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April 5, 2001

U.S. Nuclear Regulatory Commission
ATTN: Mrs. Deborah A. DeMarco
Office of Nuclear Materials Safety and Safeguards
Program Management, Policy Development, and Staff
Office of the Director
Mail Stop 8D-37
Washington, DC 20555

Subject: Transmittal of Journal Papers

Dear Mrs. DeMarco:

The purpose of this letter is to provide you copies of the attached papers that were recently published in Meteoritics and Planetary Science and Lunar and Planetary Science XXXII. The papers are entitled:

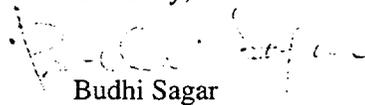
“On the origin of rim textures surrounding anhydrous silicate grains in CM carbonaceous chondrites”
by **Lauren Browning**, Harry Y. McSween, and Michael E. Zolensky

“Modeling aqueous alteration of CM carbonaceous chondrites”
by Nina D. Rosenbuerg, **Lauren Browning**, and William L. Bourcier

“Aqueous alteration of CM carbonaceous chondrites”
by N.D. Rosenberg, **L. Browning**, and W.L. Bourcier

These papers report work that Lauren Browning participated in before joining the CNWRA. Because this work was not funded by the NRC you do not need to respond to this letter. However, if you have any questions regarding the content of the papers please contact me at (210) 522-5252 or Dr. Lauren Browning at (210) 522-6642.

Sincerely,



Budhi Sagar
Technical Director

ECP: ar
enclosure

cc:	J. Linehan	K. Stablein	W. Patrick
	B. Meehan	J. Bradbury	CNWRA Directors
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On the origin of rim textures surrounding anhydrous silicate grains in CM carbonaceous chondrites

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Abstract—Fine-grained, optically opaque rims coat individual olivine and pyroxene grains in CM matrices and chondrules. Bulk chemical analyses and observations of these rims indicate the presence of phyllosilicates and disseminated opaques. Because phyllosilicates could not have survived the chondrule formation process, chondrule silicate rims must have formed entirely by late-state aqueous reactions. As such, these textures provide a useful benchmark for isolating alteration features from more complex CM matrix materials. Both chondrule silicate and matrix silicate rims exhibit morphological features commonly associated with advancing stages of replacement reactions in terrestrial serpentinites. Contacts between many matrix silicate rims and the adjacent matrix materials suggest that these rims formed entirely by aqueous reactions in a parent-body setting. This contrasts with previous assertions that rim textures can only form by the accretion of nebular dust but does not imply an origin for the rims surrounding other types of CM core components, such as chondrules.

INTRODUCTION

Although the diverse textures and phases in CM carbonaceous chondrites record a wealth of information about early solar system history, a coherent scenario for the formation of these meteorites has not yet emerged. This is, in part, because most CM chondrites experienced extensive, but incomplete, aqueous alteration. Fine-grained alteration minerals and textures obscure the nature of the original CM materials, making it necessary to extrapolate backwards in time from the most recent events. Yet, petrologic observations of CM materials are often explained in several different ways. Comprehensive scenarios for the origin of CM chondrites necessarily invoke both nebular and asteroidal processes that are poorly understood and thus cannot be easily tested.

Of the various processes that affected CM chondrites, water–rock interactions are understood best because these have been studied extensively in the context of diverse terrestrial problems (Frost, 1985; Li, 1974; Moody, 1976; Paces, 1983; Murphy and Pabalan, 1994). Consequently, we suggest that emphasis should be placed first on determining which CM features can be explained plausibly by water–rock interactions. By a process of elimination, this approach will reveal those features that must be explained by less familiar events that may have occurred in the solar nebula and on asteroids.

Fine-grained rims are the most conspicuous and ubiquitous types of CM texture, which suggests that they hold the key to understanding the larger formational history of CM chondrites. Rims are made mostly of hydrated silicates formed by water–rock interactions at temperatures below ~ 25 °C (Barber, 1981; Brearley and Geiger, 1991; Clayton, 1993; Zolensky *et al.*, 1993). These textures surround all types of coarse-grained core components in CM chondrites (Metzler *et al.*, 1992), such as chondrules, calcium-aluminum-rich inclusions, and isolated matrix silicate, sulfide, and carbonate grains.

Proposed scenarios for the formation of CM rims paint very different pictures of early solar system events. It is widely held that the original rim textures in other types of chondritic classes formed

when anhydrous dust grains physically accreted onto the surfaces of coarser-grained objects in the nebula (Grossman *et al.*, 1988; Rubin and Wasson, 1987). However, the hydrated mineralogy of CM rims indicates a more complex origin. Metzler *et al.* (1992) propose that aqueous alteration occurred before the nebular accretion of rim textures, so that the original rim materials were made of hydrated dust. This requires that aqueous alteration occurred before the accretion of the final CM asteroidal parent-body, in one of several possible "preaccretionary environments". Brearley and Geiger (1991) agree with Metzler *et al.* (1992) that rim textures formed by physical processes in the nebula but argue that the original rim materials were anhydrous, rather than hydrous. According to these authors, the hydration of CM rims occurred by subsequent aqueous processes on the CM parent-body. In contrast to these, Sears *et al.* (1993) conclude that at least some thin, fine-grained chondrule rims formed entirely on the CM parent-body, either by the solidification of mud or by aqueous reactions.

In contrast to previous CM rim studies, which focus almost exclusively on chondrule rims (King and King, 1981; Rubin and Wasson, 1987; Zolensky *et al.*, 1993), this study centers on the characterization and interpretation of rim textures surrounding individual silicate grains inside chondrules and in CM matrices. These are referred to hereafter as "chondrule silicate (CS)" rims and "matrix silicate (MS)" rims respectively. We previously referred to these textures as "rinds" (Browning, 1995), because they are typically thinner (*i.e.*, <10 μm) than chondrule rims. We show here that this distinction is unnecessary; however, because descriptive criteria used to define chondrule "rims" apply equally well to "rinds". In this paper, we characterize the bulk chemistry and petrologic features of CS and MS rims and present a petrologic interpretation for their origin. New measurements of rim thickness and core grain diameters are presented and discussed.

ANALYTICAL TECHNIQUES AND SAMPLES

We studied 36 polished sections of Mighei, Nogoya, Cochabamba, Murchison, Murray, Boriskino, Bells, Cold Bokkeveld,

Pollen, Santa Cruz, and Y791198. Each section was characterized first by optical microscopy in reflected and transmitted light. A JEOL 35C scanning electron microscope (SEM) was then operated at 20 kV to obtain backscattered electron images of selected regions. A Princeton Gamma Tech Be-window detector was used to collect energy-dispersive spectra on the mineral assemblages in these samples and these spectra were collected for at least 100 s. Finally, quantitative compositional analyses were obtained using a Cameca CAMEBAX probe operated at 20 kV and 30 nA. Natural minerals were used as standards. Cameca instrument and data-reduction software packages were used to correct for dead time, background, and matrix effects. Quantitative data are accurate within $\pm 0.5\%$.

DESCRIPTION: CM RIMS AROUND INDIVIDUAL SILICATE GRAINS

Fine-grained alteration minerals form thin (generally $<10\ \mu\text{m}$ thick), optically opaque rim textures around many of the individual olivine and pyroxene grains in CM chondrules and matrices. The distribution and abundance of these rim textures vary widely among different CM chondrites, different thin sections of an individual CM chondrite, and different portions of a single thin section. Rim textures are rarely observed in the meteorites Bells and Santa Cruz, for example, but are abundant in Mighei and Murray. A higher percentage of the anhydrous silicate grains in CM matrices are surrounded by rims (*e.g.*, MS rims) than the individual silicate grains inside chondrules (*e.g.*, CS rims).

The morphologies of CS rims exhibit a continuous range between "smooth" and "irregularly-shaped". Smooth rims form straight lines or smooth curves that define sharp contacts with the core grain and surrounding materials (Fig. 1). Most smooth rims have constant thickness and mimic the morphology of the enclosed grain (Fig. 1a). However, some smooth rims enclose one or more anhedral core grains and have highly irregular thicknesses (Fig. 1b,c). When viewed as a single object, these clusters of rimmed components often have the morphology of a single, well-defined CS grain. In contrast, most irregular rims have jagged surfaces and variable thicknesses (Fig. 2a), although some contain regions with a more subtle, fuzzy appearance (Fig. 2b, to the right of middle arrow). Irregular CS rims are often discontinuous, partially separated from the core grains they surround, or both (Fig. 2a,b). Both smooth and irregular rims fill fractures in the core grain (Figs. 1a and 2b).

Of all the different textures in CM chondrites, CS rims and MS rims are probably the most similar. These two textures have similar thicknesses and morphologies, surround the same types of core grains, and have similar bulk compositions. Like CS rims, MS rim morphologies possess smooth and irregular (Fig. 3) morphologies, as well as morphologies intermediate to these (compare Figs. 1 and 2 with Fig. 3). In some cases, individual MS rims have both smooth and irregular portions (Fig. 3b). Like some CS rims, MS rims often form around more than one core grain, and the entire cluster of rimmed components maintain the appearance of an individual MS fragment (Fig. 3c).

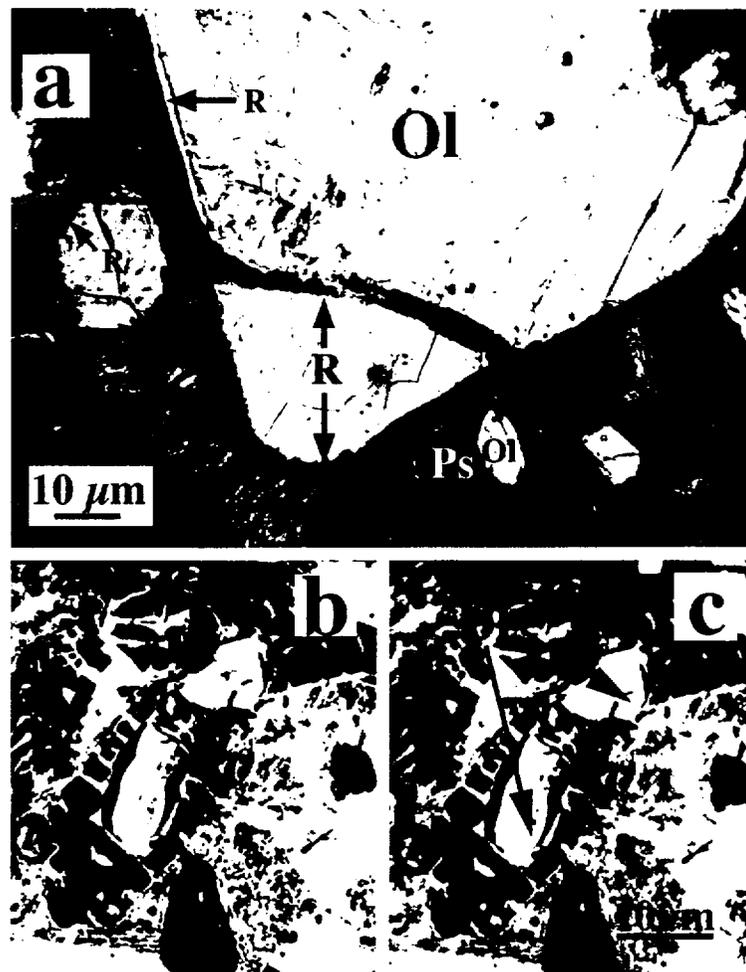


FIG. 1. Smooth CS rims. (a) Smooth chondrule rinds (R) surround olivine grains (Ol) in a Cochabamba chondrule. Note that a central parting (vertical arrow pointing up) separates the largest olivine into two portions, each of which is surrounded by a rind texture of relatively constant thickness. Rim phases also form a pseudomorph (Ps) after a smaller, euhedral olivine grain at lower right. Because a portion of the olivine (Ol) remains, this pseudomorph can be viewed as a smooth rind with variable thicknesses. Transmitted light. (b-c) Two adjacent olivine grains (ol) in a Mighei chondrule are surrounded by smooth rind textures of highly irregular thicknesses. When viewed together, these define a single fine-grained phyllosilicate and sulfide pseudomorph after an individual subhedral olivine grain. Image b is shown in transmitted light, and (c) is identical, except the contrast was artificially lowered around the pseudomorph to highlight its morphology, which is more evident when viewed in color.

