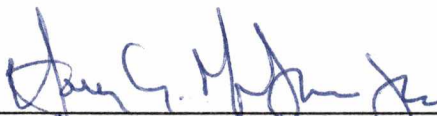


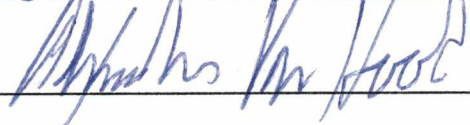
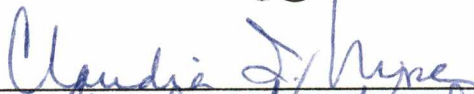
To the Graduate Council:

I am submitting herewith a dissertation written by Lauren B. Browning entitled "The Aqueous Alteration of CM Carbonaceous Chondrites." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Geology.



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We have read this dissertation and recommend its acceptance:



Accepted for the Council:



Associate Vice Chancellor
and Dean of the Graduate School

THE AQUEOUS ALTERATION OF CM CARBONACEOUS CHONDRITES

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Lauren B. Browning

December, 1995

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DEDICATION

To Ralph Browning,
who demonstrated the significance
of love in my life.

ACKNOWLEDGMENTS

I am grateful to many colleagues and friends who improved the quality of various portions of this dissertation by providing me with insightful comments, critical reviews, and thoughtful discussion. I offer here my appreciation for the valuable time that each of my committee members, Claudia Mora, Theodore Labotka, and Alexander Van Hook, generously offered in consideration of this work. Furthermore, I am pleased to take this opportunity to draw special attention to those institutions and individuals who also deserve special recognition for their influential role in my progress toward the completion of this dissertation.

I would like to acknowledge the generous financial support given to me by several corporations, institutions, and individuals. Firstly, I would like to thank the Department of Geological Sciences at the University of Tennessee for providing me with teaching and research assistantships during my first year. In addition, I offer special thanks to the NASA Graduate Student Researcher Fellowship program for generously providing full financial support, as well as access to the facilities at the NASA Johnson Space Center, for the following 3 years. In addition, I would like to thank Michael E. Zolensky, Harry Y. McSween, and Lockheed-Martin Aerospace Engineering Company for sponsoring my participation at numerous professional meetings. I also benefited from the Planetary Science Summer School Lecture Series hosted by the California Institute of Technology, and am grateful to the NASA Jet Propulsion Laboratory for providing me with the funding to attend. Finally, I would like to express my sincere gratitude to Stephen E. Dwornik and his family for setting up an endowment through the GSA Planetary Geology Division to recognize contributions made by selected students of planetary geology. I am honored to have been a recipient of this award, and am grateful for the encouragement, as well as the money, that it provided me.

Several individuals have had a profoundly positive influence on my professional development during the past few years. I'd like to thank my NASA supervisor, Michael E. Zolensky, for sharing laboratory skills and scientific insights with me on a daily basis, and, for being a friend. I am also indebted to John H. Jones for providing me with a model example of professional commitment, perseverance, and integrity. Finally, I would like to express my sincerest gratitude to my thesis advisor, Harry Y. McSween, who carefully monitored my progress, offered sound advice, and simultaneously encouraged me to develop a separate identity within the professional community to which we both belong.

Academia can be a harsh and unfriendly environment at times, and I am grateful to the many people who have instilled in me the courage to have faith in myself. In addition to those mentioned above, I would like to thank Robbie Score for her unwavering faith in my abilities, for teaching me numerous subtleties of professional etiquette and politics, and for being a reliable friend. In addition, I am beholden to Peter Bryant for the devoted attention and level-headed companionship that he gave me. Finally, I would like to mention that I continue to gain perspective from my old friend Stephen E. Bass, who offers, by way of flawless example, a constant reminder that the most significant achievements are reaped from the inner struggle to embrace the human potential for compassion.

ABSTRACT

The first multi-parameter scaling procedure for determining the relative degree of aqueous alteration that individual CM carbonaceous chondritic meteorites experienced is introduced. Modal proportions and average phyllosilicate compositions from 9 CM falls define 3 progressive alteration indices that are then used to identify 3 additional alteration trends based on whole-rock chemical data obtained from the literature. The proposed parameters produce a self-consistent order for the relative extent of alteration that the analyzed samples experienced, while the identified correlations themselves suggest constraints on asteroidal conditions during the alteration process.

Sulfide rinds are $\sim 10\ \mu\text{m}$ thick coatings of fine-grained sulfides and phyllosilicates around many individual silicate grains within CM chondrules. Two mechanisms of sulfide rind formation were considered to constrain the environmental conditions and processes that favor their production on the CM parent body: direct precipitation from a supersaturated fluid, and in situ replacement. The direct precipitation of sulfide rinds is kinetically inhibited under the most plausible of asteroidal conditions, except where S-bearing fluids are confined to olivine grain boundaries during the incipient stages of alteration. Petrological evidence supports the additional possibility that some sulfide rind textures formed by in situ replacement processes. Regardless of which mechanism prevailed, S was probably supplied to the initial CM alteration fluids in response to the equilibration of primary chondrule sulfides with grossly undersaturated alteration fluids. Sulfide rind production probably occurred at low activities of total dissolved S, pH values ranging from ~ 7 to 9, and Ehs between ~ -0.3 to -0.6 . Similar sulfide-bearing rind textures observed in CM matrices could have formed by analogous processes during parent body aqueous alteration.

The origin of altered rim materials that surround chondrules, inclusions, and mineral fragments in CM chondrites provide further insight into the location of CM alteration. An extensive petrologic investigation of the innermost and outermost contacts that separate CM rim assemblages from adjacent materials strongly supports an interactive exchange of dissolved components on the final CM parent body.

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INTRODUCTION

Much of what we currently know about solar system history has grown from investigations involving the distribution and compositions of asteroids (GEHRELS, 1979; KERRIDGE and MATHEWS, 1988). The thousands of asteroidal bodies that currently orbit in a belt between Mars and Jupiter probably formed very early in solar system history, ~4.6 b.y. ago, during a failed attempt to accrete into a full-scale planet(s) (GEHRELS, 1979). Spectral analyses indicate that groups of asteroids with similar surface compositions are confined to roughly heliocentric zones within the asteroid belt. These compositional variations probably resulted from an inhomogeneous distribution of heat across the asteroid belt which induced fractionation in those asteroids orbiting closest to the sun and affected the outermost asteroids the least. The asteroid belt thus provides a significant analog for the incipient stages of planet-building because the processing of primitive accreted materials on different asteroidal bodies was arrested in diverse states. (KERRIDGE and MATHEWS, 1988).

Asteroidal fragments are transported to Earth as meteors (ANDERS, 1978), and recovered meteoritic samples are systematically categorized according to the petrologic and chemical criteria outlined by VAN SCHMUS and WOOD(1967) and WASSON (1974). Within this classification scheme, the chondritic group of meteorites is distinguished by having relative non-volatile elemental abundances similar to those of the sun. Only one class of chondritic meteorites, the carbonaceous chondrites, also contains approximately solar ratios of volatile elements. Since the sun's composition probably reflects that of the average interstellar medium before the formation of the solar system (CAMERON, 1995), carbonaceous chondrites are commonly considered to be among the most pristine of all known solar system materials (SCOTT et al., 1989). Spectral analyses are consistent with this conclusion because they suggest that carbonaceous chondrites originated on C-type

asteroids (GAFFEY et al., 1989), which reside in the outer portions of the asteroid belt. However, petrologic investigations demonstrate that all carbonaceous chondrites experienced secondary aqueous and/or thermal processing in asteroidal settings (KERRIDGE and BUNCH, 1979).

Four major types of carbonaceous chondrites have been identified (VAN SCHMUS and WOOD, 1967; WASSON, 1974), and most of these are widely characterized as asteroidal regolith breccias (RICHARDSON and MCSWEEN, 1978; MCSWEEN, 1979; ALLEN et al., 1980; RUBIN and WASSON, 1987; ZOLENSKY and MCSWEEN, 1988). Each of these contains some combination of chondrules (~millimeter-sized spheres of igneous rock that probably formed as quenched melt droplets in the nebula), lithic clasts, and calcium aluminum inclusions, all within a fine-grained matrix host of surviving interstellar dust particles and processed mineral fragments (VAN SCHMUS and WOOD, 1967). However, CV and CO carbonaceous chondrites contain anhydrous materials that were subjected to secondary thermal metamorphism, while the primary accreted materials of CI and CM carbonaceous chondrites experienced low-temperature aqueous alteration (ZOLENSKY et al., 1993). Only one of these classes, the CM carbonaceous chondrites, preserves notable proportions of both primary anhydrous and secondary hydrous phases. As such, CM chondritic meteorites provide a rare glimpse of the petrologic, isotopic, and bulk chemical characteristics of asteroidal materials that experienced significant, but incomplete, reactions involving melted ices and anhydrous nebular components. The aqueous alteration of CM chondrites was one of the earliest parent body events in the solar system (ZOLENSKY and MCSWEEN, 1988), and has profound implications for a wide range of early solar system materials and processes.

In this dissertation, I discuss several outstanding questions regarding the aqueous alteration of CM carbonaceous chondrites, and suggest a general resolution for these on the basis of a critical evaluation of the petrologic features of individual CM chondritic samples.

The dissertation is organized into 3 autonomous parts, arranged in the given order to emphasize the general logic of my approach.

Unraveling a chronology of alteration reactions for CM chondritic meteorites cannot proceed without a reliable scaling procedure for determining the relative degree of alteration that individual CM chondritic meteorites have experienced. Part 1 introduces the first relative alteration scale for CM chondrites that relies on multiple correlated parameters. Application of the model parameters produces a self-consistent order of relative alteration for the analyzed samples and suggests constraints on the CM asteroidal parent body(ies) during the alteration process.

The asteroidal location of CM alteration has profound implications for the nature of the solar nebula and protoplanets, but has not yet been firmly established. Parts 2 and 3 of this dissertation examine the petrologic features of CM chondritic meteorites for evidence bearing on the location where CM alteration occurred. One possibility, that alteration occurred *in situ* on the CM parent body (MCSWEEN, 1979; BUNCH and CHANG, 1980, BROWNING, 1995), has recently been criticized because satisfactory explanations have not yet been provided to account for the origin of ubiquitous CM alteration textures (METZLER et al., 1992). Part 2 demonstrates that several commonly observed sulfide-bearing textures in CM chondrules and matrices are consistent with an origin by *in situ* parent body alteration. In addition, an alteration scheme is suggested which provides a general characterization of the CM fluids during incipient parent body alteration. Part 3 focuses on constraining the location where CM rim materials experienced aqueous alteration because this issue has been central to recent discussions involving the location of all CM materials (BREARLEY and GEIGER, 1991; METZLER et al., 1992; BROWNING et al., 1995). Several common rim textures are illustrated that strongly support an interactive exchange of dissolved components between rims and adjacent CM materials during parent body alteration.

REFERENCES

- ALLEN J.S., NOZETTE S., and WILKENING L.L. (1980) A study of chondrule rims and chondrule irradiation records in unequilibrated ordinary chondrites. *Geochim. Cosmochim. Acta* **44**, 1161-1175.
- ANDERS E. (1978) Most stony meteorites come from the asteroid belt. In *Asteroids: An Exploration Assessment* (eds. D. Morrison and W. C. WELLS), pp. 57-75, NASA.
- BREARLEY A.J. and GEIGER T. (1991) Mineralogical and chemical studies bearing on the origin of accretionary rims in the Murchison CM2 carbonaceous chondrite. *Meteoritics* **26**, 323.
- BROWNING L., MCSWEEN H. Y. J., and ZOLENSKY M.E. (1995) Parent body alteration features in CM rims. *Lunar and Planetary Science Conference XXVI*, 181-182.
- BUNCH T.E. and CHANG S. (1980) Carbonaceous chondrites--II. Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* **44**, 1543-1577.
- CAMERON A.G.W. (1995) Leonard Award Address - The first ten million years in the solar nebula. *Meteoritics* **30**, 133-161.
- GAFFEY M.J., BELL J.F., and CRUIKSHANK D.P. (1989) Reflectance spectroscopy and asteroid surface mineralogy. In *Asteroids II* (eds. R. Binzel et al.), Univ. of Arizona.
- GEHRELS T. (1979) *Asteroids*. University of Arizona Press.
- KERRIDGE J.F. and BUNCH T.E. (1979) Aqueous alteration on asteroids: Evidence from carbonaceous chondrites. In *Asteroids* (eds. T. GEHRELS), pp. 745-764, University of Arizona Press.
- KERRIDGE J.F. and MATHEWS M.S. (1988) *Meteorites and the Early Solar System*. University of Arizona Press.

- MCSWEEN H. Y. (1979) Alteration in CM carbonaceous chondrites inferred from modal and chemical variations in matrix. *Geochim. Cosmochim. Acta* **43**, 1761-1770.
- METZLER K., BISHOFF A., and STOFFLER D. (1992) Accretionary dust mantles in CM chondrites: Evidence for solar nebula processes. *Geochim. Cosmochim. Acta* **56**, 2873-2897.
- RICHARDSON S.M. and MCSWEEN H. Y. (1978) Textural evidence bearing on the origin of isolated olivine crystals in C2 carbonaceous chondrites. *Earth Planet. Sci. Lett.* **37**, 485-491.
- RUBIN A.E. and WASSON J.T. (1987) Chondrules, matrix and coarse grained chondrule rims in the ALLENDE meteorite: Origin, interrelationships and possible precursor components. *Geochim. Cosmochim. Acta* **51**, 1923-1937.
- SCOTT E.R.D., TAYLOR G.J., NEWSOM H.E., HERBERT F., ZOLENSKY M., and KERRIDGE J.F. (1989) Chemical, thermal and impact processing of asteroids. In *Asteroids II*, (eds. R. Binzel et al.) Univ. of Arizona Press.
- TOMEOKA K. and BUSECK P.R. (1985) Indicators of aqueous alteration in CM carbonaceous chondrites: Microtextures of a layered mineral containing Fe, S, O, and Ni. *Geochim. Cosmochim. Acta* **49**, 2149-2163.
- VAN SCHMUS W.R. and WOOD J.A. (1967) A chemical-petrologic classification for the chondritic meteorites. *Geochim. Cosmochim. Acta* **31**, 747-765.
- WASSON J.T. (1974) *Meteorites: Classification and Properties*. Springer-Verlag.
- ZOLENSKY M. and MCSWEEN H. Y. J. (1988) Aqueous Alteration. In *Meteorites and the Early Solar System* (eds. J. K. KERRIDGE and M. S. Matthews), pp. 114-143, University of Arizona Press.
- ZOLENSKY M., BARRETT R., and BROWNING L. (1993) Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **57**, 3123-3148.

PART 1

An Alteration Scale for CM Carbonaceous Chondrites

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ABSTRACT

Three parameters are proposed to determine the relative extent of alteration in CM chondritic meteorites. The mineralogic alteration index monitors the relative progress of coupled substitutions in the progressive alteration of cronstedtite to Mg-serpentine. To calculate values of the mineralogic alteration index, an algorithm is developed to estimate the average matrix phyllosilicate composition in individual CM chondrites. The second parameter is the volume percent of isolated matrix silicates, which decreases with progressive alteration due to the hydration of anhydrous phases. Finally, the volume percent of chondrule alteration monitors the extent of chondrule phyllosilicate production, and increases as alteration proceeds. These parameters define the first CM alteration scale that relies on multiple indicators of progressive alteration. The following relative order of increasing alteration is established by this model: Murchison $\leq$ Bells < Pollen $\leq$ Murray < Mighei < Nogoya < Cold Bokkeveld. The relative degrees of aqueous processing experienced by Cochabamba and Boreskino experienced is less precisely determined, although both fall near the middle of this sequence. A comparison between the mineralogic alteration index and literature values of the whole-rock chemistry of CM chondrites shows several correlations. For example, a positive, nearly linear correlation between bulk H content and progressive CM alteration suggests an approximately constant production rate of new phyllosilicates relative to the mineralogical transition from cronstedtite to Mg-serpentine. Furthermore, the abundance of trapped planetary ^{36}Ar systematically decreases in progressively altered CM chondrites, suggesting the wholesale destruction of primary noble gas carrier phase(s) by aqueous reactions. Oxygen isotopic ratios become larger as alteration proceeds, which is consistent with the low-temperature formation of phyllosilicates and a commensurate loss of ^{16}O -rich fluids.

These correlations strongly imply that individual CM chondrites were subjected to similar asteroidal processes and conditions as alteration proceeded.

INTRODUCTION

The aqueous alteration of CM chondritic meteorites provides a useful analog for other types of solar system materials that experienced interactions between melted nebular ices and anhydrous mineralogic components. Incompletely altered CM chondrites offer a superior way point for evaluating the reaction sequence of more thoroughly altered materials since the association between reactant and product phases is preserved in these meteorites. The nuclei of short-period comets, ice-bearing satellites, and many interplanetary dust particles may be thoroughly modified by aqueous alteration processes that are analogous to those which affected carbonaceous chondrite parent bodies (MCSWEEN and WEISSMAN, 1989). Furthermore, several meteorites appear to have textures and mineral assemblages that are transitional between the incompletely altered CM and thoroughly altered CI chondritic classes (IKEDA and PRINZ, 1993; ZOLENSKY and BROWNING, 1994), suggesting a relationship that may best be elucidated by extrapolation from CM, rather than CI, samples. A better understanding of the aqueous alteration of CM chondrites also provides a context for determining the conditions under which minor proportions of hydrated phases were produced in other types of chondritic meteorites. For example, some CV and unequilibrated ordinary chondrites (HUTCHISON et al., 1987; TOMEOKA and BUSECK, 1990) contain small amounts of phyllosilicates, implying that these largely anhydrous meteorite classes may have experienced alteration events that were similar to, but less extensive than, those effecting CM chondrites. Finally, uncovering the paragenetic sequence for CM

chondrites should help to establish the thermodynamic conditions on C-type asteroids, the most logical source of CM chondrites (KERRIDGE and BUNCH, 1979). Hence, understanding the progressive aqueous alteration CM chondrites has significant implications for a wide range of early solar system processes and materials.

Since individual CM chondrites have experienced various degrees of aqueous alteration (MCSWEEN, 1979; BUNCH and CHANG, 1980; TOMEOKA and BUSECK, 1985), a continuous reaction sequence for these meteorites might be constructed by determining which reactions best describe the transition between successively altered CM chondritic samples. Unfortunately, this is not a straightforward exercise. A plausible alteration scheme must simultaneously account for the effects that different degrees of aqueous processing have had on the diverse textural, mineralogical, isotopic, and bulk chemical signatures that are observed (CLAYTON and MAYEDA, 1984; VAN SCHMUS and WOOD, 1967; ZOLENSKY et al., 1993). Since the number of CM asteroidal parent bodies has not yet been determined, the possibility remains that some of the attributes that distinguish individual CM chondrites reflect inherent compositional differences on multiple CM asteroidal parent bodies. Few constraints have been imposed on the nature of the original CM parent body or bodies before their alteration, and the extent of the physical and chemical uncertainties associated with asteroidal accretion and resurfacing (HOUSEN et al., 1979) generally limit the applicability of terrestrial serpentinites as CM analogs. Moreover, the fine grain size of CM alteration phases leads to unavoidable analytical problems, while the wide range of textures and mineral associations observed within a single CM thin section readily lends itself to varied, and often self-contradictory, interpretations regarding their origin. The sum of these obstacles has impeded progress toward establishing a paragenetic sequence for CM chondritic meteorites and confused the more fundamental distinction between progressively altered CM chondritic samples.

We emphasize the need to establish a reliable scaling procedure for determining the relative degree of alteration that individual CM chondritic meteorites have experienced. Without a clearly defined alteration scale, the task of unraveling a sequence of alteration reactions from the motley collection of textures and mineral assemblages in different CM chondrites can only proceed haphazardly. We suggest that a dependable scaling procedure will employ multiple alteration parameters that act in concert to represent diverse responses to progressive CM alteration. While any one scaling parameter is, in itself, a signature of the influence of progressive alteration on a specific attribute of CM chondrites, an integrated set of scaling parameters provides a more reliable framework for the addition of new alteration parameters.

In this paper, we introduce the first relative alteration scale for CM chondrites that relies on multiple correlated parameters. Quantitative data involving modal proportions and average phyllosilicate compositions from 9 CM falls define 3 progressive alteration indicators that are then used to identify 3 additional alteration trends based on isotopic ratios and bulk chemical data. The simultaneous employment of the proposed progressive alteration indicators produces a high-resolution scale, while the identified correlations themselves provide additional insight into the asteroidal parent body conditions that may have attended CM alteration.

SAMPLES AND ANALYTICAL TECHNIQUES

We obtained samples of 9 CM chondritic falls that vary widely in their extent of aqueous alteration (MCSWEEN, 1979). Table 1 lists the meteorite names, abbreviations, thin section numbers, and sources of the CM chondrites used in this study. To minimize the effects of overlapping phases, petrographic thin sections were prepared with

Table 1. CM Chondrites Studied.

Samples	Abbreviations	Thin Section I.D's	Source
Bells	BL	B3; A3	Amer. Museum Natural History
Boreskino	BO	6495-1	Smithsonian Institute
Cochabamba	CC	1; 2	University of Vienna
Cold Bokkeveld	CB	1727a	British Museum
Mighei	MI	3; 4; 5	Field Museum
Murchison	MC	E; H	Field Museum
Murray	MY	2; 3	Field Museum
Nogoya	NG	1; 2	ASU Center for Meteoritics
Pollen	PO	3	British Museum

thicknesses somewhat less than 30 μm , when possible. Modal data were collected from these thin sections in reflected and transmitted light using a standard petrographic microscope equipped with a point counting stage. The total number of points counted for each sample was at least 1000.

We obtained chemical analyses of CM matrix material using a Cameca CAMEBAX electron microprobe at the NASA Johnson Space Center, operated at 15 kV with a beam current of ~ 30 nA. Standard data-reduction software was used to correct X-ray intensities for deadtime, background, and ZAF matrix effects. Natural minerals were used as standards. These wavelength dispersive analyses are believed to be accurate to within $\pm 0.5\%$, relative. Qualitative analyses of matrix material were also obtained on this microprobe, which is equipped with an energy-dispersive spectroscopy (EDS) detector system and scanning electron imaging capabilities.

Microprobe analyses of CM matrix material were used to estimate the average composition of the matrix phyllosilicates in individual CM chondrites. The Fe^{3+} content of matrix phyllosilicates was approximated using an algorithm that assumes charge balance (see Appendix). This information was used to calculate values of the mineralogic alteration index, which is introduced in the text.

GENERAL CHARACTERISTICS OF PROGRESSIVE ALTERATION

Because extensively altered matrix material constitutes up to 90 vol. % of CM chondritic samples (BROWNING, 1995), investigations involving the aqueous alteration of CM chondrites generally focus on the nature of matrix minerals. Resolving progressive alteration trends in CM matrices requires a knowledge of their diverse textures and mineral assemblages and an awareness of the variety of processes that are capable of

producing them. Much progress has been made in this area, and we summarize here only those results which have contributed directly to the development of our proposed alteration scale.

CM matrices contain a complex disequilibrium assemblage of minerals. Serpentine group minerals, saponite, tochilinite, tochilinite-serpentine intergrowths, olivine, pyroxene, various Fe-monosulfides, Fe-Mg oxides, carbonates, phosphates, Fe-Ni metal and amorphous material may all coexist within a single CM matrix (ZOLENSKY et al., 1993). Of these, phyllosilicates may be the most reliable indicators of progressive CM alteration because the structures and compositions of these secondary minerals strongly reflect those of the precursor silicate grains, the interacting fluids, and the environmental conditions attending aqueous alteration (MOODY, 1976). Thus, a rigorous characterization of matrix phyllosilicates is essential for the identification of mineralogical trends with advancing CM alteration.

Since most matrix phyllosilicates in CM chondrites have grain sizes on the order of a micron or less, individual phyllosilicate grains are generally evaluated by high-resolution techniques. Previous TEM analyses reveal a wide range of phyllosilicate compositions, structures, and morphologies (BARBER, 1981; TOMEOKA and BUSECK, 1985; ZOLENSKY et al., 1993). Individual phyllosilicate grains are commonly intergrown with sulfides, tochilinite, carbonates, or other phyllosilicate grains, indicating an origin by complex, *in situ* replacement processes (BUSECK and XIN, 1993). ZOLENSKY and MCSWEEN (1988) reviewed the various types of phyllosilicates that have been reported in CM chondrites and argued that these are best described as belonging to the serpentine, berthierine, chlorite, and smectite groups. Of these, the serpentine group minerals are the most volumetrically significant (MCSWEEN, 1987). Table 2 provides a list of the formulae of the mineral endmembers within the serpentine group.

Table 2. Serpentine Formulae

Mg-Bearing Members	Chrysotile	
	Lizardite	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$
	Antigorite	
Fe-Bearing Members	Cronstedtite	$\text{Fe}^{2+}_2\text{Fe}^{3+}(\text{SiFe}^{3+})\text{O}_5(\text{OH})_4$
	Greenalite	$(\text{Fe}^{2+}, \text{Fe}^{3+})_{2-3}\text{Si}_2\text{O}_5(\text{OH})_4$
	Ferroan	
	Antigorite	$(\text{Mg}, \text{Fe}, \text{Mn})_3(\text{Si}, \text{Al})_2\text{O}_5(\text{OH})_4$
Intermediate Members	Amesite	$\text{Mg}_2\text{Al}(\text{SiAl})\text{O}_5(\text{OH})_4$
	Berthierine	$(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg})_{2-3}(\text{Si}, \text{Al})_2\text{O}_5(\text{OH})_4$

Source: ZOLENSKY M. and MCSWEEN H. Y. (1988) Aqueous Alteration. In *Meteorites and the Early Solar System* (ed. J. K. KERRIDGE and M. S. MATTHEWS), pp. 114-143. University of Arizona Press.

High-resolution mineralogical characterizations are often complemented by alternative techniques that may be better suited for the identification of progressive alteration trends on a larger scale. For example, MCSWEEN (1979) proposed that the apparent content of phyllosilicate-rich matrix material in different CM chondrites should gauge the relative extent of phyllosilicate production and, therefore, the relative degree of aqueous alteration that individual CM chondrites experienced. He compared defocused beam analyses of optically homogeneous matrix with the modal matrix contents of individual CM chondrites to determine whether progressive alteration is accompanied by compositional changes in bulk CM matrices. The matrix Fe/Si ratios from different CM chondrites were found to decrease roughly with increasing modal percentages of matrix and, hence, the relative degree of aqueous alteration. Similarly, BUNCH and CHANG (1980) noted that the Mg/Fe ratios of matrix phyllosilicates probably increase during advancing alteration, and microtextural analyses of CM matrices by BARBER (1981) support the late formation of Mg-rich alteration phases.

It has long been established that terrestrial serpentinization typically involves both recrystallization and the formation of new phyllosilicates (WICKS and WHITTAKER, 1977). Since the composition of every phyllosilicate in a system must reflect the state of the surrounding alteration environment during its formation, the bulk Fe/Si and Mg/Fe trends reported earlier by MCSWEEN (1979) and BUNCH and CHANG (1980) demonstrate the large-scale evolution of matrix phyllosilicate compositions during progressive CM alteration. Microprobe analyses of CM matrices indicate that phyllosilicate compositions usually fall within a region that joins endmember cronstedtite and serpentine on a SiO_2 -MgO-FeO ternary (MCSWEEN 1987; BROWNING et al., 1991). However, the range of matrix phyllosilicate compositions for different CM chondrites varies significantly within this field (ZOLENSKY et al., 1993). Although Fe^{3+} cannot be analyzed directly by

microprobe techniques, the presence of variable amounts of Fe³⁺-rich phyllosilicates is supported by the lattice spacings of individual phyllosilicate grains (BARBER, 1981) and confirmed by Mossbauer analyses (BURNS and FISHER, 1993). Moreover, spectroscopic analyses support the presence of Fe³⁺ phyllosilicates on the surfaces of some C-type asteroids (VILAS et al., 1993). HRTEM observations (TOMEOKA and BUSECK, 1985) and mass balance calculations of bulk matrix compositions (MCSWEEN, 1987) provide a plausible explanation for the range of matrix phyllosilicate compositions in CM matrices; progressive CM alteration is accompanied by a continuous mineralogic trend from Fe³⁺-rich cronstedtite to Mg-rich serpentine.

PROGRESSIVE ALTERATION SCALE

Our scaling procedure for determining the relative alteration of CM chondrites assumes a mineralogic transition from cronstedtite to serpentine with advancing alteration, and capitalizes on variations in the range of matrix phyllosilicate compositions among different CM matrices, as well as the commensurate destruction of anhydrous silicates that necessarily attends this process. In this section, we introduce 3 new alteration parameters for determining the relative degree of aqueous alteration that individual meteorites have experienced. The first of these, the mineralogic alteration index, will be compared to all additional alteration parameters in this work.

Mineralogic Alteration Index

Because endmember phyllosilicate compositions are relatively uncommon in CM matrices (ZOLENSKY et al., 1993), phyllosilicates with intermediate compositions

collectively reflect the degree of CM alteration. Consequently, we suggest that the average phyllosilicate composition within a single CM matrix best records the overall extent of the mineralogical transition from endmember cronstedtite to serpentine. The proposed mineralogic alteration index gauges the number of incremental steps that have been taken along the alteration pathway from cronstedtite to serpentine based on an approximation of the average matrix phyllosilicate composition for a given CM chondrite.

The continuous mineralogical transition from cronstedtite to serpentine requires that recrystallized and newly-formed phyllosilicates systematically discriminate between various cations as alteration proceeds. This is most clearly evidenced by the large differences in these endmember phyllosilicate compositions (Table 2). Ferric Fe replaces one tetrahedral Si and also occupies an octahedral position in the endmember cronstedtite structure. In addition to Fe^{3+} , meteoritic cronstedtite grains incorporate up to 5 wt.% Al (BARBER, 1981), which probably occupies a portion of the structural sites that are traditionally filled by Fe^{3+} . At the other extreme of the CM mineralogic trend, the idealized serpentine structure contains a full ration of tetrahedral Si and incorporates no trivalent cations. In order to maintain an approximate mineralogic charge balance throughout the transition from endmember cronstedtite to serpentine compositions, this progressive alteration trend must have been accomplished by a sequence of coupled substitutions that systematically introduced tetrahedral Si and divalent octahedral cations into matrix phyllosilicates at the expense of Fe^{3+} and, to a lesser degree, Al.

We propose that progressive CM alteration is best monitored by evaluating the progress of Si and Fe^{3+} substitutions that necessarily attend the transition from endmember cronstedtite to serpentine. To track the redistribution of the relevant cations, we first employ a generalized stoichiometric phyllosilicate formula, $(\text{Fe}^{2+}, \text{Mg}, \text{Mn},$

$\text{Ca...})_{3-x}(\text{Al,Fe}^{3+})_x(\text{Si}_{2-x}(\text{Al,Fe}^{3+})_x\text{O}_5(\text{OH})_4$, to characterize the compositions of individual matrix phyllosilicates. This mineral formula accommodates the entire range of serpentine compositions observed in CM matrices (Table 2). The proposed mineralogic alteration index, $\text{Fe}^{3+}/(2\text{-Si})$, is intended to isolate the relevant exchange information stored in the stoichiometric phyllosilicate formula. This parameter gauges the extent to which the coupled substitution of $2(\text{Fe}^{3+},\text{Al}) = \text{Si} + (\text{Mg}, \text{Fe}^{2+} \dots)$ was completed in the average matrix phyllosilicate of an individual CM chondrite. The denominator of this ratio, 2-Si, indicates the number of trivalent atoms that replace Si in the idealized serpentine structure, while the numerator is an approximation of the total number of Fe^{3+} atoms occupying tetrahedral and octahedral sites. An endmember cronstedtite composition would be represented, then, by a $\text{Fe}^{3+}/(2\text{-Si})$ ratio of 2. In contrast, an endmember serpentine composition always yields a $\text{Fe}^{3+}/(2\text{-Si})$ ratio of 0 because it contains 2 Si atoms and no Fe^{3+} . Therefore, values of the mineralogic alteration index decrease as aqueous alteration proceeds.

A detailed account of the algorithm used to calculate values of the mineralogic alteration index is given in the Appendix, but we briefly summarize the procedure here. Phyllosilicate formulae were estimated from electron microprobe analyses of matrix material in each CM chondrite by characterizing all matrix phyllosilicates according to the generalized phyllosilicate stoichiometry described above. Since the microprobe beam is generally larger than the diameter of a single serpentine grain, we impose the requirement that each matrix analysis used in this study must reflect the composition of a mineral assemblage composed exclusively of phyllosilicates. Our procedure involves the use of multiple screening devices which exclude those analyses that contain unwanted carbonate or oxide inclusions. More than half of our original matrix analyses were eliminated from further consideration because these or additional criteria were not met

(see Appendix). Despite these efforts, corrections for small quantities of ubiquitously occurring sulfide grains had to be made for each analysis. Although sulfide inclusions clearly bias the apparent Fe content of matrix phyllosilicates, microprobe-based investigations involving the serpentine compositions in CM matrices have rarely addressed this problem. After selecting our most reliable microprobe data, the number of Fe^{3+} atoms in each matrix analysis was estimated from measured concentrations of SiO_2 , Al_2O_3 , and FeO , by allowing matrix phyllosilicates to fulfill stoichiometric requirements. Separate values of $\text{Fe}^{3+}/(2\text{-Si})$ were derived from each of the estimated phyllosilicate compositions, and then averaged to obtain the proposed alteration index number, $\text{Fe}^{3+}/(2\text{-Si})$, for each CM matrix. Table 3 gives the average serpentine formulae and mineralogic alteration indices for the CM chondrites in this study. Standard deviations for each cation demonstrate the inherent compositional variability of individual serpentine grains within each meteorite, and are not an indication of analytical errors.

Relative Proportion of Isolated Anhydrous Silicates in CM Matrices

Olivine and pyroxene grains with diameters ranging from ~5 - 100 μm are commonly imbedded within the submicron-sized alteration assemblages that compose CM matrices. These isolated anhydrous silicate grains were probably contributed to an active CM regolith by impact-fragmented chondrules (MCSWEEN, 1977; RICHARDSON and MCSWEEN, 1978; JONES, 1992). Since fluid infiltration should have been pervasive in the unconsolidated CM regolith, anhydrous matrix silicates were probably highly susceptible to fluid-rock reactions. Indeed, most isolated anhydrous silicate grains in CM matrices show clear signs of having been partially altered by aqueous reactions. The

Table 3. Estimated Chemical Formulae of Average CM Matrix Serpentine, and Mineralogical Alteration Indices (M.A.I.)

