FINE-GRAINED SERPENTINE IN CM2 CARBONACEOUS CHONDRITES AND ITS IMPLICATIONS FOR THE EXTENT OF AQUEOUS ALTERATION ON THE PARENT BODY: A REVIEW

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Abstract—Outer main-belt asteroids are predominantly of the C-type (carbonaceous), suggesting that they are likely parent bodies of carbonaceous chondrites. Abundant phyllosilicates in some classes of carbonaceous chondrites have chemical compositions, mineral associations, and textures that preserve direct evidence of the processes by which carbonaceous chondrites and their parent asteroids originated and evolved to their present state. Serpentine is the dominant hydroxyl-bearing mineral in the most abundant (CM) group of carbonaceous chondrites. Serpentine may have formed as a direct nebular condensate during cooling of the solar nebula, or by aqueous alteration of anhydrous Mg,Fe-silicate precursors. Such alteration of anhydrous precursors may have occurred in the solar nebula prior to assembly of the meteorites' parent bodies or on the parent bodies. The relative proportions of Fe and Mg in fine-grained CM2 serpentines have been used to compare the degree of aqueous alteration of different CM2 chondrites with one another. The Mg content of serpentine increases with increasing overall degree of aqueous alteration, so CM2 chondrites with Mg-rich serpentines experienced a more advanced degree of aqueous alteration than CM2 chondrites with Fe-rich serpentines. Attempts to quantify aqueous alteration of CM chondrites by interpreting electron microprobe analyses in terms of charge-balance and site-occupancy constraints from serpentine stoichiometry have met with mixed success. Despite its imperfections, one widely used alteration index based on serpentine stoichiometry is strongly correlated with the elapsed time since the fall and recovery of witnessed CM chondrite falls. Additionally, volatile organic contaminants introduced during sample processing in the laboratory are associated with serpentine and other matrix phyllosilicates. Together, these post-recovery changes in scientifically important sample attributes imply that oxidation-reduction and other types of weathering and contamination affect these meteorites even during curatorial storage and laboratory processing. The same phyllosilicates that make their carbonaceous-chondritic host rocks scientifically important research targets also render those same rocks extraordinarily vulnerable to terrestrial contamination of some of their most scientifically important attributes. This has possible implications for reconstructing pre-terrestrial (parent body) aqueous alteration phenomena from carbonaceous chondritic meteorites and eventually from samples returned by future missions to asteroids with spectral reflectance properties similar to carbonaceous chondrites.

Key Words—Aqueous Alteration, Carbonaceous Chondrites, Meteorites, Serpentine.

INTRODUCTION

Statement of purpose

Serpentine-group minerals dominate the abundant fine-grained materials of several classes of carbonaceous chondrites, which are meteorites with primitive chemical compositions that are believed to come from undifferentiated asteroids. Broad compositional trends are recognized in fine-grained CM (carbonaceous chondrite, Mighei-type) chondrite alteration minerals (*e.g.* matrix, rims) and appear to be related to trends in degree of aqueous alteration (Zolensky *et al.*, 1993; Browning *et al.*, 1996; Rubin *et al.*, 2007; Chizmadia and Brearley, 2008). Several quantitative measures of the extent of

aqueous alteration use electron probe microanalyses (EPMA) of serpentine-dominated fine-grained matrix in CM chondrites. Some of these measures are based on the assumption that matrix composition can be interpreted using charge-balance and site-occupancy constraints from serpentine stoichiometry.

Here, the literature on fine-grained serpentine in CM chondrite matrix and several previously used aqueous-alteration metrics that are based on major-element compositions of serpentine-rich matrix is reviewed. The review is illustrated with scanning electron microscope − backscattered electron (SEM-BE) and high-resolution transmission electron microscope (HR-TEM) images from ongoing work on the CM2 chondrite, Queen Alexandra Range 93005. Aqueous alteration phenomena in this meteorite have been examined previously by methods including electron probe microanalysis (EPMA) and backscattered electron imaging by Trigo-Rodriguez *et al.* (2006) and Rubin *et al.* (2007).

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Meteorites

Meteorites are naturally delivered samples from a variety of parent bodies throughout the solar system (Grady and Wright, 2006). In their chemical compositions, minerals, and textures they preserve direct evidence of the processes by which our solar system's planets and small bodies originated, were modified, and evolved to their present state. Meteorites from large, differentiated parent bodies (*e.g.* Mars, the Moon, differentiated Main Belt asteroids) complement scientific understanding of those parent bodies arrived at by other means, including ground-based astronomical observations and orbital and landed missions. Undifferentiated meteorites are important sources of information about asteroids. Other than small returned samples (*e.g.* comet dust returned by NASA's Stardust mission; Brownlee *et al.*, 2006; Zolensky *et al.*, 2006; mineral fragments recently returned from asteroid Itokawa by the ISAS Hayabusa mission) and naturally delivered interplanetary dust particles (IDPs, *e.g.* Rietmeijer, 2002), meteorites are our only direct and abundant samples of materials formed and modified during the earliest stages of solar system evolution. Studies of meteorites also contribute to the knowledge base for interpreting asteroidal and cometary composition and history (including aqueous alteration) by both direct (sample-return; *e.g.* NASA Stardust; ISAS Hayabusa) and remote (fly-by) asteroidal and/or cometary missions (*e.g.* NASA Deep Impact, EPOXI/Deep Impact Extended Mission, and Stardust NExT; ESA Rosetta).

Freshly fallen meteorites, recovered promptly after their witnessed fall, are referred to as 'falls.' Most meteorites available for scientific study are referred to as 'finds,' recovered after unwitnessed arrival and some exposure to the terrestrial surface environment, often over millennial or longer timescales. Meteorites are named for major geographic features near their recovery site. Where natural processes result in the accumulation of large numbers of meteorites, the recovery-site name is followed by a number identifying each individual object within the accumulated population. For Antarctic finds, the recovery-location name is abbreviated to one letter for meteorites recovered by Japanese research teams, and three letters for research teams from the United States of America. For example, the full name of the meteorite that is the source of the illustrations used in this review, Queen Alexandra Range (Antarctica) 93005, is condensed to QUE 93005.

At the broadest level of compositional classification, meteorites include objects that consist mainly of metal ('irons'), predominantly of silicate minerals ('stones' or 'stony meteorites'), and subequal abundances of metal and silicates ('stony irons') (Dodd, 1981; McSween, 1999; Krot *et al.*, 2003; Hutchison, 2004; Weisberg *et al.*, 2006). Stony meteorites are subdivided into those with textural evidence of familiar (to geologists) igneous differentiation processing on their parent bodies, and those containing textural evidence of cooling and solidification of individual grains from vapor and melted dust followed by assembly of the solids into rocks and parent bodies that did not differentiate to produce magmas and igneous rocks (Dodd, 1981; McSween, 1999; Krot *et al.*, 2003; Hutchison, 2004; Weisberg *et al.*, 2006). The defining features of the latter group are 'chondrules,' generally spherical mm to sub-mm-sized silicate-dominated solids that are solidified droplets formed by flash heating and rapid cooling of precursor solids in the early solar nebula (Lofgren, 1989, 1996; Lofgren and Russell, 1986; Lofgren and Lanier, 1990; McSween, 1999; Hutchison, 2004). Stony meteorites containing chondrules, and closely related meteorites in which evidence of chondrules may have been destroyed during the meteorite's history, are called 'chondrites.' (Stony meteorites with igneous textures lack chondrules and are called 'achondrites.') Three types of chondritic meteorites are known (McSween, 1999; Krot *et al.*, 2003; Hutchison, 2004; Weisberg *et al.*, 2006) — ordinary chondrites, enstatite chondrites, and carbonaceous chondrites, the subject of this paper.

Carbonaceous chondrites

Carbonaceous chondrites are naturally delivered samples from asteroidal parent bodies in the outer region of the asteroid belt (Grady and Wright, 2006). The two groups of carbonaceous chondrites with the greatest abundances of hydrous minerals (phyllosilicates) are the compositionally primitive (solar composition) and rare CI (Ivuna) group, and the much more abundant CM (Mighei) group (Dodd, 1981; McSween, 1999; Krot *et al.*, 2003; Hutchison, 2004; Weisberg *et al.*, 2006). Early research debated whether they originated as aggregates of initially hydrous dust that dehydrated and formed anhydrous silicates (*e.g.* olivine) or consisted initially of anhydrous material subsequently subjected to aqueous alteration (DuFresne and Anders, 1962). Early thermodynamic calculations suggested that the large hydroxyl and volatile content of carbonaceous chondrites was a consequence of direct equilibrium condensation (*e.g.* Grossman, 1972; Grossman and Olsen, 1974) of carbonaceous chondrite material at heliocentric distances far enough from the early/proto-Sun to permit direct condensation of hydrous mineral phases (*e.g.* serpentine) from the solar nebula. The possibility that phyllosilicates formed indirectly by nebular hydration of high-temperature anhydrous silicate condensates was subsequently dismissed on the grounds that the kinetics of gas-solid reactions in the nebula would be prohibitively slow (Prinn and Fegley, 1987), but more recent work suggests that shock waves in the nebula may have created brief episodes of conditions more favorable to formation of phyllosilicates by nebular hydration of anhydrous precursors (Ciesla *et al.*, 2003; Ciesla and Lauretta, 2005).

