

# The Action of Water

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A variety of lines of evidence show that water was widely available during the earliest geological history of the solar system. Water played a significant role in the cosmochemical and geological evolution of a range of small asteroidal bodies, by modifying the primary mineralogical and textural characteristics of pristine nebular materials and providing an agent for mass and heat transport from the interior of these bodies. The mineralogical and stable isotopic characteristics of the products of aqueous alteration, combined with geochemical and thermal modeling, can be used to place important constraints on a number of different aspects of the aqueous alteration processes, including the mechanisms of aqueous alteration reactions, the conditions of alteration, the location and timing of alteration, and the scale of mass transport. Aqueous alteration of nebular materials may have occurred in a variety of locations including the solar nebula, within ephemeral protoplanetary bodies, and within asteroidal parent bodies after final accretion.

## 1. INTRODUCTION

Among the processes that have affected primitive solar system materials, such as chondritic meteorites and interplanetary dust particles (IDPs), aqueous alteration is perhaps the most widespread. Since the discovery over 150 years ago that the CI carbonaceous chondrite fall Orgueil contained water-bearing clay minerals (*Pisani*, 1864), it has become increasingly well-recognized that water played a key role in the early geological evolution of the solar system. It is now apparent that numerous other chondrite groups, including the CM, CR, CV, CO, and ordinary chondrites, also exhibit evidence of aqueous alteration to varying degrees. Even metamorphosed ordinary chondrites, which have traditionally been regarded as being extremely dry meteorites, show evidence that they have been affected by water early in solar system history (e.g., *Zolensky et al.*, 1999; *Grossman et al.*, 2000; *Rubin et al.*, 2002). In addition to these direct observations, the spectral characteristics of C-, D-, G-, F-, and B-class asteroids (e.g., *Vilas and Gaffey*, 1989; *Vilas et al.*, 1993, 1994), which may be related genetically to carbonaceous chondrites (e.g., *Gaffey et al.*, 1993; *Pieters and McFadden*, 1994; *Hiroi et al.*, 2001; *Kanno et al.*, 2003), indicate that hydrous phyllosilicates are present on their surfaces.

These observations provide unequivocal evidence that water was widely available in the early solar system and played a significant role in the evolution of the mineralogy and cosmochemistry of a number of diverse solar system bodies. An understanding of the origin of the alteration assemblages in chondritic meteorites has the potential to place important constraints on when and where aqueous alteration in chondrites occurred, the timescales for alteration, and the effects of alteration on primary nebular components. Furthermore, it can also help constrain the role of volatiles in the solar nebula, as well as during parent-body

accretion and subsequently within asteroidal parent bodies. Finally, a knowledge of the behavior of water during the earliest stages of solar system evolution is essential to developing a full understanding of the behavior of the biogenic elements through geologic time. This chapter reviews the body of evidence that demonstrates that aqueous fluids were of major importance in the earliest geological evolution of our solar system.

## 2. MINERALOGICAL AND COSMOCHEMICAL EFFECTS OF AQUEOUS ALTERATION

The most obvious effect of aqueous alteration on chondritic meteorites is the formation of a variety of secondary phases, usually hydrous minerals such as serpentines and clays, but also carbonates, sulfates, oxides, sulfides, halides, and oxyhydroxides. In addition, alteration has had important effects on both the stable isotopic compositions of the bulk meteorites and individual components that provide very useful insights into the alteration process. In some cases, these effects are significant as in the case of the CI, CM, CR, and some CV chondrites, whereas in other chondrites such as the CO and unequilibrated ordinary chondrites (UOCs), alteration effects are more subtle. In the case of some CV chondrites, such as Allende, dark inclusions (DIs) in CV and CO chondrites, and equilibrated ordinary chondrites, alteration effects are often cryptic, but can be dramatic as in the case of halite in the Monahans (1998) (H5) and Zag (H5) ordinary chondrite breccias (e.g., *Zolensky et al.*, 1999; *Rubin et al.*, 2002).

Perhaps the most remarkable feature of alteration in chondritic meteorites is the diversity in alteration assemblages and styles of aqueous alteration. Although there are general similarities between aqueous alteration in different chondrite groups, there are also significant differences, sug-

TABLE 1. Alteration phases found in carbonaceous and ordinary chondrites (minor phases shown in italics).

CI Chondrites	CM Chondrites	CR Chondrites	CV Chondrites	CO Chondrites	Ordinary Chondrites
<b>Silicates</b>	<b>Silicates</b>	<b>Silicates</b>	<b>Silicates</b>	<b>Silicates</b>	<b>Silicates</b>
Fe-Mg serpentines Saponite (smectite)	Fe-Mg serpentines cronstedtite	Fe-Mg serpentines saponite	Fe-Mg serpentine saponite	Fe-Mg serpentine <i>chlorite</i>	smectite
<b>Carbonates</b>	<i>chlorite</i>	<b>Carbonates</b>	<i>amphibole</i>		<b>Carbonates</b>
calcite	<i>saponite</i>	<i>calcite</i>	<i>biopyribole</i>		<i>calcite</i>
dolomite	<i>vermiculite</i>		<i>talc</i>		<b>Oxides</b>
breunnerite	<b>Tochilinite</b>	<b>Oxides</b>	<i>margarite</i>		<i>maghemite</i>
<i>siderite</i>	tochilinite	magnetite	<i>clintonite</i>		
<b>Sulfates</b>	<b>Carbonates</b>	<b>Sulfides</b>	<i>muscovite</i>		<b>Sulfides</b>
gypsum	calcite	pyrrhotite	<i>Na phlogopite</i>		pyrrhotite
epsomite	dolomite	pentlandite	<i>montmorillonite</i>		pentlandite
<i>bloedite</i>	<i>aragonite</i>		<i>chlorite</i>		
<b>Sulfides</b>	<b>Sulfates</b>		fayalite		<b>Halides</b>
pyrrhotite	<i>gypsum</i>		hedenbergite		<i>halite</i>
pentlandite	<i>hemihydrate</i>		diopside		
<i>cubanite</i>	<i>anhydrite</i>		wollastonite		
<b>Oxides</b>	<b>Oxides</b>		andradite		
magnetite	<i>magnetite</i>		<i>grossular</i>		
ferrihydrite			<i>monticellite</i>		
			kirschteinite		
			nepheline		
			sodalite		
			<b>Carbonates</b>		
<b>Native elements</b>	<b>Hydroxides</b>		<i>calcite</i>		
<i>sulfur</i>	<i>brucite</i>		<b>Sulfides</b>		
	<b>Sulfides</b>		pyrrhotite		
	pyrrhotite		pentlandite		
	pentlandite		<b>Oxides</b>		
	<b>Halides</b>		magnetite		
	halite		ferrihydrite		
	sylvite				

gesting that the conditions of alteration and the availability of fluid was quite variable, both within individual asteroids and between asteroid types. In this section, the alteration assemblages and textural characteristics of alteration in these different meteorites will be summarized and the cosmochemical effects of alteration examined. Detailed discussions of the alteration mineralogy of these meteorites have been presented in extensive literature reviews (e.g., Barber, 1981; Zolensky and McSween, 1988; Buseck and Hua, 1993; Brearley and Jones, 1998; Brearley, 2003) and will only be discussed briefly here. The alteration mineralogy in the main groups of chondritic meteorites is summarized in Table 1 and mineral formulae for the principle alteration phases are presented in Table 2.

Identification of chondrites that have experienced aqueous alteration is usually based on the presence of hydrous phases such as phyllosilicates. However, over the last de-

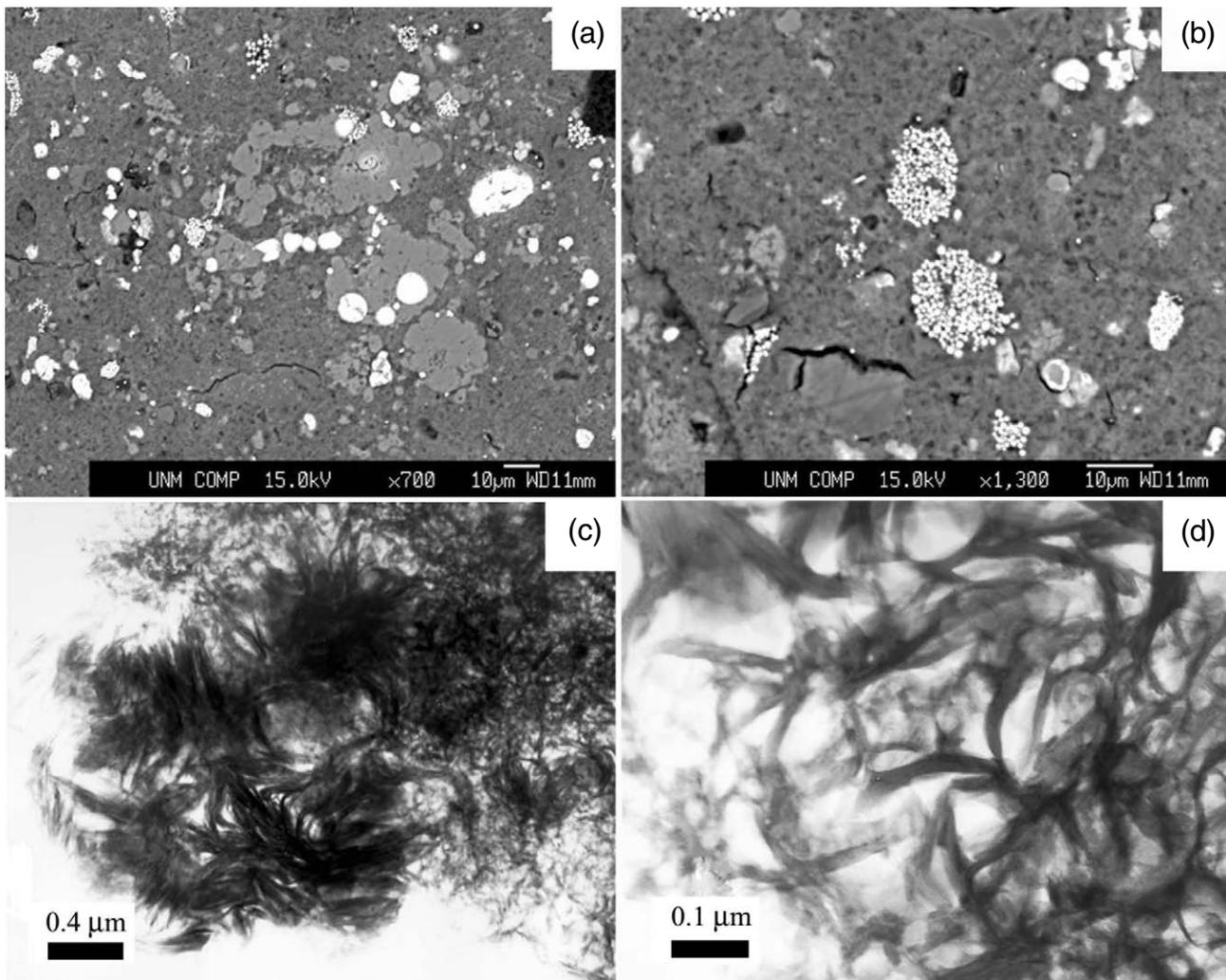
cade, it has been recognized that secondary alteration effects are present in some chondrites [e.g., CV and CO chondrites and the dark inclusions (DIs) that they contain] that may have been formed by the action of water but did not result in the widespread formation of hydrous phases (e.g., Krot *et al.*, 1995). In these cases, the effects of aqueous fluids are more cryptic and establishing the involvement of water in the formation of these mineral assemblages is more challenging and certainly controversial (see Brearley, 2003). In these situations, a combination of mineralogical studies, thermodynamic modeling, and O-isotopic data are required to demonstrate the involvement of aqueous fluids, and in some cases, the results may be equivocal. In general, aqueous alteration, which leaves a somewhat cryptic signature(s) on the rocks that it has affected, appears to have occurred at temperatures higher than those experienced during aqueous alteration that primarily resulted in the formation of

TABLE 2. Characteristics alteration phases in altered carbonaceous and ordinary chondrites.

Mineral Group	End Member	Chemical Formulae
<b>Phyllosilicates</b>		
Serpentines:		
	chrysotile	$Mg_3Si_2O_5(OH)_4$
	lizardite	$Mg_3Si_2O_5(OH)_4$
	antigorite	$Mg_3Si_2O_5(OH)_4$
	cronstedtite	$Fe_2^{2+}Fe^{3+}(SiFe^{3+})O_5(OH)_4$
Smectites	montmorillonite	$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$
	saponite	$(Ca/2)_{0.3}(Mg,Fe^{2+},Mg)_3(Si,Al)_4O_{10}(OH)_2 \cdot nH_2O$
Chlorite	clinochlore	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$
	chamosite	$(Mg,Fe^{2+},Fe^{3+})_5Al(Si_3Al)O_{10}(OH)_8$
Talc		$Mg_3Si_4O_{10}(OH)_2$
Vermiculite		$Mg_3(Si,Al)_4O_{10}(OH)_2 \cdot 4.5nH_2O[Mg]_{0.35}$
Micas	clintonite	$CaMg_3(Al_2Si_2)(OH)_2$
	margarite	$CaAl_2(Al_2Si_2)(OH)_2$
	muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$
	phlogopite	$(K,Na)Mg_3(AlSi_3O_{10})(OH)_2$
<b>Amphibole</b>		
	anthophyllite	$Mg_7Si_8O_{22}(OH)_2$
	hornblende	$(Ca,Na)_{2-3}(Mg,Fe,Al)_5Si_6(Si,Al)_2O_{22}(OH)_2$
<b>Biopyriboles</b>		
	jimthompsonite	$(Mg,Fe)_{10}Si_{12}O_{32}(OH)_4$
<b>Pyroxenes</b>		
	hedenbergite	$(CaFe)Si_2O_6$
	diopside	$(CaMg)Si_2O_6$
<b>Pyroxenoids</b>		
	wollastonite	$CaSiO_3$
<b>Garnet</b>		
	andradite	$Ca_3Fe^{3+}_2Si_3O_{12}$
	grossular	$Ca_3Al_2Si_3O_{12}$
<b>Feldspathoids</b>		
	nepheline	$(Na,K)AlSiO_4$
	sodalite	$Na_8(AlSiO_4)_6Cl_2$
<b>Olivines</b>		
	fayalite	$Fe_2SiO_4$
	kirschsteinite	$CaFeSiO_4$
	monticellite	$CaMgSiO_4$
Tochilinite	tochilinite	$2[(Fe,Mg,Cu,Ni)S] \cdot 1.57-1.85[Mg,Fe,Ni,Al,Ca](OH)_2$
<b>Sulfates</b>		
	epsomite	$MgSO_4 \cdot 7H_2O$
	gypsum	$CaSO_4 \cdot 2H_2O$
	bloedite	$Na_2Mg(SO_4)_2 \cdot 2H_2O$
	Ni-bloedite	
<b>Carbonates</b>		
	calcite	$CaCO_3$
	aragonite	$CaCO_3$
	dolomite	$(CaMg)CO_3$
	breunnerite	$(Mg,Fe,Mn,Fe)CO_3$
	siderite	$FeCO_3$

TABLE 2. (continued).

Mineral Group	End Member	Chemical Formulae
Sulfides	pyrrhotite	$\text{Fe}_{1-x}\text{S}$ ( $x = 0.0.17$ )
	pentlandite	$(\text{FeNi}_9)\text{S}_8$
	cubanite	$\text{CuFe}_2\text{S}_3$
Oxides	magnetite	$\text{Fe}_3\text{O}_4$
	maghemite	$\text{Fe}_2\text{O}_3$
	ferrihydrite	$5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$
Hydroxides	brucite	$\text{Mg}(\text{OH})_2$
Halides	halite	$\text{NaCl}$
	sylvite	$\text{KCl}$



**Fig. 1.** SEM and TEM images showing the general characteristics of CI chondrites that result from aqueous alteration. (a) BSE image of Ivuna matrix showing the presence of magnetite (Mgt) and irregularly shaped carbonate grains (Cb), set in a very fine-grained matrix of phyllosilicates. (b) BSE image of magnetite framboids (Mgt) in Ivuna matrix. (c) TEM image of coarse- and fine-grained phyllosilicates (serpentine interlayered with saponite) in Ivuna matrix. (d) TEM image showing a closeup of the textures of phyllosilicates in the CI chondrite, Ivuna.

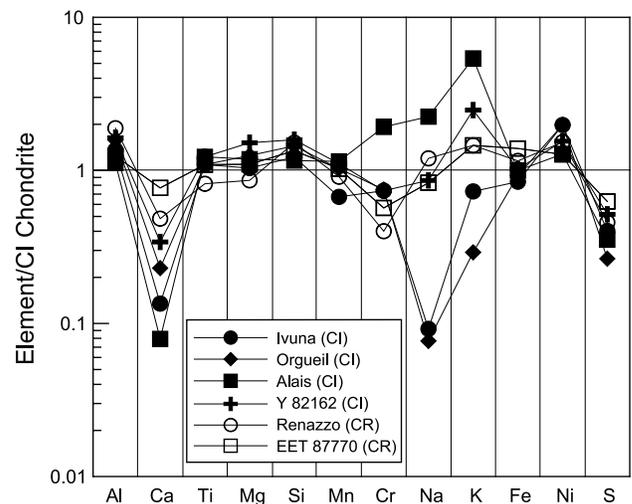
phyllosilicates. For example, the widespread development of hydrous phases that have been described in many carbonaceous and ordinary chondrites, as discussed below, is generally estimated to have occurred at temperatures below  $\sim 100^\circ\text{C}$ , although some chondrites may have experienced somewhat higher temperatures. In contrast, the formation of largely anhydrous mineral assemblages as a result of the interaction of chondritic protoliths with hydrous fluids probably occurred at temperatures in the range  $200^\circ\text{--}400^\circ\text{C}$  (Krot *et al.*, 1998a,b; Brearley, 1999). To describe alteration processes in this temperature regime, terms such as metasomatism and fluid-assisted metamorphism should be used to distinguish between lower-temperature aqueous alteration, whose primary mineralogical products are hydrous phases such as phyllosilicates.

## 2.1. CI Carbonaceous Chondrites

CI chondrites are among the rarest type of carbonaceous chondrite (only seven are currently known), but their cosmochemical significance far outweighs their relative scarcity. The CI chondrites have bulk elemental ratios that show a 1 : 1 correlation with those of the solar photosphere for most elements (Anders and Grevesse, 1989; Lodders, 2003) and are considered to have the most primitive compositions of all known solar system materials. However, despite their unfractionated chemical compositions, the CI chondrites are the most hydrated of all the chondrite groups.

The CI chondrites are complex meteorites (Figs. 1a,b) that consist of a dark, fine-grained matrix comprised largely of phyllosilicates (serpentine interlayered with saponite) with magnetite, sulfides, carbonates, and sulfates embedded within it (DuFresne and Anders, 1962; Böstrom and Fredriksson, 1966; Nagy, 1966; Tomeoka and Buseck, 1988). Magnetite development is extensive and occurs with frambooidal, plaque, and platelet morphologies (e.g., Kerridge *et al.*, 1979a) (Fig. 1b). A variety of carbonates (breunnerite, dolomite, and calcite) (Endress and Bischoff, 1996) and sulfides (pyrrhotite, pentlandite, and cubanite) occur within the matrix (e.g., Kerridge *et al.*, 1979b). The occurrence of veins of white sulfate (epsomite,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) in the CI chondrite Orgueil has been widely reported in the literature (e.g., DuFresne and Anders, 1962; Mason, 1962; Boström and Fredriksson, 1966; Richardson, 1978). This observation has been cited as evidence for aqueous alteration on the CI-chondrite parent asteroid (e.g., Zolensky and McSween, 1988). However, recent studies (Gounelle and Zolensky, 2001) provide strong evidence that the veins are, in fact, the result of remobilization and reprecipitation of soluble sulfates caused by interaction with the terrestrial atmosphere after the meteorite fell. It should also be noted that no carbonate veins have been observed in CI chondrites, although fragments of what may have been carbonate vein fillings have been described in CI chondrites (e.g., Richardson, 1978; Endress and Bischoff, 1996).

Although the bulk chemical compositions of CI chondrites are a close match to the solar photosphere abundances, aqueous alteration has caused extensive chemical

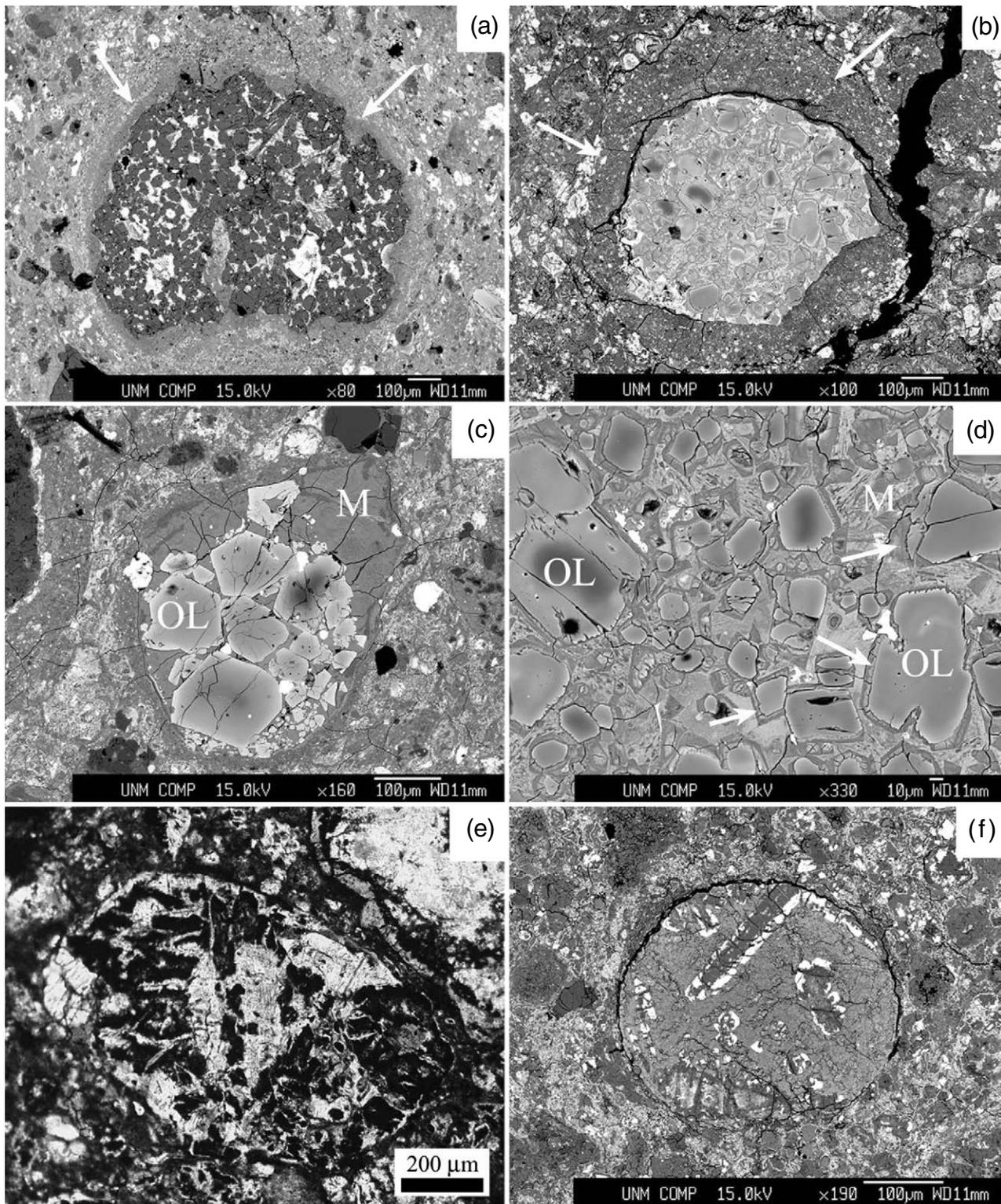


**Fig. 2.** Normalized element abundance diagram (normalized to bulk CI and Si) showing the compositions of the matrices of several CI- and CR-chondrite matrices. The data are arranged in order of decreasing condensation temperatures. The data show that the fine-grained phyllosilicate component of CI matrices represented by the data is fractionated relative to bulk CI-chondrite values. Soluble elements show variable behavior, but Ca in particular is always depleted in matrices, presumably because it has been fractionated into coarser-grained phases such as calcite and Ca-sulfates. Other soluble elements such as Na and K show variable behavior and may be enriched or depleted. CR chondrites that are less altered than CI chondrites have matrices that show less fractionation in these soluble elements than CI chondrites. Broad-beam electron microprobe data from Zolensky *et al.* (1993).