Samples	Si	Al	Cr	Fe(2+)	Fe(3+)	Mn	Mg	Ca	Na	Ni	M.A.I.
BL (25)	1.62 (.10)	0.17 (.03)	0.02 (0)	0.97 (.26)	0.59 (.20)	0.01 (0)	1.50 (.24)	0.04 (.05)	0.02 (.02)	0.04 (.03)	1.54 (.14)
BO (14)	1.73 (.13)	0.17 (.03)	0.01 (.01)	0.91 (.18)	0.36 (.25)	0.01 (0)	1.74 (.28)	0.02 (.02)	0.02 (.01)	0.02 (.02)	1.27 (.29)
CB (24)	1.77 (.13)	0.20 (.10)	0.01 (.01)	0.9 (.27)	0.25 (.22)	0.01 (0)	1.79 (.33)	0.01 (.01)	0.02 (.02)	0.02 (.02)	0.97 (.45)
CC (14)	1.58 (.12)	0.27 (.06)	0.02 (.01)	1.07 (.18)	0.58 (.19)	0.01 (0)	1.34 (.27)	0.02 (.01)	0.03 (.01)	0.08 (.02)	1.35 (.13)
MC (14)	1.58 (.19)	0.15 (.03)	0.01 (0)	0.91 (.29)	0.69 (.37)	0.01 (0)	1.59 (.40)	0.01 (.01)	0.02 (.03)	0.03 (.02)	1.57 (.20)
MI (19)	1.64 (.14)	0.25 (.10)	0.02 (.02)	0.83 (.21)	0.47 (.21)	0.01 (.01)	1.71 (.27)	0.01 (.01)	0.03 (.02)	0.02 (.03)	1.23 (.34)
MY (11)	1.56 (.14)	0.24 (.11)	0.01 (.01)	1.17 (.43)	0.65 (.24)	0.01 (0)	1.17 (.41)	0.08 (.14)	0.05 (.02)	0.04 (.03)	1.43 (.23)
NG (14)	1.80 (.10)	0.17 (.06)	0.02 (.02)	0.58 (.18)	0.23 (.19)	0.01 (0)	2.12 (.23)	0.01 (0)	0.03 (.01)	0.02 (.03)	1.03 (.34)
PO (10)	1.65 (.07)	0.18 (.02)	0.01 (0)	1.16 (.13)	0.52 (.13)	0.01 (0)	1.38 (.19)	0.01 (0)	0.03 (.01)	0.03 (.01)	1.47 (.13)

Notes: All formulae were derived from microprobe analyses that have been corrected for small amounts of sulfide, using the procedure described in the Appendix. The number in parentheses beside the sample abbreviation refers to the number of analyses averaged. Other numbers in parentheses are 2s standard deviations, which illustrate the range of matrix serpentine compositions in individual CM chondrites.

surface of the olivine in Figure 1, for example, has been etched and pitted by alteration reactions that produced phyllosilicates and minor sulfides.

The degree of whole-rock CM alteration is indirectly reflected in the degree to which anhydrous matrix silicates are preserved. As alteration proceeds, the abundance of isolated matrix silicates in an individual CM chondrite should decrease commensurably. We propose that the modal proportion of anhydrous matrix silicates in different CM matrices provides another, independent indication of the relative degree of alteration that individual samples experienced. To test this parameter, the modal proportion of isolated matrix silicates in 9 different CM chondritic falls was obtained by point counting. Results of this analysis are plotted against the mineralogic alteration index in Figure 2a.

Error bars in Figure 2a illustrate estimated 1σ counting errors, and were derived from the results of VAN DER PLAS and TOBI (1965). The method that these authors proposed for estimating counting errors from modal data is valid under the condition that the step interval between modal points is larger than the largest grain fraction. In contrast, we used the smallest possible step interval between points to maximize the coverage of each thin section. Had we used their method, we would have counted approximately 4 times fewer points in a given area. VAN DER PLAS and TOBI (1965) take the reliability of modal results as $\sigma = [p(100-P)/n]^{1/2}$, where p = the real content of a mineral in percent by volume, P = the vol. % of a mineral obtained by modal counting, and n = the total number of points counted. Since number of points that we have counted, n' , is always 4 times that of VAN DER PLAS and TOBI (1965) for a given area, we approximate the ratio of their error to our own error as $(n'/n)^{1/2} = 2$.

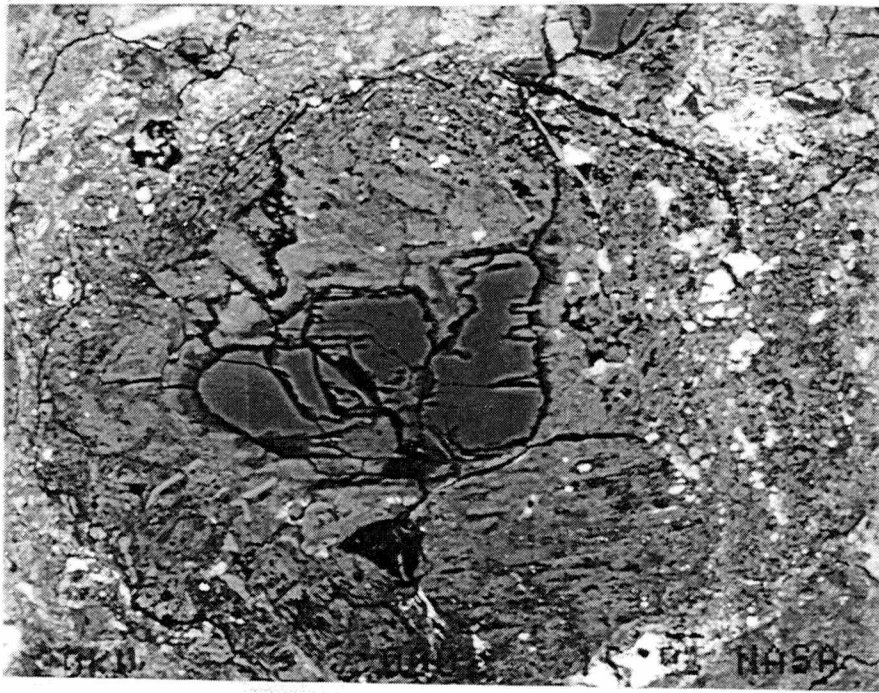


Figure 1: Olivine grain in the matrix of Cold Bokkeveld is partially altered to serpentine phases. Irregularities in the olivine surface probably resulted from the penetration of alteration fluids along the original fracture planes of the host olivine.

Figure 2. Comparison between proposed CM alteration parameters. Plots of the mineralogic alteration index number versus a) the modal proportion of isolated matrix silicates, and b) the volume percent of chondrule alteration illustrate the continual production of phyllosilicates as anhydrous silicate phases are systematically consumed during progressive CM alteration. Meteorite abbreviations are given in Table 1.

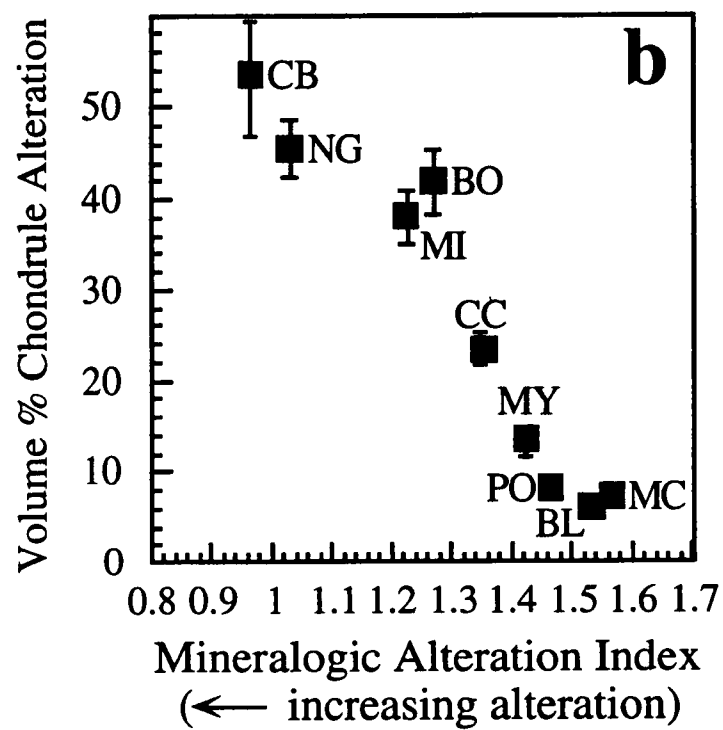
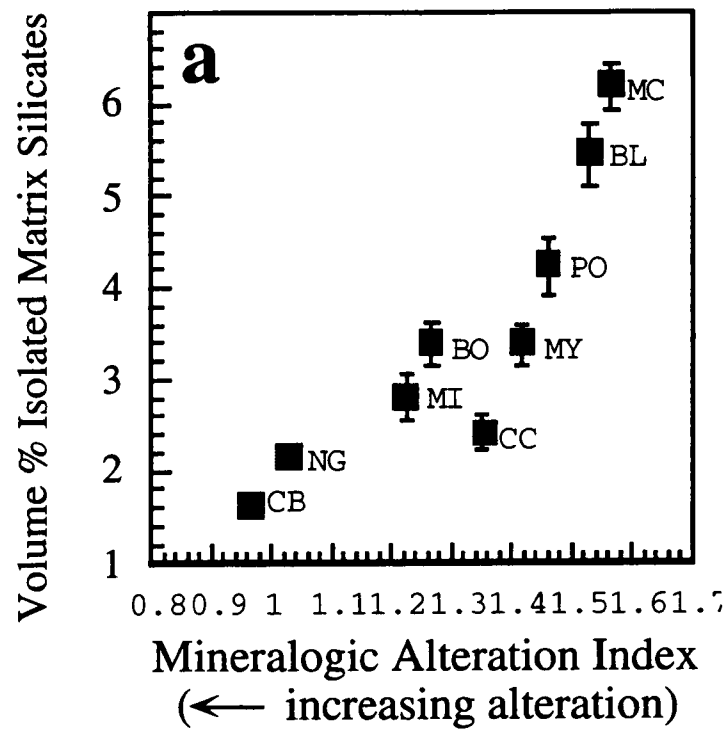


Figure 2

Relative Percentage of Chondrule Alteration

There is no reason to suppose that every olivine and pyroxene grain in the CM asteroidal regolith would have been equally susceptible to aqueous reactions. Both the low surface/volume ratio and the coarse-grained, interlocking igneous textures within chondrules, for example, must have effectively discouraged the infiltration of alteration fluids into chondrule interiors. It is no surprise, then, that the ratio of unaltered to altered silicates within CM chondrules is apparently larger than that of the surrounding fine-grained matrix or rim components. However, if differences in the extent of chondrule alteration relative to matrix alteration are systematic, then a correlation should exist between the relative degree of alteration that the chondrules and isolated matrix silicates experienced.

We propose that the percentage of chondrule alteration phases should reflect the progressive consumption of anhydrous chondrule silicates by aqueous reactions. The relative percentage of chondrule alteration phases in different CM chondrites is expected, therefore, to increase with increasing alteration. Values for this chondrule alteration parameter were obtained by point counting the chondrule phases from 9 different CM chondrites. The extent of chondrule alteration was then calculated as 100X the ratio of the number of modal points of phyllosilicate-bearing assemblages in chondrules divided by the sum of all chondrule points. The volume percentage of chondrule alteration is plotted against the mineralogic alteration index in Figure 2b. Error bars show the results of propagating counting errors across the ratio given above.

Variability and Uncertainty in Model Parameters

KERRIDGE (1985) argued that the heterogeneous nature of highly brecciated CM chondritic meteorites precludes the determination of accurate error values on analytical data. In a similar manner, we suggest that the analytical errors presented in Figures 1 and 2 should be viewed as estimations of individual sources of error, rather than a precise account of the sum of all influencing sources of error. Although this situation is not ideal, the validity of our results is not diminished. Systematic errors in the 3 proposed alteration parameters should be vanishingly small because of the collection of all data at a single laboratory by one investigator who adhered to a common procedure for each sample. Hence, we are able to emphasize the significance of relative, rather than absolute, values for individual CM chondrites. This is consistent with our goal of defining indicators of the *relative* extent of alteration that individual CM chondrites experienced. We outline here some intangible sources of error in the 3 proposed alteration parameters and describe our efforts to minimize their effects.

It is not possible to quantify errors associated with the calculation of mineralogic alteration indices. Most notably, the abundance of Fe^{3+} is an integral component of the mineralogic alteration index, but no significance can be ascribed to the absolute values of Fe^{3+} calculated in this work. However, since we use the same algorithm to calculate all Fe^{3+} values, systematic errors are minimized. Furthermore, we submit that the soundness of the logic used in devising this algorithm is demonstrated by the capacity of the mineralogic index to produce predictable alteration trends. Hence, we conclude that the mineralogic alteration index provides a sensitive gauge of the *relative* progress that individual CM chondrites have made along the progressive alteration pathway from cronstedtite to Mg-serpentine.

Biases resulting from the heterogeneity of CM samples may be realized most clearly in modal values that were obtained from a limited number of thin sections. However, every effort has been made to maximize the reliability of our modal data. For example, we have deliberately selected modal-based alteration parameters in which the relevant phases are easily distinguished by standard petrographic techniques. The proposed parameters do not require, for example, that inherently ambiguous distinctions be made between adjacent fine-grained alteration assemblages, such as rims and matrix. Very small counting distances were employed to ensure full coverage of each thin section and to maximize the total number of collected points, which improved the statistical significance of our results. In addition, we evaluated the vol. % of CM chondrules that is occupied by alteration phases to limit the influence of sampling biases that may otherwise result from different thin sections of the same meteorite having variable proportions of chondrules.

BULK CHEMICAL SIGNATURES OF PROGRESSIVE CM ALTERATION

In this section, we specifically address the possibility that the interacting alteration fluids themselves might have generated tangible signatures of the relative extent of aqueous processing that individual CM chondrites experienced. We suggest that the mineralogical changes attending progressive CM alteration should be accompanied by a suite of bulk chemical and isotopic signatures that gauge the influence, evolution, and abundance of the reacting fluids. Three types of whole rock data are discussed here which may complement the mineralogical trends attending progressive CM alteration. All whole-rock data will be compared to values of the mineralogic alteration index.

Bulk H Content

Since hydrous phyllosilicates volumetrically dominate the mineralogy of CM chondritic meteorites (MCSWEEN, 1987), it follows that a positive correlation might also exist between the degree of CM alteration and the bulk H abundance (MCSWEEN, 1979), which reflects the H₂O content of the rock. However, it should not be tacitly assumed that the total volume of interacting fluids will be represented by values of bulk rock H content. It is conceivable, for example, that advancing fluid-rock reactions may have been accompanied by phyllosilicate recrystallization and the redistribution of dissolved components, rather than by the generation of new phyllosilicates. In addition, BROWNING et al. (1995) explain how the armouring of anhydrous silicates by dense sulfide rind deposits might inhibit the continued alteration of precursor grains in CM chondrites. An inverse correlation between the bulk H content and the alteration index number is expected to occur if both parameters are sensitive to the production of phyllosilicates.

All bulk H contents in this study were taken from the literature (VAN SCHMUS and HAYES, 1974; KERRIDGE, 1985). To counter some effects of sampling heterogeneity, we utilized Si-normalized values of bulk H. In some cases, Si-normalized values were not reported directly in the literature and had to be derived from the bulk H ($\mu\text{m/g}$) values and chemical compositions of the relevant CM chondrites. A numerical approximation of errors in the bulk H abundance of CM chondrites cannot be justified (KERRIDGE, 1985), although potential sources of error include analytical limitations, intrameteorite heterogeneity and, perhaps, systematic inter-laboratory biases. Figure 3a illustrates the relationship between the mineralogic index and bulk H content in CM chondrites.

Figure 3. The mineralogic alteration index is compared to whole-rock chemical and isotopic signatures. a) The H content of individual CM chondrites increases with progressive CM alteration as more hydrous phyllosilicates are produced. b) A positive correlation between ^{36}Ar and the alteration index number indicates significant loss of trapped planetary gases with increasing CM alteration. c) The volume of isotopically heavy phyllosilicates increases during progressive CM alteration. Abbreviations for individual samples are given in Figure 2.

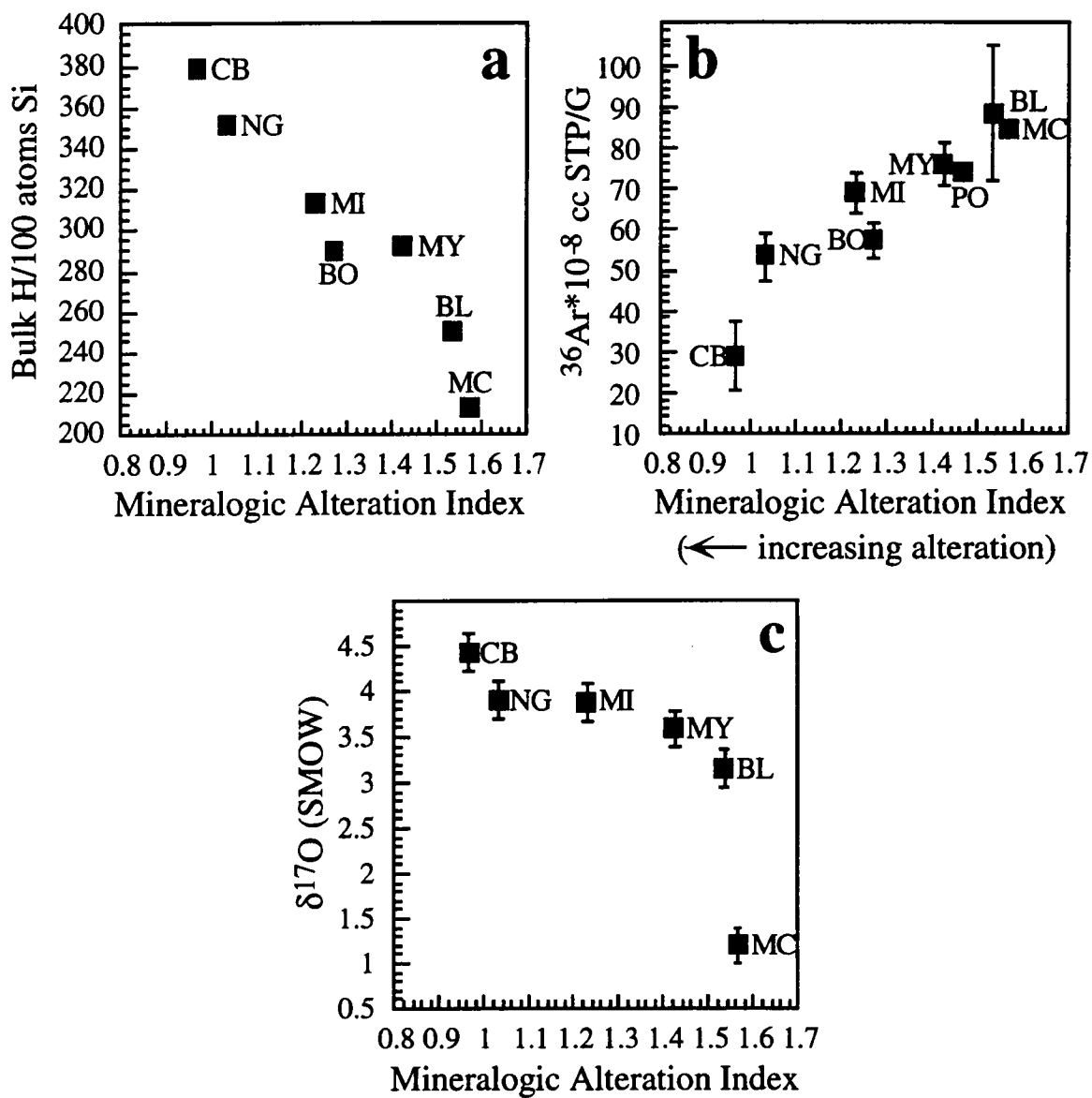


Figure 3

Abundance of Trapped Noble Gases

Trapped noble gases are present in most types of meteorites, but the abundance of these gases is highest in carbonaceous chondrites (SCHULTZ and KRUSE, 1989). The trapped gas content is subdivided into solar gas patterns, which are attributed to solar wind implantation, and planetary noble gas patterns, which are characterized by an enhancement of the heavy inert gases relative to the lighter gases (SWINDLE, 1988). Both the origin of planetary gas fractionation patterns and the cause of variations in the trapped gas abundances in different meteorites remain uncertain. Regardless, trapped noble gases are believed to have largely been incorporated into the meteorite when it formed (MAZOR et al., 1970). This suggests the possibility that secondary processes on asteroidal parent bodies may have, in some cases, led to systematic degassing events that reflect the extent of metamorphic processing. ALAERTS et al. (1977) demonstrated that the abundance patterns of trapped planetary gases exhibited by ordinary chondrites of different petrographic type were probably established in the solar nebula., rather than by variable degrees of thermal metamorphism. However, we note the obvious differences between thermal and aqueous alteration processes and explore here the possibility that partial degassing may have accompanied the progressive aqueous alteration of CM chondrites.

Aqueous reactions resulted in the wholesale dissolution of many types of primary mineralogic and organic phases in CM chondrites (ZOLENSKY and MCSWEEN, 1988). Noble gases are the most volatile elements in meteorites, and are highly insoluble in H₂O (STUTE et al., 1992). It is reasonable to suppose, then, that alteration fluids would then provide an efficient medium to transport these inert components to the surface of the CM parent body. This is consistent with suggestions that the CM alteration system was open to the loss of at least a few components, such as Cl, CH₄, and Na (BUNCH and CHANG,

1980; WOLF et al., 1980; ZOLENSKY et al., 1989). Hence, we do not suggest a process that requires the disruption of primary noble gas fractionation patterns established in the solar nebula. Instead, we propose that progressive CM alteration may have been accompanied by the systematic loss of unfractionated planetary gases as carrier phases were completely consumed by aqueous reactions. Since progressive alteration is characterized by the continued destruction of primary phases, we propose that the absolute abundance of planetary gases in different CM chondrites may reflect the relative degree of aqueous processing that individual meteorites experienced.

We take the abundance of ^{36}Ar in CM chondrites as representative of the overall trapped planetary gas content since the elemental abundance patterns of planetary gases are largely constrained. Comparisons between mineralogic alteration indices and the abundances of ^{84}Kr and ^{132}Xe produce similar, but less striking, correlations. The mean concentration of ^{36}Ar was obtained for most CM chondrites in this study from a compilation of noble gas data (SCHULTZ and KRUSE, 1989). In most cases, literature values of whole-rock ^{36}Ar were used. However, only analyses of light and dark material separates are available for Nogoya. Based on a photograph of the Nogoya sample in HEYMANN and MAZOR (1966), we visually estimated that the light material constituted 25 vol % of the analyzed sample and weighed the data accordingly. However, BLACK's (1972) data for the light and dark Nogoya separates were averaged because no indication was given of their relative proportions. To avoid extensive biases resulting from averaging a small number of ^{36}Ar analyses from compositionally heterogeneous samples, any individual data point that did not fall within 2 standard deviations from the average of the remainder of values for that meteorite was excluded from this investigation. Since the only two whole rock values of ^{36}Ar for Murchison differed significantly, we estimated an additional bulk ^{36}Ar value for this meteorite by using our modal data to weigh values of

^{36}Ar in anhydrous silicates and matrix from Murchison separates. Figure 3b is a plot of the mineralogic alteration index versus the mean ^{36}Ar abundance. Uncertainties in the mean ^{36}Ar content of each meteorite are graphically depicted.

Oxygen Isotopic Ratios

CM matrices define a mass fractionation line on a three-isotope plot of $^{17}\text{O}/^{16}\text{O}$ vs. $^{18}\text{O}/^{16}\text{O}$ (CLAYTON et al., 1976). This mass fractionation line intersects the chondritic mixing line, which separates ^{16}O -enriched and ^{16}O -depleted sources, and departs toward heavier isotopic compositions. Variations in the extent of fluid-rock reactions experienced by different CM chondrites may have produced the isotopic fractionation line (CLAYTON and MAYEDA, 1984; CLAYTON, 1993). Oxygen is an integral component of H_2O and becomes isotopically lighter in fluids during the aqueous alteration of olivines and pyroxenes at low temperatures. In contrast, the phyllosilicates that are produced during these fluid-rock reactions are enriched in heavy O isotopes. CM alteration is likely to have occurred at very low temperatures (i.e. $\sim 20\text{--}50^\circ\text{C}$) (CLAYTON and MAYEDA, 1984; ZOLENSKY et al., 1993), and the modal proportion of CM matrices may increase as alteration proceeds. Therefore, the progressive aqueous alteration of CM chondrites should be correlated with an increased production of matrix phyllosilicates and, hence, a commensurate enrichment in heavy O isotopes in the bulk sample. We suggest, then, that the extent of fractionation toward heavier O isotopes in bulk CM chondrites may be a useful indicator of the relative degree of aqueous alteration that individual meteorites experienced. Whole-rock values of $\delta^{17}\text{O}$ for the CM chondrites in this study were obtained from R. N. Clayton. Results are shown in Figure 3c. Error bars illustrate the reported analytical precision for $\delta^{17}\text{O}$, $\sim 0.2\text{‰}$. Although we have

determined that whole-rock $\delta^{18}\text{O}$ values are similarly correlated with the mineralogic index, the trend is more clearly illustrated in terms of $\delta^{17}\text{O}$.

DISCUSSION

Progressive CM Alteration Trends

We note that although the proposed alteration parameters monitor fundamental changes that are likely to accompany simple serpentinization processes, predictable trends for the aqueous alteration of CM chondrites are far from evident. These meteorites are likely to have experienced a multiplicity of parent body processes, any one of which could potentially thwart the reliability of the progressive alteration parameters.

Figure 2a implies a causal relationship between the relative degree of aqueous alteration that an individual meteorite experienced and the modal content of isolated matrix silicates. This well-defined correlation strongly suggests that each CM chondrite in this analysis must have originally contained a similar proportion of isolated matrix silicates. Hence, the original abundance of isolated silicate grains in each sample was probably at least as high as that of Murchison, but was later diminished to varying degrees depending on the extent of aqueous alteration experienced by the individual CM chondrite. Likewise, the correlation in Figure 2a argues against the addition of significantly different amounts of anhydrous silicate grains to individual CM chondrites after the onset of aqueous alteration. Throughout the alteration process, the entire group of CM chondrites probably maintained a roughly equivalent production rate of matrix silicate grains from the fragmentation of chondrules.

The percentage of chondrules that are replaced by phyllosilicate-rich assemblages increases during the mineralogical transition from cronstedtite to serpentine (Figure 2b).

The chondrule alteration parameter reveals nothing about the absolute abundance of chondrules in different CM samples. However, in a manner similar to that used for matrix silicates, we argue that the systematic behavior of the data in Figure 2b would probably not have occurred if variable proportions of unaltered chondrules had been randomly added to different CM chondrites after aqueous alteration had already begun. Thus, the flux of unaltered chondrules to the CM regolith(s) was probably nearly identical for all CM chondrites.

Phyllosilicates were continually produced throughout the course of progressive CM alteration. The trends in Figure 2 demonstrate a volumetric increase in phyllosilicates as anhydrous silicates are systematically consumed by progressive aqueous reactions. Moreover, the nearly linear increase in the bulk H content of individual CM chondrites in Figure 3a suggests a roughly constant production rate of new hydrous phases relative to the mineralogical transition from cronstedtite to serpentine. A collective evaluation of Figures 2 and 3a indicates, then, that the evolving compositions of both newly-formed and recrystallized phyllosilicates were very sensitive to the abundance and oxidation state of dissolved Fe in the fluids throughout the course of CM alteration.

The positive correlation between the median bulk ^{36}Ar content and the mineralogic alteration index of individual CM chondrites (Figure 3b) is best explained by significant degassing caused by progressive alteration reactions. It seems less likely, for example, that this trend is the result of accreting decreasing proportions of noble gas carrier phases into asteroidal parent bodies that would fortuitously experience increasing degrees of aqueous alteration at some later time. Although different analyses of the planetary gas content in a single CM chondrite may vary widely (SCHULTZ and KRUSE, 1989), Figure 3b illustrates that the effect of sample heterogeneity was not significant

enough to destroy the evidence for systematic variations between individual CM chondrites. As above, this trend suggests that the original planetary gas content of different CM chondrites was remarkably similar.

The correlation in Figure 3b indicates that the original planetary gas carrier phase(s) for CM chondrites was highly susceptible to aqueous alteration. This suggests that some portion of the CM planetary gases may currently reside in or on secondary carrier phases produced by fluid-rock reactions. Despite the apparent vulnerability of the primary noble gas carrier phase(s) to aqueous reactions, carbonaceous chondrites preserve relatively high proportions of trapped gas in comparison with most other chondritic classes (MAZOR et al., 1970). This suggests that some of the trapped gases which were released from primary retention sites may have subsequently been incorporated into the structures or onto the surfaces of recrystallized or newly-formed phyllosilicates. Any inert gases released from their primary retention sites should have been readily mobilized in the CM alteration fluids. Phyllosilicates are relatively efficient at both adsorbing noble gases onto their surfaces (REYNOLDS et al., 1978) as well as incorporating a variety of organic products into their structures (CRONIN and CHANG, 1993). In addition, the CM fluids hosted the production of a variety of additional secondary alteration phases, including carbonates, sulfides, magnetite, and tochilinite (ZOLENSKY and MCSWEEN, 1988). Most alteration may be intimately intergrown within phyllosilicate structures (BARBER, 1981). Thus, there are a variety of ways in which the planetary gases that were released from primary retention sites might subsequently become intimately associated with phyllosilicates.

Figure 3c demonstrates the systematic production of isotopically heavy phyllosilicates during progressive CM alteration. Variations between the bulk O isotopic ratios of individual CM chondrites indicate, then, that the CM alteration system must

have been open to the loss of commensurably ^{16}O -enriched fluids. This is consistent with evidence suggesting the simultaneous loss of planetary noble gases (Figure 3b), since these inert gases would have been transported to the surface of the CM parent body(s) by these same ^{16}O -rich fluids. Since the availability of liquid H_2O is the most plausible limiting factor in the extent of CM alteration, the volumetric loss of ^{16}O -rich fluids was probably also modest. This is compatible with the suggestion (BROWNING et al., 1995) that the availability of liquid H_2O in CM matrices may have been restricted to thin grain coatings during the majority of progressive CM alteration. The open-system loss of H_2O and ^{36}Ar indicated by this study may, however, be difficult to reconcile with alteration on a CM parent body that was encapsulated in a thick layer of permafrost (DUFRESNE and ANDERS, 1962), unless this containing layer was cut by extensive fractures or composed of an icy-liquid mixture.

We recall, finally, that each of the above correlations depends on the reliability of the mineralogic alteration index to gauge the relative extent of CM alteration in individual meteorites. Given the well-defined correlations between this parameter and all others, we conclude that the mineralogic alteration index is a highly sensitive indication of progressive CM alteration. Furthermore, the diversity of progressive alteration indicators that correlate with the alteration index number provides additional support for previous assertions (BUNCH and CHANG, 1980; MCSWEEN, 1987; TOMEOKA and BUSECK, 1985) that progressive CM alteration is accompanied by a mineralogical transition between meteoritic cronstedtite and serpentine.

On the Relative Order of Increasing CM Alteration

A robust alteration scale must not only explain various mineralogic, textural, and chemical trends in the CM group, but also must produce consistent assignments of the degree of alteration for specific meteorites. We begin this section by reviewing the relevant results of earlier investigations, and conclude with a discussion of the degree to which specific CM chondrites have been altered, as judged from this study.

Many conflicting suggestions have been offered regarding the relative order of increasing CM alteration. On the basis of the relative modal content of matrix materials in individual CM chondrites, for example, MCSWEEN (1979) suggested the following order of increasing aqueous alteration for the CM chondritic samples in this study (Table 1): MY (58.8%) < MI (60.7 %) < MC (63.6%) < CB (74.2%) < BO (75.8%) < PO (80%) < BL (81.7%) < NG (85.4%). Following independent petrographic analyses of Bells (BL), BREARLEY (1994) agreed that this meteorite is extensively altered, but DAVIS and OLSEN (1984) did not. In addition, GREENWOOD et al. (1994) obtained a modal matrix content for Cold Bokkeveld of 82.7 vol. %, suggesting that this meteorite is significantly more altered than suggested by MCSWEEN (1979). TOMEOKA and BUSECK (1985) supported MCSWEEN's (1979) conclusion that Mighei, Murchison, and Murray are relatively unaltered in comparison with other CM chondrites, and provided additional petrographic evidence in support of a previous suggestion (BUNCH and CHANG, 1980) that CM matrix phyllosilicates become progressively enriched in Mg and depleted in Fe as alteration proceeded. ZOLENSKY et al. (1993) tested the proposals of both MCSWEEN (1979) and TOMEOKA and BUSECK (1985) by comparing average $\text{FeO}/(\text{FeO}+\text{MgO})$ ratios for the matrix phyllosilicates in several CM chondrites with independently determined modal values of CM matrices in these same samples. The $\text{FeO}/(\text{FeO}+\text{MgO})$

ratios were found to increase in the order: NG < MC < CB < MI < MY, and no correlation was identified between values of FeO/(FeO+MgO) and the modal matrix content of individual CM chondrites. An alternative scaling parameter, the relative abundance of chlorine, was offered by BUNCH and CHANG (1980), who asserted the following order of increasing alteration: MC (1400–200 ppm Cl) < My (1000–150 ppm Cl) < CB (700–100 ppm Cl) < NG (400–50 ppm Cl). In addition, BURGESS et al. (1991) submitted that the oxidized S/reduced S ratios of individual CM chondrites should increase with the extent of progressive aqueous alteration, which results in the trend MI (1.3) < MY (1.4) < MC (2.3) < NG (3.3). The lack of agreement in these studies has prompted us to re-evaluate the types of progressive alteration parameters that might best gauge the degree of CM alteration.