The presence of non-volatile elements in CI meteorites similar in abundance to those in the solar photosphere suggested that these are the most primitive (least evolved) solids in the Solar System. At one time, such primitive and volatile-rich material (petrologic type 1) were believed to be the 'starting material' for subsequent parent-body evolution, and that other groups of meteorites had been subjected to progressively greater degrees of devolatilization and phase equilibration. Vestiges of this idea survive as the petrologic-type ("metamorphic grade") designations in the Van Schmus and Wood (1967) classification of chondritic meteorites. Petrographic research recognized that at least some hydrous phyllosilicates in carbonaceous chondrites occur as aqueous alteration products of anhydrous precursors (*e.g.* DuFresne and Anders, 1962; Bunch and Chang, 1980). The dominant recent line of thought holds that petrologic type 3 was the 'starting material;' in this view, types 4–6 represent prograde (thermal) metamorphism, and petrologic types 2 and 1 may be products of increasing degrees of hydrous alteration of type 3 starting material (McSween, 1979a; Buseck and Hua, 1993). Continued physical mixing by impacts on the parent body can result in regolith gardening, brecciation, and consequent intimate mechanical mixing of fragments sampling a broad range of degrees of alteration (petrologic types). Readers interested in more details of chondritic meteorite classification, petrologic types, and associated processes are directed to McSween (1999), Krot *et al.* (2003), Hutchison (2004), and Weisberg *et al.* (2006).

CM chondrites are mostly petrologic type 2 (CM2; Dodd, 1981; Brearley and Jones, 1998; McSween, 1999; Krot *et al.*, 2003; Hutchison, 2004; Weisberg *et al.*, 2006). Research on CM chondrites has established a range of degrees of aqueous alteration within CMs of petrologic type 2 (Zolensky *et al.*, 1993, 1997; Browning *et al.*, 1996; Rubin *et al.*, 2007; Chizmadia and Brearley, 2008; Howard *et al.*, 2009), and from petrologic type 2 to type 1 in CM chondrites (Zolensky *et al.*, 1997). However, different alteration metrics can yield varying results for the same meteorites (Howard *et al.*, 2009, their table 1), and differences in the suites of CM chondrites examined by different studies can create the appearance of broader or narrower ranges and continuous or discontinuous variations in the degree of alteration.

FINE-GRAINED PHYLLOSILICATES IN CM2 CHONDRITES

At least some phyllosilicates in CM carbonaceous chondrites are widely regarded as having formed by aqueous alteration of anhydrous precursor phases. However, in spite of the abundance of phyllosilicates in CM chondrites, the precise textural (petrographic) context in which they formed (*e.g.* matrix *vs.* chondrule

or clast) was seldom characterized rigorously in early work (Zolensky and McSween, 1988). Recent research has begun to close this gap (McSween, 1979b, 1987; Zolensky and McSween, 1988; Tomeoka *et al.*, 1989; Lauretta *et al.*, 2000; Hanowski and Brearley, 2001; Hua *et al.*, 2002; Zega and Buseck, 2003; Zega *et al.*, 2003, 2004, 2006; Brearley, 2003, 2006; Rubin *et al.*, 2007; Chizmadia and Brearley, 2008).

Textural constituents of CM carbonaceous chondrites can be classified as coarse constituents ("larger components" as identified by Zolensky and McSween, 1988, including chondrules, large mineral fragments, and refractory-element-rich calcium aluminum inclusions, CAIs), matrix (fine-grained), and fine-grained rims on coarse constituents (Figure 1). Matrix constitutes 57−85% of CM chondrites (McSween, 1979b). Because of their fine particle size, matrix and rim materials are particularly sensitive indicators of various alteration processes (*e.g.* Brearley, 2003, 2006). Much recent mineralogical and cosmochemical research has focused on fine-grained rims around chondrules in CM chondrites (Metzler *et al.*, 1992; Zolensky *et al.*, 1993, 1997; Lauretta *et al.*, 2000; Browning *et al.*, 1996, 2000; Hanowski and Brearley, 2001; Hua *et al.*, 2002; Zega and Buseck, 2003; Zega *et al.*, 2003, 2004, 2006; Brearley, 2003, 2006; Trigo-Rodriguez *et al.*, 2006; Chizmadia and Brearley, 2008). Fine-grained rims (Figure 1) on chondrules are widely thought to have accreted to the chondrule surface in the dusty nebula prior to aggregation of chondrules and rims into planetesimals, producing the "primary accretionary rock" texture recognized in several carbonaceous
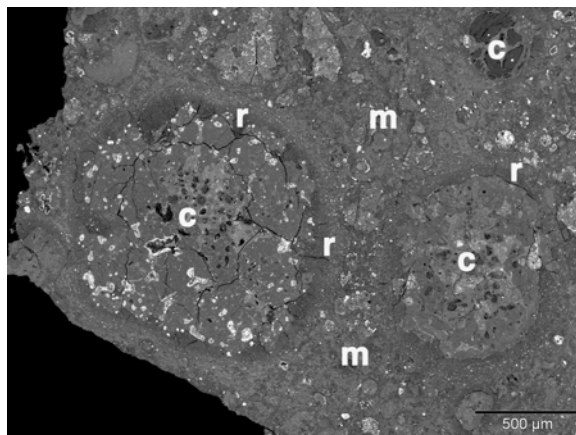

Figure 1. Two large chondrules (c) and their associated fine-grained rims (r), one smaller chondrule (c at upper right), and fine-grained matrix (m) between. Backscattered-electron SEM image of polished thin-section QUE 93005,15. The brightest (highest Z-contrast) areas are Fe-sulfide (or oxyhydroxides after sulfide); darkest areas are void space or mounting medium. Intermediate shades of gray include olivine (in chondrules, and as isolated fragments in matrix) and serpentine-group minerals (in matrix and fine-grained rims on chondrules).

Table 1. Serpentine-group minerals and their formulae.

Group	Name	Formula
Mg-bearing	Chrysotile	$Mg_3Si_2O_5(OH)_4$
	Lizardite	$Mg_3Si_2O_5(OH)_4$
	Antigorite	$Mg_3Si_2O_5(OH)_4$
Fe-bearing	Cronstedtite	$Fe_2^{2+}Fe^{3+}(SiFe^{3+})O_5(OH)_4$
	Greenalite	$(Fe_2^{2+},Fe^{3+})_{2-3}Si_2O_5(OH)_4$
	Ferroan antigorite	$(Mg,Fe,Mn)_3(Si,Al)_2O_5(OH)_4$
Intermediate	Amesite	$Mg_2Al(SiAl)O_5(OH)_4$
	Berthierine	$(Fe_2^{2+},Fe^{3+},Mg)_{2-3}(Si,Al)_2O_5(OH)_4$

Adapted from Zolensky and McSween (1988) and Browning *et al.* (1996)

chondrites by Metzler *et al.* (1992). Fine-grained rims on chondrules thus have particular scientific value, especially in CM chondrites that preserve unbrecciated primary accretionary textures. The most recent TEM studies of fine-grained rims and matrix in CM2 chondrites have emphasized texturally primitive (especially, minimally brecciated) CM2 chondrites (Lauretta *et al.*, 2000; Hua *et al.*, 2002; Zega and Buseck, 2003; Zega *et al.*, 2003, 2004, 2006; Chizmadia and Brearley, 2008). However, their layer structured minerals − coarse platy Fe-rich serpentines (cronstedtite) and curved Fe-bearing Mg-serpentines (Lauretta *et al.*, 2000) − exhibit the same attributes as their counterparts in micro-brecciated and texturally disrupted matrix typical of CM chondrites that experienced more extensive mechanical processing (*e.g.* regolith gardening by impacts on the parent body). Similarities in trace-element abundances between vein (replacement) phyllosilicates replacing anhydrous coarse-object silicates and the fine-grained rims on the coarse-grained cores suggest both cores and rims altered in the same aqueous environment, certainly after accretion of rims to core objects, and probably after assembly of rimmed objects into the parent body (Hua *et al.*, 2002).

Serpentine-group minerals

Phyllosilicate minerals of the serpentine group (Mg-serpentine, cronstedtite) (Table 1) dominate the fine-grained (matrix and chondrule-rim) materials of CM2 chondrites (Fuchs *et al.*, 1973; Mackinnon and Buseck, 1979a, 1979b; Zolensky and McSween, 1988; Howard *et al.*, 2009). The matrix mineralogy and chemistry of CM meteorites have been the subjects of numerous studies by a variety of methods. One widely used approach is the determination of the "bulk" elemental composition of matrix by area-averaging defocused-beam EPMA (*e.g.* Fuchs *et al.*, 1973; McSween and Richardson, 1977; McSween, 1979b, 1987; Bunch and Chang, 1980; Barber, 1981, 1985; Zolensky and McSween, 1988; Tomeoka *et al.*, 1989; Zolensky *et al.*, 1993; Buseck and Hua, 1993; Browning *et al.*, 1996; Howard *et al.*, 2009).