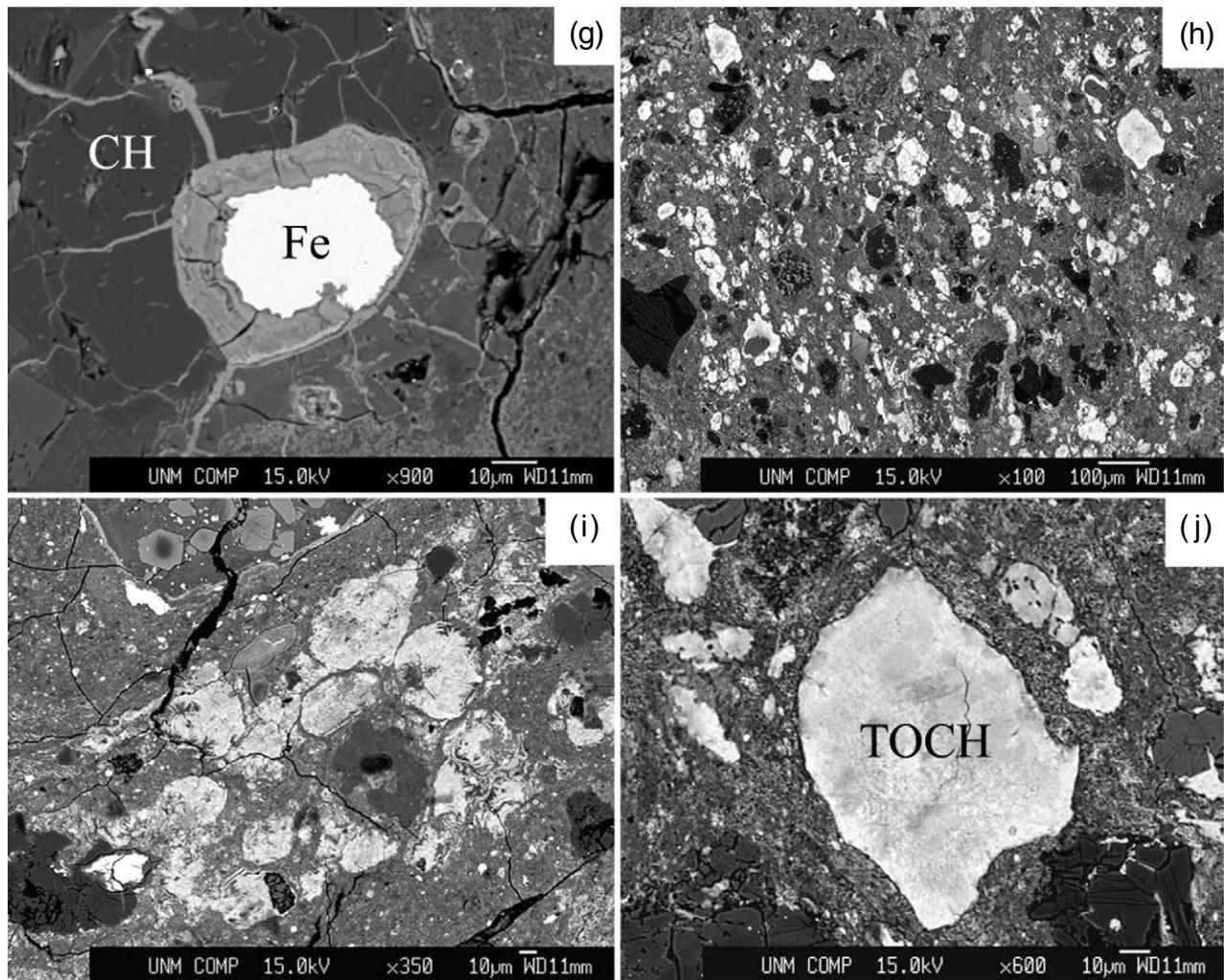
fractionation between different alteration components. Elements that are generally considered to be immobile during aqueous alteration (e.g., Al and Ti) are unfractionated in CI matrix (Fig. 2) and have solar ratios, but soluble elements such as Ca, Mn, Na, K, and S are strongly fractionated (McSween and Richardson, 1977; Zolensky *et al.*, 1993; Brearley and Prinz, 1992; Brearley, 1997a). These elements were probably mobilized and precipitated as sulfates and carbonates, although whether this process resulted in the formation of veins in the CI chondrites is open to debate, as discussed above.

## 2.2. CM Carbonaceous Chondrites

The CM chondrites are a diverse, complex group of meteorites that have undergone aqueous alteration and brecciation to different degrees (e.g., Metzler *et al.*, 1992). A significant advance in our understanding of CM chondrites has come from the work of Metzler *et al.* (1992), who recognized that the least-brecciated CM chondrites consist essentially entirely of what they described as a “primary accretionary rock.” Such primary accretionary rocks consist of coarse-grained components (chondrules, CAIs, amoeboid olivine aggregates, and mineral fragments) that are all sur-



**Fig. 3.** Images of textural and mineralogical characteristics of the effects of aqueous alteration in CM carbonaceous chondrites. (a) BSE image showing a fine-grained rim (arrowed) around a porphyritic olivine-rich type I chondrule in the relatively weakly altered CM2 Murchison; (b) BSE image of well-developed fine-grained rim (arrowed) in the unbrecciated, but relatively heavily altered CM2 chondrite ALH 81002. The rim surrounds a heavily altered type IIA chondrule in which olivine phenocrysts have been partially replaced by serpentine. (c) BSE image of a type II FeO-rich chondrule in Y 791198 showing altered mesostasis glass (M), but completely unaltered olivine (OL) phenocrysts. (d) BSE closeup showing the details of alteration of olivine (OL) to serpentine in the type IIA chondrule shown in Fig. 3b. Narrow rims of serpentine (arrowed) are present around the peripheries of all olivine grains. (e) Optical micrograph showing a completely pseudomorphed porphyritic olivine chondrule from the CM1 chondrite ALH 84034. The chondrule has been replaced by serpentine and Fe-oxides. (f) BSE image of a porphyritic chondrule in the CM1 chondrite, ALH 84034, showing perfect pseudomorphism of some of the chondrule phenocrysts.

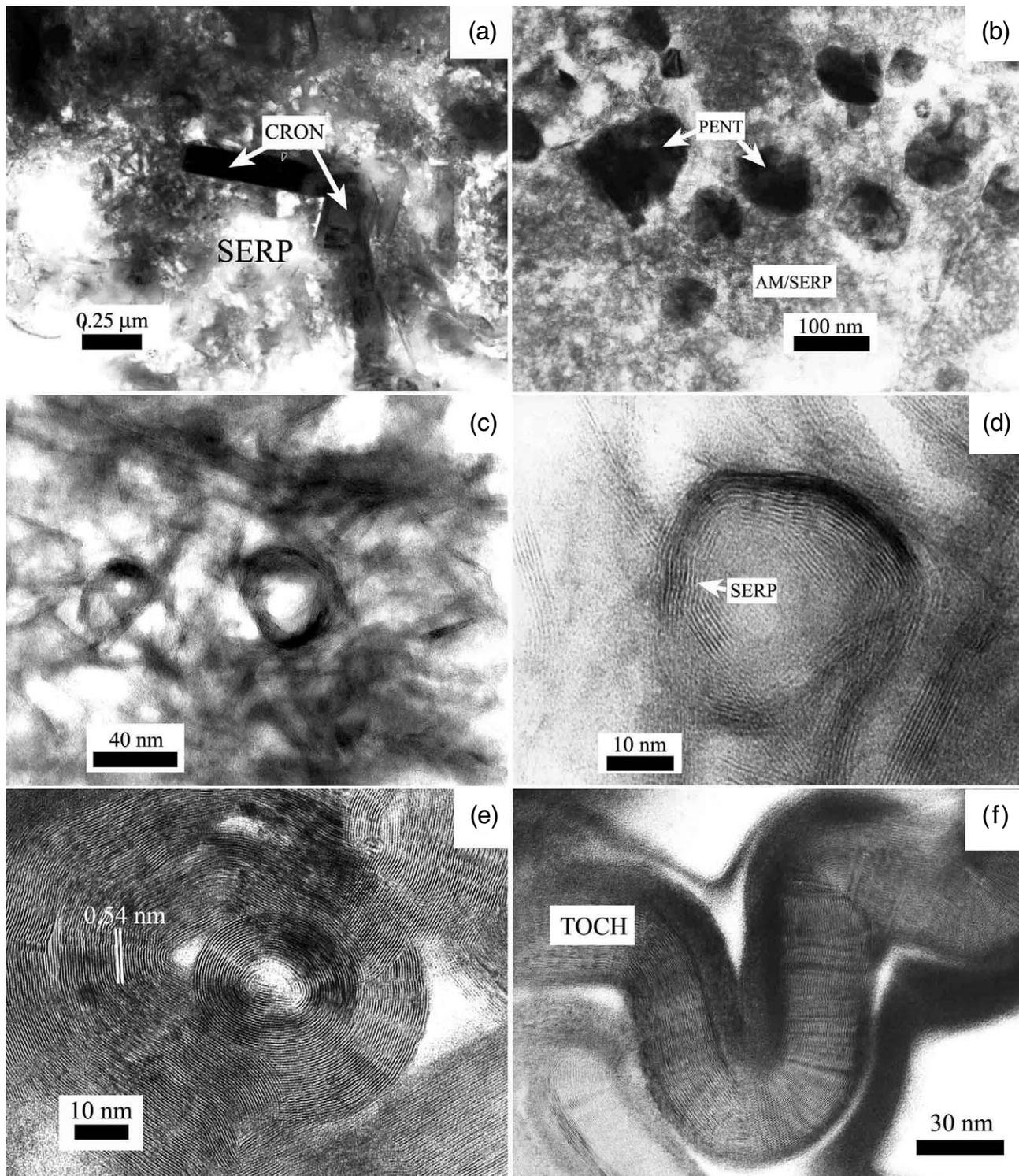


**Fig. 3.** (continued). **(g)** Partially altered metal grain (Fe) in a type I chondrule (CH) in the weakly altered CM chondrite Y 791198. The metal shows significant corrosion and is surrounded by a rim of tochilinite/cronstedtite replacement products. **(h)** BSE image of a region of matrix in Murchison containing abundant, irregularly shaped masses of tochilinite/cronstedtite intergrowths (formally termed PCP). **(i)** BSE image of tochilinite/cronstedtite intergrowths (high BSE contrast objects) in the matrix of Y 791198, a comparatively weakly altered CM2 carbonaceous chondrite, showing the fibrous characteristics of this material. **(j)** BSE image showing a closeup of a massive tochilinite/cronstedtite intergrowth (TOCH) in Murchison matrix. Compositional zoning is apparent within the aggregate.

rounded by well-developed fine-grained rims (Figs. 3a,b). *Metzler et al.* (1992) argued that the fine-grained rims represent nebular dust that accreted onto chondrules in the solar nebula, although other models for the formation of these rims have also been proposed (e.g., *Sears et al.*, 1993). Brecciation on the CM-chondrite parent body resulted in the progressive fragmentation of this primary texture and produced a clastic texture that is characteristic of many CM chondrites. As a consequence, most CM chondrites are breccias consisting of fragments of primary accretionary rocks and surviving intact chondrules, CAIs, etc., embedded within a matrix of clastic fragments derived from chondrules, fine-grained rims, etc. In extreme cases of brecciation, all evidence of the primary accretionary texture has been destroyed (e.g., in the unusual CM2 chondrite, Bells) (*Brearley*, 1995). The interaction of brecciation with aqueous alteration has resulted in remarkable textural diversity

within the CM chondrites and is a complication that makes unraveling the alteration histories of these meteorites particularly challenging.

An important characteristic of CM chondrites is that they display a wide range of degrees of aqueous alteration. Most CM chondrites are classified as petrologic type 2, indicating that they typically have essentially fully hydrated matrices, but within CM2 chondrites, the extent of alteration of chondrules is highly variable from one chondrite to another (e.g., Figs. 3a–f) and is a function of the degree of alteration of the host meteorite and the chondrule type (*Hanowski and Brearley*, 2001). A few CM chondrites exist that show essentially 100% hydration and have been termed CM1 chondrites (*Grady et al.*, 1987; *Zolensky et al.*, 1997). In the CM1s, all chondrules and other coarse-grained objects have been completely pseudomorphed by alteration phases, dominantly serpentine (Figs. 3e,f).



**Fig. 4.** Textural characteristics of fine-grained alteration phases in CM2 carbonaceous chondrites. (a) TEM image of a fine-grained rim in Murchison showing comparatively coarse-grained cronstedtite (CRON) crystals surrounded by a fine-grained matrix of serpentine. (b) TEM image of nanophase sulfide (PENT) crystals in a fine-grained rim in Murchison embedded in a groundmass of very fine-grained Mg-serpentine or amorphous material (AM/SERP) with a composition close to that of serpentine. (c) TEM image of a fine-grained rim in Murchison showing a region dominated by fine-grained Mg-serpentine with rolled and platy morphologies. (d) High-resolution TEM image of a serpentine (SERP) crystal in a fine-grained rim in Murchison showing a characteristic rolled morphology. (e) High-resolution TEM image of a cylindrical tochilinite tube from Murchison matrix. Image courtesy of K. Tomeoka. (f) High-resolution TEM image showing contorted structures in tochilinite (formerly PCP) from a tochilinite grain in Murray matrix similar to those shown in Murchison in Fig. 3h. Image courtesy of K. Tomeoka after *Tomeoka and Buseck (1985)*.

Compared with CI chondrites, the alteration mineralogy of CM2s is quite distinct. Transmission electron microscope (TEM) studies have shown that the matrices and fine-grained rims of these meteorites are dominated by fine-grained serpentines with different morphologies and variable compositions (e.g., Barber, 1981; Zolensky *et al.*, 1993; Lauretta *et al.*, 2000; Zega and Buseck, 2003; Zega *et al.*, 2003) (Figs. 4a–d). Amorphous/nanocrystalline material is also a common component of fine-grained rims in the least-altered CM chondrites (Barber, 1981; Chizmadia and Brearley, 2003). Nanometer- to micrometer-sized sulfides (pentlandite and pyrrhotite) commonly occur embedded in this groundmass of phyllosilicates and amorphous material (Fig. 4b). Magnetite is rare except in the unusual CM chondrite Bells (Rowe *et al.*, 1994; Brearley, 1995). One of the diagnostic characteristics of CM chondrites is the presence of the unusual phase tochilinite [ $6\text{Fe}_{0.9}\text{S} \cdot 5(\text{Fe,Mg})(\text{OH})_2$ ], which commonly occurs intergrown on a very fine scale with the  $\text{Fe}^{3+}$ -rich serpentine, cronstedtite (e.g., Tomeoka and Buseck, 1985). These intergrowths have commonly been called “spinach” or “poorly characterized phase (PCP)” in the literature, but both of these terms are now obsolete. These tochilinite/cronstedtite intergrowths occur throughout CM chondrites, often as distinct, irregularly shaped masses, sometimes surrounded by fine-grained rims and as a replacement product of Fe,Ni metal grains in the matrix and in chondrules (Figs. 3g–j and Figs. 4e,f). They are also a common phase within the matrix and fine-grained rims of CM chondrites, occurring in a variety of different morphologies (Figs. 4e,f).

Carbonates are ubiquitous in CM2 chondrites and are also present, with rare exceptions, in all CM1 chondrites (e.g., Johnson and Prinz, 1993; Zolensky *et al.*, 1993; Brearley and Hutcheon, 2000), occurring as 10–50  $\mu\text{m}$  grains distributed throughout the matrix (Figs. 5a–f). Calcite also occurs commonly in altered CAIs, but is rare in altered chondrules and their fine-grained rims (Brearley and Hutcheon, 2002). In CM2s, calcite is often the only type of carbonate present, except in the most heavily altered CM2s such as Nogoya that also contain dolomite (Johnson and Prinz, 1993). In some CM1s, both calcite and dolomite occur (Zolensky *et al.*, 1997). Many of these carbonate grains show previously unrecognized, complex minor-element zoning (Fig. 5) that is revealed by cathodoluminescence and electron microprobe studies (Brearley *et al.*, 1999; Brearley and Hutcheon, 2002). Compared with CI chondrites, sulfates are much less common, although they do occur in many CMs (Airieau *et al.*, 2001), in some cases as crosscutting veins (Lee, 1993). Based on the observations of Gounelle and Zolensky (2001) on CI chondrites, it is possible that these sulfate veins may actually be terrestrial in origin, but this remains to be confirmed.

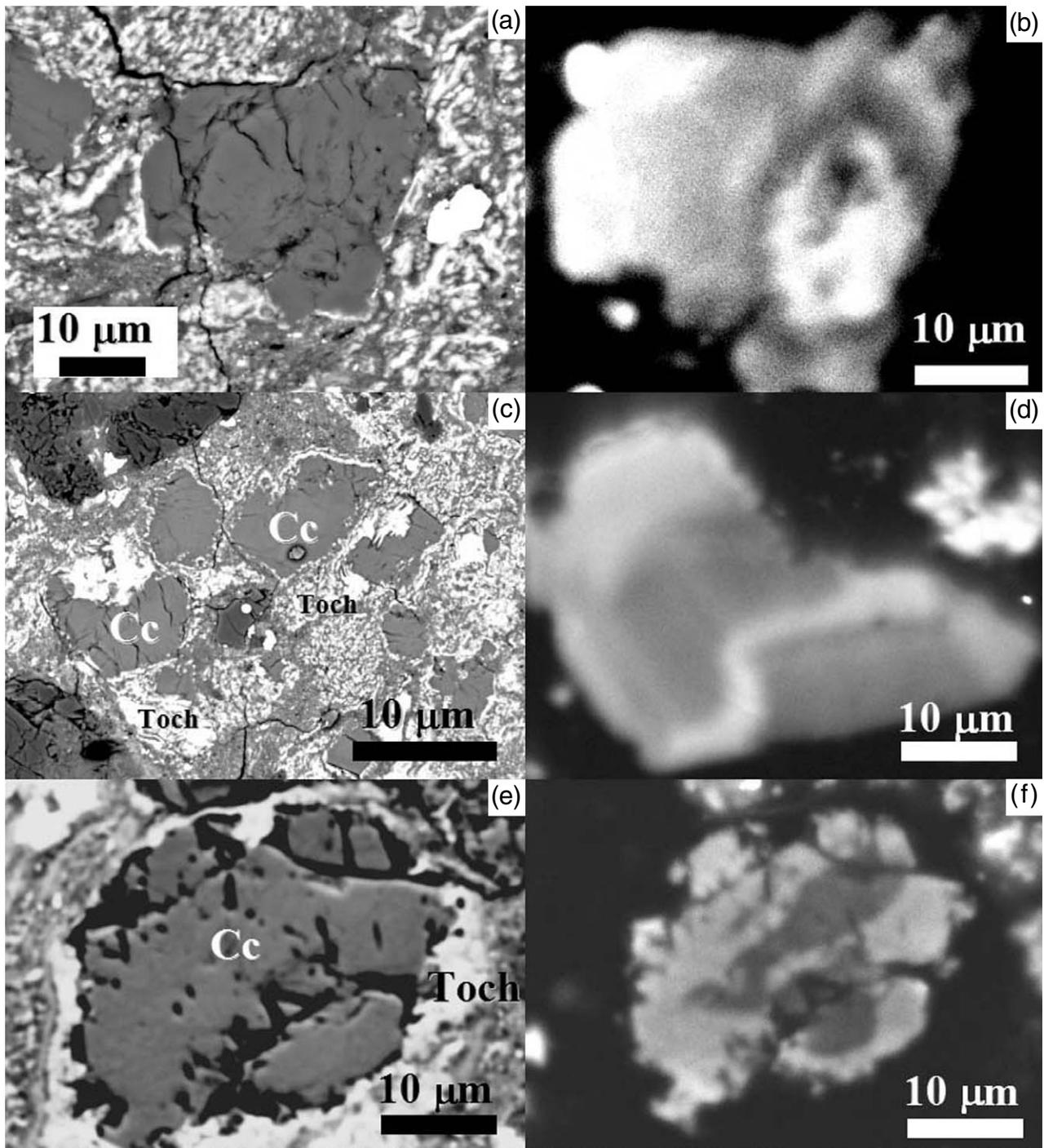
Petrographic studies show that mesostasis, Fe,Ni metal, and troilite in chondrules are highly susceptible to aqueous alteration and, even in the least-altered CM chondrites, are extensively altered (e.g., Figs. 3c,d) (Chizmadia and Brearley, 2003). Mesostasis has commonly been replaced

by serpentine with variable compositions (Richardson, 1981; Hanowski and Brearley, 2001). Metal has altered to tochilinite/cronstedtite intergrowths (Fig. 3g) and most troilite has altered to pyrrhotite or pentlandite. More advanced alteration results first in the alteration of more Fe-rich olivines in type IIA chondrules (e.g., Fig. 3d) and low-Ca pyroxene (clinoenstatite). Forsteritic olivine in type I chondrules, augite, and orthopyroxene (when present) are highly resistant to alteration (Zolensky *et al.*, 1993; Hanowski and Brearley, 2001) and only show significant replacement at the most advanced stages of alteration such as those observed in CM1 and very altered CM2 chondrites, such as Nogoya.