However, there are some differences between chondrule and MS rims. For example, smooth MS rims (Fig. 3a) are less common than their CS rim counterparts. In addition, some MS rims are significantly thicker, up to $\sim 100\ \mu\text{m}$, and grade into the surrounding matrix. These are referred to here as "gradational" MS rims. Many gradational rims surround a thinner MS rim that lies directly against the core grain (Fig. 4).

Table 1 lists the average bulk compositions of the rims surrounding 10 CS and 14 MS grains from the CM chondrites Murray and Nogoya. Rims contain significant proportions of FeO, MgO, and SiO₂, with minor amounts of CaO, Al₂O₃, and S. On average, the CaO and Al₂O₃ contents of CS rims are higher than those of MS rims, whereas the SiO₂ content of MS rims is somewhat higher. However, the large standard deviations shown in parentheses demonstrate that (1) there is a large degree of variability in

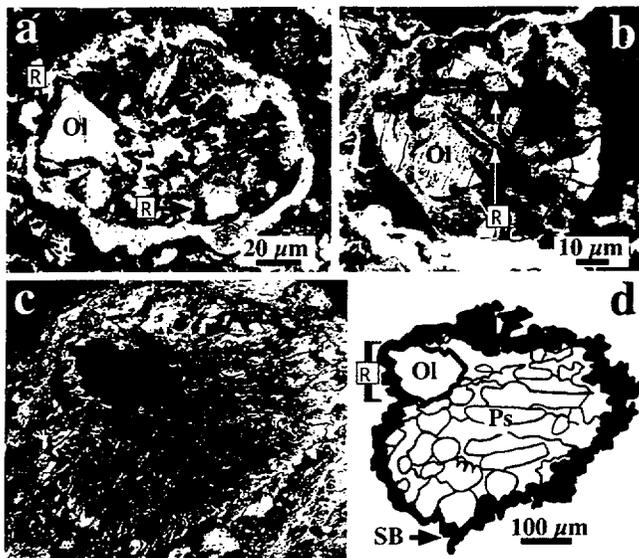


FIG. 2. The CS rims with slightly irregular to highly irregular morphologies. (a) Transmitted light image of an aqueously altered Murchison chondrule containing several irregular chondrule rinds (R) around individual olivine grains. (b) Slightly irregular chondrule rinds (R) trace the grain boundaries (lowermost arrow) and deep fracture planes (middle arrow) of an olivine grain in a Nogoya chondrule. A rind-coated central parting divides the uppermost part of the olivine into two portions (uppermost arrow). Transmitted light. (c) Backscattered electron (BSE) image of an extensively replaced Murchison chondrule. (d) Sketch of relevant textural components in (b). The chondrule contains many well-defined Mg-rich and S-poor pseudomorphs (Ps) toward the center but is lined by sulfide-rich pseudomorphs that form a sulfide-rich band (SB) around the chondrule perimeter. An irregular rind (R) partially surrounds an anomalous large olivine grain (Ol) and defines a portions of the sulfide-rich band (SB).

the compositions of individual rims and that (2) the major oxide compositions of CS and MS rims are remarkably similar.

On the basis of similar microprobe data, Metzler *et al.* (1992) assert that CM rims, which they call "accretionary dust mantles", are mixtures of "serpentine- and tochilinite-rich dust". However, there is much uncertainty in extrapolating the mineralogy of fine-grained altered materials on the basis of bulk compositional data (Barber, 1981). Despite these limitations, a few useful inferences can safely be made from the data in Table 1. The low totals suggest that hydrated phyllosilicates are a major component of rims, which is consistent with the results of petrologic observations. Also, the ubiquitous presence of S in the rim compositions suggests the presence of fine-grained, disseminated S-bearing phases. High-resolution instruments, such as the transmission electron microscope (TEM), are needed to firmly establish the mineralogy of the submicron-sized MS and CS rim materials.

Comments on the Usage of the Term "Rim"

There is no single, well-constrained definition for the "rims" in CM chondrites. Part of the problem is that the mineralogy of the CM chondrule rims is not unique. The CM chondrule rims contain the same set of minerals as the surrounding matrix materials, although the minerals occur in different proportions (Zolensky *et al.*, 1993). These authors note that mineral proportions vary between individual chondrule rims, and even between different regions of a single rim. Similarly, mineral proportions were shown to vary across small distances in the matrix.

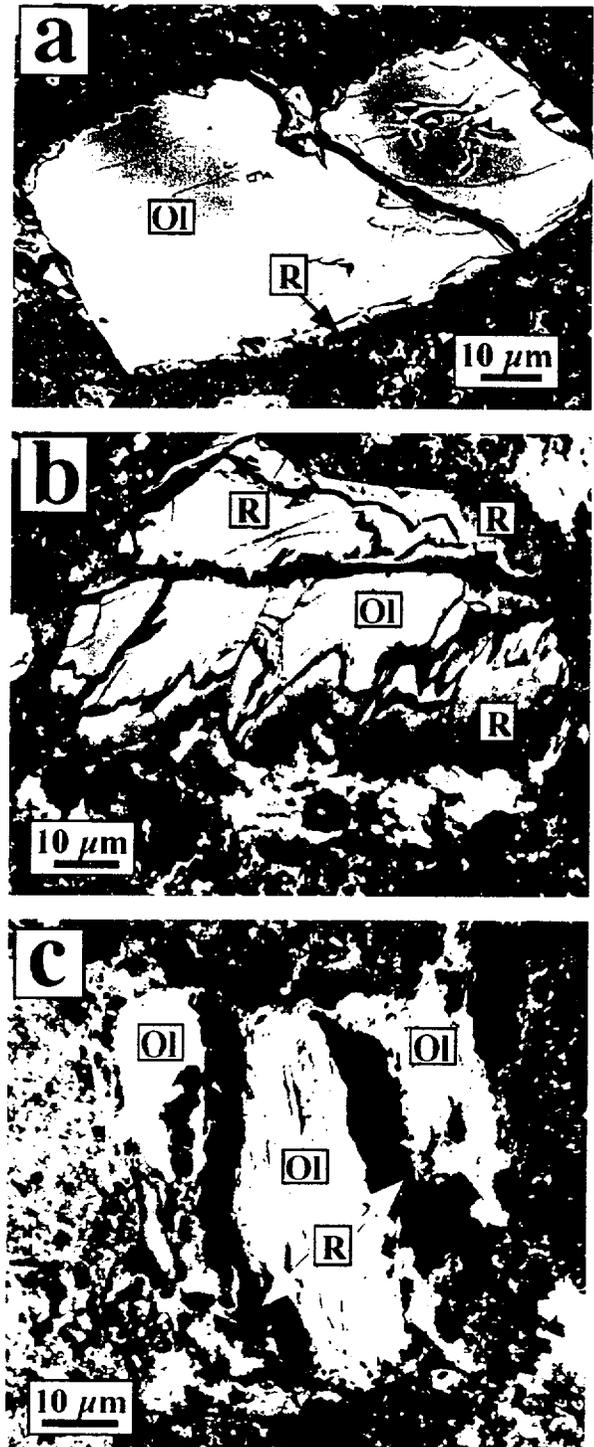


FIG. 3. Matrix silicate rims with smooth to highly irregular morphologies. (a) Smooth rind (R) around isolated matrix olivine in Mighei; BSE. (b) A matrix rind coats a matrix olivine (Ol) in Mighei and displays disparate morphological features. The most sulfide-rich portion of the rind texture (bright area at bottom) is highly irregular and intergrown with the surrounding matrix materials, whereas the portion of the rind at upper right is smooth and forms a sharp contact with the adjacent matrix. Note that the olivine is divided into two large pieces by a rind-coated central parting; BSE. (c) Slightly irregular matrix rind (R) coats three optically continuous matrix olivine (Ol) fragments in Mighei; plane light.

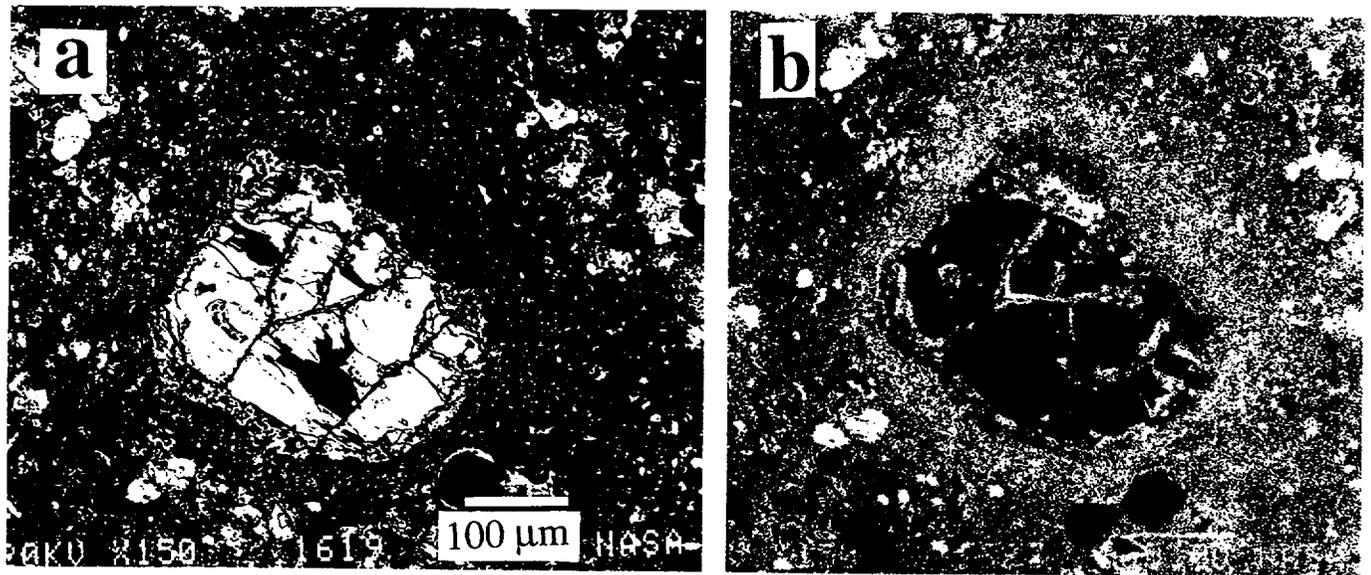


FIG. 4. (a) A gradational matrix rind (GR) surrounds an olivine grain (Ol) in Mighei and also encloses an irregular matrix rind (small arrows) that is juxtaposed against the olivine surface. The olivine grains is divided into several segments (S) that are separated by rind-filled fractures; BSE. These features suggest that the inner rim formed first by replacement and was later partially dispersed outward into the matrix by aqueous diffusion or advection. (b) An S x-ray dot map of (a), shown to scale, illustrates that the density of fine-grained S-bearing phases (bright dots) decreases away from the olivine surface until the rind is indistinguishable from the surrounding matrix materials. If the matrix represents asteroidal soils, then the gradational contact between the rim and matrix materials must have formed *in situ* on the CM parent-body.

Previous microprobe studies (Metzler *et al.*, 1992; Zolensky *et al.*, 1993) have shown that bulk CM chondrule rim compositions generally fall within a field on a Fe–Si–Mg ternary that is outlined by CM phyllosilicate analyses, cronstedtite, and tochilinite. This field was originally defined to characterize mineral proportions in CM matrix materials (McSween, 1987). According to Metzler *et al.* (1992), CM rim compositions fit within this field that is best characterized by a nearly constant Si/Mg ration and variable Fe. Figure 5 shows that most of our data for the bulk chemical compositions of MS and CS rims also fall within this field and follow the same general trends described by Metzler *et al.* (1992). Using compositional criteria therefore leads to the conclusion that "CS rims" and "MS rims" are indeed "rims".