Backscattered electron images are often published as context images for EPMA and TEM data from CM chondrites. Typical chondrules and matrix textures as seen in backscattered electron SEM images are shown in Figure 1.

In TEM imagery, micrometer-scale serpentine-group minerals appear platy (Figure 2), wavy, curved (Figure 3), and cylindrical/tubular in form. Platy varieties tend to be cronstedtite (Müller *et al.*, 1979; Barber, 1981; Lauretta *et al.*, 2000), and sub-micrometer-scale wavy, curved, and cylindrical/tubular varieties tend to be Mg-serpentine (chrysotile and/or lizardite) (Barber, 1981; Lauretta *et al.*, 2000). Tubular forms of serpentine
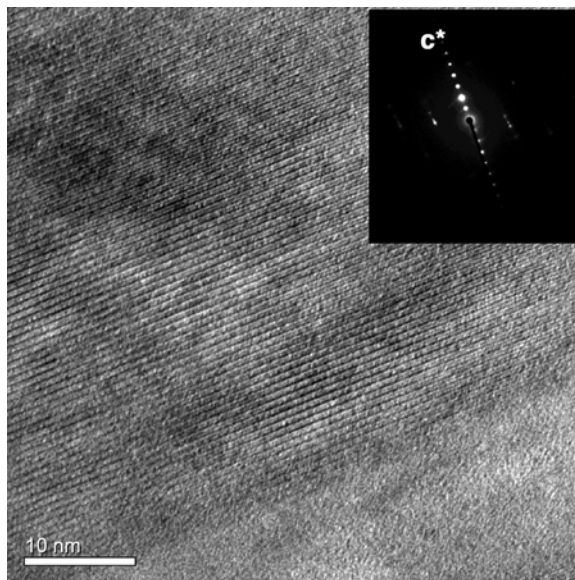
Figure 2. TEM bright-field phase-contrast image of platy serpentine in QUE 93005,16. The selected-area electron diffraction (SAED) pattern (inset) shows (00*l*) Bragg diffraction spots indicating $d_{001} = 0.72$ nm. The serpentine shown here has molar $Mg/(Mg + Fe) = 0.69$ (corrected for Fe associated with Fe-sulfide).
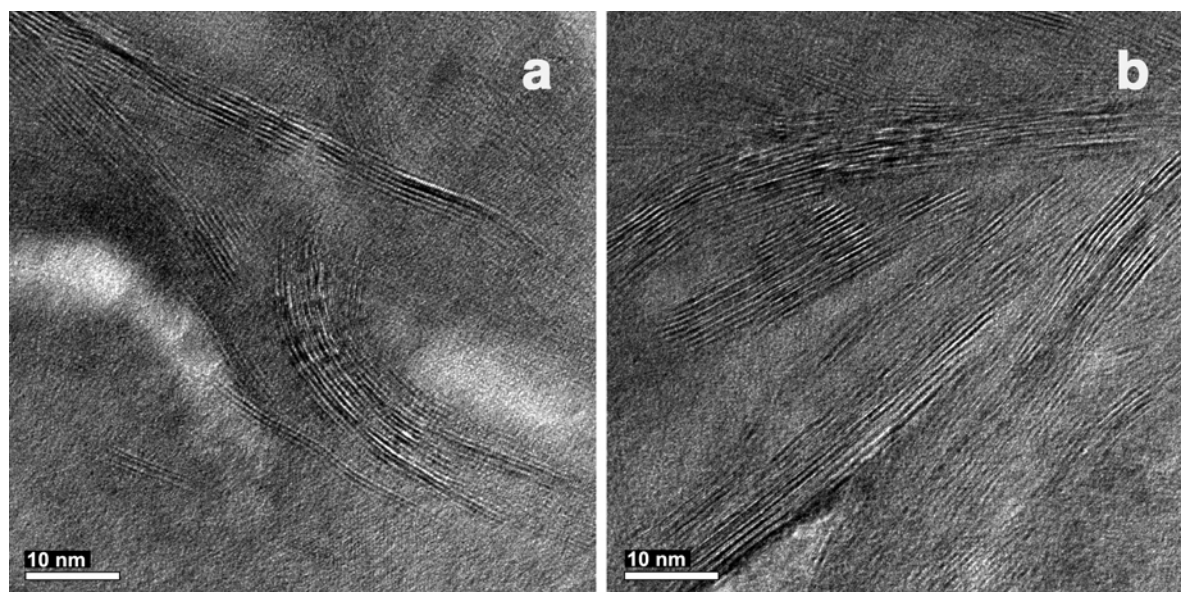
Figure 3. TEM bright-field phase-contrast image of curved serpentine in QUE 93005,16. An SAED pattern of similar material elsewhere in the same TEM grid shows (00l) Bragg diffraction spots indicating $d_{001} \approx 0.76$ nm.

are also known from CM2 meteorites (Akai, 1980; Barber, 1981; Tomeoka and Buseck, 1985; Tomeoka *et al.*, 1989; Buseck and Hua, 1993; Zega and Buseck, 2003; Zega *et al.*, 2004, 2006). However, Mg-rich and/or curved tubular serpentine is commonly observed to be especially vulnerable to preferential beam damage (Mackinnon, 1982) and may thus be under-reported.

Much of the early TEM work (Mackinnon and Buseck, 1979a, 1979b; Barber, 1981; Tomeoka and Buseck, 1983, 1985) involved the characterization of material initially termed "poorly characterized phase" (PCP; Fuchs *et al.*, 1973; Bunch and Chang, 1980; Buseck and Hua, 1993). The material initially labeled PCP (*e.g.* Fuchs *et al.*, 1973; Bunch and Chang, 1980; Barber, 1981; Tomeoka and Buseck, 1983; Rubin *et al.*, 2007) is now understood to consist of two main constituents. Type I PCP consists of discrete tochilinite [6Fe$_{0.9}$S 5(Fe,Mg)(OH)$_2$], a naturally occurring layered composite mineral with alternating coherently interstratified mackinawite-like sulfide sheets and Fe-rich brucite-like sheets (Tomeoka and Buseck, 1985; Tomeoka *et al.*, 1989; Buseck and Hua, 1993). Type II PCP is dominated by a layer-structured mineral with layer spacings (d_{001}) $\approx$ 1.7−1.8 nm, not known from naturally occurring terrestrial materials and eventually clarified as 1:1 interstratified serpentine-tochilinite (Mackinnon and Zolensky, 1984; Tomeoka *et al.*, 1989; Buseck and Hua, 1993), although other stacking variants (*e.g.* tochilinite-serpentine-serpentine, with d_{001} $\approx$ 2.4 nm) are known (Zolensky *et al.*, 1993).

Most previous TEM work dealt directly or indirectly with aqueous alteration. Previous TEM studies of fine-grained matrix mineralogy of CM2 chondrites include

Mackinnon and Buseck (1979a, 1979b), Müller *et al.* (1979), Akai (1980, 1982, 1988), Barber (1981, 1985), Mackinnon (1982), Tomeoka and Buseck (1985), Tomeoka *et al.* (1989), Zolensky *et al.* (1993, 1997), Zolensky and Ivanov (2003), and Zega *et al.* (2003, 2004, 2006). Some TEM work characterized intermediate products of prograde thermal metamorphism (Tonui *et al.*, 2003), including dehydration of serpentine to olivine (Akai, 1988). The review by Buseck and Hua (1993) summarizes the pioneering TEM studies of matrix.

PARENT-BODY AQUEOUS ALTERATION

Qualitative and quantitative models of CM chondrite aqueous alteration were summarized by Brearley (2006). Only conceptual models relevant to phyllosilicates are reviewed here. A qualitative conceptual model for CM chondrite alteration is embodied in the various alteration indices or scales that have been proposed that relate different CM chondrites to one another through observable differences (some quantitative), and linking the observed differences to alteration phenomena (*e.g.* McSween, 1979, 1987; Zolensky *et al.*, 1993, 1997; Browning *et al.*, 1996; Rubin *et al.*, 2007; Howard *et al.*, 2009; see review by Brearley, 2006). Given the abundance of matrix in CM chondrites and the reasonable expectation that fine-grained material would be especially susceptible to aqueous alteration (by virtue of its large surface-area-to-volume ratio), early efforts to quantify differences in the extent of aqueous alteration of CM chondrites emphasized matrix (*e.g.* McSween, 1979b).

