

RADIAL PYROXENE AND CRYPTOCRYSTALLINE CHONDRULES AS INDICATORS OF AQUEOUS ALTERATION AND THERMAL METAMORPHISM IN ORDINARY CHONDRITES. J. N. Grossman, United States Geological Survey, 954 National Center, Reston, VA 20192, USA, jgrossman@usgs.gov.

Introduction: Cryptocrystalline (C) and radial pyroxene (RP) chondrules are among the best understood materials found in chondrites. They formed by the complete, or nearly complete, melting of material rich in *normative* low-Ca pyroxene (>80 wt%) and plagioclase. These molten droplets cooled rapidly, and crystallized as sprays or fans of greatly elongated pyroxene crystals (<1 μm wide in C chondrules) surrounded by small amounts of glass. These chondrules are common in ordinary and enstatite chondrites (10-20 vol%), present in lower amounts in CO, CR, and CH chondrites, and nearly absent in CV chondrites.

In the ordinary chondrites (OC's), many C and some RP chondrules have a "bleached" appearance: the outer 50-200 μm appears white in broken, separated chondrules, and is lighter in color than the chondrule interior in thin section. I have shown that bleached chondrules form *in situ* when aqueous fluids flowing through the matrix around the chondrules attack and dissolve the glass just below the chondrule surface [1], consistent with earlier speculation on the subject [2-4]. The mineralogical evidence for low-temperature aqueous processes in Semarkona (LL3.0) C chondrules includes the presence in bleached zones of cavities between pyroxene crystals containing phyllosilicates, pentlandite and little or no glass; unaltered zones in the same chondrules contain interstitial glass and troilite [1]. Ion probe studies also point to aqueous alteration as the cause of bleaching in Semarkona C chondrules: the bleached zones are high in water and halogens, and low in elements that would once have been present in glass [5]. In Semarkona and Bishunpur (LL3.1), there is also good textural evidence that parent-body brecciation and aqueous alteration were approximately coeval [1].

Bleached chondrules are present in some equilibrated OC's [3,4], raising some interesting questions. If bleaching in Semarkona was caused by aqueous alteration, were metamorphosed chondrites also subject to aqueous alteration? If so, did alteration happen before, during, or after metamorphism?

Experimental procedure: Thin sections of H, L, and LL chondrites spanning a complete range of petrologic types were examined in transmitted light to search for bleached chondrules. Examples from a middle-type-3 (Chainpur, LL3.4), a high-type-3 (Dhajala, H3.8), and two type-4 chondrites (Soko-Banja, LL4, and Bjurböle, L/LL4) were selected for further study on the basis of their textural similarities to bleached chondrules in Semarkona. Core-to-rim compositional profiles were measured using a 10 \times 5 μm rastered beam (wide enough to cover many pyroxene grains) on the JEOL 8900 electron microprobe at the USGS, Reston. High-resolution X-ray maps of the chondrules were obtained on the same instrument for Na, Mg, Al, Ca, and Fe.

Occurrence of bleached chondrules: Bleached chondrules, optically identical to those in Semarkona, were ob-

served in every type-3 OC examined (H, L, and LL), from type 3.1 to 3.9. Bleached chondrules were identified in three L4 and LL4 chondrites, but were not noted in the majority of the twenty type-4 OC's examined. Well-preserved RP and C chondrules are difficult to find in most thin sections of type-5 OC's, and it was impossible to determine (optically) whether any of those found were bleached. In type-6 chondrites, which are even more metamorphosed, no bleached chondrules could be found.

Bleached chondrules in type-3 OC's: In Semarkona, bleached chondrules show fairly simple compositional profiles. In the bleached zone, all of the elements expected to be concentrated in the feldspathic glass (which is too fine-grained for microprobe analysis) are depleted: Na, K and Al are depleted by 60-90% relative to Mg, and Si/Mg is depleted by ~10%. These data are consistent with the removal of most of the glass (Si is less depleted because most of it is present in pyroxene). Ca, Ti, Cr, Mn, and S remain nearly constant across entire chondrules, as these elements are concentrated in pyroxene and sulfides which are not removed by the bleaching process. Fe shows a slight increase in the bleached zone, as will be discussed below.

