ISOTOPIC HETEROGENEITY AND CORRELATED ISOTOPE FRACTIONATION IN PURPLE FUN INCLUSIONS.


FUN isotopic anomalies appear to be relatively common (~20% of inclusions analyzed) in a class of Allende coarse-grained inclusions characterized by a distinct purple color and high abundances of spinel [1,2]. We used the ion microprobe to analyze Mg, Si, Cr and Fe isotopic compositions of two Purple Spinel-rich Inclusions (PSI=ψ) to investigate: 1) isotopic heterogeneity within an inclusion, including regions of alteration; 2) correlations of isotopic fractionation in petrographically similar inclusions; and 3) excesses in $^{26}\text{Mg}$.

The ψ consist predominantly of spinel (50%) and fassaite, and appear related to type B CAI. In both ψ, fassaite encloses euhedral, poikilitic grains of Fe-poor spinel. Clusters of Fe-rich spinel, (up to 15% FeO), surrounded by symplectic intergrowths of sodalite and Fe-rich olivine, are concentrated toward the edge of the ψ. Anorthite and melilitite are absent in B7H10, while DH8 contains minor anorthite and melilitite. Fine-grained alteration regions contain Fe-rich spinel, hibonite, hedenbergite, grossular, olivine and feldspar. Bulk compositions of the ψ differ from type B compositions in being enriched in $\text{Al}_2\text{O}_3$, TiO$_2$, FeO and Na$_2$O and depleted in SiO$_2$ and CaO. Rare earth element patterns are flat, consistent with a Group I pattern; the enrichment in DH8 is ~50 times chondritic [3]. DH8 is enriched in Zn by a factor of 6 over the average value for type B CAI, approaching the value found in fine-grained CAI. FUN inclusion C-1 was also enriched in Zn [4].

Isotopic data were collected using the PANURGE ion probe [5]. Isotope fractionation factors $F_{\text{Mg}}$ and $F_{\text{Si}}$ are obtained from deviations in the measured $^{25}\text{Mg}/^{24}\text{Mg}$ and $^{29}\text{Si}/^{28}\text{Si}$ ratios relative to the measured values in standards (Fig.1). In B7H10, most spinels show uniform Mg isotopic fractionation of 36.3 ±0.3$/\text{amu}^{-1}$. One FeO-rich spinel grain (10% FeO) from a fine-grained alteration region exhibits $F_{\text{Mg}} = 33.7 \pm 0.8$/\text{amu}^{-1}. Fassaite from B7H10 exhibits uniform $F_{\text{Mg}} = 38.5 \pm 1.6$/\text{amu}^{-1} and uniform $F_{\text{Si}} = 16.4 \pm 1.8$/\text{amu}^{-1}. In DH8, spinels exhibit a range in $F_{\text{Mg}}$ of $9.9$/\text{amu}, from 29.6 to 38.6$/\text{amu}^{-1}$. $F_{\text{Mg}}$ in spinel is not correlated with the FeO content. As in B7H10, the lowest $F_{\text{Mg}}$ in DH8 was obtained for spinel in a spinel-rich cluster surrounded by feldspars. Fassaite in DH8 shows uniform $F_{\text{Mg}} = 30.4 \pm 1.2$/\text{amu}^{-1}, but Si fractionation is variable with $-11.4 < F_{\text{Si}} < 15.0$/\text{amu}^{-1}. Cr isotopic fractionation in spinel is also variable, ranging between 7 and 15$/\text{amu}^{-1}$, with the lowest $F_{\text{Cr}}$ occurring in an Fe-rich spinel. Thermal ionization measurements of a chemically separated sample of DH8 yielded $F_{\text{Cr}} = 18$/\text{amu}^{-1} [6]. In contrast to the large $F_{\text{Mg}}$, $F_{\text{Si}}$, $F_{\text{Cr}}$ effects, Fe in DH8 spinel exhibits only small fractionation, $F_{\text{Fe}} < 3$/\text{amu}^{-1}. Analyses of anorthite in DH8 have high $^{27}\text{Al}/^{24}\text{Mg}$, but yield only an upper limit on the initial $^{26}\text{Al}/^{24}\text{Mg}$ ratio of 5x10^{-7}. The absence or extremely low level of excess $^{26}\text{Mg}$ in DH8 is also consistent with data from C-1 and HAL and demonstrates that neither F nor UN isotope effects are coupled with addition of $^{26}\text{Al}$. Evidence of UN isotopic effects are present in Si. After correcting for fractionation, Si in fassaite in both ψ show a small but resolved deficit in $^{30}\text{Si}$: $\delta^{30}\text{Si} = -2.5 \pm 1.6$/\text{amu} in DH8 and $\delta^{30}\text{Si} = -1.9 \pm 1.6$/\text{amu} in B7H10.

The ion probe data demonstrate large, positive isotope fractionation for the more volatile elements Mg, Si and Cr; thermal ionization data reveal no fractionation for the more refractory Ca and Ti [7]. The near-normal isotopic composition of "volatile" Fe suggests that Fe was introduced during alteration via Fe-Mg exchange from an isotopically normal reservoir. The magnitude of the Mg and Si isotopic fractionation in B7H10 is the largest observed for any
Allende CAI. DH8 is the first coarse-grained CAI to exhibit isotopic heterogeneity in FMg and FSi. The range in FMg among spinels (90/amu-l) is similar to the range in fine-grained CAI. Spinel in DH8 also exhibits systematically larger FMg than the surrounding fassaite. The FMg in DH8 must be interpreted in the context of the petrographic evidence. Poliklitic spinel in fassaite and anorthite laths terminating against fassaite are strongly suggestive of crystallization from a melt. The differences in FMg require either incomplete isotope exchange between fassaite and spinel during formation of DH8 or the preferential exchange of Mg in fassaite during later alteration. The variability in FMg among spinels requires that spinel also experience varying degrees of isotopic exchange with a normal Mg reservoir. DH8 is distinct from type B CAI due to the high abundance of spinel, absence of melilite, and abundance of secondary phases. The latter phases suggest that a precursor, similar to type B CAI, contained melilite which has been completely altered to olivine, hedenbergite, hibonite, grossular, and feldspathoid. The preservation of FUN isotopic effects in DH8 attests to the resistance of spinel and fassaite to mineralogical alteration and isotopic exchange.

The magnitudes of the isotopic fractionation for Mg, Si and Cr approach the values for kinetic isotope fractionation of gaseous species. A remarkably good correlation between the magnitudes of fractionation for Mg, Si and Cr in several FUN inclusions is shown in Fig. 2, in which the fractionation for each element is normalized by m^{-1/2} (Si is treated as SiO2). The tendency for the data from elements of similar volatility to lie along a 45° line emphasizes the importance of kinetic processes involving distillation and recondensation for the production of isotopically heavy Mg, Si and Cr. Because of the lack of correlation of isotope fractionation with chemical abundances, these processes need to produce a reservoir from which the inclusions subsequently formed with chemical fractionation but no further isotopic fractionation. (§606)


---

FRACTIONATION IN FUN CAI

---

Fig. 1. Mg and Si isotopic fractionation in DH8 and DH9. Note expanded scale for FMg. Fig. 2. Correlation between Mg, Si and Cr isotopic fractionation in FUN inclusions. Measured fractionation factors have been scaled by m^{-1/2}.