ALTERATION OF CV3 CARBONACEOUS CHONDRITES: PARENT BODY vs. NEBULAR PROCESSES

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Abstract. The major components of the CV3 chondrites (Ca-Al-rich inclusions, chondrules, dark inclusions and matrix) show diverse degrees of complex and heterogeneous alteration by alkali metasomatism, oxidation and sulfidation, aqueous alteration, thermal metamorphism and dehydration. Although nebular processes can not be excluded in some cases, our literature survey suggests that alteration occurred under diverse conditions mainly on the CV3 parent body and is largely responsible for the mineralogical and chemical differences between oxidized and reduced CV3 subgroups [1].

Introduction. McSween [1] divided the CV3 chondrites into reduced (CV3(red)) (with kamacite, taenite, troilite) and oxidized (CV3(ox)) (with magnetite, Fe-Ni sulfides, Ni-rich metal) subgroups. The CV3(ox) chondrites (*Allende, Bali, Grosnaja, Kaba, and Mokoia*) have higher abundances of matrix [1] and higher bulk concentrations of Na and Fe than the CV3(red) chondrites (*Arch, Efremovka, Leoville, and Vigarano*) [2]. Similarities in mineralogy, petrography, bulk chemistry and the presence of fragments of CV3(ox) material in the CV3(red) indicate that both subgroups are probably from the same parent body. But there is little agreement on how, when and where the differences between the CV3 (ox) and CV3(red) were established. Here we summarize mineralogic and chemical evidence of alteration in CV3s, to distinguish between nebular and parent-body processes.

Alkali metasomatism. All CAIs in Allende experienced secondary alteration of different degrees [3, 4]: melilite was replaced by a mixture of grossular+anorthite+feldspathoids; perovskite was replaced by ilmenite; fassaite was replaced by a mixture of ilmenite+Na-rich phlogopite+chlorite+serpentine; spinel was replaced by phyllosilicates or a mixture of olivine+feldspathoids. Hashimoto and Grossman [3] conclude that this alteration took place in the relatively low temperature (300-900 K) solar nebula; Si, Na, K, Fe, Cr, H_2O and Cl were introduced into the CAI's and Ca was lost. In contrast with Allende, fluffy type A's in Vigarano, type B in Efremovka, and fine-grained CAI's in Leoville and Efremovka appear to have escaped this alteration and have low bulk alkalis and halogens [5, 6]. Most chondrules in Allende experienced various degrees of alkali metasomatism: nepheline, sodalite, and minor amounts of grossular, wollastonite, andradite, kirschtenite and hedenbergite replace anorthite-normative glass and plagioclase in chondrule mesostases [7].

Oxidation and sulfidation. Palme and Wark [8] argue that matrix olivine in the CV3(ox) condensed before Ni-rich metal which later was converted by condensation of S to Ni-rich sulfides. However, mineralogy and chemistry of the opaques in the CV3s are consistent with their formation by exsolution, sulfidation and oxidation of originally homogeneous alloys at low-T (~770 K) and higher than solar gas fS_2 and fO_2 [9]. The similarities in the equilibration temperature, fS_2 and fO_2 for opaques in CAIs, chondrules and matrices of the CV3s suggest that these components share a late low-temperature history, probably on a parent body [9]. The formation of magnetite, Ni-rich metal, Fe-Ni sulfide, and Co-rich kamacite in a few type 3 H, L and LL chondrites during parent-body alteration [10] and redistribution of S during mild thermal metamorphism [11] support this suggestion. The planar precipitation of magnetite in Fe-rich olivine in Mokoia and Allende [12, 13] may have occurred at this time. The formation of saponite and magnetite along the planar zones in Fe-rich olivine in Mokoia indicates that the oxidation event predates aqueous alteration of this meteorite [13].

Aqueous alteration. Most CV chondrites show diverse aqueous alteration effects. A few CAIs in Allende have phyllosilicates (margarite, clintonite, Na-phlogopite, chlorite) which are thought to be formed in the low-temperature (330-470 K) solar nebula [3, 14, 15]. In contrast, in both Kaba and Mokoia the matrices, chondrules, and CAIs all contain considerable amounts of phyllosilicates which probably formed during low-temperature (<370-410 K) parent-body aqueous alteration [12, 13]. The phyllosilicates in the matrix of Mokoia are mostly Fe-bearing saponite formed by alteration of ferrous olivine, while those in chondrules and CAIs are both Fe-bearing saponite and Na-rich phlogopite formed by alteration of Ca-pyroxene, anorthite, spinel, and Ca-Al-Si-rich glass. The phyllosilicates in matrix and chondrules of Kaba consist only of saponite indicating different conditions of alteration. The formation of saponite from matrix olivine required transport of Al, alkalis, Fe and H_2O. The intimate intergrowths of magnetite and ferrihydrate with saponite in Mokoia matrix and the occurrence of submicron Fe-Ni sulfides in Kaba matrix suggest that oxidation played a more important role in the alteration of Kaba than Mokoia. Dark inclusions provide aditional evidence of heterogeneous aqueous alteration of the CV3 parent body [16, 17].

