

# STOICHIOMETRIC REACTIONS DESCRIBING SERPENTINIZATION OF ANHYDROUS PRIMARY SILICATES: A CRITICAL APPRAISAL, WITH APPLICATION TO AQUEOUS ALTERATION OF CHONDRULE SILICATES IN CM CARBONACEOUS CHONDRITES

MICHAEL A. VELBEL\*

Department of Geological Sciences, 206 Natural Science Building, Michigan State University, East Lansing, Michigan 48824-1115, USA

**Abstract**—A number of chemical reactions (mass-action expressions) have been proposed to describe serpentinization of olivine in terrestrial serpentinites. Some have been applied to interpreting the formation of serpentine-group minerals in CM carbonaceous chondrites. The widely used olivine + pyroxene → serpentine (ol + px → srp) reaction is quantitatively inconsistent with observed ratios of olivine to pyroxene and olivine to serpentine in CM carbonaceous chondrites. The reaction of 5ol → 2srp is most consistent with constraints from textural observations at the scale of individual partial and complete pseudomorphs of serpentine after coarse olivine in CM chondrites, observed co-variations in modal abundances of reactant and product minerals in CM chondrites, and experimental geochemical kinetics. Furthermore, the 5ol → 2srp reaction provides insight into the mobility of solute species in the aqueous alteration environment of CM carbonaceous chondrites.

**Key Words**—CM Chondrite, Meteorite, Olivine, Serpentine.

## INTRODUCTION

Carbonaceous chondrites are meteorites with primitive chemical compositions that are understood to come from undifferentiated asteroids (*e.g.* Dodd, 1981; Hutchison, 2004). Carbonaceous chondrites of the compositionally primitive (solar composition) and rare CI (Ivuna-like) group, the CR (Renazzo-like) group, and the much more abundant (Grady, 2000) CM (Mighei-like) group (Dodd, 1981; Hutchison, 2004) all contain appreciable modal abundances of phyllosilicates; several other varieties of carbonaceous chondrites contain little or no phyllosilicate material. Because they are much more abundant and exhibit variations in phyllosilicate abundance and composition, this paper emphasizes CM2 carbonaceous chondrites (where the number refers to the petrologic type). Current thinking is that petrologic type 3 was the ‘starting material’ and that 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). The CM chondrites are mostly petrologic type 2 (CM2; Hutchison, 2004), and a variety of subdivisions have been proposed to distinguish different 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).

Serpentine-group phyllosilicates dominate the CM chondrites, constituting 67–88 vol.% of the CM chondrites examined to date (Howard *et al.*, 2009, 2011). Textural constituents of CM carbonaceous chondrites can be classified as coarse constituents and fine material. Coarse constituents (the “larger components” of Zolensky and McSween, 1988) include chondrules (the defining textural constituent of chondrites; 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; Hutchison, 2004), large mineral fragments, and refractory-element-rich calcium aluminum inclusions, CAIs (Hutchison, 2004). Fine materials in CM chondrites include matrix (fine-grained) and fine-grained rims on coarse constituents (see review by Velbel and Palmer, 2011, and references therein). Serpentine occurs in fine matrix and rims, and in coarse constituents as partial or complete pseudomorphs after (1) anhydrous phenocryst minerals in chondrules (Figure 1), and (2) isolated coarse anhydrous minerals. Matrix consisting predominantly of serpentine constitutes 57–85% of CM chondrites (McSween, 1979b). Because of their abundance and fine particle size, matrix and rim materials are particularly sensitive indicators of various alteration processes (*e.g.* Brearley, 2003, 2006).

Matrix in CM chondrites is compositionally heterogeneous at the scale of defocused-beam electron microprobe analyses, suggesting mechanical mixing of serpentines with diverse compositions, but mean and modal serpentine compositions vary systematically with

\* E-mail address of corresponding author:

velbel@msu.edu

DOI: 10.1346/CCMN.2014.0620205

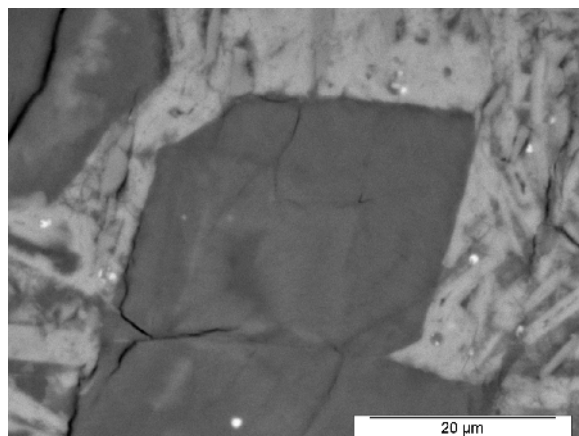


Figure 1. Pseudomorph of serpentine after altered chondrule-hosted olivine in the CM2 chondrite Nogoya. The euhedral outline of the precursor olivine is perfectly preserved. Mesostasis (intercrystalline chondrule glass) surrounding olivine crystals is altered before olivine in other CM2 chondrites. The absence of radial or concentric fractures in the altered mesostasis indicates that there was no volume change during the olivine–serpentine reaction. [This image is a close-up of the same region imaged by Velbel *et al.* (2012, figure 4a); see that paper for further discussion of this texture and phase assemblage.]

independent measures of aqueous alteration (McSween *et al.*, 1979b, 1987; Zolensky *et al.*, 1993; Browning *et al.*, 1996). Observations by transmission electron microscopy (TEM) show that ferroan serpentine-group minerals occur as solid solutions containing appreciable components of ferroan endmembers (*e.g.* cronstedtite, greenalite; Lauretta *et al.*, 2000; Zega and Buseck, 2003; Zega *et al.*, 2004, 2006; Chizmadia and Brearley, 2008) rather than as discrete endmember ferroan phyllosilicates. CM chondrite matrix, more Fe-rich than the chondrules in less-altered CM chondrites, becomes progressively enriched in more Mg-rich serpentine (more chrysotile endmember) with increase in various other measures of aqueous alteration in more altered CM chondrites (McSween and Richardson, 1977; McSween, 1979b, 1987; Zolensky *et al.*, 1993; Browning *et al.*, 1996; Howard *et al.*, 2009, 2011).

Zolensky *et al.* (1993, 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 (*e.g.* Hanowski and Brearley, 2001; Velbel *et al.*, 2012). The formation of serpentine in matrix is generally advanced even in CM chondrites in which anhydrous coarse primary-mineral constituents (*e.g.* olivine and pyroxene phenocrysts in chondrules;

isolated olivine and pyroxene fragments hosted in matrix) are unaltered. However, the increased Mg/(Fe+Mg) of matrix and rim serpentines in more altered CM chondrites suggests a shift from addition of Fe to matrix by alteration of fast-reacting minerals (especially ferroan olivine) in less-altered CM chondrites (forming Fe-rich serpentines), to increased contributions of Mg from the destruction of slower-altering forsteritic olivine at advanced-intermediate stages of aqueous alteration resulting in the formation of Mg-rich serpentines.

Matrix already exists and consists of serpentine even in CM chondrites in which the coarse chondrule olivine is unaltered, but becomes more magnesian in CM chondrites containing more altered coarse olivine. Hanowski and Brearley (2001) developed a four-stage model for the successive alteration of progressively more forsteritic olivine after the onset of the alteration of coarse olivine in chondrules. Observations from an even more altered CM chondrite were used by Velbel *et al.* (2012) to extend the Hanowski and Brearley (2001) model to Stage 5. Key attributes of the extended model are summarized in Table 1, along with related measures of aqueous alteration from the same CM chondrites on which the extended model is based, and the resulting relative abundances of mobile Fe and Mg in the solutions to which the olivine alteration would be contributing solutes at the various alteration stages. The observations and the inferences from them are all consistent with the long-expected relationship between increasingly magnesian serpentines observed in the matrices of more-altered CM chondrite and progressively more extensive alteration of the proposed Mg-source mineral, olivine (McSween and Richardson, 1977; McSween, 1979b, 1987; Zolensky *et al.*, 1993; Browning *et al.*, 1996; Howard *et al.*, 2009, 2011). The reader is directed to Velbel and Palmer (2011) and Velbel *et al.* (2012), for more detailed summaries of the recent state of knowledge of serpentine formation and compositional variation in fine-grained (matrix and rim) serpentine, and in serpentine formed by pseudomorphous replacement of coarse olivine (in chondrules and isolated fragments), respectively.