Despite their extensive degree of aqueous alteration, CM-chondrite bulk compositions show no evidence of elemental fractionations between water-soluble elements such as the alkalis and alkali-earths and refractory immobile elements, such as Al and Sc. Figure 6 shows Na/Sc, Ca/Al, and Mg/Al ratios for CM chondrites as a function of their mineralogical alteration index (MAI) (Browning *et al.*, 1996). The ratios of water-soluble Ca and Na to refractory elements are essentially constant throughout the range of alteration experienced by the CM2 chondrites. Magnesium/aluminum is also constant regardless of the extent of alteration of the host meteorite, even though Mg was clearly mobile on a localized scale during aqueous alteration as indicated by the replacement of Mg-rich chondrule silicates by Fe-rich phases and the formation of dolomite. The Na/Sc data for three CM1 chondrites are also shown for comparison with CM2 chondrites. The spread of Na/Sc ratios exhibited by these meteorites suggests that Na may have been mobilized to some degree during advanced stages of aqueous alteration. However, all three chondrites are Antarctic finds and so the possibility that the Na depletion is due to terrestrial alteration must also be considered. Calcium/aluminum data are available for only one CM1 chondrite, Yamato (Y) 82042, and suggest that Ca may have been depleted during aqueous alteration.

### 2.3. CR Carbonaceous Chondrites

CR chondrites are all petrologic type 2 (Weisberg *et al.*, 1993), with the exception of one meteorite, Grosvenor Mountains (GRO) 95577, which appears to be a CR1 (Weisberg and Prinz, 2000). Like the CM2 chondrites, the CRs exhibit significant variability of their degree of alteration. Although the general characteristics of alteration in this group of chondrites are known (e.g., Weisberg *et al.*, 1993; Zolensky *et al.*, 1993; Noguchi, 1995), the details of alteration are lacking, in comparison with CM or CI chondrites. Most CR chondrites have experienced significantly less alteration than typical CM2 chondrites. This is reflected by the fact that several CR chondrites contain chondrules with unaltered glassy mesostases or mesostases that only show the earliest stages of aqueous alteration on the periphery of chondrules (Fig. 7a) (e.g., Noguchi, 1995). In some cases, unaltered chondrule glass can occur in direct contact with hydrous matrix, as described in, for example, Y 8449

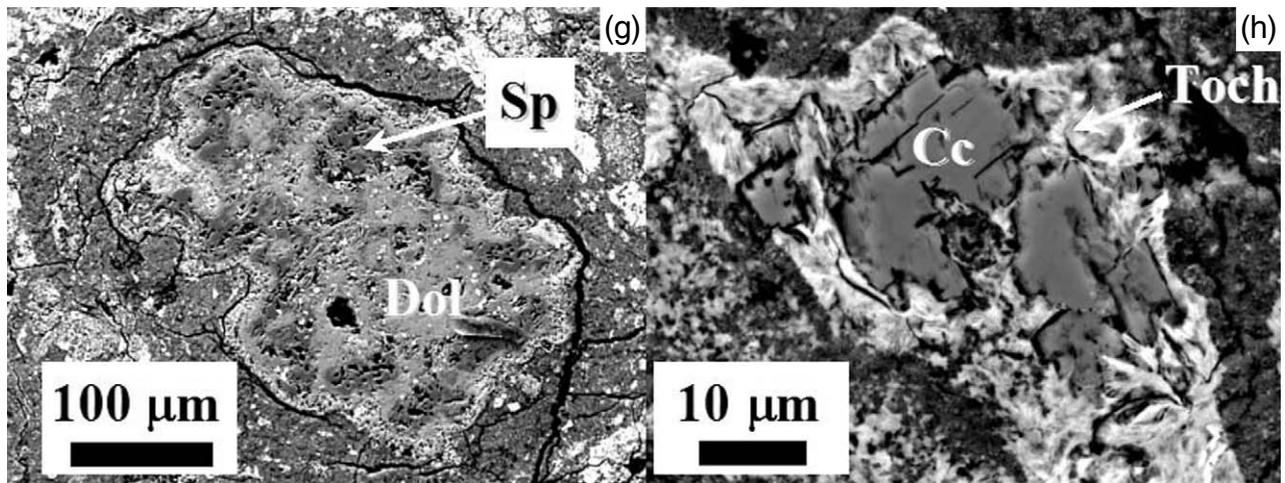


**Fig. 5.** BSE and cathodoluminescence images of carbonate occurrences in CM2 carbonaceous chondrites. **(a)** Typical occurrence of calcite in Y 791198 — anhedral, isolated grain embedded within fine-grained matrix material. **(b)** CL intensity images of the grain shown in **(a)** illustrating complex zoning characteristics with an irregularly shaped, corroded core with a zoned overgrowth. **(c)** Cluster of anhedral calcite (Cc) grains associated with tochilinite (Toch) in the fine-grained matrix of Y 791198. **(d)** CL intensity image of calcite grain in Y 791198 consisting of two subgrains that show asymmetric, but regular zoning. **(e)** Calcite (Cc) grain in Murchison matrix associated with tochilinite (Toch). **(f)** CL intensity image of grain shown in **(e)** illustrating the grain consists of two subgrains with subrounded cores, possibly indicative of dissolution, overgrown by a homogeneous rim.

(Ichikawa and Ikeda, 1995). In addition, abundant unaltered Fe,Ni metal is present in most CR chondrites. However, some CR chondrites, such as Renazzo and Al Rais, show much more advanced alteration, where the glassy mesotases in chondrules have mostly been replaced by phyllosilicates,

indicating a degree of alteration that is more comparable with typical CM2 chondrites (Weisberg *et al.*, 1993).

Most evidence of aqueous alteration is present in the matrices of CR chondrites and the style of alteration, although more limited, appears to be most similar to CI chon-



**Fig. 5.** (continued). (g) Compact altered CAI in ALH 81002 that has been extensively replaced by dolomite (Dol). The primary phases in the CAI that are unaltered are spinel (Sp) and small perovskite grains (bright blebs). (h) Calcite (Cc) in ALH 81002 associated with tochilinite (Toch). The grain has a ragged, corroded appearance indicating that it has undergone dissolution and replacement by tochilinite.

drites. Framboidal magnetite is common in the matrices of many CR chondrites (Fig. 7b), and fine-grained, Ca-rich carbonates and sulfides are also present (Weisberg *et al.*, 1993). In the matrices of two CR chondrites, Zolensky *et al.* (1993) reported unaltered olivine in addition to fine-grained phyllosilicates, predominantly serpentine, intergrown with saponite as the main alteration phases. However, in the CR Elephant Moraine (EET) 92042, Abreu and Brearley (2004, 2005a) found that the matrix consists almost entirely of fine-grained phyllosilicates that act as a groundmass for ubiquitous, submicrometer Fe,Ni sulfides (Fig. 7c,d).

CR chondrites also contain DIs that occur as lithic fragments within the host chondrites (Weisberg *et al.*, 1993; Bischoff *et al.*, 1993; Endress *et al.*, 1994) and are mineralogically similar to CR chondrite matrices, although they appear to have experienced a higher degree of hydration. These DIs have O-isotopic compositions that clearly relate them to the CR chondrites (Weisberg *et al.*, 1993), suggesting that they are derived from a region of the same parent body that has experienced more extensive aqueous alteration.

The signatures of aqueous alteration are apparent in the composition of matrices in CR chondrites, although the data for this group of chondrites is limited. The matrices of the CR chondrites are much less fractionated than CI matrices (Fig. 2), consistent with their lower degree of aqueous alteration, but nevertheless show characteristic depletions in Ca, which can be attributed to mobilization of this element to form calcite during aqueous alteration.

#### 2.4. CO Carbonaceous Chondrites

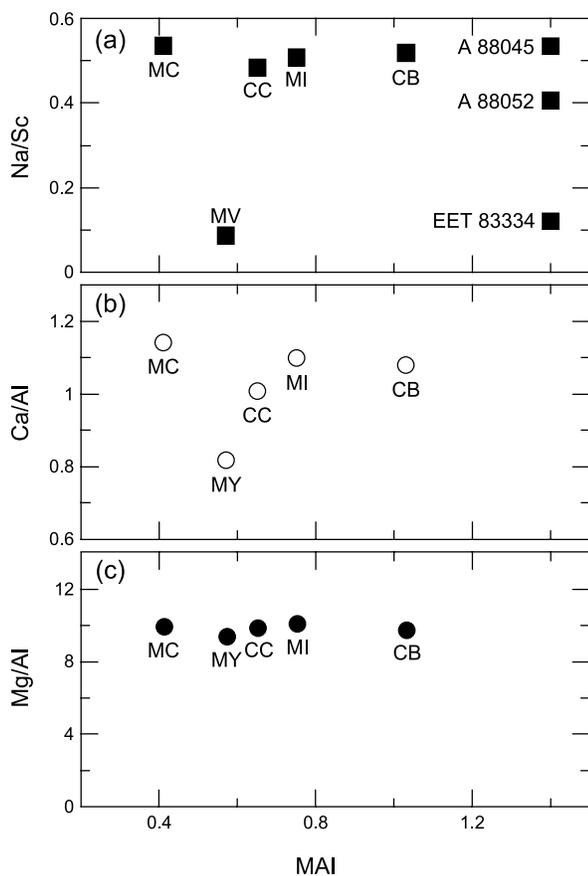
The CO3 carbonaceous chondrites as a group have been minimally affected by low-temperature aqueous alteration, although they may have been subjected to fluid-assisted metamorphism (Rubin, 1998). Evidence of alteration is variable within the CO group; most CO chondrites (e.g.,

Kainsaz, Ornans, and Warrenton) show no evidence of alteration and, in those that do, the effects are minimal even at the TEM scale (Keller and Buseck, 1990a; Brearley, 1994). The effects of alteration are almost exclusively observed within the matrix, although Ikeda (1983) and Itoh and Tomeoka (2001) have reported phyllosilicates replacing chondrule glass in Allan Hills (ALH) 77307 (3.0). Minor phyllosilicate formation is evident in the matrices of ALH 77307, Lancé, and Ornans (Brearley, 1993; Kerridge, 1964; Keller and Buseck, 1990a) with very fine-grained serpentine and saponite occurring interstitially to matrix olivines and sometimes within veins in the larger matrix olivines. CO chondrites show no evidence of the development of carbonates or sulfates and in this respect are similar to the CV chondrites, but quite distinct from CI, CR, and CM chondrites.

#### 2.5. CV Carbonaceous Chondrites and Dark Inclusions

Evidence of aqueous alteration in the CV carbonaceous chondrites is complex and controversial. In members of the oxidized and reduced CV carbonaceous chondrites, unambiguous evidence of aqueous alteration is indicated by the presence of hydrous phases, such as phyllosilicates. However, members of the oxidized CV3 chondrites also contain a variety of anhydrous phases that are also generally agreed to be of secondary origin. Although these phases have been traditionally regarded as being of nebular origin, it has been proposed more recently that these alteration assemblages are in fact the result of metasomatic processes involving an aqueous fluid on an asteroidal parent body (Krot *et al.*, 1995, 1998a,b, 2000a). The origin of these assemblages has therefore been the subject of intense debate over the last decade (see Brearley, 2003, for a recent summary).

Unlike all the other effects of aqueous alteration discussed elsewhere in this chapter, the proposed metasomatism of the oxidized CV chondrites occurred at temperatures



**Fig. 6.** Bulk-rock element/refractory element ratios for CM chondrites vs. mineralogical alteration index (MAI) as defined by *Browning et al.* (1996). The chondrites range from relatively weakly altered CM2 chondrites to fully hydrated CM1 chondrites. The CM1 chondrites are arbitrarily designated as having MAIs of 1.4. (a) Ca/Al ratio showing that despite aqueous alteration, this refractory element ratio remains constant irrespective of degree of aqueous alteration. Ca is clearly highly mobile on the scale of hundreds of micrometers to millimeters in CM chondrites, because of its high solubility in aqueous fluids, but was not depleted in the bulk rock, regardless of degree of aqueous alteration. (b) Na/Sc, showing that the moderately volatile and highly soluble element Na is not fractionated from the refractory and immobile element Sc during aqueous alteration. (c) Mg/Al vs. MAI, demonstrating that refractory element ratios remain constant during aqueous alteration. Murray appears to be anomalously low in its Ca and Na abundances, possibly because it has been extensively brecciated. Data from *Kallemeyn and Wasson* (1981); *Grady et al.* (1987); *Wlotzka et al.* (1989); *Browning et al.* (1996); *Zolensky et al.* (1997).

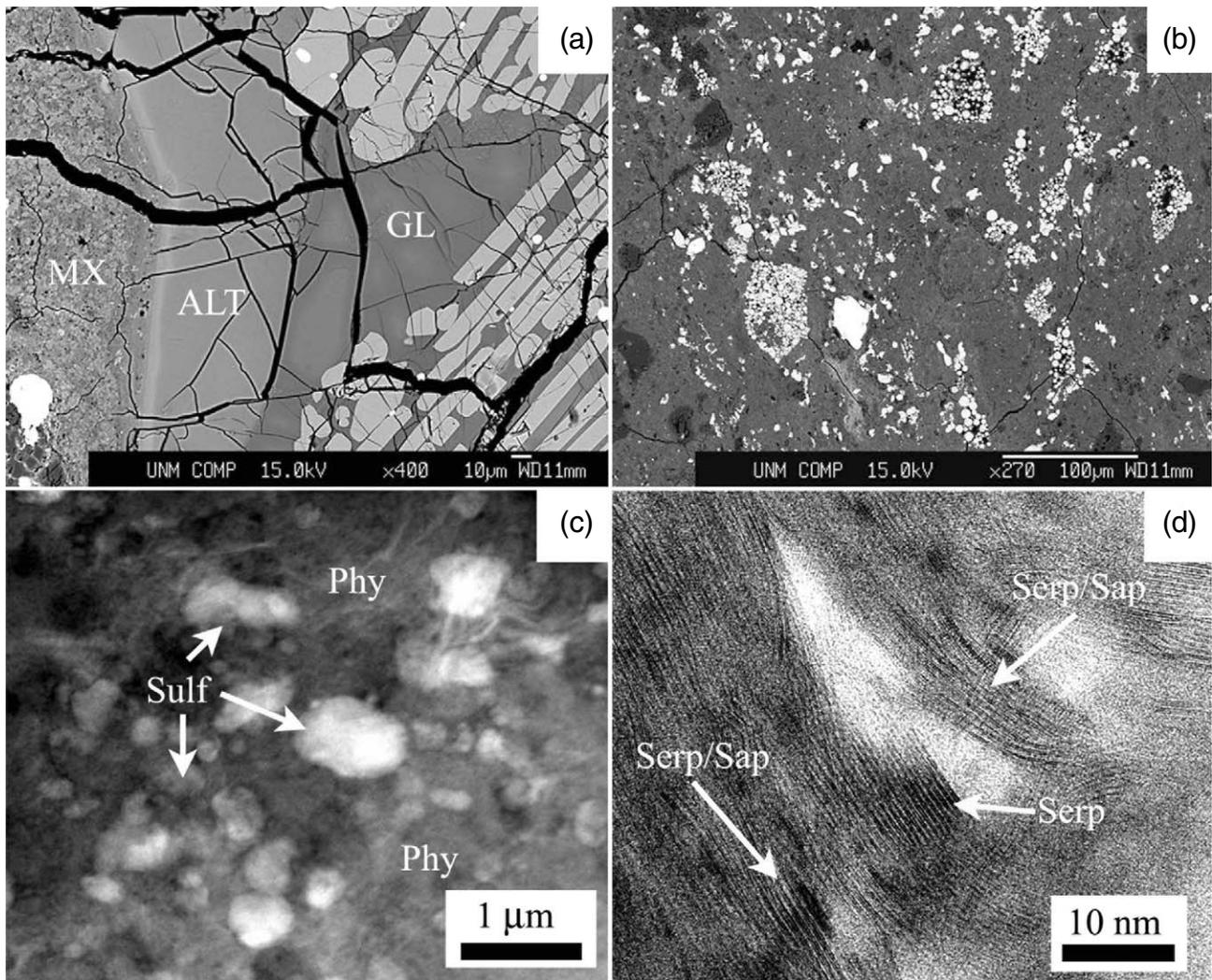
significantly higher than the alteration in most other chondrites ( $\sim 200^{\circ}$ – $300^{\circ}$ C), based on thermodynamic calculations (e.g., *Krot et al.*, 1998a,b, 2000a). As a result the dominant alteration products are anhydrous rather than hydrous phases such as phyllosilicates. It is the absence of this “smoking gun” that is, in part, responsible for the extensive debate as to the origin of these anhydrous mineral assemblages in the

Allende subgroup of the oxidized CV3 chondrites ( $CV3_{oxA}$ ). However, it should be noted that some authors have argued that the rare hydrous phases that occur in CAIs and chondrules in meteorites such as Allende were also formed during this relatively high-temperature aqueous metasomatism (e.g., *Brearley*, 1999). In the case of the Bali subgroup of the oxidized CV3 chondrites ( $CV3_{oxB}$ ), there is less ambiguity because the anhydrous phases coexist with phyllosilicate phases.

Aqueous alteration has affected the reduced CV chondrites to a very limited extent. Vigarano, the only reduced CV chondrite fall, exhibits incipient aqueous alteration within its matrix, indicated by the presence of ferrihydrite and rare, fine-grained saponite, that occur interstitially to and replacing FeO-rich matrix olivines (*Lee et al.*, 1996). Alteration in Vigarano is heterogeneous as indicated by the presence of phyllosilicate-rich fine-grained rims on some chondrules in Vigarano that have experienced more advanced alteration than typical regions of Vigarano matrix (*Tomeoka and Tanimura*, 2000). These variations in the degree of alteration are probably a reflection of the fact that Vigarano is a breccia consisting of both oxidized and reduced types that may have experienced variably alteration histories. Very minor development of carbonate that appears to be extraterrestrial in origin has also been reported in Vigarano associated with chondrules and CAIs (*Mao et al.*, 1990; *Davis et al.*, 1991; *Abreu and Brearley*, 2005b).

In the oxidized CV chondrites, phyllosilicates have been widely reported, and the range of alteration in this group varies from essential zero to regions of some chondrites where alteration is almost 50%. In members of the Bali subgroup, such as Bali, Kaba, Mokoia, and Grosnaja, matrix olivines have commonly been replaced by saponite and a variety of phyllosilicate phases including Fe-bearing saponite, Na phlogopite, Al-rich serpentine, and Na-K mica are found in altered chondrules and CAIs (*Cohen et al.*, 1983; *Keller and Buseck*, 1990b; *Tomeoka and Buseck*, 1990; *Keller et al.*, 1994; *Krot et al.*, 1998a,b). In general, evidence of significant elemental redistribution is limited in the  $CV_{oxBali}$  subgroup, with the exception of Bali itself. Bali contains distinct regions of highly altered material characterized by the formation of secondary phosphates, magnetite, and carbonates.

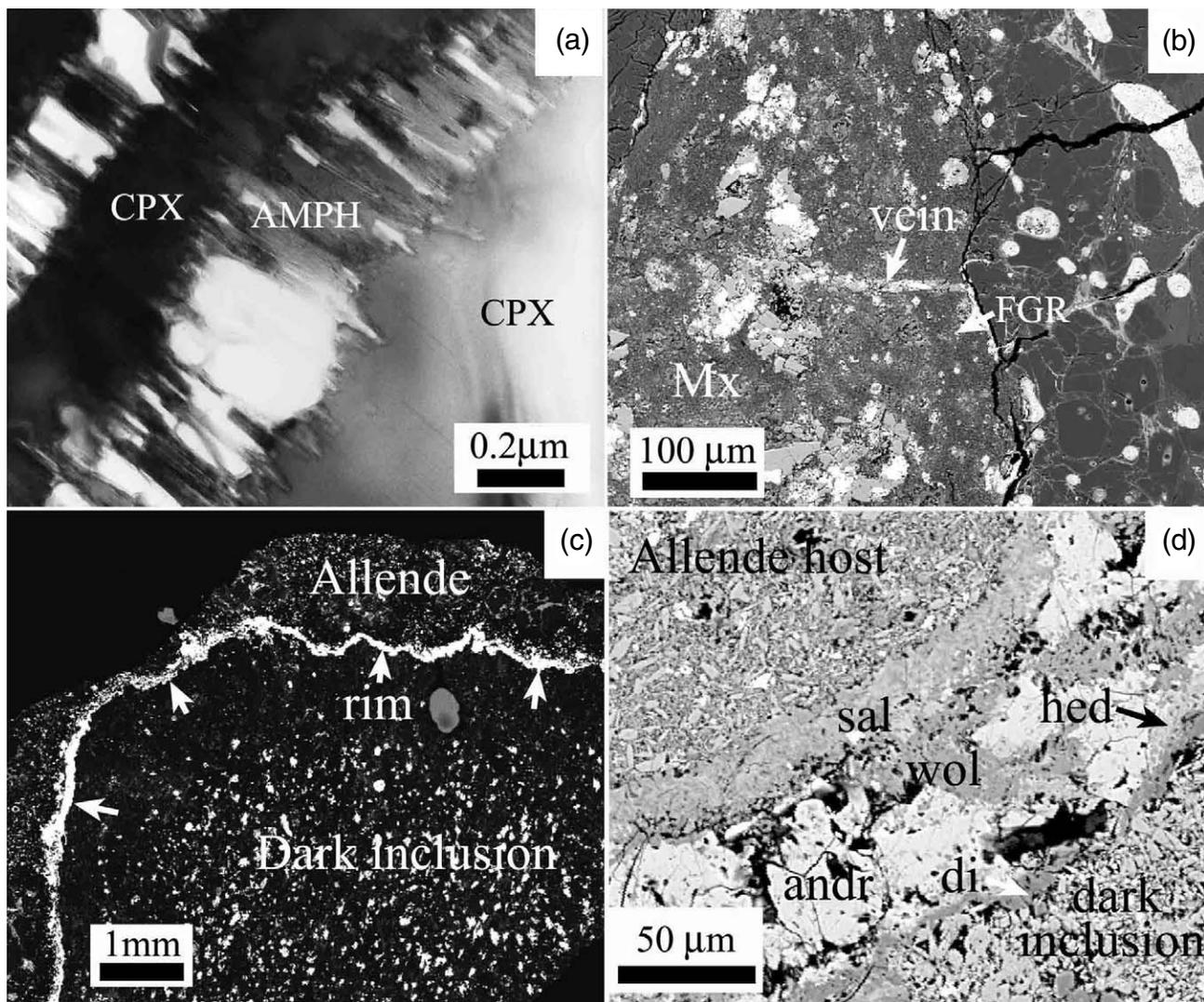
In members of the Bali subgroup, anhydrous phases that may have formed as a result of metasomatic processes involving aqueous fluids coexist with the phyllosilicate minerals described above. These secondary phases include magnetite, Ni-rich sulfides, fayalitic olivine, Ca-Fe-rich pyroxenes (Di-Hd), and andradite (Figs. 8a,b). Textural relationships between these phases indicate a complex sequence of replacement reactions that involved extensive mobilization of Ca from Ca-rich phases in chondrules and CAIs. Metal nodules in chondrules have been replaced by magnetite that has itself been replaced to varying degrees by fayalitic olivine, Ca-Fe-rich pyroxenes, and andradite. Thermodynamic analysis constrains formation of these mineral assemblages to temperatures of  $\sim 300^{\circ}$ C (*Krot et al.*, 1998a,b).