Attempts to quantify petrologic features of "rims" can be misleading. For example, Metzler *et al.* (1992) assert that there is a positive linear correlations between the diameter of all CM core components and the thicknesses of their surrounding "dust mantles" (*e.g.*, "rims"). Hanowski (1998) obtained similar results. These reports imply that CM "rims" can be identified on the basis of their

thicknesses, relative to their associated core grain. However, we do not observe the same trends. Figure 6 shows our measurements of rim and core thicknesses from the CM chondrites Murray and Murchison. Rim materials surrounding all types of coarse-grained

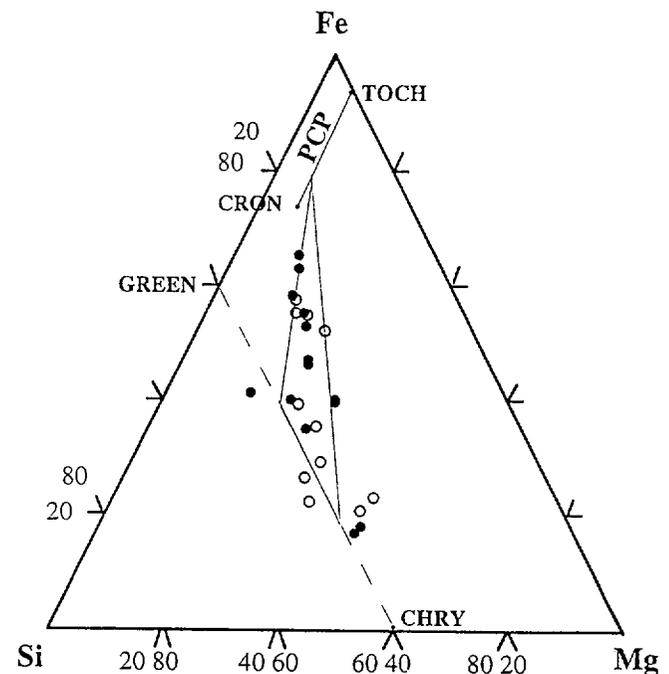


FIG. 5. An Fe–Si–Mg ternary diagram showing that the elemental bulk compositions from CS rims (hollow circles) and MS rims (filled circles) fall within the tochilinite (TOCH)–cronstedtite (CRON)–serpentine (GREEN to CHRY) fields used by Metzler *et al.* (1992) and Zolensky *et al.* (1993) to describe chondrule rim compositions in CM chondrites. Matrix silicate rims and CS rims also match petrologic descriptions for CM "rims".

TABLE 1. Average bulk compositions: matrix silicates (MS) rims and chondrule silicate (CS) rims from Murray, Nogoya and Murchison

Oxides wt%	MS rims	Std. dev.	CS rims	Std. dev.
MgO	12.94	6.87	16.76	7.61
Al ₂ O ₃	2.05	0.70	3.28	2.09
SiO ₂	23.55	5.50	26.35	7.67
CaO	1.49	3.70	4.33	10.12
MnO	0.17	0.06	0.11	0.08
FeO	37.49	11.21	25.10	12.77
Cr ₂ O ₃	0.15	0.10	0.18	0.18
S	3.94	2.83	3.57	3.08
Total	81.79	8.10	79.67	7.30

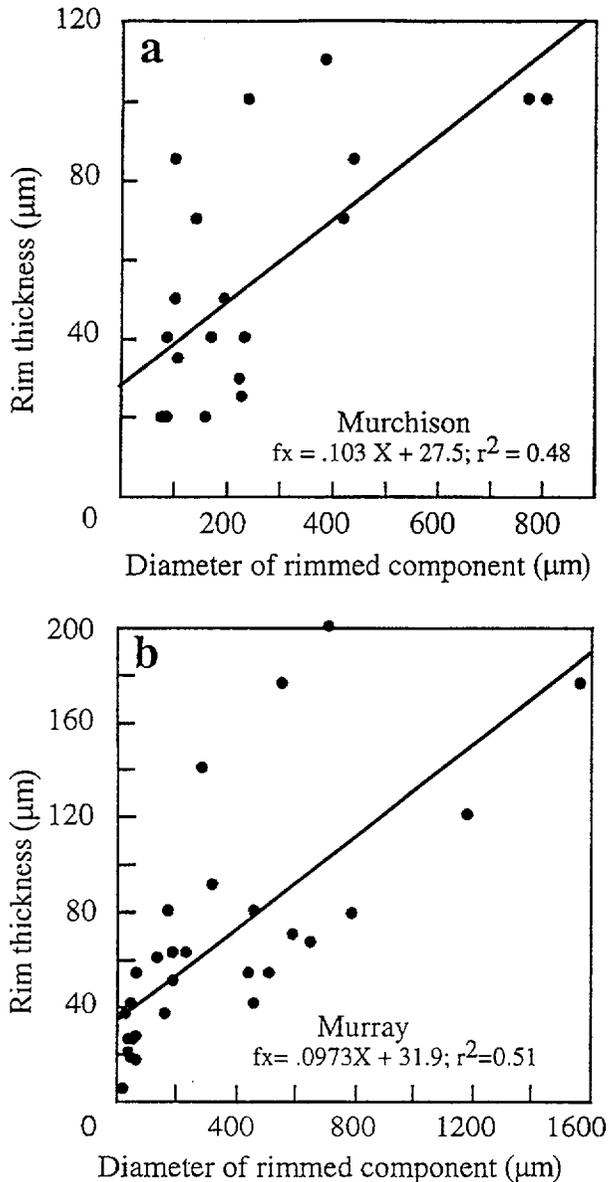


FIG. 6. No correlation is observed between the apparent thickness of the rim materials surrounding all types of core components and the apparent diameter of the rimmed cores in the CM chondrites (a) Murchison and (b) Murray. This argues against previous suggestions that we may learn something about the nebular environment from the relative sizes of associated rims and cores.

core components were measured and included in this diagram. Both plots show a wide range of rim thicknesses for any given core diameter, and correspondingly low correlation coefficients. This is the expected result, because even if the thicknesses of rims were dependent on core diameter, sectioning biases would destroy any apparent trends. For example, a large chondrule cut at an oblique angle would appear to have a small diameter with an unusually thick rim. These biases can be corrected for only if the core components have regular proportions that are known (Eisenhour, 1996). However, the vast majority of CM core components have highly irregular shapes that are not easily accounted for in correction models.

Subjective petrologic criteria provide the most useful definition for CM "rims" because these textures are readily identifiable when viewed using petrologic or SEM. Most rims are darker than the adjacent matrix materials, but some are lighter. Because rims possess a variety of petrologic features, different authors have emphasized different aspects of these textures. For example, Fuchs *et al.* (1973) describe CM rims as "narrow bands of fine-grained, inclusion-free matrix", whereas Metzler *et al.* (1992) distinguish these textures on the basis of "their dark to opaque appearance in regular thin sections, their small grain size, and their rounded or subrounded outer shape". Any of these descriptive definitions is adequate for identifying rim textures in CM chondrites, including the textures that surround individual olivine and pyroxene grains CM chondrites (*e.g.*, CS and MS rims).

We suggest that the word "rim" should not be taken to imply anything about the origin of these textures. There are many different types of rim textures in CM chondrites and the origin(s) of all of them is debated. If "rim" implied any type of genetic meaning, such as having experienced at least one episode of nebular dust accretion, then workers would have to make many judgments about the origin of individual CM textures that may be wrong, even before assigning these textures a name.

ORIGIN OF CHONDRULE SILICATE RIMS

The CS rims must have formed entirely by secondary, low-temperature water-rock interactions because these textures contain hydrous phases that could not have survived the high temperatures associated with the chondrule formation process (Hewins and Radomsky, 1990). In contrast to chondrule rims, CS rims could not have formed by mechanic processes, such as nebular accretion, because they are fully encapsulated within the igneous chondrule textures. The presence of rim textures inside chondrules clearly demonstrates that aqueous reactions, by themselves, can produce analogous rim textures. This suggests a need to reexamine the role of aqueous processing in the formation of all CM rim textures. To aid in this process, we provide interpretations of the various CS rim textures described above.

The morphologies of CS rims clearly indicate an origin by replacement. Replacement occurs when alteration phases are exchanged for a specific host mineral, rather than just precipitating in apparently random locations out of a saturated fluid. The most well-defined replacement structures, called pseudomorphs, preserve the original morphology of the host grain because the alteration reactions occur essentially within the original structure of the host mineral. In incompletely altered rocks, replacement does not go to completion, and the remnant unaltered host phase is surrounded by a zone of alteration phases that preserves the morphological features of the outer portion of the host grain. The presence of disseminated opaque grains accentuates this zone, producing a rim texture that is easily observed in both optical and backscattered electron images.

Smooth CS rims (Fig. 1) display features associated with advancing stages of pseudomorphic replacement in terrestrial serpentinites (Eckstrand, 1975; Groves *et al.*, 1974; Noack *et al.*, 1993; Wicks and Whittaker, 1977). During incipient alteration, phyllosilicates replace the core olivine or pyroxene grains along fracture planes, as well as the periphery of the host phase (Fig. 1a). Secondary opaques often co-exist with these phyllosilicates (Eckstrand, 1975; Groves *et al.*, 1974), producing opaque zones, or "rims", where incomplete replacement occurred. During the early stages of replacement, smooth rims trace the original boundaries of the core grain (Fig. 1a). With increased alteration, central partings

develop and eventually cut across the host phase separating it into two or more segments. Eventually, one or more remnant host grains becomes encased within replacement rims of irregular thicknesses (Fig. 1b,c). In this fashion, incomplete pseudomorphic replacement often results in a set of adjacent rimmed components that, when viewed together, preserve the appearance of the original intact core grain (Fig. 1b,c).

Although irregularly-shaped rims do not preserve the morphologies of the host grain, adjacent petrologic features often provide evidence that these textures also formed by replacement reactions. The highly altered chondrule shown in Fig. 2c,d consists mainly of well-defined pseudomorphs. The chondrule perimeter is defined by a wavy, sulfide-rich band that encloses the entire chondrule but is not a chondrule rim. The band is a chain made of the outer portions of individual CS grain pseudomorphs. The central, opaque-poor portions of these pseudomorphs preserve the morphology of the original host grain. In contrast, the outer portions of these same replacement structures, which lie within the opaque-rich band, have highly irregular shapes. It seems highly unlikely that the inner and outer portions of these structures formed by different types of processes. We conclude that at least some irregularly-shaped CS rim textures formed by replacement reactions. The continuous transition from smooth to irregular rim morphologies that is observed within both individual replacement structures and CS rims as a group suggests that all CS rims formed by replacement reactions.

Imperfect replacement structures develop under specific types of environmental conditions on Earth and thus might provide additional insight into the conditions during CM alteration. Wicks and Whittaker (1977) show that imperfectly formed replacement structures may result from changes in alteration conditions, or even the energetics of the post-alteration environment. Defects can also form when the cell parameters of the primary and secondary phases differ significantly (Eggleton, 1984), which may explain why many irregular rim morphologies contain relatively high proportions of opaque inclusions (Fig. 2c). Alternatively, late-stage recrystallization processes can displace the boundaries of pseudomorphs, initiate changes in the grain size of individual phases within the structure, or cause the migration of opaque inclusions (Eckstrand, 1975; Groves *et al.*, 1974; Wicks and Whittaker, 1977). Comprehensive scenarios for the formation of CM chondrites should be consistent with conditions required for the development of imperfect replacement structures.

ORIGIN OF MATRIX SILICATE RIMS

It is inherently difficult to establish the origin of rims embedded in CM matrices. Like the surrounding matrix materials, rims might have formed in response to a variety of physical and chemical processes occurring in the nebula, on the CM asteroidal parent-body, or on precursor CM planetesimals. Moreover, significant differences in proposed scenarios for the formation of CM rims (Metzler *et al.*, 1992; Zolensky *et al.*, 1993; Brearley and Geiger, 1991; Sears *et al.*, 1993) testify to the ambiguities associated with interpreting petrologic observations of rims surrounded by matrix materials. Because CS rims are formed entirely by aqueous reactions, however, they serve as an invaluable analog for identifying potential alteration features in MS rims. At the very least, this approach will reveal those features of MS rims that cannot be easily explained by aqueous reactions and that therefore justify the introduction of more complex formational scenarios involving less familiar nebular or asteroidal processes.

