COMPOSITIONAL AND MINERALOGICAL TRENDS IN FINE-GRAINED CHONDRULE RIMS IN CO CHONDRITES

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Summary The compositions and mineralogy of fine-grained chondrule rims in 6 CO chondrites, spanning the range of petrologic subtypes from petrologic types 3.0 to 3.7, have been determined by electron microprobe analysis and TEM. Based on individual electron microprobe analyses, Fe, Mg and Mn are uncorrelated and somewhat heterogeneous in rims in ALH A77307 (3.0), but rapidly become tightly clustered and develop strong positive correlations by petrologic type 3.2 (Felix). In contrast the minor elements Cr, Ti and Al are relatively homogeneous in low petrologic type CO chondrites, but become progressively more heterogeneous as the petrologic subtype increases. These changes are strongly correlated with changes in the mineralogy and mineral chemistry of the fine-grained rim materials. Olivine-Cr-spinel geothermometry from coexisting olivine and spinel grains in the rims suggest equilibration temperatures of ~600°C for Ornans and 1000°C for Warrenton.

Introduction. The CO3 carbonaceous chondrites have been shown to define a metamorphic sequence, similar to that observed in the ordinary chondrites [1,2,3]. Petrologic studies of several CO chondrites [2] have established a detailed petrologic sequence which is broadly consistent with that defined by thermoluminescence studies [3]. The detailed compositional variations in chondrule silicates reported by [2] and [4] have provided support for the concept that these meteorites were metamorphosed within a parent body environment. Although many aspects of the compositional systematics observed in chondrules through the petrologic sequence are relatively well established [2,4,5], the chemical and mineralogical changes which occur in the fine-grained matrix of these meteorites have received relatively little attention. Fine-grained rims in several CO chondrites have been studied in detail in order to provide new insights into how fine-grained matrix materials respond to metamorphism. I have studied fine-grained rims and matrix in 6 CO chondrites, ALH A77307 (3.0), Kainsaz (3.1), Felix (3.2), Ornans (3.3), Warrenton (3.6) and Isna (3.7) which span the range of degrees of equilibration found in this group. We have previously reported major, minor and trace element compositional data for ALH A77307, Kainsaz (3.1), Ornans (3.3) and Warrenton (3.6) [6-9]. This study has added additional compositional data for Felix (3.2) and Isna (3.7) and mineralogical data for matrix phases. Major and minor element compositions of fine-grained rims and matrix were measured by electron microprobe using a 10μm beam. These regions were then demounted from the thin sections and were studied by TEM techniques.

Compositional variations The elemental correlations in fine-grained rims have been examined using individual electron microprobe analyses, rather than averaged data. These data reveal complex, but extremely clear, systematic compositional variations through the petrologic sequence and provide some important additional insights into the response of matrix to increasing degrees of equilibration. The response of different groups of elements to metamorphism varies considerably and some elements appear to be highly sensitive and equilibrate rapidly, especially Fe, Mg and Mn. In ALH A77307 and Kainsaz the rim Fe/Si and Mg/Si ratios are variable, but there is no correlation between these two elements, indicating that the matrix is not a simple two component mixture of Mg and Fe-bearing phases [6]. In moving through the petrologic sequence Mg and Fe become correlated and the Mg/Fe ratios of rim analyses increase rapidly and become more tightly clustered, such that even by petrologic subtype 3.2 (Felix) they are essentially equilibrated. Mn shows very similar behavior and is positively correlated with Fe in all the subtypes except 3.0. In this respect Mn differs significantly from the other minor elements, such as Cr, Ti and Al, which become progressively more homogeneous through the petrologic sequence. In ALH A77307, Al and Cr are uncorrelated and very tightly clustered. However, with increasing petrologic subtype the spread in Cr and Al increases significantly and the two elements also become highly correlated, such that by Isna, they exhibit anextremely well-defined positive correlation.

