Aqueous Alteration and Silicon and Magnesium Isotope Measurements in CR and CV Chondrites

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Geochemistry

by

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ABSTRACT OF THE DISSERTATION

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Doctor of Philosophy in Geochemistry

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Professor Kevin McKeegan, Co-chair
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Primitive chondritic meteorites formed at the same time the planets in our solar system were forming and can offer information about the conditions present in the early solar system, provided that they have not been significantly altered by heat and water. The CR carbonaceous chondrite group contains some of the least-altered meteorites known. The members of the group have undergone minimal thermal alteration, but while on the parent asteroid CR chondrites have interacted with water to varying degrees. A numerical aqueous alteration scale was developed to rank the CR chondrites based on their interactions with water. The majority of the CR carbonaceous chondrites have had minimal interaction with water and this scale is used to select appropriate samples for the study of the early solar system.
Silicon and magnesium isotope ratios were measured in selected CR and CV chondrules using multi-collector inductively-coupled plasma mass spectroscopy to test the hypothesis that a silicon-bearing gas was present in the solar nebula and condensed into fully or partially molten chondrules. The SiO gas could react with olivine in the chondrules to form pyroxene. These data were interpreted using a condensation model for silicon. Some of the chondrules studied did show a non-equilibrium fractionation in $\delta^{29}\text{Si}$ between olivine and pyroxene that was calculated to have been caused by a supersaturated SiO gas that had condensed into the chondrule. If this SiO gas did condense into the chondrules the process happened at or near equilibrium with a undercooling of 3 K or less below the equilibrium temperature. These results provide additional evidence that a silicon-bearing gas was present in the early solar system during the time of planet formation, but not all chondrules studied show clear evidence of having incorporated this gas.
The dissertation of Ellen Renee Harju is approved.

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Chapter 1

1.1 Meteorites and the solar system

The vast majority of the meteorites in our collections come from asteroids in the main asteroid belt (e.g., Mothé-Diniz and Nesvorny, 2008). The asteroids are remnants of planet formation and formed at the same time as the planets in our solar system, approximately 4.56 billion years ago. This means that meteorites can offer clues, through elemental and isotopic compositional measurements, about the conditions present in the solar system prior to and during the epoch of planet formation.

Meteorites come from different parent asteroids, may be undifferentiated or differentiated, and may have been affected by heat and water on their parent asteroids. Meteorites with similar elemental compositions and oxygen isotope ratios are generally thought to originate from the same parent asteroid or group of related asteroids, for example a dynamical family. Many meteorites contain small, mm-size igneous spherules called chondrules. Meteorites containing chondrules are called chondrites, while meteorites lacking chondrules are generally referred to as achondrites. Some asteroids gained enough energy (through impacts, radiogenic heating, or a combination of both) to melt completely and differentiate into metal cores with rocky surface layers. The chondrites have not undergone such differentiation and some chondrites have gone through little processing over the age of the solar system.
1.2 Alteration of Meteorites

Chondrites are considered primitive unless they have been affected by heat and/or water. Some chondrites have been heated to the point where their elemental and isotopic compositions change as atoms begin to diffuse through minerals. This is referred to as thermal metamorphism. Water is present as either ice or hydrated silicate minerals on some asteroids in the outer asteroid belt. Upon heating the water can be liberated and react with anhydrous minerals causing compositional changes. This is called aqueous alteration.

Depending on the time it takes to discover them, meteorites may spend significant time on Earth’s surface. Terrestrial weathering can also alter the compositions of the meteorites. Currently, many meteorites are being recovered from the deserts of Northern Africa or from Antarctica. Meteorites found in the desert may be exposed to high temperatures and become oxidized and Antarctic meteorites may also be weathered. In order to understand alteration processes occurring on asteroids, care must be taken to select meteorites that have not been significantly affected by terrestrial weathering.

1.3 The CR Carbonaceous Chondrites

The CR carbonaceous chondrites are a group of carbon-rich meteorites that contain up to 5% carbon (Mason, 1962). They contain chondrules and are thought to originate from the same parent asteroid. Carbonaceous chondrite groups are often named for the first member of the group to be discovered. The CRs are named after the first known specimen, Renazzo, a meteorite that fell in Italy in 1824. CR chondrites are important specimens for research. Some members of the group (QUE 99177, MET
00426, and LAP 02342) are among the least-altered meteorites known. The CR chondrites were not heated significantly and are thought to have the same compositions as when they originally accreted (e.g., Weisberg et al., 1995). However, it is clear that some CR chondrites did interact with water. Some CRs have extensive interaction with water that could change the bulk composition, while others have had only incipient interaction with water.

### 1.4 CR Chondrite Aqueous Alteration Scale

The CR chondrites that are most useful for understanding aspects of accretion in the solar nebula are those samples that have had the least interaction with water (i.e., those that are the least aqueously altered). In order to provide a relative scale corresponding to a degree of thermal or aqueous alteration of a sample, a numeric scale has been devised that applies to both thermally or aqueously altered chondrites (Van Schmus and Wood, 1967). The “origin” of this petrologic classification scale is 3.0, with samples that have been progressively altered by thermal effects ranging over values of 3 to 6. In contrast, samples that have suffered primary aqueous alteration take on petrologic types < 3, with near complete aqueous alteration at 1.0. An interesting example are the CM carbonaceous chondrites, which have interacted with water to varying degrees. On the numeric scale for the CM chondrites the most aqueously altered samples are designated type 2.0. The scale progresses upward by tenths to completely unaltered samples, which would hypothetically be a type 3.0 (Rubin et al., 2007). All known CM chondrites have had significant interaction with water so there are no known type 3.0s in this group. The compositional differences between the CR and CM
chondrites are so great that the majority of the parameters used to assign a type to the CM chondrites are not appropriate for CR chondrites. Because of this, a new study was initiated to determine the changes that CR chondrites undergo when they interact with water. Approximately a third of the known CR chondrites were used to determine the effects of aqueous alteration in the group and develop a numerical alteration scale for the CR carbonaceous chondrites. This numerical scale will give insight into the processes that affected the CR parent asteroid and assist researchers in selecting the proper CR carbonaceous chondrites for their studies.

1.5 Evidence for a Silicon-Bearing Gas in the Solar Nebula

As of this writing, more than 1000 planets orbiting other stars have been confirmed by the Kepler mission (NASA Exoplanet Science Institute, 2015). It may even be possible that other planets formed in similar conditions to Earth and researchers are actively searching for Earth-like planets. In order to understand the likelihood of formation of Earth-like planets, it is important to develop constraints on the astrophysical conditions present in our own solar system at the time of planet formation. However, many open questions remain regarding the initial composition of the solar nebula just prior to planet formation.

In one important example, it has been proposed that there was a silicon-rich gas present in the early solar system. Oxygen isotope measurements from CR and CV (Vigarano-type) carbonaceous chondrites indicate that the chondrules in the meteorites interacted with an oxygen-bearing gas and silicon monoxide (SiO) has been proposed as the carrier of the oxygen (Chaussidon et al 2008). If this hypothesis is correct then there
may be evidence of this process in not just the oxygen isotopes, but the silicon isotopes as well.

Primitive CR carbonaceous chondrites and CV chondrites were chosen for a study of silicon and magnesium isotopic compositions in chondrules to determine if there is evidence of a silicon-bearing gas in the early solar nebula.

1.6 Organization of the dissertation

Chapter 2 of the dissertation discusses the development of systematic petrologic observations into a numerical scale for indexing relative degrees of aqueous alteration in the CR carbonaceous chondrites. The work has been published as Progressive aqueous alteration of CR carbonaceous chondrites in *Geochimica et Cosmochimica Acta* volume 139 in 2014.

Chapter 3 presents the data from a study of silicon and magnesium isotopes in CR and CV chondrules to search for evidence that these chondrules interacted with a silicon-bearing gas in the solar nebula.

1.7 References


Chapter 2

2.1 Introduction

The CR carbonaceous chondrites constitute one of the most primitive meteorite groups. There has been minimal thermal metamorphism: samples typically have unrecrystallized textures (e.g., Weisberg et al., 1993, 1995), highly unequilibrated mafic silicates (Wood, 1962) and abundant low-Ca clinopyroxene. Chondrules with glassy mesostases are present in some CR chondrites (Weisberg et al., 1993; Abreu and Brearley, 2010), but not others. LAP 02342 has S-rich matrix regions (Wasson, 2008; Wasson and Rubin, 2009), diagnostic of low degrees of alteration (thermal and aqueous) (Grossman and Rubin, 1999; Grossman and Brearley, 2005). However, CR chondrites also show variable degrees of aqueous alteration (e.g., Weisberg et al., 1993; Zolensky et al., 1993; Noguchi, 1995), earning members of the group the designation of petrologic type 2. Nearly half of the CR chondrites contain chondrules with chlorite- or serpentine-rich mesostases; some of the chondrules are surrounded by phyllosilicate-rich layers. The matrices of the more-altered CR chondrites contain abundant submicrometer-size grains of sulfide (typically pyrrhotite and pentlandite) and intergrowths of saponite and serpentine (Zolensky et al., 1993; Ichikawa and Ikeda, 1995; Fig. 7 of Brearley, 2006). Some CR chondrites contain magnetite platelets and framboïds (e.g., Fig. 7b of Brearley, 2006); Ca-carbonate occurs within some chondrule rims (Weisberg et al., 1993). LAP 02342 contains rare 30-100-μm-long sulfide laths encased within phyllosilicate sheaths (Wasson and Rubin, 2009). Renazzo, the CR-chondrite prototype and one of only two known CR falls, contains ~6 wt.%
bulk water (Mason and Wiik, 1962), far more than in low-type-3 ordinary-chondrite falls (~0.5 wt.% total H$_2$O; Jarosewich, 1990).

Not all CR chondrites have been altered to the same extent. Several samples (e.g., EET 87770) contain a few chondrules with glassy mesostases (and some chondrules with partially altered glass; Noguchi, 1995); others (e.g., Al Rais) contain only altered chondrules (Weisberg et al., 1993). Magnetite is present in some CR chondrites (e.g., Renazzo; Weisberg et al., 1993), but not in others (e.g., LAP 04516). Two chondrites (GRO 95577 and MIL 090292) have been so aqueously altered that nearly all of the metallic Fe-Ni and mafic silicate grains have been replaced (Weisberg and Huber, 2007; Morlok and Libourel, 2013); in contrast, other CR chondrites (e.g., LAP 02342; Acfer 097) have moderately abundant metallic Fe-Ni and unaltered mafic silicates (e.g., Wasson and Rubin, 2009).

There are additional bulk meteorite properties that correlate to different degrees with the extent of aqueous alteration: O-isotopic composition (Choi et al., 2009; Schrader et al., 2011; this study), H-isotopic composition (Bonal et al., 2011), the absolute abundance of indigenous amino acids (Martins et al., 2007; Glavin et al., 2011), and the quantity of presolar grains (Floss and Stadermann, 2009). However, the correlations of many of these parameters with petrologic subtype or with each other are not strong, thus limiting their utility as gauges for aqueous alteration. Furthermore, these properties are not determined in most laboratories. We have attempted to develop a petrography-based sequence of progressive alteration for the CR chondrites analogous to the one proposed for CM chondrites by Rubin et al. (2007). In the present manuscript we try to fill this need.
2.2 Analytical Procedures

2.2.1 Samples

Thin sections of 35 CR chondrites, probably representing 24-29 separate falls, were examined microscopically in transmitted and reflected light. The number of separate falls is a rough estimate based on proximity of recovery sites and petrographic similarities. Meteorites are listed in Table 2.1 along with their section number, recommended petrologic subtype, weathering grade and shock stage. Sizes of grains were measured microscopically with a calibrated reticle. Thirty-three of the 35 CR chondrites we examined are finds. In some cases it is difficult to use reflected light microscopy to distinguish thin rinds of magnetite (a product of asteroidal aqueous alteration) from thin rinds of goethite (produced by terrestrial weathering) around metallic Fe-Ni grains. However, goethite differs somewhat from magnetite in its shade of gray and in having a smoother appearance in reflected light; in many weathered chondrites, goethite occurs in veins that transect the sample (e.g., Hutchison, 2004). In every case where we tentatively identified magnetite petrographically, we confirmed its presence with electron microprobe analysis.

2.2.2 Mineralogical and Petrographic Techniques

The compositions of mesostasis, oxides, phyllosilicates and matrix regions were measured on the UCLA JEOL electron microprobe using natural and synthetic standards, an accelerating voltage of 15 keV, 20-s counting times per element, a focused beam and ZAF corrections. The sample current was 10 nA for carbonate and 15 nA for other analyzed phases. The carbon-dioxide component of carbonate analyses was calculated by difference from 100 wt.%. 
Table 2.1 List of 35 CR chondrites included in this study

<table>
<thead>
<tr>
<th>meteorite</th>
<th>section</th>
<th>subtype</th>
<th>weathering grade</th>
<th>shock stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acfer 097</td>
<td>AMNH 4808-1</td>
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<td>W2\textsuperscript{1}</td>
<td>S1\textsuperscript{1}</td>
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<td>AMNH 4793-2</td>
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<td>W2\textsuperscript{1}</td>
<td>S1\textsuperscript{1}</td>
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<td>S1/S2\textsuperscript{1}</td>
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<tr>
<td>Acfer 397, 399, 395, 394, 396, 398, 400</td>
<td>UCLA 2109, 2110, 2111, TK657, TK660, TK658, TK659</td>
<td>2.8</td>
<td>W1-W2\textsuperscript{1}</td>
<td>S1/S2\textsuperscript{1}</td>
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<tr>
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<td>W2\textsuperscript{1}</td>
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</table>

\textsuperscript{1}This study; \textsuperscript{2}Scott et al. (1992); \textsuperscript{3}Meteoritical Bulletin.
\textsuperscript{*}Samples that were studied mainly petrographically; their classifications are less certain.
AMNH samples from the American Museum of Natural History; USNM samples from the Smithsonian Institution; Antarctic meteorite samples from NASA – Johnson Space Center; Yamato samples from National Institute of Polar Research; UCLA samples from the UCLA collection (TK samples are thick sections); Gao-Guenie (b) courtesy of A.N. Krot, Univ. Hawaii; Only Al Rais and Renazzo are observed falls.
We made S x-ray maps of QUE 99177, Renazzo, NWA 5028, NWA 1616, GRA 06100 and Acfer 097; three different regions of Renazzo were analyzed. Back-scattered electron (BSE) maps of these same matrix areas were made simultaneously. Quantitative data for Na, Mg, Al, Si, S, K, Ca, Cr, Mn and Fe were obtained using a 3-µm-diameter electron beam to analyze points in 3×7 matrix grids in the same areas. In separate runs, also using a 3-µm beam, we analyzed matrix regions of QUE 99177, LAP 02342, Acfer 399, EET 92105, GRA 06100, NWA 5028, Renazzo, Y 790112, Acfer 097, MIL 07513 and NWA 1616. In order to exclude contributions to the matrix analyses from coarse mineral grains and holes, we followed the criteria for data exclusion similar to those in Table 2 of Wasson and Rubin (2009). Important modifications were that a variable scale was used for S and the lower limit for inclusion of FeO data was lowered from 26 to 25 wt.%.

2.2.3 Oxygen-Isotope Analysis

Using the laser-fluorination technique, we determined O-isotopic compositions for 11 CR chondrites that showed various degrees of aqueous alteration: Acfer 187, EET 87770, Gao-Guenie (b), GRO 03116, GRO 95577, GRV 021710, LAP 02342, MET 00426, MIL 090292, QUE 99177 and Renazzo. Acfer 187 is probably paired with Acfer 394; EET 87770 is paired with EET 87847 and EET 87747. Renazzo is an observed fall; all other samples for which we determined O-isotopic composition are finds, either from Antarctica or from hot deserts. Thus, most samples experienced various degrees of terrestrial weathering that modified their O-isotopic compositions.