**Fig. 7.** Textural and mineralogical characteristics of aqueous alteration in CR chondrites. **(a)** BSE image showing a zone of altered chondrule glass (ALT) in contact with fine-grained matrix material (MX) on the edge of a type II chondrule in the weakly altered CR2 EET 87770. In the interior of the chondrule, chondrule mesostasis glass (GL) is unaffected by the alteration process. **(b)** BSE image of typical region of matrix in EET 92024 showing abundant framboids of magnetite, embedded in a very fine-grained matrix. **(c)** Dark field scanning transmission electron microscope Z-contrast image of a region of typical matrix in the EET 92024 CR carbonaceous chondrite. In this image, phases with bright contrast have the highest average atomic number. Abundant submicrometer Fe,Ni sulfides, pentlandite, and pyrrhotite (Sulf) are present embedded in a groundmass of fine-grained phyllosilicates (Phy), principally serpentine and saponite. **(d)** High-resolution TEM image of typical fine-grained phyllosilicates in the matrix of the CR carbonaceous chondrite EET 92024. The matrix phyllosilicates consist of individual serpentine grains (labeled Serp) and grains that are disordered intergrowths of serpentine and the smectite group mineral saponite (labeled Serp/Sap). Image courtesy of A. M. Abreu.

The situation in the Allende-like subgroup of the oxidized CV chondrites is extremely complex, in part because Allende itself is the only chondrite of this subgroup that has been studied in any detail. Allende has an exceptionally low water content (<0.2 wt%) (Jarosewich *et al.*, 1987) and contains no hydrous phases within its fine-grained matrix (Toriumi, 1989; Brearley, 1999). Nevertheless, several occurrences of rare phyllosilicates have been described in Allende in CAIs and to a lesser extent in chondrules. Among the phases that have been described in Allende CAIs

are phlogopite, montmorillonite, clintonite, margarite, saponite, and chlorite (Wark and Lovering, 1977; Dominik *et al.*, 1978; Hashimoto and Grossman, 1987; Keller and Buseck, 1991; Tomeoka and Buseck, 1982a,b). In low-Ca pyroxene-bearing chondrules, Brearley (1999) reported the widespread occurrence of small amounts of talc, amphibole, and disordered biopyriboles (Fig. 8b). Compared with the hydrous phases observed in the Bali-subgroup, it is notable that with the exception of montmorillonite and saponite, the phases present in Allende all have higher ther-



**Fig. 8.** BSE SEM and TEM images showing a variety of styles of alteration in CV3 carbonaceous chondrites and DIs. **(a)** TEM image showing development of fibrous amphiboles replacing low-Ca pyroxene in a chondrule from Allende. Although such phases are rare, they appear to be widely developed in pyroxene-bearing chondrules in this meteorite. **(b)** BSE image showing development of a vein of alteration that crosscuts a fine-grained rim in the Mokoia CV3 (oxidized) chondrite. The vein consists of the anhydrous phases, fayalite, magnetite and Fe-sulfide. Image courtesy of A. N. Krot (after *Krot et al.*, 1998b). **(c)** Ca  $K_{\alpha}$  X-ray map of part of a DI in the oxidized CV3 chondrite Allende. The DI is surrounded by a narrow rim of Ca-rich phases that is in direct contact with the Allende host matrix. A zone around the periphery of the inclusions shows a depletion in Ca that is interpreted as a zone in which soluble Ca has been leached from the DI by aqueous fluids and has been precipitated at the boundary between the DI and the host Allende matrix. Image courtesy of A. N. Krot (after *Krot et al.*, 2000a). **(d)** BSE image showing the detailed characteristics of the Ca-rich rim between the DI and Allende host shown in **(c)**. The rim consists of a complex layered sequence of andradite garnet, wollastonite, salitic pyroxene, hedenbergite, and diopside. Image courtesy of A. N. Krot (after *Krot et al.*, 1998b).

mal stabilities. The style of aqueous alteration in Allende is therefore quite different from that observed in the Bali-like oxidized CV chondrites.

Members of the Allende subgroup have also experienced secondary alteration that has resulted in the formation of anhydrous, rather than hydrous, mineral assemblages that share some similarities with those observed in the Bali subgroup, but there are notable differences. The effects of this secondary alteration include (1) Fe-alkali-halogen metasom-

atism of CAIs, chondrules, and matrix; (2) formation of ferrous olivine rims on chondrules, isolated olivine grains, etc.; and (3) oxidation and sulfidization of opaque assemblages in CAIs, chondrules, and matrix. Additional possible effects of alteration noted by *Krot et al.* (1995) also include the formation of platy FeO-rich olivines, Ca-Fe pyroxenes, wollastonite, and andradite in the matrix. Unlike members of the Bali subgroup, phyllosilicates and pure fayalitic olivine are extremely rare. Instead, secondary alkali-rich phases

such as nepheline and sodalite are common (Krot *et al.*, 1998a,b).

The bulk compositions of the reduced and oxidized CV carbonaceous chondrites show some compositional differences that are probably a reflection of complex secondary processing. These differences are particularly apparent for elements that are mobile during aqueous alteration and metasomatism, with the oxidized CV chondrites showing enrichments in elements such as Fe and Na, relative to the reduced CV chondrites (Krot *et al.*, 1995, 1998a,b). The origin of these compositional variations appears to be strongly correlated with the fact that the oxidized subgroup has undergone extensive aqueous alteration ( $CV_{oxBali}$ ) and/or metasomatism ( $CV_{oxAll}$ ), showing that alteration for this group of chondrites did not occur under closed-system conditions.

CV chondrites commonly contain dark, lithic clasts, termed dark inclusions (DIs), that are considered to have a close genetic relationship to the host CV chondrites (see Krot *et al.*, 1995; Brearley, 2003). The same alteration features that are observed within the oxidized CV chondrites are also apparent within DIs, but the range of alteration in DIs is much wider. Consequently, DIs provide additional insights into the alteration processes that affected the CV3 chondrites. Dark inclusions have been classified into two types: type A and type B (e.g., Johnson *et al.*, 1990; Krot *et al.*, 1995). Type A inclusions resemble the host CV chondrites, but have smaller chondrules and CAIs. Type B inclusions contain no chondrules and CAIs, but consist largely of aggregates of fine-grained FeO-rich olivine with chondrule-like shapes (Kojima *et al.*, 1993; Kojima and Tomeoka, 1996; Krot *et al.*, 1997a) set in a matrix of finer-grained olivine. In DIs in the oxidized CV chondrites, the olivine aggregates contain platy olivine whereas in the reduced CVs, such as Leoville and Efremovka, chondrules have been perfectly pseudomorphed by dense aggregates of fine-grained FeO-rich olivine (Kracher *et al.*, 1985; Johnson *et al.*, 1990; Krot *et al.*, 1999).

With a few exceptions, the alteration mineralogy of DIs lacks hydrous phases such as phyllosilicates. Hence the mineralogical evidence for aqueous alteration is cryptic and other indicators such as the O-isotopic compositions of the DIs are used to infer that these complex materials interacted with water. Dark inclusions from reduced CV chondrites such as Leoville and Efremovka have bulk O-isotopic compositions that do not lie on the carbonaceous chondrite anhydrous mineral (CCAM) line. Instead, these inclusions show heavy isotope enrichments that are generally interpreted as resulting from interaction with aqueous fluids, probably on an asteroidal parent body (e.g., Clayton and Mayeda, 1999). However, not all inclusions show such heavy isotope enrichments, including most inclusions that have been studied from the Allende meteorite. In the case of Allende, the involvement of water in the genesis of these inclusions has been questioned (Clayton and Mayeda, 1999), despite the fact that some textural lines of evidence appear to provide strong support for the role of fluids in the alteration processes (Krot *et al.*, 1998a,b, 2000a), such as the

presence of Ca-rich rims at the interface of the dark inclusions with the Allende matrix (Fig. 8c,d) and veins of Ca-rich pyroxenes that crosscut the dark inclusions (see below).

## 2.6. Unique Carbonaceous Chondrites

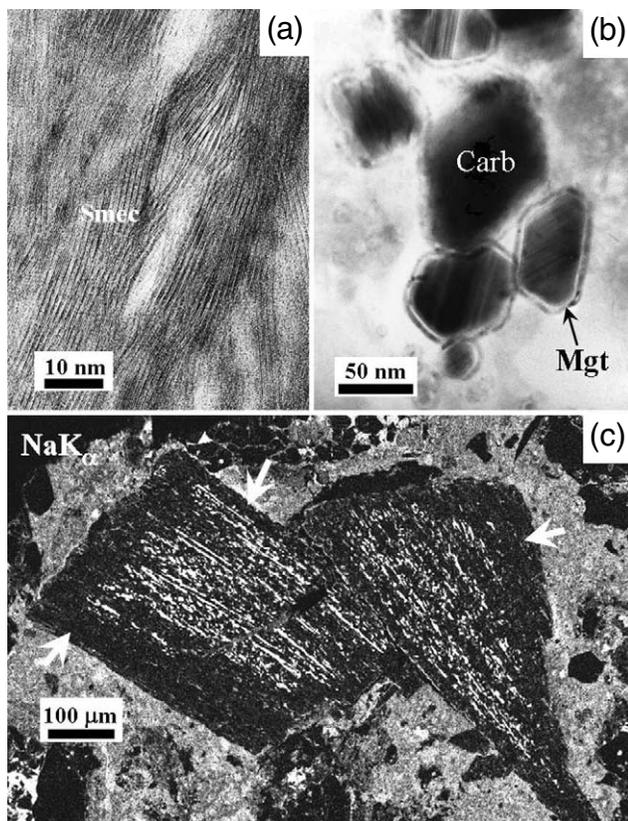
There are several unique carbonaceous chondrites such as Tagish Lake, MacAlpine Hills (MAC) 88107, Kaidun, and Lewis Cliff (LEW) 85332 that exhibit evidence of aqueous alteration. However, for brevity only Tagish Lake and MAC 88107 are discussed here. Details of aqueous alteration in LEW 85332 and Kaidun can be found in Brearley (1997a) and Zolensky and Ivanov (2003), respectively. Tagish Lake is probably the most pristine carbonaceous chondrite ever recovered. This meteorite is clearly a type 2 carbonaceous chondrite with affinities to both CI1 and CM2 chondrites, but defies a more definitive classification. Grady *et al.* (2002) have suggested that Tagish Lake is best classified as a CI2 chondrite. Tagish Lake is unusual in having an extremely low density (1.66 g/cc) (Zolensky *et al.* 2002), much lower than any other carbonaceous chondrite measured to date. Tagish Lake appears to be a breccia with two major distinct lithologies (carbonate-poor and carbonate-rich) in addition to clasts that have affinities to CM1 chondrites (Zolensky *et al.*, 2002). Sparse chondrules and CAIs, showing partial alteration, are embedded in a phyllosilicate-rich matrix. The alteration mineralogy of Tagish Lake consists of fine-grained phyllosilicates (saponite and serpentine), magnetite, Fe,Ni sulfides, and carbonates (calcite, dolomite, siderite). The fine-grained textural characteristics of the matrix phyllosilicates are typical of CI chondrites, but differ markedly from CM chondrites.

MacAlpine Hills 88107 is a unique, unequilibrated carbonaceous chondrite that has mineralogical and compositional characteristics that are intermediate between the CM and CO chondrites (Krot *et al.*, 2000b). Aqueous alteration in this chondrite has resulted in the formation of both hydrous and anhydrous phases. Saponite and serpentine occurring as intergrowths are the dominant phyllosilicates in the fine-grained matrix and coarser-grained fayalite, hedenbergite, magnetite, pyrrhotite, and pentlandite are also widely present. This alteration assemblage bears close similarities to alteration in the Bali subgroup of the oxidized CV3 carbonaceous chondrites.

## 2.7. Ordinary Chondrites

*2.7.1. Unequilibrated ordinary chondrites (UOCs).* Evidence of aqueous alteration is best developed in the matrices of a few UOCs such as Semarkona (LL3.0), Bishunpur (LL3.1), and Chainpur (LL3.4) (Hutchison *et al.*, 1987; Alexander *et al.*, 1989), but alteration effects have also been recognized recently in chondrules (Hutchison *et al.*, 1998; Grossman *et al.*, 2000, 2002). In Semarkona, alteration in the fine-grained rims and matrix is pervasive and few primary phases have survived the alteration event(s) (Hutchison *et al.*, 1987; Alexander *et al.*, 1989). Extremely fine-

grained Fe-rich smectite (Fig. 9a) is the dominant alteration mineral although roughly circular areas of coarser-grained smectite up to few micrometers in size are also present. These regions are sometimes rimmed by fine-grained magnetite and calcite. Rare primary phases that have survived alteration are Mg-rich olivine and twinned monoclinic low-Ca pyroxene, as well as partially altered grains of what appear to be densely packed aggregates of FeO-rich olivine. Sulfides of probable secondary origin, such as laths of pentlandite, also occur in the matrix. Primary sulfides in Semarkona matrix have been partially replaced along well-defined crystallographic planes by Fe-rich phyllosilicates. In the least-altered sulfides, the phyllosilicates have compositions that resemble Fe-rich chlorite or septachlorite. Sulfides that show more advanced alteration have been replaced by



**Fig. 9.** Textural characteristics of aqueous alteration in unequilibrated ordinary chondrites (UOCs). (a) High-resolution TEM image of very fine-grained FeO-rich smectite (Smec) in the matrix of the unequilibrated ordinary chondrite Semarkona. (b) TEM image of Fe-carbides (Carb) in the matrix of Semarkona surrounded by thin oxidation rims of magnetite (Mgt). (c) Na  $K_{\alpha}$  X-ray map of fragments of a bleached radial pyroxene chondrule in Semarkona. The chondrule clearly fragmented presumably as a result of brecciation and the two fragments were offset from one another. The bleached zone (arrowed) is up to 100  $\mu\text{m}$  thick on essentially all the peripheral regions of the fragment, except along the plane where fragmentation occurred. Here the bleached zone is significantly thinner, indicating that the bleaching process occurred both before and after the brecciation event that disrupted the fragment. After Grossman *et al.* (2000).

smectite with compositions that match those of smectite elsewhere in Semarkona matrix. In addition to phyllosilicates, some regions of the matrix contain the fine-grained Fe,Ni carbides (cohenite and haxonite) that are surrounded by thin oxidation rinds of magnetite (Fig. 9b) (Keller, 1998). Coarse-grained carbide-magnetite assemblages are widespread in Semarkona, replacing metal-sulfide nodules (Taylor *et al.*, 1981; Hutchison *et al.*, 1987; Krot *et al.*, 1997b). These carbide-magnetite assemblages appear to be the result of the interaction of C-O-H fluids with primary metal and sulfides during mild asteroidal metamorphism (e.g., Krot *et al.*, 1997b) and will not be discussed further here.

Compared with Semarkona, alteration of matrix and fine-grained rims in Bishunpur (Alexander *et al.*, 1989) is much less advanced. The precursor mineralogy of matrix and fine-grained rims consists of fragments of olivine and low-Ca pyroxene embedded in an amorphous material that is rich in normative feldspar. Alteration appears to have affected the amorphous material exclusively, which has been replaced by smectite with lower FeO, but higher CaO contents than smectite in Semarkona. Smectite in Bishunpur is also Cl-bearing with up to 0.3 wt% Cl, indicating that Cl-bearing fluids were certainly involved in the alteration process.

Aqueous alteration of chondrules is somewhat more cryptic and comes in the form of so-called bleached chondrules that have been reported in several UOCs (Kurat, 1969; Christophe Michel-Levy, 1976; Grossman *et al.*, 2000). In these meteorites, radial pyroxene and cryptocrystalline chondrules have porous outer zones that have a lighter appearance when viewed by optical microscopy, where mesostasis has been destroyed and alkalis and Al removed (Fig. 9c), probably by dissolution (Grossman *et al.*, 2000). Transmission electron microscope studies of chondrules in Semarkona show that partial replacement of chondrule glass by fine-grained smectite has occurred. This smectite is FeO-rich and has a composition that is essentially identical to that of smectite in the adjacent matrix (Grossman *et al.*, 2002). Hutchison *et al.* (1987) noted that calcite sometimes occurs as trains of crystals lying approximately parallel to the margins of chondrules that may represent a sink for Ca that has been mobilized from chondrule glass by aqueous fluids.

**2.7.2. Equilibrated ordinary chondrites.** Metamorphosed ordinary chondrites have been viewed for decades as being free of any effects of aqueous alteration. This view has required radical revision after the discovery of halite crystals that contain fluid inclusions, up to 15  $\mu\text{m}$  in size, in the Monahans (H5) and Zag (H4–6) ordinary chondrite breccias (Zolensky *et al.*, 1999; Rubin *et al.*, 2002). In both meteorites, halite occurs in the porous clastic matrix, which is interstitial to coarser-grained clasts of metamorphosed, and in some cases, shocked ordinary chondrite material. In Zag, halite occurs as grains up to 100  $\mu\text{m}$  in size whereas in Monahans, euhedral crystals of halite, sometimes with sylvite inclusions, can be up to 5 mm in size.

Additional evidence that metamorphosed ordinary chondrites have experienced aqueous alteration is provided by the

presence of bleached chondrules in rare petrologic type 4 and 6 chondrites (*Grossman et al.*, 2000). These chondrules have essentially identical features to those in type 3 ordinary chondrites, but appear to have experienced metamorphism that postdates aqueous alteration.

### 3. LOCATION OF ALTERATION

A critical question that has become increasingly controversial over the last 15 years concerns the environment where aqueous alteration of chondritic meteorites took place. This controversy has focused largely on the CM chondrites and, to a lesser extent, the CVs and CRs. Alteration of other chondrite groups such as the CIs, COs, and UOCs is much less contentious and there appears to be a general consensus that most evidence is compatible with asteroidal alteration.

At present, four different alteration scenarios have been proposed, three involving hydration prior to accretion of the final asteroidal parent body. These models can be summarized as (1) reaction of anhydrous, high-temperature condensate phases with water vapor as the solar nebula cooled to the condensation temperature of water ice [ $\sim 160$  K at  $P \sim 10^{-6}$  bar, e.g., *Cyr et al.* (1998)]; (2) hydration of silicate dust in the solar nebula during the passage of shock waves through regions of elevated ice/dust ratios (*Ciesla et al.*, 2003); (3) alteration within small (tens of meters), ephemeral, water-bearing protoplanetary bodies that were later disrupted (e.g., *Metzler et al.*, 1992; *Bischoff*, 1998) and their altered components dispersed and then accreted with unaltered materials into the final asteroidal parent bodies (pre-accretionary alteration); and (4) the more traditional parent-body alteration model (e.g., *Kerridge and Bunch*, 1979; *McSween*, 1979; *Browning et al.*, 1996; *Hanowski and Brearley*, 2001) in which aqueous alteration occurs entirely after asteroidal accretion. These models are not necessarily mutually exclusive: Preaccretionary alteration may have occurred, but was, in some or most cases, followed by asteroidal alteration.

In order to evaluate the evidence for and against these different alteration scenarios, it is useful to review possible criteria that can potentially be used to discriminate between alteration in different environments. These different criteria have been used in a rather *ad hoc* fashion in the literature, leading to confusion. In most cases, none of the criteria listed below provide exclusive proof of alteration in particular environment, but generally support alteration in one environment or the other. Specific criteria that can and have been used are (1) heterogeneity vs. homogeneity of the mineralogical effects of alteration within different primitive components of chondrites (e.g., CAIs, chondrules, matrix, isolated mineral grains, i.e., presence of disequilibrium mineral assemblages) (*Brearley*, 1997b; *Hanowski and Brearley*, 2001); (2) stable isotopic heterogeneity vs. homogeneity of alteration products in altered chondrites as an indicator of alteration in different or similar isotopic reservoirs; (3) correlation of mineralogical alteration effects with stable isotopic data (*Browning et al.*, 1996); (4) evidence of mass-

independent fractionation (nebular) vs. mass-dependent fractionation (asteroidal) in the O-isotopic composition of bulk chondrites and individual components (*Weisberg et al.*, 1993; *Clayton and Mayeda*, 1999); (5) evidence (or lack thereof) of bulk compositional variations that might constrain the location of alteration; (6) constraints provided by the thermodynamic stabilities of mineral phases under solar nebular and asteroidal conditions (e.g., *Krot et al.*, 1998a,b); (7) experimental and theoretical constraints on the kinetics of alteration reactions (i.e., gas-solid, liquid-solid etc); and (8) timing of alteration, i.e., evidence of the formation of alteration phases more than several million years after CAI formation is most consistent with asteroidal alteration, assuming nebular lifetimes of 5–10 m.y. (*Podosek and Cas-sen*, 1994).

A variety of lines of evidence to support both asteroidal and preaccretionary alteration have been presented in the literature. Some of the key lines of evidence are reviewed below; for an exhaustive review of the evidence for preaccretionary alteration, see *Bischoff* (1998).

#### 3.1. CI Chondrites: Evidence for Parent-Body Alteration

Since early work on the CI chondrites (*DuFresne and Anders*, 1962; *Richardson*, 1978; *Fredriksson and Kerridge*, 1988), this group of meteorites has been regarded as representing the definitive example of asteroidal aqueous alteration. As discussed above, one of the key lines of evidence for asteroidal aqueous alteration, i.e., crosscutting sulfate veins, has been brought into serious doubt. *Gounelle and Zolensky* (2001) have reinterpreted the veining as reflecting dissolution, local transport, and reprecipitation of extraterrestrial sulfates by absorbed terrestrial water. Nevertheless, other lines of textural evidence are supportive of an asteroidal scenario for alteration, such as (1) crosscutting phyllosilicate-rich veins (*Tomeoka*, 1990), (2) the presence of carbonates that appear to represent fragments of an earlier generation of carbonate veins or resemble vein fillings (*Richardson*, 1978; *Endress and Bischoff*, 1996), and (3) the ubiquitous presence of framboidal magnetite (*Kerridge et al.*, 1979a). In the latter case, *Kerridge et al.* (1979a) have argued that precipitation of magnetite from a gel-like phase is likely.