Thermal metamorphism and dehydration. The range of matrix olivine compositions decreases through the sequence Kaba-Mokoia-Vigarano-Grosnaja-Allende, possibly reflecting equilibration during thermal metamorphism [18, 19]. The apparent equilibration of matrix olivine appears to correlate with the enrichment in Fe of spinel in CAIs [4] and with the ratios of normative Ca-rich pyroxene to feldspathoid + phyllosilicates in matrices of these meteorites [18].

Formation of dark inclusions. Dark inclusions (DI) are common in all CV3 chondrites [20]. The similarities in bulk chemistry [21, 22], mineralogy and isotope compositions [21-25] between the DIs and their respective hosts indicate that the DIs formed from CV3 material. Several DIs, including DC1 and DC2 in Vigarano [16], LV-1 in Leoville [25] and All-AF in Allende [17, 22, 23] consist almost entirely of homogeneous ferrous olivine which has high Al content. The textures of these DIs indicate that olivine grains form pseudomorphs after chondrules and CAIs. Kojima and coworkers [16, 17] suggest that these DIs experienced extensive aqueous alteration which resulted in replacement all major components including chondrules and CAIs by phyllosilicates. The subsequent thermal metamorphism proceeding under mild temperatures (~600 K) transformed the phyllosilicates to the ferrous olivine. Most DIs in Allende are significantly depleted in Na and K and have slightly higher Fe, Mn and Ca than bulk Allende [21]; the All-AF inclusion has large excesses in Na, K, Cl, and Au and some depletion in Ca and Ti [22]. Most of these elements tend to be mobile during aqueous alteration in carbonaceous chondrites [26]. Many DIs show textural and chemical evidence of thermal processing, including brecciation, heating, loss of volatile elements (S, C, Cl, and Zn) and equlibration of olivine compositions [24]. The oxygen isotope compositions of the DIs in Allende, Leoville and Vigarano correlates with degree of their alteration [20]. Johnson et al. [20] conclude that the O isotopic compositions of DIs resulted from the exchange of silicates with the nebular gas below ~550 K. Extreme alteration and the heavy O isotopic composition of All-AF [22] suggest that exchange may have occurred on the parent-body instead.

Fayalitic rims. The compositionally uniform ferrous olivine rims around individual forsterite grains and type I chondrules are typical for the CV3(ox) [27-29]. Based on high abundances of minor elements (Al, Cr, Ti) in the ferrous olivines, their narrow compositional ranges (in Allende and Grosnaja), petrographic observations and thermodynamic calculations, Peck and Wood [27] suggest that these rims formed by condensation from highly-oxidized solar nebular gas. However, Hua et al. [28] and Weinbruch et al. [29] showed that high contents of Al, Cr and Ti in ferrous olivine are probably due to (a) the presence of chromite and spinel inclusions which possibly formed by oxidation of olivine and (b) diffusion of these elements from adjacent olivine. The relatively narrow compositional ranges of ferrous olivine in Allende and Grosnaja is consistent with equilibration during thermal metamorphism experienced by these meteorites. Weinbruch et al. [30] reported significant differences in oxygen isotope compositions of individual forsterite grains and fayalitic rims. The latter have similar oxygen isotope compositions to matrix olivine and bulk DIs possibly indicating genetic relationships. Because the alteration processes affecting DIs in the CV3s resulted in enrichment in ^{18}O and ^{17}O of the DIs, it seems plausible that the same processes produced ferrous olivine rims in the CV3(ox).

Dating of secondary alteration. Inferred initial $^{26}Al/^{27}Al$ ratios in primary (spinel, anorthite) and secondary (grossular, sodalite) phases in two Allende and one Leoville type B inclusions show that grossular and sodalite must have formed at least 2.4-3.9 Ma after crystallization of spinel and anorthite [31]. Varitaions in the initial $^{129}I/^{127}I$ ratio for individual temperature fractions during stepwise heating analyses of chondrules, CAIs and bulk samples of Allende have been attributed to secondary processes lasting for several Ma (2 Ma before Bjurbole to about 5 Ma after Bjurbole) [32-36]. Because the relatively unaltered Vigarano (CV3-red) has an apparent I-Xe age of 8.6 Ma before Bjurbole [32, 33], it seems likely that the alteration of the major Allende components took place on the parent body rather than in the solar nebula; but more data are needed.

Conclusion. The CV3 carbonaceous chondrites experienced various types of alteration processes, including alkali metasomatism, oxidation and sulfidation, aqueous alteration, thermal metamorphism and dehydration. Palme and Wark [8] conclude that all major components of the CV3s experienced gas-solid reactions in the highly-oxidized solar nebula; the major difference between the CV3(red) and CV3(ox) is the extent of the gas-solid reactions. In this case, the CV3(ox) and CV3(red) sampled regions of the solar nebula with different thermal history suggsting that alteration of chondrite components and the subsequent accretion took place more rapidly that the various components were able to migrate from one meteorites' formation region to the other. Although alkali metasomatism of CAIs could have taken place partly in the solar nebula [38], most of the other alteration processes appear to have operated for a long period of time on the CV3 meteorites. Most of the CV3s are breccias; Allende, Vigarano and Arch contain solar-implanted gases. The alteration and brecciation occurred prior to lithification of the CV3 parent body. These processes resulted in the formation of the oxidized subgroup of the CV3s; the reduced CV3 subgroup contains largely unaltered material. The CV3(red) chondrites are inadequately studied relative to the CV3(ox).

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