THE ROLE OF MICROCHEMICAL ENVIRONMENTS IN THE ALTERATION OF CM CARBONACEOUS CHONDRITES

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Introduction: Aqueous fluids have left their fingerprint on almost all the known chondrite groups and attest to the fact that water was a widespread agent of change in the early solar system [1,2]. The interaction of liquid or gaseous water with the primary products of nebular processes caused significant textural, mineralogical, compositional and isotopic changes that are often very complex to interpret. In particular, there has been an extensive discussion in the literature as to whether alteration of carbonaceous chondrites occurred prior to or post accretion of asteroidal parent bodies. These ideas have been best developed for the CM carbonaceous chondrites [3,4]. There is a general consensus that post accretion parent body alteration affected almost all CM chondrites, but the issue of whether preaccretionary alteration affected some or all of these meteorites has yet to be resolved [2,5].

Our systematic studies of alteration textures in CM2 chondrites have provided a significant body of evidence that many of the textural and compositional characteristics of CM chondrites can be explained by the presence of localized differences in geochemical conditions, particular pH, that occur over the scale of 10s of microns. These localized variations in pH drive dissolution and precipitation of minerals at reaction fronts where changes in fluid pH occur. The importance of these localized variations have not been recognized previously in the literature, but provide a coherent framework for the interpretation of many of the complex textural characteristics of CM chondrites, particularly those that have been used to argue for preaccretionary alteration. Specific lines of evidence to support the view that microchemical environments were of considerable importance during aqueous alteration are discussed below, focusing specifically on the evidence for differences in geochemical conditions between the interiors of altering chondrules and those in the adjacent fine-grained rims or matrix.

Alteration of FeO-rich olivines. In their classic study of the textural characteristics of CM chondrites [3] noted that fracture surfaces of FeO-rich olivine grains within broken chondrules, that are in direct contact with hydrated fine-grained rims, show no evidence of aqueous alteration. However, in the interior of these chondrules, olivine shows clear evidence of alteration. [3,4] used this evidence to argue that alteration of the chondrule had occurred prior to fragmentation, followed by accretion of a rim of hydrated dust onto the chondrule fragment before final assembly of the parent body. No further alteration had occurred on the asteroidal parent body, otherwise alteration of the olivine at the fracture surface would have occurred. Although this interpretation has its merit, [6] showed that there is an alternative and perhaps more viable explanation for such features, which are quite widespread in CM chondrites. [6] described examples of FeO-rich olivine chondrules in CM chondrites, which are surrounded by fine-grained rims (e.g. Fig. 1). FeO-rich olivine on the periphery of this chondrule, in direct contact with the fine-grained rim, shows no evidence of replacement by serpentine, whereas the bars of olivine in the chondrule interior are heavily replaced. This evidence shows unequivocally that alteration in the interior of the chondrule occurred preferentially to that on the chondrule exterior, an effect which cannot be explained by any form of preaccretionary alteration scenario. These observations are entirely consistent with the hypothesis that geochemical conditions on the interior of the chondrule are such that aqueous alteration of olivine was promoted whereas on the exterior of the chondrule, alteration is inhibited or at least retarded.

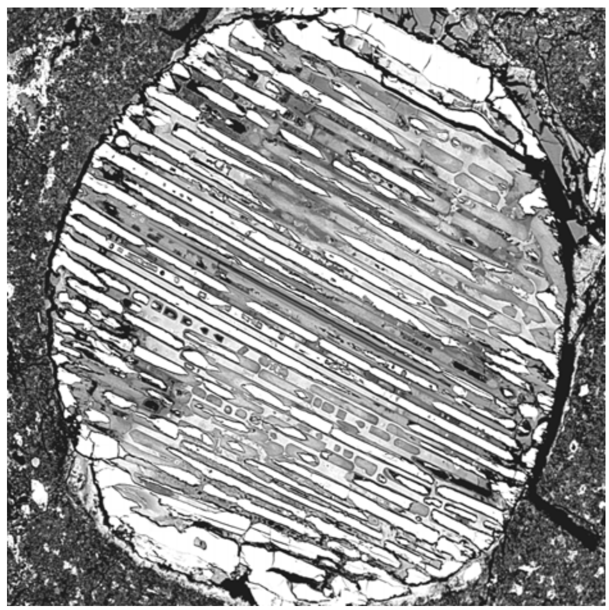

Figure 1. Barred type IIA chondrules from ALH81002 (CM2) showing extensive alteration of olivine bars in the chondrule interior, but little or no alteration where the olivine is in contact with the fine-grained rim. Field of view = 0.5 mm

Phosphate-rich zones around type IIA chondrules: We have documented narrow layers of Ca-phosphate enrichment at the interface between altered type IIA chondrules and their surrounding fine-grained rims in one of the least altered CM chondrites Y791198 [7]. In other CM chondrites that show more advanced degrees of alteration these layers of enrichment progressively disappear and the phosphate becomes distributed into the fine-grained rims [7]. These zones of enrichment are much more subdued or are absent around type IA chondrules. Chondrule mesostasis in type IIA chondrules is commonly enriched in P compared with type IA chondrules, so that the formation of these phosphate-rich layers can be related directly to the dissolution of chondrule mesostasis. The fact that phosphorus, mobilized from chondrule glass during alteration, precipitated at the chondrule/rim interface clearly shows that this feature represents a geochemical boundary at which conditions change abrubtly, driving precipitation of Ca-phosphate from solution.