Analyses of bulk CI chondrites show that they have unfractionated bulk compositions relative to the solar photosphere (*Anders and Grevesse*, 1989). This observation appears to be most consistent with alteration in an essentially closed system, i.e., within a parent body under conditions where fluid flow was minimal. Refractory and moderately volatile alkalis and alkali earths such as K, Na, Ca, Rb, and Sr, as well as the rare earth elements, have variable solubilities in aqueous fluids (e.g., *Hass et al.*, 1995) and are certainly leached at different rates from carbonaceous chondrites (*Mittlefehldt and Wetherill*, 1979). Alteration in anything other than a closed system on an asteroidal parent body would invariably cause fractionation of these elements

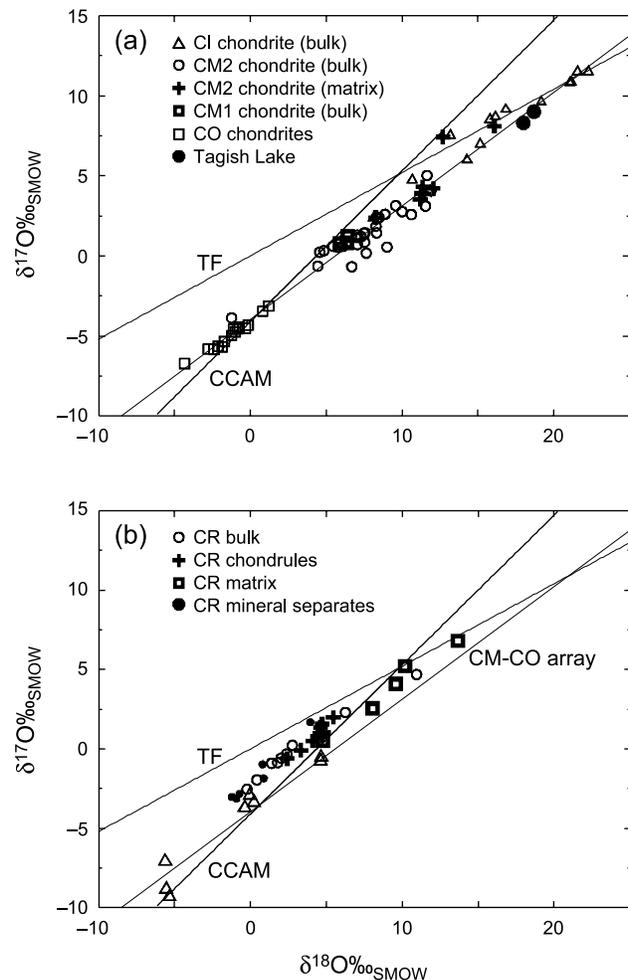
from one another, as well as from less-soluble elements such as Ti and Al. Alteration of components to varying degrees in the nebula or within ephemeral protoplanetary bodies would therefore result in a final parent body that showed fractionated elemental abundance ratios, unless all the materials from the same region of the nebula were accreted together at the same time. This is plausible, but is a scenario that is not supported by the O-isotopic composition of different components in CI chondrites. CI chondrites have bulk O-isotopic compositions that lie close to the terrestrial fractionation line on a three-isotope plot (Fig. 10a), with a  $\Delta^{17}\text{O}$  of  $+0.38 \pm 0.09\text{‰}$  ( $2\sigma_m$ ) (Rowe *et al.*, 1994). For Orgueil, the bulk rock, carbonates ( $\Delta^{17}\text{O} = \sim +0.37\text{‰}$ ), phyllosilicates (matrix:  $\Delta^{17}\text{O} = \sim +0.24\text{‰}$ ), and water released from stepwise heating ( $\Delta^{17}\text{O} = \sim +0.6\text{‰}$ ) (Baker *et al.*, 2002) all lie on or close to a mass-dependent fractionation line, indicating that they equilibrated with the same fluid. These data are most consistent with asteroidal alteration (Clayton and Mayeda, 1999; Leshin *et al.*, 2001; Baker *et al.*, 2002), although there are clearly complexities. For example, magnetites from Alais, Ivuna, and Orgueil have  $\Delta^{17}\text{O} = +1.70 \pm 0.05\text{‰}$  and are clearly not at isotopic equilibrium with the host rock.

Grady *et al.* (1988) have also argued that the C-isotopic composition of carbonates in CI chondrites is most consistent with formation on a parent body. The CI carbonates have median  $\delta^{13}\text{C}$  values of  $+50\text{‰}$  to  $+60\text{‰}$  compared with  $-15\text{‰}$  to  $-30\text{‰}$  for CI organic carbon. Formation of these isotopically-heavy carbonates has been attributed to the selective alteration of interstellar grains such as SiC that have  $\delta^{13}\text{C}$  values  $>1200\text{‰}$ , within the CI parent body. If the carbonates had formed prior to accretion, their isotopic composition would reflect the typical C-isotopic composition of the nebular gas, which is considered to have had a light isotopic composition similar to that of organic carbon (i.e.,  $\delta^{13}\text{C} \sim -15\text{‰}$ ) (Kerridge, 1993). Preservation of these heavy  $\delta^{13}\text{C}$  values requires a selective alteration process within a closed system such as an asteroidal parent body. Similar arguments can also be advanced for formation of carbonates in the CM and CR chondrites, which also have isotopically-heavy carbonates (Clayton, 1963; Halbout *et al.*, 1986; Grady *et al.*, 1988; Clayton and Mayeda, 1999).

Manganese-chromium dating of carbonates in CI chondrites also appears to be most consistent with parent-body alteration [see also Krot *et al.* (2006) and later discussion]. Carbonates in Orgueil and Ivuna (Endress *et al.*, 1996; Hutcheon and Phinney, 1996) yield formation ages of 16.5–18.3 m.y. after CAI formation, implying that alteration of CI chondrites occurred over periods of time that are significantly longer than the estimated lifetimes for the solar nebula (Podosek and Cassen, 1994) and hence are more consistent with asteroidal alteration.

### 3.2. CM Chondrites

There is a significant body of evidence to support both preaccretionary and asteroidal alteration of these complex meteorites. As a consequence, alteration in this group of



**Fig. 10.** (a) Oxygen three-isotope diagram showing the composition of bulk CI, CO, CM2, and CM1 chondrites, as well as the unique chondrite Tagish Lake. The compositions of matrix in CM2 chondrites are also shown. All the data for the CO and CM chondrites lie along the same mixing line with slope 0.7. According to the model of Clayton and Mayeda (1984), the CM chondrites were altered under fluid/rock ratios ranging from 0.3 to 0.6, whereas the CI chondrites and Tagish Lake experienced alteration under much higher water/rock ratios ( $\sim 1.2$ ). CM1 chondrites, despite their high degree of hydration, were altered under water/rock ratios similar to the least-altered CM2 carbonaceous chondrites. Data from Clayton and Mayeda (1999, 2001) and Zolensky *et al.* (1997). (b) Oxygen-isotope diagram showing the composition of bulk CR chondrites and mineral separates. The data lie along a line of slope 0.59 that is distinct from that defined by the CM and CO chondrites. Data from Clayton and Mayeda (1999).

chondrites is currently an area of significant controversy. A brief summary of the key lines of evidence that support each of the scenarios is discussed below.

#### 3.2.1. Evidence for asteroidal alteration.

3.2.1.1. Veining in CM chondrites: Unlike the CI chondrites, crosscutting veins are extremely rare in CM chondrites. However, examples of veining have been documented, including Ca sulfate veins crosscutting the matrix

of Cold Bokkeveld (*Lee, 1993*) and thin veins of Fe oxyhydroxide originating from altered metal in chondrules and extending across fine-grained rims into the clastic matrix in Murchison (*Hanowski and Brearley, 2000*). In both cases, vein formation clearly occurred after final accretion of the CM parent body.

3.2.1.2. Iron-rich aureoles: *Hanowski and Brearley (2000)* documented aureoles of Fe-enrichment surrounding large, altered metal grains in several CM chondrites that incorporate matrix, chondrules, and mineral fragments. The peripheries of the aureoles sometimes crosscut fine-grained rims and interfinger between chondrules and mineral fragments, demonstrating that they formed after asteroidal accretion. Aureole formation appears to be the result of oxidation of metal to soluble Fe<sup>2+</sup> that was transported in solution through unconsolidated chondritic materials and was finally precipitated as insoluble Fe<sup>3+</sup> oxyhydroxides.

3.2.1.3. Bulk compositional homogeneity of CM chondrites: Alteration in CM chondrites is quite variable in extent, even within CM2s. However, despite this variability, the bulk compositions of CM chondrites are quite homogeneous, suggesting that alteration was essentially isochemical in character. There is, for example, no evidence of the addition or removal of soluble elements, such as Ca, by fluids (e.g., Fig. 6). Instead, elemental mass transfer occurred on a localized scale and alteration largely involved exchange between fine-grained matrix and chondrules. Highly soluble Ca was leached from chondrules and CAIs during aqueous alteration and appears to have been precipitated in the matrix as Ca carbonate. This evidence is incompatible with the preaccretionary model, in which chondrules and matrix experienced variable degrees of alteration in different protoplanetary bodies. Preserving the homogeneous bulk composition of CM chondrites in the preaccretionary model requires mixing of altered chondrules with depleted Ca contents with an exact proportion of fine-grained dust with enriched Ca contents, in order to retain the solar Ca/Al ratio of the final chondrite.

3.2.1.4. Elemental exchange between chondrules and matrix during progressive alteration: Prior to aqueous alteration, the CM chondrites can, simplistically, be regarded as consisting of a mixture of Fe-rich, fine-grained matrix and Mg-rich chondrules. As proposed by *McSween (1979, 1987)*, progressive aqueous alteration of these meteorites should result in the redistribution of these elements between these two components. The model predicts that with progressive aqueous alteration, matrix should become more Mg-rich and chondrules Mg-depleted. Data from CM chondrites show that the Mg content of matrix and fine-grained rims does, in fact, increase with progressive alteration (*McSween, 1979; Chizmadia and Brearley, 2004*), although the trend is complicated by brecciation effects. In addition, the Fe-rich serpentine alteration products of chondrule silicates become more Mg-rich as progressive alteration of chondrules occurs (*Hanowski and Brearley, 1997*).

3.2.1.5. Homogeneity of chondrule alteration: Asteroidal aqueous alteration requires that all components within the same meteorite were altered together under the same

physicochemical conditions and for the same duration. Provided the effects of primary bulk compositions, mineralogy, grain size, and textures of different objects (e.g., chondrules) can be constrained, it would be expected that for *in situ* alteration, there should be a high degree of consistency in the style and degree of aqueous alteration of different components. Detailed studies of alteration of chondrules in two unbrecciated CM2 chondrites that have been altered to different degrees, Y 791198 (*Chizmadia and Brearley, 2003*) and ALH 81002 (*Hanowski and Brearley, 2001*) show that this is indeed the case. In the comparatively weakly altered Y 791198, only mesostasis glass, Fe,Ni metal, and sulfides are altered in all chondrules, whereas in ALH 81002 individual chondrules show highly variable degrees of alteration with extensive replacement of primary chondrule phenocryst phases such as olivine and low-Ca pyroxene. Pseudomorphic replacement of the chondrules and their phases is essentially perfect such that the morphologies of the precursors are retained exactly. When chondrules of the same type are compared, the style and extent of alteration is consistent, as are the compositions of the serpentine alteration products. These observations are consistent with *in situ* alteration in which all chondrules in an individual, unbrecciated CM chondrite interacted with the same fluid. This evidence does not necessarily preclude preaccretionary alteration. However, the probability of transporting groups of chondrules with the same degrees of alteration through a turbulent nebula as proposed in the preaccretionary model (e.g., *Metzler et al., 1992*), without mixing them with chondrules with different degrees of alteration, is small.

3.2.1.6. Oxygen-isotopic compositions: The O-isotopic data show systematic relationships between the bulk isotopic composition of CM chondrites and the degree of aqueous alteration (*Browning et al., 1996*), a relationship that would be extremely difficult to maintain in a preaccretionary environment where disruption of planetessimals occurred prior to accretion of the final parent body. Furthermore, the O-isotopic compositions of carbonates in CM chondrites also evolve with increasing degree of alteration in a manner that is most consistent with formation from a fluid that is progressively equilibrating with the host rock (e.g., *Benedix et al., 2003*). In addition, as noted earlier, the O-isotopic composition of water evolved from phyllosilicates in Murchison also appears to lie on the same mass-dependent fractionation line as carbonates (*Baker et al., 2002*), supporting the view that these two components equilibrated with the same fluid. However, it should also be noted that not all alteration components in CM2 chondrites were in isotopic equilibrium with the fluid, as indicated by the fact that Murchison matrix has a distinctly lower  $\Delta^{17}\text{O}$  than either the carbonates or water released from phyllosilicates (e.g., *Baker et al., 2002*). In addition, sulfates in CM chondrites have  $\Delta^{17}\text{O}$  values that are more positive than either carbonates or phyllosilicates (*Airieau et al., 2001*). Clearly the process of isotopic equilibration between a heterogeneous mixture of materials with variable isotopic compositions during aqueous alteration was a complex process, aspects of which are not yet fully understood.

**3.2.2. Evidence for preaccretionary alteration.** In the CM2 chondrites, most of the evidence for preaccretionary alteration focuses on the textural relationships between fine-grained rims (Fig. 3) and the objects (i.e., chondrules) they surround (Metzler *et al.*, 1992; Bischoff, 1998). In addition, the characteristics of the mineral assemblages present in the rims themselves are also important. Implicit in the preaccretionary model is the assumption that the rims formed by accretion of fine-grained dust onto chondrules within the solar nebula, a model that has received widespread support. The presence of enrichments of primordial noble gases in fine-grained rims appears to be most consistent with a nebular model (Nakamura *et al.*, 1999). However, asteroidal formation mechanisms for fine-grained rims have also been proposed (e.g., Richardson, 1981; Sears *et al.*, 1993).

**3.2.2.1. Occurrence of unaltered chondrule glass in contact with hydrated rim materials:** Metzler *et al.* (1992) described the rare occurrence of apparently unaltered chondrule glass juxtaposed against hydrated fine-grained rim materials in some CM chondrites. Chondrule glass is generally considered to be among the most susceptible of chondrule phases to aqueous alteration (see below) and therefore Metzler *et al.* (1992) argued that alteration of fine-grained rims could not have occurred without alteration of chondrule glass. They concluded that alteration of dusty rim materials must have occurred prior to accretion of rims onto the chondrules in the solar nebula, with no subsequent aqueous alteration within the asteroidal parent body. However, it is known that hydration of glasses can occur under certain conditions, but the amorphous structure of the glass is retained (e.g., Mungall and Martin, 1994). Metzler *et al.* (1992) did not report compositional data for the unaltered glass and so it is not possible to evaluate alternative explanations for this textural relationship. However, studies of other CM chondrites indicate that preserved chondrule glass is extremely rare. For example, Chizmadia and Brearley (2003) found no evidence of preserved chondrule glass in a large population of chondrules in Y 791198, a chondrite that is one of the least altered of the CM2 group.

**3.2.2.2. Unaltered chondrule olivine fracture surfaces in contact with hydrated fine-grained rim material:** In some CM chondrites, partially altered chondrule olivines with clean, unaltered fracture surfaces occur in direct contact with hydrous, fine-grained rim materials. Metzler *et al.* (1992) and Bischoff (1998) interpreted these relationships as evidence for preaccretionary alteration. In their alteration scenario, individual chondrules were altered prior to fracturing, then a fine-grained rim consisting of anhydrous and hydrated dust was accreted onto the chondrule fragments in the solar nebula. Finally, these rimmed objects were accreted into the CM parent body. Metzler *et al.* (1992) argued that if further aqueous alteration had occurred on an asteroidal parent body, the exposed fracture surfaces on the exterior of the chondrule would have undergone hydration to serpentine. However, Metzler *et al.* (1992) did not consider the possibility that the local chemical microenvironment in the fine-grained rim may have inhibited aqueous alteration

of the olivine, as appears to have occurred in some chondrules in CM chondrites (e.g., Hanowski, 1998). Hanowski reported examples of chondrules that showed evidence of advanced alteration of olivine in their interiors, but no alteration where the olivine is in direct contact with fine-grained rim materials, features that cannot be interpreted as being due to preaccretionary alteration.

**3.2.2.3. Disequilibrium mineral assemblages within fine-grained rims:** In some CM chondrites, the fine-grained rim materials appear to be a disequilibrium mixture of unaltered and altered mineral grains. In Y 791198, perhaps the least-altered CM2 chondrite currently known, Metzler *et al.* (1992) found that fine-grained rims contain an intimate mixture of primary phases such as Fe,Ni metal, troilite, and olivine and alteration phases such as phyllosilicates, tochilinite, and sulfides. In addition, in ALH 81002 Laurretta *et al.* (2000) argued that regions of unaltered olivine, pyroxene, and metal were present in fine-grained rims. These complex mineral assemblages have been interpreted as evidence that unaltered and altered nebular dust were mixed together prior to asteroidal accretion (Metzler *et al.*, 1992; Bischoff, 1998). It is expected that subsequent asteroidal alteration would have caused oxidation of Fe,Ni metal and troilite to secondary alteration products. However, Chizmadia *et al.* (2003) proposed an alternative scenario in which the survival of Fe,Ni metal is the result of hydrolysis reactions during the early stages of aqueous alteration that consume protons and drive the fluid pH to very alkaline conditions under which metal alteration is inhibited.

There is a substantial body of textural evidence to support aqueous alteration in a preaccretionary environment. However, many of these interpretations are based on simple assumptions as to how mineral phases react with aqueous fluids and do not take into consideration the complex and changing geochemical environments that were prevalent during aqueous alteration. In particular, the role of localized geochemical microenvironments and their effects on promoting or inhibiting alteration reactions needs to be examined in much greater detail. Once this understanding is developed, it will be possible to evaluate the evidence for preaccretionary alteration in a much more robust manner. Although preaccretionary alteration may have been important in CM chondrites, its effects have certainly been overprinted by later parent-body alteration. Distinguishing these preaccretionary effects from asteroidal alteration remains a significant challenge in CM chondrites.

### 3.3. CR Chondrites

**3.3.1. CR chondrites: Evidence for asteroidal alteration.** There is some ambiguity as to the location of alteration of the CR chondrites that arises in part from the fact that most CR chondrites are breccias. Weisberg *et al.* (1993) noted that chondrules in CR chondrites often show variable degrees of alteration that could be the result of alteration prior to final lithification of these meteorites. However, they also suggested that this alteration could have taken place

within the CR parent body and that the components were mixed together by later brecciation, rather than alteration occurring in a preaccretionary environment.

Evidence for parent-body alteration is provided by the alteration of chondrule glass in two chondrules from the CR2 chondrites, EET 87770 and EET 92105 (Burger and Brearley, 2004). In both meteorites, type II chondrules show evidence of partial alteration of chondrule glass to phyllosilicates where it is in direct contact with matrix. Calcium and P have been leached from the chondrule glass and the depletion in Ca is mirrored by an enrichment of Ca in the matrix that is due to the presence of fine-grained Ca phosphate. This evidence suggests that elemental exchange between chondrules and matrix has occurred during alteration with reprecipitation of Ca as Ca phosphate in the matrix immediately outside the chondrule.

Oxygen-isotope data for CR chondrites also support a parent-body alteration model. The O-isotopic compositions of bulk CR chondrites and separated components (chondrules, matrix, and mineral fragments) lie along a line of slope 0.59 (Fig. 10b) (Weisberg *et al.*, 1993; Clayton and Mayeda, 1999) that is interpreted as a mixing line between at least two O-isotopic reservoirs: a  $^{16}\text{O}$ -rich anhydrous component and a  $^{16}\text{O}$ -poor hydrous component. However, magnetite and phyllosilicate-rich matrix separates from Renazzo have O-isotopic compositions that lie on the terrestrial fractionation line, indicating that both materials formed from the same fluid (Clayton and Mayeda, 1977), a scenario that is most compatible with alteration within an asteroidal environment (Clayton and Mayeda, 1999).

**3.3.2. CR chondrites: Evidence for preaccretionary alteration.** Although Weisberg *et al.* (1993) concluded that alteration of the components in CR chondrites probably occurred within an asteroidal environment, they did not rule out the possibility of some preaccretionary alteration. Ichikawa and Ikeda (1995) have described unaltered chondrule glass in contact with hydrous matrix in Y 8449, which they attributed to preaccretionary alteration, i.e., hydrous alteration of matrix materials that were later mixed with unaltered chondrules prior to asteroidal accretion. They also noted marked compositional differences between phyllosilicates in chondrules and those in the adjacent matrix, which they argued were also the result of preaccretionary alteration.

### 3.4. CV Chondrites

**3.4.1. CV Chondrites: Evidence for asteroidal alteration.** Among the oxidized CV chondrites, members of the Bali subgroup show the strongest evidence for parent-body alteration. Aqueous alteration has affected all components (i.e., chondrules, CAIs, and matrix) of Bali, Kaba, and Mokoia, indicating that the fluid interaction occurred after all these components were assembled together (e.g., Cohen *et al.*, 1983; Keller *et al.*, 1994; Kimura and Ikeda, 1998). This conclusion is supported by evidence that Ca has been lost from chondrule mesostasis during alteration and has been redistributed into the matrix (Krot *et al.*, 1998a,b). The pres-

ence of alteration veins that postdate formation of a prominent shock-produced foliation is also consistent with this interpretation. Alteration phases in the matrices of these meteorites have clearly developed interstitially to fine-grained olivines, as well as replacing individual grains, indicating that alteration occurred after accretion.

Krot *et al.* (1998a,b) described textures in members of the Bali subgroup of the oxidized CV3 chondrites that provide strong evidence for parent-body alteration. As discussed above, in this group of chondrites, secondary phyllosilicates coexist with a variety of secondary anhydrous phases. Of particular significance is the observation that veins of fayalite, magnetite, and sulfide are present that originate in chondrules, crosscut fine-grained rims, and extend into the matrix of the meteorites (Fig. 8a), clearly indicating formation of the veins after accretion. Members of the Bali subgroup have bulk O-isotopic compositions that lie on the CCAM line. However, their O-isotopic compositions are lower in  $^{16}\text{O}$  than either the Allende subgroup or the reduced CV chondrites, an effect that may be due to aqueous alteration (Krot *et al.*, 1995; Clayton and Mayeda, 1996, 1999). The isotopic effects of aqueous alteration are especially well developed in regions of Bali that show extensive development of phyllosilicates (Keller *et al.*, 1994). Samples of such regions have O-isotopic compositions that show significant heavy isotope depletions consistent with low-temperature aqueous alteration.

In addition, ion microprobe studies of coexisting magnetite and fayalite that have replaced metal nodules in chondrules in Mokoia have O-isotopic compositions that lie close to the terrestrial fractionation line (Krot *et al.*, 1998b). The two phases appear to lie on a mass-dependent fractionation line and have a large  $\Delta^{18}\text{O}_{\text{fayalite-magnetite}}$  fractionation of  $\sim 20\%$ , indicative of a process that occurred at relatively low temperatures, most consistent with asteroidal alteration involving a fluid.