In Chainpur, which is somewhat more metamorphosed than Semarkona, the bleached chondrule examined is similar to those in Semarkona. The bleached zone is porous and depleted in alkalis, Al and Si by about the same factors as in Semarkona. Chainpur and Semarkona chondrules show a similar enrichment of Fe in the bleached zones: Fe/(Fe+Mg) rises from 25-30 mol% in the cores to 30-35 mol% near the chondrule surfaces in the bleached zones, suggesting that FeO diffused into the chondrules at some point. The Chainpur chondrule shows a curious enrichment of Ca by ~50% just *below* the bleached zone, in the apparently unaltered part of the chondrule [Fig. 1]; Ca must have been mobilized in a secondary process during or after bleaching.

Dhajala is significantly more metamorphosed than Chainpur and Semarkona: its olivine compositions are nearly homogeneous. C chondrules (two were analyzed) in Dhajala again show alkali, Al, and Si depletions in bleached zones. However, the variations of Ca, Cr, Mn and Fe are different than in type-3 chondrules. In Dhajala, Fe, Cr and Mn decrease sharply from the core of the chondrule across the bleached zone to the surface: the cores have Fe/(Fe+Mg), Mn/Mg and Cr/Mg ratios (atomic) of 30%, 0.02, and 0.15, respectively, whereas surface ratios are 17%, 0.01, and ~0.008. Ca is enriched in a zone centered on the contact between the bleached zone and the core.

Bleached chondrules in type-4 OC's. In the equilibrated ordinary chondrites, bleached chondrules can be found in meteorites with well preserved chondritic structures. They were found in four of ten L4 and LL4 chondrites, but not in about ten H4 chondrites. This may be due to the fact that the smaller chondrules in H chondrites are

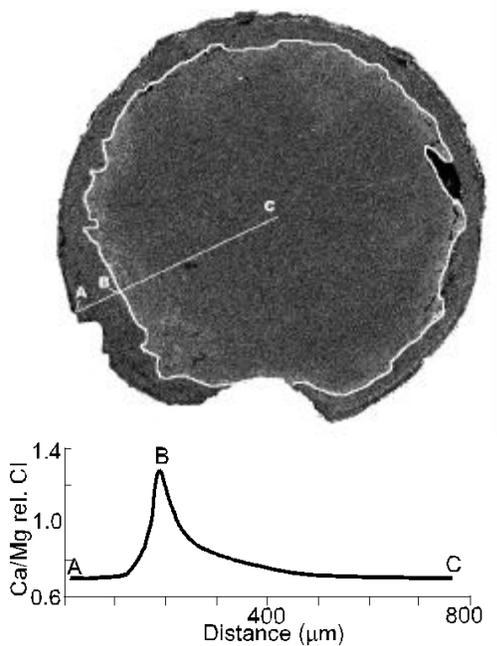


Figure 1. Calcium X-ray map of chondrule Chainpur 1251-18-1 (top). The boundary between the outer bleached zone and the core is indicated by a white line. Ca is enriched (lighter gray) just inside the boundary, as shown in the probe traverse (bottom) along line A-B-C

not as well preserved as the larger ones in L and LL chondrules.

As in type-3 chondrites, RP and C chondrules in type-4 OC's show depletions of alkalis and Al in bleached zones. But, compositional profiles of these elements across the chondrules tend to be a bit erratic due to the presence of metamorphic feldspar grains a few μm across (too coarse to allow representative local-bulk analyses given the beam size). Nevertheless, the overall signature of lower values in bleached zones is unambiguous.