The MS rims possess most of the same textural features as CS rims, which suggests a similar origin. Both sets of rims display a continuous range of morphologies from smooth (compare Figs. 1 and 3a) to irregular (Compare Figs. 2a and 3b). Some individual MS rims (Fig. 3b), like some CS rims (Fig. 2c,d), have irregular morphologies on one side and smooth morphologies on the other. The MS rims also display the same progression of textural features associated with advancing stages of replacement in terrestrial serpentinites and CS rims. Fine-grained, optically opaque materials coat the surfaces and fill the fracture planes of incipiently altered core grains (Fig. 3a). More advanced stages of core grain alteration lead to variable rim thickness (Fig. 3b) and central partings that divide the original host grain into multiple rimmed segments (Fig. 3c).

By analogy with terrestrial replacement structures and CS rims, we conclude that MS rims generally exhibit variable degrees of pseudomorphic perfection and that smooth and irregular MS rims merely represent the endmember morphologies within this series. Several lines of evidence support this hypothesis: (1) some individual MS rims display a continuum between irregular (nonpseudomorphic) and smooth (pseudomorphic) morphologies; (2) continuous transitions between nonpseudomorphic and pseudomorphic replacement features are also observed in both terrestrial serpentinites (Wicks and Whittaker, 1977) and CS rims; and (3) studies of terrestrial serpentinites (Wicks and Whittaker, 1977) suggest that physical or chemical changes in the local CM alteration environment may have caused the observed variations in the degree of pseudomorphic perfection.

We have shown that replacement reactions produced diverse and abundant textural features in CM matrices and suggest that replacement may have been the dominant mode of CM alteration reactions. We have therefore asked the question, what would MS rims with irregular morphologies look like if alteration had advanced to greater degrees? Our observations suggest that at least some "massive agglomeritic structures" (MAS) in CM matrices formed as a result of replacement that went to, or approached, completion (Fig. 7b,c). These agglomerates appear dark in plane light and bright in backscattered images, range in size from a few microns to a few hundred microns, have peripheries ranging from smooth to irregular, and are perhaps the most abundant textural components in CM matrices. Some MAS have sponge-like textures in which numerous remnant unaltered olivine grains define the "holes" (Fig. 7b). Like the clusters of olivine in Figs. 1b,c, and 2c, these fragments may represent a single grain dissected during progressive replacement. Other MAS have the same sponge-like textures, but the "holes" contain Mg-rich phyllosilicates, instead of olivine (Fig. 7c). We suggest a progression from the formation of MS rims during the earliest stages of replacement, to the development of MAS textures like those observed in Fig. 7b during advanced stages of replacement, to the fully-replaced MAS textures (Fig. 7c) that dominate some CM matrices. If this scenario is correct, then CM matrices contain a significant percentage of alteration features whose formations are not favored under energetic conditions (Wicks and Whittaker, 1977).

Gradational MS rim textures serve as a testimonial to the diversity of processes affecting CM materials that must be understood before a robust, comprehensive scenario for the formation of these meteorites can be developed. These textures appear to have formed by a combination of replacement and diffusion, advection processes, or both, and may represent modifications of thinner rim textures that formed earlier by replacement (Fig. 4). Components of

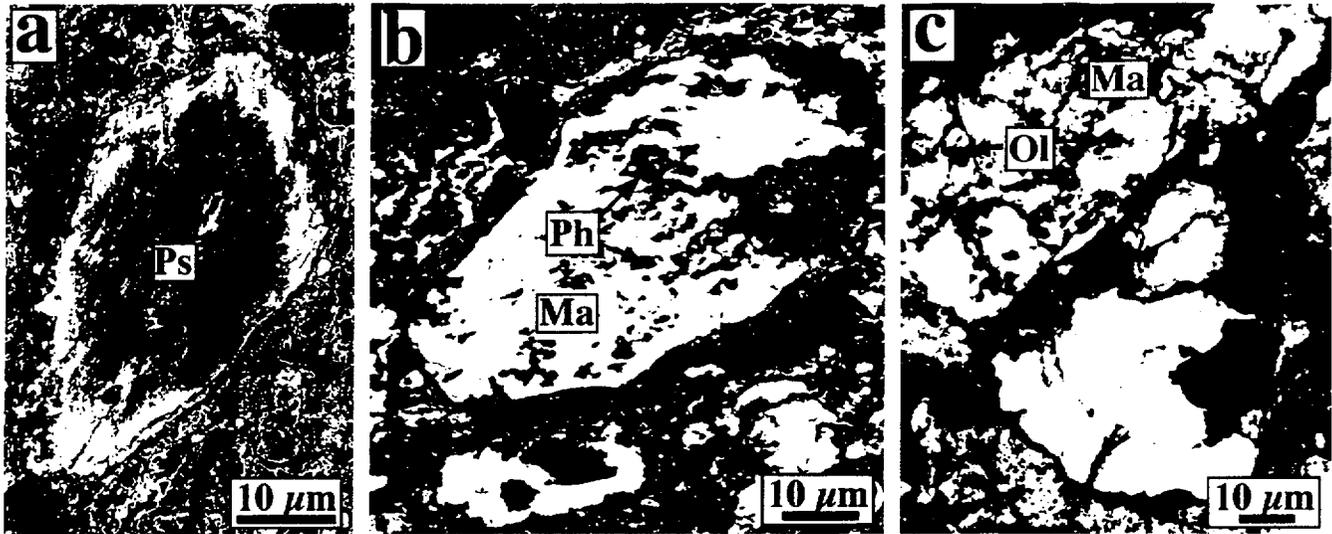


FIG. 7. Additional replacement textures in CM matrices. (a) Phyllosilicates and disseminated sulfides almost completely replace a matrix pyroxene grain in Murchison; BSE. Note that a small piece of the original pyroxene remains (arrow) and that the density of secondary sulfides is highest near the perimeter of the pseudomorph. (b) A massive agglomerate (MA) in the matrix of Murray has a sponge-like textures defined by Mg-rich phyllosilicate blebs (the "holes") set in a ground mass of fine-grained, sulfide-rich alteration minerals, and may have formed by replacement; BSE image. The left side of the massive agglomerate is smooth and has a form reminiscent of a single olivine crystal. (c) This massive agglomerate in Murray has a sponge-like texture very similar to that in (b), but the "holes" are defined by olivine grains, instead of Mg-rich phyllosilicate blebs; BSE image. With further replacement, this massive agglomerate may look like the massive agglomerate in (b).

these inner rims, however, must have migrated into the surrounding matrix by aqueous diffusion or advection processes. Hanowski and Brearley (1997) identify similar textures around metal grains that they refer to as "haloes". To produce optically opaque gradational rim textures, there must be a source of Fe, either in the core grain itself, or in a preexisting inner rim. A mechanism is therefore required to concentrate Fe around all CS and MS rims, regardless of their morphology.

THE LOCATION OF MATRIX SILICATE RIM FORMATION

The CS rims can only provide indirect evidence about the location(s) of CM alteration, because they exist entirely in chondrule interiors. The origin of CS rims is most closely tied to the alteration history of the whole chondrules surrounding them. Alteration conditions inside chondrules were probably not very different from the conditions outside chondrules, because chondrule volumes are small. However, more direct evidence for the location of CM alteration lies in the analysis of materials in contact with CM matrices.

The boundaries between matrix materials and both irregular and gradational rims (Figs. 3b and 4) show clear signs of chemical interactions in a parent-body setting. Irregular rim types are intricately interwoven with adjacent matrix materials and gradational rim types dissipate outward until they are indistinguishable from the surrounding matrix materials. If CM matrix materials represent regolith deposits on the CM parent-body, as is widely believed (Bunch and Chang, 1980; Tomeoka and Buseck, 1985), then these observed rim-matrix interactions could have only occurred on the CM parent-body after the soils formed.

Clusters of rimmed core grains in optical continuity with one another provide additional evidence for parent-body alteration. As noted previously, these are probably the remnant unaltered segments of a single, incompletely replaced core grain. Some remnant grains

may be connected in the third dimension, but replacement reactions occur *in situ*, which suggests that optical continuity ought to be preserved during the replacement process. Other scenarios, such as the nebular accretion of dust mantles around each of the individual core grains (Metzler *et al.*, 1992), do not satisfactorily explain the preservation of optical continuity.

Our approach in this paper has been to identify petrologic features that are consistent with a formation by aqueous reactions in order to identify, by a process of elimination, those features that require the introduction of alternative processes. However, we acknowledge that the simplest explanation is not always the correct explanation. For example, the small grain size of matrix materials might be explained entirely by parent-body alteration reactions, but our approach does not mandate the conclusion that the CM parent-body was never subjected to impact gardening. Instead, our approach highlights the need to critically evaluate the relative timing of aqueous alteration and brecciation. Brecciation would have destroyed the optical continuity of the core-rim clusters and erased the evidence for chemical interactions observed between matrix materials and both gradational and irregular MS rim textures. Because of the distribution and abundance of these textures, Browning and Keil (1998) conclude that CM matrices materials may not have formed in an energetic asteroidal environment (*e.g.*, regolith), as is generally believed (Bunch and Chang, 1980; Tomeoka and Buseck, 1985). Extrapolating from this concept of a quiescent alteration environment, Browning and Keil (1997) suggest the alternative hypothesis that CM chondritic materials were brecciated and buried during the initial accretion of the CM parent-body asteroid and then remained there at a sufficient depth to protect them from continued brecciation until a disruptive event finally ejected them from the parent-body asteroid.

Disagreements about the formation of CM rims center around the relative timing of aqueous alteration, accretion of the CM asteroidal parent-body, and parent-body brecciation. Our petrologic

observations suggest that some, and perhaps all, MS rims formed entirely during *in situ* parent-body aqueous alteration. Browning and Bourcier (1998a) reached a similar conclusion for the origin of some compositionally zoned rims surrounding carbonate grains in CM chondrites. This does not imply, however, that rim textures surrounding other types of CM core components, such as chondrules, necessarily formed in the same way. Complex, untestable scenarios involving processes that occur in multiple environments lose credibility, however, if the same textures could have formed by a single process in a single environment. We therefore encourage workers to focus their studies of CM rim formation on the rim textures surrounding specific types of core components.

WHAT CONCENTRATES OPAQUES INTO CHONDRULE AND MATRIX SILICATE RIMS?

Transmission electron microscopy studies have shown that the opacity of CM chondrule rims is attributable to the presence of small amounts of fine-grained, disseminated S-, Fe-, or both S- and Fe-bearing phases (Brearley and Geiger, 1991; Zolensky *et al.*, 1993). Similar studies have not yet been performed on CS and MS rims. The bulk chemical compositions of chondrule, MS, and CS rims are similar (Fig. 5), however, suggesting that disseminated opaques are common to all types of CM rims. We propose a generalized scenario explaining why opaques are concentrated around the individual olivine and pyroxene grains in CM chondrules and matrices.

We propose that CM alteration generally proceeded in the presence of thin films of intergranular fluids. Under restricted fluid flow and low-temperature conditions, diffusion would be sluggish. Relatively insoluble secondary phases, such as pyrrhotite, would be expected to occur near sources of dissolved Fe, S, or both, such as primary chondrule sulfides (Fig. 8a), and line the grain boundaries and fracture planes in many incipiently altered CM chondrules (Fig. 8b, white arrow). The heterogeneity of CM matrix minerals (Zolensky *et al.*, 1993) supports our hypothesis of thin fluid films and local precipitation–dissolution reactions. Similar local dissolution–precipitation events typify serpentinizing bodies at low temperatures attributable to the sluggish diffusion of aqueous species (Ramdohr, 1967; Noack *et al.*, 1993). The movement of thin fluid films would have been strongly affected by capillary forces and surface tensions, promoting the adhesion of the fluids on grain surfaces and slow flow rates. If local flow rates had been high, then compositional gradients would have been "washed out", and textural features produced by localized diffusion, advection, or both, such as gradational MS rims, could not have formed. Thin fluid films can thus explain why rimmed and unrimmed anhydrous MS rims may occur together in a single thin section. Moreover, the thin film hypothesis is consistent with parent-body alteration of CM materials.