Although segments of some earlier relative alteration scales for CM chondrites are reproduced by our progressive alteration parameters, the order of increasing CM alteration that is predicted by our model is generally inconsistent with previous results. However, each of our proposed alteration parameters indicate a largely self-consistent relative order of increasing CM alteration. Given the variety of factors that may have influenced the progressive alteration signatures of individual CM chondrites, however, it is not surprising that some uncertainties persist. Therefore, we note first that the correlations in Figures 2 and 3 allow the unambiguous assignment of the investigated samples to the categories of minimal (MC and BL), intermediate (PO, MY, CC, BO, MI), and extensive (NG and CB) aqueous alteration. In addition, each progressive alteration trend demonstrates the following relative order of increasing alteration for 7 of the 9 CM chondrites in this study: MC ≤ BL < PO ≤ MY < MI < NG < CB. The degree of aqueous processing that CC and BO experienced, relative to the other intermediately-altered CM chondrites, is not clearly indicated by our data. However, the extent of

Boreskino's alteration appears, on average, to be roughly equivalent to that of Mighei (MI), while Cochabamba (CC) is always more altered than Murray (MY). Disagreement between the various indices regarding the relative alteration of these two meteorites demonstrates that it is not sufficient to produce a progressive alteration scale based on a single parameter. The multiply correlated parameters in our model establish the general reliability of our results.

SUMMARY

We proposed 3 new indices for gauging the relative extent of alteration that individual CM chondrites experienced. The mineralogic alteration index gauges the relative extent to which the progressive alteration trend from cronstedtite to Mg-rich serpentine (BUNCH and CHANG, 1980; TOMEOKA and BUSECK, 1985; MCSWEEN, 1987) has been completed in individual CM chondrites. The proposed mineralogic alteration index monitors the incremental progress of coupled substitutions along this alteration pathway and is based on an approximation of the average matrix phyllosilicate composition in individual CM chondrites. The second parameter, the vol. % of isolated anhydrous matrix silicate grains, evaluates the relative extent to which the anhydrous silicates in different CM chondrites were consumed by aqueous reactions. The proportion of altered phases within chondrules defines the third alteration parameter, which is sensitive to the volumetric production of chondrule phyllosilicates as hydration reactions proceed. Hence, we propose the first alteration scale for CM chondrites that relies on multiple parameters. Correlations between the proposed parameters illustrate a systematic decrease in the vol. % of anhydrous matrix silicate grains and a commensurate

increase in the extent of chondrule alteration during the mineralogic transition from cronstedtite to Mg-serpentine.

The ability of advancing fluid-rock reactions to influence whole-rock chemical and isotopic signatures suggests the possibility of additional alteration trends in CM chondrites. Using bulk-rock data obtained from the literature, we tested the following hypotheses: 1) the abundance of bulk H reflects the extent of phyllosilicate production and, hence, the relative degree of aqueous alteration that individual CM chondrites experienced, 2) the destruction of primary noble gas carrier phases by aqueous reactions results in systematic degassing of unfractionated trapped planetary gases during progressive CM alteration, and 3) the O isotopic ratios of CM chondrites continually shift toward isotopically heavier values as the low temperature production of hydrous phyllosilicates proceeds. A comparison between the mineralogic alteration index and these bulk-rock signatures produced the predicted correlations. The predictable behavior of all proposed indicators of progressive CM alteration also suggests that individual CM chondrites may have been subjected to a similar set of asteroidal processes and conditions as alteration proceeded. In addition, the nearly linear correlation between bulk H content and progressive CM alteration implies an approximately constant production rate of phyllosilicates relative to the mineralogical transition from cronstedtite to Mg-serpentine, while oxygen isotopic systematics imply a significant loss of ^{16}O -rich fluids.

An evaluation of all proposed progressive alteration indicators clearly demonstrates the following relative order of increasing CM alteration: Murchison $\leq$ Bells $<$ Pollen $\leq$ Murray $<$ Mighei $<$ Nogoya $<$ Cold Bokkeveld. Boreskino and Cochabamba are probably best described as having experienced intermediate degrees of aqueous processing. Discrepancies between the parameter values for these 2 meteorites

demonstrate that it is not possible to produce a progressive alteration scale based on a single parameter.

REFERENCES

- ALAERTS L., LEWIS R. S. and ANDERS E. (1977) Primordial noble gases in chondrites: The abundance pattern was established in the solar nebula. *Science* **198**, 927-930.
- BARBER D. J. (1981) Matrix phyllosilicates and associated minerals in CM2 carbonaceous chondrites. *Geochim. Cosmochim. Acta* **45**, 945-970.
- BLACK D. C. (1972) On the origins of trapped helium, neon and argon isotopic variations in meteorites-II. Carbonaceous chondrites. *Geochim. Cosmochim. Acta* **36**, 377-394.
- BREARLEY A. J. (1994) Aqueous alteration and brecciation in Bells, an unusual, saponite-bearing, CM carbonaceous chondrite. *Geochim. Cosmochim. Acta*.
- BROWNING L. (1995) The Aqueous Alteration of CM Chondritic Meteorites. Ph. D. dissertation, Univ. Tennessee, Knoxville.
- BROWNING L. B., ZOLENSKY M. and BARRETT R. (1991) Serpentine and modal compositions of CM chondrites. *Lunar. Planet. Sci.* **XXII**, 145-146.
- BROWNING L., MCSWEEN H. Y. and ZOLENSKY M. (1995) On the Origin of Sulfide Rind Textures in CM Carbonaceous Chondrites. *Geochim. Cosmochim. Acta*, in preparation.
- BUNCH T. E. and CHANG S. (1980) Carbonaceous chondrites--II. Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* **44**, 1543-1577.
- BURGESS R., WRIGHT I. P. and PILLINGER C. T. (1991) Determination of sulphur-bearing components in C1 and C2 carbonaceous chondrites by stepped combustion. *Meteoritics* **26**, 54-64.

- BURNS R. G. and FISHER D. S. (1993) Nanophase mixed-valence iron minerals in meteorites identified by cryogenic mossbauer spectroscopy. *Proceedings of the International Conference on the Applications of the Mossbauer Effect*.
- BUSECK P. R. and XIN H. (1993) Matrices of carbonaceous chondrite meteorites. *Ann. Rev. Earth Planet. Sci. Lett.* **21**, 255-305.
- CLAYTON R. N. (1993) Oxygen isotopes in meteorites. *Ann. Rev. Earth Planet. Sci. Lett.* **21**, 115-149.
- CLAYTON R. N. and MAYEDA T. K. (1984) The oxygen isotope record in Murchison and other carbonaceous chondrites. *Earth Planet. Sci. Lett.* **67**, 151-161.
- CLAYTON R. N., ONUMA N. and MAYEDA T. (1976) A classification of meteorites based on oxygen isotopes. *Earth Planet. Sci. Lett.* **30**, 10-18.
- CRONIN J. R. and CHANG S. (1993) Organic matter in meteorites: Molecular and isotopic analyses of the Murchison meteorite. In *The chemistry of life's origin* (ed. J. M. Greenberg). Kluwer Academic PUBLISHERS.
- DAVIS A. M. and OLSEN E. (1984) Bells- A carbonaceous chondrite related to C1 and C2 chondrites. *Lunar. Planet. Sci.* **XV**, 190-191.
- DUFRESNE E. R. and ANDERS E. (1962) On the chemical evolution of the carbonaceous chondrites. *Geochim. Cosmochim. Acta* **26**, 1085-1114.
- GREENWOOD R. C., LEE M. R., HUTCHISON R. and BARBER D. J. (1994) Formation and alteration of CAIs in Cold Bokkeveld (CM2). *Geochim. Cosmochim. Acta* **58**, 1913-1035.
- HEYMANN D. and MAZOR E. (1966) Light-dark structure and rare gas content of the carbonaceous chondrite Nogoya. *J. Geophys. Res.* **72**, 2704-2707.
- HOUSEN K. R., WILKENING L. L., CHAPMAN C. R. and GREENBERG R. J. (1979) Asteroidal regoliths. *Icarus* **39**, 317-351.

- HUTCHISON R., ALEXANDER C. M. O. and BARBER D. J. (1987) The Semarkona meteorite: First recorded occurrence of smectite in an ordinary chondrite. *Geochim. Cosmochim. Acta* **51**, 1875-1882.
- IKEDA Y. and PRINZ M. (1993) Petrologic Study of the Belgica 7904 carbonaceous chondrite: Hydrous alteration, oxygen isotopes, and relationship to CM and CI chondrites. *Geochim. Cosmochim. Acta* **57**, 439-453.
- JONES R. H. (1992) On the relationship between isolated and chondrule olivine grains in the carbonaceous chondrite ALHA77307. *Geochim. Cosmochim. Acta* **56**, 467-482.
- KERRIDGE J. F. (1985) Carbon, hydrogen and nitrogen in carbonaceous chondrites: Abundances and isotopic compositions in bulk samples. *Geochim. Cosmochim. Acta* **49**, 1707-1714.
- KERRIDGE J. F. and BUNCH T. E. (1979) Aqueous alteration on asteroids: Evidence from carbonaceous chondrites. In *Asteroids* (ed. T. GEHRELS), pp. 745-764. University of Arizona Press.
- MAZOR E., HEYMANN D. and ANDERS E. (1970) Noble gases in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **34**, 781-824.
- MCSWEEN H. Y. (1977) On the nature and origin of isolated olivine grains in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **41**, 411-418.
- MCSWEEN H. Y. (1979) Alteration in CM carbonaceous chondrites inferred from modal and chemical variations in matrix. *Geochim. Cosmochim. Acta* **43**, 1761-1770.
- MCSWEEN H. Y. (1987) Aqueous alteration in carbonaceous chondrites: Mass balance constraints on matrix mineralogy. *Geochim. Cosmochim. Acta* **51**, 2469-2477.
- MCSWEEN H. Y. and Weissman P. R. (1989) Cosmochemical implications of the physical processing of cometary nuclei. *Geochim. Cosmochim. Acta* **53**, 3263-3271.
- MOODY J. B. (1976) Serpentinization: A review. *Lithos* **9**, 125-138.

- REYNOLDS J. H., FRICK U., NEIL J. M. and PHINNEY D. L. (1978) Rare gas separates from carbonaceous chondrites. *Geochim. Cosmochim. Acta* **42**, 1775-1797.
- RICHARDSON S. M. and MCSWEEN H. Y. (1978) Textural evidence bearing on the origin of isolated olivine crystals in C2 carbonaceous chondrites. *Earth Planet. Sci. Lett.* **37**, 485-491.
- SCHULTZ L. and KRUSE H. (1989) Helium, neon, and argon in meteorites--A data compilation. *Meteoritics* **24**, 155-172.
- STUTE M, SCHLOSSER P., CLARK J. F. and BROECKER W. S. (1992) Paleotemperatures in the southwestern United States derived from noble gases in ground water. *Science* **256**, 1000-1003.
- SWINDLE T. D. (1988) Trapped noble gases in meteorites. In *Meteorites and the Early Solar System* (ed. J. F. KERRIDGE and M. S. MATHEWS), pp. 535-564. University of Arizona Press.
- TOMEOKA K. and BUSECK P. R. (1985) Indicators of aqueous alteration in CM carbonaceous chondrites: Microtextures of a layered mineral containing Fe, S, O, and Ni. *Geochim. Cosmochim. Acta* **49**, 2149-2163.
- TOMEOKA K. and BUSECK P. R. (1990) Phyllosilicates in the Mokoia CV carbonaceous chondrite: Evidence for aqueous alteration in an oxidizing environment. *Geochim. Cosmochim. Acta* **54**, 1745-1754.
- VAN DER PLAS L. and TOBI A. C. (1965) A chart for judging the reliability of point counting results. *Amer. J. Sci.* **263**, 87-90.
- VAN SCHMUS W. R. and WOOD J. A. (1967) A chemical-petrologic classification for the chondritic meteorites. *Geochim. Cosmochim. Acta* **31**, 747-765.
- VAN SCHMUS W. R. and HAYES J. M. (1974) Chemical and petrographic correlations among carbonaceous chondrites. *Geochim. Cosmochim. Acta* **38**, 47-64.

- VILAS F., HATCH E. C., LARSON S. M., SAWYER S. R. and GAFFEY M. J. (1993) Ferric iron in primitive asteroids: A 0.43-mm absorption feature. *Icarus* **102**, 225-231.
- WICKS F. J. and WHITTAKER E. J. W. (1977) Serpentine textures and serpentinization. *Canadian Mineralogist* **15**, 459-488.
- WOLF R., RICHTER G. R., WOODROW A. B. and ANDERS E. (1980) Chemical fractionations in meteorites-XI. C2 chondrites. *Geochim. Cosmochim. Acta* **44**, 711-717.
- ZOLENSKY M. and BROWNING L. (1994) CM chondrites exhibit the complete petrologic range from type 2 to 1. *Meteoritics* **29**, 556.
- ZOLENSKY M. and MCSWEEN H. Y. (1988) Aqueous Alteration. In *Meteorites and the Early Solar System* (ed. J. K. KERRIDGE and M. S. Matthews), pp. 114-143. University of Arizona Press.
- ZOLENSKY M. E., BOURCIER W. L. and GOODING J. L. (1989) Aqueous alteration on the hydrous asteroids: Results of EQ3/6 computer simulations. *Icarus* **78**, 411-425.
- ZOLENSKY M., BARRETT R. and BROWNING L. (1993) Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **57**, 3123-3148.

APPENDIX

Determining Mineralogic Alteration Indices

The following listing describes the calculation of mineralogic alteration indices:

- 1) Thin sections of CM chondritic meteorites are selected for analysis.
 - a) Avoid terrestrially weathered samples, such as those exhibiting pervasive rust.
 - b) To lessen the possibility of analyzing non-phylllosilicate phases that may occur in the third dimension, thin sections are ideally ground to thicknesses of less than ~25 μm . If custom grinding is not feasible, look for sections that thin significantly toward the sample edge.
 - c) When possible, multiple thin sections of an individual CM chondrite should be obtained for analysis.
- 2) Electron microprobe analyses of CM matrix material are collected.
 - a) Survey the matrix material by backscattered electron imaging to characterize the grainsize distribution, textures, and mineral associations of the sample.
 - b) Select a small region (~5 μm across) of the matrix that appears to consist largely of phyllosilicates. Collect an EDS spectra of this area to demonstrate a minimal chemical contribution by non-phylllosilicate grains. Although some S will appear in almost every analysis, those spectrum with minimal peaks for S, Ca, and Cr generally produce the best analytical results for the purpose of calculating mineralogic indices.
 - c) Standard microprobe techniques are employed to collect a chemical analysis of the matrix material selected in 2b. See analytical techniques section above for recommended microprobe operating conditions.

- d) Alternate between selecting matrix points (2b) and evaluating their chemical composition (2c) until a representative selection of matrix material (2a) has been analyzed. Try to collect at least 40 points, since many of these analyses will probably be eliminated by screens.
- 3) Several initial screens are employed to ensure the quality of individual analyses.
 - a) Although microprobe analyses of CM matrices typically yield low totals, any analysis that does not produce a total of at least 83 wt. % oxides should be excluded from further consideration.
 - b) Analyses containing more than 0.5 wt. % Ca, Cr, or Na should be discarded due to an increased probability that carbonates, oxides, or non-serpentine phyllosilicates have been included in the analysis. Likewise, no more than 2 wt. % S is acceptable.
 - 4) After reducing the data, values of mineralogic alteration index are calculated from atomic proportions according to the following procedure.
 - a) Idealized sulfide grains are subtracted from each analysis. For simplicity, all S is assumed to be in the form of (Fe,Ni)_{0.877}S. This is consistent with previous assertions that Ni-bearing pyrrhotite is the predominant sulfide phase in CM matrices (ZOLENSKY et al., 1993). We define the number of Fe and Ni atoms that combine with all of the available S according to the following relationships :

$$\text{Fe} = (.875 * \text{S}) - \text{Ni}$$

$$\text{Ni} = 0.1\text{S}.$$

The number of Fe, Ni, and S atoms that are incorporated into the idealized

pyrrhotite are then subtracted from the original atomic proportions for each of these elements.

- b) Sulfide-corrected cation totals are recalculated to 5. This is accomplished by multiplying the atomic proportion of each element by a correction factor, $5/(\text{sulfide-corrected cation total})$. This step involves the assertion that the sulfide-corrected atomic proportions reflect a stoichiometric serpentine composition.
- c) New screens are imposed on the recalculated cation values to eliminate analyses that do not produce reasonable serpentine compositions. Since serpentine contains a maximum of 2 Si atoms, for example, all analyses with greater than 2 atoms of Si are excluded from further consideration. In addition, the proportions of all analyzed cations are used to determine if the resultant serpentine composition is reasonably charge-balanced. Although serpentine are seldom perfectly stoichiometric, we require that all analyses produce a total cation charge that ranges between ~13.5 and 14.
- d) The number of Fe^{3+} and Fe^{2+} atoms in each analysis are estimated by demanding that the general stoichiometric requirements of serpentine, $(\text{Fe}^{2+}, \text{Mg})_{3-x}(\text{Al}, \text{Fe}^{3+})_x(\text{Si}_{2-x}(\text{Al}, \text{Fe}^{3+})_x\text{O}_5(\text{OH})_4)$, are fulfilled. By assuming that a loss of Si is accommodated by coupled substitutions that exhaust all of the available Al, the requisite number of Fe^{3+} atoms is approximated by:

$$\text{Fe}^{3+} = (2 * (2 - \text{Si})) - \text{Al}.$$

Calculated Fe^{3+} values are then subtracted from the total number of Fe atoms to give the number of Fe^{2+} atoms that remain.

e) The mineralogic alteration index is defined as the average value of $\text{Fe}^{3+}/(2\text{-Si})$ for the matrix analyses in an individual CM chondrite. Ratios of $\text{Fe}^{3+}/(2\text{-Si})$ for individual analyses should range between 0 (Mg-serpentine) and 2 (cronstedtite). Any individual ratios that do not fall within this range are excluded from the calculation of the average $\text{Fe}^{3+}/(2\text{-Si})$ value for the sample. Ideally, at least 20 matrix analyses should be averaged into the mineralogic alteration index, but this is not always possible.

PART 2

On the Origin of Sulfide Rind Textures in CM Carbonaceous Chondrites

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ABSTRACT

Thin rinds of fine-grained sulfides and phyllosilicates are observed around many individual chondrule silicate grains in CM-type carbonaceous chondrites. The origin of this texture is evaluated to provide constraints on the alteration conditions that may have existed on some asteroidal surfaces. Some rind assemblages may have precipitated directly from supersaturated fluids at the surface of dissolving olivine grains. Kinetic controls favor the production of sulfide rind textures during the incipient stages of aqueous alteration, but continued rind growth is kinetically inhibited. However, the relative ease with which ferrous monosulfides precipitate in comparison with to endmember Mg- and Fe-serpentine suggests that sulfide-rich assemblages may have formed at the surface of reacting olivine grains when the early alteration fluids were still confined to the olivine grain boundaries. In addition, petrologic evidence strongly supports the formation of many sulfide rind textures by *in situ* replacement processes. The production of sulfide rinds around individual chondrule grains is best explained by an alteration scheme with dissolved S being mobilized during the early stages of chondrule alteration as a result of the equilibration of primary chondrule sulfides with grossly undersaturated alteration fluids. The subsequent precipitation of stable secondary sulfides is most likely to occur at low activities of total dissolved S, pH values ranging from ~7 to 9, and Eh values between ~-0.3 to -0.6. The origin of petrologically similar sulfide rind textures located in CM matrices was also considered. *In situ* fluid-rock reactions provide the most satisfactory explanations for the textures and mineral associations described in this study.

INTRODUCTION

CM carbonaceous chondrites are of particular interest because they preserve textural and mineralogical evidence of a diverse set of formational processes. These meteorites contain both anhydrous high-temperature and hydrous low-temperature phases which are intimately associated in a variety of textures that are unique to this type of meteorite. Several studies have focused on determining whether these textures were formed during nebular processes or by parent body fluid-rock reactions (MCSWEEN, 1979; BREARLEY and GEIGER, 1991; METZLER et al., 1992; BROWNING, 1994), with the result that some of the most prominent textures have alternately been assigned nebular, parent body, or combined nebular and parent body origins. This uncertainty involving the location of CM alteration needs to be resolved, because the opposing models have profoundly different implications for the nature of the solar nebula and protoplanets.

The literature contains voluminous experimental (MOODY, 1976; WOGELIUS and WALTHER, 1992) and theoretical (HELGESON et al., 1984; WICKS and WHITTAKER, 1977) studies and petrological observations of terrestrial rocks (GROVES et al., 1974; EGGLETON, 1984) bearing on the origin of specific textures and minerals resulting from fluid-rock reactions. The conclusions drawn from many of these investigations elucidate fundamental mechanisms of the serpentinization process, while the terrestrial serpentinites themselves illustrate diverse petrographic features that result from serpentinization under a range of conditions. In contrast, the viability of forming complex CM textures in a nebular environment cannot be fully assessed because there are significant gaps in the understanding of nebular processes and conditions (LEVY and JUNINE, 1993). Given the greater uncertainties in the nebular setting, we suggest that more emphasis should be placed on rigorously determining which CM textures are

consistent with an origin by aqueous processes in an asteroidal setting. By a process of elimination, such an approach may ultimately provide a means for distinguishing those textures which must *necessarily* be explained by nebular events. However, efforts to assign any type of unique origin to complex CM textures are easily stymied by ambiguities resulting from the same intricate series of formation processes that make these meteorites so interesting. To circumvent this problem, we have identified a simple CM texture that can be unambiguously ascribed to parent body alteration processes and have worked backward to quantify the conditions of its origin. We expect that these conditions should provide constraints on the broader range of CM alteration textures that can be produced by progressive alteration reactions.

Of all sites of alteration within CM chondrites, chondrules provide the clearest evidence for the formation of secondary textures by fluid-rock interactions. Chondrules crystallized from molten or partially molten droplets in the solar nebula (TAYLOR et al., 1983; GROSSMAN, 1988). Most chondrules in CM chondrites contain relatively coarse-grained olivine or pyroxene grains of primary igneous origin. In contrast, the secondary textures in CM chondrules are defined by fine-grained phases, which invariably include hydrous phyllosilicates. Numerous experiments and observations identify phyllosilicates as low-temperature alteration products of olivines, pyroxenes, and glass (MOODY, 1976; NOACK et al., 1993). The phyllosilicates observed in CM chondrules could not have formed before or during chondrule formation because they would not have survived the high melting temperatures (HEWINS and RADOMSKY, 1990), and theoretical models indicate that hydration of solidified chondrules in the nebula was probably kinetically inhibited (PRINN and FEGLEY, 1987); therefore, it seems reasonable to conclude that chondrule textures defined by phyllosilicate-bearing assemblages were produced by low-temperature aqueous reactions after accretion into a parent body.

In this work, we consider the origin of sulfide rind textures in CM chondrules. A sulfide rind is defined as any continuous or discontinuous coating of fine-grained sulfides and phyllosilicates around anhydrous silicate grains or their pseudomorphs. Unlike rims, which are complex mineral assemblages that form thick bands (up to $\sim 150\ \mu\text{m}$) around chondrules (ZOLENSKY et al., 1993), sulfide rinds enclose individual chondrule grains and are generally less than $10\ \mu\text{m}$ in thickness. Although similar rind textures have previously been described (LLORCA and BREARLEY, 1992; BUNCH and CHANG, 1980), the origin of these textures warrants additional attention. Sulfide rinds are present in abundance in most CM chondrites, implying that the production of these textures may record a common process in the alteration history of the CM parent asteroid(s). By limiting investigation to sulfide rind textures that are encapsulated inside chondrules, we avoid ambiguities involving their origin by nebular processes. For confirmation, we will present several petrological arguments that support an origin for sulfide rind textures by *in situ* aqueous reactions. We hope that an improved understanding of the origin of sulfide rinds may represent a logical step toward establishing the plausibility that parent body alteration reactions may be responsible for the development of more complex S-bearing alteration textures in CM chondrites.

We will examine critically two mechanisms that might have produced sulfide rinds in CM chondrules: direct precipitation from a supersaturated fluid, and *in situ* replacement. Both mechanisms require fluid-rock interaction, and so are parent body processes. We begin by exploring various mechanisms that might result in the preferential precipitation of sulfide-rich assemblages near the dissolving olivine surface. Toward this end, we develop a simple model to evaluate the influence of kinetic controls on the production of sulfide rinds. Predictions from this model are also useful in determining the nature of other mechanisms that may act in concert with kinetic effects to

produce sulfide rind textures from supersaturated fluids. Petrologic observations are then presented which suggest that incomplete replacement may have also played a significant role in the development of sulfide rind textures in CM chondrules. Some of the fluid parameters that favor the formation of sulfide rind textures by aqueous processes on the CM parent body are then constrained. Finally, several textures are identified in CM matrices that appear remarkably similar to those observed in altered chondrules.

ANALYTICAL TECHNIQUES AND SAMPLES

We studied 36 polished sections of 11 CM chondritic meteorites by optical and scanning electron microscopy. Thin sections of Mighei, Nogoya, Cochabamba, Murchison, Murray, Boreaskino, Bells, Cold Bokkeveld, Pollen, Santa Cruz, and Y791198 were obtained, variously, from the Field Museum, University of Vienna, ASU Center for Meteorites, British Museum, National Institute of Polar Research, and Charles Meyers/JSC.

Each section was characterized first by optical microscopy in reflected and transmitted light. A JEOL 35C scanning electron microscope (SEM) at the NASA Johnson Space Center was then operated at 20 kV to obtain back scattered electron images of selected regions. A Princeton Gamma Tech Be-window detector was used to collect EDS spectra on the mineral assemblages in these samples. Spectra were collected for at least 100 s.

PETROLOGY: SULFIDE RINDS AND CHONDRULE ALTERATION

The distinguishing characteristic of sulfide rind textures is an elevated concentration of submicron-sized sulfide grains around a partially altered mafic silicate core. The sulfide grains are almost always dispersed within a fine-grained phyllosilicate groundmass of predominantly serpentine and cronstedtite +/- chlinochlore phases. (A more comprehensive discussion of the various phyllosilicate phases in CM chondrites can be found in ZOLENSKY et al. (1993), BARBER (1981), and the references therein.) The sulfide rinds in CM chondrules are usually less than 10 μm in thickness, and may be either continuous or discontinuous around host olivine and pyroxene grains. Some rinds exhibit a jagged or irregular outline (Figure 1a), whereas others define a smooth band of roughly constant thickness around the host phase (Figure 1b). In most rind-bearing chondrules, phyllosilicates that are relatively free of sulfide inclusions fill the gaps between the individual sulfide rind segments, and fairly sharp contacts exist between the sulfide rinds and these phyllosilicates. Alternatively, the core silicate and sulfide rind may be separated by a region of sulfide-poor phyllosilicates (Figure 1c). At thin section scale, we also observe considerable variability in the amount of dispersed sulfides within the altered portions of individual chondrules. For example, sulfide rinds may be present around each olivine grain in one CM chondrule, but entirely absent in the adjacent chondrule.

Petrological observations of many CM chondrules indicate that the sulfides and phyllosilicates in sulfide rinds must have formed in concert with the dissolution of the olivine host. Figure 1b shows the typical embayed appearance of olivine grains that are surrounded by rind textures. Since secondary phyllosilicate assemblages form at the

Figure 1. Petrologic features formed by secondary sulfides in CM chondrules and aggregates. a) Fine-grained sulfides and phyllosilicates form optically opaque rinds around degraded chondrule olivines. The sulfide rinds (SR) in this Murchison chondrule are irregularly shaped and separated by sulfide-poor phyllosilicate assemblages (PH); plane light. b) Sulfide rinds trace the fracture planes and grain boundaries of chondrule olivine grains (OL) in a Nogoya chondrule. The morphology of these rinds is smooth and their thickness is roughly constant. Sulfide-poor assemblages appear grey; plane light. c) Primary sulfides (S) in Cochabamba chondrule are surrounded by secondary phyllosilicates and sulfides (SRA); BSE. d) Fine-grained phyllosilicates and secondary sulfides form pseudomorphs (PS) after precursor sulfides in Cochabamba aggregate; BSE.

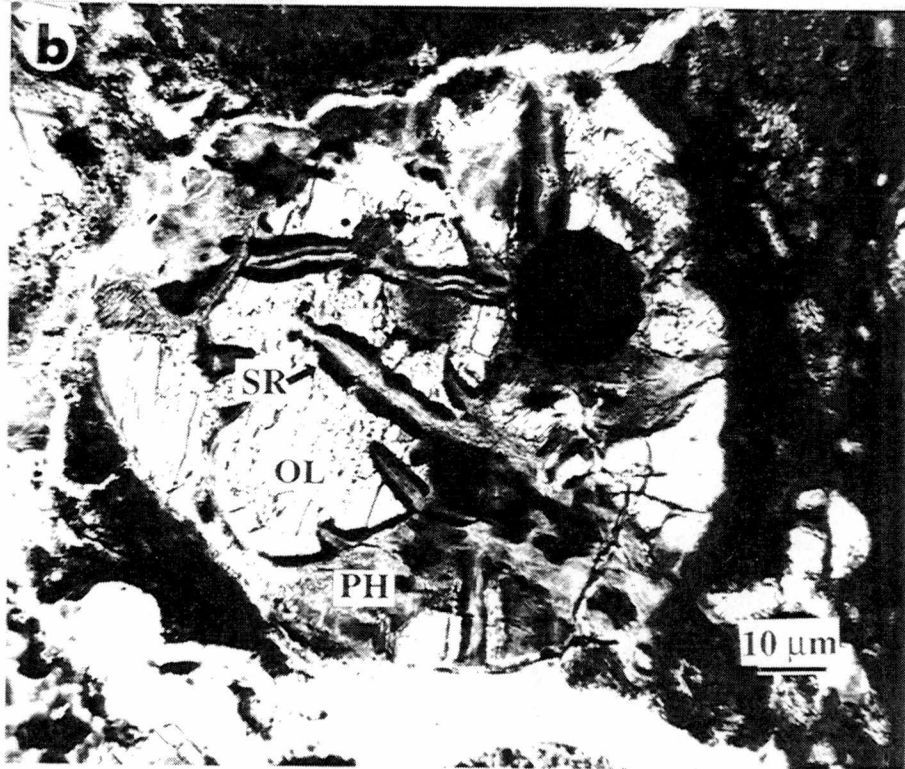
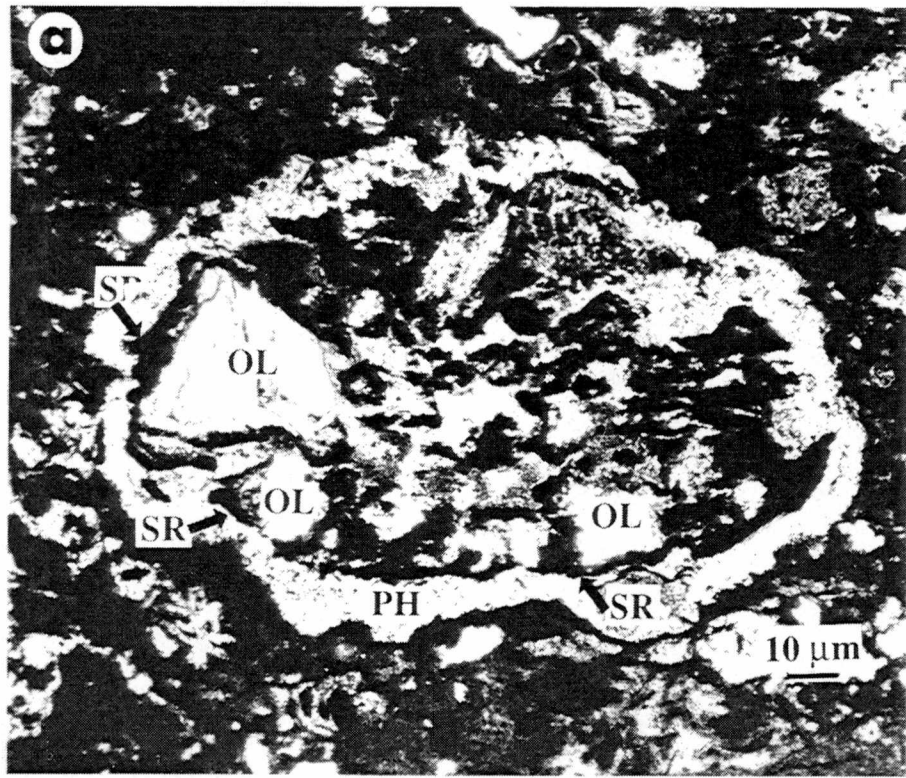


Figure 1

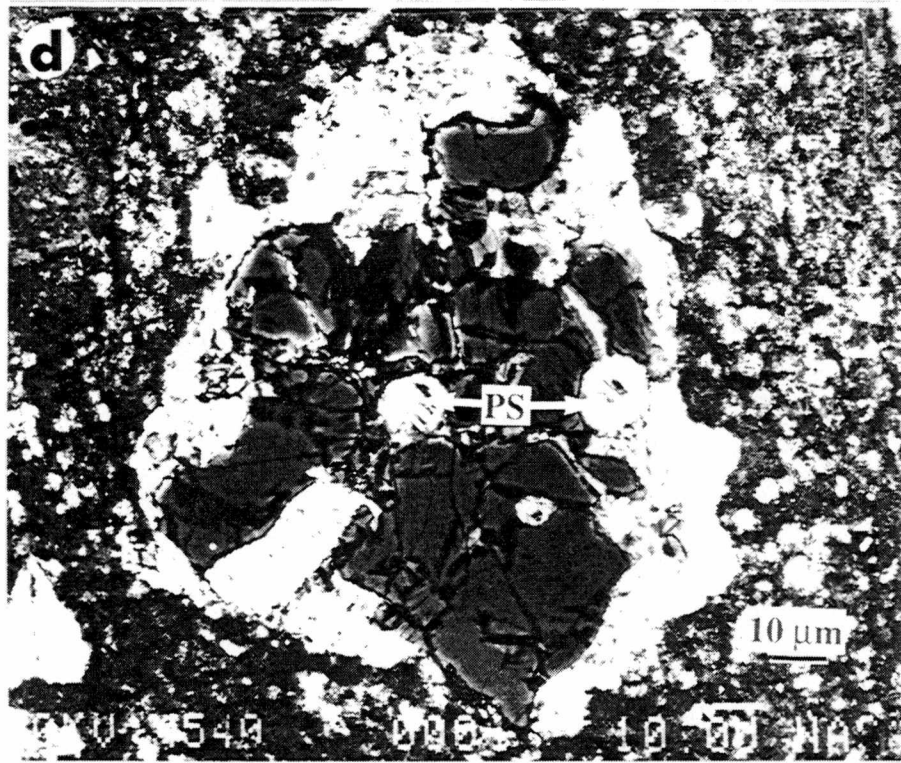
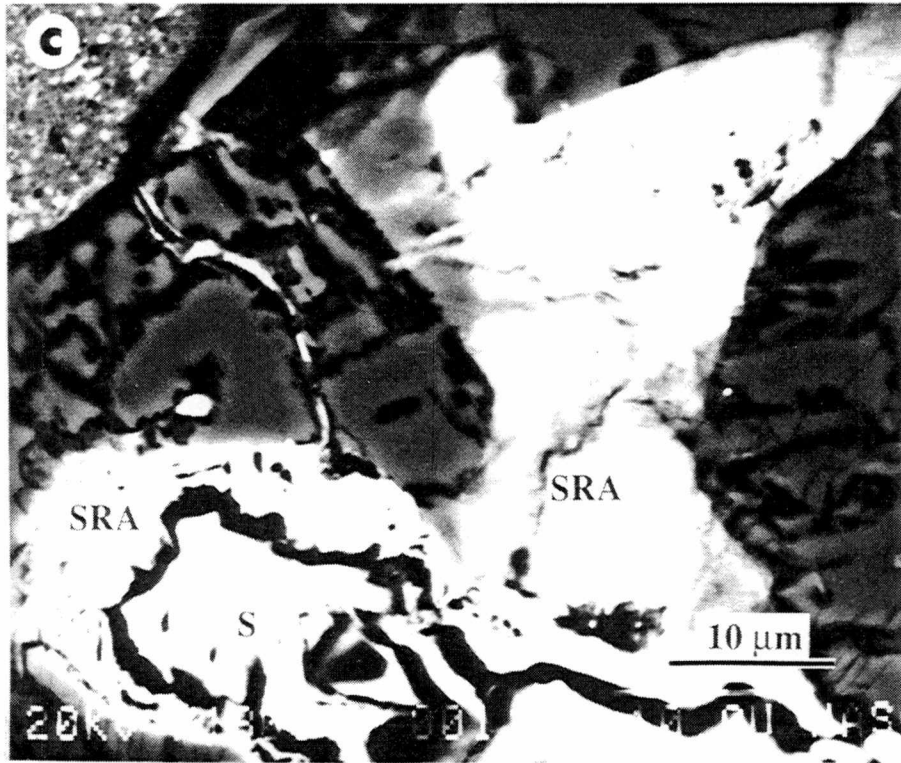


Figure 1 (continued)

expense of olivine reactants, the deteriorated olivine surfaces and associated phyllosilicate deposits clearly point to a common origin by aqueous processes. The extensive permeation of sulfide rind assemblages into the fracture planes of chondrule olivines further demonstrates that sulfides and phyllosilicates commonly formed together as secondary precipitates after chondrule olivine grains. Figure 1b shows that fracture-filling assemblages are also sometimes continuous with the surrounding sulfide rind assemblage, indicating that the sulfide and phyllosilicate assemblages that occur both within and around these chondrule silicate grains were produced during the same alteration event.

