DISTRIBUTION OF VANADIUM AND MELTING OF OPAQUE ASSEMBLAGES IN EFREMOVKA CAIs

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Abstract. A petrographic and chemical study of compact Type A CAIs from the Efremovka CV3 chondrite strongly suggests that the opaque assemblages (OAs) that they contain were molten at temperatures below the CAI silicate solidus, and that the V-rich magnetite presently observed in association with OAs formed by *in situ* oxidation of their FeNi.

Introduction. The study of the distribution of vanadium in Ca-, Al-rich inclusions can provide important information about the oxidation of their opaque assemblages and the origin of the magnetite that they commonly contain. The two different views about this problem are those of [1], who propose that formation of magnetite took place prior to incorporation into the CAI, and [2], who suggest that the magnetite originated by *in situ* oxidation of the FeNi of the OAs. Most available information about magnetite in OAs stems from study of Allende CAIs, where the often extensive sulphidization obscures the textural relationships between FeNi and magnetite in the assemblage. Ca-, Al-rich inclusions from the reduced subgroup of CV3 chondrites contain OAs that, in general, are devoid of the sulphides that characterize their Allende (oxidized CV3) relatives. In this work, we report petrographic observations and electron microprobe analyses of three compact Type A CAIs (EF1, 2 and 3) from the Efremovka CV3 chondrite. In light of trace element analyses [3] of CAIs in reduced CV3s (Vigarano, Leoville and Efremovka), including the three inclusions studied here, experimental data on metal/silicate vanadium partitioning behaviour [4], phase equilibria in the Fe-Ni-P system [5], and magnetite stability conditions [6], our results provide a plausible model for the formation of V-rich magnetite in opaque assemblages.

Results. EF1, 2 and 3 consist of melilite (>60 % by volume), spinel (8-23 %), perovskite (2-8 %), and minor to accessory amounts of fassaite and OAs. Fassaite occurs almost exclusively as amoeboid intergrowths with the perovskite and/or forming rims (of up to a few tens of microns in width) around the OAs. OAs with fassaite rims are found included in or attached to euhedral spinel grains, and enclosed in melilite crystals as well. The concentration of vanadium is constant in and among spinel grains of the same inclusion (Sp_{EF1}=0.86±0.05 wt.% V_2O_3, N=10; Sp_{EF2}=0.47±0.08, N=10; Sp_{EF3}=0.77±0.06; N=12). In contrast, fassaite grains are generally zoned: those not spatially associated with OAs display well-defined zoning profiles, with rim compositions of 0.77-1.22 wt.% V_2O_3 and cores containing up to 2.10 wt%; fassaite grains rimming OAs are also zoned and somewhat richer in V_2O_3 (1.61-2.34 wt.%) but, unlike the isolated fassaite grains, they often display complicated zoning profiles. Single perovskite grains in the studied inclusions always have homogeneous V_2O_3 contents but display a wide compositional range within an individual CAI (Pv_{EF1}: 0.32-1.32 wt.% V_2O_3; Pv_{EF2}: 0.67-2.21; Pv_{EF3}: 1.16-2.33). Melilite V contents are below the detection limit in all grains analyzed (< 50 ppm). In the OAs, vanadium exists exclusively as an oxide, in V-rich magnetite. High-resolution X-ray scans of the V, Cr and $Fe_{K\alpha}$ lines revealed that vanadium concentrates in discrete micron- to submicron-sized areas dispersed throughout the metallic FeNi of the OA. Analyses of the largest of these (5 μm across) show that they are V-, Cr-rich magnetite; thus, the vanadium is not in solid solution in the metal. Magnetite grains in EF3-OA1 (a large, 100 μm-diameter opaque assemblage in EF3) are anhedral; the coarser-grained ones occur preferentially at and near the edges of the assemblage and are somewhat poorer in vanadium (19-22 at.% V) than the ones in the interior (21-25 at.% V). EF3-OA1 contains two distinct textural components: the larger one is heart-shaped (named The Heart), 80 μm across, has a bulk Ni content of 9.2 wt.% (determined by broad-beam microprobe analyses) and consists of skeletal crystals of kamacite oriented parallel to the (111) plane of their taenite host, determined according to the method described by [7]. The Heart is partially rimmed by a band of variable width (<1-5 μm) of calcium phosphate, which locally forms euhedral crystals. The smaller mass is attached to The Heart and elongated in shape (and accordingly named The Leech). It lacks taenite and is not rimmed by phosphate (except at the contact with The Heart); it also contains a small (7x2 μm) bleb of pure powellite (W-free, $CaMoO_4$), and another even smaller inclusion (2x1 μm) of an unidentified W-Mo-S-Ca mineral (plausibly a fine intergrowth of powellite and molybdenite). Despite the fact that chemical compositions of kamacite (4.2-6.7 at.% Ni) and magnetite (19-25 at.% V) in The Heart and The Leech are indistinguishable, their distinct mineralogies and textural relationship strongly suggest that they were once individual opaque assemblages that partially coalesced in the molten state.