Primary anhydrous silicate minerals (*e.g.* pyroxene, olivine) in three groups of carbonaceous chondrites (CI, CR, and CM) were subjected to aqueous alteration (Brearley, 2003, 2006). Numerous workers (*e.g.* Bunch and Chang, 1980; Barber, 1985; Browning *et al.*, 2000; Hanowski and Brearley, 2001; Velbel *et al.*, 2012) have noted that replacement textures of primary coarse-grained olivines and pyroxenes in the abundant and well studied CM chondrites resemble terrestrial aqueous-alteration textures of ferromagnesian silicate minerals in terrestrial mafic/ultramafic rocks. Such textures include partial and complete pseudomorph and alteromorphic replacement (after euhedral and anhedral primary minerals, respectively; Delvigne, 1998), meshwork

serpentinization textures (Wicks and Whittaker, 1977), and “centripetal replacement” in which entire grains or fracture-bounded remnants are replaced from the margin inward (*e.g.* Delvigne, 1998; Boudier *et al.*, 2010). Hanowski and Brearley (2001) and Velbel *et al.* (2012) both reported textural observations from which they inferred that pseudomorphous replacement of coarse olivine by serpentine in chondrules and isolated coarse olivine grains is isovolumetric. Such textures and compositional observations constrain elemental redistribution from primary anhydrous silicates (*e.g.* olivine) to serpentine and to surrounding phases during serpentinization (*e.g.* Velbel *et al.*, 2012).

Given the apparently important role of alteration of coarse olivine in providing the Mg required to make matrices in more-altered CM chondrites more magnesian, the present study examines a number of different chemical reactions that have been proposed to describe terrestrial serpentinization, and assesses their suitability for the interpretation of serpentine pseudomorphs after coarse olivine in light of textural and modal-abundance data from CM2 carbonaceous chondrites. Note that matrix already consists predominantly of serpentine even before Stage 1 alteration (in the Hanowski and Brearley, 2001, model) of coarse constituents in chondrules begins. Furthermore, this paper distinguishes between (early) formation of matrix and the ‘cronstedtite’ that dominates it, and (late) alteration of coarse-grained/coarsely crystalline olivine. Discrete endmember cronstedtite (*sensu stricto*) does not occur in CM2 chondrites; cronstedtite occurs as one endmember in a solid-solution series. There are two solid-solution trends in the serpentine-group minerals of CM2 chondrites; one between chrysotile and greenalite endmembers, the other between chrysotile and cronstedtite. Discrete masses of serpentine-structured material with abundant ferric and tetrahedral iron (cronstedtite *sensu lato*) occur in the fine-grained constituents (matrix and rims) of many CM2 chondrites (Müller *et al.*, 1979; Lauretta *et al.*, 2000; Zega and Buseck, 2003; Zega *et al.*, 2004, 2006; Chizmadia and Brearley, 2008), but not among the serpentine pseudomorphs after coarse anhydrous primary silicates that are the target of this study. The matter of whether cronstedtite in rim and matrix might also be produced by isovolumetric reactions remains to be resolved by future work, but Müller *et al.* (1979) argued explicitly against this possibility. In summary, much of the formation of Fe-rich serpentine-group minerals in CM2 rim and matrix (*e.g.* abundant cronstedtite component in the serpentine solid-solution) has occurred before the phenomenon being investigated in the present study has begun. After exploring the usefulness of different serpentinization reactions, this paper also briefly explores some implications of the choice of reaction for interpretation of elemental mobility in the aqueous solutions that drove serpentinization on the CM2 chondrite parent-body/ies.

## MASS-ACTION EXPRESSIONS AND ASSOCIATED ELEMENTAL MASS-TRANSFER DURING AQUEOUS ALTERATION OF OLIVINE TO SERPENTINE

### *Olivine-serpentinization reactions*

At the scale of meteorite-specimen bulk chemistry, aqueous alteration of carbonaceous chondrites is isochemical (DuFresne and Anders, 1962; Clayton and Mayeda, 1999; Young *et al.*, 2003; Brearley, 2003, 2006; Rubin *et al.*, 2007; Bland *et al.*, 2009). However, every individual reaction between anhydrous primary minerals and hydrous alteration products requires and/or evolves some elements or chemical species (at minimum, water) other than those hosted entirely within the reactant and/or product minerals. The elemental mobility required by a variety of olivine-alteration and olivine-serpentinization reactions that have been proposed for terrestrial serpentinization and similar reactions in extraterrestrial materials are explored here.

A number of stoichiometric mass-action expressions for the serpentinization of olivine have been proposed. For the purposes of illustration, Mg endmembers are used here to introduce different variants of serpentinization reactions. As already noted above, much of the formation of ferroan serpentine-group minerals in matrix (*e.g.* abundant cronstedtite component in the serpentine solid-solution) has occurred before pseudomorphous replacement of olivine by Mg-rich serpentine discussed herein has begun (before Stage 1 of Table 1). After the onset of Stage 1 olivine alteration (Hanowski and Brearley, 2001), either cronstedtite-rich serpentines reacted with Mg to form more magnesian serpentine (*e.g.* Zega *et al.*, 2006), or newly formed Mg-rich serpentine diluted the previously formed matrix; in either case, CM2 matrices are more Mg-rich with more advanced progress through Stages 1 through 5 of Table 1. Thus, formation of cronstedtite-rich matrix serpentines falls outside the scope of this work, which emphasizes pseudomorphism of coarse olivine after most of the ferroan matrix material has already formed. Also, because much terrestrial serpentinization of olivine involves highly forsteritic olivine (Fo<sub>~85-95</sub>), Mg endmembers are used in most of the literature from which the reactions are cited.

The most common (*e.g.* Martin and Fyfe, 1970; Coleman, 1971; Hemley *et al.*, 1977; Wegner and Ernst, 1983; O’Hanley, 1996; Viti and Mellini, 1998; Schulte *et al.*, 2006; Evans, 2008, reaction 1) is one in which both Mg and Si are retained in mineral products at some spatial scale, so that two formula units of olivine are destroyed by reaction with water, forming one formula unit each of serpentine and brucite (reaction 1).



A reaction of the same form that conserves both Mg and Si with the same proportions of phases (2ol → srp + brc;

Table 1. Textural criteria, ratios of hydrous/anhydrous-silicate modal abundances, and examples of meteorites showing different extents of aqueous alteration in CM2 chondrules (adapted from Hanowski and Brearley, 2001).

Stage (Hanowski and Brearley, 2001)	1	2	3	4	5*	
Matrix silicates entirely of serpentine and mesostasis completely altered; alteration of:	Fa in Type IIA chondrules Fo in chondrules Metal/sulfide grains in chondrules	Unaltered	Incipient	Advanced	Nearly complete	Nearly complete
		Unaltered	Unaltered	Incipient	Moderate	Advanced
		Small grains, completely	Larger grains, completely	Larger grains completely	All grains, completely	All grains, completely
Inferred Fe and Mg content in fluid	Very high Fe	High Fe	High Mg	Very high Mg	Even higher Mg	
Phyllosilicate/anhydrous modal abundance ratio (Howard <i>et al.</i> , 2011)	Murchison (3.10) Murray (3.24)	3.74		3.94	4.09	
Meteorite(s) (and Rubin <i>et al.</i> , 2007 petrologic sub-type)	Murchison (CM2.5) Murray (CM2.4/5)	Mighei (CM2.3)	LEW 90500	ALH 81002	Nogoya (CM2.2)	

Qualitative criteria for stages 1–4 adapted from Hanowski and Brearley (2001).

