

ON THE BEHAVIOR OF PHOSPHORUS DURING THE AQUEOUS ALTERATION OF CM2 CARBONACEOUS CHONDRITES Adrian J. Brearley¹ and Lysa J. Chizmadia², ¹Dept. of Earth and Planetary Sciences, MSC03-2040, University of New Mexico, Albuquerque, NM 87131, USA (brearley@unm.edu), ²Institute for Astronomy, University of Hawaii, 2680 Woodlawn Dr., Honolulu, HI 96822

Introduction: During the earliest period of solar system formation, water played an important role in the evolution of primitive dust, both after accretion of planetesimals and possible before accretion within the protoplanetary disk. Many chondrites show evidence of variable degrees of aqueous alteration, the CM2 chondrites being among the most studied [1]. This group of chondrites is characterized by mineral assemblages of both primary and secondary alteration phases. Hence, these meteorites retain a particularly important record of the reactions that occurred between primary high temperature nebular phases and water. Studies of these chondrites can provide information on the conditions and environments of aqueous alteration and the mobility of elements during alteration. This latter question is at the core of a debate concerning the location of aqueous alteration, i.e. whether alteration occurred predominantly within a closed system after accretion (parent body alteration) or whether some degree of alteration occurred within the solar nebula or on ephemeral protoplanetary bodies prior to accretion. At the core of the parent body alteration model is the hypothesis that elemental exchange between different components, principally chondrules and matrix, must have occurred. In this study, we focus on the behavior of the minor element, phosphorus. This study was stimulated by observations of the behavior of P during the earliest stages of alteration in glassy mesostasis in type II chondrules in CR chondrites [2] and extends the preliminary observations of [3] on Y791198 to other CM chondrites.

Techniques. Data were collected for 3 CM2 chondrites; Y791198, Mighei, and ALH 81002, spanning the range from weakly to heavily altered. X-ray maps of type I and type II chondrules with well-defined fine-grained rims were collected using WDS spectrometry on a JEOL 8200 Superprobe, operating at 20 kV with a 30 nA beam current, with dwell times of 20-30 μ secs per pixel. The JEOL 8200 is equipped with 5 WDS spectrometers, including two high intensity spectrometers that allow acquisition of X-ray data at \sim 6X the count rate of a standard X-ray spectrometer.

Y791198 – Y791198 is the probably the least altered of the CM chondrites [4], but nevertheless shows complete replacement of mesostasis in all chondrules [3]. X-ray maps of 6 type II chondrules show that they are invariably surrounded by a narrow layer, \sim 10 μ m in thickness, that is enriched in Ca and P. In general, this layer appears to be exactly at the interface between the

the chondrule and the fine-grained rim, or is slightly within the fine-grained rim itself. This layer can be both continuous or discontinuous, depending on whether mesostasis is in direct contact with the fine-grained rim around the entire perimeter of the chondrule or not. The enrichments in Ca and P are also correlated with enrichments in Na and K. We interpret the correlation of Ca and P to be due to the presence of fine-grained, Ca-phosphate, probably apatite. The X-ray maps show definitively that Ca, P, Na and K have been essentially completely leached from the chondrule mesostases, although hot spots of Ca are locally present, probably due to the presence of relict unaltered Ca-pyx of quench origin. Qualitatively, the concentrations of Ca, Na, and P in the fine-grained rims appear to be indistinguishable from those in the altered mesostasis, suggesting that equilibration between the two components has occurred during the alteration process. In comparison, K appears to be present in slightly higher concentrations in the altered mesostasis than the rim.

X-ray maps of type I chondrules and their rims show that the behavior of Ca, K and Na is somewhat different. In general, no layer of Ca and P enrichment is present at the interface between the chondrule and the fine-grained rim. However, the apparent concentrations of Ca, Na, K and P in the chondrule mesostasis and associated fine-grained rims appear to be very similar, with all elements being present in low concentrations. The only evidence of elevated concentrations of P is in unaltered Fe,Ni metal in the chondrules and, to a lesser extent, within the alteration products of metal, where detectable P is still present.

Mighei – Mighei is a CM chondrite that is more highly altered than Y791198 [1]. X-ray maps of three small ($<$ 300 μ m) type II chondrules in Mighei were collected. The behavior of Ca and P in these chondrules differs from that in Y791198. Rather than a discrete narrow layer of Ca and P enrichment at the interface between the chondrules and their fine-grained rims, the Ca-phosphate appears to be distributed relatively homogeneously throughout the rim, to distances up to 25 μ m from the edge of the chondrule. Ca-phosphate grains are clearly correlated with enrichments in Na and K. A single type I chondrule was also examined. Like the type IIs in Y791198, there is no evidence of any P-rich phase in the fine-grained rims, but altered metal does show somewhat elevated concentrations of P in comparison with any other phases.

