

CHEMICAL FRACTIONATIONS IN CHONDRITES: THE ROLES OF CHONDRULE FORMATION AND THE ACQUISITION OF CAIs AND FORSTERITE-RICH DUST. Alan E. Rubin, Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90095-1567, USA (aerubin@ucla.edu).

The distinctive O-isotopic compositions of chondrules in different chondrite groups suggest that chondrules formed in local nebular regions, presumably at different heliocentric distances. Compositional and textural relationships among chondrite groups permit us to infer their relative formation locations in order of increasing distance from the Sun: EH-EL, H-L-LL, R, CR, CV-CK, CM-CO, CI [1-3]. Based on the physical and chemical properties of chondrules, Rubin [2] assigned different amounts of nebular dust to these locations: low dust in the EC and OC regions, increasing dust in the R and CR zones, maximum dust in the CV-CK zone and decreasing amounts of dust farther out.

Grossman [4] listed the six principal chemical fractionations observed among chondrites: (1) refractory lithophiles from Si, (2) Mg from Si, (3) moderately volatile lithophiles from Si and from more-refractory lithophiles, (4) highly volatile elements from other elements, (5) siderophiles from lithophiles (i.e., the metal-silicate fractionation), and (6) refractory siderophiles from common and volatile siderophiles. If some chemical fractionations were caused, at least in part, by chondrule formation [5,6], then chondrite compositions may vary with heliocentric distance.

The inference that chondrule formation is associated with whole-rock volatile depletion is supported by the anti-correlation in the five unequilibrated carbonaceous-chondrite groups (CI, CM, CO, CV, CR) between chondrule abundance and bulk CI-normalized Na/Mg ratio ($n = 5$, $r = -0.934$, $2\sigma = 0.02$, 98% confidence level). It would be difficult to produce this correlation if the fractionation of moderately volatile lithophiles from Mg (**fractionation 3**) was completed before chondrules formed [cf. 4]. The most straightforward explanation for this fractionation is that chondrule formation was associated with a bulk loss of volatiles. Lithophiles more volatile than Na would also likely have been depleted during chondrule formation.

Chondrite groups (CR, CV, CK) with large chondrules (700-910 μm) tend to have lower CI-normalized Na/Mg abundance ratios (0.43-0.46 vs. 0.56-1.27) than chondrite groups (OC, EH, EL, R, CM, CO) with smaller chondrules (150-570 μm). If chondrule formation caused volatile loss, then large chondrules were more efficient at losing volatiles than small chondrules. This may be because large chondrules were enshrouded in dust and cooled relatively slowly, allowing more time for volatile loss. Relatively slow cooling is expected for large dust-enshrouded chondrules because the dust would have absorbed heat ra-

diation from the enclosed chondrules and re-radiated some of it inward, back toward the chondrule.

The loss of highly volatile elements from chondrules could also account for **fractionation 4** (highly volatile elements from other elements). This fractionation can be represented by the In/Si ratio: it is low in chondrite groups from low-dust regions in the inner part of the nebula (e.g., EL, OC) and higher in carbonaceous chondrites that formed in dustier regions at greater heliocentric distances. An exception to this trend is the EH group which is much richer in highly volatile siderophiles (e.g., Ag, Cd, In, Tl, Bi) than EL chondrites. Rambaldi [7,8] found that coarser metal is less refractory than fine metal; EH chondrites may thus have accreted coarser metal grains than EL.

A large proportion of the volatiles lost from chondrules would have condensed on nearby dust. This is consistent with the observation that fine-grained matrix material (which formed from this dust) in unequilibrated chondrites is richer in volatiles than whole rock. Nevertheless, some fraction of the volatile phases that evaporated from chondrules could have escaped the system; they may have become suspended in nebular gas and been swept away as the nebula dissipated.

Sulfide-rich liquids readily wet silicates [9], but metallic Fe liquids do not [10]. Non-silicate melts in the interiors of solidifying droplets of the first generation of CR chondrules may have been relatively sulfide rich and migrated via porous flow to the chondrule surface. Some of these channels are still discernable. This can account for chondrules that have abundant sulfide at their surfaces and metallic Fe-Ni (and little or no sulfide) in their interiors. The fact that most CR chondrules are now sulfide free suggests that, after multiple melting episodes, the process of S evaporation in these chondrules has gone to completion.

If S in the melt was evaporating at the chondrule surface, this would have decreased the surface energy of the melts; the contact area between metal and silicate would have been reduced, tending to result in the formation of individual metal beads [11], as is commonly observed on CR chondrule surfaces. Other volatile chalcophiles (e.g., Se) as well as volatile siderophiles (e.g., Ga, Ge, As) may also have evaporated.

This scenario is consistent with the low abundances of troilite in CR chondrites and the lower bulk Mg- and CI-normalized concentrations of the volatiles Se and Ga in CR chondrites relative to those in other carbonaceous-chondrite groups (CM, CO, CV) – Se: 0.19 vs. 0.26-0.54; Ga: 0.33 vs. 0.41-0.66.

Most of the evaporated volatile chalcophiles and siderophiles would probably have condensed onto surrounding fine-grained materials, but it is plausible that some escaped the system. This loss would have contributed to the fractionation of highly volatile elements from other elements (**fractionation 4**) and the fractionation of refractory siderophiles from common and volatile siderophiles (**fractionation 6**).