\* Extended to stage 5 by Velbel *et al.* (2012). Additional data from Rubin *et al.* (2007) and Howard *et al.* (2011).

abbreviations from Kretz, 1983) but real rather than endmember mineral compositions were used by Bach *et al.* (2006). The volumetric relationships among the reactants and products for reaction 1 were illustrated by O’Hanley (1996) as follows.

$$88 \text{ cm}^3 \rightarrow 111 \text{ cm}^3 + 25 \text{ cm}^3 = 137 \text{ cm}^3 \quad (1a)$$

The 53% volume increase (equation 1a) illustrates the “Volume Problem” of serpentinization (see reviews by Coleman, 1971, and O’Hanley, 1996), in which solid volume must have increased as a consequence of serpentinization, but for which field evidence consistent with demonstrable structural volume increase was long lacking (O’Hanley, 1992). Using molar volumes (Table 2) for minerals from Smyth and Bish (1988),

the solid volume relationships before and after reaction can be expressed as follows.

$$87.2 \text{ cm}^3 \rightarrow 107.3 \text{ cm}^3 + 24.5 \text{ cm}^3 = 131.8 \text{ cm}^3 \quad (1b)$$

This corresponds to a 51% volume increase (Table 3).

Several other stoichiometric reactions have been used in support of chemical and/or isotopic modeling of aqueous alteration in carbonaceous chondrites. In one (originally written for terrestrial serpentinization by Graham, 1917; Hostetler *et al.*, 1966; Martin and Fyfe, 1970; Viti and Mellini, 1998; applied to aqueous alteration of carbonaceous chondrites by Clayton and Mayeda, 1999; Cohen and Coker, 2000; Guo and Eiler, 2007), one formula unit of olivine and one formula unit of pyroxene react with water to form one formula unit of

Table 2. Molar volumes of minerals relevant to serpentinization and/or CM chondrites.

Mineral group	Mg endmember			Fe endmember		
	Name	Symbol	Molar volume (cm <sup>3</sup> /mol)	Name	Symbol	Molar volume (cm <sup>3</sup> /mol)
Olivine	Forsterite	Fo	43.6	Fayalite	Fa	46.3
Pyroxene	Enstatite (ortho)	En	62.7	Ferrosilite (ortho)	Fs	65.9
Serpentine	Lizardite	Lz	107.3			
	Talc	Tlc	136.6			
	Brucite	Brc	24.5			
	Magnesite	Mgs	28.0			

Mineral symbols from Kretz (1983).

Molar volumes from Smyth and Bish (1988).

The actual formula for the Mg-rich lizardite for which Smyth and Bish (1988) determined the molar volume is  $(\text{Mg}_{2.79}\text{Fe}_{0.04}\text{Fe}_{0.10}\text{Al}_{0.07})^{3+}(\text{Si}_{1.83}\text{Al}_{0.17})\text{O}_5(\text{OH})_4$ .

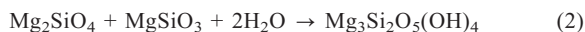
Table 3. Stoichiometric coefficients of minerals and chemical species in chondrite-relevant Mg-endmember olivine alteration reactions.

Reaction	OI	Px	Srp	Tlc	Water	CO <sub>2</sub>	H <sup>+</sup>	H <sub>4</sub> SiO <sub>4</sub>	Mg <sup>2+</sup>	Brc	Mgs	ΔV(%)	Source
1	-2	0	1	0	-3	0	0	0	0	1	0	+51	O'Hanley (1996)
2	-1	-1	1	0	-2	0	0	0	0	0	0	+0.65	Graham (1917) Clayton and Mayeda (1999) Cohen and Coker (2000) (nearly isovolumetric)
3	-4	0	0	1	-1	-5	0	0	0	0	5	+59	Young <i>et al.</i> (1999)
4	-3	0	2	0	-2	0	0	-1	0	0	0	+64	Graham (1917) O'Hanley (1996)
5	-2	0	1	0	-1	0	-2	0	1	0	0	+23	This study
6	-5	0	2	0	-2	0	-8	1	4	0	0	-1.6	This study (nearly isovolumetric)

Mineral symbols from Kretz (1983).

Stoichiometric coefficients are negative for minerals consumed during forward reactions, positive for minerals produced. Volumetric changes based on molar volumes from Smyth and Bish (1988) (see Table 2 and text).

serpentine (ol + en → srp; abbreviations from Kretz, 1983) (reaction 2).

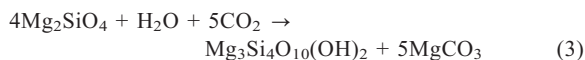


Using molar volumes (Table 2) for forsterite, enstatite, and serpentine from Smyth and Bish (1988), solid volumes before and after reaction can be determined (2a).

$$43.6 \text{ cm}^3 + 63 \text{ cm}^3 = 106.6 \text{ cm}^3 \rightarrow 107.3 \text{ cm}^3 \quad (2a)$$

Like the classic serpentinization reaction 1, all Mg and Si released by destruction of primary anhydrous silicates is retained in solid products. Unlike the classic reaction 1, solid volume is within 1% of isovolumetric for this reaction (Table 3).

In another olivine alteration reaction applied to modeling of aqueous alteration in carbonaceous chondrite parent bodies (Young *et al.*, 1999), four formula units of olivine react with water and carbon dioxide to form one formula unit of talc and five formula units of magnesite (4ol → tlc + 5mgs; abbreviations from Kretz, 1983) (reaction 3):

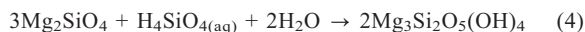


Using molar volumes (Table 2) for minerals from Smyth and Bish (1988), solid volumes before and after reaction can be calculated (3a).

$$174.4 \text{ cm}^3 \text{ olivine} \rightarrow 136.6 \text{ cm}^3 \text{ talc} + 140 \text{ cm}^3 \text{ magnesite} \\ (4 \times 43.6 \text{ cm}^3/\text{mol}) \quad (5 \times 28.0 \text{ cm}^3/\text{mol}) \quad (3a)$$

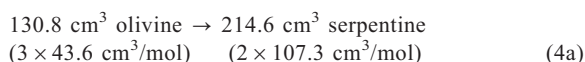
In this reaction, the product mineral assemblage invokes talc as a simplified proxy for smectite-group phyllosilicate (which occurs in the more rare petrologic type CII carbonaceous chondrites; Dodd, 1981; Hutchison, 2004), and magnesite for the carbonate minerals of carbonaceous chondrites (Young *et al.*, 1999). The 59% volume increase consequent upon this reaction is similar to that of the classic olivine to serpentine plus brucite reaction 1 (Table 3).

All the aforementioned previously used reactions assume reaction with water (plus or minus carbon dioxide), and invoke the assumption that all Mg and Si released during alteration of primary anhydrous silicate minerals is retained in their alteration products (Table 3). Less restrictive reactions involving water can be written, *e.g.* if all Mg released during destruction of olivine is retained in serpentine but Si is not similarly restricted, reaction 4 can be written.



(3ol → 2srp; modified from Graham, 1917; Hostetler *et al.*, 1966; Coleman, 1971; O'Hanley, 1996; Viti and Mellini, 1998; see also Frost and Beard, 2007; applied to CM chondrites by Howard *et al.*, 2009). Using molar volumes (Table 2) for minerals from Smyth and Bish

(1988), solid volumes before and after reaction can be shown (4a).

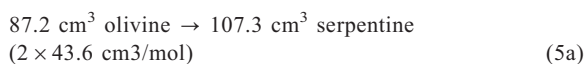


The 64% volume increase consequent upon this reaction is similar to that of the classic olivine to serpentine plus brucite reaction 1 (Table 3).

Alternatively, if all Si released during destruction of olivine is retained in serpentine but Mg is not similarly restricted, reaction 5 results.