Acid-washing and pre-fluorination aid in the removal of terrestrial weathering products. Pre-fluorination of samples is a normal pre-treatment step in all laser-fluorination analysis
procedures in order to clean the stainless steel system and to react residual traces of water or air in the fluorination chamber. However, this step can also remove oxygen in non-terrestrial materials, especially phyllosilicates that formed during asteroidal alteration because these phases may react with $\text{F}_2$ at room temperature. Therefore, we measured each sample pretreated with dilute-acid wash and pre-fluorination and also without such pretreatments. Some samples were also measured after pre-fluorination but without acid-washing. For GRO 99577, the most altered CR chondrite in the set, data were obtained without pretreatments. We tried to measure GRO 99577 after pre-fluorination, but more than half of the oxygen had already reacted during pre-fluorination, giving less than a 50% yield; in addition, the isotopic ratios of the retained $\text{O}_2$ were no longer representative.

A few tens of milligrams of each meteorite were gently crushed using an agate mortar and pestle; relatively fresh-looking fragments were carefully selected under a binocular microscope. A small amount of each meteorite (5-10 mg) was washed with diluted $\text{HCl}$ (6 M), rinsed with high-purity alcohol and distilled water, and dried in a 60ºC oven. About 2 mg of each sample (consisting of about 10 fragments) were used for each analysis. It is difficult to recover fine-grained materials completely after acid washing and it is likely that acid-treated samples preferentially lost matrix materials relative to chondrules and CAIs.

The O-isotopic compositions were determined using the CO$_2$-laser fluorination facilities at UCLA, the Korea Polar Research Institute (KOPRI) and the University of New Mexico (UNM): $\text{F}_2$ is used as the oxidant at UCLA; BrF$_5$ is used at KOPRI and UNM. San Carlos olivine was used as the oxygen standard at UCLA and UNM; Juan de Fuca basalt (JFB) glass was used at KOPRI. When we measured samples without pre-fluorination, the sample chamber was evacuated overnight while being heated with an IR lamp (~70ºC). Detailed analytical
procedures at UCLA, KOPRI and UNM can be found in Young et al. (1998), Ahn et al. (2012) and Sharp (1990), respectively.

Oxygen-isotopic compositions are given in units of per mil (‰) and expressed as $\Delta^{17}O$, defined as the deviation from the terrestrial fractionation (TF) line on the standard three-isotope graph, where:

$$\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O,$$

$$\delta^{17}O = [((^{17}O/^{16}O)_{\text{sample}}/(^{17}O/^{16}O)_{\text{SMOW}}) - 1] \times 1000,$$

$$\delta^{18}O = [((^{18}O/^{16}O)_{\text{sample}}/(^{18}O/^{16}O)_{\text{SMOW}}) - 1] \times 1000,$$

and SMOW is the acronym for Standard Mean Ocean Water.

2.3 Results

It facilitates the discussion to describe the CR chondrites in the order of increasing degrees of aqueous alteration. These descriptions include new and literature data and mention our assigned petrologic subtypes. The justifications for the boundaries between adjacent subtypes are presented in a later section. Descriptions of a few additional CR chondrites appear in Appendix A1.

2.3.1 Descriptions of Representative CR Chondrites

QUE 99177 is one of the least-altered CR chondrites, designated in Table 2.1 as type 2.8. It is weathering stage W2. The rock contains well-defined chondrules (Fig. 2.1a). Although only one of the nine porphyritic and barred-olivine chondrules we examined petrographically contains clear, colorless glassy mesostases (Table 2.2), the available section is thick, making identification of isotropic glass difficult. A classification of type-3.0 was proposed based on the
rarity of phyllosilicate in the fine-grained matrix measured in a few TEM sections (Abreu and Brearley, 2010); however, some chondrules are surrounded by phyllosilicate-rich rims, implying appreciable aqueous alteration. The presence of these phyllosilicates and the paucity of isotropic glassy mesostases in chondrules suggest that QUE 99177 is more appropriately classified as type

<table>
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<th>chondrite</th>
<th>subtype</th>
<th>weathering stage</th>
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<th>chondrules appearing in the microscope to have glassy mesostases</th>
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<td>Y 793495</td>
<td>2.8</td>
<td>W2</td>
<td>9</td>
<td>0</td>
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</table>

*There are uncertainties in these data. Many of these mesostases appear to be fine-grained (i.e., not glassy) when imaged by BSE and hence, may have experienced minor aqueous alteration.

2.8 than 3.0. Mafic silicate phenocrysts in the chondrules appear unaltered. Metallic Fe-Ni is moderately abundant, occurring as nodules in chondrules, discontinuous rings of blebs at chondrule surfaces and as large nodules in the matrix. Also present are a few patches of troilite. Coarse grains of magnetite are absent. Limited transmission-electron microscope (TEM) studies (Abreu and Brearley, 2010) show that the matrix and fine-grained chondrule rims consist mainly
Fig. 2.1. Back-scattered electron (BSE) images of mesostasis-rich portions of chondrules in CR2.8 chondrites. (a) Low-FeO porphyritic olivine-pyroxene (POP) chondrule K3l in QUE 99177 contains clear, colorless, isotropic glassy mesostasis (light gray) that appears smooth in BSE images. Calcium-rich pyroxene (very light gray) forms rims on some low-Ca pyroxene phenocrysts (dark gray) as well occurring as a few individual grains within the mesostasis. Fine white lines are iron-oxide-rich terrestrial weathering veins. (b) Low-FeO POP chondrule 1 in EET 92062. This chondrule also contains clear, colorless, isotropic glassy mesostasis (light gray) that appears smooth under BSE imaging. Only small amounts of metallic Fe-Ni blebs (white) occur in the mesostasis. (c) Low-FeO POP chondrule I2r in LAP 02342 contains clear, colorless, isotropic glassy mesostasis (dark gray); the glass appears smooth in the BSE image. Small crystallites of Ca-pyroxene precipitated from the liquid prior to vitrification. (d) Low-FeO POP chondrule B5f in LAP 02342 that contains microcrystalline mesostasis (mottled, medium gray), probably formed by divitification of glass. Such mesostasis textures are typical for most chondrules in LAP 02342. White lines are iron-oxide-rich terrestrial weathering veins. meso = glassy mesostasis; ol = olivine; Ca-pyx = Ca-rich pyroxene.

of amorphous ferroan silicate typically surrounding tiny particles of troilite and Fe-Ni sulfide; phyllosilicates, magnetite and Ca-carbonate are rare (probably ≤1 vol.%) in these sections. Fine-
grained alkali-rich material associated with nanoglobules within a large C-rich vein (Nguyen et al., 2008) suggests local alteration by a fluid (Peeters et al., 2012).

**MET 00426** is similar to QUE 99177 in being one of the least-altered CR chondrites, i.e., type 2.8 (Table 2.1). It is weathering stage W2. It also contains well-defined chondrules, but only one of the eight porphyritic and barred-olivine chondrules we examined petrographically and by BSE imaging has a clear, light-brown glassy mesostasis (Tables 2.2, 2.3). Mafic silicate phenocrysts are unaltered; moderately abundant, unaltered metallic Fe-Ni is present. Like QUE 99177, MET 00426 contains some chondrules with phyllosilicate-rich rims. There are no coarse magnetite grains. The matrix is similar to that in QUE 99177 in containing little phyllosilicate, magnetite or Ca-carbonate in two TEM sections (Abreu and Brearley, 2010).

### Table 2.3 Mean composition (wt.%) of glassy mesostasis in CR-chondrite chondrules

<table>
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<th>EET 92062 POP chondrule 1</th>
<th>MET 00426 POP chondrule E21</th>
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<tr>
<td>mesostasis type</td>
<td>clear, colorless, isotropic glass</td>
<td>clear, light brown isotropic glass</td>
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<td>2</td>
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<tr>
<td>SiO₂</td>
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<td>52.0 ± 0.3</td>
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<tr>
<td>Al₂O₃</td>
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<td>Cr₂O₃</td>
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<td>0.23 ± 0.09</td>
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<tr>
<td>FeO</td>
<td>2.2 ± 0.2</td>
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<tr>
<td>MnO</td>
<td>0.47 ± 0.06</td>
<td>0.56 ± 0.03</td>
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<tr>
<td>MgO</td>
<td>5.1 ± 0.4</td>
<td>5.7 ± 0.5</td>
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<tr>
<td>CaO</td>
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<td>14.8 ± 0.6</td>
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</tr>
<tr>
<td>total</td>
<td>98.5±0.4</td>
<td>98.9±0.1</td>
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n.d. = not determined

**EET 92062**, classified as type 2.8 (Table 2.1), contains a few chondrules with clear, colorless glassy mesostases (Burger and Brearley, 2004, 2005; Fig. 2.1b); three of the 10 porphyritic and barred-olivine chondrules we examined petrographically and by BSE imaging
contain light-brown isotropic glass (Table 2.2). It is weathering stage W1. The average composition of glassy mesostasis in one porphyritic olivine-pyroxene (POP) chondrule from this meteorite is given in Table 2.3. The slightly low analytical total (98.5 wt.%) could reflect minor hydration of the glass (cf. Grossman et al., 2002). A few chondrules have fine-grained mesostases, some of which contain Ca-pyroxene crystallites. Mafic silicate phenocrysts in all of the chondrules appear unaltered. Metallic Fe-Ni is moderately abundant and unaltered; magnetite is absent. The sample is paired with EET 92105, and according to the Meteoritical Bulletin, is probably also paired with EET 87770, 87747, 87847, 92062 and several other samples from this site.

**LAP 02342** contains well-defined chondrules with unaltered mafic silicate phenocrysts and is classified as type 2.8 (Table 2.1). It is weathering stage W1. Three of the 11 porphyritic and barred-olivine chondrules we examined petrographically (Table 2.2) appear to contain glassy mesostases (Fig. 2.1c); however, back-scattered electron (BSE) imaging shows that the mesostasis in two of these chondrules is microcrystalline (Fig. 2.1d), possibly indicative of minor alteration. Some chondrules have patches of “smooth” phyllosilicate rims. Metallic Fe-Ni is moderately abundant (e.g., Wasson and Rubin, 2010); there are several patches of troilite, and no recognizable magnetite. The matrix has a high, relatively uniform, FeS content (e.g., Wasson, 2008). Additional studies of the matrices and chondrule rims show the presence of minor phyllosilicates and accessory Ca-carbonate (Wasson and Rubin, 2009, 2013).

**GRA 95229** has well-defined chondrules, but none of the 10 porphyritic and barred-olivine chondrules we examined microscopically and by BSE imaging contain clear, colorless glass. Chondrule phenocrysts appear unaltered. Metallic Fe-Ni is moderately abundant;
incipient magnetite is present (Trigo-Rodriguez et al., 2013). The rock is classified as type 2.7 (Table 2.1). It is weathering stage W1.

**NWA 1616**, classified as type 2.6 (Table 2.1), is appreciably more altered than the CR2.8 samples. Chondrules lack glassy mesostases, but mafic-silicate phenocrysts are unaltered. Although the rock is weathering stage W3 and much of the metallic Fe-Ni has been weathered, some unoxidized metal remains. There are large patches of magnetite in the rock; some opaque blebs within chondrules and at chondrule margins consist of magnetite-sulfide intergrowths. Goethite veins transect several chondrules and matrix regions; larger patches of goethite appear to mark the location of former metal nodules.

**GRA 06100** (type 2.5) has fairly abundant metallic Fe-Ni, but the metal appears more (pre-terrestrially) altered than that in NWA 1616 – the edges of some large metal nodules contain 2-5-μm-size magnetite grains interspersed with 4-20-μm-size troilite grains. It is weathering stage W2. Chondrules do not contain glassy mesostases. Although Abreu and Stanek (2009) and Abreu and Singletary (2011) reported some aqueous alteration of chondrule mafic-silicate phenocrysts, we did not observe this. Rare Ca-carbonate is present (Abreu, 2012). Some analyses of matrix regions total ~95 wt.% (compared to an average of ~82 wt.% in average CR matrix regions), consistent with matrix compaction or the growth of new phases within pores. The occurrence in the matrix of tiny silica grains with planar deformation features suggest that the rock has been shock heated (Abreu et al., 2014).

**Renazzo**, the only normal CR observed fall (weathering stage W0), is classified here as type 2.4 (Table 2.1). Weisberg et al. (1993) found it to be more altered than most CR chondrites. Chondrules are well-defined, but do not contain glassy mesostases. The edges of some low-Ca pyroxene chondrule phenocrysts that exhibit polysynthetic twinning have been altered along the
twin boundaries (Fig. 2.2a-c); some have been stained brown and contain linear trails of submicrometer inclusions. The edges of these pyroxene grains exhibit micrometer-size microdenticles (Fig. 2.2a,b), a common characteristic of chain silicates that have been subject to low-temperature aqueous alteration (e.g., Velbel, 2011). Although metallic Fe-Ni is fairly abundant in Renazzo, some 10-20-µm-size metal blebs within chondrules and chondrule fragments have 1-3-µm-thick layered rinds of magnetite and sulfide. Ca-phosphate is associated with magnetite in some chondrule rims (Jilly and Huss, 2012). Some larger (~100-µm-size) metal nodules are surrounded by 20-µm-thick rinds of troilite. In between the troilite and the unaltered interior metal, there are small patches of magnetite. Chondrules in the rock are preferentially aligned (Rubin and Harju, 2012), indicative of impact-induced shearing (cf. Rubin, 2012).

Fig. 2.2a. Altered low-Ca pyroxene phenocryst in a chondrule in CR2.4 Renazzo. Transmitted light image showing mesostasis near the edge of the pyroxene grain. The grain edge (arrows) has a sawtooth pattern (microdenticles) characteristic of aqueous dissolution of chain-silicate minerals (Velbel, 2011).
Fig. 2.2b. Altered low-Ca pyroxene phenocryst in a chondrule in CR2.4 Renazzo. Higher-magnification view of microdenticles in the pyroxene grain from Fig. 2.2a.

Fig. 2.2c. Altered low-Ca pyroxene phenocryst in a chondrule in CR2.4 Renazzo. Transmitted light image showing the entire polysynthetically twinned crystal with alteration along the twin boundaries. pyx = pyroxene
**Al Rais** (type 2.3) is the second of two observed falls (weathering stage W0), but the meteorite is texturally and compositionally anomalous (CR-an). It contains appreciably more matrix material than normal CR chondrites and higher volatile contents. Chondrules are well-defined, but do not contain glassy mesostases; twin boundaries in many low-Ca pyroxene phenocrysts exhibit significant aqueous alteration. There are large nodules of metallic Fe-Ni at chondrule margins and in chondrule interiors, but many of these nodules show extensive alteration. The metal interiors of the nodules are surrounded by rinds consisting of 6-10-μm-thick iron-oxide layers intercalated with 2-3-μm-thick S-rich layers (Fig. 2.3) that are difficult to analyze; the entire series typically contains five to six layers, although Fig. 2b of Morlok and Libourel (2013) shows ten 3-10-μm-thick layers around one metal grain. The layers in many of the nodules are scalloped, forming convex intrusions into the metal interiors. In some cases,

![Fig. 2.3a. BSE image of an altered kamacite grain at the margin of a chondrule in CR2.3 Al Rais. Kamacite (white) is largely replaced by alteration products (gray) at the margin of the chondrule. kam = kamacite; mgt = magnetite.](image-url)
Fig 2.3b. BSE image of an altered kamacite grain at the margin of a chondrule in CR2.3 Al Rais. Kamacite (white) is surrounded by a multi-layered complex intergrowth of oxide (medium gray) and a S-rich phase (light gray). chd = chondrule; kam = kamacite; mgt = magnetite.