There are many unresolved questions regarding alteration in the Allende subgroup of the oxidized CV chondrites, the location of alteration being but one of them. Evidence of hydrous alteration in this group of chondrites is minimal and the O-isotopic compositions of bulk Allende and Allende matrix show no evidence of the heavy isotope enrichments that are the characteristic signature of aqueous alteration. However, laser fluorination O-isotopic mass spectrometric analyses of individual chondrules in Allende (Young and Russell, 1998) show clear evidence of limited heavy isotope enrichments, consistent with aqueous alteration. Mineralogically, Brearley (1997b) found that the same rare, hydrous phases occur in all low-Ca pyroxene-bearing chondrules studied within a single thin section and the style and abundance of the phases is consistent from one chondrule to another. This observation suggests that all the chondrules were altered under similar conditions, for similar lengths of time, consistent with an asteroidal environment. However, this evidence is difficult to reconcile with the evidence that Allende matrix shows no direct mineralogical or isotopic evidence of aqueous alteration. An

asteroidal environment for alteration is therefore somewhat equivocal at this point, the data also being suggestive of pre-accretionary alteration.

Studies of DIs in CV chondrites have provided quite an extensive body of textural and isotopic evidence for *in situ* parent-body alteration. *Krot et al.* (1998a,b, 2000a) have described DIs from Allende that are crosscut by veins of salitic pyroxenes and Fe,Ni sulfides. In addition, each inclusion is surrounded by continuous, layered rims consisting of Ca-Fe-rich mineral phases (Figs. 8c,d). The inner layer consists of diopside-salitic pyroxene, followed by a central zone of hedenbergite, wollastonite, andradite, and kirschsteinite. The outermost zone, in contact with Allende host matrix, is composed of salitic pyroxene. The thickness of the Ca-Fe-rich rim appears to be quite well correlated to observed depletions in Ca in the outer parts of each DI (Fig. 8c).

*Krot et al.* (2000a) have argued that these characteristics are consistent with at least two periods of aqueous alteration, both of which postdate the aggregation and lithification of the DIs. The first stage resulted in the formation of secondary mineral phases such as fayalitic olivine, nepheline, sodalite, and Fe,Ni sulfides as well as the crosscutting veins of Ca-Fe pyroxene and andradite. Following this stage of alteration, the DIs were transported from their formation location, probably by impact processes on the CV3 asteroid, and were mixed into Allende host material. The alteration assemblages in the DI were out of equilibrium with fluids in host Allende, causing dissolution of Ca-Fe pyroxenes in the DIs. Reprecipitation of these phases occurred at the interface between the DI and Allende host, a process that appears to have been initiated at temperatures of ~250°C, based on thermodynamic calculations (*Krot et al.*, 2000a). Diffusional exchange between the DIs and Allende host evidently occurred during this event, requiring that this episode of alteration occurred *in situ* within an asteroidal parent body.

Oxygen-isotopic data for DIs (*Clayton and Mayeda*, 1999) provide some important insights into their possible origins. Like Allende matrix, Allende DIs have compositions that are not displaced from the CCAM line to <sup>16</sup>O-rich composition (*Krot et al.*, 1998b). However, inclusions from Efremovka, Leoville, and Vigarano are displaced to the right of the CCAM line, forming an array that extends toward the terrestrial fractionation line and shares a number of similarities with the arrays found in the CR and CM chondrites. *Clayton and Mayeda* (1999) have argued that large heavy isotope enrichments in these DIs are likely to be the result of low-temperature aqueous alteration processes, although mineralogically there is little evidence of hydrous phases in these inclusions. For some inclusions (e.g., Efremovka) (*Krot et al.*, 1999), there is a clear correlation between degree of replacement of primary phases with heavy isotope enrichment, providing further support for such a model.

**3.4.2. CV chondrites: Evidence for preaccretionary alteration.** Most studies of aqueous alteration in the Bali subgroup of the oxidized CV chondrites favor alteration in

an asteroidal environment (e.g., *Keller et al.*, 1994; *Krot et al.*, 1998a), whereas *Kimura and Ikeda* (1998) did not rule out the possibility of preaccretionary alteration. In the Allende subgroup, the heterogeneous development of rare phyllosilicate phases in CAIs has been widely attributed to formation of these phases in the solar nebula prior to accretion. For example, *Hashimoto and Grossman* (1987) and *Keller and Buseck* (1991) have proposed that phyllosilicate phases formed by reaction of individual CAIs with a nebular gas that also caused Fe-alkali-halogen metasomatism. In this scenario, heterogeneous development of hydrous phases depends on whether an individual CAI interacted with the gas or not.

### 3.5. CO Chondrites

**3.5.1. CO chondrites: Evidence for asteroidal alteration.** Definitive evidence for the location of the low-temperature aqueous alteration in the CO chondrites is limited, but points largely toward an asteroidal environment. In the matrix, development of hydrous phases has occurred interstitially to fine-grained matrix phases, filling pore space and partially replacing FeO-rich matrix olivine. This evidence indicates that alteration probably occurred after all the matrix grains accreted together and is most consistent with parent-body alteration. In the CO3.4, for example, Lancé, matrix olivines that have equilibrated Fa contents (Fa<sub>45-50</sub>), indicative of thermal metamorphism (*Keller and Buseck*, 1990a), also show evidence of aqueous alteration, indicating that interaction with an aqueous fluid was a late-stage event and postdated parent-body metamorphism.

*Rubin* (1998) has argued that parent-body metamorphism in the CO chondrites occurred in the presence of an aqueous fluid and that aqueous alteration and metamorphism are closely related (i.e., fluid-assisted metamorphism). This suggestion appears to be supported by the bulk O-isotopic data for CO carbonaceous chondrites, which show a weak correlation with petrologic type. *Clayton and Mayeda* (1999) showed that CO bulk-rock data can be fitted well to a single mixing line with slope 0.70 that is also defined by CM whole-rock and matrix separates (Fig. 10a). *Clayton and Mayeda* (1999) tentatively interpreted these data as indicating that the CO chondrites probably interacted with an external O-bearing (aqueous?) reservoir during parent-body metamorphism. At least some alteration in the CO chondrites probably occurred post-metamorphism as a result of interaction of residual aqueous fluids that were not lost during the metamorphic event.

**3.5.2. CO chondrites: Evidence for preaccretionary alteration.** Despite the body of evidence for parent-body alteration in the CO chondrites, there is some evidence for preaccretionary alteration in the most primitive member of the group, ALH 77307 (3.0). This chondrite has a bulk O-isotopic composition that lies very close to the average value for anhydrous silicate minerals in Murchison, a value that *Clayton and Mayeda* (1984, 1999) have interpreted as being the primary nebular precursor composition of Murchison

minerals, prior to aqueous alteration/thermal metamorphism. However, *Itoh and Tomeoka* (2001) have described phyllosilicates in chondrules in ALH 77307 that are embedded in a very fine-grained matrix that shows essentially no evidence of aqueous alteration and is very primitive in its textural and mineralogical characteristics (*Brearley*, 1993). Further studies are needed, but these data appear to be indicative of aqueous alteration of chondrules prior to parent-body accretion, although *Itoh and Tomeoka* (2001) attributed these phyllosilicates to parent-body alteration.

### 3.6. Unique Carbonaceous Chondrites

The unique carbonaceous chondrite MAC 88107 contains both textural and isotopic evidence of aqueous alteration within an asteroidal parent body (*Krot et al.*, 2000b). The most notable textural characteristic indicative of *in situ* alteration is the presence of widespread veins of fayalite and hedenbergite up to 30  $\mu\text{m}$  in thickness. These veins originate at opaque nodules within chondrules and cross-cut the surrounding fine-grained rims, extending into the matrix. These observations indicate that chondrules and their fine-grained rims must have accreted and been compacted together with matrix before alteration occurred. Additional evidence for asteroidal alteration comes from the Mn-Cr-isotopic systematics of fayalite in MAC 88107 (see *Krot et al.*, 2006). The initial  $^{53}\text{Mn}$  of fayalite [ $(1.58 \pm 0.26) \times 10^{-6}$ ] indicates a formation age  $\sim 9$  or 18 m.y. after Allende CAI formation, depending on the choice of the solar system initial abundance of  $^{53}\text{Mn}$  used in the age calculation.

### 3.7. Ordinary Chondrites

Aqueous alteration of the ordinary chondrites appears to have occurred dominantly in an asteroidal environment based on several independent lines of evidence. *Hutchison et al.* (1987) showed that alteration veins in the matrix of Semarkona penetrate into chondrules. They also described trains of calcite crystals that decorate the margins of chondrules and clasts, indicating formation after accretion. This conclusion is also supported by the observations of *Grossman et al.* (2000), who described a radial pyroxene chondrule in Semarkona (Fig. 9c) that underwent an early stage of alteration that produced a bleached zone around its exterior. This chondrule was later fragmented as a result of regolith processes and a second bleached zone developed along the surfaces exposed by the fracture. Smectite, with a composition essentially identical to that in the matrix, occurs replacing mesostasis glass, suggesting that alteration products of matrix and glass equilibrated with the same fluid on an asteroid.

The D/H ratios of chondrules and matrix in Semarkona provide evidence to support *in situ* exchange of aqueous fluids between these two different components. *Deloule and Robert* (1995) reported very elevated D/H ratios in the matrix of Semarkona that are indicative of the presence of

interstellar water. A similar range of D/H ratios occurs in bleached chondrules in Semarkona (*Grossman et al.*, 2000), although these ion microprobe measurements are complicated by the fact that D/H ratios vary as a function of depth into the sample. This variability may be due to exchange of terrestrial water with interlayer water in smectite. Nevertheless, despite some ambiguity, the elevated D/H ratios in both matrix and altered chondrules indicate that they both exchanged with an isotopically similar reservoir, implying that alteration occurred within an asteroidal environment.

Although halite in the equilibrated ordinary chondrites Zag and Monahans appears to be unambiguously asteroidal in origin (*Zolensky et al.*, 1999; *Rubin et al.*, 2002), there is debate over whether it precipitated from fluids that were derived internally from within the ordinary chondrite parent body. *Rubin et al.* (2002) proposed a scenario in which extensive parent-body processing (metamorphism, breccia, regolith gardening) occurred before precipitation of halides from aqueous solutions within porous regions of the asteroidal regolith. However, *Zolensky et al.* (1999) and *Bridges et al.* (2004) have suggested that the halite was derived from water-rich materials that were added at a late stage to the ordinary chondrite regolith and hence is not indigenous to the ordinary chondrite parent body.

## 4. MODELS FOR PARENT-BODY ALTERATION

Several different approaches have been taken to develop models for various aspects of the alteration history of carbonaceous chondrite parent bodies and include both empirical and theoretical treatments. These models have attempted to address (1) the evolution of mineralogic alteration assemblages with progressive alteration using observations and computer modeling (e.g., *Zolensky et al.*, 1989; *Rosenberg et al.*, 2001), (2) the stable isotopic evolution of solid and fluid phases during the alteration process (e.g., *Clayton and Mayeda*, 1984, 1999; *Young et al.*, 1999), and (3) the thermal evolution of asteroids undergoing alteration (*Grimm and McSween*, 1989; *Wilson et al.*, 1999; *Cohen and Coker*, 2000). In general, the focus of the bulk of these models has been directed toward understanding alteration of CM and CI chondrites, although the work of *Young et al.* (1999) and *Young* (2001) is more global in character.

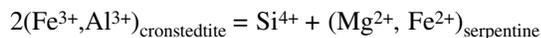
### 4.1. CM Chondrite Alteration Models

*McSween* (1979, 1987) proposed a model for progressive aqueous alteration of CM chondrites, based on mineralogical and compositional criteria, that stems from the recognition that CM chondrites exhibit variable degrees of alteration. This model has been refined progressively by further studies (*Tomeoka and Buseck*, 1985; *Zolensky et al.*, 1993; *Browning et al.*, 1996; *Hanowski and Brearley*, 2001) and various petrographic and isotopic indices to track the degree of aqueous alteration have been proposed (e.g., *Browning et al.*, 1996).

At the core of the progressive alteration model is the concept that as alteration proceeds and phases with different alteration susceptibilities react, elemental exchange occurs between the FeO-rich, fine-grained matrix and chondrules that are dominated by Mg-rich phenocryst phases such as olivine and low-Ca pyroxene. Hence, the model predicts that with increased degrees of alteration, fine-grained matrix should become more Mg-rich. Compositional data for CM matrices suggest that such a general trend does exist, although it shows considerable complexities, indicating that other factors also need to be considered (*McSween, 1979*). For example, in the original model proposed by *McSween (1979, 1987)*, the extent of alteration was closely coupled to brecciation. As chondrules altered they were broken apart by regolith comminution, causing a progressive increase in the modal abundance of matrix as these fragments were mixed with existing matrix materials and underwent alteration. Although this model holds for many CM chondrites, more recent studies show that advanced aqueous alteration can also occur entirely independent of brecciation as indicated by relatively heavily altered CM chondrites, such as ALH 81002 and several CM1 chondrites that are essentially unbrecciated (*Llorca and Brearley, 1992; Zolensky et al., 1997; Hanowski and Brearley, 2001*).

Petrographic and mineralogic studies of CM chondrites have established a general sequence of alteration of primary phases that is consistent with this model (e.g., *McSween, 1979; Tomeoka and Buseck, 1985; Zolensky et al., 1993; Browning et al., 1996; Hanowski and Brearley, 2001*). This sequence is based on the observed relative alteration susceptibilities of the major primary phases in the presence of aqueous fluids. Iron-nickel metal, troilite, and chondrule glass are most susceptible to alteration. In comparison, olivine and low-Ca pyroxene appear to be much more resistant, although there is clearly a compositional dependence on olivine alteration, with FeO-bearing olivine in type IIA chondrules (Fa<sub>20-45</sub>) altering more rapidly than forsteritic olivine in type IA chondrules and amoeboid olivine aggregates. These observations are consistent with experimental studies of olivine dissolution (*Wogelius and Walther, 1991, 1992*). Only in very heavily altered CM2 chondrites and CM1s are Mg-rich olivines altered to a significant degree.

Following *McSween (1979, 1987)*, *Browning et al. (1996)* made an important effort to correlate alteration based on mineralogic criteria with other parameters that may be potential monitors of aqueous alteration in the CM chondrites. Their primary mineralogic criterion is based on the progressive increase in Mg content of matrix serpentine as alteration proceeds. This reaction can be formalized as a progressive change from cronstedtite to Mg-rich serpentine, described by the idealized coupled substitution



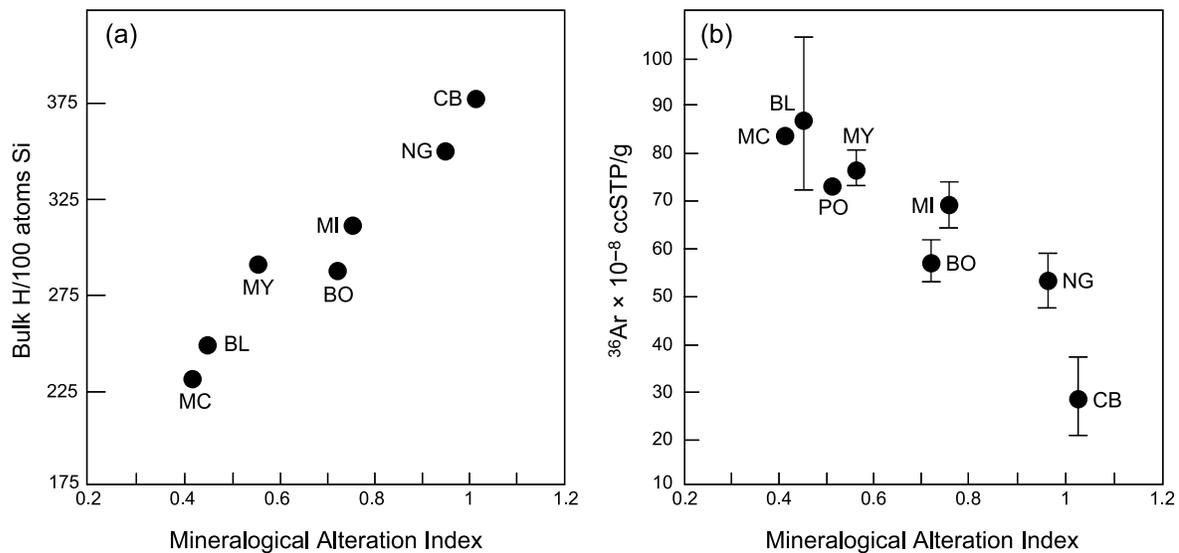
the so-called mineralogic alteration index (MAI). Additional criteria that were used as indicators of aqueous alteration are the abundance of isolated, anhydrous mineral fragments

in the matrix and the relative percentage of chondrule alteration. These parameters were chosen based on the assumption that as alteration proceeds, anhydrous phases that occur as isolated mineral grains and in chondrules should progressively alter to serpentine and hence will decrease in abundance. Despite the errors involved in measuring these different parameters because of the effects of brecciation in CM chondrites, *Browning et al. (1996)* were able to demonstrate that there are reasonable correlations between these three different independent measures of extent of alteration. Most importantly, the relative sequence of alteration for different CM chondrites is reproduced to a large extent in each case, with some minor differences. Good correlations are observed between the MAI and key bulk properties of CM chondrites, including H content and planetary noble gas content (Ar) (Fig. 11). As expected, the H content increases progressively as degree of hydration increases, whereas the <sup>36</sup>Ar content shows the reverse relationship. The decrease in <sup>36</sup>Ar content is attributed to progressive degassing of Ar as a result of destruction of the noble gas carrier phases by aqueous fluids.

Similar results were also obtained by *Eiler and Kitchen (2004)*, who investigated the H-isotopic composition and highly volatile element contents of CM chondrites that straddle the range of alteration found in this group. In this study, δD was found to be highest for the least-altered chondrites and shows a decrease as alteration proceeds that is coupled to decreases in bulk-rock Na content and planetary noble gas content (Ar). These correlations are especially strong when δD for matrix separates is compared with whole-rock data for Na and Ar contents. Although Na shows an apparent decrease with increasing degree of alteration, *Eiler and Kitchen (2004)* suggested that this was not necessarily due to removal of Na during alteration, but could be due to a dilution effect caused by water that is structurally bound in the rock during aqueous alteration. The decrease in δD is also correlated with a decrease in whole-rock N/H and C/H ratios that is probably attributable to loss of C and N as CH<sub>4</sub> and NH<sub>3</sub> that are evolved from organic material during asteroidal hydration reactions.

## 4.2. Isotopic Constraints on Alteration in CM Chondrites

The O-isotopic compositions of CM chondrites provide some important constraints on the alteration process and can be used to constrain water/rock ratios and temperatures of alteration. Bulk CM chondrites and mineral separates have O-isotopic compositions that lie along a mixing line with slope 0.7, rather than the slope 0.5 CCAM line (*Clayton and Mayeda, 1984, 1999*). The slope of this mixing line is attributed to the fact that CM chondrites consist of a mixture of <sup>16</sup>O-rich primitive nebular silicate material in chondrules and CAIs with compositions that lie along the CCAM line and hydrated <sup>16</sup>O-poor material, principally phyllosilicates that occur in the matrix (Fig. 10a) (*Clayton and Mayeda, 1984, 1999*). Formation of the hydrated material occurs



**Fig. 11.** Correlation of mineralogical alteration index (MAI) of *Browning et al.* (1996) with bulk properties of CM2 carbonaceous chondrite falls. **(a)** MAI vs. bulk H contents (plotted as bulk H/100 atoms Si), showing a progressive increase with increasing degree of alteration. **(b)** MAI vs. bulk  $^{36}\text{Ar}$  concentration showing an inverse correlation that is interpreted as the destruction of the carrier(s) of planetary noble gas composition as alteration advances. Meteorite abbreviations: Murchison (MC), Bells (BL), Murray (MY), Boriskino (BO), Mighei (MI), Nogoya (NG), Cold Bokkeveld (CB), Pollen (PO).

by reaction of anhydrous precursors with a  $^{16}\text{O}$ -poor aqueous reservoir with a composition above the terrestrial fractionation line. Based on the fractionation of  $^{18}\text{O}$  between phyllosilicates and precursor hydrous phases (17‰), *Clayton and Mayeda* (1996) estimated the water/rock ratio during aqueous alteration to be  $\sim 0.35$  by oxygen atoms ( $\sim$ the ratio by volume). CM2 chondrites show a range of bulk O-isotopic compositions that appear to be roughly correlated with the degree of alteration (*Browning et al.*, 1996). For the CM2 chondrites, this correlation may be attributable to higher degrees of alteration due to higher water/rock ratios ranging between 0.3 and 0.6, with the most highly altered CM2 having seen the highest water/rock ratios. This model does not appear to hold for the CM1 chondrites that have O-isotopic compositions that are similar to the least-altered CM2 chondrites, despite their more extensive degree of alteration (Fig. 10a). *Zolensky et al.* (1997) have interpreted this observation as indicating that alteration of CM1 chondrites occurred under similar fluid/rock ratios as relatively weakly altered CM2 chondrites. However, alteration of the CM1 chondrites occurred either at a more elevated temperature or for a more extended period of time.

Details of the complex alteration history of the CM chondrites have come from studies of the isotopic compositions of individual components, such as phyllosilicates, carbonates, sulfates, magnetite, and water in these meteorites. *Clayton and Mayeda* (1984) found that calcite and phyllosilicate separates from Murchison lie on a mass-dependent fractionation line with  $\Delta^{17}\text{O}$  of  $-1.4\text{‰}$ , indicating that they formed at equilibrium from the same aqueous reservoir. The magnitude of the fractionation of  $^{18}\text{O}$  (22.0‰) be-

tween these two phases requires a very low temperature of formation, probably around  $0^\circ\text{C}$ , depending on the initial assumptions made in the model. *Clayton and Mayeda* (1984, 1999) have argued that this is a process that was most likely to have occurred within an asteroidal parent body. However, more recent measurements of carbonates from Murchison (*Benedix et al.*, 2003) yield  $\Delta^{17}\text{O}$  of  $-0.72\text{‰}$ , suggesting that the carbonates may not actually be in isotopic equilibrium with the phyllosilicates.

Measurements of the O-isotopic composition of water released by stepwise heating of Murchison (*Baker et al.*, 2002) also provide evidence that isotopic equilibration between various phases in CM chondrites is not complete. *Baker et al.* (2002) found that most water is released in a broad peak at  $\sim 350^\circ\text{C}$ , corresponding to the release of structurally bound water in serpentine group minerals. This water has a  $\Delta^{17}\text{O}$  of  $-0.77\text{‰}$ , very similar to that of carbonates in the same rock, suggesting that these two components lie on a mass-dependent fractionation line and are in isotopic equilibrium. However, the water is not in isotopic equilibrium with the matrix in Murchison, which has a  $\Delta^{17}\text{O}$  of  $-1.88\text{‰}$ , an effect that *Baker et al.* (2002) suggested may be due to differences in the isotopic composition of O on different structural sites within alteration phases. One possibility is that tetrahedrally coordinated O in precursor silicate phases does not undergo complete isotopic equilibration with O in the altering fluids during the alteration process. Hence, the product phases of alteration, such as serpentine, may retain a proportion of  $^{16}\text{O}$  from the precursor silicates, whereas O associated with hydroxyl records the O-isotopic composition of the altering water with higher fidelity.