Although much of the dissolved S needed to precipitate the opaques in CS rims was probably supplied by the dissolution of primary chondrule sulfides, there are several possible sources for dissolved Fe. Many individual source grains were probably destroyed by alteration and are no longer present in the meteorites. However, estimates of the relative proportions of minerals in the unaltered CM materials, on the basis of observations of the minerals still present in these meteorites, provide some insight into the most likely types of sources (Browning and Bourcier, 1998b). Dissolved Fe was probably supplied from the dissolution of primary metal and sulfide grains that are sometimes associated with CS rims (Ramdohr, 1967; Tomeoka and Buseck, 1985). A less obvious, yet

potentially more important, source of dissolved Fe is olivine. Although the FeO content of chondrule olivine is generally low (Wood, 1967; Rubin and Wasson, 1986), these phases volumetrically dominate the mineralogy of chondrules and could have contributed a significant fraction of total dissolved Fe²⁺ needed to precipitate the relatively insoluble opaques observed in CM chondrites. For example, Browning (1995) modeled the precipitation of secondary pyrrhotite at the surface of a reacting olivine grain, assuming that all the requisite Fe²⁺ is supplied by dissolving olivine grains that are separated by a few hundred microns of dilute S-bearing fluids. These calculations suffice to show that even FeO-poor olivine will rapidly release enough dissolved Fe²⁺ to form Fe-sulfides at its surface. Recrystallization of matrix phyllosilicates may have released Fe into the fluids during the late stages of alteration, because Fe was progressively exchanged for Mg in these minerals as the

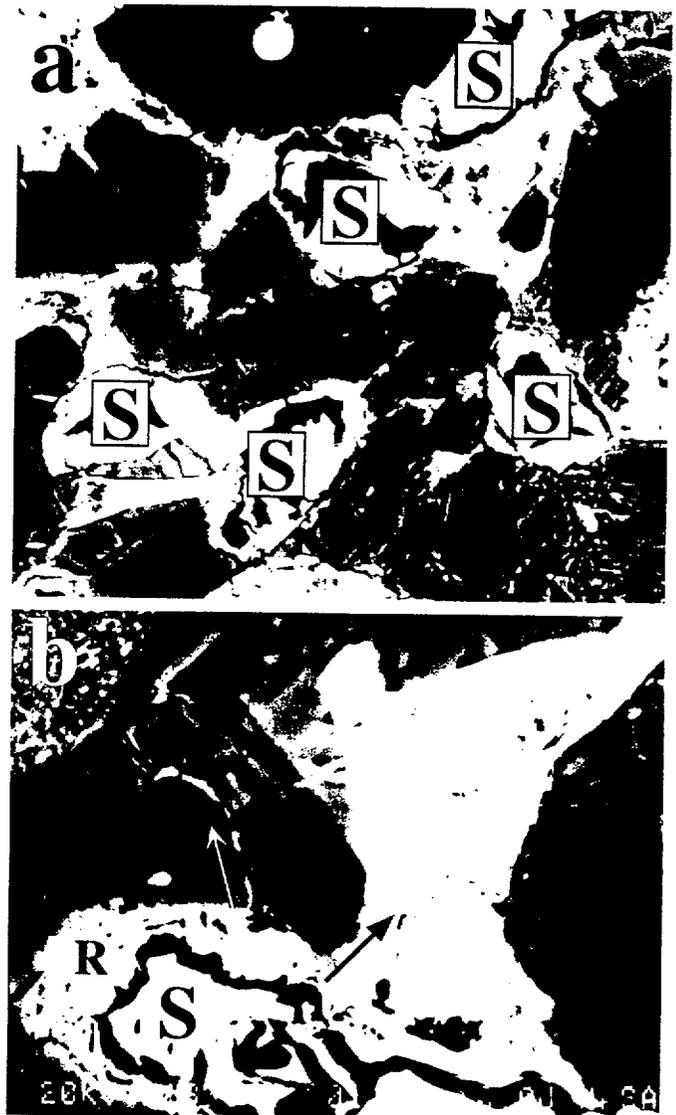


FIG. 8. Incipient alteration in a Cochabamba chondrule; BSE. (a) Fine-grained secondary sulfides (bright areas) form near primary sulfide (S) in area of altered mesostasis during the initial stages of chondrule alteration. (b) Fine-grained secondary sulfides form a rim texture around a highly degraded primary sulfide bleb (S), and line the grain boundaries between adjacent olivines (white arrow).

meteorites experienced increasing degrees of alteration (Browning *et al.*, 1996; Tomeoka and Buseck, 1985).

CONCLUSIONS

Optically opaque rim textures surrounding individual chondrule silicate grains must have formed by *in situ* aqueous processes and thus provide a useful benchmark for identifying structures outside of chondrules that may have formed by similar alteration processes. Because matrix silicate rims are embedded in matrix materials that are generally thought to represent portions of the parent-body regolith, a large number of nebular or parent-body scenarios might be constructed to explain their origin. With one exception, however, the same set of diverse morphological features are observed in both CS and MS rims, and the simplest explanation is that both types of rims formed exclusively by *in situ* aqueous processes on the CM parent body.

The only type of rim morphology identified in this study that is not present in both CS and MS rims is gradational matrix silicate rims. The unique morphological features of these rims provide strong evidence for an origin involving *in situ* parent-body alteration and would not be expected to form inside chondrules. We note that if the formation of chondrule rims involved nebular accretion, as is generally thought, then this study implies that more than one scenario may be needed to explain the origin of the CM rims in general. The rims surrounding different types of coarse-grained core components may have formed in different ways. Until the alteration history of CM rim textures is understood better, it seems premature to develop comprehensive, multi-environment scenarios for the formation of CM chondrites on the basis of analyses of CM rims.

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Modeling aqueous alteration of CM carbonaceous chondrites

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Abstract—Results from an inorganic geochemical modeling study support a scenario in which low-temperature aqueous alteration of an anhydrous CM asteroidal parent body and melt water from H₂O and CO₂ ices produces the altered assemblage observed in CM carbonaceous chondrites (chrysotile, greenalite, tochilinite, cronstedtite and minor calcite and magnetite). We consider a range of possible precursor mineral assemblages, varying with respect to the Fe-oxidation state of the initial anhydrous phases. The aqueous solutions produced by this alteration are generally strongly basic and reducing and a large quantity of H₂, and possible CH₄, gas can be released during aqueous alteration.

INTRODUCTION

CM carbonaceous chondrites are believed to be fragments of some of the most primitive material in our solar system. In addition to nebular components (*e.g.*, chondrules), these meteorites contain abundant hydrous minerals, primarily Fe and Mg-rich serpentines and tochilinite, an interlayered Fe sulfide-Fe hydroxide mineral. Several lines of evidence suggest that these hydrated minerals formed by low-temperature aqueous alteration, possibly *in situ* on CM asteroidal parent bodies (Clayton and Mayeda, 1999; Zolensky *et al.*, 1993; Zolensky and McSween, 1988; Bunch and Chang, 1980). Grimm and McSween (1989) suggested a scenario in which primitive asteroidal bodies, initially made up of ice and anhydrous minerals, underwent extensive aqueous alteration when the ice melted in response to heating, perhaps from radioactive decay of ²⁶Al (Fig. 1), or possibly from solar electromagnetic induction heating.

We are interested in understanding aqueous alteration on CM asteroidal parent bodies because of what this might tell us about conditions in the early solar system. Of particular interest is the question of the origin and delivery of water to primordial Earth. The Earth formed in a region of the protoplanetary nebula where temperatures were too hot for water to condense (Wetherill, 1990). For a long time it was thought that water was delivered to Earth by a late bombardment of comets, but recent isotopic (*e.g.*, Meier *et al.*, 1998) and dynamical modeling (Levison and Duncan, 1997) studies suggest otherwise. It now appears that water must have been delivered to Earth in the form of volatile-rich planetesimals from more distant regions of the early solar system where conditions were cool enough for water to condense, and that perturbations from

Jupiter and Saturn scattered these bodies inwards. If water was delivered to Earth in this manner, some of this water may have arrived sequestered in hydrous mineral phases.

Understanding aqueous alteration on CM asteroidal parent bodies is also of interest with respect to questions concerning the origin of life. Carbonaceous chondrites contain a complex suite of organic compounds (Cronin *et al.*, 1988), many of which may have been synthesized in the aqueous alteration processes that resulted in the formation of the hydrous mineral phases (Bunch and Chang, 1980; Schulte, 1997). The aqueous alteration of CM carbonaceous chondrites may also be a useful guide to understanding the history of other meteorites, icy-satellites such as Europa, comets, and C-type asteroids which show spectral evidence for hydrous minerals (Jones *et al.*, 1990; Barucci *et al.*, 1998).

This paper reports on the results of an inorganic geochemical modeling study of the aqueous alteration of CM asteroidal parent bodies. A modeling study by Zolensky *et al.* (1989) examined alteration scenarios for CM and CV asteroidal parent bodies for a wide range of temperatures and water–rock ratios. We focus here on simulations that start with CM asteroidal parent bodies and produce alteration assemblages consistent with CM carbonaceous chondrites. A major difference between these two studies is the assumed CM asteroidal parent body composition. The earlier study relied on visual estimates of the anhydrous mineralogy preserved in Murchison, a well-studied CM carbonaceous chondrite. Our estimates rely on a range of possible precursor assemblages reported in a recent study by Browning and Bourcier (1998). These assemblages are based on the preserved anhydrous phases in numerous CM carbonaceous chondrites, including Murchison, and are constrained by detailed elemental mass

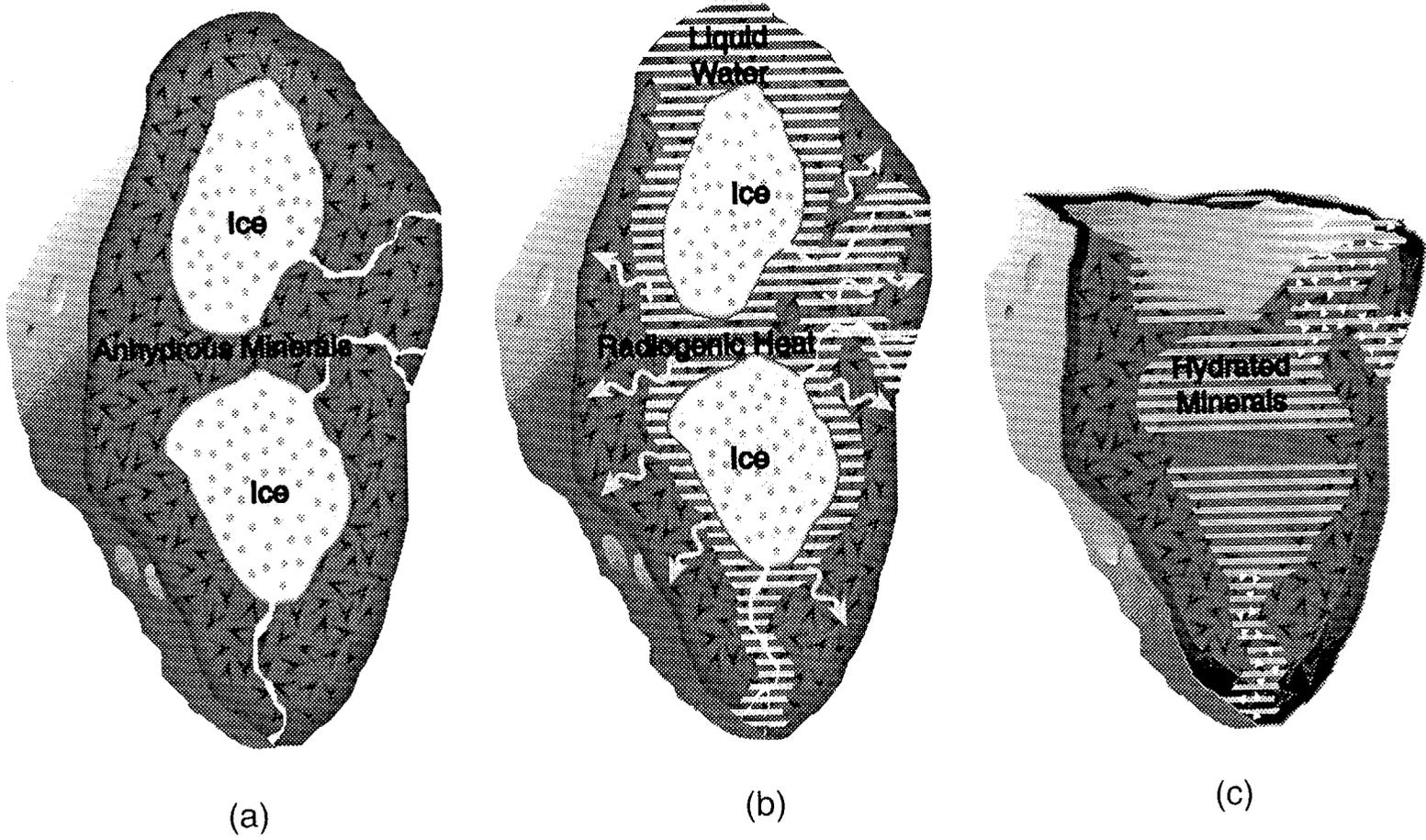


FIG. 1. Possible aqueous alteration scenario that produced CM carbonaceous chondrites.

balance analyses. This allows for consideration of the original proportions of unaltered precursor phases, which differs from those preserved in the altered meteorites. These additional constraints on precursor mineral proportions greatly increases our understanding of CM asteroidal parent bodies and consequently enhances our efforts to understand the aqueous alteration that produced CM carbonaceous chondrites.