ALH81002 – ALH81002 is a quite highly altered CM2 chondrite that represents a more advanced stage of alteration than Mighei. X-ray maps of three type IIA and two type I chondrules were collected. Like Mighei, Ca and P occur in a diffuse zone around the periphery of the chondrules that extends into the fine-grained rim for about 20 μm . The low X-ray intensities of Ca and P indicate that if Ca-phosphate is present it is extremely fine-grained and is disseminated throughout the rim material, rather than as distinct coarse-grained crystals. Our preliminary data indicate that there is a general positive relationship between the size of the chondrule and the thickness of the Ca,P-enriched zone in the fine-grained rim, but this requires confirmation with further data. One notable difference in ALH81002 is that Ca and P have not been entirely removed from all the chondrules. Two of the chondrules studied contain Ca concentrations in altered mesostasis that is clearly higher than in the fine-grained rims. In one chondrule, the Ca is clearly correlated with P, but in a second chondrule P shows only a partial correlation with Ca.

Discussion. Our data provide some important new insights into the behavior of Ca, P, Na, and K during aqueous alteration. In particular, they show conclusively that transport of these elements from chondrules into their associated fine-grained rims occurred during alteration, entirely consistent with parent body alteration. All these elements have been recognized to be mobile during aqueous alteration, but with the exception of Ca, the sinks for Na, K and P in CM chondrites are poorly understood. Prior to aqueous alteration of CM chondrites, Ca, Na and K are particularly concentrated in chondrule mesostases. Rare analyses of unaltered glass and glass inclusions in olivine in CM2 chondrites suggest concentrations of up to 22 wt% CaO and 8 wt% Na₂O [5], although both elements show considerable variation. No data are available for P in chondrule mesostases in CMs. However, based on data for OCs [8] and CRs [2], it appears that P is enriched significantly in type II chondrule mesostasis (~3 wt% P₂O₅ [6]) relative to type I. In type I chondrules, P is dominantly present in Fe, Ni metal. Our data show that during alteration of mesostases in type II chondrules, Ca, P, Na and K are all highly mobile and are readily leached from the glass. However, exactly how far each of these elements is transported appears to be strongly dependent on local geochemical conditions. The presence of a layer of Ca-phosphate at the interface between the chondrules and fine-grained rims in Y791198 indicates that an abrupt change in fluid geochemistry must have been present at this boundary to drive phosphate precipitation during the earliest stages of aqueous alteration. Ca-phosphate solubility in-

creases in acidic solutions, whereas precipitation of phosphate is favored by increasing alkalinity [7]. One possible explanation for the formation of Ca-phosphate is that there is a abrupt change in pH at the boundaries between the chondrules and their fine-grained rims that results in precipitation of Ca-phosphate in a boundary layer. Thermodynamic modeling indicates that during the earliest stages of CM chondrite alteration [8], fluid pH rapidly rises to alkaline values due to the consumption of protons by hydrolysis reactions [9], conditions under which Ca-phosphate precipitation is favored. However, it seems likely that in the interior of chondrules the hydrolysis of Si-rich mesostasis glass will actually generate local fluid compositions that are more acidic due to the formation of H₂SiO₄, a weak acid [9]. Dissolved Ca and P, moving from the interior of the chondrule outward into the rim will encounter fluid with a higher pH and will precipitate at this interface. The occurrence of enhanced Na associated with the Ca-phosphate is consistent with the fact that Na can substitute into Ca-phosphates via the coupled substitution $\text{Na}^+ + \text{S}^{6+} = \text{Ca}^{2+} + \text{P}^{5+}$.

At more advanced stages of alteration, as recorded in Mighei and ALH81002, phosphate dissolution and reprecipitation appears to have occurred. In these cases, the phosphate is transported further away from the chondrule into the rim, resulting in dissemination of Ca-phosphates in a diffuse zone surrounding the chondrule. The occurrence of Ca-bearing altered mesostasis in chondrules in ALH81002 requires further study, because it implies that in these chondrules Ca was not fully leached, despite the advanced degree of aqueous alteration. It is not clear whether this is typical behavior of type II chondrules in ALH81002 or is perhaps due to the presence of Ca-rich quench pyroxenes that are more resistant to aqueous alteration in some chondrules. The association of P with this Ca-bearing mesostasis could be the result of advanced alteration of P-bearing FeO-rich olivines in these chondrules. For example, [6] showed that in ordinary chondrites such olivines can contain as much as 0.13 wt% P.

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