Carbonate occurrences. Further evidence supporting the view that geochemical conditions in the interior of the chondrules was different from the surrounding fine-grained rims and matrix comes from the occurrence of carbonate in CM chondrites. Our detailed studies CM chondrites [8] show that Ca-carbonate rarely occurs within the interior of chondrules and is essentially absent from fine-grained rims. Carbonates typically occur outside chondrules associated with aggregates of PCP or distributed within clastic matrix in brecciated CM chondrites. Excluding CAIs, chondrule mesostasis contains the most elevated concentrations of Ca in CM chondrites, so that carbonate formation within chondrule mesostasis would be anticipated. Certainly, this has happened in altered CAIs, which are frequently pseudomorphed by significant abundances of carbonates (both calcite and dolomite). The absence of Ca carbonate within chondrules shows that geochemical conditions were not favorable locally for carbonate precipitation. However, Ca leached from chondrule mesostasis by altering fluids was able to precipitate outside chondrules within the matrix where conditions were favorable for carbonate precipitation.

Discussion: This evidence suggests that geochemical conditions in the interior of chondrules were different from those in fine-grained rims and matrix for at least some period of aqueous alteration. In all the cases documented above, the observed behavior is entirely consistent with the presence of localized differences in the pH of the fluid, with the interior of the chondrules having a lower pH than the fine-grained rims and matrix. For the case of the alteration behavior of FeO-rich olivine on the interior vs exterior of chondrules, it is well-known from experimental studies [9], that the rate of alteration of olivine decreases as pH increases. The lack of alteration of FeO-rich olivine in direct contact with fine-grained rims is consistent with this scenario, i.e. the higher alkalinity of solutions outside the chondrule have inhibited olivine alteration whereas in the interior, where solutions are more acidic, olivine alteration is enhanced. Further, the solubility of Ca-carbonate and Ca-phosphate both increase in acidic solutions and hence precipitation of these phases within the chondrule will be inhibited by lower pH values. However, as these species migrate down chemical potential gradients within the fluid, they will eventual reach the chondrule exterior where they will encounter more alkaline fluids that favor phosphate and carbonate precipitation. The occurrence of Ca-phosphate immediately adjacent to the edge of the chondrules in Y791198 suggests either that Ca-phosphate precipitates more readily at lower pHs than Ca-carbonate or that once precipitated, the solubility of the phosphate is relatively low compared with Ca-carbonate.

What causes the differences in geochemical conditions between chondrule exteriors and their surrounding fine-grained rims? The initial pH of water that interacted with the solid anhydrous components of CM chondrites would have been essentially neutral assuming that it was derived by melting of accreted water ice. The earliest phase of alteration would have involved hydrolysis reactions with the very fine-grained materials that constitute matrix and fine-grained rims. These hydrolysis reactions consume protons rapidly as metal-oxygen bonds in silicates are broken [10]. Hence the fluid will evolve rapidly to become alkaline in character. Geochemical modeling of the alteration of carbonaceous chondrite mineral assemblages consistently predicts that such an increase occurs. Hence, the rapidly altering fine-grained material will coexist with a strongly alkaline fluids. This fluid will begin to interact progressively with the coarser-grained components of chondrules. Mesostasis is perhaps the most susceptible component of chondrules to alteration and will begin to alter early. This material has unique properties compared with any other chondritic component, but the most important in this context is the fact that it is SiO_2-rich with 45-75 wt% SiO_2 [11]. The increase in pH associated with hydrolysis of minerals increases with the cation content of the mineral in question. Solutions in contact with minerals with low cation contents and high numbers of Si-O-Si bonds show smaller increases in pH. It is therefore plausible that the high Si content of mesostasis glass results in a smaller increase in pH on the interior of chondrules compared with the exterior. Hence although pH in the chondrule interiors will increase, it may not reach such elevated values as occurs in the fine-grained rims or matrix. Differences in pH between the interior of altering chondrules and fine-grained rims probably only existed for limited periods of time and eventually dissipated as alteration became more advanced.

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Acknowledgements: Research funded by NASA grant NAG5-13046 to A.J. Brearley (PI).