Table 2.4 Compositions (wt.% ) from individual analyses of three oxide-sulfide layers surrounding kamacite in an opaque assemblage in CR2.3 Al Rais

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<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
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<td>Si</td>
<td>2.0</td>
<td>3.3</td>
<td>0.10</td>
</tr>
<tr>
<td>Al</td>
<td>0.21</td>
<td>0.29</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>Fe</td>
<td>44.4</td>
<td>43.7</td>
<td>49.2</td>
</tr>
<tr>
<td>Cr</td>
<td>0.65</td>
<td>1.1</td>
<td>0.10</td>
</tr>
<tr>
<td>Mn</td>
<td>0.10</td>
<td>0.15</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>Mg</td>
<td>1.8</td>
<td>2.6</td>
<td>0.36</td>
</tr>
<tr>
<td>Na</td>
<td>0.31</td>
<td>0.65</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>Ni</td>
<td>7.3</td>
<td>1.2</td>
<td>13.0</td>
</tr>
<tr>
<td>S</td>
<td>20.0</td>
<td>13.3</td>
<td>31.3</td>
</tr>
<tr>
<td>O</td>
<td>23.4</td>
<td>31.1</td>
<td>3.6</td>
</tr>
<tr>
<td>total</td>
<td>100.2</td>
<td>97.4</td>
<td>97.7</td>
</tr>
</tbody>
</table>

Oxygen was analyzed as a separate element. Low analytical totals in analyses 2 and 3 may reflect minor porosity. Analysis 3 has an Fe/Ni ratio is in the range of mackinawite [(Fe,Ni)₉S₈] compositions.

there is little residual metal in the nodules. The S-rich layers may contain sulfide and/or sulfate (Table 2.4). Analyses 1 and 2 in Table 2.4 are rich in Fe, Ni, S and O. They are probably
mixtures of iron (±nickel) oxide and sulfide or sulfate. Analysis 3 has appreciably more S and much less O; its Fe/Ni ratio is in the compositional range of mackinawite (Fe,Ni)$_9$S$_8$. The low analytical totals of analyses 2 and 3 (97.4-97.7 wt.%) may reflect minor porosity rather than OH.

**GRO 95577 and MIL 090292** (both type 2.0 and weathering category B) are the most-altered CR chondrites known. GRO 95577 was described by Weisberg and Huber (2007) as CR1; MIL 090292 is listed as CR1 in the Meteoritical Bulletin Database. Chondrules in GRO 95577 were completely altered (mainly to phyllosilicates and oxides), but remain as spheroidal pseudomorphs. The mesostases of these chondrules consist of phyllosilicates that appear light green in plane-polarized transmitted light. In MIL 090292, only a few rare olivine grains survive.

Four opaque assemblages (A – D) in GRO 95577 were studied (Table 2.5, Figs. 2.4, 2.5).

![BSE images of rare residual kamacite cores (white) surrounded by iron oxide rinds (medium gray) in CR2.0 GRO 95577. Grains within a chondrule pseudomorph. The dark-gray core at the bottom of the large grain (assemblage D) is compositionally equivalent to a mixture enriched in iron carbonate (siderite) and ferrous sulfate. A similar image of this assemblage was given in Weisberg and Huber (2007); a mirror image of this same assemblage appears in Morlok and Libourel (2013). Kamacite is white, iron oxide is medium gray, and silicate is black. kam = kamacite; sid = siderite/ferrous sulfate; sil = silicate.]

Fig 2.4a.
Metallic Fe-Ni is very rare and occurs only as kamacite cores surrounded by iron oxide (e.g., Fig. 2.4a,b). The GRO 95577 matrix contains elongated patches of iron-oxide framboids (Fig. 2.4b). The chondrule/matrix modal abundance ratio of GRO 95577 is similar to that of typical CR chondrites (1.5±0.5). The center of assemblage A (Fig. 2.5a) has a composition consistent with that of siderite (FeCO$_3$) mixed with lesser amounts of ferrous sulfate (possibly hydrated) and additional NiO-rich phases (Table 2.5). The oxide layers in assemblage A (Table 2.5) consist mainly of magnetite with phosphate and sulfate components. Oxides with similar compositions throughout GRO 95577 (e.g., Fig. 2.5b), vary in NiO and SO$_3$ through a narrow compositional range. Assemblage B contains these oxides along with phyllosilicate and an ilmenite-rich phase. [The Ti may have been derived from chondrule mesostases and/or from small perovskite
Fig. 2.5a. BSE images of altered opaque grains (formerly metallic Fe-Ni) in CR2.0 GRO 95577. Assemblage A has a center (black) consisting of a mix of iron carbonate (siderite), ferrous sulfate, and additional NiO-rich phases. This mixture is surrounded by at least eight distinct layers of iron oxide containing sulfate and phosphate chemical components (different shades of light-to-medium gray).

Fig 2.5b. BSE images of altered opaque grains (formerly metallic Fe-Ni) in CR2.0 GRO 95577. Large opaque assemblage B showing distinct layers of oxides (dark and light shaded) arranged concentrically with respect to grain boundaries and fractures. The center of the assemblage (medium-dark gray) consists of phyllosilicate. Also present are two oxide grains (medium gray) that are enriched in ilmenite. ilm = ilmenite-rich grains; phyllo = phyllosilicate.
Table 2.5 Compositions (wt.%) of layers within opaque assemblages in CR2.0 GRO 95577

<table>
<thead>
<tr>
<th>assemblage A</th>
<th>layer 1</th>
<th>layer 2</th>
<th>layer 3</th>
<th>layer 4</th>
<th>carbonate-rich grain</th>
</tr>
</thead>
<tbody>
<tr>
<td>no. analyses</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.15</td>
<td>0.51</td>
<td>0.53</td>
<td>0.92</td>
<td>--</td>
</tr>
<tr>
<td>TiO₂</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>--</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>1.1</td>
<td>1.1</td>
<td>0.98</td>
<td>0.83</td>
<td>--</td>
</tr>
<tr>
<td>FeO</td>
<td>84.7</td>
<td>86.7</td>
<td>86.5</td>
<td>85.6</td>
<td>51.8</td>
</tr>
<tr>
<td>MnO</td>
<td>0.06</td>
<td>0.14</td>
<td>0.12</td>
<td>0.09</td>
<td>0.44</td>
</tr>
<tr>
<td>NiO</td>
<td>5.2</td>
<td>2.7</td>
<td>2.4</td>
<td>1.9</td>
<td>6.4</td>
</tr>
<tr>
<td>MgO</td>
<td>&lt;0.04</td>
<td>0.10</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>2.0</td>
</tr>
<tr>
<td>CaO</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.05</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.07</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>0.05</td>
<td>--</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.92</td>
<td>0.78</td>
<td>0.80</td>
<td>0.44</td>
<td>1.2</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.32</td>
<td>2.0</td>
<td>2.3</td>
<td>2.5</td>
<td>13.3</td>
</tr>
<tr>
<td>CO₂</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>24.8</td>
</tr>
<tr>
<td>total</td>
<td>92.5</td>
<td>94.0</td>
<td>93.6</td>
<td>92.3</td>
<td>100.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>assemblage B</th>
<th>light oxide</th>
<th>dark oxide</th>
<th>ilmenite-rich phase</th>
<th>oxide rim</th>
<th>oxide</th>
<th>carbonate-rich grain</th>
</tr>
</thead>
<tbody>
<tr>
<td>no. analyses</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.26</td>
<td>0.94</td>
<td>0.18</td>
<td>0.14</td>
<td>0.46</td>
<td>0.04</td>
</tr>
<tr>
<td>TiO₂</td>
<td>&lt;0.04</td>
<td>0.16</td>
<td>46.6</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.13</td>
<td>0.15</td>
<td>&lt;0.04</td>
<td>0.24</td>
<td>0.20</td>
<td>0.26</td>
</tr>
<tr>
<td>FeO</td>
<td>88.5</td>
<td>86.5</td>
<td>42.4</td>
<td>88.7</td>
<td>86.2</td>
<td>60.9</td>
</tr>
<tr>
<td>MnO</td>
<td>0.05</td>
<td>&lt;0.04</td>
<td>5.1</td>
<td>0.04</td>
<td>0.09</td>
<td>0.70</td>
</tr>
<tr>
<td>NiO</td>
<td>3.0</td>
<td>2.8</td>
<td>1.8</td>
<td>3.3</td>
<td>3.6</td>
<td>5.2</td>
</tr>
<tr>
<td>MgO</td>
<td>0.07</td>
<td>0.06</td>
<td>0.08</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>2.2</td>
</tr>
<tr>
<td>CaO</td>
<td>0.05</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Na₂O</td>
<td>&lt;0.04</td>
<td>0.13</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>0.07</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.51</td>
<td>0.18</td>
<td>0.22</td>
<td>0.50</td>
<td>0.31</td>
<td>0.52</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.7</td>
<td>4.0</td>
<td>2.4*</td>
<td>2.3</td>
<td>5.9</td>
<td>10.1</td>
</tr>
<tr>
<td>CO₂</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>20.0</td>
</tr>
<tr>
<td>total</td>
<td>95.3</td>
<td>94.9</td>
<td>98.8</td>
<td>95.2</td>
<td>96.8</td>
<td>100.0</td>
</tr>
</tbody>
</table>

The CO₂ concentrations in the carbonate-rich grains were calculated by difference from 100 wt.%.. All iron is assumed to be FeO.

The dash line means not determined. The carbonate-rich grain in assemblage A has a composition of a mixture enriched in siderite and ferrous sulfate; that in assemblage D is broadly similar in composition.

The layers in assemblage A are ordered so that layer 1 is closest to the center of the grain and layer 4 is the outermost layer.

*The S value in the ilmenite-rich phase assemblage B is for elemental S, not SO₃.
(CaTiO$_3$) grains in refractory inclusions; e.g., Weisberg et al. (1993).] Oxide layers are arranged symmetrically outwards from the assemblage boundary (Fig. 2.5a) or from fractures within the assemblage (Fig. 2.5b). The low analytical totals in these oxides may be due to ferric iron. Only rare metallic Fe-Ni occurs in MIL 090292; the principal opaque phases are Fe-oxides and sulfide. Some oxide grains contain 1–6-µm grains of metallic Fe-Ni.

2.3.2 Phyllosilicate Rims Around Chondrules

“Smooth” rims, largely consisting of phyllosilicates (Fig. 2.6), were observed around

Fig 2.6a. BSE images of “smooth” phyllosilicate-rich rims around chondrules in slightly altered CR chondrites. Two-tone phyllosilicate rim around chondrule F4f in QUE 99177. The thin bright layer between the outer phyllosilicate and the matrix contains small blebs of metallic Fe-Ni. Chd = chondrule, mtx = matrix.
Fig. 2.6b. BSE images of “smooth” phyllosilicate-rich rims around chondrules in slightly altered CR chondrites. Two-tone phyllosilicate rim around chondrule D3d in MET 00426. Large metal bleb (white) at left is in the host chondrule. A discontinuous chain of tiny metal grains parallels the two-tone rim and separates different fine-grained regions. chd = chondrule; kam = kamacite.

several porphyritic olivine (PO) and porphyritic olivine-pyroxene (POP) chondrules in three CR2.8 chondrites: QUE 99177, MET 00426 and LAP 02342. The rims are 5-30-μm thick. Some appear to consist of a single phyllosilicate phase (which we dub “one-tone” rims). In some cases, the smooth rims around the chondrules in these meteorites occur as two distinct layers of different shading with a sharp boundary between them (Harju et al., 2010); we refer to this variety as “two-tone rims.” [We examined BSE mosaic images of several other CR chondrites (i.e., Acfer 097, El Djouf 001, Renazzo, Al Rais) and were unable to find additional occurrences
of two-tone phyllosilicate rims.] Rims with the lighter BSE shade have ~7 wt.% more FeO than the darker rims. The average compositions of the light and dark rims in QUE 99177, MET

Fig. 2.6c. BSE images of “smooth” phyllosilicate-rich rims around chondrules in slightly altered CR chondrites. Two-tone phyllosilicate rim around chondrule J5l in LAP 02342. The light inner rim penetrates cracks. The oval region near upper left is a distinct phyllosilicate phase containing ~2 wt.% S, and lower SiO₂, FeO and K₂O than the light-colored portion of the two-tone rim. A kamacite nodule (white) surrounded by terrestrially produced goethite (light gray with a chunky texture) occurs at upper right. chd = chondrule; kam = kamacite; mtx = matrix.

00426 and LAP 02342 are shown in Table 2.6. In each case where both rims are present, the dark rim lies farther from the chondrule. The rims have low analytical totals (~82-86 wt.%;
Table 2.6), characteristic of phyllosilicates and porous materials; like phyllosilicates, the rims are damaged by the electron beam during microprobe analysis.

Table 2.6 Average compositions (wt.%) of light and dark phyllosilicates in chondrule rims from CR2.8 chondrites and pyroxene and silica in the “honeycomb” structure in QUE 99177

<table>
<thead>
<tr>
<th>BSE-light phyllosilicate</th>
<th>QUE 99177</th>
<th>MET 00426</th>
<th>LAP 02342</th>
</tr>
</thead>
<tbody>
<tr>
<td>no. analyses</td>
<td>15</td>
<td>8</td>
<td>24</td>
</tr>
<tr>
<td>SiO₂</td>
<td>37.0 ± 4.9</td>
<td>37.2 ± 2.0</td>
<td>38.3 ± 2.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.7 ± 2.3</td>
<td>0.68 ± 0.33</td>
<td>0.88 ± 0.71</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.09 ± 0.07</td>
<td>0.06 ± 0.06</td>
<td>0.06 ± 0.07</td>
</tr>
<tr>
<td>MnO</td>
<td>0.25 ± 0.15</td>
<td>0.31 ± 0.09</td>
<td>0.61 ± 0.31</td>
</tr>
<tr>
<td>CaO</td>
<td>0.49 ± 0.37</td>
<td>0.32 ± 0.31</td>
<td>0.26 ± 0.23</td>
</tr>
<tr>
<td>MgO</td>
<td>3.7 ± 2.7</td>
<td>4.4 ± 0.9</td>
<td>3.8 ± 1.5</td>
</tr>
<tr>
<td>FeO</td>
<td>39.4 ± 1.8</td>
<td>37.6 ± 1.1</td>
<td>38.1 ± 2.8</td>
</tr>
<tr>
<td>S</td>
<td>0.19 ± 0.17</td>
<td>0.37 ± 0.41</td>
<td>0.23 ± 0.22</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.10 ± 0.07</td>
<td>0.38 ± 0.16</td>
<td>0.50 ± 0.37</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.18 ± 0.09</td>
<td>0.30 ± 0.05</td>
<td>0.20 ± 0.11</td>
</tr>
<tr>
<td>total</td>
<td>84.1 ± 2.6</td>
<td>81.5 ± 1.0</td>
<td>82.9 ± 2.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>BSE-dark phyllosilicate</th>
<th>QUE 99177</th>
<th>MET 00426</th>
<th>LAP 02342</th>
</tr>
</thead>
<tbody>
<tr>
<td>no. analyses</td>
<td>4</td>
<td>10</td>
<td>26</td>
</tr>
<tr>
<td>SiO₂</td>
<td>39.2 ± 1.2</td>
<td>39.1 ± 0.9</td>
<td>39.3 ± 0.8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.8 ± 0.6</td>
<td>1.5 ± 0.4</td>
<td>1.5 ± 0.5</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.24 ± 0.09</td>
<td>0.11 ±</td>
<td>0.13 ± 0.20</td>
</tr>
<tr>
<td>MnO</td>
<td>0.29 ± 0.08</td>
<td>0.28 ±</td>
<td>0.06</td>
</tr>
<tr>
<td>CaO</td>
<td>0.93 ± 0.29</td>
<td>0.23 ±</td>
<td>0.06</td>
</tr>
<tr>
<td>MgO</td>
<td>11.1 ± 1.4</td>
<td>9.7 ± 0.5</td>
<td>7.38 ± 1.47</td>
</tr>
<tr>
<td>FeO</td>
<td>29.9 ± 2.5</td>
<td>30.3 ± 1.5</td>
<td>32.7 ± 1.6</td>
</tr>
<tr>
<td>S</td>
<td>0.25 ± 0.05</td>
<td>0.24 ±</td>
<td>0.05</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.16 ± 0.07</td>
<td>0.15 ±</td>
<td>0.05</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.12 ± 0.05</td>
<td>0.14 ±</td>
<td>0.21 ± 0.21</td>
</tr>
<tr>
<td>total</td>
<td>86.0 ± 1.3</td>
<td>81.8 ± 1.8</td>
<td>82.7 ± 1.8</td>
</tr>
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</table>