Hydrogen-isotope studies of bulk CM chondrites and separated chondrules and matrix samples (*Eiler and Kitchen, 2004*) show that the whole-rock  $\delta D$  values have a general negative correlation with  $\Delta^{17}O$ , decreasing from a maximum value of  $\sim 0\text{‰}$  in the least-altered CMs to  $\sim -200\text{‰}$  for the most heavily altered examples. This correlation is particularly strong when data for matrix separates alone are compared with the difference  $\delta^{18}O_{\text{matrix}} - \delta^{18}O_{\text{whole rock}}$ , a parameter used by *Clayton and Mayeda (1999)* as a preferred measure of aqueous alteration.

A significant outcome of the *Eiler and Kitchen (2004)* study is that any direct relationship between CI and CM chondrites based on their H-isotopic compositions is highly improbable, although this is a relationship that has been suggested by some authors. Despite their intense degree of aqueous alteration, the CI chondrites have bulk  $\delta D$  values of  $\sim 100\text{‰}$ , distinctly higher than the least-altered CM chondrites. The H-isotopic composition of CM chondrites becomes less, rather than more, CI-chondrite-like with increasing aqueous alteration, the reverse of the trend observed for their O-isotopic compositions. These data preclude an origin for the CI chondrites by very advanced aqueous alteration of CM chondrites.

### 4.3. Thermal Modeling of Asteroidal Aqueous Alteration

Over the last 15 years, there have been important efforts to model aqueous alteration processes in the asteroidal parent bodies of carbonaceous chondrites. These efforts have involved developing viable thermal models for asteroidal-sized parent bodies and provide an important theoretical framework for interpreting petrographic and cosmochemical observations of altered carbonaceous chondrites. Essentially all the models assume that the source of water for asteroidal alteration is water ice that was accreted along with the anhydrous precursor components of carbonaceous chondrites (i.e., chondrules, CAIs, matrix, etc.). A number of assumptions have to be made about the initial physical states of primitive asteroids as well as the important processes that control their development. There are important differences between each of the models in regard to processes such as fluid flow, venting of gases, convection, etc.

Most models assume an asteroid diameter of 100 km and an initial accretion temperature of 170–180 K (*Grimm and McSween, 1989; Wilson et al., 1999; Cohen and Coker, 2000*), although *Young (2001)* has explored alteration on asteroids with larger radii. In all cases, melting of accreted water ice occurs as a result of heat released by the decay of  $^{26}\text{Al}$ , which is typically assumed to have been accreted into the asteroid at initial  $^{26}\text{Al}/^{27}\text{Al}$  ratios lower than the canonical value of  $5 \times 10^{-5}$  (*MacPherson et al., 1995*). The models require a knowledge of a large number of physical and chemical parameters, such as porosity, permeability, thermal conductivity, reaction kinetics, etc. Some of these parameters are reasonably well known based on studies of

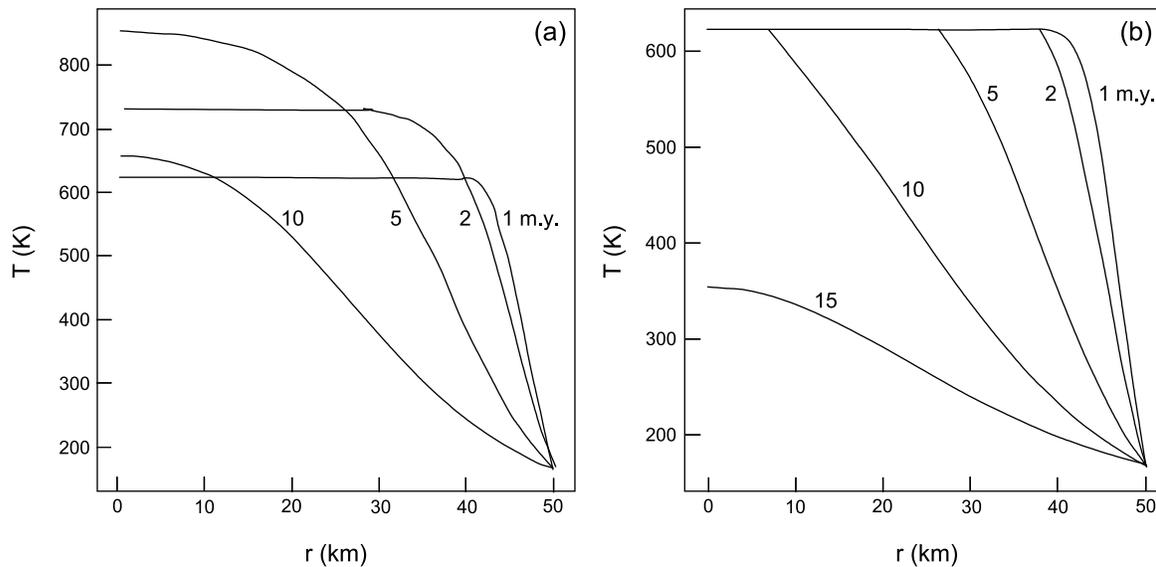
meteorites, but many are poorly constrained and have to be estimated or are varied within what are considered to be a reasonable range of plausible values (e.g., initial ice/silicate ratio, etc.). As with any modeling effort of this type, an assessment of the sensitivity of the models to different parameters has to be made.

*Grimm and McSween (1989)* investigated aqueous alteration for two endmember models. In both models, the accreted materials consist of a mixture of anhydrous silicate materials and ice (volume fraction  $< 0.4$ ), and the mixing is homogeneous throughout the parent body. In the first model, alteration occurs throughout the interior of an asteroidal parent body and hydrothermal circulation can occur if sufficiently large thermal gradients develop. In the second model, alteration occurs within an accretional regolith and water to drive aqueous alteration is supplied to the regolith by a variety of mechanisms, including melting of ice *in situ*, hydrothermal circulation, venting through fractures, or vapor diffusion through fractures and pores.

In both models, rates of aqueous alteration reactions are considered to be essentially instantaneous, in comparison with the timescales of asteroidal thermal evolution. Among the many parameters that affect thermal evolution, the initial  $^{26}\text{Al}/^{27}\text{Al}$  ratio, the latent heat of fusion of ice, and the exothermic character of dehydration reactions are especially significant. *Wilson et al. (1999)* calculated that for an initial volume fraction of ice of 0.3, almost 6 $\times$  as much heat is available from the exothermic hydration reactions as is required to melt ice. The consequence of this process is that once aqueous alteration reactions commence, a runaway reaction process occurs.

For an initial  $^{26}\text{Al}/^{27}\text{Al}$  ratio of  $1.2 \times 10^{-6}$ , and an ice fraction of 0.2 (chosen to be consistent with the final hydration level of a CM chondrite, i.e., 1 : 1 hydrous/anhydrous mineral ratio), melting of ice occurs over a period of approximately 3 m.y. and the internal temperature in the asteroid is maintained at 0°C from the core out to within 10 km of the asteroid surface (*Grimm and McSween, 1989*). Once all the ice has melted, however, exothermic alteration reactions cause the interior temperature to rise rapidly to maximum values of 150°C and marked thermal gradients develop within the asteroid (Fig. 12a). All the water in the asteroid is consumed by the hydration reactions. At a higher  $^{26}\text{Al}/^{27}\text{Al}$  ratio ( $5 \times 10^{-5}$ ), the rise in temperature is so rapid that temperatures high enough to cause dehydration of alteration products (350°C) occurs within 1 m.y. If this occurs, *Grimm and McSween (1989)* argue that internal pressurization of the parent body will occur as the pore volume is filled with near-critical  $\text{H}_2\text{O}$ . With pressures of several kilobars in the interior of a 100-km body, venting of  $\text{H}_2\text{O}$  along fractures will occur, so that  $\text{H}_2\text{O}$  will be lost from the asteroid.

A similar model with a higher starting water volume fraction (0.4) to simulate alteration in CI carbonaceous chondrites (i.e., near complete hydration of anhydrous rock) also predicts a rapid rise in temperature to the dehydration



**Fig. 12.** Examples of calculated thermal histories for 100-km-diameter CM and CI chondrite parent bodies after *Grimm and McSween* (1989). **(a)** Thermal model for CM-chondrite-like alteration with initial ice fraction of 0.2 and  $^{26}\text{Al}/^{27}\text{Al}$  ratio of  $1.2 \times 10^{-6}$ . Following absorption of latent heat of fusion of  $\text{H}_2\text{O}$  after 2 Ma, temperatures show a rapid increase due to heat released by exothermic hydration reactions. **(b)** Calculated model thermal history for CI-chondrite-like parent body with initial ice fraction of 0.4 (required to achieve complete hydration of the precursor anhydrous materials) and an  $^{26}\text{Al}/^{27}\text{Al}$  ratio of  $5 \times 10^{-6}$ .

temperature, but not beyond it (Fig. 12b). The lower maximum temperature (~620 K) reached in this model compared to that for the CM model is due to the fact that at least some of the heat produced from exothermic hydration reactions is consumed in melting the larger fraction of ice.

To extend the work of *Grimm and McSween* (1989), *Cohen and Coker* (2000) have developed a thermal model to clarify the temperature distribution and duration of liquid water on a 100-km-diameter CM chondrite parent body. By solving the one-dimensional radially symmetric heat conduction equation for a range of different initial conditions (i.e., accretion temperature, ice fraction, accretion time, abundance of radionuclides, permeability), they showed that liquid water can exist near the center of the asteroid for up to several million years. If water is not a limiting agent (i.e., is not completely consumed by hydration reactions), high ice fractions (0.4) result in lower temperatures in the asteroid core. This effect is the result of (1) the lower volume fraction of anhydrous material, hence a lower abundance of radionuclides that provide heat; (2) the fact that the higher fraction of ice requires a higher heat budget to melt the higher proportion of ice; and (3) liquid water, where present, buffers the increase in temperature because it has a higher heat capacity than rock.

One important outcome of the model is that liquid water never exists in the regolith of the asteroid over any range of model parameters. Depending on the choice of initial parameter values, the thickness of the outer part of the asteroid that remains frozen varies from as little as 6 km to about

15 km for estimated “canonical” values for CM-chondrite alteration (i.e., accretion 3 m.y. after nebular collapse, 3 AU from the Sun, permeability of  $10^{-12} \text{ m}^2$ , and ice fraction of 0.3).

Essentially all the thermal models discussed above assume that the asteroid remains as a single body throughout the period of alteration, which may last for several millions of years. However, *Wilson et al.* (1999) have examined the possibility that gas production during aqueous alteration with a subsequent internal pressurization could have resulted in partial to complete disruption of the parent body. Modeling of fluid-rock interactions in carbonaceous chondrites indicates that significant amounts of gas are released, such as  $\text{H}_2$  from alteration of silicates,  $\text{CO}_2$ , and possibly methane due to the breakdown of organic compounds (e.g., *Rosenberg et al.*, 2001).

A possible outcome of rapid gas generation is that the asteroid can become internally pressurized, resulting in the progressive development of fractures, provided the gas pressure exceeds the tensile strength by about a factor of 2. Once a pathway that allows pressurized gas to escape to the surface has developed, runaway fragmentation of the material on either side of the fracture can occur. Expansion of pressurized gas as it escapes to the surface will entrain fragments of material. For small asteroids (3 km to a few tens of kilometers radius), this process could result in disruption of the asteroid. If the fragments produced in this process are small (<a few tens of millimeters in size), complete disruption of the asteroid will occur. On the other hand, for

larger fragments, partial reaccretion may occur on the time-scale of hours, resulting in the formation of an asteroidal body in which the original radial distribution of materials has been completely changed. Hence, the outer portion of an asteroid, containing frozen water ice, could be buried in the interior of the asteroid, enabling it to undergo melting and initiating a new wave of aqueous alteration, provided that disruption occurs before  $^{26}\text{Al}$  content has decreased too much. Such a disruption process could be responsible for the widespread brecciated characteristics of CI, CM, CV, and CR chondrites, rather than being the result of impact brecciation on asteroidal surfaces.

*Young et al.* (1999) and *Young* (2001) have developed finite difference codes to model aqueous alteration in carbonaceous chondrite parent bodies with diameters <100 km, which differ from other models in that they include the mineralogical and isotopic effects of aqueous alteration as well as vapor advection. *Young et al.* (1999) have argued that the O-isotopic composition of the components of different carbonaceous chondrites can only be explained by significant fluid flow through asteroidal parent bodies, an important effect that is not considered in detail in other thermal models. The effects of fluid flow on the thermal evolution of asteroidal parent bodies are significant, because fluid-rock reactions are much more limited when fluid flow occurs, compared with stationary fluid. This significantly reduces the heating effects of exothermic hydration reactions that are important in other models.

In comparison with other models, in which pressure buildup in the asteroid interior is released by episodic fracturing and venting, *Young* (2001) argued that the internal pressurization drives fluid flow from the interior of the asteroid through porosity to the asteroid surface, where water can be lost into space. This process is likely to occur on asteroids that have diameters that are too large to disrupt by internal pressurization.

This model provides useful additional insights into the possible evolution of parent bodies that were heated uniformly throughout their interiors. First, it appears that asteroids with radii <50 km maintain high thermal gradients, whereas larger bodies have essentially uniform internal thermal gradients except near their outer surfaces. As with other models, aqueous alteration is predicted to commence within a few 100,000 years after heating commences, assuming an initial  $^{26}\text{Al}/^{27}\text{Al}$  ratio of  $1 \times 10^{-5}$ . As ice melting commences, liquid water migrates toward the exterior of the asteroid driven by pressure gradients and generates a region between the asteroid core and surface where fluid flow occurs for an extended period of time. This is a region where significant aqueous alteration occurs; the O-isotopic compositions of carbonates and hydrous minerals generated in the model calculations are in good agreement with those observed in CI, CM, and CV chondrites, supporting the notion that alteration on the parent bodies of these chondrites occurred under conditions of significant fluid flow. The model is remarkably successful at matching the observed increases in  $\Delta^{17}\text{O}$  of the solids during the

alteration process, assuming an initial  $\Delta^{17}\text{O}$  of ice of 16.0 and rock of  $-2.7$ . The very elevated  $\Delta^{17}\text{O}$  for ice assumed in the calculation is consistent with values used by *Clayton and Mayeda* (1984) to explain the O-isotopic evolution of CM and CI chondrites.

Second, for parent bodies with radii greater than 50 km in size, the modeling suggests that alteration will occur much later than for small asteroids. If the initial  $^{26}\text{Al}/^{27}\text{Al}$  ratio is quite high (e.g.,  $5.0 \times 10^{-6}$ ), then the rate of heating for a 1 Ceres-sized body (1025 km diameter) will be fast and water will be lost from the asteroid, before significant alteration can occur. For an initial  $^{26}\text{Al}/^{27}\text{Al}$  ratio of  $6.8 \times 10^{-7}$  heating is sufficiently slow so that maximum temperatures just above the melting temperature of water ice are reached 5–6 m.y. after accretion. In this situation, alteration occurs principally in a region near the asteroid surface, because this is the region of highest fluid flow. These timescales are consistent with the extended durations for aqueous alteration that are indicated by Mn-Cr dating of carbonates in CI and CM chondrites, which suggest that alteration occurred over periods of up 9 m.y. (e.g., *Krot et al.*, 2006).

A significant issue that remains to be addressed for the fluid-flow models concerns the effects that such flow would have on the chemistry of carbonaceous chondrites. If significant fluid movement had occurred through carbonaceous chondrite parent bodies, elemental mass transfer of the most soluble elements, such as the alkalis (e.g., Na, K) and alkali earths (e.g., Ca, Sr), would be expected. The bulk compositions of the most-altered carbonaceous chondrites (CI and CM) show no evidence of elemental fractionations that would indicate either addition or removal of these elements from the protolith material, arguing against fluid flow. In the case of the CI chondrites, these elements are unfractionated relative to the solar photosphere and in the case of the CMs display fractionations that are consistent with their cosmochemical behavior (i.e., refractory Ca is unfractionated relative to other refractory elements; Na is depleted according to its volatility). These data indicate that the elemental abundances in carbonaceous chondrites were established prior to accretion and have been essentially unaffected by later secondary processing, i.e., that alteration occurred isochemically in a closed system. There is little doubt however, that on the scale of millimeters, these elements were clearly highly mobile and were redistributed between components during aqueous alteration.

## 5. FLUID COMPOSITIONS

Among the most challenging aspects of understanding aqueous alteration in chondritic meteorites is constraining the compositions of the altering fluids in terms of both their chemistry and isotopic composition. This problem is particularly complex, because alteration in chondrites commenced under conditions where the fluid was in chemical and isotopic disequilibrium with the solid phases. The fluid composition therefore changed progressively with time as

the altering system evolved toward equilibrium and may also have been variable within different regions of the same parent body (e.g., *Richardson, 1978; Fredriksson and Kerridge, 1988; Johnson and Prinz, 1993, Riciputi et al., 1994*). Furthermore, unlike terrestrial rocks where fluid inclusions are quite common, direct samples of altering fluids are extremely rare in chondrites or are very small and difficult to analyze. Despite these problems, progress has been made that puts useful constraints on the elemental and isotopic composition of the fluids, particularly in the CI and CM chondrites.

### 5.1. Elemental Composition of Altering Fluids: Evidence for Brines

Among the phases that have proved most useful in constraining fluid compositions are highly soluble phases such as carbonates, sulfates, and halides. Assuming appropriate mineral/fluid element partitioning data are available, minor- and trace-element analyses of such phases can be used to constrain element ratios in the altering fluids. *Riciputi et al. (1994)* demonstrated the feasibility of this approach based on ion microprobe analyses of a suite of elements (Fe, Mg, Mn, Sr, Na, B, and Ba) in dolomites and carbonates from CI and CM chondrites. These data indicate that carbonates either precipitated from, or recrystallized in equilibrium with, low-temperature aqueous solutions with element/Ca ratios that are comparable with buried terrestrial brines (defined here as highly saline solutions). Sodium/calcium ratios are notably enriched in both dolomite and calcite in CM and CI chondrites. Dolomite in CI and CM chondrites appears to have precipitated from compositionally similar fluids, but calcite and dolomite in CM chondrites are clearly not in chemical equilibrium. This evidence suggests that these phases grew at different times, possibly during different alteration events, and provides evidence that fluid compositions varied temporally in the CM parent body.

*Riciputi et al. (1994)* observed significant variability in the element/Ca ratios in the carbonate grains that they analyzed, sometimes up to 2 orders of magnitude. This variation is probably the result, at least in part, of the presence of complex, fine-scale zoning in individual carbonate grains that has only recently been recognized (e.g., *Brearley et al., 1999; Brearley and Hutcheon, 2002*). The presence of such zoning suggests that rather than recording fluid compositions from single events, calcite and dolomite both record complex variations in fluid composition through time.

A unique opportunity to study the composition of asteroidal fluids directly has come from the discovery of fluid inclusions in halite in the Monahans and Zag equilibrated ordinary chondrites (*Zolensky et al., 1999; Rubin et al., 2002; Bridges et al., 2004*). In Monahans, primary and secondary fluid inclusions up to 15  $\mu\text{m}$  in size are present, whereas in Zag the inclusions are typically <10  $\mu\text{m}$  in size. The primary inclusions were trapped during the initial growth of the halite from asteroidal fluids, whereas the

secondary inclusions formed as a result of healing of fluid-filled fractures in existing halite. Fluid inclusion studies show that vapor bubbles are rare in fluid inclusions in Zag halites, suggesting that the trapping of the fluids occurred at temperatures  $\leq 100^\circ\text{C}$ , perhaps in the range  $25^\circ\text{--}50^\circ\text{C}$  (*Rubin et al., 2002*). In Monahans, the fluid inclusions appear to contain Fe, Mg, and/or Ca, indicated by the fluid-freezing temperatures (*Zolensky et al., 1999*).

Halite in these ordinary chondrites appears to have formed by precipitation from concentrated brines. *Rubin et al. (2002)* have speculated that these brines formed in a near-surface environment in which evaporation caused a progressive increase in alkali and chloride ions until the solutions became supersaturated and halite precipitated. As discussed earlier, however, the halite may in fact be derived from water-rich materials that were mixed into the ordinary chondrite during the waning stages of asteroidal metamorphism.

### 5.2. Oxygen-Isotopic Evolution of Aqueous Fluids

The O-isotopic systematics of altered chondrites have been discussed earlier and in *Clayton and Mayeda (1984, 1999)*. Here we focus specifically on data from individual mineral phases that provide information about how the O-isotopic composition of the fluids may have evolved during aqueous alteration. *Benedix et al. (2003)* have reported data for carbonates (dolomite and calcite) from several CM2 chondrites. They found that the carbonate  $\Delta^{17}\text{O}$  values become progressively lower as a function of the degree of alteration of the host chondrite based on the MAI of *Browning et al. (1996)*. *Airieu et al. (2001)* found similar behavior for sulfates in CM2 chondrites, but  $\Delta^{17}\text{O}$  for sulfates is more positive than for either carbonates or phyllosilicates in the same chondrite. These data indicate that the change in  $\Delta^{17}\text{O}$  may be due to precipitation of the carbonates and sulfates from a fluid that becomes progressively more equilibrated with the host chondrite as alteration proceeds, assuming that the altering fluid had a higher  $\Delta^{17}\text{O}$  than anhydrous precursor phases in the chondrite (*Clayton and Mayeda, 1999*). *Airieu et al. (2001)* argued that the differences in  $\Delta^{17}\text{O}$  between sulfate and carbonate were due to precipitation of sulfate earlier than carbonate, from a fluid that was less isotopically equilibrated with the host rock.

There also appears to be some isotopic variability in carbonates within individual CM chondrites that might represent a record of changing fluid composition with progressive alteration, although alternative explanations are also possible. For example, *Benedix et al. (2003)* found  $\Delta^{17}\text{O}$  values between  $-0.54\text{‰}$  and  $-0.84\text{‰}$  for four different splits from Murchison, significantly different from the value measured by *Clayton and Mayeda (1984)* ( $-1.4\text{‰}$ ). This difference may in part reflect the fact that Murchison is a complex breccia and contains clasts with different alteration histories. The data also show a range of  $\delta^{18}\text{O}$  values (26.6–35.5 $\text{‰}$ ) that is consistent with the range of values measured

TABLE 3. Summary of estimated conditions of parent-body alteration for chondritic meteorites.