Formation of V-rich magnetite in OAs: Vanadium-rich magnetite in CAIs is <u>always</u> spatially associated with opaque assemblages. On the other hand, there is no relationship between the bulk vanadium content of CAIs in reduced CV3 chondrites and the amount of opaque assemblages that they contain. Although the OAs may have been previously enriched in vanadium relative to the CAI through reduction of this element from the CAI liquid (since $D_V^{liq.met./liq.sil.}$ ~5000 at 1533°K and log f_{O_2}=-19, according to extrapolation from experimental data by [4] for partitioning of V between S-bearing liquid metal and a silicate liquid of basaltic composition), it is likely that

some vanadium was already present in the reduced state dissolved in the metal of the OA. However, the lack of correlation between the V and, for instance, the Ir concentrations in CAIs [3], indicates that the bulk vanadium enrichment of the CAI relative to CI (factors of 16, 3 and 24, for EF1, 2 and 3, respectively) is not due to the presence of different amounts of OAs. Experimental data by [6] show that magnetite and an Fe_xNi_y alloy can coexist at equilibrium only at T<950°K if the composition of the alloy is such that y<15 (as observed in our Efremovka OAs). At those temperatures, the oxygen fugacity required for magnetite-metal equilibrium (log f_{O_2}=-22) is about six orders of magnitude higher than that of a gas of solar composition. Therefore, even if magnetite were present in the OAs prior to their incorporation into CAIs, the magnetite would have been unstable and, consequently, reduced to metal under the f_{O_2}-T conditions typical of CAI silicate liquids (T≥1500°K, log f_{O_2}~-19; [8]). Incorporation of the OAs into the CAIs at subsolidus (and more oxidizing) conditions is unlikely since OAs, especially the smaller ones, are commonly mantled by fassaite and enclosed in euhedral spinel grains (an early-crystallizing phase). Then, despite the probable effect of the high V contents of magnetite on the magnetite-FeNi equilibrium conditions, it is safe to say, in light of these data and in agreement with [2], that the magnetite nucleated at temperatures well below the solidus of the CAI, and therefore must have formed *in situ*.

Vanadium in CAI silicates: Spinel compositions suggest that vanadium is compatible in this mineral. Then, the homogeneity of the vanadium contents among different spinel grains within the same CAI suggests that crystallization of this mineral in EF1, 2 and 3 occurred in a narrow temperature interval. Subsequent cooling would induce the oxidation of vanadium [2] that may then be included as V $^{3+}$ in perovskite and fassaite crystallizing from the late CAI residual liquid. The fassaite grains that crystallized around OAs may have incorporated more vanadium (from the locally V-enriched OAs) than the isolated ones. This can explain the higher V concentrations in fassaite rims (relative to isolated fassaite grains) and the relative depletion of V in the magnetites from the exterior (relative to the ones in the interior) of the OAs, due to nucleation and growth of magnetite at lower temperatures in areas that had been depleted in V by the earlier crystallization of fassaite.

OA-CAI equilibrium: If the currently observed V contents reflect equilibrium partitioning for this element between the opaque assemblages and the CAI silicates, it is possible to estimate the OA/CAI vanadium distribution coefficient when final (after cooling and oxidation) OA-CAI equilibrium was achieved. Thus, the apparent metal/silicate distribution coefficient can be calculated according to the expression: $D_v^{OA/CAI}$ = $[V]_{OA}/[V]_{sil}$, where $[V]_{OA}$= $x_{mt}[V]_{mt}$ and $[V]_{sil}$=$x_{sp}[V]_{sp}$ +$x_{fas}[V]_{fas}$ +$x_{pv}[V]_{pv}$, x_i and $[V]_i$ being the mass fractions and vanadium concentrations, respectively, of the indicated minerals. Modal and microprobe analyses yield values of $D_v^{OA/CAI}$ = 9 for EF1, 5 for EF2, and 8 for EF3, which are in very good agreement with V-distribution values in three Allende CAIs ($D_v^{OA/CAI}$ =6-60) estimated by [2].

Melting of OAs: The metal that now constitutes the major part of the OAs must have been at least partially molten at the time of complete solidification of CAI silicates. According to experimental results on the phase relationships in the Fe-Ni-P system [5], an alloy containing >8.9 wt.% Ni and 1.2 wt.% P will melt at 1333°K, well below the considered CAI solidus temperature (~1500°K). The bulk P content of EF3-OA1 must have been at least 1.2 wt.% (estimated by assuming that all P currently in phosphate was dissolved in the metal at those f_{O_2}-T conditions). Therefore, and at least in Efremovka, the presence of sulphur is not necessary to induce melting of the OA since the P contents of the FeNi alloys were high enough to maintain the metal partially molten until after their host CAI silicates were completely crystallized.

In summary, based on considerations of magnetite-FeNi equilibrium conditions, the observed spatial association between V-rich magnetite and metal in the OAs, and the close textural relationship between the OAs and euhedral spinel grains, we conclude that V-rich magnetite formed *in situ* in CAIs by oxidation of the metal of OAs at low temperatures (below 950°K). Considering also that the OAs probably remained molten after the complete solidification of the CAI silicates, a plausible sequence of events in the history of the OAs in CAIs from EF1, 2 and 3 is as follows: (1) melting of the CAI-OA and reduction of some V from the CAI liquid at T≥1500°K and log f_{O_2}~-19; (2) nucleation and growth of euhedral spinel crystals and melilite above 1500°K; (3) cooling of the CAI and oxidation of V; (4) crystallization of fassaite and perovskite from the residual, Ti-rich, CAI liquid; (5) solidification of the FeNi alloys in the OAs (approximately at 1333°K); and (6) nucleation and growth of magnetite (T≤950°K) within and around opaque assemblages. The investigation of OAs in CAIs from the reduced CV3 chondrites opens an interesting field of further research aimed at understanding the origin of opaque assemblages and the relationships with their CAI hosts.

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