end member

F_{523.3}W_{4.8}

<table>
<thead>
<tr>
<th>BSE-dark phyllosilicate</th>
<th>_que 99177</th>
<th>MET 00426</th>
<th>LAP 02342</th>
</tr>
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<tbody>
<tr>
<td>no. analyses</td>
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<td>26</td>
<td>5</td>
</tr>
<tr>
<td>SiO₂</td>
<td>54.7 ± 0.7</td>
<td>94.3 ± 1.5</td>
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</tr>
<tr>
<td>Al₂O₃</td>
<td>0.32 ± 0.25</td>
<td>1.3 ± 0.7</td>
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</tr>
<tr>
<td>Cr₂O₃</td>
<td>1.2 ± 0.3</td>
<td>0.06 ± 0.03</td>
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</tr>
<tr>
<td>MnO</td>
<td>2.9 ± 0.6</td>
<td>0.12 ± 0.08</td>
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</tr>
<tr>
<td>CaO</td>
<td>2.3 ± 0.5</td>
<td>0.12 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>24.5 ± 1.5</td>
<td>0.62 ± 0.62</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>14.3 ± 2.1</td>
<td>1.8 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.21 ± 0.08</td>
<td>0.39 ± 0.22</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>total</td>
<td>100.5 ± 0.5</td>
<td>98.7 ± 0.4</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 2.7. BSE image of the “honeycomb” structure in an igneous rim surrounding chondrule H9c in CR2.8 QUE 99177. The structure consists of patches of silica (dark gray) residing within a pyroxene rim (medium gray). Patches of phyllosilicate within the pyroxene are also present. Chondrule (medium-dark gray) is at right; fine-grained matrix material (medium gray) occurs beyond the honeycomb rim at the left. chd = chondrule; mtx = matrix.

Several 35-150-µm-long sections of the rim around chondrule H9c in QUE 99177 have a “honeycomb” texture (Harju et al., 2010) consisting of distinct 3-8-µm-size patches of nearly pure SiO₂ and moderately ferroan (Fs₂₃.₅Wo₄.₈) low-Ca pyroxene (Fig. 2.7; Table 2.6). It seems possible that the individual patches of silica are connected in three dimensions. This honeycomb structure averages 8-10 µm in width in most places in the chondrule rim, but is somewhat wider (15-30 µm) where there are chondrule embayments. The honeycomb sections of the rim are
separated by regions consisting of low-Ca pyroxene grains and small patches of phyllosilicates.

Grains of nearly pure silica (Table 2.6) are also present; we do not know if the silica is amorphous, but the presence of impurities in the silica suggests that, if crystalline, the phase has an open structure and is more likely to be tridymite or cristobalite than quartz. The minor amounts of FeO, MgO and Al\textsubscript{2}O\textsubscript{3} in the silica phase are not likely to be an artifact caused by overlap of the electron beam on adjacent pyroxene – the silica phase has more Al\textsubscript{2}O\textsubscript{3} than the pyroxene (1.3 vs. 0.32 wt.%) and a much higher FeO/MgO ratio (2.9 vs. 0.58) (Table 2.6).

### 2.3.3 Variations in Oxide Composition

Although coarse magnetite is not present in the least-altered CR chondrites, the more-altered samples contain magnetite and other iron oxides of similar composition (Table 2.7).

<table>
<thead>
<tr>
<th>Table 2.7 Compositions of iron oxides (wt.%) in CR chondrites.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NWA 2196</strong></td>
</tr>
<tr>
<td>no. analyses</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>Cr\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>FeO</td>
</tr>
<tr>
<td>MnO</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>Na\textsubscript{2}O</td>
</tr>
<tr>
<td>total</td>
</tr>
</tbody>
</table>

All Fe computed as FeO. The oxides in NWA 2196, Renazzo and Al Rais are compositionally equivalent to magnetite.
Magnetite occurs in Renazzo, Al Rais and NWA 2196 (Table 2.7); other CR chondrites such as NWA 5028 contain iron oxides with somewhat lower analytical totals, presumably reflecting a greater concentration of ferric iron, i.e., they are enriched in a hematite (Fe$_2$O$_3$) compositional component. These ferric oxides appear to be systematically enriched in Al$_2$O$_3$ relative to magnetite in Renazzo, Al Rais and NWA 2196 (0.22-0.48 vs. $\leq$0.07 wt.%; Table 2.7). The low degree of terrestrial weathering of NWA 5028 (i.e., W1; Table 2.1) is consistent with the supposition that the iron oxides in this rock formed on the CR parent asteroid.

2.3.4 Glass in Chondrule Mesostases

During the earliest stages of alteration and metamorphism, the alkali contents of clear isotropic chondrule glass become inhomogeneous as albite crystallizes and the residual glass becomes richer in K (Grossman and Brearley, 2005). There is a large diversity of chondrule mesostasis compositions even in individual highly unequilibrated chondrites (e.g., LL3.0 Semarkona; Table C36 of Gooding, 1979). At present there are too few data to determine if this characteristic might be useful for gauging the extent of whole-rock aqueous alteration. We searched for isotropic glass with the petrographic microscope in sections of 16 CR chondrites having petrographic subtypes $\geq$2.7 (Table 2.2). Mesostases that appear “glassy” in the microscope were identified in five sections: EET 92062 and LAP 02342 had the highest fraction in our search (three occurrences in 10 and 11 chondrules, respectively). “Glassy” mesostases were found in $\sim$12% of the chondrules in MET 00426 and <5% in EET 92062 and Gao-Guenie (b). Only one chondrule with isotropic glass out of nine was identified in QUE 99177.
However, there are uncertainties in these data. First, these are the statistics of small numbers. Second, some chondrules with petrographically clear mesostases appear to be fine-grained (i.e., microcrystalline, not glassy) when examined by back-scattered-electron (BSE) imaging and may have suffered minor aqueous alteration. This suggests that microscopic observations tend to overestimate the true abundance of glassy chondrules. In contrast, there are two processes that could act to underestimate the abundance of glassy chondrules: (1) CR chondrites of weathering stage >W2 could have had patches of clear, isotropic glass that were destroyed by terrestrial weathering. (2) Thin sections that are too thick can have phenocrysts occurring beneath patches of glass, obscuring the isotropism of the glass when viewed in transmitted light. This could be the case for QUE 99177.

2.3.5 Compositional Zoning in Chondrule Mesostases

Grossman et al. (2002) found that 35% of type-I (low-FeO) porphyritic chondrules in LL3.0 Semarkona exhibit compositional zoning in their mesostases: glass in the outer parts of these chondrules tends to be enriched in Na and K and depleted in Ca, Ti, and Cr. They concluded that aqueous alteration on the parent body caused glass in the outer parts of the chondrules to hydrate and undergo structural modification; this aided elemental exchange between the outer mesostasis and the surrounding chondrite matrix.

We analyzed mesostases throughout two low-FeO (type-I) chondrules in LAP 02342 (POP chondrule C4q and PO chondrule H2f) and one low-FeO POP chondrule (chondrule 1) in EET 92062. Mesostasis in chondrule C4q and chondrule 1 is enriched in Na and depleted in Ca, Ti, and Cr near the edge of the chondrule, adjacent to matrix (e.g., Fig. 2.8); K shows no trend in C4q and was not determined in chondrule 1. Mesostasis in chondrule H2f is enriched in Na and
depleted in Ti near the edge of the chondrule; K, Cr and Ca show no trends (e.g., Fig. 2.8). Despite the K and Ca discrepancies, these results are roughly consistent with the data for Semarkona chondrules (Grossman et al., 2002) and appear attributable to parent-body aqueous alteration.

![Graphs showing compositional zoning profiles of mesostasis in two low-FeO porphyritic chondrules](image)

Fig. 2.8. Representative compositional zoning profiles of mesostasis in two low-FeO porphyritic chondrules [C4q (POP) and H2f (PO)] in CR2.8 LAP 02342. Mesostasis in chondrule C4q is depleted in Cr$_2$O$_3$, CaO and TiO$_2$ and enriched in Na$_2$O near its edge. Mesostasis in chondrule H2f is depleted in TiO$_2$, but CaO shows no trend. These zoning profiles are similar to those in LL3.0 Semarkona and are attributable to parent-body aqueous alteration. The detection limits are ~0.04 wt.% for all of the oxides in this diagram. Uncertainties in the measurements are on the order of 0.1 wt.% oxide as determined by multiple analyses of a homogeneous olivine grain in H4 Bath (Rubin, 2005).
2.3.6 Matrix-Grid Compositions Including S

The least-altered CR chondrites have relatively high, relatively uniform S contents in the matrix; this is illustrated in the images of LAP 02342 matrix regions published by Wasson (2008). We used the matrix grid approach of Wasson and Rubin (2009) to measure S and nine other elements in matrix grid areas in a number of CR chondrites. As discussed in more detail in the experimental section, we used a 3-µm electron microprobe beam to analyze a grid of points spaced about 7 µm apart. Anomalous points (for most elements, those plotting ~>2.5 standard deviations outside the grand mean) were discarded. Our results for 10 CR chondrites (including paired Acfer samples) are listed in Table 2.8. The number of analyzed points and the number discarded are listed in the last line of each grid area.

We obtained data for ten elements. All elements show scatter from point to point and from one grid area to the next. The most variable element is S, reflecting its sensitivity to the degree of aqueous alteration.

As discussed by Wasson and Rubin (2009), most of the elemental variations in grid areas of primitive CR chondrites (such as LAP 02342) seem to reflect nebular formation. These workers suggested that, during chondrule formation, slightly melted assemblages of dust particles formed weakly bound structures that, in some cases, differed from the mean matrix composition. This compositional record was preserved even after the structure was compacted during asteroid formation. The challenge is to separate primary nebular effects from those produced during aqueous alteration.

At the bottom of Table 2.8 we list some of the grid areas that were discarded because the compositions are unrepresentative. In general, the reason for deciding that these particular regions are unrepresentative is that many points have anomalous compositions. We show
examples of unrepresentative data for four CR chondrites including two that also yielded representative data shown in the central section of Table 2.8.

The last lines show that we discarded >50% of all unrepresentative grid areas except in NWA 1616. In fact, all but two of the points for NWA 1616 have Al contents above the limits; we averaged them despite their systematically high Al values. We're confident that the high Al is the result of aqueous alteration. Wasson et al. (2013) reported a large depletion in Al in a grid area that overlapped a smooth rim (a product of aqueous alteration) in LAP 02342.

We obtained much data on two of the least-altered CR chondrites, QUE 99177 and LAP 02342. In the top section of the table we list concentration data for five grid areas in QUE and four in LAP. With the exception of one region in QUE, S means range from 2.25 wt.% to 4.06 wt.%; the range is similar in the two chondrites. We included QUE region I5l to show an anomalous grid area with high Mg and Si and low Fe and S. Mean S contents (excluding QUE I5l and including data not included in Table 2.8) are 3.18% (QUE) and 3.33 wt% in LAP. Relative standard deviations in the grid-area S concentrations are generally about 25 to 35%. Our working interpretation is that these concentrations, small ranges and low analytical totals (78.5 – 83.9 wt.%) are representative of the least-altered CR chondrites. Wasson and Rubin (2009) interpreted such low totals as due mainly to voids, and to a lesser extent, structural H₂O.

Grid areas in six other CR chondrites are also shown in the central section of Table 2.8. The S content (3.3 wt.%) and the total and general compositions of EET 92105 matrix regions imply that this meteorite is largely unaltered. The next highest S (present in the matrix of Y-790112) is much lower, its analytical total is slightly high, its Fe is slightly high, and its Mg slightly low. The next highest S (1.8 wt.%) is in Renazzo r1 dark; it has a low analytical total
and very low FeO; two other Renazzo grid areas are designated unrepresentative in the bottom portion of Table 2.8. As discussed below, low-FeO contents are indicative of aqueous alteration.

The Acfer samples were found in close proximity to each other and appear to be paired. The Acfer 399 grid area is designated representative, the other two unrepresentative. All of the Acfer samples show moderate weathering; the pre-weathering S content was probably about 1.0 to 1.5 wt.%.

Some data on CR samples that experienced relatively little aqueous alteration are plotted in Fig. 2.9; we plot S, SiO$_2$ and MgO against FeO. The four QUE and four LAP samples offer evidence of the variability of matrix grid areas in the least aqueously altered CR chondrites. Two other relatively unaltered samples (EET and Acfer) are plotted as test cases.

The S-Fe plot (Fig. 2.9a) shows a positive linear trend. We interpret the cluster of two QUE and two LAP points on the upper right of the diagram as showing the compositional range of the least-altered regions in CR matrix; the remaining QUE and LAP samples seem to have been affected by asteroidal aqueous alteration. The EET sample plots within error of the four fairly primitive QUE and LAP samples; we interpret this to mean that EET has experienced about the same level of aqueous alteration as QUE and LAP. Acfer 399 has a high Fe content, consistent with relatively little aqueous alteration, but the S content (0.7 wt.%) is far outside the range of primitive CR matrix. This is plausibly due to the hot-desert weathering experienced by the Acfer samples.

