BULK CHEMICAL COMPOSITIONS OF TYPE B REFRACTORY INCLUSIONS.

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Introduction: Both the chemical and isotopic compositions of Types A and B refractory inclusions in CV3 chondrites suggest that they may be evaporation residues of high-temperature condensate assemblages [1]. The MgO and SiO_2 contents of these objects are generally consistent with evaporative loss of the amounts of these oxides indicated by their F_{Mg} and F_{Si}, but it is rare when bulk chemical and Mg and Si isotopic data exist for the same inclusion. We report on our efforts to solve this problem by obtaining accurate bulk chemical and Mg and Si isotopic data on each of a suite of inclusions from various CV3s.

Sampling: As discussed previously [1], accurate determination of bulk chemical compositions of refractory inclusions is fraught with difficulties primarily related to sample heterogeneity and the small sample sizes typically used for this purpose. For example, a 1 cm-diameter inclusion weighs 1.75 g, so a bulk chemical composition obtained by modal recombination of an equatorial, 30 µm-thick, thin section of it would be based on only 8 mg, or 0.4 %, of the sample. Similarly, a bulk composition obtained by instrumental neutron activation analysis (INAA) of a relatively large, 30 mg fraction of it would be based on only 1.7 % of the sample. The inclusions employed in this study were large enough that multiple thin sections were prepared from each and relatively large quantities of material were excavated from each. In some cases, material was removed from inclusions that had been sampled and studied previously. The excavated material from each inclusion was ground into a homogeneous powder (5-200 mg but most ~40 mg) which was divided into separate aliquots for INAA determination of major elements; Mg isotopic analysis; O and Si isotopic analysis; and, in some cases, U-Pb geochronologic investigation [2].

INAA: Na, Mg, Al, Ca, Ti, V and Mn abundances were determined in a rabbit irradiation, and Fe in a long irradiation, at the University of Missouri Research Reactor, and SiO_2 was obtained by difference, in each of 6 inclusions from Efremovka, 5 from Allende and one from Leoville. Uncertainites due to counting statistics and standardization were always ≤0.9% of the amounts present for CaO and MgO, and ≤0.6% for Al_2O_3. It was postulated in [1] that each Type A or B inclusion has a chondritic CaO/Al_2O_3 weight ratio of 0.792, and that deviation of the measured ratio from this value in any sample is a measure of the non-representativeness of the sample. Despite the relatively large sample sizes, however, none of the samples in this study appears to be representative according to this criterion, with the ratios obtained ranging from 0.52-1.06. When the data obtained here are commingled with the INAA data reported for 15 other inclusions in [1] and unpublished data for two other Allende inclusions, the mean CaO/Al_2O_3 ratio is 0.88±0.21 (1σ). After removal from consideration of very small samples (≤2mg), leaving only one inclusion from [1], the mean ratio of the remaining 15 samples closely approaches the chondritic value and has a smaller standard deviation, 0.80±0.18. This includes 7 Type As with a mean ratio of 0.86±0.17 and 8 Type Bs with a mean ratio of 0.75±0.20.

Modal Recombination: Using an electron microprobe, wavelength-dispersive point analyses were obtained at spacings ranging from 10-25 µm along automated traverses across the polished surfaces of multiple thin sections of samples from three of the Allende inclusions and the one from Leoville studied by INAA. All are of Type B. From the analyses of all points with analytical sums between 97 and 102%, the volume proportions of each pure phase and phase mixture were determined in each section. For Type B1 inclusions, characterized by a core and a mantle of distinct mineralogy, the volume proportions of phases within each of the units were determined separately, and the areal proportions of core and mantle in thin section were converted to volume proportions assuming an inner sphere is surrounded by a spherical shell in three dimensions. The weight proportions were calculated using the densities of the pure phases and a mean density of 3.3 g/cc for all mixtures. The bulk composition of each section was computed from the mean composition of each phase and phase mixture, and their weight proportions. Golfball is a Type B inclusion with a fassaite-rich mantle and a melilite-rich core. Results for two, 6 mm-diameter, equatorial thin sections, L1 and L2, of this inclusion are shown on a CaO *vs* Al_2O_3 plot in Fig. 1. The point analyses (1280 for L1 and 1422 for L2) cluster at the compositions of the pure phases, and the triangle joining the mean compositions of fassaite, melilite and spinel encloses the analyses of almost all of the spots containing phase mixtures. Intersecting the triangle is a line whose slope is the chondritic CaO/Al_2O_3 ratio. The mean compositions of L1 and L2 have CaO/Al_2O_3 ratios of 0.69 and 0.65, resp., and are plotted on Fig. 1. Also shown is the INAA measurement of 15 mg of Golfball which yields a CaO/Al_2O_3 ratio of 0.70. It was suggested in [1] that analysis of a non-representative sample could be corrected for sample heterogeneity by addition or subtraction of sufficient spinel to obtain the chondritic CaO/Al_2O_3 ratio. If each inclusion actually possesses this ratio, this method works very well for Type A inclusions, which are almost completely composed of

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only two phases, melilite and spinel. Because Type B inclusions also contain major amounts of fassaite and minor anorthite, there are additional ways by which any particular sample of a Type B may be non-representative. For each sample of every Type B inclusion, three different corrected compositions were calculated by adding or subtracting sufficient amounts of each of spinel, melilite or fassaite to obtain the chondritic CaO/Al_2O_3 ratio. Some of the corrected compositions for the three samples of Golfball are visible along the chondritic line in Fig. 1. Because the true bulk composition of each subsample probably lies between its three corrected compositions, the best estimate of the true bulk composition of each subsample is their mean and standard deviation, unless one or two of the estimates lead to unreasonable bulk mineralogical compositions. The best estimate of the bulk chemical composition of an inclusion is the average of the mean corrected compositions of its different subsamples. These are given in the Table for each of the inclusions of this study, along with previously obtained Mg and Si isotopic data for two of them [3].