Several widely used alteration indices are framed in terms of how matrix Mg and Fe abundances vary with the overall degree of aqueous alteration experienced by any individual CM chondrite (Zolensky *et al.*, 1993; Browning *et al.*, 1996). Both alteration indices reviewed here involve the abundances of major serpentine-forming elements. The ratio Fe/(Mg+Fe) (and its counterpart, Mg/(Mg+Fe)) (Zolensky *et al.*, 1993) uses the analyzed matrix abundances of major elements − Mg and total Fe − that occur predominantly in the octahedral sites of serpentine-group minerals (Table 1). The Mineralogical Alteration Index (MAI) of Browning *et al.* (1996) is based on the abundance of Fe^{3+}, which is estimated from stoichiometric and charge-balance requirements of serpentine-group structural formulae, and which can occur in either tetrahedral or octahedral sites in serpentine-group minerals (Table 1). These two related but non-identical alteration metrics are discussed in the following sections.

Matrix Mg-Fe systematics

Throughout the literature on fine-grained rims and matrix in CM chondrites, an explicit connection is seen between the composition of fine-grained alteration products and the differential destruction of anhydrous silicates. In both matrix and fine-grained rim material, broad compositional trends are recognized in likely alteration minerals (*e.g.* matrix, rims) and believed to be related to trends in degree of aqueous alteration (*e.g.* Zolensky *et al.*, 1993; Browning *et al.*, 1996).

CM chondrite matrix, initially more Fe-rich than the chondrules in the same meteorite, becomes progressively more Mg-rich with aqueous alteration (McSween and Richardson, 1977; McSween, 1979b, 1987; Zolensky *et al.*, 1993; Browning *et al.*, 1996). Zolensky *et al.* (1993, their figure 4) illustrated that specimen-average Fe/(Fe+Mg) (wt.%) values vary from 0.4 to 0.9 in a suite of nine CM chondrites. Increasing Mg/Fe (decreasing Fe/(Fe+Mg) (wt.%) (Zolensky *et al.*, 1993) and corresponding increasing Mg/(Fe+Mg) (wt.%)) in matrix phyllosilicates with increasing CM chondrite alteration is generally (*e.g.* Zolensky *et al.*, 1993) attributed to differences in dissolution rates of olivines of the different compositions that co-exist in CM chondrites (Wood, 1967; Fuchs *et al.*, 1973; Goswami and Macdougall, 1983). In mineral solid-solution series with complete substitution of Fe for Mg (*e.g.* olivines), the dissolution rates of Fe-rich varieties are faster than rates for Mg-rich varieties (*e.g.* Velbel, 1999, and primary references therein). Early in the evolution of a closed aqueous system with both Fe-rich and Mg-rich olivines (Wood, 1967; Fuchs *et al.*, 1973; Goswami and Macdougall, 1983), rapid consumption of Fe-silicates releases Fe to aqueous media in preference to Mg, and early formed products are Fe-rich, high-Fe/(Fe+Mg), low-Mg/(Fe+Mg) matrix serpentines (Zolensky *et al.*, 1993). At later stages of reaction, primary anhydrous Fe

silicates have been preferentially depleted; dissolution of the surviving Mg-rich silicates results in later-stage solutions being dominated by Mg (rather than Fe), and later-formed Mg-rich, high-Mg/(Fe+Mg), low-Fe/(Fe+Mg) matrix serpentines form from the resulting Mg-rich aqueous medium (Zolensky *et al.*, 1993).

Alternatively, Howard *et al.* (2009) argued that the Mg/Fe ratios of CM chondrite serpentines are inherited directly from the compositions of the anhydrous minerals they replace, and that the Fe-rich matrix serpentines indicate that their precursor olivines were more Fe-rich than chondrule olivines.

The mineralogical alteration index

More recent work has expanded the number and diversity of parameters measured in attempts to quantify different degrees of progressive aqueous alteration. Browning *et al.* (1996) examined a number of non-Antarctic CM chondrite falls and ranked those meteorites from least altered to most altered using a variety of measurable parameters, many of which appear to be broadly correlated with one another. Parameters used by Browning *et al.* (1996) in establishing their rankings include modal percent isolated anhydrous silicate grains in matrix; modal percent replacement of anhydrous chondrule silicates by hydrous alteration products; and the MAI, a parameter of matrix-phyllosilicate major-element chemistry that was shown to be reasonably well correlated with other measures.

Browning *et al.* (1996) attempted to place the previous observation (Zolensky *et al.*, 1993) that initially formed matrix phyllosilicates are Fe-rich whereas more advanced matrix phyllosilicates are Mg-rich on a crystal-chemical foundation based on the stoichiometries of serpentine-group minerals (Table 1). A general stoichiometric expression for serpentine-group minerals including cronstedtite and Mg-serpentines is equation 1 (adapted from Browning *et al.*, 1996)

$$((Fe^{2+},Mg,Mn,Ca,...)_{3-x}(Al,Fe^{3+})_x)(Si_{2-x}(Al,Fe^{3+})_x)O_5(OH)_4 \qquad (1)$$
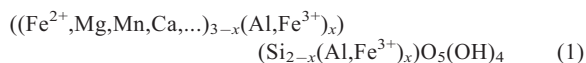
where $0 < x < 1$. The coupled substitutions of two trivalent ions (Fe^{3+}, Al) by one tetrahedral tetravalent Si and one divalent octahedral cation (Mg, Fe^{2+}) can be described as

$$2(Fe^{3+},Al) \leftrightarrow Si + (Mg, Fe^{2+} \ldots) \qquad (2)$$
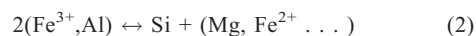
To maintain charge balance, every trivalent cation that substitutes for Si in a tetrahedral site (and contributes to x) and thereby reduces the positive charge associated with tetrahedral cations must be compensated by an equal increase in positive charge in octahedral sites. This is achieved in cronstedtite by substituting the same number of trivalent cations for divalent cations in octahedral sites (x) as the number of trivalent cations substituted for Si in tetrahedral sites (x). Consequently, the total amount of trivalent cations substituted for other

cations is $2x$, with equal amounts (x) in tetrahedral and octahedral sites. Equation 1 yields the composition of Mg-serpentine when $x = 0$ and Fe-rich serpentine (*e.g.* cronstedtite) when $x = 1$. Note that Al, which resembles Fe^{3+} in that it can occur in both octahedral and tetrahedral sites in serpentine-group minerals (Table 1), is not treated separately from Fe^{3+} in this general stoichiometric expression.

The index proposed by Browning *et al.* (1996) assumes that the volume of material analyzed by an electron microprobe spot is homogenous and consists only of a serpentine-group mineral, with no contribution to the microprobe analysis by other minerals containing Si, Mg, Fe, or Al, except for a correction for S-associated Fe based on the amount of S present ($Fe' = Fe - .975$ S; Browning *et al.*, 1996, Appendix, item 4a), assuming idealized pyrrhotite to be the primary S-bearing phase. (The matter of correcting for Fe and Mg hosted by minerals other than discrete serpentine or discrete sulfides, in particular the role of the brucite layer in tochilinite which hosts Fe and Mg that obey neither sulfide stoichiometry nor serpentine stoichiometry, remains to be resolved. Browning *et al.* (1996) corrected for Fe associated with tochilinite indirectly by excluding high-S spots from further consideration; whether the S is hosted in pyrrhotite or tochilinite, the correction for divalent metals associated with S is generally small.) After correction for S-associated Fe, the treatment is equivalent to assuming that all Fe, Mg, and Si in a microprobe analysis of CM matrix obey serpentine stoichiometry. Invoking the further assumption that a deficiency of Si is accommodated by tetrahedral substitutions that exhaust all of the analyzed Al (Browning *et al.*, 1996 Appendix, item 4d), the number of Fe^{3+} ions required for charge-balance and tetrahedral-site occupancy per $O_5(OH)_4$ formula unit (p.f.u.) is approximated as

$$Fe^{3+} = 2(2 - Si) - Al \qquad (3)$$

Fe^{3+} abundances estimated in this way are subtracted from the total Fe measured by the microprobe analysis to determine the abundance of octahedral Fe^{2+}.