The SiO$_2$ data (Fig. 2.9b) show considerable scatter, but the total range is only 10% relative. We tentatively conclude that the least-altered CR chondrites have low SiO$_2$, but due to the high degree of scatter, this is not a very useful parameter for assessing CR aqueous alteration.
Fig. 2.9. Compositions of matrix grid areas in slightly altered, type-2.8 CR chondrites. (a) S vs. FeO. These two components are sensitive to aqueous alteration; the least-altered CR chondrites have 3-4 wt.% S and 31-34 wt.% FeO in most grid regions. (b) SiO$_2$ vs. FeO. Although SiO$_2$ shows a narrow range, it has too much scatter to be useful for taxonomy. (c) MgO vs. FeO. The MgO content increases with increasing degrees of aqueous alteration; see text for a more-detailed discussion.
### Table 2.8 Matrix grid elemental concentration data for CR chondrites with subtypes ≥2.4

#### Representative samples

<table>
<thead>
<tr>
<th>Element</th>
<th>QUE M7</th>
<th>QUE E45mRm</th>
<th>QUE E5</th>
<th>QUE G9</th>
<th>QUE I51</th>
<th>LAP J2s</th>
<th>LAP K1i</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂O₃</td>
<td>0.40</td>
<td>0.08</td>
<td>0.33</td>
<td>0.06</td>
<td>0.40</td>
<td>0.20</td>
<td>0.32</td>
</tr>
<tr>
<td>SiO₂</td>
<td>29.7</td>
<td>3.6</td>
<td>26.6</td>
<td>3.2</td>
<td>29.8</td>
<td>1.9</td>
<td>26.4</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.11</td>
<td>0.05</td>
<td>0.32</td>
<td>0.13</td>
<td>0.17</td>
<td>0.05</td>
<td>0.18</td>
</tr>
<tr>
<td>MnO</td>
<td>0.23</td>
<td>0.05</td>
<td>0.20</td>
<td>0.06</td>
<td>0.18</td>
<td>0.03</td>
<td>0.16</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.05</td>
<td>0.02</td>
<td>0.07</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.87</td>
<td>0.45</td>
<td>1.73</td>
<td>0.33</td>
<td>1.86</td>
<td>0.15</td>
<td>1.62</td>
</tr>
<tr>
<td>CaO</td>
<td>1.12</td>
<td>0.27</td>
<td>1.04</td>
<td>1.03</td>
<td>0.95</td>
<td>0.83</td>
<td>0.43</td>
</tr>
<tr>
<td>MgO</td>
<td>18.3</td>
<td>4.3</td>
<td>13.2</td>
<td>1.6</td>
<td>16.8</td>
<td>1.3</td>
<td>14.2</td>
</tr>
<tr>
<td>FeO</td>
<td>30.0</td>
<td>5.6</td>
<td>33.4</td>
<td>2.2</td>
<td>27.3</td>
<td>1.4</td>
<td>33.7</td>
</tr>
<tr>
<td>S</td>
<td>2.75</td>
<td>0.66</td>
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<td>1.00</td>
<td>2.25</td>
<td>0.85</td>
<td>3.96</td>
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<tr>
<td>total</td>
<td>83.2</td>
<td>2.2</td>
<td>78.5</td>
<td>3.3</td>
<td>78.6</td>
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<td>79.0</td>
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<td>7</td>
<td>21</td>
<td>5</td>
<td>21</td>
<td>6</td>
<td>36</td>
</tr>
</tbody>
</table>

#### Representative samples (LAP 55f, LAP 55y, Acfer 399, EET 92105, GRA06100r1, NWA 5028r2, Renazzo r1lt, Y790112)

<table>
<thead>
<tr>
<th>Element</th>
<th>LAP 55f</th>
<th>LAP 55y</th>
<th>Acfer 399</th>
<th>EET 92105</th>
<th>GRA06100r1</th>
<th>NWA 5028r2</th>
<th>Renazzo r1lt</th>
<th>Y790112</th>
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<tbody>
<tr>
<td>Cr₂O₃</td>
<td>0.36</td>
<td>0.10</td>
<td>0.33</td>
<td>0.07</td>
<td>0.32</td>
<td>0.07</td>
<td>0.36</td>
<td>0.07</td>
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<tr>
<td>SiO₂</td>
<td>29.1</td>
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<td>26.4</td>
<td>2.72</td>
<td>30.3</td>
<td>3.0</td>
<td>28.7</td>
<td>3.0</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.50</td>
<td>0.07</td>
<td>0.90</td>
<td>0.16</td>
<td>1.07</td>
<td>0.03</td>
<td>1.14</td>
<td>0.13</td>
</tr>
<tr>
<td>MnO</td>
<td>0.20</td>
<td>0.09</td>
<td>0.24</td>
<td>0.09</td>
<td>0.26</td>
<td>0.40</td>
<td>0.23</td>
<td>0.08</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.05</td>
<td>0.02</td>
<td>0.08</td>
<td>0.02</td>
<td>0.28</td>
<td>0.04</td>
<td>0.11</td>
<td>0.02</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.67</td>
<td>0.18</td>
<td>1.88</td>
<td>0.24</td>
<td>2.04</td>
<td>0.26</td>
<td>1.69</td>
<td>0.34</td>
</tr>
<tr>
<td>CaO</td>
<td>0.53</td>
<td>0.25</td>
<td>1.36</td>
<td>0.64</td>
<td>2.35</td>
<td>0.29</td>
<td>0.68</td>
<td>0.52</td>
</tr>
<tr>
<td>MgO</td>
<td>16.4</td>
<td>2.4</td>
<td>16.3</td>
<td>1.89</td>
<td>13.0</td>
<td>2.00</td>
<td>16.1</td>
<td>2.2</td>
</tr>
<tr>
<td>FeO</td>
<td>33.0</td>
<td>2.7</td>
<td>30.5</td>
<td>2.22</td>
<td>33.9</td>
<td>3.21</td>
<td>30.4</td>
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</tr>
<tr>
<td>S</td>
<td>4.06</td>
<td>0.82</td>
<td>2.67</td>
<td>0.81</td>
<td>0.66</td>
<td>0.33</td>
<td>3.33</td>
<td>0.98</td>
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<tr>
<td>total</td>
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<td>2.2</td>
<td>79.3</td>
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<td>83.0</td>
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<td>56</td>
<td>23</td>
<td>66</td>
<td>12</td>
</tr>
</tbody>
</table>

#### Unrepresentative samples (many discarded or discardable points)

<table>
<thead>
<tr>
<th>Element</th>
<th>Acfer097r1</th>
<th>Acfer 395</th>
<th>MIL 07513</th>
<th>NWA 1616</th>
<th>Renazzo r1lt</th>
<th>Renazzo r2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂O₃</td>
<td>0.35</td>
<td>0.09</td>
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<td>0.22</td>
<td>0.42</td>
<td>0.27</td>
</tr>
<tr>
<td>SiO₂</td>
<td>30.6</td>
<td>2.6</td>
<td>28.9</td>
<td>3.76</td>
<td>28.4</td>
<td>1.74</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.26</td>
<td>0.10</td>
<td>0.11</td>
<td>0.06</td>
<td>0.3</td>
<td>0.05</td>
</tr>
<tr>
<td>MnO</td>
<td>0.18</td>
<td>0.07</td>
<td>0.24</td>
<td>0.25</td>
<td>0.28</td>
<td>0.04</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.18</td>
<td>0.07</td>
<td>0.2</td>
<td>0.05</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.64</td>
<td>0.42</td>
<td>2.54</td>
<td>0.47</td>
<td>1.8</td>
<td>0.43</td>
</tr>
<tr>
<td>CaO</td>
<td>1.27</td>
<td>0.29</td>
<td>1.81</td>
<td>0.39</td>
<td>0.42</td>
<td>0.14</td>
</tr>
<tr>
<td>MgO</td>
<td>15.2</td>
<td>3.0</td>
<td>15</td>
<td>6.86</td>
<td>17.2</td>
<td>1.33</td>
</tr>
<tr>
<td>FeO</td>
<td>33.8</td>
<td>4.2</td>
<td>33.3</td>
<td>7.22</td>
<td>43.5</td>
<td>2.42</td>
</tr>
<tr>
<td>S</td>
<td>1.35</td>
<td>0.84</td>
<td>0.87</td>
<td>0.45</td>
<td>0.35</td>
<td>0.05</td>
</tr>
<tr>
<td>total</td>
<td>85.0</td>
<td>2.6</td>
<td>82.8</td>
<td>4.61</td>
<td>92.4</td>
<td>1.59</td>
</tr>
</tbody>
</table>
The MgO data (Fig. 2.9c) show a larger (20%) relative range and a relatively strong negative trend. We conclude that low (ca. 14 wt.%) MgO is indicative of low degrees of aqueous alteration. We note that EET has a MgO content just below that of one of the two primitive LAP samples. More interestingly, our Acfer sample has the lowest MgO content on the diagram, but is the same within error as the two most primitive QUE samples. Acfer also has a total (83 wt.%) that is within the normal range for the least-altered CR chondrites. We conclude that Acfer has experienced relatively little asteroidal aqueous alteration and that its anomalous compositional features are mainly the result of terrestrial weathering.

2.3.7 Carbonate-Rich Clast in MIL 07525

MIL 07525 is a breccia; the host is subtype 2.8 and has experienced little alteration, but the section includes a heavily altered 600-µm-size clast (Fig. 2.10) probably of subtype 2.0 – 2.1.

Fig. 2.10. BSE image of an aqueously altered clast in CR2.8 MIL 07525. The clast consists of a Ca-carbonate grain containing iron-oxide grains (small gray inclusions) as well as phyllosilicates. The metallic Fe-Ni blebs (white) in an adjacent chondrule are completely unaltered (except for minor terrestrial weathering). Ca-carb = Ca-carbonate.
The clast consists of Ca-carbonate that surrounds 4-35-µm-size grains of iron oxide (compositionally equivalent to a mixture of magnetite and hematite) and Fe- and Mg-rich phyllosilicate (Table 2.9). The low analytical total of the oxide phase is attributed to the presence of ferric iron; the low total of the phyllosilicate is attributed to the presence of hydroxyl. The clast is situated next to a chondrule with unaltered metal.

**Table 2.9 Average compositions (wt.%) of phases in a carbonate-rich clast in MIL 07525**

<table>
<thead>
<tr>
<th></th>
<th>Ca carbonate</th>
<th>oxide</th>
<th>phyllosilicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>no. analyses</td>
<td>5</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>--</td>
<td>2.3 ± 1.5</td>
<td>34.3 ± 0.1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>--</td>
<td>0.27 ± 0.21</td>
<td>--</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>--</td>
<td>0.05 ± 0.03</td>
<td>2.3 ± 0.3</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>--</td>
<td>0.21 ± 0.12</td>
<td>--</td>
</tr>
<tr>
<td>FeO</td>
<td>1.1 ± 0.5</td>
<td>86.8 ± 2.0</td>
<td>28.0 ± 1.2</td>
</tr>
<tr>
<td>MnO</td>
<td>0.14 ± 0.03</td>
<td>0.08 ± 0.03</td>
<td>0.46 ± 0.03</td>
</tr>
<tr>
<td>MgO</td>
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<td>0.58 ± 0.38</td>
<td>20.6 ± 1.0</td>
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<tr>
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<td>0.77 ± 0.16</td>
<td>0.73 ± 0.06</td>
</tr>
<tr>
<td>Na₂O</td>
<td>--</td>
<td>0.04 ± 0.04</td>
<td>--</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>&lt;0.04 ± 0.05</td>
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<tr>
<td>SO₃</td>
<td>0.31 ± 0.15</td>
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<tr>
<td>CO₂</td>
<td>44.5 ± 4</td>
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<td>--</td>
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<tr>
<td>total</td>
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The CO₂ concentration was calculated by difference from 100 wt.%. All Fe is assumed to be FeO. NiO was not determined.

### 2.3.8 Oxygen-isotopic compositions

The O-isotopic compositions of 11 CR chondrites are summarized in Table 2.10 and Fig. 2.11. Preliminary results were reported in Choi et al. (2009). Similar to the results of Choi et al. (2009) and Schrader et al. (2011), our CR data fall along a roughly linear mixing line with a slope appreciably lower than that of the carbonaceous-chondrite anhydrous minerals (CCAM) line (0.94). [Earlier CR-chondrite results by Clayton and Mayeda (1999) showed a still-lower slope.] The CR mixing line in the present study (n = 11) has a slope of 0.74 with a δ¹⁷O intercept of -2.69 (using the average value for each sample and giving equal weight to the 11
analyzed CR chondrites; Table 2.10). Very similar CR mixing lines were obtained from the UCLA and KOPRI data sets: slopes are 0.75±0.2 and 0.74±0.06 and $\delta^{17}\text{O}$ intercepts of -2.75±0.09 and -2.65±0.13‰, respectively. Our mixing-line slope is steeper than the value of 0.70±0.04 reported previously by Schrader et al. (2011). The 10 CR chondrites studied by Clayton and Mayeda (1999) form a line of slope 0.64 and a $\delta^{17}\text{O}$ intercept of -1.96‰;

![Standard three-isotope oxygen diagram for 11 CR chondrites showing that they lie along a CR mixing line (dashed line: $\delta^{17}\text{O} = 0.74 \times \delta^{18}\text{O} - 2.69$). Highly altered CR2.0 GRO 95577 has higher $\Delta^{17}\text{O}$ values and plots at upper right. The least-altered samples have lower $\Delta^{17}\text{O}$ values and plot at lower left. Thus, there is a general correlation between $\Delta^{17}\text{O}$ and the degree of parent-body aqueous alteration. The terrestrial fractionation (TF) line and the carbonaceous-chondrite anhydrous minerals (CCAM) line are shown for reference. Filled symbols represent untreated samples; open symbols represent treated samples; open symbols with an enclosed cross represent pre-fluorinated samples that were not treated with acid. The dashed regression line (slope = 0.74±0.03) is based on a simple average for each meteorite; see text for details.](image-url)
if CR-an Al Rais is omitted from the Clayton-Mayeda trend, the line has a slope of 0.72 and a δ\textsuperscript{17}O intercept of -2.12‰.

Instead of grinding the whole rock into power to produce homogenous samples, we crushed meteorites into small fragments that were still large enough to be picked up by tweezers;

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<th>δ\textsuperscript{17}O (‰)</th>
<th>δ\textsuperscript{17}O (‰)</th>
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<td>10.25</td>
<td>5.00</td>
<td>-0.33</td>
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</tr>
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</table>
we selected relatively fresh-looking fragments under a binocular microscope. We suspect that this procedure (as well as acid-washing and pre-fluorination) helped minimize the amount of terrestrial oxygen in our measurements. Our data are generally lower in Δ^{17}O than previous data (Fig. 2.12), suggesting that our technique minimized the amount of terrestrial oxygen (resulting from weathering).

![Oxygen-isotopic compositions of CR chondrites in this study are compared with previous data in a Δ^{17}O vs. δ^{18}O diagram. Our Δ^{17}O values are generally lower than previous data with similar δ^{18}O values, implying that our data have less low-δ^{18}O terrestrial contamination. Sources of data: B93 (Bischoff et al., 1993), C&M (Clayton and Mayeda, 1999), S11 (Schrader et al., 2011).](image)

Fig. 2.12. Oxygen-isotopic compositions of CR chondrites in this study are compared with previous data in a Δ^{17}O vs. δ^{18}O diagram. Our Δ^{17}O values are generally lower than previous data with similar δ^{18}O values, implying that our data have less low-δ^{18}O terrestrial contamination. Sources of data: B93 (Bischoff et al., 1993), C&M (Clayton and Mayeda, 1999), S11 (Schrader et al., 2011).
In general, $\Delta^{17}$O data from acid-washed samples plot lower on the CR-mixing line, followed by samples that were treated by pre-fluorination only, and then by samples with no pretreatments (Table 2.10). This sequence implies that these cleaning steps for terrestrial weathering also removed some fine-grained matrix minerals and phases that formed during low-temperature aqueous alteration.

2.4 Discussion

2.4.1 Processes and products indicative of CR alteration

During aqueous alteration of CR chondrites, a large number of changes take place in texture, mineralogy, bulk chemistry, bulk isotopic composition and in the modal abundances of presolar grains and organic materials. Some parameters are affected primarily at low degrees of alteration (e.g., alteration of chondrule glass, development of phyllosilicate), some at high degrees (e.g., growth of coarse carbonate grains, creation of chondrule pseudomorphs), and some change more-or-less continuously throughout the alteration sequence (e.g., bulk O-isotopic composition, alteration of coarse mafic silicate grains). A few parameters are sensitive indicators of alteration (e.g., S loss from matrix material), whereas others appear to vary only slightly (e.g., the abundance of insoluble organic matter).