Iron and Mn are unzoned across the type-4 bleached chondrules, while Cr shows a similar decrease in the bleached zones to that observed in Dhajala. Ca is extremely enriched in the bleached zones, present as abundant 5-10 μm grains of Ca-rich pyroxene in approximately the same location as the Ca-rich zones seen in Dhajala.

Discussion

Metamorphic effects. Bleached chondrules are apparently sensitive recorders of metamorphic effects in OC's. The opposite Fe-zoning trends in bleached chondrules from H3 and LL3 chondrites are easily understood as the result of equilibration of the tiny pyroxene crystals in the bleached zones with minerals outside the chondrules; equilibration is facilitated by the absence of interstitial glass in the bleached zones that might otherwise afford protection from metamorphic fluids. The analyzed RP and C chondrules in Dhajala, have higher Fe/(Fe+Mg) ratios than the H-chondrite equilibrium value of ~18 mol%, so that metamorphism should

result in Fe depletion of the pyroxene, as observed. The zoning trends in Cr and Mn are also consistent with equilibration of pyroxenes in the bleached zones with minerals outside the chondrules, as Cr/Mg and Mn/Mg ratios approach values typical of equilibrated H chondrite pyroxene. Conversely, the cores of bleached chondrules in the LL3 chondrites have lower Fe/(Fe+Mg) ratios than the "equilibrated" LL ratio of ~30 mol%, and the expected trend during metamorphism should be toward Fe enrichment of pyroxene.

In the type-4 OC's, exchange of Fe, Mg, and Mn between minerals in RP and C chondrules and elsewhere in the rock has proceeded to completion. Cr/Mg ratios, however, are still lower in bleached zones than in chondrule cores. Either Cr never achieved equilibrium among pyroxene grains in type 4 chondrites, or there is an additional, unobserved Cr-bearing phase present.

Calcium zoning in bleached chondrules. With increasing metamorphic grade, one observes the following progression in bleached chondrules: type 3.0—no Ca zoning; type 3.4—development of a Ca-rich zone below the bleached zone; type 3.8—broadening of the Ca-rich zone into the bleached area; type 4—growth of Ca-rich pyroxenes in the bleached zone. Why the Ca-rich zone is developed in apparently unaltered parts of bleached chondrules in type-3.4 Chainpur, but not type-3.0 Semarkona is not obvious. Perhaps the explanation lies in some kind of a metamorphic effect post-dating aqueous alteration, related to the incipient crystallization of feldspar from glass in Chainpur. Another possibility is that the conditions of aqueous alteration were different in Semarkona and higher-grade chondrites, resulting in the mobilization of Ca in the latter meteorites.

The timing of aqueous alteration. The fact that one can find a metamorphic effect in OC's that is dependent upon the pre-existence of bleached chondrules, as is the case for the sequence of Ca zoning profiles described above, proves that aqueous alteration occurred prior to thermal metamorphism. The preferential growth of secondary feldspar and calcic pyroxene grains in the bleached zones of RP and C chondrules in equilibrated chondrites also demonstrates that alteration predated metamorphism. The metamorphic minerals formed in the porous framework of pyroxene (and, presumably, hydrous minerals) where there was ample room for grain growth.

Thus, aqueous alteration must have been a common early process in many OC's, including metamorphosed ones. In the higher petrologic type chondrites, the fluids must have been driven off at relatively low temperature, before metamorphic reactions such as serpentinization or amphibole formation could become extensive.

References: [1] J.N. Grossman and A.J. Brearley (1997) *Meteorit. Planet. Sci.* 32, A53. [2] G. Kurat (1969) in *Meteorite Research*, Reidel Publ. Co., 185-190. [3] M. Christophe Michel-Levy (1976) *Earth. Planet. Sci. Letts.* 30, 143-150. [4] W. R. Skinner et al. (1989) *Meteoritics* 24, 326. [5] J.N. Grossman et al. (1997) *LPI Tech. Rept.* 97-02, Part 1, 19-20.