Matrix mineralogy Mineralogically, matrix in the least equilibrated chondrite of the group, ALH 77307, differs significantly from the other CO chondrites. It consists of a complex unequilibrated assemblage of olivines, pyroxenes, amorphous material, sulfides, oxides and iron nickel metal. Many different aggregates, with distinct textures and mineralogies have been recognized in this meteorite, which may represent distinct nebular dust components [6]. In contrast, matrices and fine-grained chondrule rims in Kainsaz are essentially completely crystalline with fine-grained olivine as the dominant phase, and low-Ca pyroxene, aluminous Cr-bearing spinel and kamacite with ~4.5 at.% Ni as the accessory phases. The mineralogy of

Ornans rims differs in some respects from Kainsaz. Certainly olivine is the dominant phase, but low-Ca pyroxene appears to be extremely rare. Very fine-grained Cr-bearing, hercynitic spinel (<200 nm) is extremely common interstitial to fine-grained olivine and rare crystals of awaruite have also been found. The mineralogy of Warrenton matrix is essentially identical to that in Ornans, being dominated by olivine, with common Cr-spinel and accessory awaruite.

Mineral chemistry There are significant changes in the mineral chemistry of olivine and spinel through the petrologic sequence. Olivine in ALH A77307 is highly unequilibrated and ranges in composition from Fo_{100-30}. In Kainsaz the range in composition is much more restricted (Fo_{28-52}) with a mean of 44.28. None of the very Fo-rich compositions which are present in ALH A77307 have been found in Kainsaz. The olivine compositions become progressively more Mg-rich and the range of compositions more restricted in moving up the petrologic sequence. In Ornans the mean is $Fo_{46.57}$ with a range of Fo_{40-52}, and by Warrenton the mean Fo is 59.52 with a range of Fo_{54-64}. The ranges for Kainsaz and Warrenton are very consistent with those reported by [10]. The spinel composition also changes as a function of petrologic type, but these variations are more complex than for olivine and do not appear to be systematic. Ornans is intermediate in petrologic type to Kainsaz and Warrenton, but has lower Mg/(Mg+Fe) and Cr/(Cr+Al) ratios than either Kainsaz and Warrenton which have similar Mg/(Mg+Fe). Warrenton has the highest Cr/(Cr+Al) ratio of all three meteorites. Analyses of spinels in Kainsaz carried out on TEM samples mounted using C grids rather than the conventional Cu to avoid Zn-Cu peak interferences show that there is detectable Zn present. The concentrations are low and lie in the 0.5 to 1 wt% ZnO range, but confirm that spinel is probably the major carrier of Zn in the rims of these meteorites as suggested previously [8].

Olivine-spinel geothermometry. The compositions of coexisting fine-grained Cr-spinel and olivine have been used to calculate the possible metamorphic temperatures for Kainsaz, Ornans and Warrenton using the calibration of [11]. The data for Ornans consistently give temperatures around 600°C and show a small spread in the data. In contrast, values for Warrenton are much higher and cluster around 1000°C. Kainsaz on the other hand gives much higher temperatures, in excess of 1400°C, which would suggest that these values do not represent equilibrium.

Discussion The compositional observations present above confirm earlier observations that the matrices of the CO chondrites become more Mg-rich with increasing petrologic type [1,2]. However, it is clear that the behavior of different elements is complex and they respond differently during the process of equilibration. Fe, Mg and Mn rapidly become homogeneous, whereas Cr, Ti and Al become progressively more heterogeneous. These variations can be closely correlated with the changes in mineralogy and chemistry of the fine-grained phases. Olivine, the dominant Fe, Mg and Mn-bearing phase, becomes equilibrated and its composition moves to more Mg-rich values. The progressive increase in the heterogeneous distribution of Cr, Al and Ti is evidently the result of the increase in the abundance of Cr-spinel, the major carrier of these elements. Olivine-spinel geothermometer provides the first quantitative determination of metamorphic temperatures for the CO chondrites, but significance of the data are not clear. For Kainsaz, the very high temperatures are obviously unrealistic and suggest that the spinel and olivine are not equilibrated. In view of the heterogeneity of olivine compositions in this meteorites, this is a reasonable conclusion. In contrast, olivine compositions in Ornans and Warrenton are quite homogeneous and the spinel compositions show little variation indicating that they are at equilibrium. The equilibration temperature determined for Ornans of ~600°C is a reasonable value and is within 100°C of the peak metamorphic temperatures estimated by [12] based on Fe-Mg diffusion modeling of zoning in chondrule olivines. However, the temperature of 1000°C for Warrenton appears to be too high and would be close to the melting point of troilite. It is noteworthy, however, that the increase in temperature is consistent with petrologic type. One possible explanation is that the matrix in Warrenton experienced a short excursion to much higher temperatures and these are recorded in the fine-grained olivine and spinel which would respond rapidly to such changes. Further studies of equilibration temperatures in other CO chondrites may help clarify this problem.

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