Browning *et al.* (1996) defined the MAI as

$$MAI = 2 - \frac{Fe^{3+}}{2 - Si} \qquad (4)$$

The MAI was intended to represent the extent to which the coupled substitutions described in expression 2 were completed in the average matrix phyllosilicate of a given CM chondrite. The MAI increases from 0 for cronstedtite (initial alteration) to 2 for Mg-serpentine (continued alteration), and it is intended to reflect two tendencies with increased alteration of CM matrix phyllosilicates; (1) the tendency toward more Mg-rich phyllosilicates with increasing degree of aqueous alteration (*e.g.* McSween and Richardson, 1977;
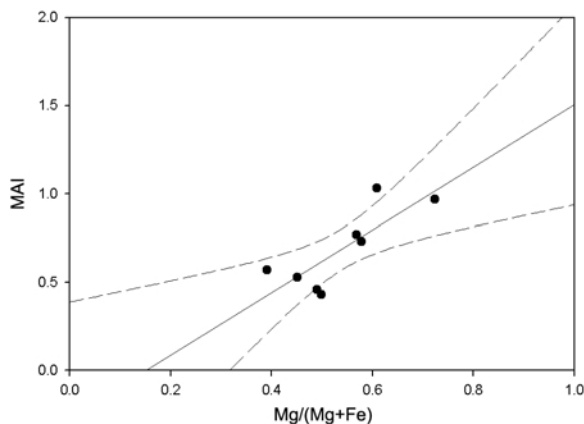

Figure 4. MAI *vs.* Mg/(Mg+Fe) for the eight CM chondrite falls analyzed by Browning *et al.* (1996). $r^2 = 0.65$; 95% confidence limits. This plot compares the MAI of Browning *et al.* (1996) with Mg/(Mg+Fe) of Zolensky *et al.* (1993), previously shown to increase with increased aqueous alteration of CM2 chondrites. The MAI increases as the proportion of Mg to Fe in CM2 matrix increases.

McSween, 1979b, 1987; Zolensky *et al.*, 1993); and (2) the tendency toward lower abundances of both total Fe and oxidized Fe as Mg-serpentine comes to dominate over cronstedtite (Browning *et al.*, 1996). The correlation of the MAI with Mg/(Mg+Fe) for the eight CM2 falls studied by Browning *et al.* (1996) is not strong (Figure 4) but is consistent with the idea that the MAI increases as the proportion of Mg to Fe in CM matrix increases (Zolensky *et al.*, 1993; Browning *et al.*, 1996). The counterpart ratio, Fe/(Fe+Mg), decreases with increasing MAI (Fig. 5).

If previous work (McSween and Richardson, 1977; McSween, 1979b, 1987; Zolensky *et al.*, 1993) is correct that CM matrix serpentine is more Mg-rich in more altered CM2s, then the Browning *et al.* (1996) correlation of MAI with other compositional and
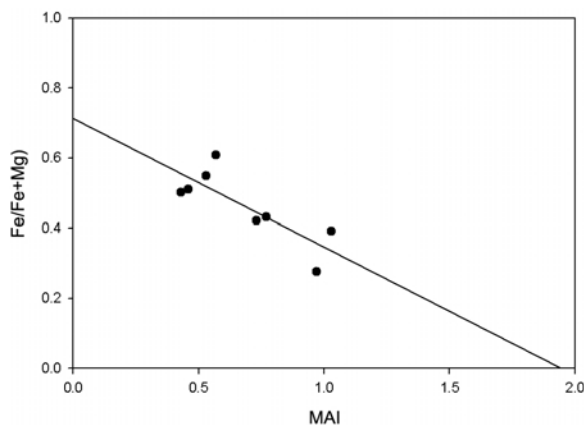

Figure 5. Fe/(Fe+Mg) *vs.* MAI for the eight CM chondrite falls analyzed by Browning *et al.* (1996). Fe decreases with increasing MAI.

petrographic measures of alteration requires that the serpentines in high-MAI CM2s must achieve charge balance with predominantly divalent octahedral cations and not require as much charge balance from Fe^{3+} as less altered CM2s (Figure 5). That requires that the Fe in highly altered (and high MAI) serpentines be divalent (Figure 6). The implied reduced state is consistent with the abundant divalent Fe in sulfides in highly altered CM2s (*e.g.* Rubin *et al.*, 2007).

Browning *et al.* (1996) showed that, for a suite of CM chondrite falls, the rank-order of the extent of aqueous alteration as determined by this matrix geochemical measure is broadly consistent with rank ordering in other petrographic and chemical parameters (*e.g.* Mg/(Mg+Fe), bulk H content, abundance of trapped noble gases, and oxygen isotope compositions; see also Benedix *et al.*, 2003). The relative order of increasing alteration among CM chondrites determined by Browning *et al.* (1996) was broadly consistent with other published rankings (see recent summary by Howard *et al.*, 2009, their table 1). However, a number of difficulties with the MAI have recently been recognized (Bland *et al.*, 2006; Rubin *et al.*, 2007; Howard *et al.*, 2009; Palmer and Lauretta, 2010). Some likely reasons for these difficulties with the MAI are explored here.

The primary goal of the MAI is to determine the amount of alteration the meteorite has undergone by calculating the amount of Fe that is in the Fe^{3+} state (Browning *et al.*, 1996). In general the matrix is richer in Fe than most Mg-serpentine can accommodate, and as a result, cronstedtite serves as a host phase that can accommodate a higher metal to Si ratio, (Mg+Fe)/Si. However, the MAI as calculated by Browning *et al.* (1996) does not evaluate this ratio accurately. The

determination of the amount of Fe^{3+} is correct (equation 3), but when equation 3 is substituted into the formula for the MAI (equation 4), the result is

$$MAI = \frac{Al}{2 - Si} \qquad (5)$$

The MAI is shown by equation 5, which is intended to represent site occupancies of Fe and ions that substitute for it with more advanced aqueous alteration, depends for its estimates of Fe distribution primarily on the measured abundance of Al, which has not been shown previously to be a good indicator of aqueous alteration in CM chondrites. The Al content of CM chondrite matrix is a function of the amount of Al in the sample, not the oxidation state of altered minerals or the amount of chondritic anhydrous silicates that have been altered. Although Al does show a preference for the cronstedtite phase rather than Mg-serpentine, continued alteration does not deplete the amount of Al. The denominator in equation 5 (the $(2 - Si)$ term) does provide some indication of the ratio of metal cations to Si in the matrix, but it is not a direct measurement.

The largest problems of the MAI are mathematical, division by zero, and biases caused by the exclusion of data. As the matrix composition approaches pure serpentine, the number of Si cations approaches 2, which drives the denominator of equation 5 toward zero. A serpentine sample with only Si in tetrahedral sites – for example, exact stoichiometric greenalite or chrysotile – would have $x = 0$, $Fe^{3+} = 0$, and Si = 2, and the determination of the MAI by equation 5 would involve division by zero in the ratio. This can have a large distorting effect as Si approaches 2, resulting in division by a very small number that makes the MAI (equation 5) very large (greater than 2). This in turn would require the exclusion of the data point, even though it is likely to be an analysis of a valid phyllosilicate with acceptable values of x and Fe^{3+}. Furthermore, when the abundance of Al is low or zero, or if Al abundance was not determined, the MAI is low or zero (equation 5) regardless of the analyzed Fe and Mg abundances. The MAI may reasonably estimate Fe siting and valence under limited circumstances at intermediate abundances of Si, but at high Si abundances and at any Al abundance, the use of the MAI is potentially problematic.

The other mathematical problem with the MAI is that excluding data that fall outside of allowable boundaries (0 to 2) causes a preferential bias of the data by removing half of the Gaussian distribution. Probe microanalyses assumes that the error, both above and below the actual values, has a Gaussian distribution. The criteria for the MAI will exclude individual, valid data points because they fall outside of the accepted range, even though they are part of a distribution in which the average value does not. This causes a bias that shifts the MAI average value as a function of standard deviation.
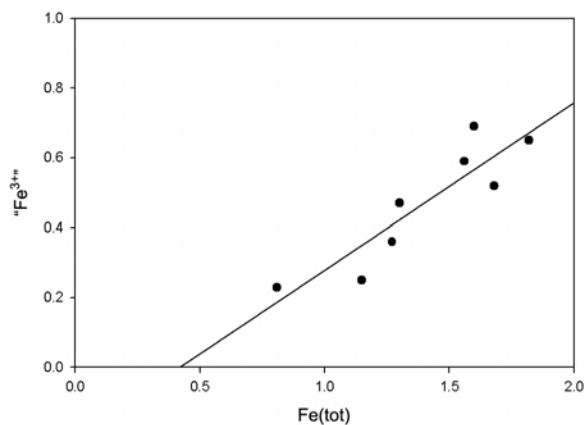

Figure 6. "Fe^{3+}" (estimated by Browning *et al.*, 1996, from analyzed Si, analyzed Al, and site- and charge-balance; equation 3) *vs.* Fe(tot) (from EPMA analysis reported as sum of Fe^{2+} and Fe^{3+}), the latter estimated for the eight CM chondrite falls analyzed by Browning *et al.* (1996). More Fe is ferrous as total Fe decreases.