The precipitation of rind sulfides requires that fluids contained dissolved S. Previous investigations have concluded that primary sulfide grains in chondrules are the most likely source of dissolved sulfide ions in CM fluids (DUFRESNE and ANDERS, 1962; MCSWEEN, 1979; BUNCH and CHANG, 1980). This is consistent with our petrological observations of altered CM chondrules. Figure 1c shows a CM chondrule that contains several primary sulfides. Fine-grained sulfides and phyllosilicates surround the primary sulfides and also trail off into adjacent chondrule materials. The textural association of fine-grained sulfide-phyllosilicate assemblages and primary sulfide blebs suggests that aqueous species were released by the dissolving precursor sulfides and subsequently incorporated into secondary sulfides during chondrule alteration. Some rind-bearing chondrules do not preserve any primary sulfides, but contain fine-grained sulfides and phyllosilicates that pseudomorph precursor sulfide or metal grains (Figure 1d). These observations are consistent with geochemical modeling (ZOLENSKY et al., 1989), which predicts the formation of secondary sulfides during aqueous alteration. The proximity of primary and secondary sulfides further suggests that movement of dissolved S-bearing species was limited.

The precipitation of secondary sulfides also requires that the CM fluids contained dissolved Fe^{2+} . Some of this Fe^{2+} must have been released during the dissolution of precursor chondrule sulfides. The early dissolution of small metal grains may also have contributed some Fe^{2+} to the fluids in CM chondrules. Although metal is less abundant than sulfides in CM chondrules, small metal grains are often observed in and around many chondrule silicate grains and some sulfides (RAMDOHR, 1973). Additional Fe^{2+} would have been contributed to the fluids in chondrules from the dissolution of Fe-bearing olivines. Although the Fe-content of chondrule olivine is generally low in type II carbonaceous chondrites (WOOD, 1967), the high rates of olivine dissolution (WOGELIUS and WALTHER, 1992) and the large proportion of olivine grains in CM chondrules strongly suggest that olivine dissolution may have been an important source of dissolved Fe^{2+} . The role that Fe-bearing olivine plays in the formation of sulfide rind textures is discussed in the sections below.

PRECIPITATION OF RINDS FROM SUPERSATURATED FLUIDS

Petrographic observations of altered CM chondrules illustrate that precursor sulfides and olivines experienced dissolution processes that may have provided a significant proportion of the dissolved components needed for the precipitation of rind assemblages. However, the development of sulfide rind textures requires an additional mechanism to concentrate the fine-grained sulfides at, or near, the surface of dissolving olivine grains. In the sections below, we consider the possibility that kinetic controls and/or the size of alteration conduits may have strongly influenced the precipitation of sulfide rind textures directly from supersaturated fluids.

Brief Description of the Kinetic Model

Experimental alteration of Fe-bearing olivine grains in an oxidizing aqueous environment has shown that the host phase may be armored by oxidized Fe-bearing precipitates at the olivine-fluid interface (LUCE et al., 1979; SIEVER and WOODFORD, 1979). We suggest that the rind textures observed in CM chondrules may have also formed by analogous processes. Under extremely reducing conditions it is possible that ferrous sulfide might precipitate rapidly enough to produce rind textures before the released Fe^{2+} has equilibrated in the alteration fluids (SIEVER and WOODFORD, 1979). The viability of a kinetically driven mechanism for sulfide rind production depends, then, on the ability of the alteration system to encourage sulfide precipitation near the olivine surface while discouraging its random precipitation in a larger reservoir of compositionally homogeneous fluid.

We will focus on characterizing the distribution of sulfide precipitates that form by kinetically driven reactions between aqueous sulfide species and Fe^{2+} released from dissolving olivine grains at STP. Unfortunately, only two ferrous monosulfides in CM chondrites have adequate thermodynamic data sufficiently well characterized for modeling purposes: troilite (a stoichiometric pyrrhotite of composition FeS) and $\text{Fe}_{.877}\text{S}$ (a somewhat Fe-depleted member of the pyrrhotite series). Both sulfides have been incorporated into the model as precipitating rind phases. Unless otherwise stated, both sulfides are collectively referred to as "pyrrhotite". A detailed account of all model equations is given in the Appendix.

Our model defines two infinite and parallel planes of olivine that are separated by 200 μm of dilute S-bearing solution that is assumed to behave ideally at all times. The assumption of an ideal solution requires that we restrict our calculations to the incipient

stages of rind production, when the concentration of dissolved species is still very small. The total concentrations and relative proportions of dissolved S-bearing species in the model solution are calculated from the solubility of pyrrhotite in pure water at each pH from 7 to 12, and are held constant in the model solution at all times. The pH range considered in this model encompasses the values suggested by previous workers (ZOLENSKY et al., 1989; DUFRESNE and ANDERS, 1962). We then determine the constant flux of $\text{Fe}^{2+}_{\text{aq}}$ from dissolving olivine with homogeneous compositions ranging from an XFa of 0.1 to 0.6 at each pH. The selected range of olivine compositions approximates that of CM chondrites. The Fe^{2+} that is released from each olivine plane diffuses into the S-bearing solution from both olivine planes.

The distribution of the diffusant is closely monitored because a gradient of $\text{Fe}^{2+}_{\text{aq}}$ is requisite to the incipient production of sulfide rind textures by kinetic processes. Precipitation occurs under the condition that the concentration of $\text{Fe}^{2+}_{\text{aq}}$ exceeds the solubility of pyrrhotite. Thus, if the solubility product of an Fe-bearing phase is exceeded under the influence of a strong gradient in $\text{Fe}^{2+}_{\text{aq}}$, then precipitation is favored near the Fe^{2+} source (e.g. the olivine planes) but suppressed toward the center of the fluid volume. The distribution of $\text{Fe}^{2+}_{\text{aq}}$ continues to evolve through time because additional Fe^{2+} is constantly supplied to the solution while diffusion acts to destroy any concentration gradients. Therefore, the $\text{Fe}^{2+}_{\text{aq}}$ gradient is continually monitored. Following the appearance of a Fe-bearing phase, the evolution of the $\text{Fe}^{2+}_{\text{aq}}$ gradient is considered by balancing the effects that diffusion, Fe^{2+} release, and precipitation have on the distribution of Fe^{2+} in the model solution. In this manner, we determine the locations where pyrrhotite should begin to precipitate with respect to the olivine boundary under a range of initial conditions. Finally, we evaluate the extent that the model fluid is saturated with respect to endmember Fe- and Mg-serpentine at the instant that pyrrhotite

first begins to precipitate at each pH. These calculations provide a basis for determining the relative timing of serpentine and pyrrhotite precipitation throughout the model solution.

Kinetic Model Results and Discussion

Dissolved Fe and S in the model solution

Differences in troilite and pyrrhotite solubilities provide information regarding both the initial S content of the model solution and the amount of $\text{Fe}^{2+}_{\text{aq}}$ that is required to precipitate each sulfide. Table 1 lists the results of these calculations for pH 7 to 12. The solubilities of both sulfides increase with decreasing pH, due to hydrolysis of the sulfide ion, which favors the production of larger proportions of H_2S and HS^- . As a result, more $\text{Fe}^{2+}_{\text{aq}}$ is required to precipitate ferrous monosulfides at nearly neutral pH values than at high pHs. Under all pH conditions, less $\text{Fe}^{2+}_{\text{aq}}$ is required to precipitate $\text{Fe}_{.877}\text{S}$ than troilite because the former incorporates less Fe^{2+} into its structure. Hence, non-stoichiometric pyrrhotite is predicted to be the more likely secondary sulfide precipitate in CM chondrites, consistent with compositional analyses of fine-grained sulfides in CM chondritic samples (ZOLENSKY et al., 1993).

At the onset of alteration, a constant flux of $\text{Fe}^{2+}_{\text{aq}}$ is released into the model solution from the dissolution of olivine. For simplicity, the surfaces of the model olivine are treated as uncharged. As shown by WOGELIUS and WALTHER (1992), the rate of olivine dissolution is largely dependent on pH and XFa. This result can be depicted on a plot of the log rate of the Fe^{2+} flux rate versus pH (Fig. 2) because the olivine dissolution equations portray the steady-state, stoichiometric release of components. The rate that

Table 1. Concentrations of dissolved Fe^{2+} and S^{2-} in equilibrium with pyrrhotite ($\text{Fe}_{.877}\text{S}$) and troilite (FeS) in pure water as a function of pH. Solubilities decrease with increasing pH, and are always lower for pyrrhotite than troilite.

Pyrrhotite ($\text{Fe}_{.877}\text{S}$)			Troilite (FeS)	
pH	Fe^{2+} (mol/L)	S^{2-}	Fe^{2+} (mol/L)	S^{2-}
7	1.99E-07	3.21E-14	6.69E-06	9.43E-13
8	1.99E-08	3.21E-13	6.69E-07	9.43E-12
9	1.99E-09	3.21E-12	6.69E-08	9.43E-11
10	2.13E-10	3.10E-11	7.15E-09	8.83E-10
11	7.75E-11	8.25E-11	2.60E-09	2.43E-09
12	7.49E-11	8.53E-11	2.51E-09	2.51E-09

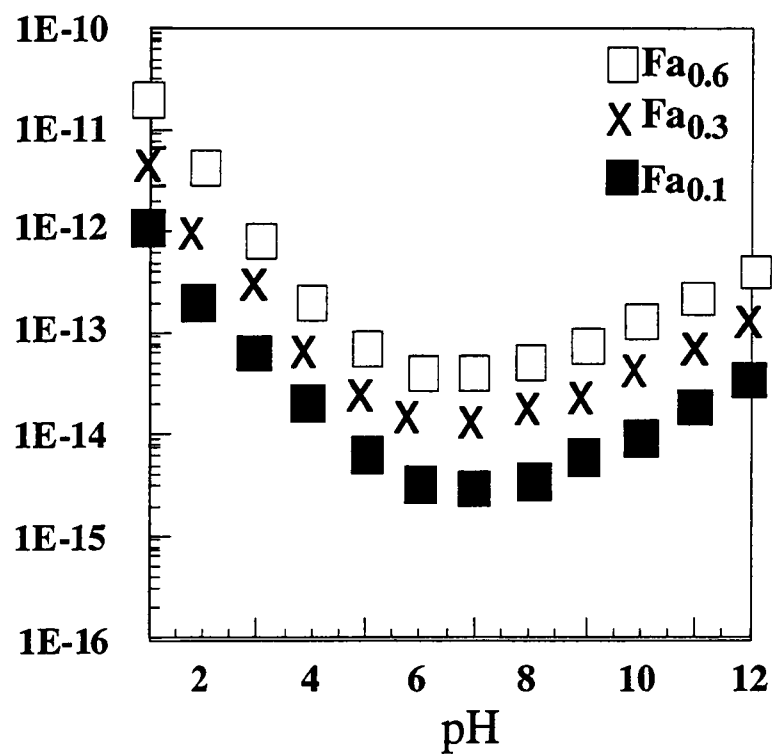


Figure 2. Flux rate of $\text{Fe}^{2+}_{\text{aq}}$ from dissolving olivine as a function of pH and olivine composition. Release rates are highest for Fe-rich olivines under acidic and alkaline conditions.

Fe^{2+} is released is slowest at nearly neutral pHs and increases at both acidic and basic pH values. Since we have restricted our model solution to pH values between 7 to 12 and considered olivine compositions varying from $\text{XFa}_{0.1}$ to $\text{XFa}_{0.6}$, the highest rate of olivine dissolution occurs at pH 12 and $\text{XFa}_{0.6}$. At any fixed pH, the rate of $\text{Fa}_{0.6}$ dissolution is approximately an order of magnitude more rapid than that of $\text{Fa}_{0.1}$. For any given olivine composition, there is roughly an order of magnitude difference between the rate of dissolution at pHs 7 and 12.

Incipient formation of sulfides and serpentine

Figure 3a compares the times of initial precipitation for troilite and pyrrhotite at 1 μm from the surface of the dissolving olivine planes as a function of pH and XFa . Since the solubility products for troilite and pyrrhotite are both very low, precipitation is initiated on the order of a few seconds or less after olivine dissolution begins. We note that even Mg-rich olivine grains ($\text{XFa}=0.1$) will release enough Fe^{2+} to begin precipitating either sulfide quickly. At any given pH, however, the time required to initiate sulfide precipitation decreases as the dissolving olivine source becomes more Fe-rich. The time of initial precipitation also varies with pH, as demonstrated by the strong negative slopes. The fluid is saturated more readily as pH increases from a neutral value because the flux rate of released Fe^{2+} increases and sulfide solubilities decrease. As expected, comparison of the troilite and pyrrhotite curves for any given olivine composition indicates that pyrrhotite will precipitate almost an order of magnitude faster than troilite at all solution pH's due to differences in their solubilities. Consequently, troilite is omitted from further discussions involving sulfide and production.

Figure 3b shows the distribution of $\text{Fe}^{2+}_{\text{aq}}$ when pyrrhotite begins to precipitate at a pH of 10. The calculated solubility for pyrrhotite at this pH is shown by a solid line.

Figure 3. Distribution of $\text{Fe}^{2+}_{\text{aq}}$ from dissolving olivine as a function of pH and olivine composition. a) Log values of the times required for the model solution to exceed the calculated solubilities of FeS and $\text{Fe}_{.877}\text{S}$ as a function of pH. Saturation occurs most rapidly when the dissolving model olivines are Fe-rich and the pH values are high. The model solution is always saturated more rapidly with respect to pyrrhotite than troilite. b) Distribution of $\text{Fe}^{2+}_{\text{aq}}$ in a solution of pH 10 at the instant that the solubility for pyrrhotite is first exceeded between olivine planes of $\text{XFa} = 0.1$. The strong gradient results in the preferential precipitation of pyrrhotite near the olivine surfaces.

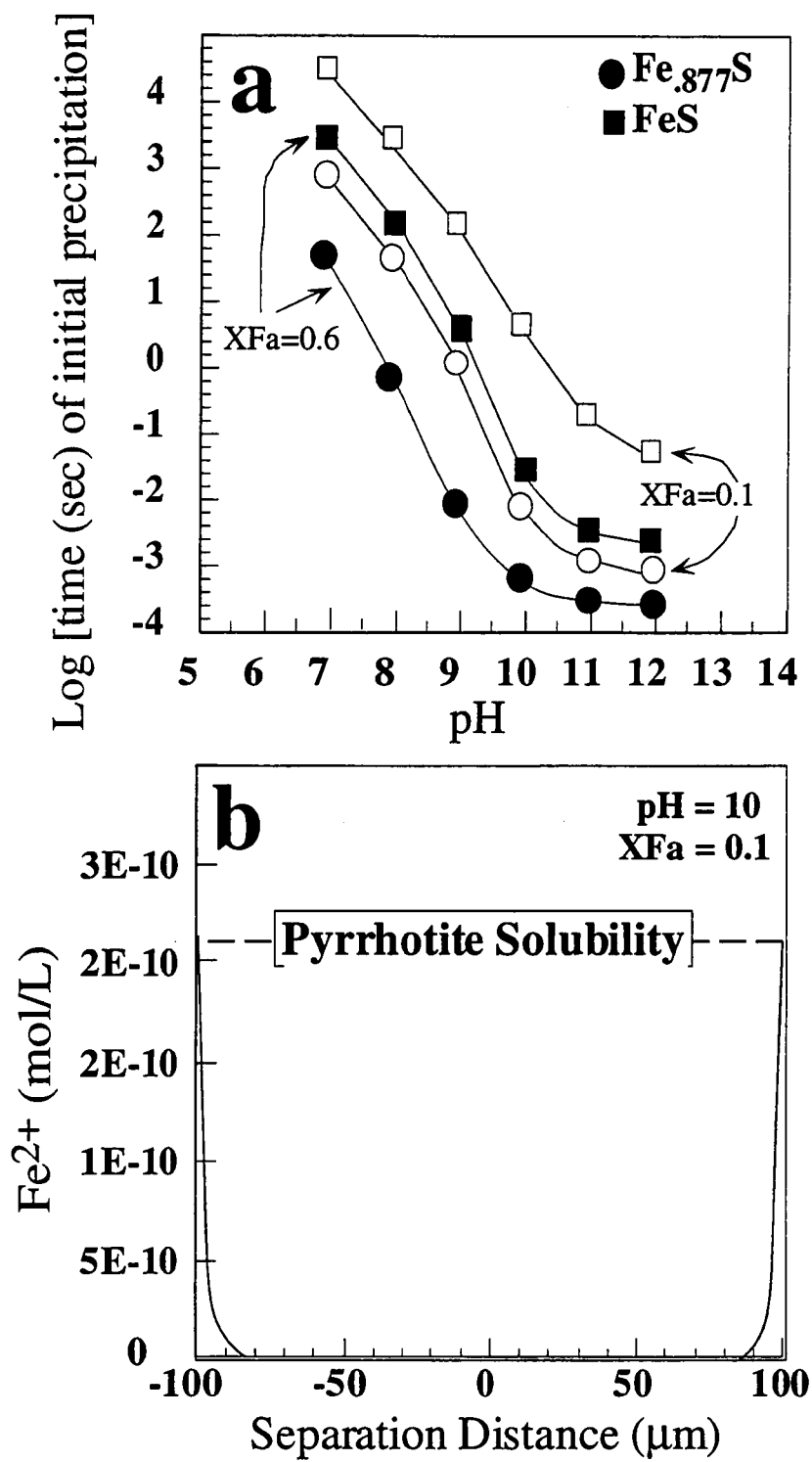


Figure 3

Since the solubility of pyrrhotite is preferentially exceeded near the olivine boundaries, pyrrhotite begins to form directly against the surface of the dissolving olivine in a rind-like texture. In a similar manner, pyrrhotite precipitation is initiated at the olivine-fluid interface for all pH values between ~9 and 12 because its solubility under these conditions is exceedingly small while the rates of olivine dissolution are high. In contrast, a gradient is not present when the solubility of pyrrhotite is first exceeded at pH values of 7 or 8, and precipitation occurs randomly throughout the model solution. Therefore, the formation of sulfide rind textures is not favored by kinetic processes at pH 7 to 8.

Figure 4a is a plot of the calculated log ion activity product for Mg-serpentine as a function of pH. The log of the equilibrium constant for Mg-serpentine is illustrated for reference. The two curves show the extent to which the fluid is saturated in Mg-serpentine at the instant the pyrrhotite first begins to precipitate at a distance of 1 μm from the surface of dissolving olivines of compositions $\text{XFa}_{0.1}$ and $\text{XFa}_{0.6}$. The extent that the fluid is saturated with respect to Mg-serpentine increases with the Mg-content of the dissolving olivine. Even when the olivine source is very Mg-rich ($\text{XFa}_{0.1}$), the model solution is grossly unsaturated in Mg-serpentine at the instant that pyrrhotite first precipitates. Therefore, the precipitation of pyrrhotite will always be initiated before Mg-serpentine under the conditions of this model. As the composition of dissolving olivine approaches that of pure forsterite ($\text{XFa} \ll 0.1$), however, the efficiency of pyrrhotite formation may rely increasingly on the availability of an Fe^{2+} source not accounted for in this model.

Since the equilibrium constant for Fe-serpentine is nearly 15 orders of magnitude lower than that of Mg-serpentine (Fig. 4b), the fluid is significantly closer to saturation in Fe-serpentine when pyrrhotite precipitation is initiated. The fluid is nearest saturation in

Figure 4. Extent that the model fluids are saturated in a) Mg-serpentine and b) Fe-serpentine at the instant that pyrrhotite ($\text{Fe}_{0.877}\text{S}$) first begins to precipitate as a function of pH and olivine composition. The fluid is undersaturated in Mg- and Fe-endmember serpentine when pyrrhotite first appears in the model solution.

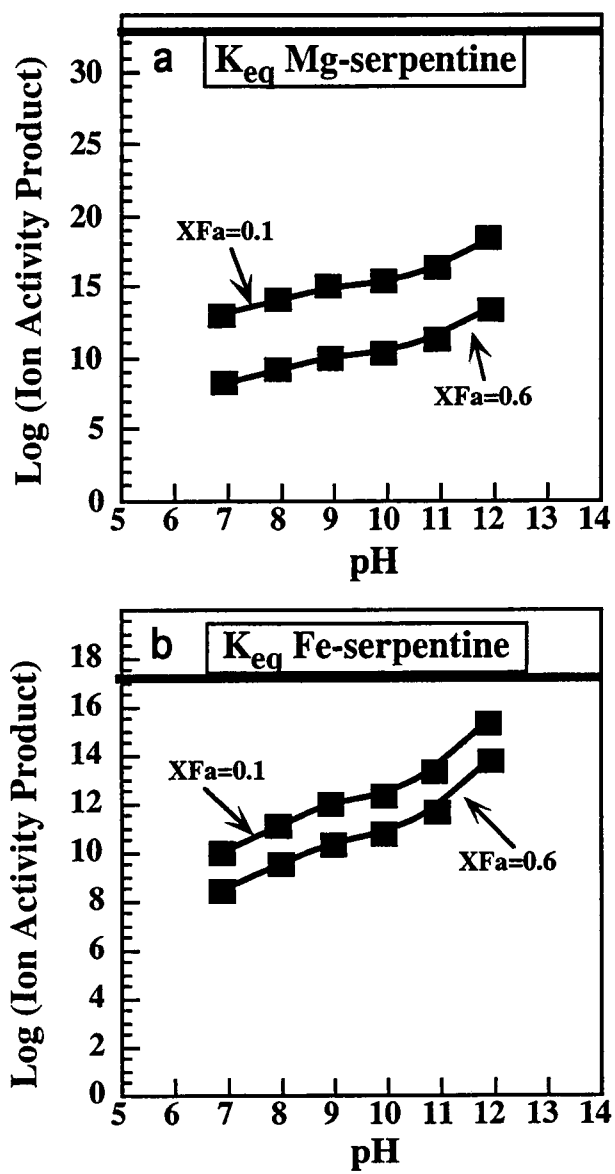


Figure 4

Fe-serpentine under alkaline conditions when the XFa of the dissolving olivine is low. Increasing the XFa content of the dissolving olivine reduces the time required to initiate the precipitation of pyrrhotite, but decreases the amount of Si that is available for the production of serpentine. However, Fe-serpentine does not precipitate before pyrrhotite under any of the investigated model conditions. Therefore, pure endmember Fe-serpentine will probably not form rinds around dissolving olivine grains unless the precipitation of pyrrhotite is inhibited by processes not accounted for in this model.

We conclude that pyrrhotite will always begin to precipitate from aqueous reactions before the model fluid is saturated in either endmember Mg- or Fe-serpentine. At pH 9 to 12, pyrrhotite begins to precipitate preferentially near the surface of the dissolving olivine planes. The efficient precipitation of pyrrhotite implies a decrease in the amount of $\text{Fe}^{2+}_{\text{aq}}$ that is available for the subsequent production of serpentine. Therefore, it is likely that the first phyllosilicate to precipitate after pyrrhotite will have a significant Mg component, despite the lower equilibrium constant for endmember Fe-serpentine. Under the conditions of this model, where dissolving olivine grains are widely spaced, incipient pyrrhotite production should begin randomly throughout the fluid at pH 7 to 8 and be joined by the production of serpentine. Since rind production is not favored at pH 7 and 8 by kinetically-controlled processes, these conditions are omitted from further discussion in the next section.

Development of full-scale sulfide rind textures

The precipitation of an Fe-bearing phase decreases the amount of dissolved Fe^{2+} that is available in the model fluid. Once the solubility of pyrrhotite has been exceeded, precipitation rates are incorporated into the model calculations to account for these changes. Our results indicate that the maximum rate of pyrrhotite precipitation is always

much smaller than the concentration of $\text{Fe}^{2+}_{\text{aq}}$ that is continuously being supplied to the fluids by the dissolving olivine. Therefore, pyrrhotite can never utilize more than a fraction of the released Fe^{2+} that is present in excess of the pyrrhotite solubility product. Once precipitation has begun, the majority of the newly released Fe^{2+} is efficiently removed from the olivine boundaries by diffusion. As a result, the effect of pyrrhotite precipitation on the calculated distribution of $\text{Fe}^{2+}_{\text{aq}}$ is insignificant because most of the $\text{Fe}^{2+}_{\text{aq}}$ equilibrates in the model solution. Thus, Fe^{2+} -bearing precipitates will be somewhat randomly distributed throughout the fluid, rather than being incorporated into sulfide precipitates that armor the surfaces of each olivine plane.

Under the conditions of this model, a Fe^{2+} gradient is not maintained in the inter-olivine fluids for a sufficient period of time to continue to develop significant sulfide deposits around the dissolving olivine source by kinetic processes alone. Figure 5 shows the distribution of pyrrhotite precipitates in the model solution after several increments of time have elapsed at pH 10. The shape of the precipitation curve remains roughly constant with time, but shifts upward toward larger absolute values of precipitation. As a result, the ratio of grain-boundary to mid-plane precipitates diminishes on a time scale that follows the dissipation of the $\text{Fe}^{2+}_{\text{aq}}$ gradient. Our calculations indicate that after approximately 30 seconds, the $\text{Fe}^{2+}_{\text{aq}}$ gradient is effectively destroyed and significant sulfide deposits will begin to develop throughout the entire region between the olivine planes. We conclude that, although the conditions are favorable for sulfide rind growth during the incipient stages of chondrule alteration, the development of $\sim 10 \mu\text{m}$ thick sulfide rinds is kinetically inhibited in each evaluated case.

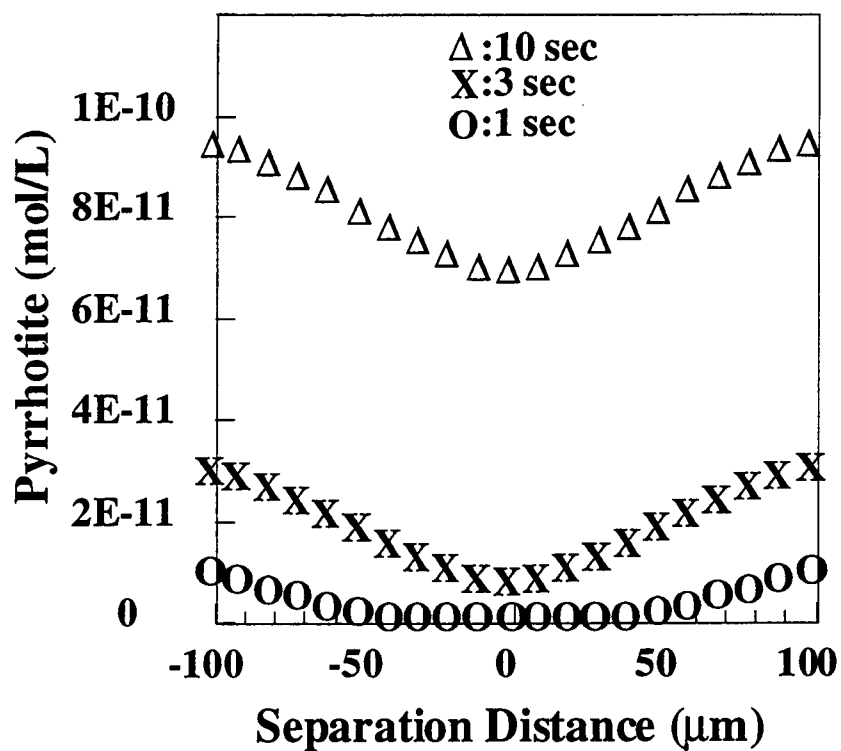


Figure 5. Distribution of pyrrhotite ($\text{Fe}_{0.877}\text{S}$) precipitates across the model solution after 1, 3, and 10 sec of olivine dissolution. Precipitation is initiated at the olivine-fluid interface, but the proportion of sulfides near the olivine planes compared to the sulfides in the midpoint between the olivine planes decreases rapidly with time.

Effect of Narrow Conduits on the Formation of Sulfide Rinds

We conclude above that kinetic processes alone will not result in large enough variations in the spatial distribution of sulfide precipitates to account for the formation of the sulfide rinds that we observe in CM chondrules. However, conditions are favorable for sulfide rind precipitation during the early stages of aqueous alteration. Particularly compelling are the points that 1) pyrrhotite will always precipitate from supersaturated S-bearing fluids before serpentine, even when the dissolving olivine is Fe-poor, and 2) the incipient formation of pyrrhotite at pH 9 through 12 occurs preferentially at the olivine-fluid interface. We note that, ultimately, production of sulfide rinds is not favored under the conditions of the model because most of the Fe^{2+} released from the dissolving olivine diffuses away from the olivine boundary before it can be incorporated into a significant rind deposit. Therefore, we will explore the possibility that non-diffusive processes may have concentrated $\text{Fe}^{2+}_{\text{aq}}$ near the surface of dissolving olivine grains to allow the continued precipitation of sulfide rind textures from supersaturated fluids.

The precise dissolution mechanism of Fe-bearing olivine is not clearly understood. Since we concern ourselves here with the formation of sulfide rind textures by reactions between the surface of dissolving olivines and S-bearing fluids, this produces some uncertainties in the nature of the aqueous environment that immediately surrounds dissolving olivine grains. Although olivine dissolution experiments have not yet been conducted in the presence of reducing S-bearing fluids, the experimental dissolution of Fe-bearing olivine grains in an oxygenated environment provides some insight into the formation of sulfide rind textures in CM chondrites. As previously mentioned, these experiments often produce a ferric-oxide or -hydroxide armor around the dissolving olivine grains (LUCE et al., 1979; WOGELIUS and WALTHER 1992).

Unfortunately, experimental results have not been sufficient to determine if these armoring precipitates 1) develop immediately on, or in, an oxidized surface layer of the dissolving olivine (WHITE and YEE, 1985), or 2) form directly on the olivine surface following the oxidation of $\text{Fe}^{2+}_{\text{aq}}$ in solution (SIEVER and WOODFORD, 1979). Regardless, both possibilities indicate that the mechanisms which control fluid parameters at, or very near, the surface of the dissolving olivine may be significantly different from those of the general fluid reservoir. This suggests, by analogy, that the dissolution of Fe-bearing olivine grains in a deoxygenated atmosphere may also produce a unique environment at the olivine-fluid interface which favors the formation of sulfide rind textures.

Another approach to the problem of precipitating sulfide rinds directly from supersaturated fluid involves considering the effect of a small separation distance between dissolving chondrule olivines. Recall that, under the conditions of our kinetic model, we consider the distribution of precipitates in an aqueous environment between widely spaced olivine grains. From a practical standpoint, this represents the case where sulfide precipitation was initiated after aqueous alteration had already proceeded for a sufficient period of time for dissolution to have produced broad conduits in chondrules. However, the juxtaposition of phyllosilicates and secondary sulfides directly against the surface of chondrule olivines suggests the possibility that sulfide rind textures may have formed significantly earlier. During the incipient stages of chondrule alteration, adjacent olivine grains were probably separated by very small distances, since the initial infiltration of fluids occurs between precursor grains where minute interstitial voids facilitate the passage of fluids (WICKS and WITTAKER, 1977). As a result, much of the Fe^{2+} needed for the precipitation of sulfides may have been effectively trapped within these narrow fluid-filled conduits.

Petrological observations support the production of sulfide rind textures during the incipient stages of CM alteration. In many slightly altered CM chondrules where olivine grains are joined by interlocking igneous textures, the alteration fluids appear to have intruded the chondrule along narrow conduits between adjacent chondrule grains. Figure 6a shows an incipiently altered chondrule in Murray. In this example, fine grained sulfide and phyllosilicate deposits are confined to narrow regions between unaltered chondrule olivines, suggesting that favorable conditions for sulfide rind formation occurred during the early stages of aqueous alteration along narrow conduits.