For convenience, the alteration sequence of CR chondrites can be divided into early, intermediate and final-stage alteration processes. Useful comparisons can be made with the alteration of other carbonaceous-chondrite groups (e.g., CM; Rubin et al., 2007). Some CR chondrites may have experienced aqueous alteration at different temperatures (Abreu, 2012); a few CR chondrites may have experienced short-duration impact heating after alteration (Briani et
Finally, it is important to understand that terrestrial weathering has played a significant role in the alteration of specific samples, especially those from hot deserts.

2.4.1.1 Early-Stage Alteration Processes

(1) Alteration of initially clear isotropic glass (e.g., Ichikawa and Ikeda, 1995; Grossman and Brearley, 2005; Brearley, 2006). Chondrule glass can be leached, undergo chemical and isotopic exchange with the fluid, become compositionally zoned with respect to the chondrule interface with the matrix, and become hydrated to form phyllosilicates. Glass that is sequestered within mafic silicate grains will remain unaltered for longer periods. Reproducible low analytical totals of undevitrified chondrule glass (e.g., ≤98.0 wt.%) can indicate hydration. Elemental zoning (wherein glass near the surface of low-FeO (type-I) porphyritic chondrules is enriched in Na and depleted in Cr and Ti relative to glass near the chondrule center) is also indicative of the early stages of parent-body alteration (Grossman et al., 2002). Calcium can be leached from the glass in high-FeO (type-II) porphyritic CR chondrules and deposited in the matrix to help form CaCO$_3$ during the early stages of parent-body aqueous alteration (Burger and Brearley, 2004, 2005). (Fine, reactive organic matter in the matrix may contribute C to CaCO$_3$ produced during alteration; Wasson and Rubin, 2009.)

(2) Changes in O and H isotopes. We infer from the observed trends on O-isotope diagrams (Fig. 2.11) that as individual CR chondrites interact with aqueous fluids on their parent body, they gain O with high $\Delta^{17}$O. There is also some evidence
that they exchange H with fluids having low $\delta^D$ values (Alexander et al., 2012a,b, 2013).

(3) **Amino acids and presolar grains.** The sparse data imply that large decreases in the abundances of amino acids (Martins et al., 2007) and O-anomalous presolar grains (Floss and Stadermann, 2009; Haenecour and Floss, 2011; Zhao et al., 2011) occur at the beginning stages of aqueous alteration, but there are too few data to define trends among the subtypes.

(4) **Phyllosilicates.** Three of the least-altered CR chondrites (QUE 99177, MET 00426 and LAP 02342) contain smooth phyllosilicate rims around some chondrules (Fig. 2.6). Aqueous alteration on the CR parent asteroid seems to have converted some primary igneous-rim materials into phyllosilicates; the preservation of abundant metallic Fe-Ni indicates that this process took place with minimal whole-rock alteration. On the other hand, limited TEM data indicate that phyllosilicates are relatively rare in the matrices of QUE 99177 and MET 00426 (Abreu and Brearley, 2010); they appear to be more common in the (relatively few) studied matrices of more-altered samples. TEM studies are needed to ascertain matrix hydration in samples in which phyllosilicate grains are too small to be recognized optically or analyzed with the electron microprobe. However, because TEM sections are very small and relatively few have been studied, one cannot be sure that the sections are representative of the whole rocks. We therefore consider the presence of smooth rims to be a more-reliable indicator of asteroidal aqueous alteration.
(5) *S in the matrix.* As discussed above, S is distributed fairly uniformly at a concentration of ~3 wt.% in the matrix of LAP 02342 (Table 1 of Wasson and Rubin, 2009). In type-3 ordinary chondrites, the matrix S concentration falls off rapidly at the onset of metamorphism (Grossman and Brearley, 2005) and is thus a sensitive indicator of petrologic subtype. Aqueous alteration produces a similar S depletion in CR chondrites: the S content of fine-grained matrix material decreases from ~3 wt.% in the least-altered CR chondrites (type-2.8) to <1 wt.% in CR chondrites of type ≤2.6. An exception is the matrix in CR2.4 Renazzo (2.7±1.0 wt.% S, n=12) which is moderately rich in S, but shows a large degree of scatter. The electron beam overlapped two coarse sulfide grains in this patch of Renazzo matrix and these points were omitted from the mean and standard deviation. Sulfide-poor matrix areas in Renazzo have as little as 0.08 wt.% S.

In their study of CM chondrites, Rubin et al. (2007) found that with increasing degree of alteration of CM chondrites, S formed relatively coarse sulfide grains at the expense of S in both the fine-grained matrix and within tochilinite-cronstedtite-rich (PCP) clumps. Sulfide coarsening may have also occurred in CR chondrites – with increasing alteration, coarse sulfide formed at the expense of matrix S. We conclude that immediately after Renazzo was aqueously altered, its fine-grained matrix had very low S contents (probably ≤~0.1 wt.%). Also present were randomly scattered coarse sulfide grains. It is possible that post-alteration impact-induced brecciation shattered and dispersed these sulfide grains throughout the matrices of these meteorites. Renazzo has a strong petrofabric (Rubin and Harju, 2012), probably a result of impact processes (e.g., Gattacceca et al., 2005). Such processes may have introduced crushed FeS and might account for the anomalously high but variable S contents of its matrix regions.
2.4.1.2 Intermediate-Stage Alteration Processes

(1) *Oxide-rich assemblages.* Interaction of CR chondrites with water produces magnetite and/or other iron-oxides from metallic Fe-Ni and FeS. These oxides are very rare to absent in the least-altered CR samples (Table 2.11). Ca-phosphate formed along with magnetite in some regions, replacing metallic Fe-Ni (Jilly and Huss, 2012). In CI, CK and R chondrites, Ni was incorporated into Fe-Ni sulfides (e.g., Fredriksson and Kerridge, 1988; Kallemeyn et al., 1991; Bischoff et al., 2011) during this stage of oxidation; a related process is most likely responsible for producing Ni- and S-rich layers around altered metallic Fe-Ni grains in CR-an Al Rais (Fig. 2.3). In CR chondrites, fine-grained S in the matrix was dissolved and transported out of the matrix to form Fe-Ni sulfide rinds near metallic Fe-Ni grains.

(2) *Phenocryst alteration.* In the least-altered CM and CR chondrites, chondrule mafic phenocrysts remain pristine, but at high degrees of aqueous alteration they alter to phyllosilicates at their edges and along twin boundaries and fractures. In moderately altered CR chondrites, incipient alteration of phenocrysts occurs at subtype 2.5 (Table 2.11), and in CM chondrites at subtype 2.3 (Table 5 of Rubin et al., 2007), suggesting that these stages mark a comparable degree of aqueous alteration in these two chondrite groups. Moderate phenocryst alteration is petrographically evident in CR2.4 chondrites.

2.4.1.3 Final-Stage Alteration Processes

(1) *Formation of coarse carbonate.* Ca- and Mg-Ca-carbonate in CM and CI chondrites (Endress and Bischoff, 1996; de Leuw et al., 2010, Fredriksson and Kerridge, 1988)
are associated with high degrees of aqueous alteration. Several CR chondrites (including relatively pristine samples; Wasson and Rubin, 2009; Abreu and Brearley, 2010) contain accessory carbonate (Weisberg et al., 1993), and Al Rais contains carbonate veins. However, coarse carbonate occurrences have been observed only in (a) CR2.0 GRO 95577, (b) in a highly altered, phyllosilicate- and oxide-bearing clast in the MIL 07525 CR2.8 breccia, and (c) in CR2.4 MIL 090001 by Keller et al. (2012). Coarse carbonate grains may be forming largely within voids in the meteorite matrix.

(2) Sulfate. Some of the S dissolved from the matrix during aqueous alteration was partly oxidized to form sulfate. Textural evidence suggests that the ferrous sulfate associated with oxides in opaque assemblages in GRO 95577 (Figs. 2.4a, 2.5a) was produced on the asteroid and is not a product of terrestrial weathering.

(3) Chondrule pseudomorphs. In type-2.0 CM and CR chondrites, mafic silicates are very rare to absent and all (or almost all) of the chondrules have been completely replaced by phyllosilicates, oxides and other minor secondary phases (Rubin et al., 2007; Weisberg and Huber, 2007; this study) with little or no apparent change in chondrule shape. In CM2.1 chondrites (e.g., QUE 93005), several chondrule pseudomorphs in every thin section contain rare grains of mafic silicate (Rubin et al., 2007); it seems likely that, in CR2.1 chondrites, a larger fraction of mafic-silicate-bearing chondrule pseudomorphs should be present than in CR2.0 chondrites.
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<tr>
<td>replacement of coarse metal and silicate by phyllosilicate and oxide</td>
<td>little</td>
<td>little</td>
<td>most metal and mafic silicates replaced</td>
<td>almost all metal and mafic silicates replaced</td>
<td>complete or nearly complete</td>
<td></td>
</tr>
<tr>
<td>abundance of phyllosilicate in matrix and chondrule rims</td>
<td>very high</td>
<td>very high</td>
<td>very high to extremely high</td>
<td>very high to extremely high</td>
<td>very high to extremely high</td>
<td></td>
</tr>
</tbody>
</table>
2.4.2 Possible Terrestrial Weathering Products

Some secondary phases in CR chondrites were produced by terrestrial weathering rather than by parent-body alteration and it is important to be able to distinguish the responsible process. Many CR chondrites are from hot deserts; these environments cause more profound weathering effects than cold deserts. All but two CR chondrites are finds, and the two observed falls (Renazzo and Al Rais) have been on Earth for many decades. Terrestrial weathering products include goethite or maghemite (e.g., Rubin, 1997; Cadogan and Devlin, 2012) occurring as rinds around metal grains and as veins and patches in the matrix (e.g., area B4 of CR2 LAP 02342; Fig. 1 of Wasson and Rubin, 2009).

Because heavily weathered chondrite finds tend to contain substantial amounts of bulk Fe$_2$O$_3$ and, in some cases, SO$_3$ (Jarosewich, 1990), it is plausible that sulfates and ferric-iron-bearing oxides in CR chondrites were formed by terrestrial weathering. Sulfates occurring as veins or flakes (e.g., Figs. 1 and 2 of Gounelle and Zolensky, 2001) are more likely to be terrestrial-weathering products than smooth, thick coherent layers around or within metal grains (or former metal grains), especially if those grains are in observed falls. It seems likely that all the nodules of oxide and S-rich phases in the Al Rais fall (Fig. 2.3) are pre-terrestrial alteration products. The thick, coherent iron-oxide layers around kamacite grains in GRO 95577 (Fig. 2.4) closely resemble magnetite rims around metal grains in other chondrites and are also likely pre-terrestrial. This conclusion is supported by the occurrence of iron-oxide frambooids in the matrices of the GRO 95577 and MIL 090292 CR2.0 chondrites. The cores of some of the former metal grains in GRO 95577 (Fig. 2.4a, 2.5a) consist of an intergrowth of siderite and ferrous sulfate and are probably pre-terrestrial – they are not made of essentially pure sulfate (nor do they occur as flakes) as the terrestrially produced sulfate in CI Orgueil (Fig. 2 of Gounelle and
The core of the metal grain in Fig. 2.4a has fractures (presumably impact induced) and forms a sharp boundary with the surrounding iron oxide. The core of the grain in Fig. 2.5a is more texturally ambiguous, but it is surrounded by smooth iron-oxide layers and is similar in composition to the core in Fig. 2.4a. We infer that it also is probably a product of pre-terrestrial parent-body alteration.

The two-tone phyllosilicate-rich rims around chondrules (Fig. 2.6) are coherent and smooth and form sharp boundaries; they appear to be pre-terrestrial. In contrast, the segmented mottled oxide rind around the kamacite grain in Fig. 2.6c in LAP 02342 is definitely (and entirely) a terrestrial weathering product.

2.4.3 Petrographic Properties Used in Assessing Aqueous Alteration of CR Chondrites

We suggest that an aqueous-alteration scale for CR chondrites should range from 2.0 to 3.0, with type-3.0 representing unaltered samples. On the basis of the textural, mineralogical and bulk-compositional characteristics of the fine-grained matrices of MET 00426 and QUE 99177, Abreu and Brearley (2010) proposed that these meteorites are in fact type 3.0, but as discussed below, we reclassify these meteorites as type 2.8.

Although the Semarkona LL chondrite has experienced very little thermal metamorphism, earning its status as type 3.00 on the thermal metamorphism scale (e.g., Grossman, 1985; Grossman and Brearley, 2005), it has experienced a moderate amount of aqueous alteration and has an extensively hydrated matrix (Brearley et al., 1989). In fact, Hutchison et al. (1987) suggested that Semarkona should be designated petrologic type 2. Fine-grained chondrule rims and matrix material throughout Semarkona consist mainly of fine-grained Fe-rich phyllosilicate (smectite); also present are grains of Fe-Ni carbide (cohenite and haxonite), maghemite (Fe$_2$O$_3$),
calcite, magnetite and pentlandite (Taylor et al., 1981; Hutchison et al., 1987; Alexander et al., 1989; Krot et al., 1997; Keller, 1998; Brearley, 2006). The absence of thermal-metamorphic effects and the presence of aqueous-alteration effects in Semarkona imply that chondritic meteorites could be classified along two separate tracks, one designating its metamorphic grade, the other its degree of aqueous alteration. On an aqueous alteration scale, Semarkona should probably be classified as type 2.8.

Like Semarkona, MET 00426 and QUE 99177 show no signs of thermal metamorphism (and, hence, would be type 3.0 on such a metamorphic scale), but they have experienced moderate aqueous alteration as indicated by their “smooth” phyllosilicate-bearing chondrule rims. These two CR chondrites appear to be approximately equivalent to Semarkona in their degree of aqueous alteration. Because our classification scheme is concerned with aqueous alteration and not thermal metamorphism, we reject the type-3.0 designation of Abreu and Brearley (2010) for MET 00426 and QUE 99177.

In the development of subtypes for CM chondrites, Rubin et al. (2007) deliberately did not use types 2.7-3.0 because they found that the least-altered CM chondrite in their study (QUE 97990) has abundant phyllosilicates. These authors decided to leave room in the scale for less-aqueously-altered chondrites. The goal was for the CM and CR alteration sequences to be roughly comparable, but because of substantial petrologic differences between CM and CR chondrites, this goal has not met with full success.

Table 2.11 summarizes the proposed diagnostic parameters for the CR chondrites. Useful parameters include the abundance of chondrules with isotropic glass, the presence of magnetite, the degree of mafic silicate alteration, and the extent of replacement of coarse metal and silicate grains with phyllosilicate and oxide. Other properties that correlate to greater or lesser extents
with the amount of aqueous alteration include O and H isotopes, the abundance of presolar grains and amino acids, the textures of insoluble organic matter, chondrule mesostasis compositions, and the whole-rock water content. These are discussed in Appendix A2.

On a scale gauging aqueous alteration, CR3.0 chondrites would have experienced no alteration. They would possess unhydrated matrices (e.g., as determined by TEM analyses) containing >3 wt.% S. They would have no phyllosilicate-rich smooth rims, no sulfide laths sheathed with phyllosilicates, and no magnetite. They would contain a moderate fraction of low-FeO and high-FeO chondrules (≥30%) with clear, isotropic glassy mesostases, unaltered mafic silicate grains, and abundant metallic Fe-Ni. There are currently no CR chondrites that match all these characteristics.

Type-2.9 CR chondrites should exhibit only incipient hydration of the fine-grained matrix and chondrule rims; smooth rims would be absent. Porphyritic and barred-olivine chondrules containing clear, colorless, isotropic glassy mesostases would be moderately abundant. As is the case for type 3.0, there are no CR chondrites that match these criteria.