A similar 2ol  $\rightarrow$  srp reaction with different descriptions of the mobile solute species was used by Coleman (1971). Using molar volumes (Table 2) for minerals from Smyth and Bish (1988), solid volumes before and after reaction can be calculated (5a).

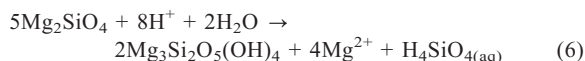


The 23% volume increase consequent upon this reaction (2ol  $\rightarrow$  srp) is smaller than that of the classic olivine to serpentine plus brucite reaction 1 (Table 3). Condie and Madison (1969) invoked both importation of Si (as in reaction 4, but unlike reaction 5) and export of Mg (not a phenomenon of reaction 4, but common in many other reactions including reaction 5) to explain observed whole-rock bulk-compositional relationships of serpentinized dunite, and also inferred volume expansion; these relationships are consistent with both reactions (4) and (5) for whole-rock-scale serpentinization.

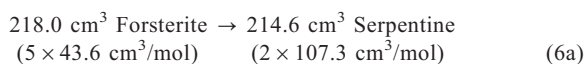
An isovolumetric reaction for the hydration of forsterite to serpentine + brucite was written by O'Hanley (1996, p. 15) who noted that mobile products included excess Mg and Si. The reaction was dismissed by O'Hanley (1996) on the grounds that Mg and Si metasomatism is not observed in the rocks surrounding terrestrially serpentinized rock bodies. Other isovolumetric reactions (*e.g.* reactions not producing brucite) have not yet been considered for application to carbonaceous chondrites. Velbel and Barker (2008) and Velbel *et al.* (2009) observed replacement textures consistent with isovolumetric replacement by several different phyllosilicates after several different primary minerals (chain-silicates) during terrestrial weathering. They also reported that unexpected elemental mobility is required during early weathering for phyllosilicates of the observed compositions to isovolumetrically replace primary minerals of known composition. According to Velbel and Barker (2008), Fe had to be imported into the pseudomorphic-replacement micro-environment in order to produce nontronitic smectite of the observed composition from the weathering of pyroxenes of the observed composition in the naturally weathered terrestrial pyroxenite they studied. Similarly, Al had to be imported into the partially pseudomorphic

(Velbel *et al.*, 2009) (septoalteromorphic, in the terminology of Delvigne, 1998) microenvironment to produce kaolin-group minerals from hornblende, and Price *et al.* (2013) identified the external source mineral of the required Al.

Following the approach of Velbel and Barker (2008) and Velbel *et al.* (2009), a reaction describing isovolumetric replacement of olivine by serpentine can be written (reaction 6):



A similar 5ol  $\rightarrow$  2srp isovolumetric reaction with different descriptions of the mobile solute species was used by Hostetler *et al.* (1966) and Thayer (1966). Using molar volumes (Table 2) for minerals from Smyth and Bish (1988), solid volumes before and after reaction are expressed as follows (6a):



This reaction (5ol  $\rightarrow$  2srp) is nearly isovolumetric, with a decrease in volume of <2% (Table 3). This reaction explicitly embodies the hydrolysis and hydration aspects of serpentinization reactions discussed by Evans (2008).

The discussion of Plümper *et al.* (2012) on isovolumetric replacement of olivine by serpentine during terrestrial serpentinization is for the most part superb. However, their reaction 8 is based on oversimplifications (by rounding) of the molar volumes of olivine and serpentine. The molar volume of forsterite was over-estimated by Plümper *et al.* (2012) (they used 50 cm<sup>3</sup>/mol instead of the actual value of 43.6 cm<sup>3</sup>/mol) and underestimated the molar volume of serpentines (they used 100 cm<sup>3</sup>/mol instead of the actual value of 107.3 cm<sup>3</sup>/mol). This results in some misleading consequences for the resulting mass-action expression, specifically the ratios of olivine to serpentine formula units and the stoichiometric coefficients of the mobile solutes. Using oversimplified molar volumes resulted in a 2:1 olivine:serpentine ratio instead of the correct value of 5:2 (reaction 6 in the present study). The 2:1 ol:srp reaction of Plümper *et al.* (2012) does not produce mobile Si as isovolumetric serpentinization of olivine by serpentine should when written in the volumetrically correct form of Hostetler *et al.* (1966), Thayer (1966), and reaction 6 above. As Plümper *et al.* (2012) were not concerned with and, therefore, did not discuss Si mobility, their sound qualitative conclusions about Mg mobility are not affected by this approximation, but this is an example of how seemingly inconsequential simplifications useful in one context can have negative consequences in other contexts.

The six reactions examined above are not an exhaustive survey of all possibilities (for some other reactions, see also Hostetler *et al.*, 1966; Schulte *et al.*,

2006; and Frost and Beard, 2007). They do, however, include several that have been applied previously to carbonaceous chondrites, and they illustrate several important aspects of choosing appropriate reactions for interpreting the geochemical/cosmochemical conditions under which aqueous alteration occurred:

(1) All describe aqueous alteration of olivine, but to different phyllosilicate products; most reactions apply to production of serpentine, but reaction 3 invokes talc as a proxy for smectite-group minerals known from a small number of chondrites.

(2) Some reactions produce ancillary non-phyllosilicate products (brucite, magnesite) and may not be appropriate to situations lacking the required abundances of such products within pseudomorphs/alteromorphs after olivine. For example, note that direct application of reaction 1 would be appropriate for systems in which serpentine and brucite were formed in equimolar abundances. Brucite is documented from Nogoya (Bunch and Chang, 1980), and the brucite-like hydroxide layer in discrete tochilinite and interstratified tochilinite-serpentine common in CM chondrites (Mackinnon and Zolensky, 1984; Tomeoka *et al.*, 1989; Buseck and Hua, 1993) also occurs in Nogoya (Zolensky *et al.*, 1993) and may serve as a brucite-like sink for Mg not taken up in other alteration products. Recent whole-sample quantitative X-ray diffraction analyses detected but could not quantify abundances of tochilinite or tochilinite-serpentine intergrowths (Howard *et al.*, 2009, 2011). Furthermore, all previously documented occurrences of tochilinite or interstratified serpentine-tochilinite have been in matrix and rims; the fact that these brucite-like layers occur 'outside' the pseudomorphs/alteromorphs after olivine means that brucite-like layers are not among the products the volume of which must be considered 'within' the pseudomorphs/alteromorphs described by the proposed reactions.

(3) The ratio of olivine destroyed to serpentine formed varies among serpentine-forming reactions, from 1.5 (reaction 4) to 2.5 (reaction 6), even if no other reactants (*e.g.* pyroxene; reaction 2) are involved (Table 3). Consequently, the mere coexistence of olivine and serpentine (or olivine and serpentine and brucite, or olivine and serpentine and interstratified tochilinite-serpentine) in a phase assemblage is not sufficient to identify the reaction responsible. Instead, quantitative modal analysis (*e.g.* Howard *et al.*, 2009, 2011) is required, and must be of sufficient sensitivity to discriminate among the different co-variations of olivine and serpentine expected from the different reactions.

#### *Assessing the suitability of different serpentinization reactions for application to CM chondrites*

Generally, the material immediately surrounding pseudomorphs/alteromorphs after individual coarse olivine crystals/grains in carbonaceous chondrites contains no systematic evidence (*e.g.* demonstrably pre-terrestrial,

indigenous radial or concentric fractures) of volume change (Hanowski and Brearley, 2001; Velbel *et al.*, 2012). Within porphyritic olivine chondrules, mesostasis is usually the first chondrule silicate phase to alter to phyllosilicates (Fuchs *et al.*, 1973) while ferroan olivine is still unaltered (Hanowski and Brearley, 2001, their Stage 1). The commonly observed perfect pseudomorphism of serpentine after olivine (*e.g.* figure 4b of Velbel *et al.*, 2012) combined with the absence of radial or concentric fractures within the pseudomorphs, between them and their surroundings, and in the surrounding previously altered mesostasis (Figure 1), all suggest negligible volume change during serpentinization of single olivine crystals. Therefore, at the scale of the individual coarse primary olivine grains and their alteration products in CM chondrites, partial and complete replacement of olivine by serpentine in CM2 chondrites was isovolumetric (*e.g.* Hanowski and Brearley, 2001). On this basis, reactions 1, 3, 4, and 5 can be dismissed; they are not accurate descriptions of 'mineral-scale' alteration in CM2 chondrites (although they may still be applicable to 'larger-than-grain-scale' alteration such as that reported by Lee *et al.* (2012), which is beyond the scope of this paper).