Given small olivine separation distances, dissolved Fe^{2+} probably collected within regions of restricted fluid access and did not readily equilibrate with the larger reservoir of CM fluids because the diffusive transport of $\text{Fe}^{2+}_{\text{aq}}$ out of these narrow fluid conduits would have been severely limited. If the fluids that filled these conduits contained sufficient quantities of dissolved S, then sulfide production would have continued unabated in the narrow interstitial regions between adjacent chondrule olivines. This mechanism for sulfide production does not require the accumulation of significant amounts of dissolved Fe^{2+} and S in the interstitial spaces because, as indicated by the results of our kinetic model, the precipitation of sulfides can proceed from the $\text{Fe}^{2+}_{\text{aq}}$ released by Fe-poor olivine with very low concentrations of dissolved S. Thus, one plausible effect of shortening the separation distance between dissolving olivine grains is the formation of sulfide rind textures. The importance of narrow fluid conduits in determining the types of secondary phases that form is illustrated by observations of dense sulfide deposits within the narrow fracture planes of many chondrule olivines (see Fig. 1b). Similarly, sulfides are often present within both the restricted confines of olivine fracture planes and the interstitial regions between adjacent grains in some of the least altered terrestrial serpentinites (GROVES et al. 1974). These observations imply that

Figure 6. Additional textures formed by fine-grained sulfides and phyllosilicates in chondrules and aggregates. a) Fine-grained phyllosilicates and secondary sulfides (SRA) are restricted to narrow conduits between olivine grain boundaries in this incipiently altered chondrule in Murray; BSE. The initial alteration of CM chondrules may be characterized by the precipitation of rind assemblages along the surfaces of dissolving chondrule silicates. b) Secondary sulfides and phyllosilicates form pseudomorphic structures (PS) after host olivine grains in a Cochabamba chondrule while coarser-grained sulfides line the relict boundaries of each structure; BSE. The incorporation of secondary sulfides within these structures illustrates the *in situ* replacement of chondrule olivine grains by sulfide rind assemblages. c) Sulfide rinds in Mighei chondrule preserve the relict grain boundaries of incompletely replaced olivine grains; plane light. d) Diagrammatic sketch of Figure 6c. Original olivine (OL) grain boundaries of pseudomorphic structures (PS) are punctuated with central partings. Central portion of chondrule is filled by relatively sulfide-free phyllosilicate assemblage (PH). e) BSE image of sulfide-rich Murchison chondrule containing many pseudomorphic structures and one irregularly-shaped sulfide rind. f) Diagrammatic sketch of relevant textural features in Figure 6e. The extent of the sulfide rind (SR) is restricted to the portion of the large olivine grain (OL) that falls within the sulfide-rich band (SRB) around the chondrule. Since the sulfide-rich band is defined by sulfide-rich pseudomorphic structures (PS), this suggests that the sulfide rind within this band must have formed by the same pseudomorphic processes.

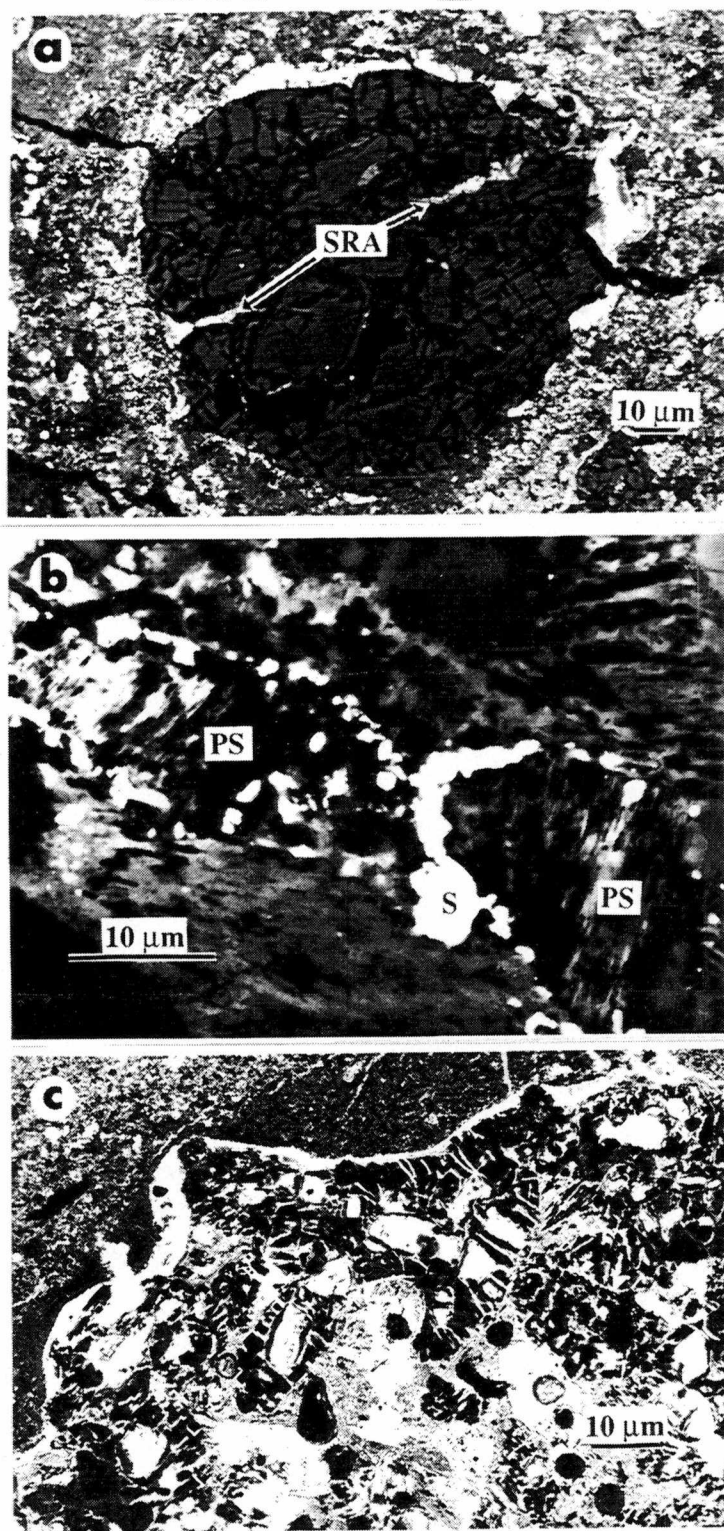


Figure 6

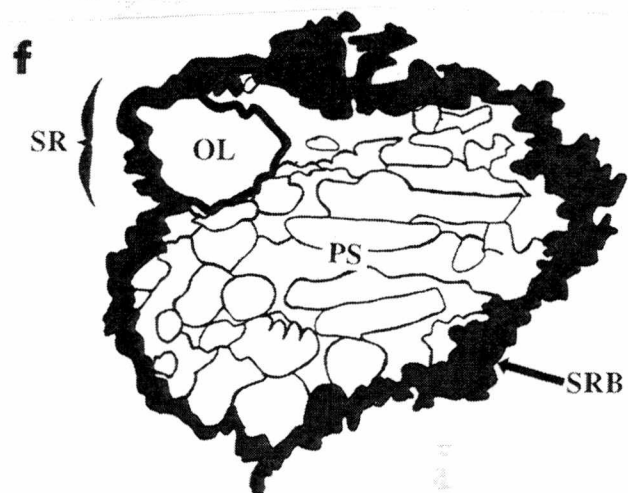
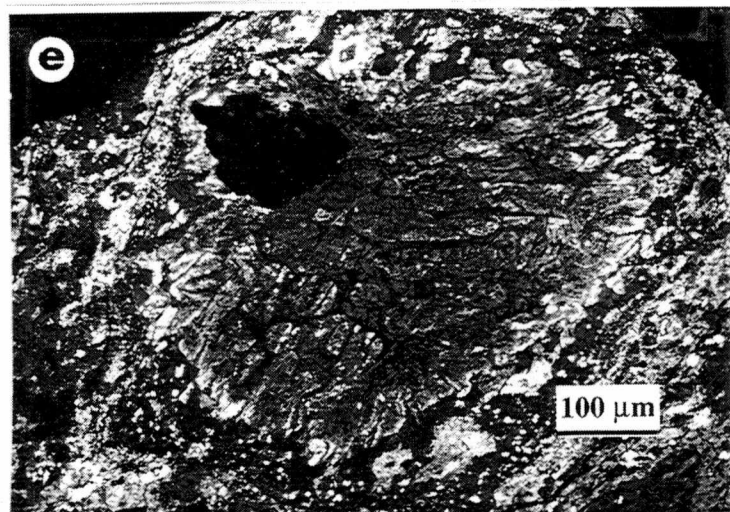
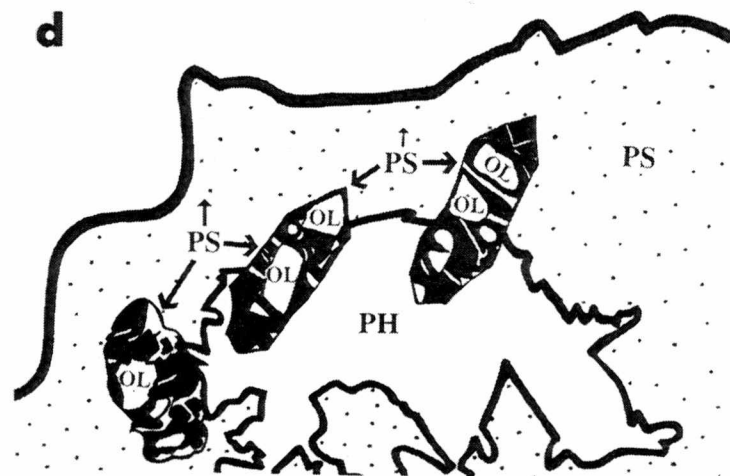


Figure 6 (continued)

most of the Mg and Si released from dissolving olivines may have preferentially escaped from the narrow conduits. This is consistent with the results of our kinetic model, which indicate that reactions between S-bearing fluids and olivine favor the precipitation of sulfide over serpentine, because it implies that much of the dissolved Mg and Si would have remained in the expelled fluid as sulfides rapidly sealed off the narrow conduits.

Although alternative possibilities exist, we suggest that the most obvious explanation for the juxtaposition of sulfide-rich and sulfide-poor assemblages in CM chondrules (see Figs. 1a and 1b) is the limited availability of dissolved S in the alteration fluids. As noted above, textural evidence suggests that the dissolution of precursor chondrule sulfides may have contributed dissolved S to the chondrule fluids. The presence of dense concentrations of secondary sulfides around partially dissolved primary sulfides suggests that finite concentrations of dissolved S may have been largely restricted to the regions immediately surrounding precursor sulfide sources. Since secondary sulfides precipitate efficiently from dilute solutions, these observations suggest that the sulfide-poor assemblages probably formed next to sulfide-rich assemblages when the local supply of dissolved S became exhausted in the fluids.

In a broad sense, the effect that varying the separation distance between dissolving olivine grains has on the alteration process leads to a more general conclusion: the original geometry and phase associations of CM chondrules must have also played a significant role in the pathways of alteration fluids and, hence, the types of secondary textures that were produced. In addition to the assertion that the early fluids were restricted to intergranular pathways, we suggest that CM fluids probably infiltrated preferentially along pre-existing chondrule fractures or regions filled by glassy mesostasis that dissolved rapidly. Therefore, several controlling factors may have ultimately helped

to define the conditions favorable for the precipitation of sulfide rind deposits in any given locale.

SULFIDE RINDS BY IN SITU REPLACEMENT PROCESSES

Serpentine commonly forms as an in situ replacement product after most minerals in ultramafic terrestrial rocks (MOODY, 1976; FROST, 1985). When replacement occurs with little or no disruption of the precursor grain boundaries (WICKS and O'HANLEY, 1988), a pseudomorphic texture is produced. Many phyllosilicate pseudomorphs after terrestrial olivine contain minor Fe-bearing inclusions such as magnetite or sulfides (RAMDOHR, 1967; GROVES et al., 1974; FROST, 1985). The formation of these Fe-bearing inclusions may be related to a low tolerance for Fe in some phyllosilicate structures (WICKS and WHITTAKER, 1977). Similarly, we observe the nearly ubiquitous presence of fine-grained sulfides within most phyllosilicate pseudomorphs after olivine in hydrated CM chondrules. Petrological observations of altered CM chondrules suggest that some sulfide rind textures may have formed by the incomplete replacement of chondrule olivine grains.

Pseudomorphic textures are common in CM chondrules. Figure 6b shows a highly altered CM chondrule that contains sulfide-bearing pseudomorphs after olivine. Fine-grained sulfides are present as inclusions within the pseudomorphic structures, while larger sulfide grains demarcate the relict grain boundaries. Likewise, many sulfide rind textures form well-defined pseudomorphic structures which clearly display the original morphology of the host phase. Relict olivine grain boundaries in Figures 6c and 6d, for example, are sharply defined by an opaque assemblage of fine-grained sulfides and phyllosilicates. In this example, replacement has largely occurred along the outer

portions of euhedral chondrule olivine grains, but central partings divide the pseudomorphic structure into two or more segments containing the remnants of unaltered olivine grains. Each of the partially replaced remnant olivine grains is surrounded by individual sulfide rind textures. We observe many similar examples that illustrate the formation of sulfide rind textures by incomplete replacement processes.

Many sulfide rinds in CM chondrules exhibit irregular or serrated outlines (Figs. 1a and 6e). The lack of well-defined pseudomorphic features complicates the unambiguous assignment of a replacement origin to these sulfide rind textures. However, the irregular morphology of these rinds may, in part, be attributed to the partial replacement of host silicates that have experienced a prior episode of surface dissolution (Figures 1a and 1b). This is consistent with observations of rinds that fill the degraded fracture planes and trace the anhedral grain boundaries of the core silicate. Yet, a prior event of surface dissolution can not fully account for the serrated morphology of many sulfide rind textures. WICKS and WHITTAKER (1977) indicate that the perfection of pseudomorphic textures in terrestrial serpentinites varies widely. These authors also note that some replacement textures do not exhibit any of the features typically associated with pseudomorphic textures. Therefore, a replacement origin for the irregularly-shaped sulfide rind textures in CM chondrules must be inferred from additional petrological evidence.

Petrological observations suggests that some irregularly-shaped sulfide rind textures formed by the incomplete and imperfect replacement of chondrule silicates. Figure 6e, for example, shows a chondrule that contains one sulfide rind texture and multiple pseudomorphic structures. The juxtaposition of the sulfide rind and sulfide-bearing pseudomorphs within this single chondrule setting facilitates their comparison. For clarity, the relevant features of this image are depicted in a diagrammatic sketch

(Figure 6f). Note that the highest concentrations of fine-grained sulfides in this example define a narrow band around the chondrule perimeter. Since the width of this band is generally thinner than the width of a single pseudomorphic structure, the pseudomorphs toward the outside of the chondrule display a heterogeneous distribution of sulfide inclusions. Dense sulfide deposits are only present in those portions of pseudomorphic structures that lie within the sulfide-rich band. The sulfide rind in this example defines one segment of the continuous sulfide-enriched band that traces the outer portion of this chondrule. In contrast, a rind texture is not present around any part of the olivine host that does not fall within the sulfide-rich band. The shape of the sulfide rind also exhibits the same serrated irregularity as those portions of the adjacent pseudomorphs which lie within the sulfide-rich band. The remarkable similarity between the appearance of the sulfide rind and the sulfide-enriched portions of neighboring pseudomorphs strongly suggests that both textures were formed by the same alteration process. We suggest that the only difference between these textures is that the sulfide rind partially encloses a large olivine grain which has not been fully replaced. This may be due to the smaller surface/volume ratio of this grain relative to its neighbors. The poorly defined relict grain boundaries associated with the pseudomorphs in this example demonstrate that imperfect replacement processes did occur in CM chondrites.

CONSTRAINTS ON ALTERATION FLUIDS

CM alteration fluids probably represent water and possibly other components released from ices that accreted along with stony materials to form the original CM parent body (GRIMM and MCSWEEN, 1989), along with extra components derived by fluid-rock reactions. Although the composition of CM ices remains largely unknown, several

inferences can be made about the early alteration fluid from the textures and mineral associations observed in altered CM chondrules. Since olivine does not contain S, the presence of fine-grained sulfides within rind and pseudomorphic structures clearly demands some other source of dissolved S. Furthermore, the occurrence of dense concentrations of Fe-sulfides around relatively Fe-poor chondrule olivines strongly suggests that Fe^{2+} was also present in the CM fluid during rind production. Although we have shown that sulfide production can proceed from reactions between a S-bearing fluid and the Fe^{2+} released from the dissolution of even Fe-poor olivine, backscattered electron images of sulfide rind textures demonstrate that the bulk composition of these rinds is significantly more Fe-rich than the olivine grains that they surround. Therefore, additional $\text{Fe}^{2+}_{\text{aq}}$ must have been contributed to the alteration fluid by an alternate source. As suggested earlier, the predominant source for dissolved Fe and S-bearing species in CM chondrules was probably precursor sulfide and Fe metal grains. We seek a single set of fluid parameters at STP that is adequate to explain both the local control of dissolved sulfide components and the formation of secondary sulfides.

Figure 7a is an Eh-pH diagram for Fe- and S-bearing phases which was constructed by GARRELS and CHRIST (1965) assuming a total activity of dissolved S = 10^{-1} . This is perhaps the most commonly depicted Eh-pH stability diagram for the Fe-S- H_2O - O_2 system because 10^{-1} is approximately the activity of $\text{H}_2\text{S}_{\text{aq}}$ in a solution saturated with H_2S gas at STP. Although there is no a priori reason why specific geological settings should adhere to these conditions, Figure 7a provides a useful starting place for the initial investigations of phase relations. These are, for example, the conditions suggested by DUFRESNE and ANDERS (1962) for the alteration of CM chondrites. This diagram shows that pyrrhotite is only stable under very reducing conditions. The pH stability for pyrrhotite at an activity of total dissolved S equal to 0.1

Figure 7. Eh-pH diagrams of iron-bearing phases at activities of $\Sigma S = 0.1$ and 10^{-6} . a) Eh-pH diagram of iron-bearing phases at activity of $\Sigma S = 0.1$. Fe-monosulfides (FeS) are stable under very alkaline, reducing conditions and may occur together with pyrite; after Garrels and Christ (1965). b) Eh-pH diagram of iron-bearing phases at activity of $\Sigma S = 10^{-6}$. Fe-monosulfides (FeS) are stable under reducing conditions at neutral pH and may occur together with pyrite, $\text{Fe}^{2+}_{\text{aq}}$, or magnetite; after Garrels and Christ (1965).

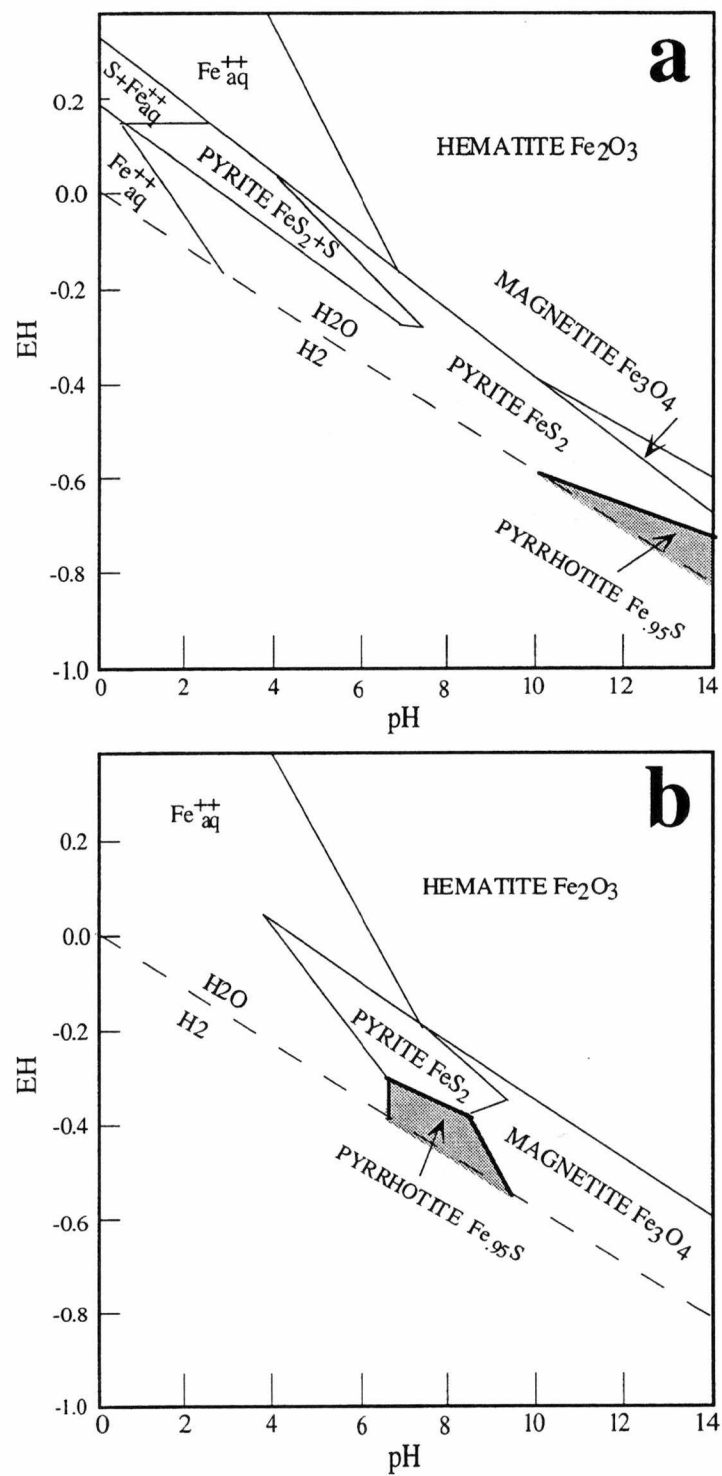


Figure 7

ranges from ~10 to 14, consistent with the pH values of most experimentally-derived and naturally-occurring serpentinization fluids (MOODY, 1976). As the fluids become more oxidizing, pyrite becomes the stable phase.

The secondary textures and mineral associations within altered CM chondrules are not easily reconciled with the phase relations depicted in Figure 7a. Since fine-grained secondary sulfides usually occur in close association with precursor sulfide blebs in CM chondrules (see Figures 1c and 1d), a specific set of fluid conditions is needed to explain both the destruction of the precursor sulfide and the immediate formation of secondary sulfide precipitates. Figure 7a indicates that the dissolution of precursor sulfides would require an Eh or pH excursion that would necessarily constrain the fluid to pass through the stability field for pyrite. Yet, no pyrite has ever been observed in any CM chondritic meteorites (ZOLENSKY et al., 1993). Although minor magnetite is observed in CM chondrites (BARBER, 1981; ZOLENSKY et al., 1993), the alteration fluid would again be constrained to pass through the pyrite field before magnetite became stable.

The conditions of Figure 7a mandate an external control to maintain the activity of dissolved S at a value of 0.1 that is difficult to justify. This would require a source of dissolved S in the CM fluids that is independent of the dissolution of precursor chondrule sulfides. Moreover, any type of external control in the dissolved S content of chondrule fluids is inconsistent with petrological observations indicating that the S content of the CM fluid was dependent on the local dissolution of precursor sulfide grains. It is difficult to imagine an alternate source of dissolved S species that could reasonably account for the elevated S activities prescribed in Figure 7a. For example, it seems unlikely that high concentrations of dissolved S originated in the accreted CM ices since cometary ices, which may provide a reasonable analog for the CM ices, are notably depleted in S-

bearing species (JESSBERGER et al., 1989). We conclude, then, that the conditions prescribed by Figure 7a are probably not applicable to the CM alteration fluids.

We suggest, instead, that the fluids that first infiltrated CM chondrules contained little or no dissolved components that are required for the production of Fe-sulfides. The dissolution of primary chondrule pyrrhotite could be accomplished, then, as these sulfides equilibrated with grossly undersaturated fluids. Under these conditions, some dissolution will occur regardless of the stability of the precursor sulfide relative to other Fe-bearing phases. If the initial CM chondrule fluids were undersaturated with respect to sulfide, the precursor sulfides in chondrules would have essentially been the sole contributor of dissolved sulfide ions. When these precursor sulfides equilibrated with the CM fluids, the concentration and proportion of the various S-bearing species in solution would largely be determined by the solution pH. Once the local concentration of dissolved sulfide ions and Fe^{2+} exceeded the solubility product of pyrrhotite, secondary sulfides probably began to form.

Following the suggestion of GARRELS and CHRIST (1965), the first appearance of secondary sulfides at STP is most likely to occur at intermediate pH values and an activity of total dissolved S that is on the order of 10^{-6} (Figure 7b). Results of geochemical modeling of the aqueous alteration of asteroidal materials support a low S content in the CM fluids (ZOLENSKY et al., 1989). A comparison between Figures 7a and 7b demonstrates the significant effect that lowering the activity of total dissolved S has on phase relations. The stability field for pyrrhotite in Figure 7b occurs at significantly higher Eh and lower pH than in Figure 7a. Under the low S conditions of Figure 7b, pyrrhotite is stable at pH values between ~7 and 10, while its Eh stability varies from ~-0.35 to -0.55. Pyrite is no longer the sole phase that can be stable with pyrrhotite. Instead, the pyrrhotite field is now joined on the alkaline side by magnetite and on the

acidic side by $\text{Fe}^{2+}_{\text{aq}}$. The juxtaposition of the pyrrhotite and magnetite stability fields is sufficient to explain the observation of both phases in CM chondrites, without co-existing pyrite.

The scenario outlined above is adequate to characterize the basic fluid conditions needed to encourage sulfide rind growth in CM chondrules. Both the dissolution of precursor sulfides and the subsequent precipitation of secondary sulfides in CM chondrules could occur without having to evoke an excursion in the Eh-pH conditions of the alteration fluid. Furthermore, fluid compositions are locally controlled by this process so that large concentrations of dissolved S do not need to be maintained in the fluid by an undetermined external source. We conclude, then, that precursor sulfides in CM chondrules probably equilibrated with undersaturated fluids and released dissolved Fe^{2+} and S^{2-} ions into the fluid which subsequently precipitated as secondary sulfides under conditions roughly equivalent to those suggested by GARRELS and CHRIST (1965) for the incipient production of stable sulfides (Fig. 7b).

ON THE ORIGIN OF SULFIDE RINDS IN CM MATRICES

Matrix material composes up to 90 vol. % of CM chondritic samples (ZOLENSKY et al., 1993; BROWNING, 1995). In a broad sense, CM matrices can be described as the fine-grained groundmass of a regolith breccia containing lithic clasts, chondrules, CAI's, chondrule fragments, and isolated anhydrous silicate grains. However, CM matrices are best distinguished from other types of chondritic matrices by an enigmatic suite of alteration textures and mineral assemblages. CM alteration phases constitute, for example, concentrically layered chondrule rims (BREARLEY and GEIGER, 1991; METZLER et al., 1992; ZOLENSKY et al., 1993), sulfide rind textures, and massive

agglomerates of fine-grained sulfides and phyllosilicates (this work). Much of the discussion regarding the location where CM alteration occurred has focused on the interpretation of these textures (BREARLEY and GEIGER, 1991; METZLER et al., 1992; SEARS et al., 1993; BROWNING et al., 1994). Unfortunately, determining a unique origin for any of these alteration textures is inherently complicated by overprinted, diverse formation events, such as the accretion of nebular components, the subsequent mechanical disruption of accreted components by regolith gardening, and one or more forms of parent body processing. Consequently, no consensus has been reached on the location(s) where these alteration textures formed.

Sulfide rinds are observed around many isolated matrix silicates within CM matrices (Figs. 8b through 8d). All these examples were taken from the same thin section of Mighei to demonstrate variations in sulfide rind textures that are observed at this scale. Some rinds share sharp, smooth contacts with the surrounding matrix (Fig. 8b), whereas others possess irregular outlines (Fig. 8c). Some rinds have sharp contacts on one side of the core grain, but poorly defined contacts on the other side (Fig. 8d). However, all sulfide rinds within CM matrices are fine-grained intergrowths of sulfide and phyllosilicate grains that line the surfaces and fracture planes of partially degraded host grains.

The petrologic characteristics of sulfide rinds in CM matrices are remarkably similar to those that are observed inside chondrules, suggesting that they may have formed during the same aqueous alteration event that produced the rind textures in chondrules. Although the identification of chondrule-type alteration textures within the CM matrix does not preclude an origin for these features by a more complex combination of nebular and parent body processes, a retreat to multiple settings of aqueous alteration produces many questions that can not be addressed given our lack of constraints on early

Figure 8. Textures and mineral associations in CM matrices that are consistent with an origin by in situ aqueous alteration. a) Phyllosilicate-filled vein (V) in Murchison matrix indicates that alteration fluids must have infiltrated CM parent body; BSE. b) Sulfide rind (SR) around isolated matrix olivine (OL) in Mighei displays well-defined pseudomorphic features; BSE. c) Sulfide rind around optically continuous fragments of a disrupted olivine grain in the matrix of Mighei suggest a formation by incomplete and imperfect replacement processes; plane light. d) Replacement zone around an isolated matrix olivine in Mighei defines a sulfide rind texture. The most sulfide-rich portion of the rind texture (brightest area toward bottom) is highly irregular, but the remainder of the sulfide rind preserves the straight-edged relict grain boundaries of the host olivine. Fine-grained sulfides and phyllosilicates form massive agglomeritic structures (MA) at left center and upper right; BSE.

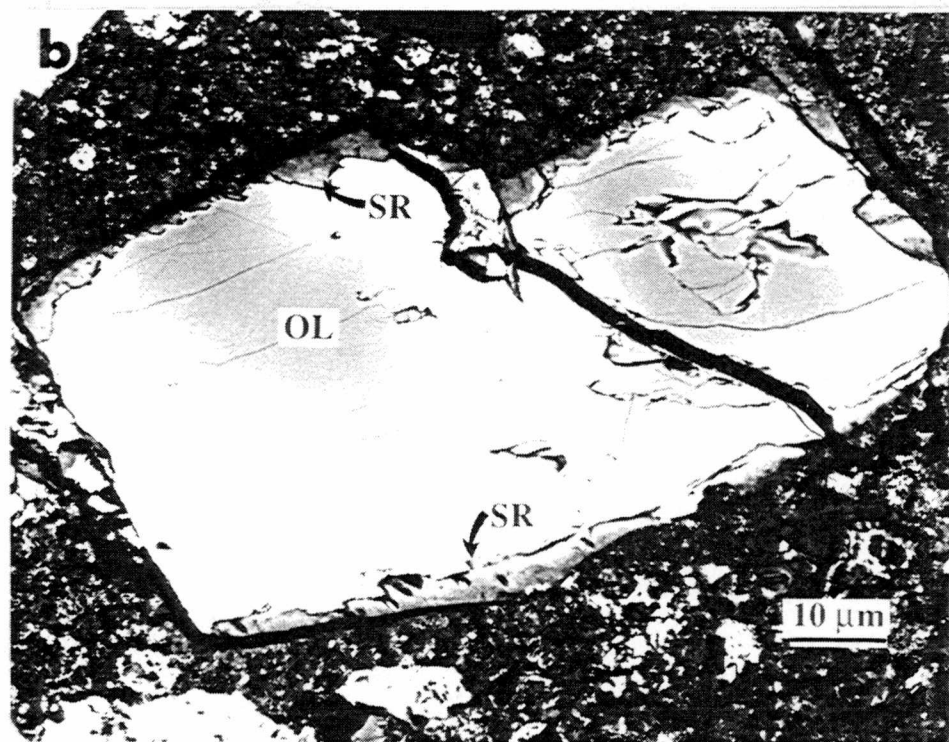
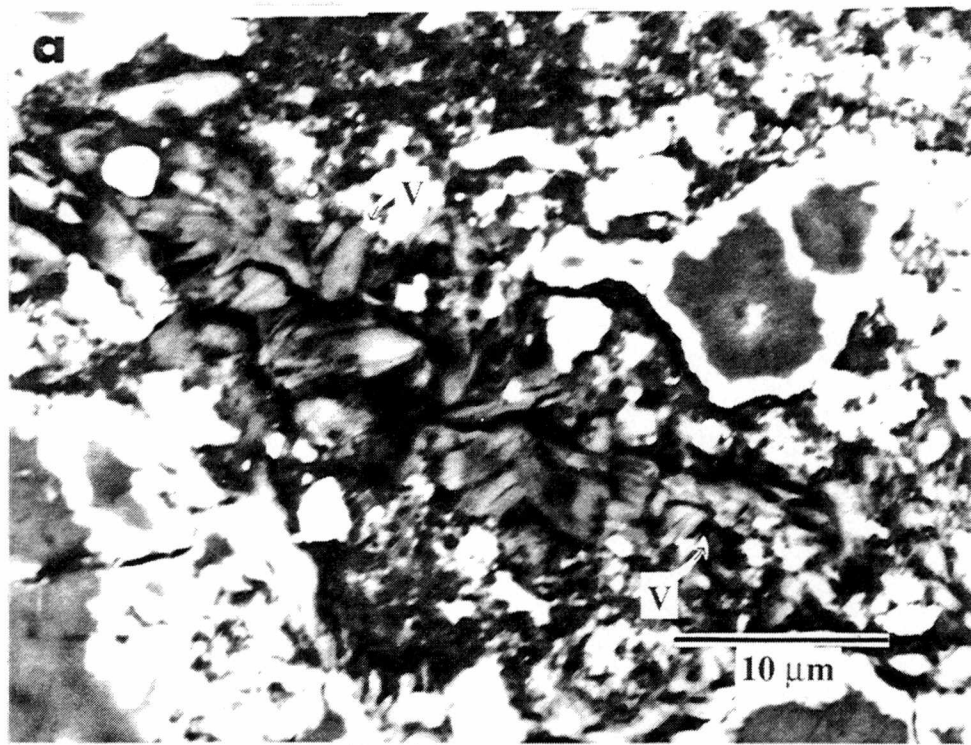


Figure 8

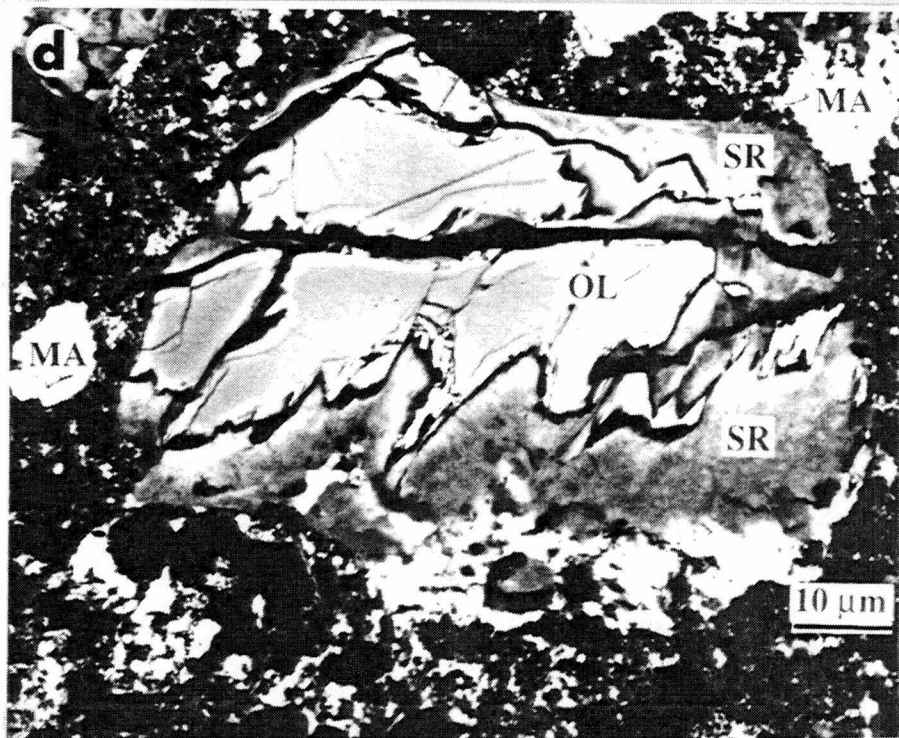
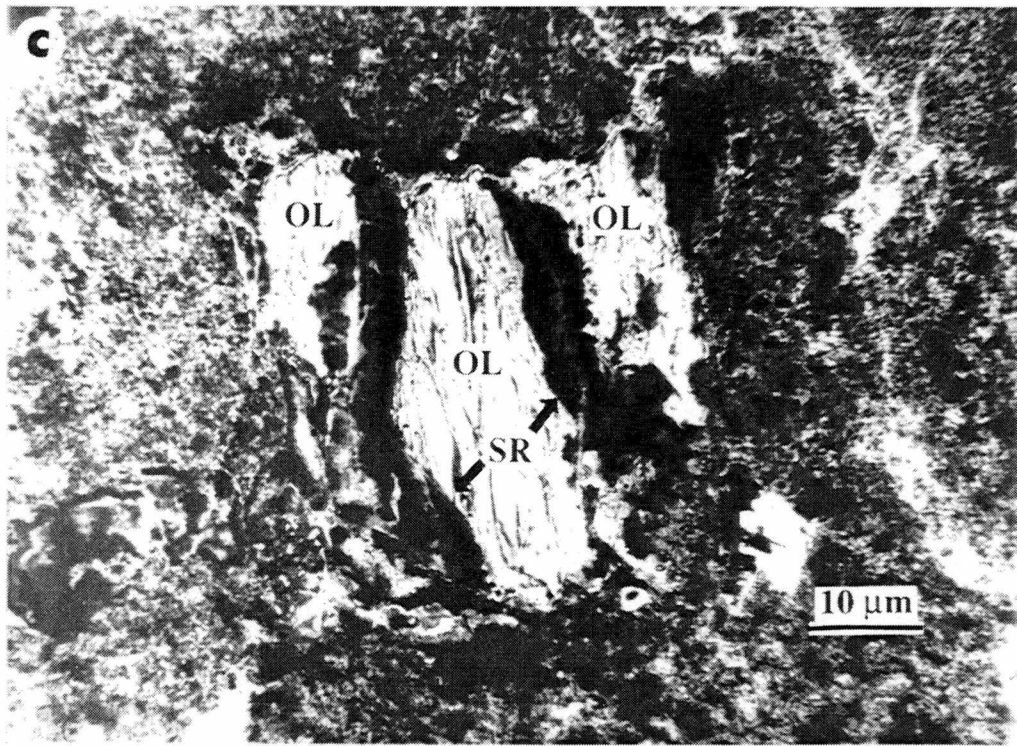


Figure 8 (continued)

nebular processes. Instead, we offer *in situ* fluid-rock reactions as a unifying explanation for the textures and mineral associations described in this study. In the sections below, we evaluate specific mechanisms which might have produced the sulfide rind textures in CM matrices by *in situ* aqueous reactions. For comparison, the plausibility of forming sulfide rind textures in CM matrices without introducing parent body alteration is also explored.