Some problems in using and interpreting the MAI (*e.g.* MAI being not well correlated with the amount of alteration in the meteorite in some previous studies) probably result from difficulties in accounting properly for the amount of Al in CM matrix regions analyzed. Others may involve difficulties in apportioning Fe analyzed by EPMA among multiple possible host phases in which the Fe can occur in a variety of oxidation states. In addition to serpentine, Fe in CM2 chondrites can occur in the serpentine and brucite sheets of interstratified serpentine-tochilinite (Mackinnon and Zolensky, 1984), in sulfides (*e.g.* pyrrhotite, pentlandite: Rubin *et al.*, 2007), in oxides (*e.g.* magnetite: Fuchs *et al.*, 1973; Bunch and Chang, 1980; Barber, 1981; Brearley and Jones, 1998), and in metal (*e.g.* kamacite: Metzler *et al.*, 1992; Palmer and Lauretta, 2010). The presence of any of these minerals in matrix volumes analyzed by EPMA influences Fe abundances in ways unrelated to the charge balance requirements of serpentine stoichiometry or site occupancy in serpentine layers, both of which together are the basis (equations 1–3) for the MAI. Direct determination of Fe distributions and oxidation state in matrix phases by Mössbauer spectroscopy combined with electron energy loss spectroscopy in TEM (Zega *et al.*, 2003, 2004, 2006) is probably required to determine the extent to which Fe abundances in CM2 matrix represent true stoichiometries and site occupancies of serpentine-group minerals as distinct from larger-scale properties of polymineralic assemblages of bulk matrix. Previous work shows no correlation between Fe^{3+} and degree of alteration (Zega *et al.*, 2003).

TERRESTRIAL WEATHERING IN CURATORIAL AND LABORATORY ENVIRONMENTS

In order to interpret aqueous alteration phenomena in meteorites, scientifically informative pre-terrestrial (parent body) alteration must be distinguished from terrestrial alteration. Chemical and mineralogical properties of meteorites, including indicators of pre-terrestrial aqueous alteration, may be affected by whether their journey from their parent body to the laboratory involved a long hiatus at Earth's surface prior to recovery. In freshly fallen meteorites (falls) recovered promptly after their witnessed fall, aqueous alteration minerals crosscut by or metamorphosed near the fusion crust (which formed on the meteorites during their passage through Earth's atmosphere upon their arrival) are predominantly pre-terrestrial and record aqueous alteration on their parent body (Gooding, 1986). When available, falls are preferred for studies of parent-body and solar-system phenomena. Most carbonaceous chondrite meteorites available for scientific study are 'finds,' recovered after unwitnessed arrival and some exposure to the terrestrial surface environment, often over millennial or longer timescales. In 'finds,' effects of

terrestrial aqueous weathering and contamination are superimposed upon the aqueous-alteration mineral assemblages of pre-terrestrial origin, potentially complicating interpretation of the latter.

Many important pre-terrestrial attributes appear to be preserved in many finds despite terrestrial weathering. Falls are expected to show minimal evidence of terrestrial exposure, since they usually enter scientific collection (curatorial storage and analytical laboratory) environments promptly after Earth arrival and recovery. However, Bland *et al.* (2006) reported a strong correlation between the MAI and the year of the fall in CM chondrite falls – the longer the time elapsed since an historic witnessed fall, the higher the MAI (Figure 7). This implies that even among falls that spent most of their terrestrial history in curatorial (*e.g.* natural history museum) environments, CM chondrites that were exposed to such curatorial environments longer have matrices that are more Mg-rich and (to the extent the MAI is a proxy indicator) have less abundant (Figure 5) and more reduced Fe (Figure 6) than more recent CM falls with shorter terrestrial exposure. The remainder of this discussion examines in greater detail the possibility of terrestrial CM-chondrite weathering during curatorial storage.

THE CHEMICAL INDEX OF ALTERATION

The chemical index of alteration (CIA) is a widely used major-element measure of depletion of mobile alkalis and alkaline earths relative to immobile Al from analyzed volumes of terrestrially weathered rocks (Nesbitt and Young, 1982; Price and Velbel, 2003).

$$CIA = (100)[Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O)] \qquad (6)$$

The CIA ranges from a value constrained by the abundances of alkalis, Ca, and Al in the fresh parent rock to 100 for a weathered sample from which all
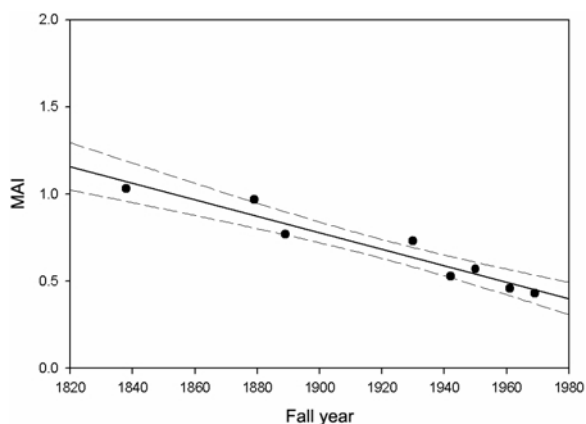

Figure 7. MAI *vs.* fall year (Grady, 2000); after Bland *et al.* (2006). $r^2 = 0.92$; 95% confidence limits. The longer the elapsed time since an historic witnessed fall, the higher the MAI.

mobile elements (represented in this index by Na, K, and Ca) have been leached (Price and Velbel, 2003).

The CIA increases with increasing recovery age of the same CM chondrite falls examined by Browning *et al.* (1996) and Bland *et al.* (2006) (Figure 8), consistent with common patterns of elemental mobilization during terrestrial weathering. The poorer correlation of the CIA than the MAI with time since fall may be influenced by heterogeneity in the parent material (pre-weathering) abundances of Na, K, Ca, and Al (all of which are present in abundances of <3 wt.% in CM chondrites; Hutchison, 2004) among the different CM chondrites examined. However, although variations in parent-material composition can result in different values of the CIA in the starting materials of weathering (Price and Velbel, 2003), the sequence of eight CM2 chondrite falls are unlikely to reflect, coincidentally, both more pre-terrestrial aqueous alteration and more terrestrial weathering solely as a result of variations in initial elemental abundances unrelated to alteration. If the MAI and the CIA both increase in older CM chondrite falls (Figures 7, 8) for reasons other than alteration and weathering either before or during curation, the alternative reason appears to require an unlikely pattern of fall of compositionally variable CM2s over the past several centuries that produces the same distribution of chemical alteration/weathering indicators as alteration and/or weathering would have produced. Parsimony favors post-fall pre- or post-recovery (and possibly curatorial) weathering of CM2 falls.

The increase of both the MAI and the CIA with time elapsed since fall (Figures 7, 8) suggests that the MAI varies with terrestrial "weathering" of CM chondrites, even falls "weathered" after collection and during curation (Bland *et al.*, 2006). Oxidation of ferrous and metallic iron is visually recognized as rust and is the

Figure 8. CIA *vs.* fall year (Grady, 2000). $r^2 = 0.32$; 95% confidence limits. The CIA, a measure of leaching of alkalis and alkaline earths relative to aluminum during terrestrial open-system weathering, is higher in CM2 chondrites that fell and were recovered longer ago.

basis of the most widely used meteorite-weathering classifications (Wlotzka, 1993, for ordinary chondrite falls; and the Antarctic weathering scale used by the NASA Meteorite Working Group of the Astromaterials Acquisition and Curation Office; see review by Velbel and Gooding, 1990). The prevalence of oxidation as a terrestrial weathering phenomenon of stony meteorites combined with the fine grain size and consequent high reactivity of chondritic matrix and rim materials cause rim and matrix materials to be preferentially susceptible to terrestrial oxidation, whether in curatorial and/or laboratory weathering environments (for falls) or in natural Earth-surface environments (for finds).

The CIA is predicated on the assumption of differential leaching of alkalis and alkaline earths relative to Al during terrestrial weathering. Such leaching may have occurred on a local scale even in meteorite falls recovered promptly after arrival and curated away from liquid water. In chondrites, some elements are hosted in phases that are so reactive in the presence of water (even as vapor) that even exposure to water in ostensibly dry environments (*e.g.* Antarctic cold deserts; laboratory atmosphere) results in elemental mobilization and the formation of secondary minerals (usually evaporites) (*e.g.* Velbel, 1988; Jull *et al.*, 1988; Velbel and Gooding, 1990; Velbel *et al.*, 1991). Efflorescences consisting of sulfate and carbonate evaporites (Velbel, 1988; Jull *et al.*, 1988; Velbel *et al.*, 1991; Gounelle and Zolensky, 2001; Losiak and Velbel, 2011) can form by oxidation of meteoritic sulfide and hydrolysis of anhydrous meteoritic silicates by sulfuric and terrestrial carbonic acids. Antarctic weathering of chondritic meteorites is known to leach small amounts of Mg and minor elements liberated by weathering of chondritic anhydrous silicate minerals such as olivine (Velbel *et al.*, 1991). Carbonaceous chondrites are especially vulnerable (Velbel, 1988; Losiak and Velbel, 2011). Carbonate- and sulfate-forming weathering in curatorial and laboratory processing environments have been documented for several carbonaceous chondrite groups. Reactive soluble species were remobilized and formed sulfates during curatorial storage of the CI carbonaceous chondrite Orguiel (Gounelle and Zolensky, 2001), and redistribution of carbonate during sample storage has been documented in Vigarano (CV3) (Abreu and Brearley, 2005).