Reactions 2 and 6 are both isovolumetric within a few volume percent. However, they are not equally consistent with the ensemble of available observations. Olivine alteration in CM chondrites can and must proceed with mass-action expressions other than reaction 2 ( $ol + px \rightarrow srp$ ). The mole-for-mole stoichiometric coupling of olivine and pyroxene destruction required by reaction 2 is inconsistent with a number of observations. These include: (1) The generally unequal abundances of olivines and pyroxenes in CM chondrites (*e.g.* Rosenberg *et al.*, 2001; Bland *et al.* 2004; Howard *et al.*, 2009, 2011); (2) the observed depletion ratios of CM olivine and pyroxene during aqueous alteration (data from Howard *et al.*, 2011); (3) the observed ratios of CM olivine decrease to CM serpentine increase during aqueous alteration (data from Howard *et al.*, 2011); (4) the known unequal mineral-solution reaction rates of these minerals over the temperature range of interest (*e.g.* Goldich, 1938; Velbel, 1993; Brantley, 2005, 2008).

The next several paragraphs elaborate on several of these points.

Some CM and CM-like primitive chondrites (Murchison, Cold Bokkeveld, Nawapali, Cochabamba, Acfer 094, El-Quss Abu Said) contain abundant fine-grained pyroxene along with olivine in their matrices (Barber, 1981; Greshake, 1997; Nakamura *et al.*, 2008), which may have reacted simultaneously with matrix olivine consistent with reaction 2, but this is only relevant to the alteration of coarse-grained olivine if coarse or matrix pyroxene were available in abundances sufficient for reaction 2 ( $ol + px \rightarrow srp$ ) to both proceed in matrix olivine and continue in coarse olivine (as observed by Hanowski and Brearley, 2001, and Velbel *et*

*al.*, 2012) before the matrix pyroxene was exhausted. The paucity of primitive (petrologic type 3) CM chondrites presently limits the ability to quantitatively test such modal-abundance relationships. However, some CM chondrites reach high levels of olivine depletion even after pyroxene has been completely depleted (Howard *et al.*, 2011). This could be taken to mean that the pyroxene was depleted in a coupled ol + px → srp reaction, that olivine occurred in excess of pyroxene, that olivine reacted more slowly, and, therefore, that the olivine was not completely altered. Alternatively, this could indicate that olivine alteration can continue even in the absence of simultaneous pyroxene alteration. In the absence of better quantitative evidence for high pre-alteration pyroxene abundances in what are now petrologic type 2 CM chondrites, the case for applying reaction 2 to pseudomorphic replacement of coarse olivine is weak.

From the least altered to the most altered CM2 chondrites examined by quantitative X-ray diffraction (XRD), the modal volume percentage sum of anhydrous silicates (olivine and pyroxene) decreases by almost exactly same amount as the modal volume percentages of serpentine-group phyllosilicates increase (Howard *et al.*, 2011: table 1, figure 5). Within uncertainties (~20% relative), these measurements appear consistent with replacement reaction 2 in which the volume of serpentine produced equals the volume of olivine and pyroxene destroyed. More detailed examination of the ‘molar’ ratios associated with the aforementioned modal proportions reveals the failure of reaction 2 to conform to observations, however. From the least altered to the most altered CM2 chondrites examined by quantitative XRD, modal volume percentages of olivine decrease from 23.1% to 4.0% (a difference of 19.1% modal) while pyroxene decreases from 9.8% to 0% (a difference of 9.8% modal)

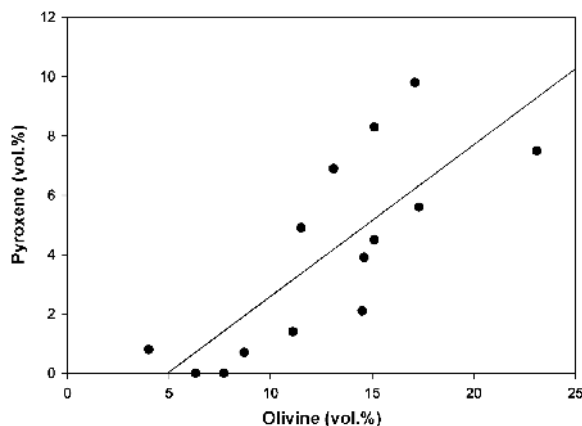


Figure 2. Modal percentages of olivine and pyroxene in CM chondrite falls and finds QUE 97990, Y 791198, Murchison, Murray, Mighei, ALHA81002, Nogoya, Essebi, Cold Bokkeveld, QUE 93005, ALH 83100, MET 01070, MET 01070 (2), and SCO 06043, (from highest to lowest modal olivine abundance) with linear regression. (Data from Howard *et al.*, 2011, table 1.)

(Figure 2, data from Howard *et al.*, 2011). In other words,  $\Delta\text{ol(modal)} \approx 2 \times \Delta\text{px(modal)}$ ; ~2 modal % olivine is consumed by the actual alteration reaction for every 1 modal % pyroxene consumed. Because the molar volumes of olivine and pyroxene differ substantially (reaction 2a), the ‘molar’ proportion of olivine/pyroxene consumed is substantially different (7).

$$(19.1 \text{ cm}_{\text{ol}}^3/9.8 \text{ cm}_{\text{px}}^3) \times (63 \text{ cm}_{\text{px}}^3 \text{ mol}_{\text{px}}^{-1}/43.6 \text{ cm}_{\text{ol}}^3 \text{ mol}_{\text{ol}}^{-1}) = 2.82 \text{ mol}_{\text{ol}}/\text{mol}_{\text{px}} \quad (7)$$

Observed modal-abundance depletions of olivine and pyroxene (Figure 2; Howard *et al.*, 2011) thus show that  $\Delta\text{ol(molar)} \approx 3 \times \Delta\text{px(molar)}$ ; nearly three moles of olivine are depleted by aqueous alteration reactions for each mole of pyroxene depleted. These ‘observed’ proportions ( $\Delta\text{ol(molar)} \neq \Delta\text{px(molar)}$  by nearly a factor of three) are incompatible with the equimolar consumption of olivine and pyroxene ( $\Delta\text{ol(molar)} = \Delta\text{px(molar)}$ ) as required by widely used reaction 2.

Finally, the observed value of the ratio of molar olivine depleted to molar serpentine produced in CM2 chondrites (determined from the ranges of modal depletion of olivine and modal increase of serpentine as measured by Howard *et al.*, 2011, as shown in equation 8) is 2.9.

$$(19.1 \text{ cm}_{\text{ol}}^3/16.2 \text{ cm}_{\text{srp}}^3) \times (107.3 \text{ cm}_{\text{srp}}^3 \text{ mol}_{\text{srp}}^{-1}/43.6 \text{ cm}_{\text{ol}}^3 \text{ mol}_{\text{ol}}^{-1}) = 2.90 \text{ mol}_{\text{ol}}/\text{mol}_{\text{srp}} \quad (8)$$

This demonstrates that reaction 6 (5ol → 2srp), which yields the highest ol:srp ratio (2.5) of any reaction considered here (Table 3), conforms most closely to the observed co-variations between olivine depletion and serpentine enrichment in altered CM carbonaceous chondrites.