Discussion: In the Table, the data for F12 are based on a complete, 5 mm-diameter, semicircular section (CaO/Al_2O_3 =0.81); the fassaite-rich core was totally absent from another, 2x2 mm, polar section. For F7, the data are based on two, nearly complete, circular sections, 7x9 and 6x8 mm in size (CaO/Al_2O_3 =0.73 and 0.81, resp.). INAA of a 5 mg sample removed from one end of each of these inclusions gave virtually the same composition as the mantle portion for F12 and of a spinel-melilite mixture for F7, as inferred from analyses of thin sections of the inclusions. The data for Leoville 3537-2 are based on the nearly complete, 7 mm-diameter, circular section seen in [4], INAA of a 1 mg sample studied previously [5], and INAA of 25 mg of a 90 mg, homogenized powder in the present study. The CaO/Al_2O_3 ratios of these three samples are 0.87, 0.72, and 0.52, resp. Corrections to the INAA data on the larger sample for each of spinel and fassaite yielded fassaite contents >75 wt %, which were deemed unreasonable, and were thus disregarded. Subtraction of fassaite from the thin section-based analysis to yield a chondritic CaO/Al_2O_3 ratio gave a bulk composition outside the three-phase triangle; this correction was disregarded. Modal recombination of three additional, 2x2 mm chips of 3537-2 yielded CaO/Al_2O_3 ratios of 0.57, 0.43 and 0.27. Comparison of their mineralogical compositions to that of the large section showed that they were all fragments of the core, and were thus disregarded as being too non-representative for bulk composition purposes.

The data given in the Table are thought to be the best estimates of the bulk compositions of Type Bs obtained to date. Although the data base for superior analyses of Type B inclusions is still limited, none of the data presented here fall on the low-SiO_2, high-MgO side of the condensation curve, or in the region with SiO_2>30% and MgO<12%, unlike the Type B data plotted in [1, Fig. 9]. This is an improvement, as neither of these regions can be reached by evaporation of reasonable condensate precursors.

Measured major element compositions of refractory inclusions may not be representative, even if obtained from powders weighing as much as 90 mg by INAA, or from thin sections of chips as large as 2x2 mm by modal recombination, if such samples are excavated in the normal way from an exposed surface of one side of an inclusion. To increase the probability of obtaining accurate results, either a powder approaching half the mass of an inclusion should be analysed, or an equatorial thin section containing the entire outline of an inclusion should be obtained.

References: [1] Grossman L. *et al*. (2000) *GCA 64*, 2879. [2] Amelin Y. *et al*. (2002) This vol. [3] Clayton, R.N. *et al*. (1988) *Phil. Trans. R. Soc. Lond. A325*, 483. [4] Caillet C. *et al*. (1993) *GCA 57*, 4725. [5] Sylvester P. J. et al. *al*. (1992) *GCA 56*, 134.

Fig. 1
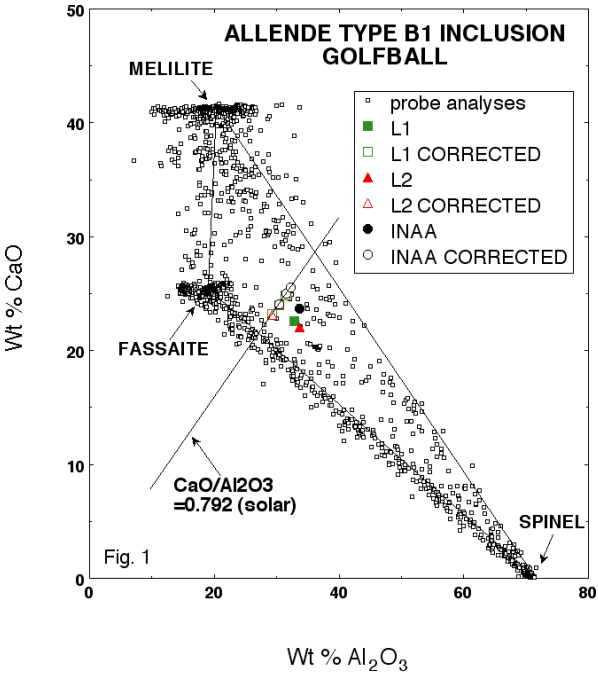
Inclusion	Type	CaO	Al_2O_3	MgO	SiO_2	TiO_2	F_{Mg} (‰/amu)	F_{Si}(‰/amu)
Golfball	B1	24.3±0.5	30.7±0.6	13.0±0.3	29.4±0.5	2.6±0.4		
Leo 3537-2	B1	26.5±0.7	33.5±0.9	11.4±1.4	26.8±2.2	1.8±0.5		
Allende F12	B1	28.8±0.3	36.3±0.4	11.2±0.1	22.3±0.2	1.4±0.4	10.9±0.3	2.4±0.1
Allende F7	B2	25.0±0.4	31.6±0.5	11.7±0.1	29.6±0.6	2.1±0.2	4.9±0.6	1.5±0.1