The observation that the MAI and the CIA increase with terrestrial age of witnessed falls (Figures 7, 8) probably indicates terrestrial oxidation of highly reactive matrix sulfides. Sulfuric acid produced by oxidation of sulfide could react with anhydrous meteoritic Mg-silicates (*e.g.* olivine). The sulfate anion can become incorporated into evaporite veins or efflorescences such as those widely recognized on finds (Velbel, 1988; Losiak and Velbel, 2011) and more recently recognized in long-curated CI carbonaceous chondrite falls (Gounelle and Zolensky, 2001). Acid-driven dissolution of primary anhydrous
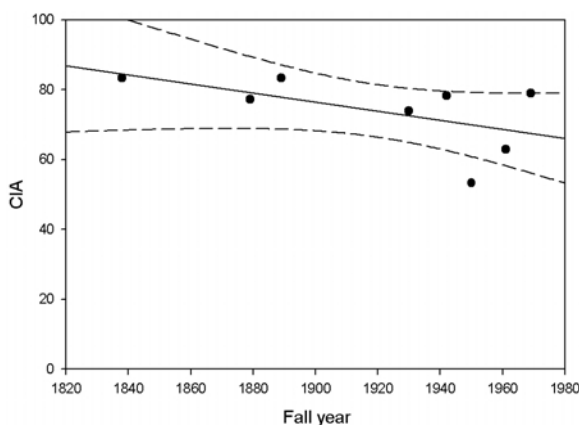
meteoritic Mg-silicates contributes Mg to terrestrial weathering products (*e.g.* Velbel *et al.*, 1991). This does not necessarily mean that CM chondrite serpentine becomes more magnesian during curatorial storage. As the MAI assumes that all analyzed elements obey serpentine stoichiometry (Browning *et al.*, 1996), analyses of matrix by methods with spatial resolutions larger than grain sizes (*e.g.* electron microprobe) may erroneously attribute to matrix silicates the redistributed Mg in locally distributed Mg-hosting weathering products.

Defocused-beam analyses of matrix would indicate depletion of highly mobile alkalis and alkaline earths because, during curatorial (and natural?) weathering, mobile species would migrate out of the matrix toward fractures and surfaces during evaporative formation of (alkali and alkaline-earth) sulfate efflorescences. The greater the extent to which such mobile elements were removed from analyzed volumes of matrix into nearby fractures, the higher the CIA of the matrix (Figure 8). Velbel *et al.* (1991) observed that during the formation of Mg-carbonate efflorescences on a terrestrially weathered ordinary chondrite, Na, K, and Ca (the mobile cations, the depletion of which is measured by the CIA) all occur in the terrestrial Mg-carbonate efflorescences at abundances within an order of magnitude of their chondritic ratios with Mg. The implied relatively low degree of fractionation between alkalis or Ca relative to Mg favors a meteoritic rather than contaminant source of the Na, K, and Ca in the efflorescences (Velbel *et al.*, 1991). Alkalis and alkaline earths leached from chondritic matrix are removed from matrix and conveyed to loci of product-mineral (evaporite efflorescence) formation (Velbel *et al.*, 1991). The CIA of carbonaceous chondrite matrix thus increases as the matrix is depleted in mobile alkalis and alkaline earths during weathering, whether that weathering is natural or curatorial (Figure 8).

Silicon, aluminum, weathering, and MAI

The MAI may not be the direct proxy for oxidized Fe that it was originally intended to be. Of the Fe values plotted (Figures 5, 6), only Fe(tot) comes more or less directly from EPMA. The "Fe^{3+}" reported by Browning *et al.* (1996, their table 3) and plotted in Figure 6 is estimated using Si and Al abundances measured by EPMA and invoking charge-balance and site-occupancy constraints for serpentine (equation 3). The (divalent) Fe reported by Browning *et al.* (1996, their table 3) and plotted in Fe/(Fe+Mg) (Figure 5) is estimated by difference from measured Fe(tot) and the Fe^{3+} estimated using equation 3 and measured Si and Al abundances (Browning *et al.*, 1996). The MAI is shown in equation 5 to depend entirely on: (1) a number of assumptions about cation site occupancies and charge balance in the tetrahedral and octahedral sheets of serpentine; and (2) analyzed abundances of Si and Al. The MAI can increase if the numerator (Al) increases or if the denominator ($2 - Si$) decreases; the denominator

decreases if Si increases from values of <2 characteristic of cronstedtite toward the ideal two tetrahedral Si per formula unit of Mg-serpentine.

Much of the following analysis (especially that linked to Figures 8 and 9) assumes that Al is immobile during the fall-age-related alteration phenomenon indicated by Figure 7. Because Al mobilization is strongly pH dependent, Al mobilization during weathering in localized acidic microenvironments may complicate the scenario described above. Mobilization of Al during terrestrial weathering of mafic rocks has recently been documented by Velbel *et al.* (2009). However, increasing the MAI by adding Al to analyzed volumes of matrix would require both acidic conditions and an abundant and/or kinetically reactive mineral source of Al. Al is not an abundant constituent of CM2 chondrites (Hutchison, 2004) and it is not commonly hosted in minerals that dissolve faster than common rock-forming silicates (Brearley and Jones, 1998). Consequently, interpreting the MAI in terms of Si mobilization appears more likely to be useful than invoking mobilization of Al.

Consider the likely greater mobility of Si than Al. Si/Al increases with increasing CIA among the CM2 falls examined by Browning *et al.* (1996) (Figure 9). Cochabamba, the only CM2 find examined by Browning *et al.* (1996), has a high CIA and the lowest Si/Al of all CM2s they studied (Figure 9). Alkalis, alkaline earths, and silica are depleted relative to aluminum from this find, consistent with open-system leaching during its pre-recovery exposure to the natural terrestrial weathering environment at its recovery site.

Similarly, alkalis and alkaline earths are depleted from the analyzed matrix volumes relative to aluminum (as indicated by increasing CIA; Figure 8) among the CM2 falls studied by Browning *et al.* (1996). However, Si/Al increases slightly with increasing CIA (Figure 9). This indicates that Si is not being leached relative to Al
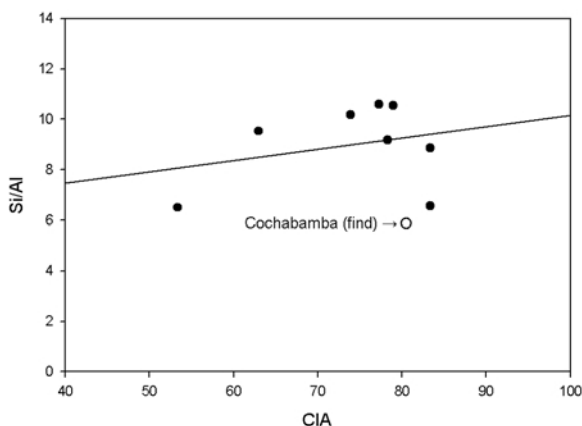

Figure 9. Si/Al (data from Browning *et al.*, 1996) *vs.* CIA (chemical index of alteration; Nesbitt and Young, 1982). Falls are indicated by filled circles; the CM2 chondrite find at Cochabamba is shown by an open circle. See text for discussion.

as is usual during open-system leaching, and may even be slightly enriched in matrix with increased weathering in CM2 falls (Figure 9), and that alteration in the falls was not simple open-system leaching of elements usually mobile (relative to Al) during weathering. Post-recovery terrestrial weathering during curation and storage, and processing (*e.g.* cutting) of samples in water might have mobilized highly mobile elements (*e.g.* alkalis and alkaline earths) but elements of intermediate mobility during moisture-driven weathering (*e.g.* silica) may have exhibited behavior more similar to closed-system weathering.

In light of equation 5, the data in Figure 8 are most simply interpreted to indicate some combination of Al increase and/or Si increase in the longest-curated CM2 falls. Silicon is released to solution during hydrolytic dissolution of olivine (*e.g.* Velbel *et al.*, 1991, their reaction 1). Thus, if an environmental acid (either terrestrial carbonic acid or terrestrial sulfuric acid formed by oxidation of meteoritic sulfides) reacts with olivine, alkali and alkaline earth cations can be leached from matrix to form evaporites (Velbel, 1988; Jull *et al.*, 1988; Velbel *et al.*, 1991; Losiak and Velbel, 2011). Such a reaction and ensuing mobilization of alkalis and alkaline earths result in depletion of those elements relative to Al (which is normally immobile during weathering) and an increase in the CIA of the analyzed matrix volume (Figure 8). The analyzed amount of Si in matrix may possibly be enriched because, unlike alkalis and alkaline earths, it appears not to be leached away from the analyzed matrices of CM2 falls (Figure 9).