It is difficult to distinguish different degrees of alteration among the least-altered CR chondrites in our collections. Some of the ambiguities are listed below:

The limited TEM observations of Abreu and Brearley (2010) for MET 00426 (one chondrule rim and one matrix region) and QUE 99177 (two chondrule rims and one matrix region) suggest that these two meteorites are less altered than EET 87770 and paired specimens (Abreu and Brearley, 2004). In contrast, EET 87770 contains a higher proportion of chondrules with patches of clear, isotropic glass than these samples (e.g., Table 2.2; Burger and Brearley, 2004), suggesting that EET is less altered. But the occurrence of some altered zones in these same chondrules in EET (Burger and Brearley, 2004, 2005) and the occurrence of fine-grained
magnetite in the matrix of this meteorite (Abreu and Brearley, 2004) show that EET 87770 is far from pristine.

LAP 02342 contains sulfide laths surrounded by phyllosilicate sheaths (Wasson and Rubin, 2009), whereas QUE 99177 contains sulfide laths with no such sheaths. This suggests that QUE may be less altered than LAP. On the other hand, LAP has a larger fraction of chondrules that contain mesostases that appear glassy in transmitted light than MET 00426 or QUE 99177 (Table 2.2), suggesting that LAP may be less altered than QUE or MET. All three meteorites (QUE, MET and LAP) have some smooth, phyllosilicate-rich chondrule rims suggesting comparable degrees of aqueous alteration.

For the slightly altered CR chondrites, heterogeneities in the degree of alteration (plainly visible in individual meteorites such as EET 92042 and such paired specimens as EET 92105 and EET 92062; Abreu and Brearley, 2004) may indicate that there was too little water to saturate the matrix, and that, during impact compaction, water was distributed heterogeneously.

We assign all the slightly altered CR chondrites to type 2.8. Petrographic examination and BSE imaging show that chondrules with isotropic glass are rare (typically <15%) in these samples. There are no signs of alteration affecting metallic Fe-Ni grains or chondrule phenocrysts. There are minor amounts of phyllosilicates in the matrix and/or within chondrule rims. Type-2.7 CR chondrites contain no chondrules with isotropic glass and exhibit incipient magnetite formation. A significant fraction of the matrix consists of phyllosilicates. Chondrites containing significant magnetite replacing ≥2 vol.% metallic Fe-Ni are classified as type 2.6; these samples have major amounts of phyllosilicate in the matrix. Type-2.5 chondrites exhibit incipient mafic phenocryst alteration, whereas type-2.4 chondrites exhibit moderate phenocryst alteration. (Mafic silicate phenocrysts should be examined in reflected light, plane-polarized
transmitted light, and transmitted light with crossed polars.) Phenocryst alteration is more advanced in CR2.3 samples wherein partial oxidation of sulfides also occurs. Currently there are no samples of types-2.2 and -2.1 CR chondrites, but in our scheme, subtype 2.2 rocks would show that most of the metallic Fe-Ni has been oxidized; these samples would also exhibit extensive phyllosilicate formation. Type-2.1 samples would be even more altered – almost all of the metal and mafic silicate grains would have been replaced. In type-2.0 CR chondrites, mafic silicate grains and metallic Fe-Ni are very rare to absent. The rare surviving metal grains are surrounded by layered iron-oxide rinds. The metal alteration is very complex; iron-oxide phases, ilmenite-rich phases, carbonate-rich phases and phyllosilicates have been identified in type-2.0 rocks. We prefer labeling these highly altered rocks CR2.0 rather than CR1 in order to emphasize the continuous nature of aqueous-alteration features throughout the CR sequence.

Some alteration features (e.g., coarse carbonate or phyllosilicate occurrences) in CR chondrites may be heterogeneously distributed; some, such as matrix hydration, are determinable only through TEM analyses (and because little area is typically studied, may have appreciable sampling errors). Nevertheless, we estimate the uncertainty from petrographic data in the assignment of CR subtype to be ±0.1.

Several parameters used in the CM scale (Rubin et al., 2007) are not appropriate for CR chondrites. The amount and size of metal grains are much larger in unaltered CR than CM chondrites. CR chondrites that have not been extensively altered (i.e., subtypes ≥2.4) retain 6-8 vol.% metal on average (Weisberg et al., 1993), whereas even the least-altered CM chondrite studied by Rubin et al. (2007), CM2.6 QUE 97990, contains only ~1 vol.% metal. (CM2.7 Paris contains 1.2 vol.% metal; Rubin, 2014.) The CM alteration scale also relies heavily on the composition of PCP (intergrowths of tochilinite and cronstedtite formerly dubbed “poorly-
crystallized phases” that are difficult to study mineralogically). However, PCP is not observed in CR chondrites, perhaps because, in CR chondrites, the concentrations of S and oxidized Fe are much lower than in CM chondrites. For example, the Renazzo CR fall contains 1.31 wt.% S and has an (Fe-in-FeO)/(total Fe) ratio of 0.46 (Mason and Wiik, 1962), whereas the Murchison CM fall contains 2.64 wt.% S and has an (Fe-in-FeO)/(total Fe) ratio of 0.79 (Jarosewich, 1990). In addition, carbonates are relatively rare in CR chondrites, but are an important classificatory parameter of CM-chondrite alteration.

Additional potential complicating factors for the alteration scale include brecciation and unrepresentative sampling. These are discussed in Appendix A3.

2.4.4 Episodic Aqueous Alteration

Carbonates in Renazzo appear to have formed a few million years before those in GRO 95577 (Jilly et al., 2013) suggesting that the CR parent asteroid experienced more than one aqueous-alteration event. By analogy with less-altered CR chondrites, the opaque assemblages in CR2.0 GRO 95577 (Figs. 2.4, 2.5) and CR2.0 MIL 090292 must have been composed initially of metallic Fe-Ni. They now consist mainly of oxide-rich layers (with minor sulfate and phosphate components). The 200×330-µm-size assemblage in Fig. 2.5a has at least eight oxide-rich layers surrounding a rounded patch compositionally equivalent to a mixture enriched in siderite and ferrous sulfate (Table 2.5).

Oxidation of metallic Fe-Ni proceeds initially from the exterior of the grain inwards as evidenced by the oxide rinds surrounding residual kamacite cores (Figs. 2.4, 2.5). The inner layers of assemblage A tend to have higher contents of NiO than outer layers (Table 2.5). [Nickel is more noble than Fe and less readily oxidized; oxides derived from late-altered metal
would tend to have higher Ni contents, assuming that Ni could diffuse during aqueous alteration.] BSE light-shaded oxide zones differ from dark-shaded zones (Figs. 2.4, 2.5) mainly in having slightly higher FeO and slightly lower S (calculated here as SO$_3$; Table 2.5). Each of the dozen separate patches of concentric oxide layers in assemblage B (Fig. 2.5b) has the same initial sequence of alternating light-shaded and dark-shaded layers (starting from the outside and moving toward the interior). Such complex layering probably involves episodic influxes of aqueous fluids, perhaps accompanied by variations in temperature.

2.5 Conclusions

The CR chondrites exhibit a large range of aqueous alteration from slightly altered type-2.8 samples to fully altered type-2.0 rocks. CR2.8 chondrites show a range of aqueous-alteration features; they contain chondrules with phyllosilicate-bearing rims (“smooth rims”), although limited TEM studies of QUE 99177 and MET 00426 by Abreu and Brearley (2010) showed minimal matrix hydration. We found one chondrule each in our single thin sections of QUE 99177 and MET 00426 with clear isotropic glassy mesostases; in contrast, we found that 30% of the chondrules in LAP 02342 and EET 92062 contain mesostases that appear glassy in transmitted light.

Bulk S contents are generally high (~3 wt.%) in small (~50×50 µm) matrix patches in CR2.8 chondrites and appreciably lower (~1 wt.%) in more-altered CR samples. Other petrographic techniques used to gauge the degree of alteration among CR chondrites include the abundance of chondrules with glassy mesostases, the presence of altered mafic silicate phenocrysts in chondrules, and the proportion of metallic Fe-Ni transformed into magnetite.
As whole-rock alteration progresses, chondrule mesostasis is hydrated to form phyllosilicates, metallic Fe-Ni is partially replaced by magnetite and other iron-oxides (as in CR2.4 Renazzo and CR2.3-an Al Rais), and mafic-silicate phenocrysts in chondrules are altered, initially at their edges, along twin boundaries and within cracks. The two CR2.0 chondrites (GRO 95577 and MIL 090292) are the most aqueously altered members of the CR group; mafic silicates and metallic Fe-Ni are very rare to absent in these rocks. There are no CR2.1 or 2.2 chondrites and the only type 2.3 is the anomalous, matrix-rich CR chondrite Al Rais.

Although the CR-chondrite group includes slightly altered and completely altered samples, the majority of CR chondrites are relatively unaltered. Of the 24-29 independent CR chondrites in this study, ~70% of the samples are slightly altered type 2.8 rocks and ~20% are in the severely altered 2.0-2.3 range.

2.6 References


Chapter 3

3.1 Introduction

Chondrite meteorites contain spherical, sub-millimeter size objects that were molten for brief periods of time called chondrules. Primitive chondrites are disequilibrium assemblages that offer information about the conditions that existed in the early solar system. The extent to which partially molten or fully molten chondrules interacted with nebular gas is a subject of current research. Interaction of molten chondrules with nebular gas containing oxygen could explain varying O-isotope results from different objects in CV chondrites. Clayton et al. (1983) suggested that chondrules interacted with a nebular gas containing CO and H$_2$O, but no silicon. Chaussidon et al. (2008) proposed that chondrules in CV and CR chondrites interacted with a nebular gas containing SiO. They proposed a new model where chondrules are heated until they are molten or partially molten at which point relict olivine is dissolved and SiO gas is incorporated into the melt. In this scenario pyroxene is produced at the expense of olivine in a reaction similar to:

$$\text{Mg}_2\text{SiO}_4 + \text{SiO} + \text{H}_2\text{O} \rightarrow \text{Mg}_2\text{Si}_2\text{O}_6 + \text{H}_2$$  \hspace{1cm} (1)

Experimental oxygen isotope data from CR and CV chondrites agree with the prediction from Reaction (1) that 2/3 of the oxygen atoms in pyroxene come from relict olivine and
1/3 come from SiO$_2$ in the melt (as a result of SiO$_{(g)}$ + O dissolved into the melt). Krot et al. (2004a) reported silica-rich rims on chondrules in CR chondrites that may have interacted with an SiO-rich gas. Their petrographic results agree with those of Tissandier et al. (2002), who allowed synthetic chondrules to react with SiO-rich gas. If the nebular gas contained SiO there could be detectable isotopic fractionations for silicon in pyroxene and silica grains situated at chondrule peripheries and within igneous rims. Thermal and aqueous alteration alters isotopic ratios, so primitive meteorites that have undergone minimal alteration are the ideal samples for these measurements.

### 3.2 Previous Work

#### 3.2.1 Oxygen Isotopes

Chaussidon et al. (2008) used an ion microprobe to measure oxygen isotopes of olivine and pyroxene phenocrysts in-situ in CR and CV chondrites. To explain the data they assumed that pyroxene phenocrysts formed from relict olivine grains that were heated to a molten or partially molten state and then reacted with gaseous silicon that reacted with nebular oxygen (O$_2$) and dissolved in the melt to form SiO$_2$. These workers suggested the reaction:

$$\text{Mg}_2\text{SiO}_4 + \text{SiO}_2 \rightarrow \text{Mg}_2\text{Si}_2\text{O}_6$$  \hspace{1cm} (2)

We infer that Reaction (2) should be modified to include water, the more likely source of oxygen needed to balance the reaction rather than molecular oxygen. Nonetheless, within the context of the proposed reaction, and assuming that the oxygen isotope composition
of SiO and O$_2$ gas are the same, the resulting pyroxene is hypothesized to contain four oxygen atoms from the relict olivine and two oxygen atoms from SiO$_2$ dissolved in the melt. The following model for the oxygen isotope composition of the pyroxene is obtained:

\[
\delta^{18}\text{O} \text{(pyroxene)} = \frac{2}{3} \times \delta^{18}\text{O}_{\text{ Olivine}} + \frac{1}{3} \times \delta^{18}\text{O}_{\text{Gas}} \tag{3}
\]

\[
\delta^{17}\text{O} \text{(pyroxene)} = \frac{2}{3} \times \delta^{17}\text{O}_{\text{ Olivine}} + \frac{1}{3} \times \delta^{17}\text{O}_{\text{Gas}} \tag{4}
\]

Regression of the oxygen isotope data presented by Chaussidon et al. yields

\[
\delta^{18}\text{O} \text{(pyroxene)} = 0.72 \times \delta^{18}\text{O}_{\text{ Olivine}} + 1.21 \tag{5}
\]

\[
\delta^{17}\text{O} \text{(pyroxene)} = 0.81 \times \delta^{17}\text{O}_{\text{ Olivine}} + 0.60 \tag{6}
\]

The data agree with the model within error. The slope for the regression line predicted by the model is 0.67. Taking into account errors the $\delta^{18}$O regression slope is between 0.56 and 0.85 and the value of the slope for the $\delta^{17}$O regression line is between 0.66 and 0.94.

The oxygen isotopic composition of the nebular oxygen gas that interacted with both CR and CV chondrules was calculated using the intercepts of the regression lines to be $\delta^{18}$O = $3.6 \pm 1\%e$ and $\delta^{17}$O = $1.8 \pm 1\%e$.

### 3.2.2 Magnesium and silicon isotopes

Davis et al. (1990) measured mass fractionation in olivine experimentally. They found that evaporated molten forsterite was enriched in the heavy isotopes of Mg and Si
by 30 and 15 per mil, respectively (12% of the initial mass remained). However, solid forsterite that was evaporated had fractionations of only ~1 per mil. Mass fractionation due to evaporation from a molten olivine melt is likely measurable.

Weisberg et al. (1992) measured oxygen isotopes for layered chondrules in CR2.8 El Djouf 001 and found that the rims were depleted in $^{16}$O relative to $^{17}$O and $^{18}$O. If the oxygen isotopic fractionation were due to evaporation then mass dependent fractionations should be observed in Si and Mg isotopes as well. Huss et al. (1996) measured Mg and Si isotopes in the interior portions and rims in chondrules in the CR2.8 El Djouf 001. Huss et al. were not able to find evidence of evaporative mass fractionation in El Djouf 001. Mass fractionation was not observed between interior olivine and rim olivine or interior pyroxene and rim pyroxene to a precision greater than 1 per mil. This meteorite has experienced minimal aqueous alteration (CR subtype 2.8), but has been extensively terrestrially weathered (W3). Due to the limited data set, weathering grade of the chondrite, and advances in resolving Mg and Si isotopic effects it would be worthwhile to gather more Mg and Si isotopic data for chondrules with pyroxene-rich rims. Galy et al. (2002) concluded that chondrules formed in a high-pressure ($10^{-3}$ bar) environment where isotopic effects from the kinetics of volatilization are not observed.

Young et al. (2002) used UV laser ablation MC-ICPMS to measure magnesium isotopes in calcium-aluminum-rich inclusions and chondrules in Allende. Depletions in $^{25}$Mg were found at the edges of some chondrules and were attributed to aqueous alteration.
Armytage et al. (2012) measured silicon isotopic compositions of chondrules from Allende and found a small variation in $\delta^{30}$Si from -0.71 to -0.10 per mil. They attribute this to heterogeneity in Si isotopes inherited in the nebula.