During the cooling of chondrule precursor droplets, surface tension could have caused the ejection of metal droplets from the silicate melt [12]. Large metal clumps present near chondrule margins and in the matrix of CR chondrites attest to such a process. If some metal escaped the system, this could have contributed to the metal-silicate fractionation (**fractionation 5**), which also varies with heliocentric distance. This fractionation can be represented by the CI-normalized Ni/Mg ratio. It is highest in enstatite chondrites (1.04-1.50), lower in OC (0.61-1.04) and R chondrites (0.91), and slightly lower in CR chondrites (0.89). The ratio is lowest (0.78-0.84) where the dust is most abundant, in the CV-CK region. At somewhat greater heliocentric distances, the dust distribution falls off and the Ni/Mg ratio begins to climb from 0.88-0.93 in CM-CO chondrites to 1.00 in CI. Preferential loss of some metal from large, relatively slow-cooling chondrules from dusty nebular regions caused siderophile depletions in chondrite groups that formed in these regions.

Fractionation 1 (refractory lithophiles from Si) can be represented by the Ca/Si ratio which is low in enstatite, ordinary and R chondrites (groups that formed in the inner part of the nebula), higher in CR chondrites (which formed at greater heliocentric distances), and highest in CV and CK chondrites (which formed at still greater distances). The Ca/Si ratio declines with increasing distance from the Sun in CM-CO chondrites and declines further in CI chondrites.

The CAI modal abundance correlates with the abundances of refractory lithophiles and refractory siderophiles (e.g., Os and Ir) among chondrite groups. Although refractory elements are more abundant outside CAIs (in chondrules, matrix and metal-rich nodules) than within them, the mechanism responsible for incorporating CAIs into chondrites helped determine the chondrites' bulk refractory-element abundances.

Differences among chondrite groups in their abundances of refractory lithophiles (**fractionation 1**) and refractory siderophiles (**fractionation 6**) are attributable, at least in part, to the modal abundances of CAIs. There is a positive correlation among chondrite groups between the abundance of CAIs and the abundance of matrix; this suggests that chondrite groups that formed in dustier nebular regions acquired greater numbers of CAIs. The inferred amount of nebular dust at the chon-

drite-formation locations correlates with the abundance of CAIs; both peak in the CV-CK region.

The aerodynamic behavior of a particle is a function of the product of its size and density [13]. Because CAIs appear to have been concentrated in dusty nebular zones, Rubin [3] inferred that much of the dust existed as highly porous multi-mm-to-cm-size dustballs, ~100 times more massive than compact, mm-size CAIs (but with similar aerodynamic properties). Experimental and theoretical studies indicate that nebular fines would tend to agglomerate into dustballs with ~90% porosity that resemble interplanetary dust particles.

Many workers (e.g., [4,6]) have suggested that the Mg-Si fractionation (**fractionation 2**) among chondrite groups was caused by the acquisition or removal of forsterite (which has a Mg/Si atomic ratio of 2.0). Forsterite-rich dust was certainly present in the nebula at the time CAIs formed: e.g., the innermost layer of fine-grained accretionary rims around some CAIs in CV chondrites contains forsteritic olivine [14-16].

The EH and EL chondrites (which formed in the low-dust inner part of the nebula), have low CI-normalized Mg/Si ratios (0.69 and 0.82, respectively). The dust abundance was higher in the OC region; they have higher Mg/Si ratios (0.87-0.90). The carbonaceous chondrite groups have similar CI-normalized Mg/Si ratios (0.98 to 1.06), but because the amount of nebular dust peaked in the CV-CK region, one might expect that particular region to have the highest bulk Mg/Si ratios (assuming the dust was forsterite rich). This is indeed the case. This same region also has the most CAIs and the highest bulk refractory lithophile element abundances. It thus seems likely that the amount of forsterite that was concentrated in the different nebular regions was largely responsible for their varying Mg/Si ratios (**fractionation 2**).

References: [1] Wasson J. T. (1988) In: *Mercury* (eds. Vilas F. et al.), 622-650. [2] Rubin A. E. (2010) *GCA* 74, 4807-4828. [3] Rubin A. E. (2011) *Icarus* 213, 547-558. [4] Grossman J. N. (1996) In: *Chondrules and the Protoplanetary Disk (CPD)* (ed. Hewins R. H., et al.), 243-253. [5] Larimer J. W. and Anders E. (1967) *GCA* 31, 1239-1270. [6] Larimer J. W. and Anders E. (1970) *GCA* 34, 367-387. [7] Rambaldi E. (1976) *EPSL* 31, 224-238. [8] Rambaldi E. R. (1977) *EPSL* 36, 347-358. [9] Barnes S. J. et al. (2008) *Geology* 36, 655-658. [10] Minarik W. G. et al. (1996) *Science* 272, 530-533. [11] Yu Y. et al. (1996) In: *CPD* (ed. Hewins R. H. et al.), 213-220. [12] Uesugi M. et al. (2008) *MPS* 43, 717-730. [13] Weidenschilling S. J. (1977) *MNRAS* 180, 57-70. [14] MacPherson G. J. et al. (1985) *GCA* 49, 2267-2279. [15] Cosarinsky M. et al. (2001) *MPS* 36, A44-A45. [16] Cosarinsky M. et al. (2002) *MPS* 37, A38.