Formation of Matrix Rind Textures by In situ Aqueous Reactions

There are several lines of evidence that strongly suggest that significant aqueous alteration must have occurred on the CM parent body. For example, veins are observed in some CM matrices (Figure 8a). The infilling of these veins by phyllosilicates requires the presence of alteration fluids on a parent body that was at least partially lithified. In addition, the carbonates that are present in most CM chondrites are most likely to have precipitated from parent body fluids because the CO₂ pressure in the solar nebula was presumably too low to stabilize carbonates (ARMSTRONG et al., 1982). Other factors, such as the identification of a correlation in the composition of matrix phyllosilicates with increasing degrees of alteration (MCSWEEN, 1979; BROWNING et al., 1993) and the observation that the whole-rock O isotopic compositions of CM chondrites approximate a mass fractionation line (CLAYTON et al., 1976), point to systematic changes in the bulk properties of CM chondrites with progressive *in situ* alteration.

If chondrule alteration occurred on the final CM parent body, then the same fluids that infiltrated CM chondrules probably reacted even more effectively with adjacent regolith materials. The diminished grain size and relatively high porosity that generally typify mechanically churned regoliths suggest an ideal setting for fluid infiltration and

subsequent alteration reactions on the CM parent body. Because CM chondrites are breccias, there is no requirement for chondrule and matrix alteration to have occurred simultaneously. However, similarities between the secondary phase assemblages that are observed in the chondrules and matrices of CM chondrites provide encouragement that these two types of chondritic material may have been derived from related precursor phases that were subjected to similar alteration conditions.

Precipitation of matrix rinds from supersaturated fluids

One mechanism for precipitating sulfide rind textures involves constraining the alteration fluids to exist within a narrow space between dissolving olivine grains. As discussed in the context of chondrule alteration, this forces secondary alteration phases to precipitate very near the surface of the dissolving olivine grains. Since S-bearing fluids react efficiently with small amounts of dissolved $\text{Fe}^{2+}_{\text{aq}}$, sulfide rind textures are likely to form under these conditions. For the case of chondrule alteration, it is easy to envision how incipient alteration could provide a favorable environment for sulfide rind production by limiting the diffusion of released Fe^{2+} out of the narrow alteration channels that form between interlocking chondrule grains. In contrast, the original CM matrix material is generally characterized as a loosely-consolidated regolith, which suggests an environment marked by the potential for efficient fluid flow through a porous medium. However, these factors do not necessarily hinder the precipitation of sulfide rind deposits from supersaturated matrix fluids.

We suggest that the surfaces of reacting matrix silicates may have never been exposed to more than a thin film of fluid. Under these conditions, rind textures would form because secondary phases would be constrained to precipitate within the thin fluid film at the olivine surface. One explanation for the presence of fluid coatings around

precursor grains is that the total amount of alteration fluids in the CM matrix may have been severely limited. Also, it is only necessary that the total amount of water in contact with individual matrix grains be limited to a thin film at any given time. Matrix alteration could have proceeded through the action of thin layers of "unfrozen water" around matrix grains (GOODING et al., 1984). Alternatively, the instantaneous flux of liquid water supplied to the porous CM regolith might have been restricted by the rate that liquid water was derived from accreted ices in the interior of the asteroidal parent body.

Formation of sulfide rind textures by replacement processes

Replacement textures in CM matrices are remarkably similar to those observed within the confines of altered CM chondrules (Fig. 9a; compare with Fig. 6b). Some fully-replaced structures preserve relict grain boundaries or cleavage planes (Figs. 9a and 9b). In addition, many partially degraded matrix olivines are surrounded by a zone of alteration that retains the morphological features of the original host grain (Fig. 8b and 8d). Since these replacement zones are enriched in sulfides compared to the surrounding matrix, sulfide rind textures are produced. Thus, some sulfide rind textures in CM matrices clearly demonstrate an origin by incomplete replacement processes.

Replacement processes were probably much more common than is unambiguously indicated by the number of well-defined pseudomorphic structures. The pseudomorphic structures in CM matrices, like those in CM chondrules, may display a wide degree of perfection across a single structure. In Figure 9b, for example, only the relict grain boundary on the right side of this pseudomorph is clearly delineated. Likewise, a disparity in the degree of pseudomorphic perfection is also observed across many individual rind textures (Fig. 8d).

Figure 9. Sulfide-rich pseudomorph textures in CM matrices. a) Phyllosilicates and secondary sulfides form a well-defined pseudomorph structure (PS) after a matrix silicate grain in Murchison; BSE. This matrix pseudomorph closely resembles the appearance of the chondrule pseudomorph shown in Figure 6b. b) Fine-grained phyllosilicates and sulfides pseudomorph a matrix silicate in Mighei. Relict grain boundary is well defined on the right side of the structure, but degraded and irregular toward the left. An amorphous agglomerate is also present at lower right; BSE. c) Cluster of massive agglomerates (MA) in the matrix of Mighei. A sponge-like texture is formed by the inclusion of remnant olivine grains (OL) within the fine-grained massive agglomerates toward the top of the BSE image. d) Matrix agglomerate in Murray has similar appearance to the sponge-like texture shown in the preceding image, suggesting a similar origin by replacement processes. The presence of sharply defined relict grain boundaries in the upper part of the agglomeritic structure further support a replacement origin. Unlike the sponge-like agglomerate in Figure 9c, however, the remnant olivine grains in this example have been fully altered to phyllosilicates (PH); BSE.

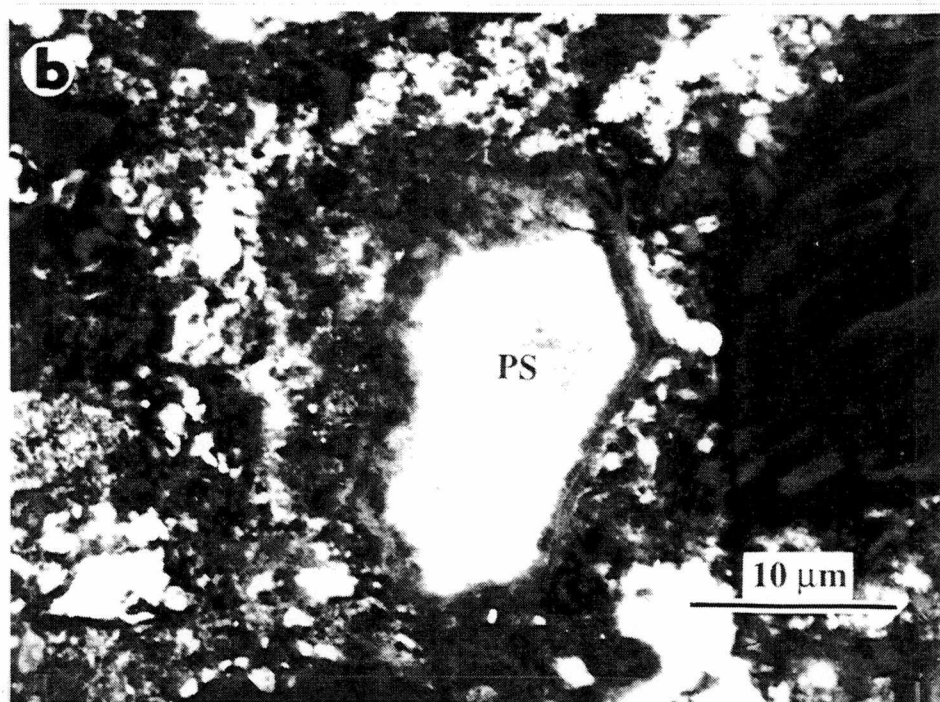
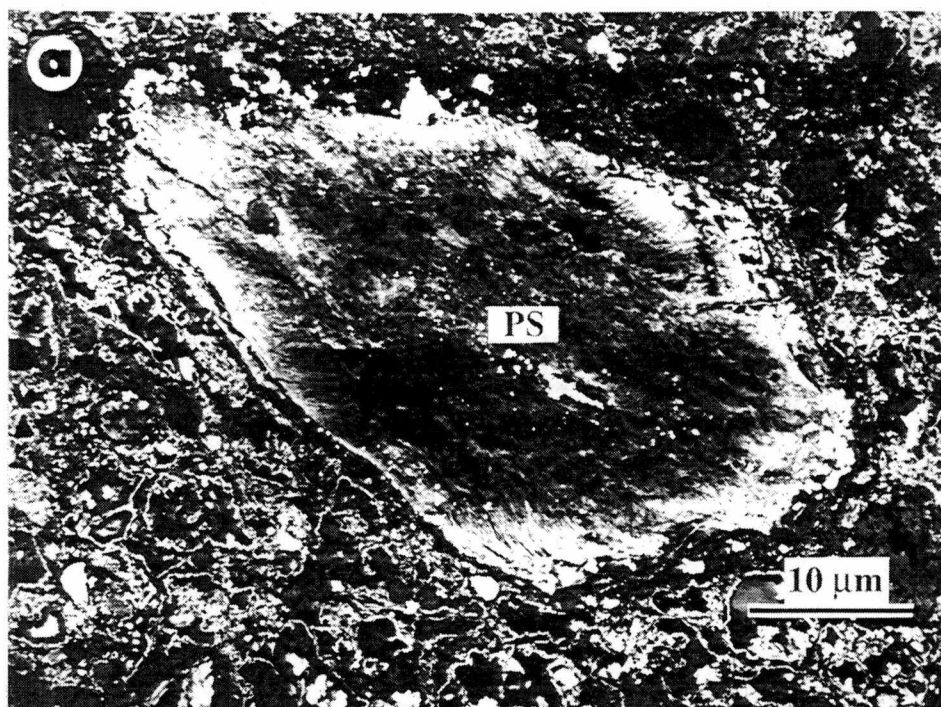


Figure 9

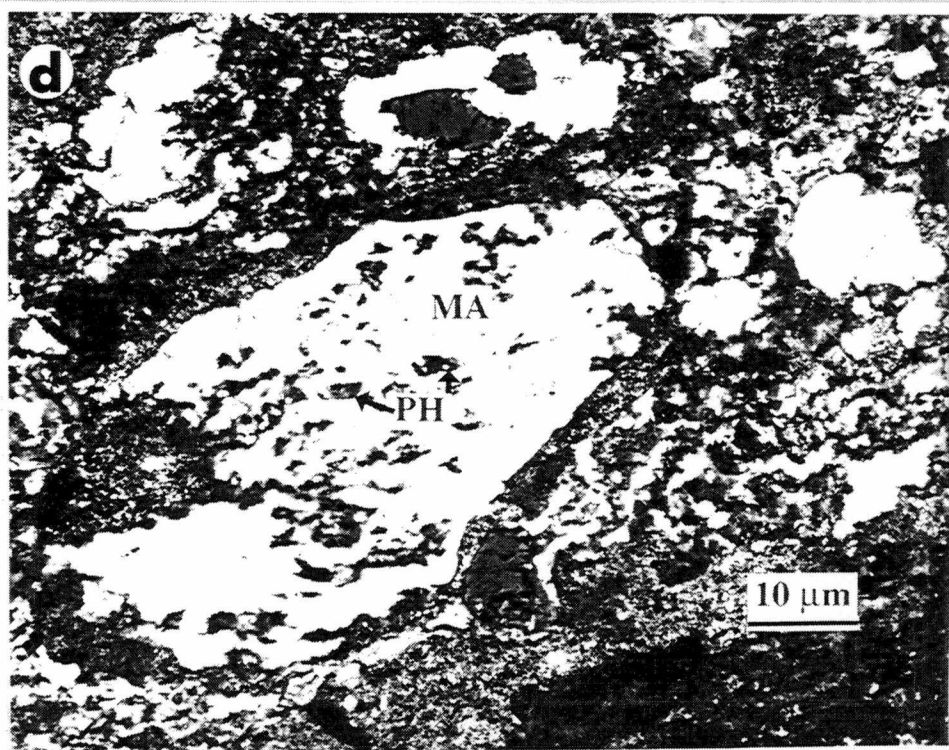
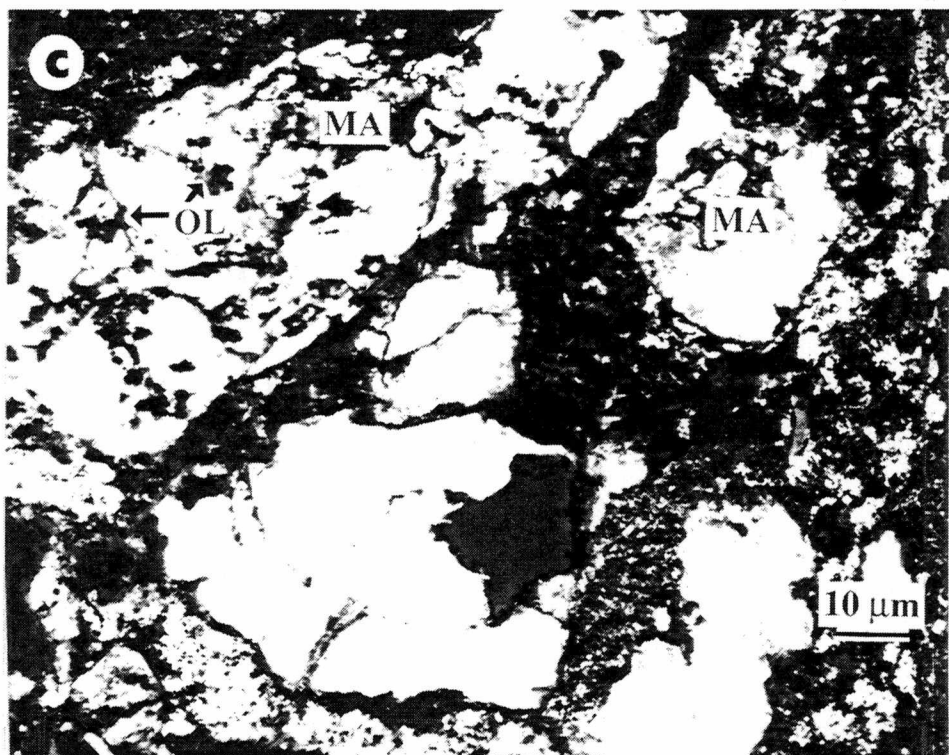


Figure 9 (continued)

Massive agglomerates are the single most common textural component of CM matrices and, perhaps, CM chondrites as a whole. Most of these are composed of fine-grained phyllosilicates and sulfides. However, our petrographic observations suggest that tochilinite may dominate the mineral assemblages of some massive agglomerates in CM matrices. Although the conditions of tochilinite formation are poorly known (ZOLENSKY et al., 1993), there is some evidence that it may form from the replacement of sulfides and phyllosilicates during the advanced stages of aqueous alteration (RAMDOHR, 1973). Regardless, the focus of this discussion is on those massive agglomerates that are composed of the same mineral assemblage as the replacement textures typically observed within altered CM chondrules, phyllosilicates and sulfides. Example of these massive agglomerates are shown in Figures 8d and 9b. These matrix textures display a continuous range of morphologies from irregular stringers to compact clumps and vary in length from a few microns to several tens of microns.

A replacement origin for massive agglomerates can be inferred by comparison with zones of morphological irregularities that are exhibited in clearly defined pseudomorphic structures. Most massive agglomerates resemble the imperfectly replaced segments of the pseudomorphic structures given in Figures 8d and 9b. In addition, some matrix agglomerates display a sponge-like texture containing multiple remnants of the unaltered host silicate (Fig. 9c). These incompletely replaced structures are very similar to many phyllosilicate and sulfide agglomerates that contain no remnant of the unaltered host silicate (Fig. 9d; and compare to Fig. 9c). This strongly suggests, by analogy, that all massive agglomerates in CM matrices may have formed by the imperfect replacement of relict matrix silicates during progressive aqueous alteration. The variety and abundance of massive replacement structures that are observed in CM matrices suggests

that replacement, rather than precipitation from supersaturated fluids, may have been the dominant mechanism of matrix alteration.

Although pseudomorphic replacement occurs *in situ* within a host phase, no inherent information is provided from these structures regarding the location of this process. Therefore, it may be instructive to compare the nature and distribution of the replacement textures within CM chondrules and matrices. We recall, first, that the degree of perfection of the replacement process in both CM chondrules and matrices ranges from very good to poor. In addition, the replacement structures in both locations are composed of fine-grained phyllosilicates and disseminated sulfides. These similarities strongly suggest that the chondrule and matrix replacement structures formed under nearly equivalent environmental conditions in a single parent body setting. A similar conclusion can be drawn from differences in the distribution of the different types of replacement structures between chondrules and matrices. Completely pseudomorphed textures are generally much more common in CM matrices than in chondrules, whereas sulfide rind textures are more common in chondrules than matrices. These observations are fully consistent with the hypothesis that the porous CM regolith would have experienced a greater extent of alteration than chondrules during aqueous alteration on the final CM parent body.

Formation of Sulfide Rind Textures Without *In situ* Aqueous Reactions

Parent body alteration alone may not adequately account for all the features of CM chondritic matrices. Suggested problems include unaltered matrix grains juxtaposed against fully altered grains, small areas composed of highly unequilibrated mineral assemblages, and a negative correlation between the reported amount of clastic matrix

and the abundance of solar wind-implanted gases (METZLER et al., 1992). These observations imply that diverse processes affected the evolution of CM matrix material. Since the relative importance of these processes is not known, any number of mechanisms might be introduced to explain the formation of matrix rind textures. In the sections below, we address some of the specific concerns of previous workers which might bear on the origin of sulfide rind textures.

The nebular accretion of sulfide rind textures

There is no a priori reason to assume that the sulfide rinds that are observed in either CM chondrules or matrices must have formed *in situ* on the *final* CM parent body. METZLER et al. (1992) argue, for example, that aqueous alteration occurred at some point before the accretion of the final CM parent body. Their extensive petrological study of CM textures has revealed that all types of coarse-grained components in CM chondrites are rimmed by fine-grained serpentine and S-bearing phases. These authors conclude that most or all of the secondary hydrous phases observed in CM chondrites were produced some time before the accretion of the final CM parent body. This precursor CM material was then dispersed into the nebula, forming multiple dust clouds of fine grained alteration phases. Consequently, all rim textures in CM chondrites are interpreted as resulting from the accretion of these secondary phases around coarse-grained core components in a strictly nebular setting. Finally, these authors propose that the final CM parent body formed largely from the agglomeration of these rimmed components, and experienced little or no subsequent aqueous alteration. The obvious similarities between a sulfide-rich "accretionary rim" and a "sulfide rind" suggests the possibility that these textures may be equivalent.

Our observations indicate that a nebular origin for sulfide rind textures leads to the frequent enlistment of extenuating circumstances to explain specific textural observations. For example, Figure 8c shows a matrix olivine that is separated into three distinct segments, each of which are in optical continuity. Each individual olivine fragment is enclosed by a sulfide rind. We observe several similar examples and, for the purpose of argument, we assume that the olivine fragments in at least some of these cases are not connected in the third dimension. Following the basic tenets of the accretionary rim model (METZLER et al., 1992), a nebular origin for these rinds may require the following sequence of events: an olivine grain was energetically disrupted; these individual olivine fragments preserved their original optical orientation as they traveled together through nebular dust clouds accreting rim material; and, finally, the conglomerate of rimmed olivine fragments accreted intact onto the final CM parent body.

An alternative, and much simpler, explanation for the features in Figure 8c involves incomplete replacement processes on the final CM parent body; since pseudomorphic replacement necessarily occurs *in situ* within the structure of the host phase, the optical orientation of any unaltered olivine remnants is not disturbed. Therefore, clusters of optically oriented olivine fragments with individual rinds separated from one another by matrix material could have formed by one process, the partial replacement of fine-grained sulfides and phyllosilicates after a single olivine grain.

Our observations strongly suggest that it is not likely that matrix rind textures formed at any point during the early solar system chronology suggested by the accretionary rim model. First, we have shown above that many sulfide rinds must have been produced by pseudomorphic replacement processes. Clearly, well-defined replacement morphologies would probably not be reproduced by the mechanical accretion of dust particles in a nebular environment. It might plausibly be argued that

these pseudomorphic structures were transported wholesale to the final CM parent body from another location, such as a violently disrupted precursor parent body, where the majority of CM alteration may have occurred (METZLER et al., 1992). However, we noted above that 1) the extent of pseudomorphic replacement, and hence, the degree of aqueous alteration, is greatest in CM matrices, and 2) CM matrices and chondrules contain the same type of alteration structures, and these are strikingly similar in texture and mineralogy. These observations suggest a single alteration environment in which fine-grained matrix materials experienced preferential alteration and all CM components reacted with the same reservoir of alteration fluids. Therefore, if there was a precursor CM parent body, then it must have shared many of the same characteristics as the parent body that has provided us with samples. Hence, although the evolution of CM chondritic materials clearly involved a variety of nebular and parent body processes, our observations of sulfide rind textures provide no compelling reason to enlist multiple environments of fluid-rock interactions.

Impact-induced formation of sulfide rind textures

There are several impact-related hypotheses which may support the parent body formation of secondary mineral coatings around coarse-grained matrix components. One of these involves the clumping of fine-grained matrix material onto the surfaces of coarse-grained matrix components during regolith gardening processes. Although the original advocate of this hypothesis is unknown, the possibility of a regolith origin for rimming textures has been discussed informally for years and was critically evaluated by METZLER et al. (1992). These authors present several convincing arguments against the production of secondary mineral coatings in an active regolith environment. We add to this list by noting that an origin for sulfide rinds involving energetic regolith processes is

inadequate to explain the observation of sulfide rinds around brecciated olivine fragments that maintain their original crystallographic orientation (Fig. 8c).

We consider another possibility, that the sulfide rinds surrounding isolated matrix silicates might have been released from rind-bearing chondrules during regolith gardening. This hypothesis is consistent with previous suggestions that a significant fraction of isolated matrix silicates may have been derived from the comminution of chondrules (MCSWEEN, 1977; RICHARDSON and MCSWEEN, 1978; JONES, 1992). Furthermore, TOMEOKA and BUSECK (1985) have proposed the separation of similar alteration materials from disrupted chondrules by regolith gardening processes. Hence, we can apply these concepts to the origin of sulfide rinds in CM matrices without undue extrapolation. Since the basic conclusion of previous workers, that chondrule components were supplied to the matrix during parent body impacts, does not specify the relative timing of aqueous alteration and chondrule disruption, we will evaluate several cases.

If aqueous alteration never occurred on the CM parent body, then all sulfide rinds in CM matrices might plausibly be attributed to the mechanical disruption of chondrules that experienced alteration in a pre-accretionary environment. In this case, one might reasonably suppose that regolith gardening processes, which are forceful enough to fracture chondrules, should produce a representative proportion of rind-silicate textures with morphologies that suggest violent disruption from a chondrule source. However, matrix fragments possessing sharply truncated rind-silicate boundaries are not commonly observed. In addition, if pre-altered chondrules were disaggregated into a parent body regolith that never experienced aqueous alteration, then the CM matrix should contain roughly similar proportions of the various types of replacement textures that are observed in altered chondrules. This would hold, even if fine-grained nebular material was added

to the CM regolith. Yet, as noted above, CM matrices contain a significantly higher proportion of fully-replaced structures than chondrules. Consequently, the possibility of supplying all sulfide rind textures to the CM matrix by a scenario involving the impact of rind-bearing chondrules into a dry regolith is dismissed.

A second possibility is that all of the sulfide rind textures in CM matrices were released from disrupted chondrules into an active regolith that was simultaneously experiencing aqueous alteration. However, any scenario which implies the formation of rind textures by parent body aqueous reactions in chondrules might just as well explain the production of rind textures in the surrounding matrix during the same alteration event. Furthermore, this scenario, like the previous one, is driven by collisionary forces that should produce a higher proportion of sharply truncated rind textures than is observed. Hence, if aqueous alteration and regolith gardening did occur simultaneously, then most of the sulfide rinds in CM matrices probably formed by *in situ* fluid-rock reactions in a regolith environment that was only sporadically disrupted by impact brecciation.

The remaining possibility, that pervasive aqueous alteration occurred sometime after the major regolith gardening event, is inadequate to account for the redistribution of sulfide rinds from chondrules to matrices because unaltered chondrules do not contain any sulfide rind textures. However, this does not mean that aqueous alteration could not have followed regolith gardening since the formation of sulfide rind textures is accomplished by aqueous reactions involving unaltered silicate grains. We conclude, then, that all of the sulfide rinds that are observed in CM matrices could not have been released from disrupted chondrules. Instead, sulfide rind production probably occurred by *in situ* aqueous reactions in a regolith environment some time during or after impact brecciation.

SUMMARY

Fine-grained sulfides and phyllosilicates form rind textures around many chondrule olivine grains in CM chondrites. Since hydrous phyllosilicates would not have survived the high temperatures associated with chondrule formation, these textures must have formed by secondary aqueous reactions. The alteration processes responsible for the formation of the sulfide rinds in chondrules should provide further insight into the origin of other sulfide-bearing alteration textures in CM chondrites. We have evaluated critically the mechanisms and environmental conditions that may result in the production of sulfide rinds by fluid-rock reactions. If pervasive CM alteration did indeed occur in a parent body setting, then the conclusions of this investigation should apply to the alteration of all components in CM chondrites.

The possibility that the sulfide rind textures precipitated from supersaturated chondrule fluids was considered. A model was devised to test the idea that sulfide rind textures may have formed by kinetically-controlled processes involving reactions between Fe-bearing olivine and a S-bearing alteration fluid. It was determined that rind production should proceed during the incipient stages of aqueous alteration. Sulfides always precipitate more efficiently than either Fe- or Mg-endmember serpentine, and Fe-depleted pyrrhotite is more likely to form than stoichiometric troilite. However, continued rind growth is kinetically-inhibited because the Fe^{2+} that is released from dissolving olivine grains quickly equilibrates in the chondrule fluids. Therefore, sulfides will begin to precipitate somewhat randomly in the chondrule fluids before a full-scale rind texture can be produced near the olivine boundaries. However, if the initial alteration fluids penetrated CM chondrules along narrow conduits between closely-spaced olivine grains, then dense sulfide deposits would probably have formed rind

textures at the chondrule-fluid interface. Similarly, sulfide rind textures in CM matrices might have precipitated from supersaturated fluids under the condition that the alteration fluids were restricted to thin films around individual chondrule grains.

Textural analyses of altered CM chondrules suggest that rind textures may have also formed by the incomplete replacement of chondrule silicates. Although many sulfide rinds in CM chondrules possess well-defined pseudomorphic textures, other rinds do not preserve the original morphology of the host olivine. Similarly, some sulfide rinds in CM matrices also display a wide variety in their degree of pseudomorphic perfection. The formation of the most irregularly shaped sulfide rinds cannot be unambiguously attributed to replacement processes. However, petrological arguments support a replacement origin for many of these structures. In addition, we observed a large proportion of amorphous sulfide and phyllosilicate agglomerates in CM matrices that are also interpreted as poorly-defined replacement structures.

Constraints were imposed on the CM fluids to explain local dissolution and precipitation of sulfides, by devising a alteration scheme to account for a range of petrologic observations. We suggest that the initial CM fluids probably contained negligible proportions of dissolved S. The predominant source of the dissolved S-bearing species needed for subsequent rind production was probably precursor sulfide grains. Under these conditions, precursor sulfides would have partially dissolved as they equilibrated with grossly undersaturated chondrule fluids. Secondary sulfides probably began to form very near precursor sulfide grains where the solubility product for these phases was most rapidly exceeded. The first appearance of stable secondary sulfides may have occurred at roughly intermediate pH, strongly reducing conditions, and an activity of total dissolved S on the order of 10^{-6} .

We have illustrated that the petrologic characteristics of sulfide rinds in CM matrices are remarkably similar to those that are observed in chondrules. Unfortunately, assigning a formational mechanism to the sulfide rinds in CM matrices is complicated by uncertainties in the evolution of an asteroidal regolith. However, after weighing the plausibility that these rind textures formed by either parent body alteration or some alternative processes suggested by some previous investigations, we conclude that *in situ* fluid-rock reactions provide the most satisfactory explanations for the textures and mineral associations described in this study.

REFERENCES

- ARMSTRONG J. T., MEEKER G. P., HUNEKE J. C., and WASSERBURG G. J. (1982) The blue angel: I. The mineralogy and petrogenesis of a hibonite inclusion from the Murchison meteorite. *Geochim. Cosmochim. Acta* **46**, 575-596.
- BARBER D. J. (1981) Matrix phyllosilicates and associated minerals in CM2 carbonaceous chondrites. *Geochim. Cosmochim. Acta* **45**, 945-970.
- BEZMEN M. I. and SMOLYAROVA T. A. (1977) Enthalpy of formation of monoclinic pyrrhotite and its stability in the system Fe-S. *Intl. Geol. Rev.* **19**, 761-765.
- BREARLEY A. J. and GEIGER T. (1991) Mineralogical and chemical studies bearing on the origin of accretionary rims in the Murchison CM2 carbonaceous chondrite. *Meteoritics* **26**, 323.
- BROWNING L. (1995) The Aqueous Alteration of CM Chondritic Meteorites. Ph. D. dissertation, Univ. Tennessee.
- BROWNING L. B., MCSWEEN H. Y., and ZOLENSKY M. (1993) An alteration scale for CM chondrites and implications for planetary noble gas abundances. *Meteoritics* **28**, 331-332.
- BROWNING L., MCSWEEN H. Y. and ZOLENSKY M. (1994) Alteration and formation of rims on the CM parent body. *Lunar Planet. Sci.* XXV, 181-182.
- BUNCH T. E. and CHANG S. (1980) Carbonaceous chondrites--II. Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* **44**, 1543-1577.
- CLAYTON R. N. and MAYEDA T. K. (1984) The oxygen isotope record in Murchison and other carbonaceous chondrites. *Earth Planet. Sci. Let.* **67**, 151-161.
- CRANK J. (1975) *The Mathematics of Diffusion*. Oxford Univ. Press.