CONCEPTUAL MODEL FOR AQUEOUS ALTERATION

We do not attempt to elucidate all of the complicated history of CM carbonaceous chondrites in this study, focusing instead on the major aspects of alteration. We begin by describing our assumptions regarding initial rock and fluid compositions.

It is difficult to determine the original, unaltered mineral composition of CM asteroidal parent bodies because alteration is so extensive. As stated in the Introduction, we rely on the Browning and Bourcier (1998) study of possible precursor mineralogy of CM carbonaceous chondrites. Each assemblage contains mostly Fe-poor phases consistent with observations of existing unaltered phases. The major uncertainty in the original mineral composition is the form of the original Fe-rich phases, since most of these phases are gone. A range of possible precursor mineral assemblages is reported, mainly to address this uncertainty. Of the 19 assemblages listed in that study, we consider two here: the most reduced Fe composition and the most oxidized Fe composition (Table 1). It is also difficult to make estimates of the composition of the original fluid phase, since no direct evidence is preserved in CM carbonaceous chondrites. We assume that water and carbon ices were present and that the original fluid phase in CM asteroidal parent bodies was melt water from these ices. We do not know the original proportions of rock and water. Recent estimates of the bulk densities of C-type asteroids suggest that these bodies may have been very porous (e.g., Ververka *et al.*, 1997).

Alteration minerals in CM carbonaceous chondrites include Mg-serpentine (chrysothite), Fe-serpentine (greenalite, cronstedtite) and tochilinite, with minor amounts of magnetite

TABLE 1. Anhydrous precursor mineralogy and mineral formulae.

Mineral name	Mineral formula	Reduced-Fe endmember (vol%)*	Oxidized-Fe endmember (vol%)*
Pyrrhotite	Fe _{0.875} S	9.25	8.79
Forsterite	Mg ₂ SiO ₄	7.71	44.04
Fayalite	Fe ₂ SiO ₄	0.00	27.75
Enstatite	Mg ₂ Si ₂ O ₆	57.93	4.65
Native iron metal	Fe	10.09	0.02
Diopside	CaMgSi ₂ O ₆	10.81	10.20
Glass	SiO ₂	1.75	1.40
Other (neglected)		2.46	3.05

*Based on Browning and Bourcier (1998).

TABLE 2. Alteration phases and mineral formulae.

Mineral name	Mineral formula
Greenalite	Fe ₃ Si ₂ O ₅ (OH) ₄
Cronstedtite	Fe ₄ SiO ₅ (OH) ₄
Tochilinite	6FeS*5Fe(OH) ₂
Chrysothite	Mg ₃ Si ₂ O ₅ (OH) ₄
Calcite	CaCO ₃
Magnetite	Fe ₃ O ₄

and calcite (Table 2). A general alteration history for CM carbonaceous chondrites can be discerned from petrologic studies (e.g., Browning *et al.*, 1996; Tomeoka and Buseck, 1985). Briefly, this evidence suggests that reduced Fe-phase minerals reacted with water to form more oxidized Fe phases, and that Mg-silicates reacted with water to form Mg-rich serpentines. Some Fe-rich alteration phases may have formed relatively early and evolved to more Mg-rich alteration phases over time. The geochemical data indicate that alteration occurred between about 0–25 °C (with water possibly flowing from higher temperature to lower temperature regions) in a closed system (allowing for some volatile loss), and did not require large volumes of water interacting with the rock (see Clayton and Mayeda, 1999; Young *et al.*, 1999).

The aqueous alteration of CM asteroidal parent bodies is in many ways similar to the serpentinization of ultramafic rocks on Earth (O'Hanley, 1996). This alteration also occurred at low temperatures and the minerals that make up ultramafic rocks, mainly Mg-rich olivines and pyroxenes, are among the unaltered phases found in CM carbonaceous chondrites.

DESCRIPTION OF NUMERICAL MODELING STUDY

We use a numerical model, based on the conceptual model described in the previous section, to explore possible water-rock interactions on a CM asteroidal parent body. Our calculations are performed using the REACT computer code (Bethke, 1996). (REACT is a geochemical modeling tool nearly identical to the more commonly used EQ3/6 code (Wolery, 1992). The differences are primarily in the user interface.)

REACT models equilibrium states in systems containing an aqueous fluid, with or without mineral phases present, and the evolution of the system in response to changes in temperature or boundary conditions or the addition or removal of reactants. REACT calculates the equilibrium distribution of aqueous species, fluid saturation state with respect to various mineral phases, and the fugacities of dissolved gases. REACT also calculates the equilibrium mineral assemblage and total mass and volume of fluid present. Kinetically controlled reactions can also be considered.

REACT is used in conjunction with a thermodynamic dataset containing data for the relevant mineral, gas and

aqueous species. We use a slightly-modified version of the commonly-used "sup" database (v. 7) based on SUPCRT92 (Johnson *et al.*, 1992) and add data for the minerals cronstedtite and greenalite from the much larger composite "com" database (v. 7) (Delany and Lundeen, 1990). Thermodynamic data for Fe-endmember tochilinite were estimated by assuming ideal mixing between pyrrhotite and iron hydroxide layers (Browning and Bourcier, 1996). Thermodynamic data for pyrrhotite were estimated from the experimental mixing properties and approach described in Powell (1983).

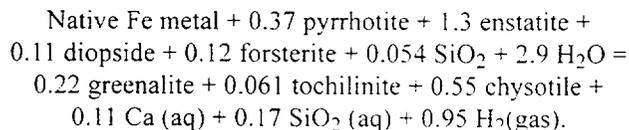
We consider equilibrium assemblages as a function of water-rock ratio, suppressing the precipitation of mineral phases well-known to be kinetically inhibited at these low temperatures (*e.g.*, garnets, amphiboles, quartz). The only Mg-phyllisilicate allowed to form is chrysotile, the Mg-alteration phase observed in CM carbonaceous chondrites. We do not consider the evolution of Fe-alteration phases to Mg-rich alteration phases with reaction time.

We start each calculation with a set amount of dilute fluid, representing melt water from CM asteroidal parent body ices. To this initial fluid system, we add the equivalent of a 1 m³ volume of asteroid in terms of specific mineral volumes. We examine the effects of initial mineral assemblage, water-rock ratio (1–10, based on mass), temperature, fluid composition, and whether the system is open or closed with respect to gas escape. We report results in terms of alteration mineral assemblages, amount of water consumed during alteration, change in mineral volume, gases produced, pH, Eh, and major aqueous species.

MODEL RESULTS AND DISCUSSION

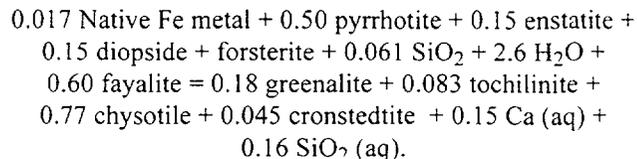
We begin by considering aqueous alteration in a closed system at 25 °C for the reduced-Fe endmember initial mineral assemblage. We start with 3000 kg of nearly pure water with a pH of ~7, and incrementally react 3000 kg of rock. To put these quantities into perspective, when fully reacted, these amounts are equivalent to 1 m³ of asteroid with a porosity of 20% and 15× the amount of water needed to fill all the pores.

The overall reaction for the aqueous alteration in this system, as determined by REACT, is described by the following equation:



The altered mineral composition includes, in vol%, 61% chrysotile, 25% greenalite and 14% tochilinite. The alteration assemblage is the same for the range of water-rock ratios considered. The pH increases from 12.2 to 13.1 and the Eh decreases from -0.80 to -0.88 as the water-rock ratio decreases from 10 to 1.

The aqueous alteration for the oxidized-Fe endmember initial mineral assemblage is similar in most respects. In this case, we start the calculation with 2500 kg of water to allow for a water-rock ratio of 1 after all the rock is reacted (*i.e.*, this assemblage is less dense). As with the reduced-Fe endmember initial assemblage, aqueous alteration produces chrysotile, greenalite, and tochilinite, but in this case, cronstedtite, a more oxidized Fe-serpentine than greenalite, forms as well. The overall water-rock reaction for the aqueous alteration for the oxidized-Fe system is described by the following equation:



The altered composition includes 57% chrysotile, 15% cronstedtite, 14% greenalite, and 13% tochilinite by volume. The alteration assemblage is the same for the range of water-rock ratios considered. The pH increases from 12.5 to 13.3 and the Eh decreases from -0.59 to -0.64 as the water-rock ratio decreases from 10 to 1.

For both initial mineral assemblages, there is a significant increase in the mineral volume (~50%), and in both cases, the aqueous solutions are dominated by Ca and Si complexes. Both reactions are dominated by hydration reactions, consuming large amounts of water, 600 and 370 kg of water for the reduced-Fe and oxidized-Fe assemblages, respectively. For perspective, consider a 20% porosity asteroid. Complete alteration would require the equivalent of the amount of water needed to fill all the pores of the asteroid 2–3 times. We also note that both reactions are exothermic.

The major difference between the two initial mineral compositions is the large amount of H₂ gas produced when water reacts with the reduced-Fe assemblage (7.3 g per kg of asteroid reacted) and the nearly zero amount produced with the oxidized-Fe assemblage, with the consequent greater Eh in the latter case. The H₂ gas is produced as reduced iron is oxidized (Fe⁰ + 2H⁺ = Fe⁺⁺ + H₂(gas)). The amount of H₂ gas produced in the reduced-Fe initial assemblage cases is directly proportional to the amount of reduced Fe present that reacts with water. This amount is therefore inversely correlated with porosity for a given volume of asteroid. A reacted 1 m³ volume of reduced-Fe assemblage asteroid can therefore produce 22 kg of H₂ gas if the porosity is 20%, and 5.5 kg of H₂ gas if the porosity is 80%.

In the simulations discussed so far, we have not included any carbonate in the water, and as a result, we have not seen any calcite in the alteration assemblages. We now reconsider the calculations discussed above adding different levels of dissolved carbonate as [HCO₃⁻] to the initial fluid, which gives the initial fluid a pH closer to 4. The amount of calcite that forms, as a volume percent of the mineral assemblage, varies

between 0 and about 4% and is a function of both the dissolved carbonate concentration and water-rock ratio. For example, there is not enough carbonate in the system to react all the available Ca at $[\text{HCO}_3^-]$ levels of 0.01 or 0.1 molal. In the 0.01 molal case, the carbonate is exhausted upon addition of just a small amount of rock to the system. In the 0.1 molal case, the carbonate is exhausted by a water-rock ratio of about 4. For a $[\text{HCO}_3^-]$ level of 0.2 molal, the carbonate is not exhausted until a water-rock ratio of nearly 2. Not surprisingly, the presence of large amounts of dissolved carbonate creates a more acidic and more oxidizing environment, but the alteration assemblages are not much affected.

