

COMPOSITIONALLY ZONED FASSAITE IN AN ALLENDE COARSE-GRAINED INCLUSION; S.B. Simon<sup>1</sup> and L. Grossman<sup>1,2</sup>, <sup>1</sup>Department of the Geophysical Sciences, <sup>2</sup>Enrico Fermi Institute, University of Chicago, Chicago, IL 60637

We have analyzed two euhedral, concentrically zoned fassaite crystals in TS22F1, an Allende Type B Ca-, Al-rich inclusion (CAI) to determine how their compositions varied as crystallization proceeded. With no Fe/Mg fractionation (due to the absence of FeO in these inclusions) and wide ranges of MgO, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and Ti<sub>2</sub>O<sub>3</sub> contents, it is not obvious what a "typical" fassaite crystallization trend might be. The latter feature, however, makes fassaite a good recorder of CAI residual liquid compositions. In addition, these crystals provide an opportunity to test some of the predictions of Stolper and Paque [1] regarding zoning in fassaite crystallized from a CAI-like liquid.

The sample consists of 0.5-1 mm crystals of melilite, pyroxene, and anorthite, all of which poikilitically enclose numerous spinel crystals. Based on textural relationships, spinel crystallized first, followed by melilite, fassaite, and anorthite. Electron microprobe traverses were conducted across two ~ 1 mm fassaite crystals. We can use Sc as an index of pyroxene fractionation because it is incompatible in spinel and melilite but compatible in pyroxene. As Fig. 1 shows, pyroxene Sc contents are highest at the cores and drop with increasing degrees of crystallization, as is also the case for the TiO<sub>2</sub><sup>tot</sup> (all Ti calculated as Ti<sup>4+</sup>) contents (Fig. 2), whereas MgO (Fig. 2) and SiO<sub>2</sub> contents increase from core to rim. Al<sub>2</sub>O<sub>3</sub> does not exhibit a clear trend because it is affected by coupled substitutions in addition to changes in liquid composition. Determination of correlation coefficients shows, however, that Al<sub>2</sub>O<sub>3</sub> is positively correlated with Ti (the correlation is stronger for Ti<sup>4+</sup> than Ti<sup>3+</sup>) and strongly anticorrelated with Mg and Si.

An important feature of these pyroxenes is their Ti<sub>2</sub>O<sub>3</sub> systematics. Ti<sub>2</sub>O<sub>3</sub> contents were calculated assuming stoichiometric pyroxenes with four cations per six oxygens. The results (Fig. 3) show that both TiO<sub>2</sub> and Ti<sub>2</sub>O<sub>3</sub> contents decrease from core to rim, and Ti<sub>2</sub>O<sub>3</sub> contents vary much more across the crystals than TiO<sub>2</sub> contents. The Ti<sup>3+</sup> present in the melt was preferentially taken up by the fassaite, efficiently depleting the melt in Ti<sup>3+</sup> relative to Ti<sup>4+</sup>. This suggests that  $D_{\text{Ti}^{3+}}^{\text{cpx/L}} > D_{\text{Ti}^{4+}}^{\text{cpx/L}}$ , as found in [2]. This makes sense, because the larger ionic radius [3] of Ti<sup>3+</sup> allows it to fit better than Ti<sup>4+</sup> into the pyroxene M1 site. Thus, the Ti<sup>3+</sup>/Ti<sup>4+</sup> ratios in the pyroxene were strongly affected by crystal/liquid fractionation; attempts to determine oxygen fugacity at the time of crystallization must take this effect into account by using bulk pyroxene Ti<sup>3+</sup>/Ti<sup>4+</sup> ratios.

Stolper and Paque [1] correctly predicted that pyroxene which crystallized before plagioclase and after the onset of spinel and melilite crystallization would have decreasing TiO<sub>2</sub> contents from core to rim. We observe increasing Mg, however, whereas they predicted decreasing Mg, from core to rim. Their prediction was based on their observation of decreasing MgO and TiO<sub>2</sub> contents in residual liquids produced in crystallization experiments. Apparently in TS22, as Ti<sup>3+</sup> became depleted in the melt, Mg increasingly substituted for it in the pyroxene. Because of the formation of initially Ti-rich, Mg-poor (7-8 wt % MgO) pyroxene in TS22, Mg depletion of the residual melt probably did not occur, whereas the experiments of [1], probably due in part to the absence of Ti<sup>3+</sup>, yielded relatively Mg-rich (10-12 wt % MgO) pyroxene, and an Mg-poor late liquid.

Based on our pyroxene analyses and the estimated  $D_{\text{Ti}^{4+}}^{\text{cpx/L}}$  of ~ 1 [2], the melt contained about 2 wt % TiO<sub>2</sub> at the onset of pyroxene crystallization. Using the bulk composition calculated by [2] for this inclusion and assuming that spinel and melilite TiO<sub>2</sub> and Ti<sub>2</sub>O<sub>3</sub> contents are negligible, we estimate that the inclusion was 60 % solidified when the fassaite started growing. This is reasonable because it is less than the modal sum (68 %) of spinel + melilite + alteration products [2], consistent with the onset of pyroxene crystallization after much spinel + melilite crystallization but before its completion. If TS22 were indeed 60 % crystallized at the onset of pyroxene formation, the Ti<sub>2</sub>O<sub>3</sub> content of the fractionated liquid should have been ~ 3.9 wt %, requiring a  $D_{\text{Ti}^{3+}}^{\text{cpx/L}}$  of about 2. This is lower than the value obtained by [2]. Because the latter value was determined by isothermal experiments on a relatively Ti-rich, non-CAI composition selected to yield Ti<sup>3+</sup>-rich pyroxenes, it

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may not be applicable to all natural CAI's.

This work also allows us to estimate the initial  $D_{Sc}^{cpx/L}$ . This inclusion has a bulk Sc content of 131.3 ppm [4]. Crystallization of 60 % of the liquid to spinel + melilite containing no Sc should yield a residual liquid with 328 ppm Sc. The fassaite cores contain ~ 1400 ppm Sc, and therefore fassaite began crystallizing with a  $D_{Sc}^{cpx/L}$  of ~ 4.3.

REFERENCES: [1] Stolper, E. and J.M. Paque (1986) *GCA* 50, 1785-1806. [2] Beckett, J.R. (1986) Ph.D. thesis, Univ. of Chicago, 373 pp. [3] Shannon, R.D. and C.T. Prewitt (1969) *Acta Cryst. B25*, 925-946. [4] Grossman, L. and R. Ganapathy (1976) *GCA* 40, 331-344.

