+/Eu3+ in melilite is also too low to explain the observed
positive Yb anomaly in melilite. By applying Philpotts' method (11) Eu$^{2+}$/Eu$^{3+}$
ratios in melilite and pyroxene in HN3-1 are calculated to be 6.7 and 0.81,
respectively. Taking free energy change of the reaction, EuO + YbO$_5$ = EuO$_4$ +
YbO, as a conservative value of 80 kJ/mol and an activity coefficient of YbO
which is twice as large as that of EuO in melilite, Yb$^{2+}$/Yb$^{3+}$ is calculated to
be less than 0.1, which is too small to produce the observed Yb anomaly.

The observed Yb anomalies appear to be due to mixing of a Yb-rich component
or components in melilite and anorthite. The core melilite which has a quite
different crystal appearance compared with the mantle melilite (10) is a possible
candidate for the Yb-carrier. Considering that anorthite which also shows a Yb anomaly contain the third O isotopic component, the core melilite
may also show an O isotope anomaly, if the O isotope ratio in the core melilite
was not homogenized with that in the mantle melilite by diffusion.

The results of the present study suggest, (1) positive Yb anomalies in
melilite and anorthite REE patterns are due to mixing of Yb-rich component in
core melilite and anorthite, which have not been equilibrated with pyroxene
and mantle melilite, (2) apparent equilibration of REE in melilite and pyroxene
have been established at the time of a heating event, which have caused diffusion of REE in pyroxene and mantle melilite.

Fig. 1. Mineral REE pattern for the Alende CAI HN3-1. Note the distinct positive Yb anomaly in melilite and anorthite patterns.

Fig. 2. The observed REE pattern for melilite in HN3-1 and EK1-07(5) compared with the calculated REE pattern for melilite. The calculated values are obtained by postulating that melilite was the first mineral to crystallize from the bulk liquid, and totalled to 40%. Spinal was neglected since spinal does not contain appreciable amount of REE. The bulk REE pattern for HN3-1 was calculated assuming that melilite: fassait:anorthite = 3:3:2.

References.