In this calculation, we decoupled the oxidized and reduced aqueous carbon species, so that no CH_4 was able to form from the dissolved carbonate. This assumption is based on studies showing very low rates for these redox reactions in nature (*e.g.*, Shock, 1988). It may, however, be possible for HCO_3^- to be converted to CH_4 in the presence of ultramafic rocks under reducing conditions ($2\text{H}_2 + \text{C} = \text{CH}_4$). Evidence comes from recent laboratory studies on H_2 and CH_4 generation from native metal reacted with water (Horita and Berndt, 1999) and observations of $\text{H}_2 - \text{CH}_4$ gas seeps in serpentinized zones on Earth (Abrajano *et al.*, 1990). We ran calculations with $[\text{HCO}_3^-]$ levels = 0.2 m again, this time allowing CH_4 formation from the dissolved carbonate. In this case, for the reduced-Fe initial assemblage, calcite only formed at high water-rock ratio. At a water-rock ratio of 1, both H_2 (17.1 kg) and CH_4 (9.5 kg) formed. The results for the oxidized-Fe initial assemblage were not changed.

We also investigated allowing gases generated by the water-rock interaction to escape (*i.e.*, an open system rather than a closed system). If the H_2 fugacity for the reduced-Fe endmember case in the "atmosphere" of the CM asteroidal parent body is held to a level of 1.2×10^{-5} (the equilibrium H_2 fugacity calculated by REACT for the oxidized-Fe endmember case), the effects on aqueous alteration are minor. The alteration mineral assemblage does not change. The only difference is the absence of a build-up of H_2 gas (by definition) which results in a higher oxidation state. If the "atmospheric" H_2 levels are set about an order of magnitude lower (*e.g.*, 1×10^{-6}), the alteration mineral assemblage includes cronstedite, a more oxidized Fe-serpentine than greenalite.

We were able to produce a few percent magnetite as an alteration mineral with relatively minor changes in the amounts of Fe minerals and SiO_2 in the initial mineral assemblage. Such changes are not unreasonable given the fact that local heterogeneity likely existed on CM asteroidal parent bodies. For example, we produce 1% by volume magnetite by reducing the amount of pyrrhotite in the reduced-Fe initial mineral composition by an order of magnitude, or by reducing this amount by one-half and also eliminating the SiO_2 phase. In the oxidized-Fe case, 1% by volume magnetite forms when one-half of the pyrrhotite is removed from the original

composition. In both cases, the volume of greenalite increases, using up the all the dissolved SiO_2 and leaving a very alkaline, Ca-OH fluid. These fluids strongly resemble the high-pH, Ca-OH waters from some springs associated with ultramafic rocks on Earth (Barnes and O'Neil, 1969).

CONCLUSIONS

These model results support a scenario in which low-temperature aqueous alteration of an anhydrous CM asteroidal parent body and melt water from H_2O and CO_2 ices produces the main alteration minerals found in CM carbonaceous chondrites.

The aqueous alteration for reduced-Fe and oxidized-Fe endmember mineral assemblages for CM asteroidal parent bodies is similar in most respects. In both cases, aqueous alteration results in approximately a 50% increase mineral volume and produces chrysotile, greenalite, and tochilinite; cronstedite only forms in the more oxidized assemblage. We are able to simulate the formation of minor calcite by adding dissolved carbonate to the system. A large quantity of H_2 gas can be released during aqueous alteration, in direct proportion to the amount of reduced Fe present that reacts with water (*e.g.*, about 7.3 g per kg asteroid with the reduced-Fe assemblage). If dissolved carbonate is present, CH_4 gas may also be produced. The aqueous solutions produced by this alteration are dominated by Ca and Si, and are strongly basic and reducing. The alteration involves primarily hydration reactions that consume large amounts of water. For example, complete reaction of a 20% porosity CM asteroidal parent body requires 2–3× the amount of water needed to fill all the pores (*i.e.*, 0.4–0.6 m^3 for a 1 m^3 asteroid).

These model results have several interesting implications. With respect to conditions in the early solar system, the large volume of gas that can be released during aqueous alteration of CM asteroidal parent bodies, and possibly the significant increase in the volume of the mineral assemblage as well, support the suggestion of Wilson *et al.* (1999) that internal gas pressurization may have led to partial or complete disaggregation of early asteroid bodies. Also, our model results suggest that if the core of the icy-satellite Europa has a composition similar to a CM carbonaceous chondrite, as has been suggested by Fanale *et al.* (1998) and Bass *et al.* (2000), the ocean on Europa is likely to be very alkaline and reducing.

Our current research efforts are focused on integrating thermohydrologic models with our geochemical models to achieve a more comprehensive picture of aqueous processes on primitive bodies in the early solar system. The addition of organic geochemistry to these models also needs to be considered.

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AQUEOUS ALTERATION OF CM CARBONACEOUS CHONDRITES. N. D. Rosenberg¹, L. Browning² and W. L. Bourcier³ ¹LLNL (MS L204, Livermore CA 94550; rosenberg4@llnl.gov) ²Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, (San Antonio TX, 78238; lbrowning@swri.edu) ³LLNL (MS L219, Livermore CA 94550; bourcier1@llnl.gov)

Introduction: Several lines of evidence suggest that the hydrated minerals found in CM carbonaceous chondrites formed by low-temperature aqueous alteration, possibly in situ on CM asteroidal parent bodies. One scenario is that primitive asteroidal bodies, initially made up of ice and anhydrous minerals, underwent extensive aqueous alteration when the ice melted in response to heating, perhaps from radioactive decay of ²⁶Al [1] or possibly from solar electromagnetic induction heating. We report on results of an inorganic geochemical modeling study of the aqueous alteration of CM asteroidal parent bodies, building on earlier work [2].

Conceptual Model: Our estimates for precursor assemblages are based on a study [3] which considered the preserved anhydrous phases in numerous CM carbonaceous chondrites, constrained by detailed elemental mass balance analyses. Each assemblage contains mostly Fe-poor phases consistent with observations of existing unaltered phases. The major uncertainty in the original mineral composition is the form of the original Fe-rich phases, since most of these phases are gone. A range of possible precursor mineral assemblages is reported, mainly to address this uncertainty. We consider two: the most reduced Fe composition and the most oxidized Fe composition. The most volumetric abundant mineral in the reduced-Fe endmember is enstatite (58%), with diopside, native iron metal, pyrrhotite and forsterite present at levels of 5-11%. The oxidized-Fe endmember contains mainly forsterite (44%), with 4-11% fayalite, diopside, and pyrrhotite and enstatite. We assume that water and carbon ices were present and that the original fluid phase in CM asteroidal parent bodies was melt water from these ices.

Alteration minerals in CM carbonaceous chondrites include Mg-serpentine (chrysotile), Fe-serpentine (greenalite, cronstedtite) and tochilinite, with minor amounts of magnetite and calcite. A general alteration history for CM carbonaceous chondrites can be discerned from petrologic studies [e.g., 4,5]. Briefly, this evidence suggests that reduced Fe-phase minerals reacted with water to form more oxidized Fe phases, and that Mg-silicates reacted with water to form Mg-rich serpentines. The isotope and phase stability data indicate that alteration occurred between about 0-25°C (with water possibly flowing from higher temperature to lower temperature regions) in a closed system (al-

lowing for some volatile loss), and did not require large volumes of water interacting with the rock [6,7].

Numerical Modeling Study: We use a numerical model, based on the conceptual model described above, to explore possible water-rock interactions on a CM asteroidal parent body. Our calculations are performed using the REACT computer code [8] in conjunction with a thermodynamic dataset containing data for the relevant mineral, gas and aqueous species. We consider equilibrium assemblages as a function of water-rock ratio, suppressing the precipitation of mineral phases well-known to be kinetically inhibited at these low temperatures (e.g., quartz). The only Mg-phyllsilicate allowed to form is chrysotile, the Mg-alteration phase observed in CM carbonaceous chondrites.

We start each calculation with a set amount of dilute fluid, representing melt water from CM asteroidal parent body ices. To this initial fluid system, we add the equivalent of a 1 m³ volume of asteroid in terms of specific mineral volumes. We examine the effects of initial mineral assemblage, water-rock ratio (1-10, based on mass), temperature, fluid composition, and whether the system is open or closed with respect to gas escape. We report results in terms of alteration mineral assemblages, amount of water consumed during alteration, change in mineral volume, gases produced, pH, Eh, and major aqueous species.

Model Results and Discussion: We begin by considering aqueous alteration in a closed system at 25°C for the reduced-Fe endmember initial mineral assemblage. We start with 3000 kg of nearly pure water with a pH of ~7, and incrementally react 3000 kg of rock. To put these quantities into perspective, when fully reacted, these amounts are equivalent to 1 m³ of asteroid with a porosity of 20% and 15 times the amount of water needed to fill all the pores. The altered mineral composition includes, in volume percent, 61% chrysotile, 25% greenalite and 14% tochilinite. The alteration assemblage is the same for the range of water-rock ratios considered. The pH increases from 12.2 to 13.1 and the Eh decreases from -0.80 to -0.88 as the water-rock ratio decreases from 10 to 1.

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reduced-Fe endmember initial assemblage, aqueous alteration produces chrysotile, greenalite, and tochilinite, but in this case, cronstedtite, a more oxidized Fe-serpentine than greenalite, forms as well. The altered composition includes 57% chrysotile, 15% cronstedtite, 14% greenalite, and 13% tochilinite by volume. The alteration assemblage is the same for the range of water-rock ratios considered. The pH increases from 12.5 to 13.3 and the Eh decreases from -0.59 to -0.64 as the water-rock ratio decreases from 10 to 1.

For both initial mineral assemblages, there is a significant increase in the mineral volume (~50%), and in both cases, the aqueous solutions are dominated by Ca and Si complexes. Both reactions are dominated by hydration reactions, consuming large amounts of water, 600 and 370 kg of water for the reduced-Fe and oxidized-Fe assemblages, respectively. For perspective, consider a 20% porosity asteroid. Complete alteration would require the equivalent of the amount of water needed to fill all the pores of the asteroid 2-3 times. Both reactions are exothermic; the heat generated from initial water-rock reactions could melt additional ice, leading to the alteration of additional rock.

The major difference between the two initial mineral compositions is the large amount of H₂ gas produced when water reacts with the reduced-Fe assemblage (7.3 g per kg of asteroid reacted) and the nearly zero amount produced with the oxidized-Fe assemblage, with the consequent greater Eh in the latter case. The H₂ gas is produced as reduced iron is oxidized ($\text{Fe}^0 + 2\text{H}^+ = \text{Fe}^{2+} + \text{H}_2(\text{gas})$). The amount of H₂ gas produced in the reduced-Fe initial assemblage cases is directly proportional to the amount of reduced Fe present that reacts with water.

In the simulations discussed so far, we have not included any carbonate in the water, and as a result, we have not seen any calcite in the alteration assemblages. We next reconsider the calculations discussed above adding different levels of dissolved carbonate as [HCO₃⁻] to the initial fluid, which gives the initial fluid a pH closer to 4. The amount of calcite that forms, as a volume percent of the mineral assemblage, varies between 0 and about 4% and is a function of both the dissolved carbonate concentration and water-rock ratio. For example, there is not enough carbonate in the system to react all the available Ca at [HCO₃⁻] levels of 0.01 molal or 0.1 molal. In the 0.01 molal case, the carbonate is exhausted upon addition of just a small amount of rock to the system. In the 0.1 molal case, the carbonate is exhausted by a water-rock ratio of about 4. For a [HCO₃⁻] level of 0.2 molal, the carbonate is not exhausted until a water-rock ratio of nearly 2. Not surprisingly, the presence of large amounts of dissolved carbonate creates a more acidic and more oxi-

dizing environment, but the alteration assemblages are not much affected. In this calculation, we did not allow CH₄ to form from the dissolved carbonate. This assumption is based on studies showing very low rates for these redox reactions in nature, but this may not be a good assumption for system that contain metal [9]. We reran calculations with [HCO₃⁻] levels = 0.2 m allowing CH₄ formation from the dissolved carbonate. In this case, for the reduced-Fe initial assemblage, calcite only formed at high water-rock ratio. At a water-rock ratio of 1, both H₂ (17.1 kg) and CH₄ (9.5 kg) formed. The results for the oxidized-Fe initial assemblage were not changed.