The scenario described in the previous paragraph is consistent with increase of the MAI among long-curated falls by transfer of Si from anhydrous silicates such as olivine to analyzed volumes of phyllosilicate-rich CM2 matrix analyzed for determination of the MAI. Addition of Si derived from weathering of anhydrous silicates to the analyzed volumes of matrix would increase the MAI (Figure 7) by decreasing the denominator in equation 5. Alkalis and alkaline earths appear to be largely removed from analyzed matrix volumes (Figure 8) during the same process that appears to result in addition of Si to analyzed matrix volumes (Figure 9). Both Mg and Fe are released by destruction of anhydrous silicates such as olivine (*e.g.* Velbel *et al.*, 1991, their reaction 1). Neither element factors directly into either the MAI (equation 5) or the CIA (equation 6), but the long-established inverse relationship between Mg and Fe abundances in matrices of different degrees of alteration (Zolensky *et al.*, 1993) is preserved in the correlation between the MAI of Browning *et al.* (1996) and the Mg/(Fe+Mg) ratio of Zolensky *et al.* (1993) (Figure 4).

The fate of the Mg and Fe released by the proposed terrestrial weathering of anhydrous CM2 silicates such as olivine is uncertain in that any number of scenarios would satisfy requirements from observational constraints. Being major elements, small changes in either are difficult to

constrain from bulk chemical analyses of solids (Velbel, 1988). Mg and Fe may be redistributed into matrix phyllosilicates in the same manner previously proposed for pre-terrestrial aqueous alteration of CM2 chondrites by Zolensky *et al.* (1993) and, thereby, modify the MAI. Alternatively, they may be redistributed into non-phyllosilicate weathering products (*e.g.* carbonates, sulfates, oxides) retained within the analyzed volumes and attributed to serpentine structure and stoichiometry, thereby affecting the MAI. Finally, they may be removed from analyzed volumes along with other elements, the export of which increases the CIA (Figure 8), and hosted outside the analyzed volumes in efflorescence-forming minerals. Mobilization of Fe during terrestrial weathering is not a commonly expected behavior for normal weathering under oxidizing conditions (*e.g.* Velbel, 1993, and many primary references), but Fe mobilization during weathering has been documented at a variety of scales and in a variety of mineral assemblages (*e.g.* Velbel, 1989; Price and Velbel, 2000; Velbel and Barker, 2008).

The preceding paragraphs explain the observed relationships shown in Figures 4 and 7−9, including changes in the MAI with fall age, without direct reference to Fe or its oxidation state. Although MAI is intended as a proxy for Fe oxidation state, equation 5 shows that the proxy relates to Fe oxidation state at best indirectly, through the stoichiometric and charge-balance relationships embodied in the equations leading to equation 5. If sulfide oxidation contributes sulfuric acid which in turn dissolves olivine hydrolytically, thereby releasing olivine-hosted Fe, Mg, and Si, then the phenomena measured by CIA and Si/Al, including export of alkalis and Ca from matrix volumes relative to immobile Al, import of olivine-sourced Si into matrix volumes relative to immobile Al, and difficult-to-constrain mobilization behavior of Mg and Fe, may be related indirectly to Fe oxidation state, mobilization, and hosting in a manner at least somewhat consistent with the original intent of the MAI. Such a relationship as might exist is evidently not simple.

An alteration index that relates strongly to oxidation-reduction chemistry of highly reactive fine-grained constituents (as does the MAI) and is demonstrably equivocal in distinguishing terrestrial from pre-terrestrial alteration even for falls (Bland *et al.*, 2006) is probably even less useful for finds known to have long exposures (usually of uncertain duration) to terrestrial weathering before recovery. Thus, for chondritic finds in particular (but also for at least the fine-grained constituents of falls), distinguishing pre-terrestrial from terrestrial aqueous alteration poses challenges. "Whether the MAI is recording terrestrial or preterrestrial alteration remains an open question. What is apparent is that carbonaceous chondrites falls are susceptible to terrestrial weathering: determining where asteroidal alteration ends and terrestrial alteration begins is clearly a non-trivial task." (Bland *et al.*, 2006, p. 863).

Phyllosilicates and their role in the preservation of indigenous properties in carbonaceous chondrites

In addition to being the basis for MAI, serpentine-group minerals and other phyllosilicates play an important role in other phenomena in which scientifically important pre-terrestrial attributes of some carbonaceous chondrites are compromised by modifications that occur during sample processing for analysis. The search for organic carbon compounds indigenous to the parent bodies of meteorites and intentionally returned samples from solar system objects is a high priority for planetary materials research (Kebukawa *et al.* 2009; Committee on the Planetary Science Decadal Survey, 2011). Using Fourier-transform infrared (FTIR) spectroscopy to characterize organic-chemical compounds in several carbonaceous chondrite falls, Kebukawa *et al.* (2009) found that C2 chondrites with phyllosilicates in their matrices adsorbed volatile organic-carbon compounds from laboratory sample-storage materials within 1 day, between sample preparation and analysis. Similar contamination affected identically processed serpentine (antigorite), smectite (montmorillonite), and silica gel. In contrast, no such contamination occurred in an identically processed phyllosilicate-free carbonaceous chondrite of a different compositional class. Phyllosilicate minerals are expected to be among the possible host phases for organic-carbon compounds in samples to be returned by future sample return missions to carbonaceous-chondrite-like asteroids, but the same phyllosilicates will be attractive host phases for terrestrial contaminant organic-carbon compounds (Kebukawa *et al.*, 2009).

Several missions have been proposed that are designed to return samples from asteroids related to carbonaceous chondrites. The Russian Space Agency (RosCosmos) Phobos-Grunt mission (Galimov, 2010), The Japan Aerospace Exploration Agency (JAXA) Hayabusa-2 mission (Hasegawa *et al.*, 2008; Campins *et al.*, 2009), and NASA's recently selected OSIRIS-REx mission (Campins *et al.*, 2010; Delbo and Michel, 2011; Committee on the Planetary Science Decadal Survey, 2011) are all intended to return to Earth samples from asteroids (or Phobos, a moon of Mars that may be a captured asteroid) with spectroscopic indications of carbonaceous-chondrite affinities. Not all carbonaceous chondrite classes contain phyllosilicates (Dodd, 1981; McSween, 1999; Krot *et al.*, 2003; Hutchison, 2004; Weisberg *et al.*, 2006). However, experience with carbonaceous chondrite falls indicates several categories of serious oxidation-reduction, elemental mobilization, and volatile-organic contamination challenges, all involving fine-grained matrix phyllosilicates, that need to be anticipated to ensure the integrity of sought-after indigenous compositional properties of the samples after the samples are returned and enter the scientific curatorial and laboratory processing environments.

CONCLUSIONS

Carbonaceous chondrites are naturally delivered samples from asteroidal parent bodies in the outer region of the asteroid belt. Serpentine-group minerals dominate the fine-grained (rim and matrix) constituents of the CM group of carbonaceous chondrites. Fine-grained serpentines in CM2 chondrites are known to become more magnesian with increasing degree of alteration (Zolensky *et al.*, 1993). The MAI is intended to measure the extent of serpentine compositional evolution from cronstedtite to Mg-serpentine during progressive aqueous alteration, by estimating the amount of Fe that is in the Fe^{3+} state from EPMA and charge-balance and site-occupancy requirements assumed from serpentine stoichiometry. However, the estimate of Fe^{3+} depends heavily on the abundance of Al in the matrix and takes on physically unreasonable values when measured Si abundances approach complete occupancy of tetrahedral sites by Si. An additional challenge arises from the fact that, even among CM chondrite falls, with minimal exposure to Earth's ambient environment and decade- or century-scale exposure to only curatorial and laboratory environments, the MAI increases with elapsed time since fall. Furthermore, the MAI also scales with the CIA, a widely used major-element index of terrestrial weathering. Consequently, the possibility that the MAI measures pre-terrestrial (asteroidal, parent-body) aqueous alteration of serpentine-rich matrix in CM chondrites cannot be distinguished from the possibility that the MAI measures the effects of terrestrial weathering in the presence of terrestrial moisture in curatorial environments. Additionally, serpentine- and smectite-group minerals in the matrices of C2 chondrites (and probably other phyllosilicate-bearing primitive solar-system materials) are highly vulnerable to contamination by terrestrial volatile organic compounds during sample processing, storage, and analysis.

Changes in a major-element carbonaceous-chondrite alteration index based on serpentine stoichiometry and detection of terrestrial volatile-organic contaminants associated with serpentine and other phyllosilicates in carbonaceous chondrites have been documented to affect promptly recovered meteorite samples after they enter the terrestrial curatorial and analytical laboratory environments. Both examples show that scientifically important properties of carbonaceous chondritic materials can be compromised during interactions of carbonaceous-chondrite matrix with the terrestrial curatorial and laboratory environments. The association of these sample-integrity vulnerabilities with phyllosilicates must be taken into account in planning for preservation of sample integrity during processing of returned samples from proposed future sample-return missions to asteroids with spectral reflectance properties similar to carbonaceous chondrites.

ACKNOWLEDGMENTS

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