The several lines of reasoning summarized in the previous paragraphs demonstrate that reaction 2 (ol + px → srp) is not a satisfactory description of serpentinization phenomena in CM chondrites. In contrast, the isovolumetric 5ol → 2srp reaction 6 as written is appropriate for replacement of anhydrous silicates ‘at the grain scale’, as water in the products was not initially present within the volume of the anhydrous reactant-mineral grain that was replaced, and was instead added to the volume within which replacement of the initially parent-mineral occurred. Volumes computed for all the reactions summarized above are for silicate and hydroxide (and in one case, carbonate) mineral phases only. If the water involved in the reactions was initially present as ice, initial (reactant) solid volumes would have to include the volume of reactant ice. This can be an important concern at the whole-rock scale (*e.g.* Clayton and Mayeda, 1999; Cohen and Coker, 2000; Bland *et al.*, 2009; Lee *et al.*, 2012). The reactions written above apply without such modification, however, in the case of ‘grain-scale’ replacement (isovolumetric or otherwise) of initially anhydrous silicates (*e.g.* olivine). Any water incorporated



into a pseudomorph or alteromorph after an anhydrous reactant silicate (and that may or may not result in product volume being different from reactant volume) originated from outside the anhydrous reactant mineral, would not be part of the pre-alteration volume of the reactant mineral grain, and would have been added to the pseudomorph or alteromorph from outside its initial volume.

There exists a hierarchy of spatial scales in rocks subjected to aqueous alteration, including individual pseudomorphs (each of which must generally be a small open geochemical alteration microsystem, *sensu* Nahon, 1991 and Delvigne, 1998) and the whole rock. At the bulk-sample scale, hydration of CM2 chondrites appears isochemical (except for the O and H of water), with little evidence for metasomatic element mobility beyond the whole-rock scale (DuFresne and Anders, 1962; Clayton and Mayeda, 1999; Young *et al.*, 2003; Brearley, 2003, 2006; Rubin *et al.*, 2007; Bland *et al.*, 2009). On the basis of the preceding examination of reactions 1–6, however, isovolumetric replacement of coarse olivine by serpentine as described by reaction 6 ( $5\text{ol} \rightarrow 2\text{srp}$ ) satisfies presently understood textural, modal-abundance, and kinetic constraints for replacement of olivine by serpentine at the scale of an individual pseudomorph. At the scale of an individual pseudomorph, reaction 6 requires open-system behavior – several mobile species must be added to ( $\text{H}^+$ ,  $\text{H}_2\text{O}$ ) or removed from ( $\text{Mg}^{2+}$ ,  $\text{H}_4\text{SiO}_{4(\text{aq})}$ , and in real, non-endmember solid solutions, Fe) the pseudomorphic/alteromorphic replacement volume, by elemental mass transfer between the pseudomorphed volume and its surroundings. Each such individual volume described by reaction 6 (or a similar reaction for other primary-secondary mineral pairs) is only a small fraction of the whole rock.

Alteration may be isochemical at the whole-rock scale if smaller contained ‘importing’ and ‘exporting’ volumes experienced compensating mass transfers resulting in whole-rock scale mass balance (i.o.w., the large closed system consists of small local open systems). The import-export (open system) behavior of the volumes that are pseudomorphic after olivine as described by reaction 6 can be used to gain additional insight about elemental mass transfer among different volumes within an altered CM2 chondrite from compositional data on olivines and the serpentines that replace them (*e.g.* Hanowski and Brearley, 2001; Velbel *et al.*, 2012), as will be demonstrated for  $\text{H}^+$ ,  $\text{H}_2\text{O}$ ,  $\text{Mg}^{2+}$ ,  $\text{H}_4\text{SiO}_{4(\text{aq})}$ , and Fe in the next contribution in this series.

### CONCLUSIONS

A number of chemical reactions (mass-action expressions) have been proposed to describe serpentinization of olivine in terrestrial serpentinites. Among those serpentinization reactions that have been proposed to explain replacement of olivine by serpentine in CM2 carbonaceous chondrites, the isovolumetric  $5\text{ol} \rightarrow 2\text{srp}$  reaction

best satisfies presently understood textural, modal-abundance, and kinetic constraints. This isovolumetric replacement of olivine by serpentine requires that several solute and/or solvent chemical species be added to or removed from the pseudomorphic/alteromorphic replacement volume. Isochemical whole-rock-scale aqueous alteration of CM2 chondrites may be a consequence of element exchange between smaller (*e.g.* individual-pseudomorph-scale) volumes with ‘importing’ and ‘exporting’ (open system) behavior for different elements, that sum over all microsystem volumes to whole-rock-scale mass balance and bulk-sample isochemical alteration because of compensating mass transfers among the smaller-scale internal alteration microsystems.

### ACKNOWLEDGMENTS

The author thanks his colleagues Mike Zolensky, Eric Tonui, Ian Mackinnon, Oliver Plümer, Joe Nuth, Hap McSween, Adrian Brearley, Alexander Krot, Maggie McAdam, Jessica M. Sunshine, Kieran T. Howard, Tim McCoy, Bob Clayton, Alan Rubin, Ed Young, Eric Palmer, Frans Rietmeijer, Jeff Grossman, and Anton Kearsley, for helpful discussions and correspondence; Craig Schwandt, Loan Le, Jason Price, Cari Corrigan, Amy McAdam, Angela Donatelle, Dan Snyder, Anna Losiak, Kathleen Jeffery, Gabrielle Tepp, Laurel Eibach, and Mike Wright for assistance in the laboratory and stimulating discussions; the Meteorite Working Group and the staff of the Astromaterials Acquisition and Curation Office at NASA-JSC for samples; Ewa Danielewicz and Abigail Tirrell (Michigan State University Center for Advanced Microscopy) for assistance with the scanning electron microscopy; and Brother Guy Consolmagno, S.J., for helpful and encouraging perspectives on long-term scholarly enterprises. This research was supported by two Michigan Space Grant Consortium Research Seed Grants, a Michigan State University Honors College Honors Research Seminar, and NASA Grant NAG 9-1211. Thoughtful, thorough reviews by Kieren Howard and an anonymous reviewer are greatly appreciated. This paper was written during the first author’s tenure as a Smithsonian Senior Fellow at the Division of Meteorites, Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution. He is most grateful to Cari Corrigan and Ed Vicenzi for hosting the visit, and to his co-hosts, and Glenn MacPherson, Tim McCoy, and Linda Welzenbach, for stimulating conversations.

### REFERENCES

- Bach, W., Paulick, H., Garrido, C.J., Ildefonse, B., Meurer, W.P., and Humphris, S.E. (2006) Unraveling the sequence of serpentinization reactions: petrography, mineral chemistry, and petrophysics of serpentinites from MAR 15°N (ODP Leg 209, Site 1274). *Geophysical Research Letters*, **33**, L13306, doi:10.1029/2006GL025681
- Barber, D.J. (1981) Matrix phyllosilicates and associated minerals in C2M carbonaceous chondrites. *Geochimica et Cosmochimica Acta*, **45**, 945–970.
- Barber, D.J. (1985) Phyllosilicates and other layer-structured materials in stony meteorites. *Clay Minerals* **20**, 415–454.
- Bland, P.A., Cressey, G., and Menzies, O.N. (2004) Modal mineralogy of carbonaceous chondrites by X-ray diffraction and Mössbauer spectroscopy. *Meteoritics and Planetary Science*, **39**, 3–16.