We were able to produce a few percent magnetite as an alteration mineral with relatively minor changes in the amounts of Fe minerals and SiO₂ in the initial mineral assemblage. Such changes are not unreasonable given the fact that local heterogeneity likely existed on CM asteroidal parent bodies.

Conclusions: These results support a scenario in which low-temperature aqueous alteration of an anhydrous CM asteroidal parent body and melt water from H₂O and CO₂ ices produces the main alteration minerals found in CM carbonaceous chondrites. There are several interesting implications. With respect to conditions in the early solar system, the large volume of gas that can be released during aqueous alteration of CM asteroidal parent bodies, and possibly the significant increase in the volume of the mineral assemblage as well, support suggestions that internal gas pressurization may have led to partial or complete disaggregation of early asteroid bodies [10]. Also, our model results suggest that if the core of the icy-satellite Europa has a composition similar to a CM carbonaceous chondrite [11,12], the ocean on Europa is likely to be very alkaline and reducing.

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COMPOSITIONAL ZONING AND MN-CR SYSTEMATICS IN CARBONATES FROM THE Y791198 CM2 CARBONACEOUS CHONDRITE Adrian J. Brearley¹, Ian D. Hutcheon² and Lauren Browning³. ¹Dept. of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA (brearley@unm.edu), ²Analytical and Nuclear Chemistry Division, Lawrence Livermore National Laboratory, Livermore, CA 94551, ³Southwest Research Institute, San Antonio, TX 78238.

Introduction: The record of primitive solar system processes recorded within the CM carbonaceous chondrites has been extensively compromised by the effects of aqueous alteration [1]. The effects of aqueous alteration are widespread, but manifest themselves to different degrees within CM meteorites and are, in many cases, complicated by the effects of brecciation [2,3]. One of the key issues to understanding the process of aqueous alteration is determining where alteration took place. Although alteration within a parent body environment unequivocally affected many CM chondrites [4], there is also evidence that some alteration may have occurred prior to accretion of asteroidal parent bodies [5]. This "preaccretionary" alteration may have occurred in transient protoplanetary bodies that were subsequently disrupted by impacts, prior to incorporation of the final components in the CM carbonaceous chondrite parent bodies [5,6].

One of the products of aqueous alteration are carbonates, disseminated in low abundances (<~3 vol%) in all CM chondrites [7]. We have shown that carbonates in CM chondrites ranging from weakly to highly altered (Murchison, ALH81002 and ALH84034 (CM1)) [8-10] have complex compositional zoning that provides new insights into the origin of these grains. To extend these observations we studied the unbrecciated and weakly altered CM2 chondrite, Yamato 791198. Our goals are to understand how carbonate mineralogy, chemistry and isotopic systematics evolve as a function of increasing degrees of alteration and the role that brecciation may play in affecting carbonate formation. We studied carbonates in Y791198 using SEM techniques (BSE, CL) and EPMA. In addition, to understand the timing of carbonate formation, we investigated the ⁵⁵Mn-⁵³Cr isotope record of selected Y791198 carbonates to search for radiogenic ⁵³Cr* using the LLNL ims-3f ion microprobe (SIMS) [11].

Observations: Y791198 has been classified as a primary accretionary rock in which essentially all the macroscopic components are mantled by fine-grained rims [6]. Our observations are generally consistent with these studies. In Y791198, the carbonate grains appear to occur exclusively within the fine-grained matrix. We have not observed any carbonates associated with chondrules and due to the rarity of CAIs in the small thin sections studied, it is not clear whether CAIs have been replaced by carbonates.

EPMA studies show that the only carbonate phase present is CaCO₃, which optically appears to be exclusively calcite although some minor aragonite may also be present [7]. Calcite occurs typically as irregularly-shaped grains, which may be either single crystals or aggregates of several crystals. The grain sizes vary from <50 μm, ranging down to <10 μm. Most grains have a highly angular morphology, although some grains may have well-developed facets. Inclusions of sulfides or phyllosilicates, probably serpentines, are sometimes present. None of the carbonate grains are surrounded by fine-grained rims. Instead, the carbon-

ates occur embedded within fine-grained matrix material that is often associated with abundant tochilinite/serpentine aggregates (formerly PCP) that are distributed throughout this meteorite.

We studied about 20 of the carbonates in detail by

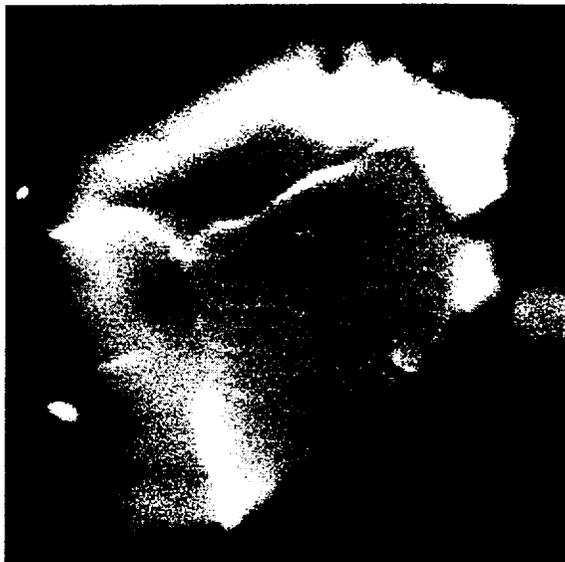


Figure 1. SEM CL image of calcite grain in Y791198 showing asymmetric zoning. Field of view = 55 microns. CL and EPMA and several grains were analysed for ⁵⁵Mn-⁵³Cr dating by SIMS. All of the grains show evidence of complex zoning and two distinct types can be distinguished based on the CL characteristics. Asymmetric zoning (Fig. 1) is present within individual crystals and rarely in aggregates of grains. Within aggregates, the outer parts (and cores) of the constituent grains have low CL and zone to bright CL rims, where the grains meet in the interior of the aggregate. In individual crystals, a similar type of zoning is present with one part of the grain having a relatively homogenous, low CL core and an overgrowth with consistently brighter CL intensity. We infer that this region is an overgrowth because the crystals often have well-developed facets (Fig.1). Compositionally, all these grains exhibit similar zoning characteristics. The lower CL intensity cores generally have MgO, MnO and FeO contents of ~0.4 wt% or less. The zoning profiles are relatively flat or show slight increases towards the outer parts of the low CL cores. All three elements show exactly the same behavior. In the rim, which can vary in thickness from 5 to 15 μm, FeO, MnO and MgO all increase rapidly. In several of the grains studied, the MnO contents increase to remarkably similar values at the rim of 1.2 ± 0.1 wt%. The increase in CL intensity at the rims and in hotspots in the interiors of grains appears well correlated with elevated MnO contents.

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An additional feature, found in three grains, is the present of relict, complexly zoned cores. In each case, the core shows evidence of reverse zoning and has a subrounded outline indicating it may have experienced a period of dissolution, prior to the growth of the main part of the crystal. The 3 relict cores we have observed are $<5 \mu\text{m}$ in size. It is possible such relict cores may be more widespread, but are simply not present in the plane of the section. In each grain, the cores contain elevated FeO contents in comparison with the rims (1.5-3 wt% vs. 0.8-1 wt%), but MnO concentrations can be variable, ranging from $<0.4 \text{ wt}\%$ up to 1.6 wt%.

The second type of zoning occurs only in two aggregates of calcite grains. In these aggregates, the CL intensity shows complex variations not readily related to individual grains. These grains are characterized by core regions with low CL intensity having very irregular and curved shapes. The morphology of these low CL intensity cores is suggestive of resorption, followed by continued carbonate precipitation. The core regions are overgrown by higher intensity CL rims and the interface between cores and rims is sharp and not transitional in nature.

The Cr isotopic composition of six calcite grains was determined. The SIMS analyses are characterized by large variations (>100 -fold in some grains) in Mn/Cr within individual calcites, indicative of Cr-rich inclusions or matrix located in fractures. Ion imaging was used to locate regions free of extraneous Cr and with high Mn/Cr; the large uncertainties in $\delta^{53}\text{Cr}$ values reflect the limited number of analyses for any Mn/Cr. Three of six calcites contain enrichments in ^{53}Cr with $\delta^{53}\text{Cr}$ values ranging up to $\sim 600\%$. The magnitudes of the ^{53}Cr excesses are linearly correlated with the respective $^{55}\text{Mn}/^{52}\text{Cr}$ ratios, indicating *in situ* decay of ^{53}Mn and demonstrating that short-lived ^{53}Mn was extant at the time of carbonate formation. The slope of the correlation line on a $^{53}\text{Mn} - ^{53}\text{Cr}$ evolution diagram (Fig. 2), determined by a weighted least squares fit, corresponds to an initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $(1.3 \pm 0.6) \times 10^{-5}$.

Discussion: Carbonates in Y791198 share some similarities with those in the weakly altered, but brecciated CM2 chondrite, Murchison [8]. Calcite is the only carbonate phase present in both meteorites and commonly shows complex zoning, as revealed by CL imaging. This contrasts with carbonate in the more highly altered, but unbrecciated CM2 chondrite ALH81002, in which calcite shows little or no zoning [9]. Carbonates in Murchison show considerably more variability in the styles of zoning than those in Y791198, an effect which may result from extensive brecciation in Murchison.

In Y791198, most calcites appear to record a similar evolutionary history that involved a change in fluid chemistry recorded in a correlated increase in the Mn, Fe and Mg contents of the carbonates at their rims. This similarity in the zoning behavior indicates these grains probably grew from a fluid of similar, but evolving composition. In contrast, the group of calcites exhibiting patchy compositional zoning clearly formed under different conditions, and apparently experienced periods of dissolution and reprecipitation. This group could represent the very earliest carbonates that formed within the CM2 parent body and became unstable as the fluid composition changed as alteration proceeded. It is also possible that these grains represent a generation of grains that formed prior to accretion of

the final CM2 parent body. In principle, these scenarios

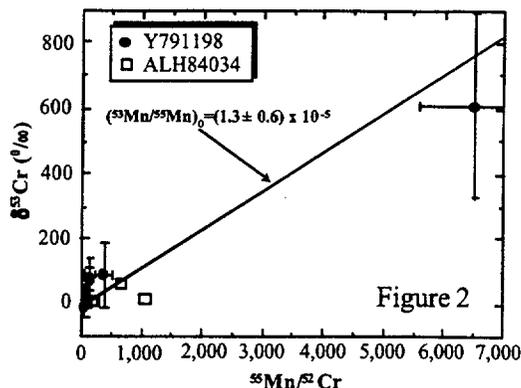


Fig. 2. ^{53}Mn - ^{53}Cr evolution diagram for Y791198 carbonates; line is fitted to data for Y791198 only.

can be distinguished based on the ^{53}Mn - ^{53}Cr ages of carbonates but our preliminary data do not provide sufficient temporal resolution. The initial $^{53}\text{Mn}/^{55}\text{Mn}$ ratio inferred for the Y791198 carbonates generally encompasses the range of values found for carbonates in two other CM chondrites, ALH84034 and Nogoya [10] and in Kaidun [12]. Due to the uncertainty in the solar system initial abundance of ^{53}Mn [13,14], the age of the Y791198 carbonates is best determined by comparing the $^{53}\text{Mn}/^{55}\text{Mn}$ ratio determined here with the Angrite value [14]. The difference in $^{53}\text{Mn}/^{55}\text{Mn}$ corresponds to an age difference of $12.6 \pm 3.7 \text{ Ma}$ or an absolute age of $4570 \pm 4 \text{ Ma}$. The data for Y791198 extend the evidence for the early onset of aqueous activity on chondrite parent bodies and support the view that formation of secondary minerals most plausibly occurred in an asteroidal setting, consistent with our mineralogical observations [4]. It appears that water played an important role in the chemical/mineralogical evolution of primitive planetary bodies over an extended period of time, perhaps 15 Ma, and that carbonate formation on the CM planetesimal may have been episodic, with periods of dissolution and reprecipitation, involving fluids of different compositions.

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