Meteorite Group	Temperature (°C)	pH	eH	$f_{O_2}$	W/R*
CI	~20 <sup>[1]</sup> 50–150 <sup>[2]</sup> 100–150 <sup>[3]</sup>	8–10 <sup>[1]</sup> , 7–10 <sup>[2]</sup>	–0.2 <sup>[1]</sup> –0.3 to –0.8 <sup>[2]</sup>	>10 <sup>–55</sup> –10 <sup>–70</sup> †	1.1–1.2 <sup>[4,7]</sup>
CM2	0 <sup>[4]</sup> , ~20 <sup>[1]</sup> , 1–25 <sup>[2]</sup> 80 <sup>[5]</sup>	6–8 <sup>[1]</sup> , 7–12 <sup>[2]</sup> ,	–0.75–0.5 <sup>[2]</sup> 7–13 <sup>[6]</sup>	<10 <sup>–85</sup> ‡	0.3–0.6 <sup>[4,7]</sup>
CM1	~120 <sup>[7]</sup>	—	—	<10 <sup>–55</sup> –10 <sup>–70</sup> †	0.3 <sup>[7]</sup>
CV(All ox)	200–300 <sup>[9,10]</sup> <340 <sup>[11]</sup>	—	—	—	—
CV (Bali ox)	50–150 <sup>[8]</sup>	—	—	<10 <sup>–55</sup> –10 <sup>–70</sup> †	0.8–1.1 <sup>[8]</sup>
CO	0–50 <sup>[8]</sup>	—	—	>10 <sup>–55</sup> –10 <sup>–70</sup> †	0.1–0.6 <sup>[8]</sup>
CR	50–150 <sup>[8]</sup>	—	—	>10 <sup>–55</sup> –10 <sup>–70</sup> †	0.4–1.1 <sup>[8]</sup>
MAC 88107	<200 <sup>[10]</sup>	—	—	—	—
UOC	<260 <sup>[12]</sup>	—	—	—	—
EOC	<100 <sup>[13]</sup>	—	—	—	—

\*W/R = water/rock ratio — based on proportions of oxygen atoms (~ equal to the relative volumes of water to rock).

†Range of oxygen fugacities based on the calculated position of the sulfide-sulfate boundary in the temperature range 0°–150°C (*Bourcier and Zolensky, 1992*). CI chondrites are the only group of chondrites that contain significant amounts of sulfates.

‡Based on the calculated stability of tochilinite (*Browning and Bourcier, 1996*).

References and methods used for estimations: [1] *DuFresne and Anders (1962)*, mineral equilibria; [2] *Zolensky et al. (1989)*, thermodynamic modeling of mineral assemblages; [3] *Clayton and Mayeda (1999)*, O-isotopic fractionation between carbonate and phyllosilicates; [4] *Clayton and Mayeda (1999)*, modeling of bulk-rock O-isotopic composition; [5] *Baker et al. (2002)*, O-isotopic fractionation between structural bound water in phyllosilicates and calcite; [6] *Rosenberg et al. (2001)*, thermodynamic modeling of mineral assemblages; [7] *Zolensky et al. (1997)*, modeling of bulk-rock O-isotopic composition; [8] *Zolensky et al. (1993)*, mineral assemblages and thermodynamic modeling; [9] *Krot et al. (1998a,b)*, thermodynamic modeling of phase equilibria; [10] *Krot et al. (2000b)*, thermodynamic modeling; [11] *Brearley (1997b)*, phase equilibria; [12] *Alexander et al. (1989)*, thermodynamic calculations; [13] *Rubin et al. (2002)*, fluid inclusions in halite.

conventionally by *Grady et al. (1988)* and by ion probe by *Brearley et al. (1999)*. These data indicate that carbonate was either forming at constant temperature from an evolving reservoir and that the carbonate grains may show isotopic zoning or have grown at different times, or that temperature was varying during carbonate growth.

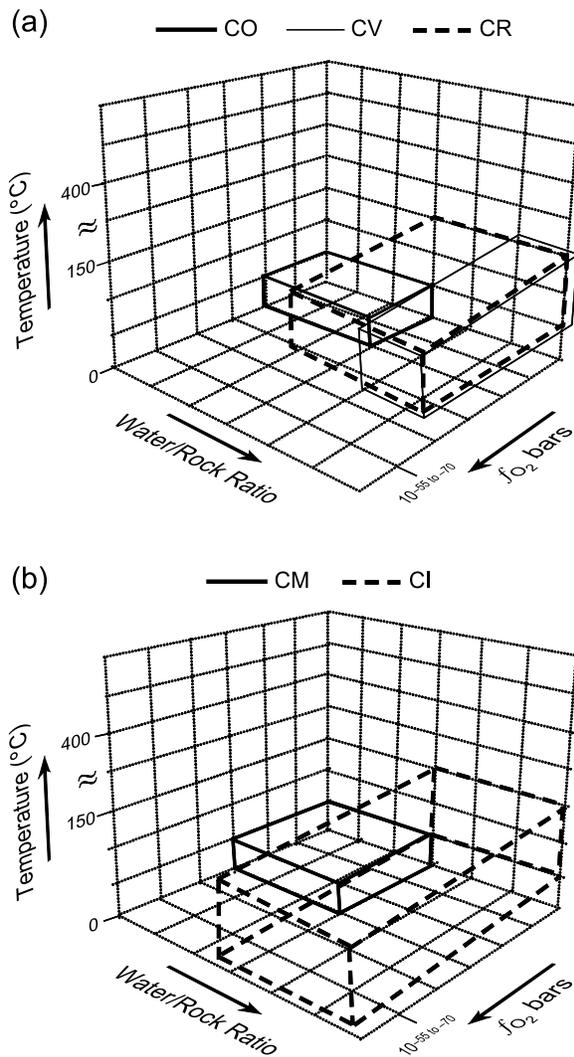
## 6. CONDITIONS OF AQUEOUS ALTERATION

General constraints on the conditions of alteration observed in carbonaceous chondrites come from undepleted volatile trace-element abundances, the survival of organic compounds that are sensitive to thermal processing, highly unequilibrated mineral compositions, and lack of evidence of any metamorphic equilibration of even submicrometer grains. These data indicate collectively that the temperatures of aqueous alteration were certainly less than 300°C, in some cases 200°–300°C lower than this value, with the exception of some of the oxidized CV3 chondrites as discussed above. However, beyond this upper limit, putting exact constraints on the physical conditions (T,  $f_{O_2}$ , fluid/rock ratios, pH, etc.) of alteration is one of the most challenging problems of studying alteration in chondritic me-

teorites. Constraints on the conditions of alteration come from a variety of sources, including stable-isotope data, mineralogical phase equilibria, experimental data, and thermodynamic modeling. In all these approaches, there are significant uncertainties because of assumptions in the models and the fact that mineral assemblages in altered chondrites may not always be in thermodynamic equilibrium. Despite these uncertainties, these different approaches do at least provide a plausible envelope of the alteration conditions experienced by different chondrite types. The possible ranges of alteration conditions estimated for carbonaceous and ordinary chondrites are summarized in Table 3 and are illustrated graphically in Fig. 13 for the carbonaceous chondrites.

### 6.1. CI Carbonaceous Chondrites

*DuFresne and Anders (1962)* examined the mineralogical phase relations present in CI chondrites in considerable detail and concluded that aqueous alteration by liquid water occurred under equilibrium conditions at temperatures of ~20°C. They constrained fluid Eh to –0.2 V and pH in the range 8–10. Efforts to constrain the alteration conditions of the CI chondrites by *Zolensky et al. (1989)* using thermo-



**Fig. 13.** Estimated temperature-water/rock ratio-oxygen fugacity conditions of aqueous alteration in carbonaceous chondrites after Zolensky *et al.* (1993). **(a)** Alteration conditions for weakly altered CO, CV, CR, and unique carbonaceous chondrites. **(b)** Alteration conditions for more pervasively altered carbonaceous chondrites (CI and CM). The oxygen fugacity indicated ( $f_{O_2} = 10^{-55}$ – $10^{-70}$ ) represents the range over which the boundary between sulfate and sulfide occurs in the temperature range 0°–150°C, based on the calculations of Bourcier and Zolensky (1992). Sulfates are generally absent in all but the CI chondrites. Sulfides are the dominant S-bearing phases in the CO, CV, and CR chondrites. The CM chondrites appear to have formed under more reducing conditions than the other chondrite groups due to the presence of tochilinite that is stable at values of  $f_{O_2} < \sim 85$  (Browning and Bourcier, 1996).

dynamic modeling yield higher-temperature conditions of alteration ranging from 50 to (at least) 150°C, over a wide range of plausible fluid/rock ratios. In these calculations, solution pH was found to vary from 7 up to between 9 and 10, and Eh from  $-0.3$  to  $-0.8$  V, with the low pH and higher Eh values being prevalent during the earliest stages of alter-

ation. Other efforts to constrain the conditions of aqueous alteration of the CI chondrites also suggest higher temperatures of alteration for these meteorites. The relatively small O-isotopic fractionation between carbonate and phyllosilicates in Orgueil of 8‰ suggests that alteration occurred at a relatively high temperature, certainly higher than that of CM2 chondrites, probably in the range 100°–150°C. Based on the bulk O-isotopic composition of CI chondrites, the integrated water/rock ratio (oxygen atoms) during alteration appears to have been high, probably  $\sim 1.1$ – $1.2$  (Clayton and Mayeda, 1999). This appears to be consistent with the presence of saponite, a phase that appears to require relatively high water/rock ratios to be stable (Bourcier and Zolensky, 1992). The oxygen fugacity during alteration of CI chondrites appears to be relatively high based on the presence of magnetite rather than tochilinite in this group of meteorites. This observation is supported by the presence of sulfate in CI chondrites. Bourcier and Zolensky (1992) determined that in neutral solutions  $f_{O_2}$  of the sulfide-sulfate boundary lies between  $10^{-70}$  and  $10^{-55}$  bars in the temperature range 0°–150°C.

## 6.2. CM Carbonaceous Chondrites

Estimates for the conditions of alteration of the CM chondrites using different approaches are in better agreement than for the CI chondrites. DuFresne and Anders (1962) and Zolensky *et al.* (1989) reported temperatures of alteration of  $\sim 20^\circ\text{C}$  and  $1^\circ$  to  $\sim 25^\circ\text{C}$ , respectively. Using a simple closed-system hydration reaction model, Clayton and Mayeda (1999) also found that the O-isotopic systematics of CM chondrites were consistent with alteration near 0°C, with fluid/rock ratios of 0.3–0.6. However, more recent work (Baker *et al.*, 2002) based on the O-isotopic fractionation between calcite and structurally-bound water released from phyllosilicates in Murchison indicates somewhat higher alteration temperatures of  $\sim 80^\circ\text{C}$ . The discrepancies between these estimates are a reflection of uncertainties in the extent to which different components are in isotopic equilibrium with one another.

Like the CI chondrites, fluid pH values in CMs appear to have ranged from mildly acidic to alkaline in character. DuFresne and Anders (1962) calculated a pH range of 6–8, compared with 7 to slightly above 12 determined by Zolensky *et al.* (1989) for a wide range of rock/fluid ratios.

Mineralogical and thermodynamic constraints show that alteration conditions in the CM2 chondrites were more reducing than the CIs. Mineralogically, this is indicated by the unique presence of tochilinite in CMs as the dominant Fe-bearing phase compared with magnetite in CIs and the rarity of sulfates in CM2 chondrites (e.g., Lee, 1993). Zolensky *et al.* (1989) calculated an Eh range from 0.5 to  $-0.75$  V for the development of the mineral assemblages observed in CM chondrites. Very reducing conditions appear to be required to stabilize tochilinite according to phase equilibria calculations based on estimated thermodynamic data (Browning and Bourcier, 1996) and observations on the stability of tochilinite in the terrestrial environment (van de

Vusse and Powell, 1983). The upper thermal stability of tochilinite appears to be  $\sim 120^\circ\text{C}$ . The calculated phase relations are consistent with the mineralogical associations in CM chondrites and indicate that tochilinite is only stable at  $\text{PO}_2$  values ( $\log \text{PO}_2 < -80$ ), conditions under which  $\text{PH}_2$  would be high. Tochilinite could plausibly coexist with low Ni,Fe metal in CM chondrites. In contrast, tochilinite is a relatively rare phase in CM1 chondrites, suggesting that the most heavily altered CMs experienced conditions of alteration higher than  $\sim 120^\circ\text{C}$  or more oxidizing than the CM2 chondrites (Zolensky *et al.*, 1997).

More detailed geochemical modeling provides support for low-temperature alteration ( $25^\circ\text{C}$ ) under reducing conditions for the CM2 carbonaceous chondrites (Rosenberg *et al.*, 2001). Using two different potential anhydrous precursor CM-chondrite mineral assemblages (Browning and Bourcier, 1998), a reduced Fe endmember (Fe present dominantly as  $\text{Fe}^0$  in Fe metal) and an oxidized Fe endmember (Fe present as  $\text{Fe}^{2+}$ ), Rosenberg *et al.* (2001) found that good matches to the observed alteration assemblages in CM chondrites could be produced. Chrysotile, greenalite, and tochilinite are formed as alteration products from both precursor assemblages, but cronstedtite only develops from the oxidized precursor. In both cases, the pH of the altering solutions evolve from an initial value of 7 to highly basic values (12–13). Alteration of the reduced precursor results in the generation of large quantities of  $\text{H}_2$  due to the oxidation of Fe metal, whereas essentially no H is evolved during alteration of the oxidized precursor assemblage.

### 6.3. Other Carbonaceous Chondrites

The conditions of alteration in other carbonaceous chondrites remain less well constrained although estimates are available, in part, based on comparisons with other carbonaceous chondrites. Zolensky *et al.* (1993) summarized plausible alteration conditions for CR, CV, and CO chondrites (in addition to CI and CM as discussed above), based principally on mineralogical criteria. The alteration mineralogy of CR chondrites, mainly serpentinite/saponite and magnetite, suggests alteration under relatively oxidizing conditions and temperatures, similar to those experienced by the CI chondrites, although under a somewhat more restricted range of  $f_{\text{O}_2}$ . Water/rock ratios for alteration in both CI and CR chondrites may have been similar as indicated by the presence of saponite. Krot *et al.* (1998a,b) have carried out detailed thermodynamic calculations to constrain the conditions of metasomatic alteration of the oxidized CV chondrites. These studies indicate that the coexistence of phyllosilicates, magnetite, fayalite, Ca-Fe-rich pyroxenes, and andradite in members of the Bali subgroup of CV3 chondrites is consistent with formation at temperatures  $< 300^\circ\text{C}$  during fluid-rock interactions. Using these same calculations, Krot *et al.* (2000b) were able to infer that the coexistence of fayalite, hedenbergite, and magnetite in the unique chondrite MAC 88107 is indicative of alteration at lower temperatures or less-oxidizing conditions than for the

CV3 chondrites. Alteration is constrained to have occurred at temperatures between  $\sim 120^\circ$  and  $220^\circ\text{C}$ , assuming a confining pressure of 100 bars.

### 6.4. Unequilibrated Ordinary Chondrites

Alexander *et al.* (1989) used a variety of mineralogical and thermodynamic constraints to estimate the conditions of aqueous alteration in the UOCs Semarkona and Bishunpur. They concluded, based on the presence of Na-bearing smectite and the behavior of K-rich smectite in the terrestrial environment, that alteration temperatures could not have exceeded  $260^\circ\text{C}$ . They also examined the variation in gas phase composition as a function of temperature under two sets of limiting conditions: (1) the minimum partial pressure of  $\text{H}_2\text{O}$  needed to stabilize smectite, and (2) a maximum  $\text{PH}_2\text{O}$  assuming that liquid water is present. The calculations demonstrated that under both these limiting conditions,  $\text{H}_2\text{O}$  and  $\text{H}_2$  dominate the gas phase and smectite can be stabilized with or without liquid water in the system.

## 7. TIMING OF ALTERATION

Constraints on the timing and duration of aqueous alteration are key components in unraveling the alteration history of chondritic meteorites. For example, evidence that alteration occurred for extended periods (5–20 m.y.) after CAI formation favors an asteroidal scenario for alteration vs. time periods  $< 5$  m.y. that could also be reconciled with alteration prior to accretion of asteroidal parent bodies. A detailed discussion of the timescales of aqueous alteration based on the Mn-Cr and I-Xe systems are discussed in Krot *et al.* (2006). Only a brief discussion of the implications for aqueous alteration will be discussed here.

Manganese-chromium-isotopic studies have focused on dating the formation of carbonates in CI and CM chondrites and the unusual chondrite Kaidun (Endress *et al.*, 1996; Hutcheon *et al.*, 1999; Brearley *et al.*, 2001; Brearley and Hutcheon, 2000, 2002). Dating of carbonates in CIs and Kaidun is facilitated by the presence of Mn-bearing breunnerites and dolomites; for the CM chondrites this task is much more challenging because Mn-poor calcite is the dominant carbonate, although Mn-bearing dolomite does occur in the most highly altered CM2s (Johnson and Prinz, 1993) and is relatively common in some CM1s (Zolensky *et al.*, 1997).

Using the constraints provided by Al-Mg and Mn-Cr systems, combined with the results of thermal modeling of asteroidal parent bodies, it is possible to put some constraints on the onset and duration of aqueous alteration in asteroidal parent bodies. If it is assumed that the measured difference in initial  $^{27}\text{Al}/^{26}\text{Al}$  ratios between CAIs and chondrules is real, then accretion of the carbonaceous chondrite parent bodies must have occurred at least 3 m.y. after CAI formation. Thermal modeling (see above) indicates that temperatures within these asteroids will have increased to the melting temperature of water ice within 0.03–0.6 m.y.,

assuming initial  $^{26}\text{Al}/^{27}\text{Al}$  ratios in the range  $1.6 \times 10^{-6}$  to  $2 \times 10^{-5}$  (e.g., *Wilson et al.*, 1999). In addition, aqueous alteration had to have commenced shortly after chondrule formation (i.e., within ~3–4 m.y. of CAI formation), otherwise  $^{26}\text{Al}$  would have decayed to values that were too low to heat asteroidal parent bodies to temperatures sufficiently high to melt ice (e.g., *Cohen and Coker*, 2000).

Measured initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios in carbonaceous chondrites range from  $(1.42 \pm 0.6) \times 10^{-6}$  to  $(8 \pm 4) \times 10^{-6}$  for CIs to  $(1.3 \pm 0.6) \times 10^{-5}$  to  $(5.0 \pm 1.5) \times 10^{-6}$  in CMs and  $(9.4 \pm 1.6) \times 10^{-6}$  in Kaidun. Assuming a solar system initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $(4.4 \pm 1.0) \times 10^{-5}$  (*Lugmair and Shukolyukov*, 2001), these differences in initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios correspond to a time period of ~9 Ma. Perhaps the key issue that arises from the Mn-Cr system ages is exactly what events are being dated. Aqueous alteration of asteroidal parent bodies was a complex process and probably involved different episodes of carbonate growth. A conservative assumption is that the carbonate ages record the last stage of aqueous alteration in carbonaceous chondrite parent bodies. If this is the case, then the following inferences about the duration of aqueous alteration can be made. Aqueous alteration in CM chondrites clearly lasted for a significantly shorter time than the CI chondrites. If alteration commenced within 4 m.y. of CAI formation, the measured initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios for carbonates in CM chondrites suggest aqueous alteration in the CM chondrites could have occurred for periods of  $\sim 7.5 \pm \sim 2$  m.y. There is some indication that CM2 chondrites may have been altered for a shorter period of time than the more heavily altered CM1 chondrites, but given the significant uncertainties in the initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios, this remains rather speculative (*Brearley and Hutcheon*, 2000, 2002). Further studies are necessary to refine the alteration chronology more precisely. The much lower initial  $^{53}\text{Mn}/^{55}\text{Mn}$  in CI chondrites suggests that alteration extended for ~12.5 m.y. after accretion, and possibly longer if carbonates do not record the last period of asteroidal aqueous alteration.

The occurrence of halite in the equilibrated ordinary chondrites Monahans and Zag has provided a unique opportunity to study the timing of formation of this mineral using I-Xe dating (*Whitby et al.*, 2000; *Busfield et al.*, 2004). However, the data from both meteorites show significant scatter in their initial  $^{129}\text{I}/^{127}\text{Xe}$ , presumably due to disturbance of the I-Xe system, precluding a simple interpretation of the formation age of these minerals. However, based on these data, *Busfield et al.* (2004) proposed a model involving formation of halite in both meteorites ~5 m.y. after the Shallowater enstatite achondrite, which has an absolute age of 4559 Ma. This would place halite formation at about the same time as carbonate formation in CI chondrites. However, for the case of halite, this does not necessarily imply that water was present continuously for several million years on the ordinary chondrite parent body.

Taken together, these data clearly demonstrate that liquid water was available for extended periods of time (several million years) on asteroidal parent bodies. Based on

the thermal modeling discussed above, it appears that these timescales are inconsistent with small asteroidal parent bodies and require larger asteroids with radii >50 km. These bodies would have to accrete with initial  $^{26}\text{Al}/^{27}\text{Al}$  ratios that were high enough to generate enough heat to melt water ice, but not high enough to allow rapid heating and ensuing early loss of water, which would prevent significant aqueous alteration.

## 8. EPISODIC OR CONTINUOUS AQUEOUS ALTERATION

One issue of importance for aqueous alteration in chondrites is whether alteration was continuous, extending over several million years (as indicated by Mn-Cr and I-Xe dating), or was episodic. Evidence from studies of carbonates in CM chondrites provides some indication that alteration may have been episodic and involved periods of carbonate dissolution followed by reprecipitation (e.g., *Brearley et al.*, 1999; *Brearley and Hutcheon*, 2000, 2002). One possible explanation for the complex zoning in carbonate minerals in some CM chondrites is that carbonate dissolution and/or growth may be related to changes in the fluid composition as a result of perturbations caused by impact-related brecciation or degassing (e.g., *Wilson et al.*, 1999). An additional possibility is that liquid water produced during the main phase of heating may diffuse back from the outer regions of the asteroid into the interior as the asteroid cools (e.g., *Cohen and Coker*, 2000). This process can only occur provided that water is not lost into space either by diffusional loss through the outer icy regolith or by venting along fractures.

## 9. CONCLUSIONS

Over the last two decades, significant advances have been made in our understanding of the aqueous alteration processes that have affected chondritic meteorites. However, many important questions remain that are currently active areas of debate. The issues of where and over what time periods aqueous alteration took place are first-order questions that require much more extensive investigation. Significant advances to address these questions are likely to come in the future from the application of modern microbeam techniques to understand the microstructural, trace-element, and isotopic characteristics of individual alteration phases. The recognition that phases such as carbonates record compositional zoning at the microscale provides the opportunity to examine the chemical and isotopic evolution of fluids, in addition to constraining the timescale of alteration using short-lived radionuclide chronometers such as the Mn-Cr system. The integration of petrographic observations with improved asteroidal thermal models is likely to be an especially important area of investigation. This work has special significance in integrating observations made at the microscale with macroscopic modeling efforts. Finally, an improved understanding of the role of microchemical en-

vironments during all stages of aqueous alteration of complex heterogeneous mineral assemblages that characterize chondritic meteorites is essential in developing robust criteria for evaluating asteroidal vs. preaccretionary environments for aqueous alteration.

**Acknowledgments.** Supported by NASA Grants NAG5-9798 and NAG5-11862 to A.J.B. (P.I.).

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