- DUFRESNE E. R. and ANDERS E. (1962) On the chemical evolution of the carbonaceous chondrites. *Geochim. Cosmochim. Acta* **26**, 1085-1114.
- FROST B. R. (1985) On the stability of sulfides, oxides, and native metals in serpentinite. *J. Petrol.* **26**(1), 31-63.
- GARRELS R. M. and CHRIST C. L. (1965) *Solutions, Minerals, and Equilibria*. Freeman, Cooper & Co.
- GOODING J. L. (1984) Aqueous alteration on meteorite parent bodies: Possible role of "unfrozen water" and the Antarctic meteorite analogy. *Meteoritics* **19**, 228-229.
- GROVES D. I., HUDSON D. R., and HACK T. B. C. (1974) Modification of iron-nickel sulfides during serpentization and talc-carbonate alteration at Black Swan, Western Australia. *Econ. Geol.* **69**, 1265-1281.
- HELGESON H. C., MURPHY W. M., and AAGAARD P. (1984) Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions. II. Rate constants, effective surface area, and the hydrolysis of feldspar. *Geochim. Cosmochim. Acta* **48**, 2405-2432.
- JESSBERGER E. K., KISSEL J., and RAHE J. (1989) The composition of comets. In *Origin and Evolution of Planetary and Satellite Atmospheres* (ed. S. K. Atreya, J. B. Pollack, and M. S. Matthews), pp. 167-191. Univ. Arizona Press.
- JONES R. H. (1992) On the relationship between isolated and chondrule olivine grains in the carbonaceous chondrite ALHA77307. *Geochim. Cosmochim. Acta* **56**, 467-482.
- LEVY E. H. and JUNINE J. I. (1993) *Protostars and Planets III*. Univ. Arizona Press.
- LLORCA J. and BREARLEY A. J. (1992) Alteration of chondrules in ALH 84034, an unusual CM2 carbonaceous chondrite. *Lunar Planet. Sci.* **XXIII**, 753-754.
- LUCE R. W., BARTLETT R. A., and PARKS G. A. (1979) Dissolution Kinetics and the weathering of mafic silicates. *Geochim. Cosmochim. Acta* **43**, 717-724.

- MATSUNAGA T., KARAMETAXAS G., VON GUNTEN H. R., and LICHTNER P. C. (1993) Redox chemistry of iron and manganese minerals in river-recharged aquifers: A model interpretation of a column experiment. *Geochim. Cosmochim. Acta* **57**, 1691-1704.
- MCSWEEN H. Y. (1977) On the origin and nature of isolated olivine grains in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **41**, 1145-1161.
- MCSWEEN H. Y. (1979) Alteration in CM carbonaceous chondrites inferred from modal and chemical variations in matrix. *Geochim. Cosmochim. Acta* **43**, 1761-1770.
- MCSWEEN H. Y. (1987) Aqueous alteration in carbonaceous chondrites: Mass balance constraints on matrix mineralogy. *Geochim. Cosmochim. Acta* **51**, 2469-2477.
- METZLER K., BISHOFF A., and STOFFLER D. (1992) Accretionary dust mantles in CM chondrites: Evidence for solar nebula processes. *Geochim. Cosmochim. Acta* **56**, 2873-2897.
- MOODY J. B. (1976) Serpentinization: A review. *Lithos* **9**, 125-138.
- NAHON D. B. and COLIN F. (1982) Chemical weathering of orthopyroxenes under lateritic conditions. *Amer. J. Sci.* **282**, 1232-1243.
- NOACK Y., COLIN F., NAHON D., DELVIGNE J., and MICHAUX L. (1993) Secondary-mineral formation during natural weathering of pyroxene: Review and thermodynamic approach. *Amer. J. Sci.* **293**, 111-134.
- NORDSTROM D. K., PLUMMER L. N., LANGMUIR D., BUSENBERG E., MAY H. M., and PARKHURST D. L. (1990) Revised chemical equilibrium data for major water-mineral reactions and their limitations. In *Chemical Modeling of Aqueous Systems II* (ed. D. C. Melchior and R. L. Bassett), pp. 398-413. American Chemical Society.

- PELTZER E. T., BADA J. L., SCHLESINGER G., and MILLER S. L. (1984) The chemical conditions on the parent body of the Murchison meteorite: Some conclusions based on amino, hydroxy and dicarboxylic acids. *Adv. Space Res.* **4**, 69-74.
- PRINN R. G. and FEGLEY B. J. (1987) The atmospheres of Venus, Earth and Mars: A critical comparison. *Ann.Rev.Earth Planet. Sci. Lett.* **15**, 171-212.
- RAMDOHR P. (1967) A widespread mineral association, connected with serpentinization. *N. Jb. Miner. Abh.* **107**(3), 241-265.
- RAMDOHR P. (1973) *The Opaque Minerals in Stony Meteorites*. Elsevier.
- RICHARDSON S. M. and MCSWEEN H. Y. (1978) Textural evidence bearing on the origin of isolated olivine crystals in C2 carbonaceous chondrites. *Earth Planet. Sci. Lett.* **37**, 485-491.
- SEARS D. W. G., BENOIT P. H., and JIE L. (1993) Two chondrule groups each with distinctive rims in Murchison recognized by cathodoluminescence. *Meteoritics* **28**(5), 669-675.
- SIEVER R. and WOODFORD N. (1979) Dissolution kinetics and the weathering of mafic minerals. *Geochim. Cosmochim. Acta* **43**, 717-724.
- TAYLOR G. J., SCOTT E. R. D., and KEIL K. (1983) Cosmic setting for chondrule formation. In *Chondrules and Their Origins* (ed. E. A. King), pp. 262-278. Lunar Planet. Inst.
- WHITE A. F. and YEE A. (1985) Aqueous oxidation-reduction kinetics associated with coupled electron-cation transfer from iron-containing silicates at 25°C. *Geochim. Cosmochim. Acta* **49**, 1263-1275.
- WICKS F. J. and O'HANLEY D. S. (1988) Serpentine minerals: Structures and petrology. In *Hydrous Phyllosilicates*, Vol. 19 (ed. S. W. Bailey), pp. 91-159. Mineralogical Society of America.

- WICKS F. J. and WHITTAKER E. J. W. (1977) Serpentine textures and serpentinization. *Canadian Mineralogist* **15**, 459-488.
- WOGELIUS R. A. and WALTHER J. V. (1992) Olivine dissolution kinetics at near-surface conditions. *Chem. Geol.* **97**, 101-112.
- WOOD J. A. (1967) Olivine and pyroxene compositions in Type II carbonaceous chondrites. *Geochim. Cosmochim. Acta* **31**, 2095-2108.
- ZOLENSKY M., BARRETT R., and BROWNING L. (1993) Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **57**, 3123-3148.
- ZOLENSKY M. E., BOURCIER W. L., and GOODING J. L. (1989) Aqueous alteration on the hydrous asteroids: Results of EQ3/6 computer simulations. *Icarus* **78**, 411-425.
- ZOLENSKY M. and MCSWEEN H. Y., JR. (1988) Aqueous Alteration. In *Meteorites and the Early Solar System* (ed. J. K. Kerridge and M. S. Matthews), pp. 114-143. University of Arizona Press.

APPENDIX

Kinetic Model Formulation

We devise here a simple model to determine if kinetically controlled processes are responsible for the formation of sulfide rinds in CM chondrules. This is accomplished by evaluating the distribution and relative timing of incipient pyrrhotite and serpentine precipitation with respect to the surface of dissolving olivine in contact with a S-bearing alteration fluid. Thermodynamic data at STP were taken from BEZMEN and SMOLYAROVA (1977), GARRELS and CHRIST (1965), NORDSTROM et al. (1990), and NOACK et al. (1993).

Model geometry and initial aqueous solution

The surfaces of the adjacent CM precursor grains are approximated as parallel planes of Fe-bearing olivine, since Fe-sulfide rinds are generally associated with olivine host grains. These parallel Fe sources are separated by a distance of 200 μm , which is filled by an aqueous solution. This geometry represents the case of olivine dissolution in a water-rich environment where the grains are widely separated. However, we will see that the separation distance between Fe sources has a direct impact on the abundance and distribution of $\text{Fe}^{2+}_{\text{aq}}$ in the model solution. The effect of shortening the separation distance between olivine planes is discussed in the text.

For the purpose of this model, the initial alteration fluid of this model is defined as pure water plus a small amount of various S-bearing species. The total concentration of dissolved S-bearing species added to the model solution is just sufficient to be in equilibrium with pyrrhotite. Given a solubility product for pyrrhotite, K_{pyr} , the

equilibrium concentrations of both dissolved Fe^{2+} and S^{2-} can be obtained from general solubility calculations by

$$[\text{Fe}^{2+}] = [\text{K}_{\text{pyr}} (1 + \text{H}^+/\text{K}_2 + (\text{H}^+)^2 / \text{K}_1 \text{K}_2)]^{1/2}, \quad (1)$$

assuming that the distribution of S is determined by the equilibria:



For troilite, we substitute $\text{K}_{\text{pyr}} = \text{K}_{\text{FeS}} = 6.31 \times 10^{-18}$ into Eqn. (1). Alternately, $\text{K}_{\text{pyr}} = \text{K}_{\text{Fe}_{0.877}\text{S}} = 6.39 \times 10^{-21}$ is substituted into a slightly modified version of Eqn. (1):

$$[\text{Fe}^{2+}] = 0.877 \{ [\text{K}_{\text{pyr}} (1 + \text{H}^+/\text{K}_2 + (\text{H}^+)^2 / \text{K}_1 \text{K}_2)] / 0.877 \}^{1/2} \quad (4)$$

to account for the non-stoichiometry of $\text{Fe}_{0.877}\text{S}$. Calculations were performed for conditions of pH 7 to 12, which account for the most general range of pyrrhotite stability. A partial list of these results is given in Table 1. For simplicity, the concentration of the various S-bearing species is held constant throughout the remaining model calculations. This approach allows us to test the capacity of Fe-bearing olivine to react with dilute S-bearing fluids in order to produce sulfide rind textures.

Incipient Precipitation of Pyrrhotite

At the onset of alteration, each plane of olivine begins to dissolve. Rate equations for the surface-controlled dissolution of forsterite (R_{Fo}) and fayalite (R_{Fa}) are given by (WOGELIUS and WALTHER, 1992):

$$R_{Fa} \text{ (mol cm}^{-2}\text{s}^{-1}\text{)} = 1.1 \cdot 10^{-10} a_{H^+}^{0.69} + 3.22 \cdot 10^{-14} + 1.2 \cdot 10^{-16} a_{H^+}^{(-0.3)} \quad (5)$$

$$R_{Fo} \text{ (mol cm}^{-2}\text{s}^{-1}\text{)} = 9.07 \cdot 10^{-12} a_{H^+}^{0.54} + 5.25 \cdot 10^{-15} + 2.33 \cdot 10^{-17} a_{H^+}^{(-0.31)}. \quad (6)$$

These equations are based on steady-state release patterns from the experimental dissolution of Fa_{94} and Fa_9 , and are valid in the pH range 2 to 12. Values of R_{Fa} and R_{Fo} were calculated for solutions of pH 7 to 12, and used to determine the dissolution rate, (R_{Ol}), for olivines of intermediate composition by

$$R_{Ol} \text{ (mol cm}^{-2}\text{s}^{-1}\text{)} = X_{Fa}R_{Fa} + X_{Fo}R_{Fo}, \quad (7)$$

with X_{Fa} , X_{Fo} = mol fraction fayalite and forsterite, respectively. This equation was formulated by WOGELIUS and WALTHER (1992) under the assumption that olivine dissolution rates increase on a molar basis with Fe content. Solutions for Eqn. (7) were obtained using different combinations of olivine composition ($0.1 < X_{Fa} < 0.6$) to account for a range of initial starting materials. Since Eqn. (7) was formulated from experiments involving Fo_{91} , reliable dissolution rates cannot be calculated for olivines with compositions still more Mg-rich. Excluding nearly pure forsterite, however, the evaluated range approximates the observed compositions of CM olivines (WOOD, 1967).

Since the model solution maintains equilibrium proportions of dissolved S-

bearing species, the precipitation of pyrrhotite is contingent on the release of aqueous Fe^{2+} from each plane of dissolving olivine. Thus, we are interested in the flux of released Fe^{2+} from dissolving olivines of intermediate composition. Since the dissolution rates given above describe the steady-state stoichiometric release of olivine components, we calculate the Fe^{2+} flux, R_d , by

$$R_d (\text{mol cm}^{-2}\text{s}^{-1}) = 2 X_{\text{Fa}} R_{\text{Ol}} . \quad (8)$$

This relationship is derived from Eqn. (7) in WOGELIUS and WALTHER (1992) to provide solutions in the form of constant flux rates, which are needed for diffusion equations. We calculate the constant flux rate of Fe^{2+} that is released from each plane of dissolving olivine from pH 7 to 12. This provides a set of representative flux rates for the time-dependent contribution of $\text{Fe}^{2+}_{\text{aq}}$ from adjacent olivine grains during chondrule alteration.

Released Fe^{2+} is allowed to diffuse away from each olivine plane and react with the S-bearing model fluids. We take the diffusivity of $\text{Fe}^{2+}_{\text{aq}}$, D , as $7 \times 10^{-6} \text{ cm}^2 / \text{s}$, and evaluate the solution of the one-dimensional diffusion equation (CRANK, 1975):

$$C - C_0 = R_d l D^{-1} \{ D t l^{-2} + (3x^2 - l^2)/6l^2 - 2\pi^{-2} \sum (-1)^n n^{-2} \exp(-D n^2 \pi^2 t / l^2) \cos n \pi x l^{-1} \}, \quad (9)$$

where l is the distance, measured in units of x , from each plane to the midpoint between the planes, and C and C_0 are the final and initial concentrations, respectively. We accommodate the conditions of our model, which represent the case of a constant flux from two surfaces into an interior region that initially contains no Fe^{2+} , by setting $C_0 = 0$. Since the model solution maintains equilibrium concentrations of dissolved sulfide ions,

pyrrhotite will precipitate under the condition that the concentration of $\text{Fe}^{2+}_{\text{aq}}$ has exceeded its calculated solubility. By setting C equal to the solubility of pyrrhoitite, we evaluate the time of precipitation at various distances from the olivine surface. Similarly, the distribution of Fe^{2+} can be determined after specified amounts of time have elapsed. In this manner, the behavior of released $\text{Fe}^{2+}_{\text{aq}}$ is tracked in the model solution as a function of of time and distance from the olivine boundaries.

The rate of pyrrohtite precipitation is dependent on the extent of fluid saturation, which is influenced by competition for reactants with other types of secondary precipitates. For simplicity, we begin by inhibiting the precipitation of all secondary phases except pyrrhotite. If pyrrohtite is not capable of producing rind textures around the dissolving olivine under these conditions, then there is no need to incorporate additional complexities into the model. Following the onset of saturation, the kinetic rate expression (MATSUNAGA et al., 1993)

$$(\delta F_r / \delta t) = -\alpha k_r (1 - K_r Q_r) \quad (10)$$

is used, where

αk_r : Effective rate constant; ($\text{mol L}^{-1}\text{s}^{-1}$),

F_r : 1000 mol of precipitate per liter (mol L^{-1}),

K_r : equilibrium constant,

Q_r : instantaneous ion activity product,

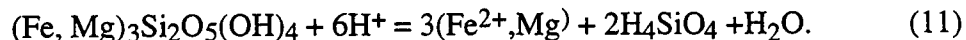
t: time (s).

Eqn. (10) relates the precipitation rate of pyrrhotite to the extent of supersaturation in a system where the reactant is diffusing away from a fixed source. We use MATSUNAGA et al.'s (1993) effective rate constant for troilite, $1 \times 10^{-11} \text{ mol L}^{-1} \text{ s}^{-1}$, and also assign this value to pyrrhotite, for which there are no experimental data. Since hydrolysis of the sulfide ion has already been incorporated into solubility calculations (Eqns. 1 and 4), we evaluate the formation of pyrrhotite from its ionic components. The concentration of precipitates across the model solution is then obtained at several time increments to characterize the relative distribution of precipitates during progressive alteration.

Formation of Fe- and Mg-endmember serpentine

Serpentine is the volumetrically dominant secondary phase in CM chondrites (MCSWEEN, 1987) and can form from aqueous species that are released by dissolving olivines. We have determined the extent that the model fluid is saturated with respect to endmember Fe- and Mg- serpentine at the instant that troilite first begins to precipitate at the various pH's. By assessing the effects of competition between sulfides and serpentine for dissolved ions at the onset of precipitation, we are able to predict which alteration products will form preferentially at the olivine-fluid boundaries. The relative stabilities of Fe-oxides and pyrite with respect to pyrrhotite are discussed in the text.

At the instant when the model fluids first become saturated in pyrrhotite, ion activity products are calculated for endmember serpentine compositions according to the reaction



We assume that the model system is closed with respect to all aqueous components that are released from the stoichiometric dissolution of olivine, and take $K_{\text{Fe-serp}} = 10^{17.541}$ and $K_{\text{Mg-serp}} = 10^{32.2}$. Therefore, we calculate the flux rates of released Mg^{2+} and Si^{4+} by comparison with that of Fe^{2+} . The subsequent diffusive behavior of dissolved Mg^{2+} and Si^{4+} in the model solution is treated as above. However, we require additional information regarding the speciation of dissolved silica species because the proportion of H_4SiO_4 at equilibrium in the solution at any time is a function of both the pH and the sum of dissolved silica species, ΣSi . We assume that local equilibrium occurs spontaneously between water and released silica, and determine $m\text{H}_4\text{SiO}_4$ from the general relation

$$\Sigma\text{Si} = m\text{H}_4\text{SiO}_4(1 + K_1/a\text{H}^+ + K_1K_2/a^2\text{H}^+) \quad (12)$$

where $\text{H}_4\text{SiO}_4 = \text{H}^+ + \text{H}_3\text{SiO}_4^-$ with $K_1 = 1.26 \times 10^{-10}$
 and $\text{H}_3\text{SiO}_4^- = \text{H}^+ + \text{H}_2\text{SiO}_4^{2-}$ with $K_1 = 5.01 \times 10^{-11}$.

Since the values of pH and ΣSi are known, we are able to compare the relative timing of Mg- and Fe-endmember serpentine precipitation with that of pyrrhotite at pH 7 to 12.

Additional considerations

It has been necessary to incorporate several simplifying approximations of the natural CM system into the model. However, some of these considerations have not been previously mentioned. Although calculations were restricted to STP in accordance with previous estimates large variations in the temperature of alteration may have a significant effect on the rates of olivine dissolution, the diffusivity of Fe^{2+} , and the precipitation rates of secondary phases. Unfortunately, lack of experimental data prohibits the

quantification of these effects. In addition, the presence of S-bearing organics has been neglected, despite some evidence suggesting that reactions between organic and inorganic materials may have influenced the direction of CM alteration (PELTZER et al., 1984). Also, the possibility of advective transport is not considered. However, the effects of these processes would have to act in concert to significantly increase the flux rate of released Fe^{2+} and decrease its diffusive capacity in the inter-olivine fluids to influence the fundamental results of this model.

PART 3

Petrologic Evidence for the Parent Body Aqueous Alteration of CM Carbonaceous Chondrites

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ABSTRACT

A petrologic investigation of the rim-core and rim-matrix boundaries in CM chondritic meteorites was undertaken to determine the location of CM alteration. Two endmember interpretations for the observed rim features are compared; that all CM materials experienced in situ aqueous reactions on the CM parent body and that all CM materials were altered on a precursor CM planetesimal prior to both nebular rim formation and the accretion of the CM parent body. Petrologic evidence for chemical communication between CM rims and adjacent materials strongly supports an origin by in situ alteration because adjacent materials must have first been admixed on the CM parent body. Adjacent CM rim and core materials probably exchanged significant amounts of dissolved materials during CM parent body alteration, implying a causal relationship between the compositions of some CM rim and core components. Moreover, petrologic features suggest that in situ CM alteration probably produced some new rim textures and mineralogies. Three types of rim-matrix contacts were also critically evaluated: gradational, irregular, and sharp. The origin of the latter is poorly constrained. However, gradational and irregular rim-matrix contacts strongly suggest an origin during CM parent body alteration. Neither of these can be easily reconciled with an origin involving the alteration of CM materials on a precursor CM planetesimal. Overall, the petrologic characteristics of rim contacts in CM chondrites strongly support aqueous alteration on the CM parent body.

INTRODUCTION

Although significant progress has been made in characterizing and interpreting CM chondritic materials, the relationship between individual CM samples or the distinct

textural components within them is less certain. For example, was there was one asteroidal source for all CM chondrites, a different CM parent body for each sample, or, some intermediate number of CM parent bodies? Notable similarities, as well as differences, exist between the petrologic (BROWNING et al., 1995b), chemical (KALLEMEYN and WASSON, 1981), and isotopic (CLAYTON and MAYEDA, 1984) signatures of individual CM chondrites, and their origin probably need to be more clearly understood before the total number of CM asteroidal parent bodies can be deduced with some certainty. This requires a greater appreciation of the types of processes and materials involved in the origin and evolution of a single CM parent body. Hence, attention is turned toward deducing the origin of diverse textures and mineral associations within *individual* CM chondrites.

Petrologic features of individual CM chondrites suggest the possibility that CM materials may have been exchanged between multiple CM parent bodies. Most notably, lithic clasts of CM material are commonly embedded within the petrologically distinct matrix material of host CM chondrites (FUCHS et al., 1973; MCSWEEN, 1979; METZLER et al., 1992). Although these lithic clasts could plausibly have been both disrupted and implanted on a single, compositionally heterogeneous parent body, a simpler explanation may be that lithified CM clasts were ejected from one CM parent body and then transported to another. If different CM parent bodies did indeed exchange lithified materials during early solar system history, then it is reasonable to suppose that unconsolidated CM materials might also have resided on one or more precursor planetismals before finally lithifying on a CM parent body. Recent discussions involving the location of CM chondrite alteration reflect different views on this possibility (BREARLEY and GEIGER, 1991; METZLER et al., 1992; BROWNING et al., 1995a).

Although it is likely that all types of CM components were simultaneously subjected to aqueous alteration, recent investigations have focused on the location where

CM rim material was altered (BREARLEY and GEIGER, 1991; METZLER et al., 1992; BROWNING et al., 1995a). Complex assemblages of secondary alteration phases form rims around all types of coarse-grained CM components (METZLER et al., 1992; ZOLENSKY et al., 1993), except lithic fragments, and are among the most conspicuous textures in CM chondrites. Rim formation is widely believed to have occurred in the nebula (KING and KING, 1981; RUBIN, 1984; CONNOLLY, 1992), but theoretical calculations strongly suggest that aqueous alteration in the nebula is kinetically inhibited (PRINN and FEGLEY, 1987). However, although it can be concluded that CM rim materials were probably altered in an asteroidal environment, there is no a priori reason to assume that this alteration occurred either before, or after, the nebular rim forming event.

Two opposing multi-stage models have emerged to explain the formation of CM rims, and these prescribe fundamentally different locations for the alteration of CM rim materials. Both models are based on petrologic features that are commonly observed in individual CM chondrites. The first model claims that, like the rims observed in other types of chondritic meteorites (KING and KING, 1981; RUBIN, 1984), the primary rim textures in CM chondrites probably formed when fine-grained anhydrous phases accreted onto coarse-grained components in the solar nebula. This model advocates the subsequent hydration of these anhydrous rim materials on the CM parent body (BUNCH and CHANG, 1980; BREARLEY and GEIGER, 1991). In contrast, the second model proposes that the final CM parent body experienced little or no aqueous alteration (METZLER et al., 1992). Instead, it is submitted that loosely consolidated chondritic materials were aqueously altered on a precursor CM planetesimal, which ultimately disrupted, releasing coarse-grained components and generating multiple dust clouds of altered materials. CM rims formed, then, when coarse-grained components passed through one or more of these dust clouds, accreting fine-grained alteration phases onto their surfaces. Finally, this "accretionary rim model" describes the agglomeration of

these altered rimmed components onto the CM parent body. These two models for the location of CM alteration have fundamentally different implications for the distribution and interactive roles of nebular dust clouds, planetismals, and ices during the early stages of solar system evolution, and a resolution is needed.

Since aqueous reactions generally result in the redistribution of dissolved components between adjacent materials (MOODY, 1976; MATSUNAGA et al., 1993), we suggest that the location of CM alteration may be resolved by examining the textures and mineral associations of contacts that separate rim materials from enclosed core and surrounding matrix components. If all CM materials were altered on the CM parent body, then there should be tangible petrologic evidence for an interactive exchange of dissolved components between rims and adjacent CM materials, except in cases of subsequent regolith gardening. In contrast, if the alteration of CM materials occurred prior to both rim formation and the accretion of the CM parent body (METZLER et al., 1992), then CM rims should never display evidence for fluid-rock interactions with neighboring materials. By thus evaluating the nature of contacts that separate CM rims from adjacent materials, the location of CM alteration ought to be constrained.

We have undertaken an extensive petrographic examination of the rim contacts in 10 CM chondrites to search for evidence of in situ fluid-rock reactions. Both the innermost and outermost contacts that separate rims from adjacent CM materials are critically evaluated using optical and scanning electron microscopy. We present here several commonly observed petrologic features that are fully consistent with aqueous alteration on the CM parent body. As such, we introduce evidence that is inconsistent with the accretionary rim model (METZLER et al., 1992). However, our discussion of this model is restricted to the specific CM rim textures discussed in this work.

SAMPLES AND ANALYTICAL TECHNIQUES

We acquired samples of 9 CM chondritic falls and 1 CM find for this study. Thin sections of each sample were either obtained from an external source or prepared at NASA Johnson Space Center. Prepared thin sections were ground to less than the standard 30 μm , to decrease the effects of evaluating overlapping phases. Table 1 gives the meteorite names, thin section numbers, and sources for each of the investigated samples.

Each thin section was analyzed at NASA Johnson Space Center using both optical (transmitted and reflected light) and scanning electron microscopy. We used a JEOL 35C SEM operated at 20 kV to obtain backscattered electron images of relevant regions within the thin sections. The JEOL 35C SEM is equipped with a Princeton Gamma Tech Be-window detector, which was used to obtain both EDS analyses of selected CM materials and x-ray dot maps of selected elements. X-ray data was collected for 360 s to produce the dot images.

RESULTS

This discussion is separated into two sections that focus on the petrologic interpretation of boundaries that separate CM rim materials from adjacent core components and matrix, respectively. Specific illustrative examples given in this work are not unique; all highlighted features are commonly observed in CM chondritic samples.

Table 1. CM Chondrites Studied.

Meteorite	Thin Section IDs	Source
Bells	B3; A3	Amer. Museum Natural History
Boreskino	6495-1	Smithsonian Institute
Cochabamba	1; 2	University of Vienna
Cold Bokkeveld	1727a	British Museum of Natural History
Mighei	3; 4; 5	Field Museum
Murchison	E; H	Field Museum
Murray	2; 3	Field Museum
Nogoya	1; 2	ASU Center for Meteoritics
Pollen	3	British Museum of Natural History
Y791198	1; 2; 3	National Institute of Polar Research

Rim-Core Boundaries

We present here petrologic evidence that the rim-core contacts in CM chondrites are often overprinted by secondary alteration phases that probably formed during CM parent body alteration. We first note, however, the potential for disagreement over what constitutes "primary" and "secondary" rim textures. Proponents of the accretionary rim model (METZLER et al., 1992) define the petrologic features of a "primary accretionary rock" based on the textures and mineral associations that are observed in the meteorite Y791198. These authors submit that this particular meteorite is composed of pristine, unbrecciated accretionary materials. If it is thus unequivocally true that the meteorite Y791198 experienced no aqueous alteration on the CM parent body, then every single rim-core contact in this meteorite should be devoid of petrologic evidence for in situ fluid-rock reactions. For clarity, then, we first consider a rim-aggregate contact from the meteorite Y791198 (Fig. 1).

Primary textures of the rim-aggregate boundary in Figure 1a have been overprinted by secondary alteration phases during parent-body alteration reactions. A fragment of the Y791198 aggregate is imbedded in the adjacent sulfide-rich rim layer (Fig. 1b). This fragment is connected to the host aggregate by a series of phyllosilicate stringers which cut across the rim deposit. These cross-cutting phyllosilicate stringers must have formed by in situ aqueous reactions sometime during or after the production of the sulfide-rich rim, and are thus inconsistent with the hypothesis that the aqueous alteration of all Y791198 materials was completed before the nebular formation of rims (METZLER et al., 1992). Additional phyllosilicates are present within the aggregate, along the rim-aggregate contact, and throughout the sulfide-rich rim material, strongly suggesting that the same parent body fluids caused significant changes in the primary textures and mineralogies of both the aggregate and rim. Moreover, significant

Figure 1. Rim-core boundary in Y791198. a) BSE image of a rimmed aggregate in the meteorite Y791198. Small arrows show the locations where Mg-rich rim materials (dark) protrude into the adjacent matrix. Big arrow shows area enlarged in Figure 1b. b) A disrupted fragment (DF) from the aggregate is bridged to the aggregate core by several phyllosilicate stringers (PST). Sulfide-rich rim materials (bright) intrude into the aggregate forming stringers and ponds (IS). Additional examples can be seen in Figure 1a.

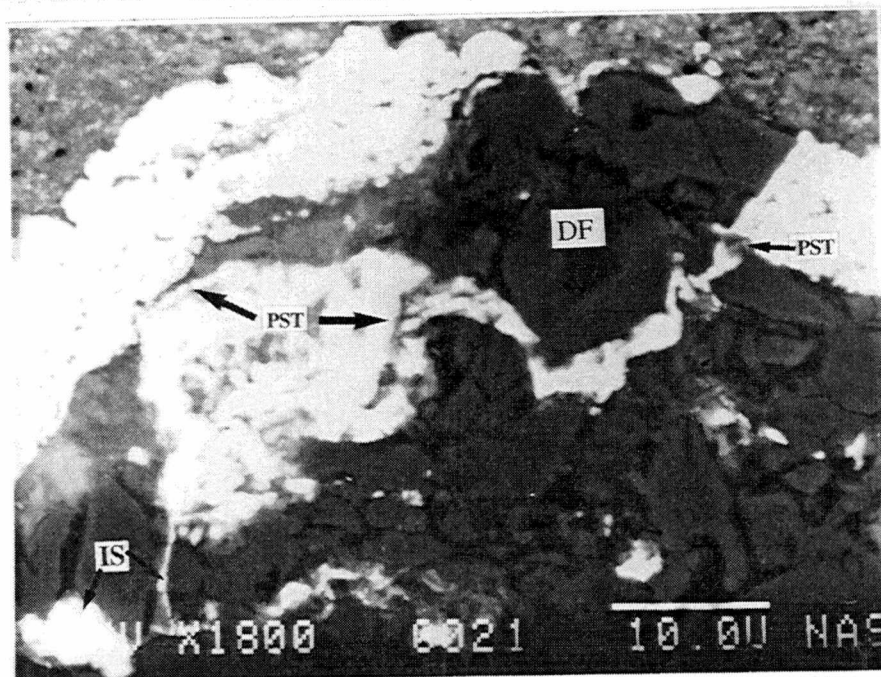
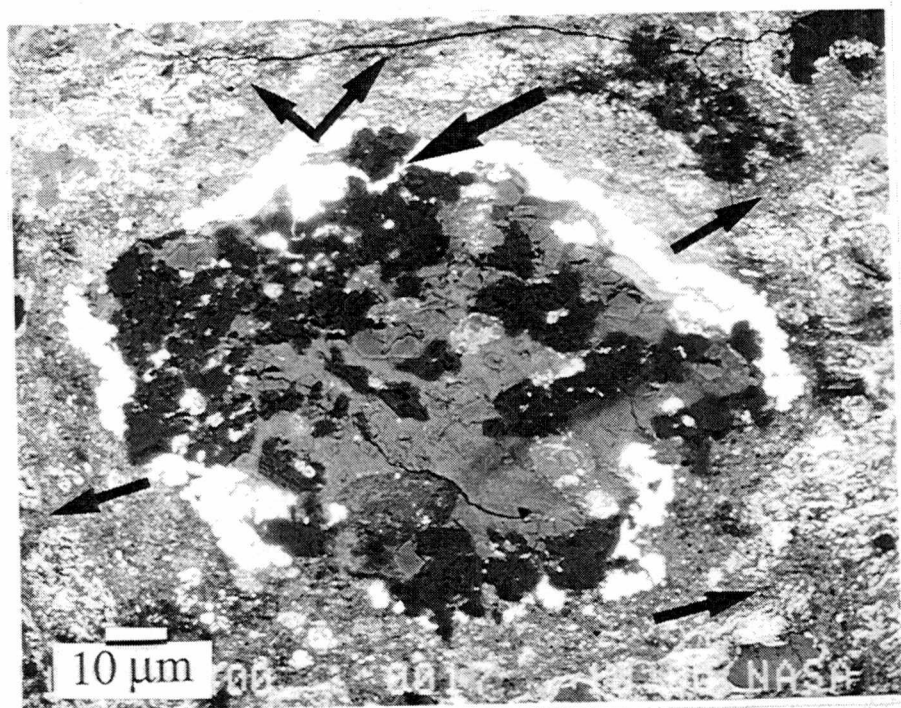


Figure 1

proportions of fine-grained sulfides have penetrated the interior of this highly altered aggregate, implying that rim materials were also mobilized during parent body alteration. Hence, petrologic observations of the meteorite Y791198 strongly suggest that at least some dissolved components were exchanged between adjacent materials during parent body alteration; a point that sharply conflicts with the assertion that this meteorite possesses pristine accretionary textures (METZLER et al., 1992).

Petrologic evidence for an additional type of rim-core interaction is illustrated in Figure 2. The perimeter of this Cochabamba aggregate has been extensively eroded by aqueous reactions, and altered rim materials fill the various embayments. We focus here on that portion of the aggregate and rim which includes the largest of these alteration cavities (Fig. 2b). In addition to reacting with the surface of the aggregate, alteration fluids must have also penetrated the aggregate since incompletely altered primary sulfides are surrounded by a secondary alteration assemblage of fine grained sulfides and phyllosilicates. One of these primary sulfides (see arrow in Fig. 2b) is partially enclosed within the aggregate, while the remaining portion protrudes into the embayment. Additional sulfides are exposed at the surface of the aggregate near the base of the cavity. A S X-ray dot map of this same region (Fig. 2c) indicates that the concentration of fine-grained secondary sulfides within the rim-filled cavity is highest near the primary sulfide grains that are exposed at the surface of the corroded aggregate. This strongly implies that significant amounts of dissolved S were released during the aqueous alteration of this sulfide-bearing aggregate and subsequently incorporated into the adjacent rim material within the embayment. Hence, a fine-grained rimming material was probably already in place around the aggregate in Figure 2 when aqueous alteration occurred.