- Bland, P.A., Jackson, M.D., Coker, R.F., Cohen, B.A., Webber, J.B.W., Lee, M.R., Duffy, C.M., Chater, R.J., Ardakani, M.G., McPhail, D.S., McComb, D.W., and Benedix, G.K. (2009) Why aqueous alteration in asteroids was isochemical: High porosity  $\neq$  high permeability. *Earth and Planetary Science Letters*, **287**, 559–568.
- Boudier, F., Barronet, A., and Mainprice, D. (2010) Serpentine mineral replacements of natural olivine and their seismic implications: Oceanic lizardite versus subduction-related antigorite. *Journal of Petrology*, **51**, 495–512.
- Brantley, S.L. (2005) Reaction kinetics of primary rock-forming minerals under ambient conditions. Pp. 73–117 in: *Surface and Ground Water, Weathering, and Soils* (J.I. Drever, editor). Treatise on Geochemistry Vol. **5** (H.D. Holland and K.K. Turekian, series editors). Elsevier-Perгамon, Oxford, UK.
- Brantley, S.L. (2008) Kinetics of mineral dissolution. Pp. 151–210 in: *Kinetics of Water–Rock Interaction* (S.L. Brantley, J.D. Kubicki, and A.F. White, editors). Springer, Berlin.
- Brearely, A.J. (2003) Nebular versus parent-body processing. Pp. 247–268 in: *Meteorites, Comets, and Planets* (A.M. Davis, editor). Treatise in Geochemistry Vol. **1** (H.D. Holland and K.K. Turekian, series editors). Elsevier-Perгамon, Oxford, UK.
- Brearely, A.J. (2006) The action of water. Pp. 587–624 in: *Meteorites and the Early Solar System II* (D.S. Lauretta and H.Y. McSween, Jr., editors). University of Arizona Press, Arizona, USA.
- Browning, L.B., McSween, H.Y., Jr., and Zolensky, M.E. (1996) Correlated alteration effects in CM carbonaceous chondrites. *Geochimica et Cosmochimica Acta*, **60**, 2621–2633.
- Browning, L.B., McSween, H.Y., Jr., and Zolensky, M.E. (2000) On the origin of rim textures surrounding anhydrous silicate grains in CM carbonaceous chondrites. *Meteoritics and Planetary Science*, **35**, 1015–1023.
- 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. *Geochimica et Cosmochimica Acta*, **44**, 1543–1577.
- Buseck, P.R. and Hua, X. (1993) Matrices of carbonaceous chondrite meteorites. *Annual Reviews of Earth and Planetary Science*, **21**, 255–305.
- Chizmadia, L.J. and Brearely, A.J. (2008) Mineralogy, aqueous alteration, and primitive textural characteristics of fine-grained rims in the Y-791198 CM2 carbonaceous chondrite: TEM observations and comparison to ALHA81002. *Geochimica et Cosmochimica Acta*, **72**, 602–625.
- Clayton, R.N. and Mayeda, T.K. (1999) Oxygen isotope studies of carbonaceous chondrites. *Geochimica et Cosmochimica Acta*, **63**, 2089–2104.
- Cohen, B.A. and Coker, R.A. (2000) Modeling liquid water on CM meteorite parent bodies and implications for amino acid racemizations. *Icarus*, **145**, 369–381.
- Coleman, R.G. (1971) Petrologic and geophysical nature of serpentinites. *Geological Society of America Bulletin*, **82**, 897–918.
- Condie, K.C. and Madison, J.A. (1969) Compositional and volume changes accompanying progressive serpentinization of dunites from the Webster-Addie ultramafic body, North Carolina. *American Mineralogist*, **54**, 1173–1179.
- Delvigne, J. (1998) *Atlas of Micromorphology of Mineral Alteration and Weathering*. The Canadian Mineralogist, Special Publication **3**, Mineralogical Association of Canada, Ottawa, Ontario, Canada, 495 pp.
- Dodd, R.T. (1981) *Meteorites: A Petrologic-Chemical Synthesis*. Cambridge University Press, Cambridge, UK, 368 pp.
- DuFresne, E.R. and Anders, E. (1962) On the chemical evolution of the carbonaceous chondrites. *Geochimica et Cosmochimica Acta*, **26**, 1085–1114.
- Evans, B.W. (2008) Control of the products of serpentinization by the  $\text{Fe}^{2+}\text{Mg}_{-1}$  exchange potential of olivine and orthopyroxene. *Journal of Petrology*, **49**, 1873–1887. doi:10.1093/petrology/egn050
- Frost, B.R. and Beard, J.S. (2007) On silica activity and serpentinization. *Journal of Petrology*, **48**, 1351–1368.
- Fuchs, L.H., Olsen, E. and Jensen, K.J. (1973) *Mineralogy, Mineral-Chemistry, and Composition of the Murchison (C2) Meteorite*. Smithsonian Contributions to Earth Science **10**, 39 pp.
- Goldich, S.S. (1938) A study in rock weathering. *Journal of Geology*, **46**, 17–58.
- Grady, M.M. (2000) *Catalog of Meteorites* (fifth edition). Cambridge University Press, Cambridge, UK, 689 pp.
- Graham, R.P.D. (1917) Origin of massive serpentine and chrysotile-asbestos, Black Lake-Thetford area, Quebec. *Economic Geology*, **12**, 154–202.
- Greshake, A. (1997) The primitive matrix components of the unique carbonaceous chondrites Acfer 094: A TEM study. *Geochimica et Cosmochimica Acta*, **61**, 437–452.
- Guo, W. and Eiler, J.M. (2007) Temperatures of aqueous alteration and evidence for methane generation on the parent bodies of CM chondrites. *Geochimica et Cosmochimica Acta*, **71**, 5565–5575.
- Hanowski, N.P. and Brearely, A.J. (2001) Aqueous alteration of chondrules in the CM carbonaceous chondrite, Allan Hills 81002: Implications for parent body alteration. *Geochimica et Cosmochimica Acta*, **65**, 495–518.
- Hemley, J.J., Montoya, J.W., Christ, C.L., and Hostetler, P.B. (1977) Mineral equilibria in the  $\text{MgO-SiO}_2\text{-H}_2\text{O}$  system: I Talc-chrysotile-forsterite-brucite stability relations. *American Journal of Science*, **277**, 322–351.
- Hostetler, P.B., Coleman, R.G., and Mumpton F.A. (1966) Brucite in alpine serpentinites. *American Mineralogist*, **51**, 75–98.
- Howard, K.T., Benedix, G.K., Bland, P.A., and Cressey, G. (2009) Modal mineralogy of CM2 chondrites by X-ray diffraction (PSD-XRD). Part 1: Total phyllosilicate abundance and the degree of aqueous alteration. *Geochimica et Cosmochimica Acta*, **73**, 4576–4589.
- Howard, K.T., Benedix, G.K., Bland, P.A., and Cressey, G. (2011) Modal mineralogy of CM2 chondrites by X-ray diffraction (PSD-XRD). Part 2: Degree, nature and settings of aqueous alteration. *Geochimica et Cosmochimica Acta*, **75**, 2735–2751.
- Hutchison, R. (2004) *Meteorites: A Petrologic, Chemical and Isotopic Synthesis*. Cambridge University Press, Cambridge, UK, 506 pp.
- Kretz, R. (1983) Symbols for rock-forming minerals. *American Mineralogist*, **68**, 277–279.
- Lauretta, D.S., Hua, X., and Buseck, P.R. (2000) Mineralogy of fine-grained rims in the ALH 81002 CM chondrite. *Geochimica et Cosmochimica Acta*, **64**, 3263–3273.
- Lee, M.R., Lindgren, P., Sofe, M.R., Alexander, C.M.O'D., and Wang, J. (2012) Extended chronologies of aqueous alteration in the CM2 carbonaceous chondrites: Evidence from carbonates in Queen Alexandra Range 93005. *Geochimica et Cosmochimica Acta*, **92**, 148–169.
- Lofgren, G.E. (1989) Dynamic crystallization of chondrule melts of porphyritic olivine composition: Textures: Experimental and natural. *Geochimica et Cosmochimica Acta*, **53**, 461–470.
- Lofgren, G.E. (1996) A dynamic crystallization model for chondrule melts. Pp. 187–196 in: *Chondrules and the Protoplanetary Disk* (R.H. Hewins, R.H. Jones, and E.R.D. Scott, editors). Cambridge University Press, Cambridge, UK.
- Lofgren, G.E. and Lanier, A.B. (1990) Dynamic crystallization