Although in situ alteration requires a single set of alteration conditions for adjacent CM materials, similar constraints are not imposed by the accretionary rim model (METZLER et al., 1992). We note the possibility, however unlikely, that the association

Figure 2. Rim-core boundary in Cochabamba. a) An extensively altered aggregate in Cochabamba is pitted by embayments, or alteration cavities; BSE. The arrow shows the location of the enlarged region shown in Figure 2b. b) The largest alteration cavities in the Cochabamba aggregate is filled by fine-grained rim material (bright). The arrow points to a primary sulfide that is halfway in the aggregate and halfway in the alteration cavity. Two additional primary sulfides are exposed at the surface of the aggregate near the base of the alteration cavity. These are surrounded by a fine-grained assemblage of sulfides and phyllosilicates (gray). c) A S x-ray dot map of Figure 2b, taken at the same magnification. The line demarcates the position of the rim-aggregate contact. The highest density of fine grained sulfides (bright dots) in the alteration cavity is located near the primary sulfides. d) a Fe x-ray dot map of Figure 2b, taken at the same magnification. Fine-grained Fe-bearing phases (bright dots) are distributed somewhat homogeneously throughout the alteration cavity.

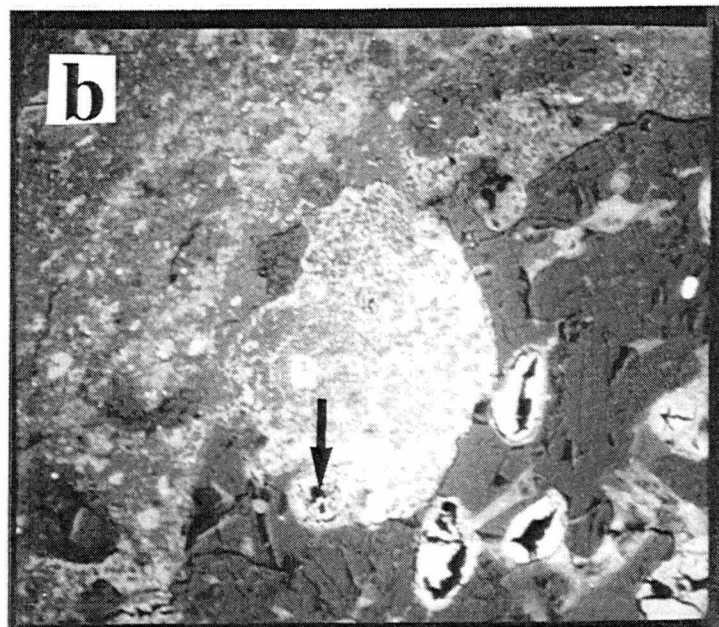
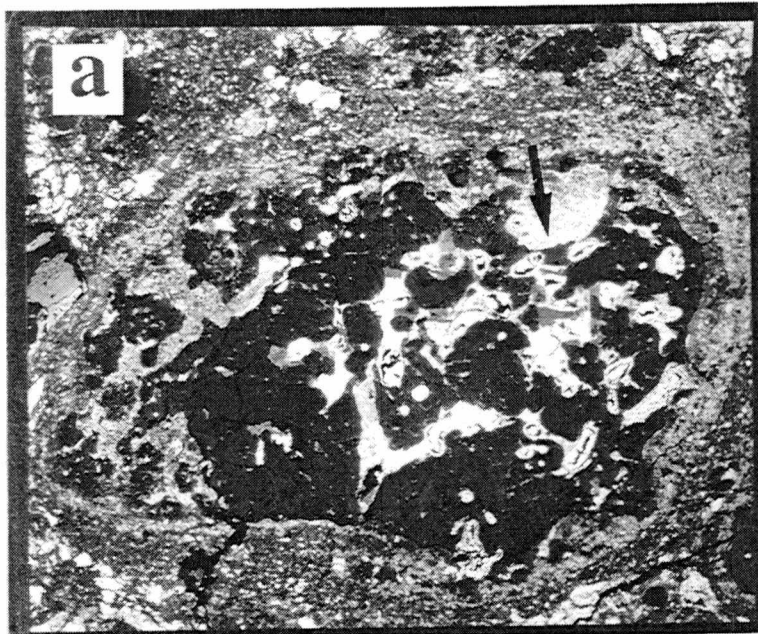


Figure 2

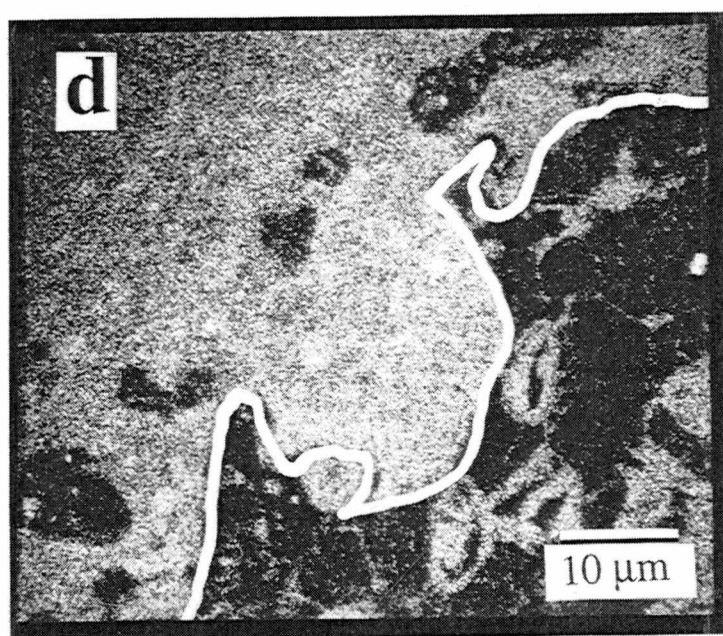
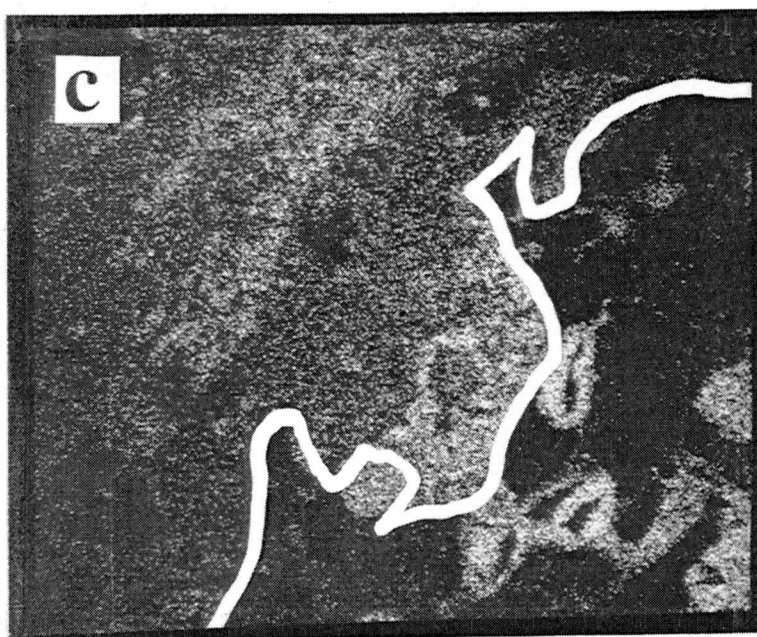


Figure 2 (continued)

between the primary and secondary sulfides in Figure 2 is fortuitous, and test the hypothesis that the mineral associations in this example are consistent with a common origin by fluid-rock reactions. As such, we expand our investigation to include materials within the entire Cochabamba embayment. An Fe X-ray dot map of this region (Fig. 2d) illustrates a somewhat homogeneous distribution of Fe across the entire embayment. Although secondary Fe-sulfides are largely restricted to the lower portion of this alteration cavity, EDS analyses indicate that the upper half of the embayment is dominated by Fe-enriched phyllosilicates. Hence, we seek now a reasonable alteration scenario that is adequate to explain the dissolution of precursor sulfides within the aggregate, the limited distribution of secondary sulfides, and the juxtaposition of sulfide-rich and Fe-phyllosilicate-rich rim assemblages within the alteration cavity.

DUFRESNE and ANDERS (1962) imposed Eh-pH constraints on the CM alteration system based on the $\text{FeO-SiO}_2\text{-H}_2\text{O-O}_2$ phase relations that occur when the activity of total dissolved S is held constant at a value of 0.1 in the fluids. However, a maintenance of this elevated S activity is not consistent with a common origin for juxtaposed Fe-serpentine-rich and Fe-sulfide-rich assemblages by aqueous reactions. BROWNING et al. (1995) demonstrated that sulfide precipitation will occur more efficiently than Fe-serpentine, even when Fe-bearing alteration fluids contain as little as 5 orders of magnitude less dissolved S than is assumed by DUFRESNE and ANDERS (1962). As more S is added to the fluids, sulfide precipitation is further encouraged. Therefore, if the activity of dissolved S in the Cochabamba fluids had been externally controlled at a value of 0.1, then the entire alteration cavity in Figure 2 should have been dominated by Fe-sulfides, not just the lower portion. Therefore, the Eh-pH conditions proposed by DUFRESNE and ANDERS (1962) are inadequate to explain the juxtaposition of sulfide-rich and Fe-phyllosilicate-rich assemblages by a single infiltration of Fe-bearing alteration fluids.

BROWNING et al. (1995a) proposed an alteration scenario for CM chondrites which is fully consistent with the petrologic features illustrated in Figure 2. We submitted that the initial alteration fluids which infiltrated CM chondrites contained essentially none of the dissolved components required for the production of Fe-sulfides. The dissolution of primary sulfides within chondrules or aggregates would be accomplished, then, as these sulfides equilibrated with grossly undersaturated fluids. As noted in studies of terrestrial serpentinites (RAMDOHR, 1967; GROVES et al., 1974), secondary sulfides are often closely associated with precursor sulfides because the solubility products of sulfides are rapidly exceeded near a local source of dissolved S and Fe. In eliciting negligible concentrations of dissolved S in the initial CM fluids, local, rather than external, controls apportion the amount of dissolved S-bearing species available to precipitate secondary sulfides from the CM alteration fluids. Under these conditions, stable secondary sulfides would begin to precipitate when the concentrations of dissolved S and Fe were just sufficient to exceed the solubility product for sulfides. Hence, reasonable parent body alteration processes provide a logical explanation for the initial dissolution of precursor sulfides exposed at the surface of the dissolving aggregate shown in Figure 2, the concentration of secondary sulfides in the immediate vicinity of these primary sulfides, and the juxtaposition of sulfide- and Fe-phyllosilicate-rich rim assemblages in the adjacent alteration embayment.

We conclude that typical rim-core boundary features in CM chondrites strongly support parent body aqueous alteration. The identification of compelling petrologic evidence for rim-core boundary interaction within the meteorite Y791198 argues directly against the fundamental conclusions of the accretionary rim model. We note, in addition, that we have presented here sound petrologic arguments for 1) a causal relationship between the compositions of some rim materials and core components, and thus, 2) the development of specific rim textures and mineralogies during CM alteration.

Rim-Matrix Contacts

Gradational rim-matrix contacts in CM chondrites strongly suggest an origin by in situ aqueous alteration. Figure 3a shows an isolated matrix olivine grain that is surrounded by a rim assemblage that is distinguished from the outlying matrix material by an elevated concentration of optically opaque sulfide grains. A S x-ray dot map (Fig. 3b) demonstrates the gradual dissipation of these fine-grained sulfides into the surrounding matrix. In situ alteration fluids provide a logical median for the exchange of dissolved S between these adjacent CM materials. Therefore, gradational rim-matrix contacts are fully consistent with the synchronous alteration of CM rim and matrix materials on the CM parent body. In contrast, it is difficult to reconcile the production of gradational rim-matrix contacts with an origin that restricts the mode of communication between adjacent components to accretionary or regolith gardening processes. Moreover, these processes would then have to account for the orderly redistribution of fine-grained sulfides across the rim material itself. If altered rim materials adhered onto core components before the accretion of the CM parent body, this results in the unlikely situation of having to account for the migration of sulfides across rim materials that were already lithified. Hence, gradational rim-matrix contacts are inconsistent with the accretionary rim model, and probably formed, instead, by parent body aqueous alteration.

Many rim-matrix contacts in CM chondrites are highly irregular due to the extension of rim materials into the adjacent matrix. To illustrate this texture, we re-visit the rimmed component from the meteorite Y791198 (Fig. 1a). This aggregate is surrounded by 2 roughly concentric rim layers: a sulfide-rich inner layer, and an outer layer composed of more Mg-rich material. The arrows in Figure 1a show several locations where Mg-rich rim material protrudes into the surrounding matrix materials

Figure 3. Gradational rim-matrix boundary in Mighei. a) An olivine grain in the matrix of Mighei is rimmed by sulfide-rich rim material (bright); BSE. b) A S x-ray dot map of Figure 3a, shown to scale. The density of fine-grained S-bearing phases (bright dots) decreases away from the olivine surface and eventually grades into the surrounding matrix materials.

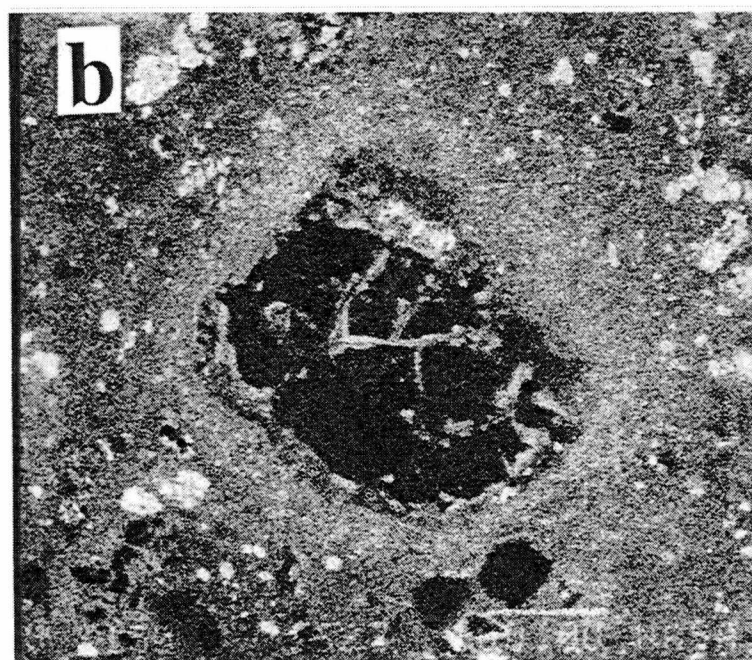
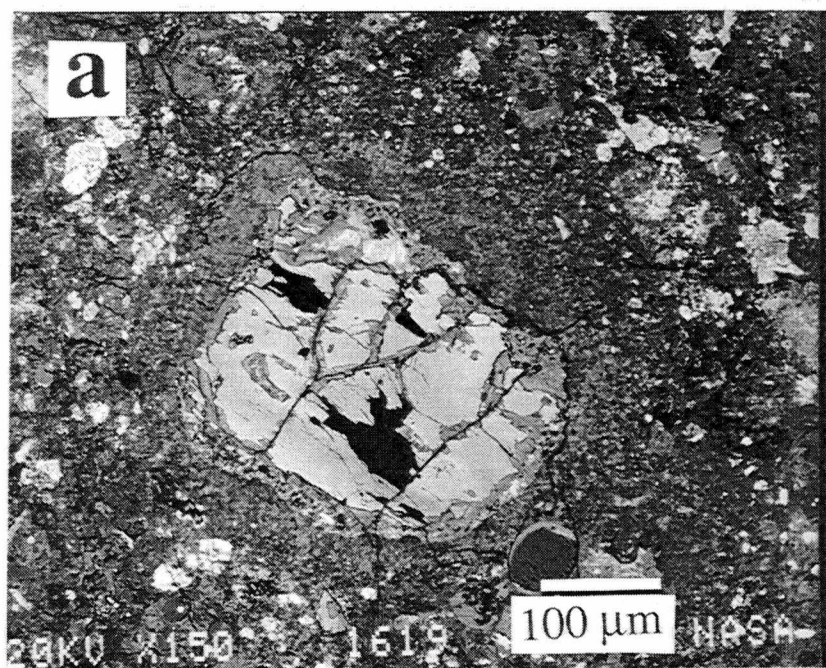


Figure 3

along convoluted pathways. A closer examination of these regions reveals that the protrusions themselves contain delicate offshoots of rim material that form dendritic patterns into the surrounding matrix. The mobilization of rim materials argues for in situ CM alteration. In contrast, it is difficult to imagine how these delicate, often bifurcating protrusions would have survived impact and subsequent regolith gardening processes if they had formed before the accretion of the Y791198 parent body, as suggested by METZLER et al. (1992). Furthermore, since compression on the CM parent body(ies) was probably just sufficient to produce a very weak preferred orientation of elongate phyllosilicates (FUJIMURA et al., 1983), it seems unreasonable to attribute the origin of rim extensions to plastic deformational processes. Instead, rim extensions, like gradational rim-matrix contacts, strongly suggest the transport and exchange of CM materials between adjacent CM components during in situ aqueous alteration.

Many CM rim-matrix contacts are sharp (Fig. 4). Sharp rim-matrix contacts provide compelling petrologic support for the accretionary rim model because rim and matrix materials would necessarily maintain their inherent petrologic differences after being juxtaposed by physical mixing processes on a chemically inactive CM parent body. However, we note that this explanation is not unique. For example, BREARLEY and GEIGER, 1991 argue for the in situ alteration of rim and matrix materials because, despite differences in their bulk composition, CM rims and matrices contain precisely the same assemblage of alteration phases. Hence, sharp rim-matrix contacts might result from a limited, or at least selective, exchange of dissolved components between compositionally distinct, primary rim and matrix materials during parent body alteration. An alternative explanation is that some rimmed components may have been altered on one portion of the CM parent body and then implanted into dissimilar matrix material elsewhere on the CM parent body during regolith gardening processes. We emphasize that while the accretionary rim model relies strictly on accretionary and regolith gardening processes to

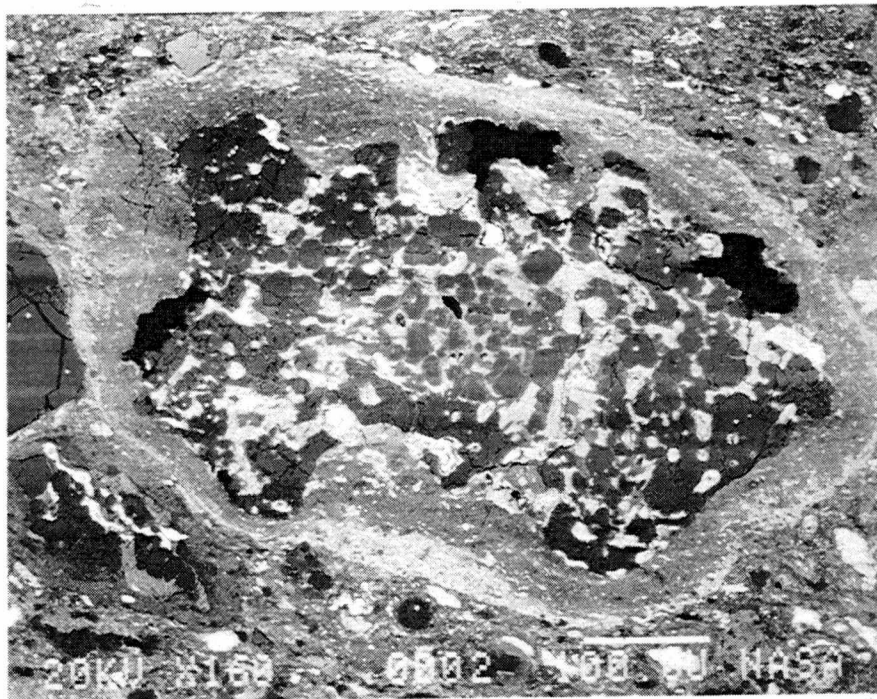


Figure 4. A sharp rim-aggregate boundary in Murchison; BSE. Sulfide-rich rim materials (bright) are petrologically distinct from the adjacent, more Mg-rich rim materials.

explain the petrologic relationship between all adjacent CM components (METZLER et al., 1992), there is no reason to suppose that these same processes would not effect the petrologic features of a parent body that was also subjected to pervasive aqueous reactions.

We conclude, then, that gradational and irregular rim-matrix contacts offer a less ambiguous interpretation regarding the location of CM alteration than sharp rim-matrix contacts. While aqueous alteration on the CM parent body can produce all 3 types of rim-matrix contacts, the accretionary rim model can only account for the development of sharp rim-matrix boundaries. Therefore, petrologic observations of the rim-matrix contacts in CM chondrites strongly support in situ alteration on the CM parent body.

SUMMARY

We performed an extensive petrologic examination of CM chondritic meteorites to determine the location where CM materials experienced aqueous alteration. Two different possibilities were considered, that the aqueous alteration of CM materials occurred either 1) on a precursor CM planetismal *before* nebular rim formation (METZLER et al., 1992), or, 2) on the CM parent body(ies) (MCSWEEN, 1979; BUNCH and CHANG, 1980; TOMEOKA and BUSECK, 1985; BREARLEY and GEIGER, 1991; BROWNING et al., 1995a). To distinguish between these two endmember hypotheses, we critically evaluated the petrologic features of the innermost and outermost boundaries that separate CM rims from adjacent materials. Since all secondary alteration features that relate CM rims to adjacent materials must have been produced after the nebular rim formation event, these are interpreted as being strictly consistent with an origin involving final CM parent-body alteration. In contrast, we identify no unambiguous criteria with which to confirm alteration on a precursor CM planetismal. Although attention was thus

focused on identifying petrologic evidence in support of CM parent-body alteration, we also assessed the possibility that the individual petrologic features discussed in this work might also be accounted for by the alternative possibility (METZLER et al., 1992). Each of the specific examples presented in this work are representative of features commonly observed in CM chondritic samples.

Many of the petrologic features of rim-core boundaries in CM chondrites strongly support aqueous alteration on the CM parent body. For example, delicate phyllosilicate stringers bridge a host aggregate to a fragment of the aggregate which is fully embedded within the surrounding rim material. These secondary cross-cutting stringers could not have formed before the emplacement of the rim material, and are thus inconsistent with the alteration of CM components on a precursor CM planetesimal. In addition, significant amounts of sulfide-rich rim material are shown within the interior of a highly altered aggregate core, suggesting the transport of CM rim materials during in situ alteration. We also illustrated that the concentration of fine grained secondary sulfides in one CM rim is highest near the primary sulfide grains that are exposed at the surface of an adjacent aggregate. This strongly suggests that significant amounts of dissolved S were released during the aqueous alteration of the sulfide-bearing aggregate and subsequently incorporated into the adjacent rim material. In addition, we argued that the more general petrologic features in this example are compatible with a reasonable scenario for in situ aqueous alteration. Overall, our observations of rim-core boundaries indicate that CM rims and adjacent core components exchanged materials during in situ aqueous alteration and that new rim textures and mineralogies were produced during this process.

We illustrated 3 common types of rim-matrix boundaries in CM chondrites, gradational, irregular, and sharp. Gradational rim-matrix contacts demonstrate a communication between adjacent CM materials which could not result from accretionary or regolith gardening processes on a chemically inactive CM parent body. Therefore,

these contacts probably formed as alteration fluids redistributed selected materials across rim-matrix boundaries. The protrusion of CM rims into adjacent matrix materials results in highly irregular rim-matrix boundaries that probably formed in a manner analogous to that of the gradational rim-matrix contacts. Many of these rim extensions are intricately interwoven within the surrounding matrix materials and are probably too delicate to have survived the disruption of a precursor CM planetismal, nebular rim formation, the accretion of the CM parent body, and subsequent regolith gardening processes. Therefore, they probably formed by in situ alteration reactions on the CM parent body. In addition, we argue that some sharp rim-matrix contacts would probably be produced regardless of whether CM materials were altered on a precursor CM planetismal or the CM parent body. Hence, while aqueous alteration on the CM parent body can produce all 3 types of rim-matrix contacts, alteration on a precursor CM planetismal can only account for the development of one of these. Therefore, we conclude that the petrologic features of rim-matrix contacts in CM chondrites strongly support in situ alteration on the CM parent body.

REFERENCES

- BREARLEY A.J. and GEIGER T. (1991) Mineralogical and chemical studies bearing on the origin of accretionary rims in the Murchison CM2 carbonaceous chondrite (abst.). *Meteoritics* **26**, 323.
- BROWNING L., MCSWEEN H., and ZOLENSKY M. (1995a) On the Origin of Sulfide Rind Textures in CM Carbonaceous Chondrites. *Geochim. Cosmochim. Acta* in preparation.
- BROWNING L., MCSWEEN H., and ZOLENSKY M. (1995b) An alteration scale for CM carbonaceous chondrites. *Geochim. Cosmochim. Acta* in preparation.
- BUNCH T.E. and CHANG S. (1980) Carbonaceous chondrites--II. Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* **44**, 1543-1577.
- CLAYTON R.N. and MAYEDA T.K. (1984) The oxygen isotope record in Murchison and other carbonaceous chondrites. *Earth Planet. Sci. Lett.* **67**, 151-161.
- CONNELLY H.C.J. (1992) The production of accretionary rims around chondrules by drop quenching into dust: A test for parent body origin (abst.). *Lunar and Planetary Science Conference XXIII*, 243-244.
- DUFRESNE E.R. and ANDERS E. (1962) On the chemical evolution of the carbonaceous chondrites. *Geochim. Cosmochim. Acta* **26**, 1085-1114.
- FUCHS L.H., OLSEN E., and JENSEN K.J. (1973) Mineralogy, crystal chemistry and composition of the Murchison (C2) Meteorite. *Smithsonian Contrib. Earth Sci.* **10**, 399 pp.
- FUJIMURA A., KATO M., and KUMAZAW M. (1983) Preferred orientation of phyllosilicate [001] in matrix of Murchison meteorite and possible mechanisms of generating the oriented texture in chondrites. *Earth Planet. Sci. Lett.* **83**, 25-32.

- GROVES D.I., HUDSON D.R., and HACK T.B.C. (1974) Modification of iron-nickel sulfides during serpentinization and talc-carbonate alteration at Black Swan, Western Australia. *Econ. Geol.* **69**, 1265-1281.
- KALLEMEYN G.W. and WASSON J.T. (1981) The compositional classification of chondrites -I. The carbonaceous chondrites. *Geochim. Cosmochim. Acta* **45**, 1217-1230.
- KING T.V.V. and KING E.A. (1981) Accretionary dark rims in unequilibrated chondrites. *Icarus* **48**, 460-472.
- MATSUNAGA T., KARAMEYAS G., VON GUNTEN H.R., and LICHTNER P.C. (1993) Redox chemistry of iron and manganese minerals in river-recharged aquifers: A model interpretation of a column experiment. *Geochim. Cosmochim. Acta* **57**, 1691-1704.
- MCSWEEN H. Y. (1979) Alteration in CM carbonaceous chondrites inferred from modal and chemical variations in matrix. *Geochim. Cosmochim. Acta* **43**, 1761-1770.
- METZLER K., BISHOFF A., and STOFFLER D. (1992) Accretionary dust mantles in CM chondrites: Evidence for solar nebula processes. *Geochim. Cosmochim. Acta* **56**, 2873-2897.
- MOODY J.B. (1976) Serpentinization: A review. *Lithos* **9**, 125-138.
- PRINN R.G. and FEGLEY B.J. (1987) The atmospheres of Venus, Earth and Mars: A critical comparison. *Annual Review of Earth and Planetary Science Letters* **15**, 171-212.
- RAMDOHR P. (1967) A widespread mineral association, connected with serpentinization. *N. Jb. Miner. Abh.* **107**, 241-265.
- RUBIN A.E. (1984) Coarse-grained chondrule rims in type 3 chondrites. *Geochim. Cosmochim. Acta* **48**, 1779-1789.

- TOMEOKA K. and BUSECK P.R. (1985) Indicators of aqueous alteration in CM carbonaceous chondrites: Microtextures of a layered mineral containing Fe, S, O, and Ni. *Geochim. Cosmochim. Acta* **49**, 2149-2163.
- ZOLENSKY M., BARRETT R., and BROWNING L. (1993) Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **57**, 3123-3148.

PART 4

Summary

SUMMARY

The investigation of CM carbonaceous chondritic material provides one of the most logical approaches toward gaining a better understanding of aqueous interactions in the early solar system. However, the unraveling of a detailed origin for these meteorites has long since proven to be a formidable challenge as a result of the extremely diverse materials and processes involved. This thesis was motivated by the need to identify and address the outstanding fundamental questions and assumptions that continue to hinder this process.

The ultimate goal of identifying the chronological reaction sequence for the fluid-rock reactions affecting CM materials cannot be achieved without a reliable procedure for distinguishing progressive alteration signatures. In Part 1, we proposed the first multi-component scaling procedure to determine the relative extent of aqueous alteration that individual CM chondrites experienced. The first parameter, the mineralogic alteration index, gauges the relative extent to which the progressive alteration trend from cronstedtite to Mg-rich serpentine has been completed in individual CM chondrites. The second parameter, the vol. % of isolated matrix silicate grains, evaluates the relative extent to which the anhydrous silicates in different CM chondrites were consumed by aqueous reactions. In addition, we proposed that the proportion of altered phases within chondrules is a sensitive indicator of the volumetric production of chondrule phyllosilicates as hydration reactions proceed. Finally, mineralogic alteration indices were compared to literature values of bulk oxygen isotopic ratios, trapped ^{36}Ar , and H content to demonstrate that the CM alteration fluids influenced the whole-rock signatures of CM chondrites during progressive aqueous alteration.

The proposed progressive alteration indicators produced a self-consistent order of increasing CM alteration: Murchison $\leq$ Bells $<$ Pollen $\leq$ Murray $<$ Mighei $<$ Nogoya $<$

Cold Bokkeveld. Boreskino and Cochabamba are probably best described as having experienced intermediate degrees of aqueous processing. Comparisons with whole-rock chemical and isotopic data demonstrated the systematic loss of ^{16}O -rich fluids and trapped planetary noble gases, and the nearly constant production rate of new phyllosilicates as the mineralogic transition from cronstedtite to serpentine phases proceeded. The predictable behavior of each of these progressive alteration parameters suggests that individual CM chondrites may have been subjected to a similar set of asteroidal processes and conditions as alteration proceeded.

For many years the consensus was that CM materials experienced aqueous alteration on the CM parent body, but this conclusion has recently been challenged by a compelling new model. In Part 2, an origin is suggested for "sulfide rinds" and similar sulfide-bearing textures which provides strong support for the parent body alteration of CM chondrites. "Sulfide rinds" are defined as an armor of fine-grained sulfides and phyllosilicates around olivine grains that are fully encapsulated within CM chondrules. Part 2 describes the mechanisms and environmental conditions that favor the production of sulfide rinds by in situ aqueous reactions. These conclusions were then used to constrain the origin of sulfide rind and related sulfide-bearing textures located in CM matrices.

A model was developed to determine if sulfide rind assemblages could have precipitated directly out of S-bearing fluids at the surface of dissolving Fe-bearing olivine grains. The production of representative sulfide rinds ($\sim 10\ \mu\text{m}$ thick) is kinetically inhibited when adjacent olivine grains are separated by significant distances (i.e. $\sim 200\ \mu\text{m}$), but it is argued that sulfide rind textures could have formed at the surface of reacting olivine grains when the incipient CM fluids were restricted to olivine grain boundaries. A second possibility, supported by petrological evidence, is that many sulfide rind textures formed by in situ replacement processes. One or both of these mechanisms

could have produced the sulfide rinds that are observed in CM chondrules by in situ alteration processes. Regardless of the actual mode of formation, the dissolved S needed for sulfide rind production was probably mobilized during the early stages of chondrule alteration in response to the equilibration of primary chondrule sulfides with grossly undersaturated alteration fluids. The subsequent precipitation of stable secondary sulfides is most likely to have occurred at low activities of total dissolved S, pH values ranging from ~7 to 9, and Ehs between ~-0.3 to -0.6. If all CM materials did indeed experience in situ aqueous alteration, then these fluid conditions must have been pervasive on the CM parent body.

An extensive petrologic examination of matrix textures and mineral associations revealed that situ fluid-rock reactions provide the most satisfactory explanation for sulfide rind and related sulfide-bearing textures in CM matrices. For example, many sulfide rind textures around isolated matrix silicates possess well-defined pseudomorphic textures. In addition, irregularly-shaped sulfide rind textures in CM matrices were probably produced by incomplete, and imperfect, replacement processes. Similarly, the most prevalent textural structures in CM matrices, massive sulfide and phyllosilicate agglomerates, are likely to have formed by imperfect replacement processes.

In Part 3, petrologic evidence was introduced which further supports the parent body alteration of CM chondritic materials. For example, many rim-core and rim-matrix boundaries in CM chondritic meteorites are overprinted by secondary alteration phases, indicating that dissolved components were exchanged between adjacent CM materials during in situ aqueous reactions. The in situ alteration of some of these coarse-grained core components probably contributed enough dissolved components to the adjacent CM rim materials to significantly affect the mineralogy and texture of the rim itself. In one such example, the plausibility of a significant material exchange between the aggregate and surrounding rim was demonstrated by determining the capability of the alteration

scenario given in Part 2 to produce the observed results. Moreover, gradational rim-matrix contacts and highly irregular rim-matrix boundaries with delicate rim material extensions into the surrounding matrix strongly suggest an origin by in situ alteration reactions. In contrast, none of the observed rim-matrix or rim-core contacts provided compelling support for the alteration of CM rim materials prior to the accretion of the CM parent body.

VITA

Lauren B. Browning was born on October 28, 1959 in Coconut Grove, Florida. She attended many public schools in both Florida and Texas, and received her High School diploma in early 1977. After a brief enrollment at the University of Texas at Austin, Lauren performed an assortment of odd jobs in Austin, Texas, for 8 years. During this period she held positions as a construction worker, maid, sales person, gardener, race horse groom, waitress, and chef. Afterwards, Lauren re-entered the University of Texas in earnest. During the summer of 1990, she accepted a Lunar and Planetary Institute Summer Internship, and was introduced to meteorite research. In 1991, she earned a Bachelor of Science degree in Geology, with honors. After completing one semester in graduate school at the University of Arizona, Lauren transferred to the University of Tennessee at Knoxville. One year later, Lauren was awarded support from NASA to pursue her investigation of CM chondritic meteorites at the NASA Johnson Space Center in Houston, Texas. Lauren alternately resided in Texas and Tennessee for the next three years and received her Doctor of Philosophy in Geology in 1995.