- study of barred olivine chondrules. *Geochimica et Cosmochimica Acta*, **54**, 3537–3551.
- Lofgren, G.E. and Russell, W.J. (1986) Dynamic crystallization of chondrule melts of porphyritic and radial pyroxene composition. *Geochimica et Cosmochimica Acta*, **50**, 1715–1726.
- Mackinnon, I.D.R. and Zolensky, M.E. (1984) Proposed structures for poorly characterized phases in C2M carbonaceous chondrite meteorites. *Nature*, **309**, 240–242.
- Martin, B. and Fyfe, W.S. (1970) Some experimental and theoretical observations on the kinetics of hydration reactions with particular reference to serpentinization. *Chemical Geology*, **6**, 185–202.
- McSween, H.Y., Jr. (1979a) Are carbonaceous chondrites primitive or processed? A review. *Reviews of Geophysics and Space Physics*, **17**, 1059–1078.
- McSween, H.Y., Jr. (1979b) Alteration in CM carbonaceous chondrites inferred from modal and chemical variations in matrix. *Geochimica et Cosmochimica Acta*, **43**, 1761–1770.
- McSween, H.Y., Jr. (1987) Aqueous alteration in carbonaceous chondrites: Mass balance constraints on matrix mineralogy. *Geochimica et Cosmochimica Acta*, **51**, 2469–2477.
- McSween, H.Y., Jr. and Richardson, S.M. (1977) The composition of carbonaceous chondrite matrix. *Geochimica et Cosmochimica Acta*, **41**, 1145–1161.
- Müller, W.F., Kurat, G., and Kracher, A. (1979) Chemical and crystallographic study of cronstedtite in the matrix of the Cochabamba (CM2) carbonaceous chondrite. *Tschemak's Mineralogische und Petrographische Mitteilungen*, **26**, 293–304.
- Nahon, D.B. (1991) *Introduction to the Petrology of Soils and Chemical Weathering*. John Wiley and Sons, Inc., New York, 313 pp.
- Nakamura, T., Noguchi, T., Okazaki, R., Jogo, K., and Ohtsuka, K. (2008) Mineralogical and stable isotope signatures of El-Quss Abu Said CM2 carbonaceous chondrite: Pristine material from the outer asteroid belt. Abstract, 71<sup>st</sup> Annual Meteoritical Society Meeting, #5124.
- O'Hanley, D.S. (1992) Solution to the volume problem in serpentinization. *Geology*, **20**, 705–708.
- O'Hanley, D.S. (1996) *Serpentinities: Records of Tectonic and Petrological History*. Oxford University Press, New York, 277 pp.
- Plümper, O., King, H.E., Vollmer, C., Ramasse, Q., Jung, H., and Austrheim, H. (2012) The legacy of crystal-plastic deformation in olivine: High-diffusivity pathways during serpentinization. *Contributions to Mineralogy and Petrology*, **163**, p. 701–724.
- Price, J.R., Bryan-Ricketts, D.S., Anderson, D., and Velbel, M.A. (2013) Weathering of almandine garnet: Influence of secondary minerals on the rate-determining step, and implications for regolith-scale Al mobilization. *Clays and Clay Minerals*, **61**, 34–56.
- Rosenberg, N.D., Browning, L. and Bourcier, W.L. (2001) Modeling aqueous alteration of CM carbonaceous chondrites. *Meteoritics and Planetary Science*, **36**, 239–244.
- Rubin, A.E., Trigo-Rodríguez, J.M., Huber, H., and Wasson, J.T. (2007) Progressive alteration of CM carbonaceous chondrites. *Geochimica et Cosmochimica Acta*, **71**, 2361–2382.
- Schulte, M., Blake, D., Hoehler, T., and McCollom, T. (2006) Serpentinization and its implications for life on early Earth and Mars. *Astrobiology*, **6**, 364–376.
- Smyth, J.R. and Bish, D.L. (1988) *Crystal Structures and Cation Sites of the Rock-Forming Minerals*. Allen & Unwin, Boston, USA, 332 pp.
- Thayer, T.P. (1966) Serpentinization considered as a constant-volume metasomatic process. *American Mineralogist*, **51**, 685–710.
- Tomeoka, K., McSween, H.Y., Jr., and Buseck, P.R. (1989) Mineralogical alteration of CM carbonaceous chondrites: A review. *Proceedings of the National Institute of Polar Research Symposium on Antarctic Meteorites* **2**, 221–234.
- Velbel, M.A. (1993) Constancy of silicate-mineral weathering-rate ratios between natural and experimental weathering: Implications for hydrologic control of differences in absolute rates. *Chemical Geology*, **105**, 89–99.
- Velbel, M.A. and Barker, W.W. (2008) Pyroxene weathering to smectite: Conventional and low-voltage cryo-field emission scanning electron microscopy, Koua Bocca ultramafic complex, Ivory Coast. *Clays and Clay Minerals*, **56**, 111–126.
- Velbel, M.A. and Palmer, E.E. (2011) Fine-grained serpentine in CM2 carbonaceous chondrites and its implications for the extent of aqueous alteration on the parent body: A review. *Clays and Clay Minerals*, **59**, 416–432.
- Velbel, M.A., Donatelle, A.R., and Formolo, M.J. (2009) Reactant-product textures, volume relations, and implications for major-element mobility during natural weathering of hornblende, Tallulah Falls Formation, Georgia Blue Ridge, U.S.A. *American Journal of Science*, **309**, 661–688.
- Velbel, M.A., Tonui, E.K. and Zolensky, M.E. (2012) Replacement of olivine by serpentine in the carbonaceous chondrite Nogoya (CM2). *Geochimica et Cosmochimica Acta*, **87**, 117–135.
- Viti, C. and Mellini, M. (1998) Mesh textures and bastites in the Elba retrograde serpentinites. *European Journal of Mineralogy*, **10**, 1341–1359.
- Wegner, W.W. and Ernst, W.G. (1983) Experimentally determined hydration and dehydration reaction rates in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O. *American Journal of Science*, **283-A**, 151–180.
- Wicks, F.J. and Whittaker, E.J.W. (1977) Serpentine textures and serpentinization. *The Canadian Mineralogist*, **15**, 459–488.
- Young, E.D., Ash, R.D., England, P., and Rumble, D., III (1999) Fluid flow in chondritic parent bodies: Deciphering the compositions of planetesimals. *Science*, **286**, 1331–1335.
- Young, E.D., Zhang, K.K., and Schubert, G. (2003) Conditions for pore water convection within carbonaceous chondrite parent bodies – implications for planetesimal size and heat production. *Earth and Planetary Science Letters*, **213**, 249–259.
- Zega, T.J. and Buseck, P.R. (2003) Fine-grained-rim mineralogy of the Cold Bokkeveld CM chondrite. *Geochimica et Cosmochimica Acta*, **67**, 1711–1721.
- Zega, T.J., Garvie, L.A.J., Dodony, I., and Buseck, P.R. (2004) Serpentine nanotubes in the Mighei CM chondrite. *Earth and Planetary Science Letters*, **223**, 141–146.
- Zega, T.J., Garvie, L.A.J., Dódony, I., Friedrich, H., Stroud, R.M., and Buseck, P.R. (2006) Polyhedral serpentine grains in CM chondrites. *Meteoritics and Planetary Science*, **41**, 681–688.
- Zolensky, M. and McSween, H.Y., Jr. (1988) Aqueous alteration. Pp. 114–143 in: *Meteorites and the Early Solar System* (J.F. Kerridge and M. Shapley Matthews, editors). The University of Arizona Press, Arizona, USA.
- Zolensky, M.E., Barrett, R., and Browning, L. (1993) Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites. *Geochimica et Cosmochimica Acta*, **57**, 3123–3148.
- Zolensky, M.E., Mittlefehldt, D.W., Lipschutz, M.E., Wang, M.-S., Clayton, R.N., Mayeda, T.K., Grady, M.M., Pillinger, C., and Barber, D. (1997) CM chondrites exhibit the complete petrologic range from type 2 to 1. *Geochimica et Cosmochimica Acta*, **61**, 5099–5115.

(Received 21 January 2014; revised 20 June 2014; Ms. 845; AE: W. Huff)