### 3.3 Methods

#### 3.3.1 Sample Selection and Preparation

Type 1AB chondrules are intermediate between 1A and 1B chondrules and contain 20-80% olivine phenocrysts (Jones 1994). Type 1AB chondrules often have coarse pyroxene grains near the outer chondrule margin; these regions, which we refer to as “rims” may have formed in a reaction similar to reaction 1. Type 1AB chondrules were selected to test this model.

Existing thin sections of CV and CR chondrites were examined using a petrographic microscope to find type 1AB chondrules with pyroxene rims and olivine phenocrysts in the interior. An image taken with a digital camera attached to a petrographic microscope of one such chondrule in a thin section of the CV chondrite Allende is shown in Fig. 3.1. Once the type 1AB chondrules were identified, the UCLA LEO 1430 VP SEM was used to confirm that the chondrules contained pyroxene and olivine. The SEM was operated in variable pressure mode for sections that were not previously carbon coated. Energy dispersive spectroscopy (EDS) was used to determine if mineral phases present in the chondrules were olivine or pyroxene. The Mg/Si ratio in olivine ($\text{Mg}_2\text{SiO}_4$) is twice that of the ratio in pyroxene ($\text{MgSiO}_3$) which renders the two phases readily distinguishable using EDS. Maps were made of the chondrules highlighting areas that contained pyroxene. It was important to verify that there were
patches of pyroxene at least 70 µm in diameter because the spot size used to analyze the pyroxene by mass spectrometry is 69 µm. A typical patch of pyroxene in a chondrule rim from a chondrule in Allende is shown in Fig. 3.2.

Fig. 3.1. Allende thin section 458 Type 1AB Chondrule 1 in transmitted light with cross polars prior to ablation. An arrow is pointing to pyroxene in the rim of the chondrule, which appears darker gray.

Although several thin sections of Allende were identified as having type 1AB chondrules, not all of the sections could be successfully ablated. In some cases the thin section would break instead of ablating and in some cases the laser would burn through the thin section and would ablate SiO$_2$ glass. To overcome these challenges, it was decided that thick sections would be more appropriate samples for the study.

A thick section of a relatively unaltered CR2.8 chondrite was requested from the Meteorite Working Group (MWG) at NASA’s Johnson Space Center. A thick section of CR2.8 EET 87747 (section 17) was provided by the MWG and is shown in Fig. 3.3. The UCLA Materials Science and Engineering Nova Nano 230 Field Emission SEM and the UCLA LEO 1430 VP SEM were used to confirm type 1AB chondrules and make maps.
highlighting pyroxene in the chondrule. Chondrules 2 and 3 in EET 87747 are type 1AB and are seen in Figs. 3.4 and 3.5. Both chondrules are type 1AB chondrules with pyroxene rims.

Two additional CR2.8 samples were requested from the MWG. Thick sections of EET 92052 (section 12) and EET 87770 (section 21) were obtained. Both sections contained one type 1AB chondrule. X-ray maps of the elements Si, Mg, Ca, Al, and Fe were obtained using the UCLA Tescan Vega SEM for both sections to distinguish among pyroxene, olivine, and other phases such as mesostasis. The maps were made in variable pressure mode with a 660-nm beam size.

To prepare the samples for mass spectrometry, any existing carbon coats were polished away using ¼-µm diamond paste. The sections were sonicated in 95% ethanol for 10 minutes to remove any oil.

Fig. 3.2. BSE image of pyroxene in the rim of a type 1AB chondrule in Allende (thick section F1, Chondrule 4).
Fig. 3.3. Reflected light image of a thick section of CR2.8 EET87747.

Fig. 3.4. BSE image of EET 87747 Chondrule 2. This is a type 1AB chondrule with a pyroxene rim. The inner and outer edge of the pyroxene rim is indicated by two arrows.
Fig. 3.5. BSE image of EET 87747 Chondrule 3. This is a type 1AB chondrule with a pyroxene rim. Arrows indicate the inner and outer boundaries of a portion of the pyroxene rim.

3.3.2 Mass Spectroscopy

Si and Mg isotopic compositions were measured in-situ using UV laser ablation and the ThermoFinnigan Neptune MC-ICPMS at UCLA (LA-MC-ICPMS). The standards used include San Carlos olivine, glass doped with $^{26}$Mg, spinel, and vesuvianite. A 69-µm spot was used to measure Si isotope ratios in silicates and a 52-µm spot was used to measure Mg isotope ratios.

There is the potential for matrix effects with LA-MC-ICPMS. The potential for such effects for the method used here was assessed by Shahar et al. (2007) in the UCLA
laboratory. Shahar et al measured silicon isotopes in an igneous CAI using LA-MC-ICPMS. They determined that matrix effects were not significant by measuring silicon isotope ratios in a synthetic diopside glass (Di$_{0.59}$An$_{0.41}$) both dissolved in solution and using laser ablation to introduce the sample to the mass spectrometer. The synthetic glass was doped with $^{28}$Si and the solution measurements showed that $\delta^{29}$Si=-10.7‰ and $\delta^{30}$Si=-10.72‰ relative to NBS-28. The synthetic glass contains Ca and Al cations and is far from an equilibrium isotopic composition. Despite this the results obtained by laser ablation were indistinguishable from the results obtained by having the glass dissolved in solution and separating the Ca and Al by cation exchange.

### 3.3.3 Confirmation of Mineral Phases

The UCLA JEOL JXA-8200 electron microprobe (EMP) was used to image the sections and confirm the mineral phases that were analyzed by MC-ICPMS. The sections were carbon coated prior to EMP analyses. Wavelength Dispersive Spectroscopy (WDS) and EDS were both used to confirm that the laser ablation spots were pyroxene or olivine. An accelerating voltage of 15 keV, counting times of 20 seconds per element, and ZAF corrections were used. Electron microprobe data were used to obtain a Ca/Mg ratio for pyroxene samples to determine if there was enough calcium present in a sample such that a correction for $^{48}$Ca$^{++}$ was required. Spots which contained a mixture of phases or mesostasis were discarded for this study. A back-scattered electron (BSE) image of Allende thin section 458 Chondrule 1 post ablation is shown in Fig. 3.6.

The UCLA Tescan Vega SEM was used to confirm the mineral phases present in EET 87770 and EET 92052 by EDS.
3.3.4 Condensation Model

A condensation model which takes into account both collision frequency and zero-point energy effects was developed by Young and Schauble (2012). The isotopic data will be analyzed using this model. The isotope fractionation due to condensation ($\alpha_{\text{cond}}$) can be calculated by the following equation:

$$ \alpha_{\text{cond}} = \frac{\alpha_{\text{Eq}} \alpha_{\text{Kin}} s_i}{\alpha_{\text{Eq}} (s_i - 1) + \alpha_{\text{Kin}}} $$  \hspace{1cm} (7)

where $s_i$ is the degree of undercooling in the system and is equal to the partial pressure of gaseous species $i$ divided by the equilibrium partial pressure of gas $i$. The term $\alpha_{\text{Kin}}$ takes
into account the collision frequencies and zero point energy differences of different isotopes of Si. The term $\alpha_{\text{Eq}}$ is the equilibrium isotope fractionation. At equilibrium ($s_i=1$) the equation gives the equilibrium isotope fractionation for Si ($\alpha_{\text{cond}} = \alpha_{\text{Eq}}$).

A new value of $\Delta H_{\text{rxn}} (-495,735 \text{ J/mol})$ was calculated to reflect the process of silicon dissolving into a chondrule melt and being incorporated into pyroxene as shown in Reaction (1):

$$\text{Mg}_2\text{SiO}_4 + \text{H}_2\text{O} + \text{SiO} \rightarrow \text{Mg}_2\text{Si}_2\text{O}_6 + \text{H}_2$$

This new value was used in the Van’t Hoff Equation (Simon and DePaolo 2010) to calculate the reaction temperature and the degree of undercooling ($s$) as is shown in Equation 8.

$$\ln(s) = \frac{\Delta H^*}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{Eq}}} \right)$$

3.4 Results

3.4.1 Allende Thin Section 458 Chondrule 1

Silicon isotope ratios were measured in-situ in a type 1AB chondrule in Allende (CV$_{\text{ox}}$) using LA-MC-ICPMS. Measurements were made in the pyroxene rim of the chondrule and in the interior olivine phenocrysts. The data that were obtained are shown in Fig. 3.7. Delta values ($\delta = (R/R_{\text{std}} -1) \times 1000$, where $R$ is the relevant isotope ratio and std refers to a reference, or standard, composition), calculated relative to the silicon
standard NBS 28, are shown. The error ellipses represent 1-sigma analytical errors. Pink error ellipses are olivine and black ellipses are pyroxene. The mass dependent terrestrial fractionation line is also plotted. On average the there is a difference of ~0.3‰ in δ^{29}\text{Si} between olivine and pyroxene.

A Raleigh-type condensation model was used to predict the expected isotope shift in ^{29}\text{Si} based on the fraction of gas remaining (F) at 1700 K. This is shown in Fig. 3.8 with a horizontal line at δ-δ°=−0.33‰ which is the experimentally determined isotope shift between pyroxene and olivine. The model provides more than one possible solution depending on the amount of silicon remaining in the gas phase.
Fig. 3.8. The expected isotope shift for $\delta^{29}$Si as a function of the fraction of gas remaining in a Raleigh-type condensation. The curves represent different values of $s_i$, which is $p_{SiO}/p_{SiO, Eq}$. The horizontal line represents the experimentally determined value of $\delta-\delta^0$. $s=1.1$ corresponds to an undercooling of -4.6 K and $s=1.5$ corresponds to an undercooling of -19.4 K.

A second, non-Raleigh-type condensation model was also used. This model predicts the isotope shift for $^{29}$Si/$^{28}$Si based on the partial pressure of SiO divided by the equilibrium partial pressure of SiO (i.e., $s_{SiO}$). The results are shown in Fig. 3.9 along with the experimentally determined value of $\delta-\delta^0$ for $^{29}$Si which is -0.33‰. The experimentally determined isotope shift intersects the model curve at a value of $s_{SiO}=1.04$. This value of $s_{SiO}$ corresponds to an undercooling of -1.9 K. This model does not change significantly when temperatures of 1400-1700 K are used.

The values for $\delta^{29}$Si measured in olivine and pyroxene in Allende 458 Chondrule 1 are shown in a probability density plot (Fig. 3.10).
Fig. 3.9. The expected isotope shift for $\delta^{29}\text{Si}$ as a function of $s_i$, which is $p_{\text{SiO}}/p_{\text{SiO, Eq}}$. The horizontal line represents the experimentally determined value of $\delta-\delta^0$. The intersection of the two curves is at $s_i=1.04$, which corresponds to an undercooling of $-1.9$ K.

Fig. 3.10. Probability density plot for $\delta^{29}\text{Si}$ measured in olivine and pyroxene in Allende Section 458 Chondrule 1 relative to NBS 28. Olivine data (n=5) are in green and pyroxene data (n=5) are in red.
3.4.2 EET 87747 Chondrules 2 and 3

Silicon isotope ratios were measured in two type 1AB chondrules in CR2.8 EET 87747. Delta values obtained for Chondrule 2 are shown in Fig. 3.11 and those for Chondrule 3 are shown in Fig. 3.12. Error ellipses represent 1-σ analytical errors. There is a fractionation of approximately 0.2‰ between the $\delta^{29}\text{Si}$ values measured in olivine and pyroxene in EET 87747 Chondrule 3.

Chondrule 3 contains a pyroxene rim, olivine phenocrysts in the interior, interior pyroxene, and an igneous rim containing both pyroxene and olivine. The average $\delta^{29}\text{Si}$ value for olivine is -0.05‰ (n=6). The average value of $\delta^{29}\text{Si}$ for pyroxene in the interior rim is -0.21‰ (n=16). The olivine in the secondary shell is heavier than most of the other olivine analyses and has a $\delta^{29}\text{Si}$ value of -0.019‰ (n=1). Pyroxenes in the igneous rim are heavier than those in the pyroxene rim and have a $\delta^{29}\text{Si}$ value of -0.11‰ (n=2). The interior pyroxene is similar to the pyroxene in the rim and had a $\delta^{29}\text{Si}$ value of -0.27‰ (n=2).

The values for $\delta^{39}\text{Si}$ measured in olivine and pyroxene in EET 87747 Chondrules 2 and 3 are shown in probability density plots (Figs. 3.13 and 3.14). Magnesium three isotope plots are shown for these chondrules in Figs. 3.15 and 3.16. Probability density plots of $\delta^{25}\text{Mg}$ measured in olivine and pyroxene in Chondrules 2 and 3 are shown in Figs. 3.17 and 3.18.
Fig. 3.11. Silicon three-isotope plot for EET 87747 Chondrule 2. Error ellipses show 1-$\sigma$ analytical errors on pyroxene (black) and olivine (pink) measurements. The mass-dependent fractionation line is shown for reference. Mass interferences on $\delta^{30}$Si cause deviations from the terrestrial fractionation line.

Fig. 3.12. Silicon three-isotope plot for EET 87747 Chondrule 3. Error ellipses show 1-$\sigma$ analytical errors on pyroxene (black) and olivine (pink) measurements. The mass-dependent fractionation line is shown for reference.
Fig. 3.13. Probability density plot for $\delta^{29}\text{Si}$ measured in olivine and pyroxene in EET 87747 Chondrule 2. Olivine data (n=6) are in green and pyroxene data (n=11) are in red.

Fig. 3.14. Probability density plot for $\delta^{29}\text{Si}$ measured in olivine and pyroxene in EET 87747 Chondrule 3. Olivine data (n=6) are in green and pyroxene data (n=16) are in red. Magnesium isotope ratios were measured in EET 87747 Chondrules 2 and 3.
Fig. 3.15. Magnesium three-isotope plot for EET 87747 Chondrule 2. Error ellipses represent 1-σ analytical errors. Black ellipses are pyroxene and pink ellipses are olivine. The mass-dependent fractionation line is shown for reference.

Fig. 3.16. Magnesium three-isotope plot for EET 87747 Chondrule 3. Error ellipses represent 1-σ analytical errors. Black ellipses are pyroxene and pink ellipses are olivine. The mass-dependent fractionation line is shown for reference.
Fig. 3.17. Probability density plot for $\delta^{25}$Mg measured in olivine and pyroxene in EET 87747 Chondrule 2.

Fig. 3.18. Probability density plot for $\delta^{25}$Mg measured in olivine and pyroxene in EET 87747 Chondrule 3.
3.4.3 EET 87770 Chondrule 1

A silicon three-isotope plot for EET 87770 Chondrule 1 is shown in Fig. 3.19. The silicon terrestrial fractionation line is shown for reference. The corresponding probability density plot for $\delta^{29}\text{Si}$ in olivine and pyroxene is shown in Fig. 3.20. The magnesium three-isotope plot is shown in Fig. 3.21 with the terrestrial fractionation line for reference. Error ellipses represent 1-sigma analytical errors on both three-isotope plots. Olivine data are shown in pink and pyroxene data are shown in black.

Fig. 3.19. Silicon three-isotope plot for EET 87770 Chondrule 1. Olivine analyses are shown in pink and pyroxene analyses are shown in black. Error ellipses represent 1- $\sigma$ analytical uncertainties.
Fig. 3.20. Probability density plot for $\delta^{29}$Si measured in olivine (green, n=7) and pyroxene (red, n=10) in EET 87770 Chondrule 1.

Fig. 3.21. Magnesium three-isotope plot for EET 87770 Chondrule 1. Olivine analyses are shown in pink and pyroxene analyses are shown in black. Error ellipses represent 1-$\sigma$ analytical uncertainties.
3.4.4 EET 92052 Chondrule 1

The silicon three isotope plot for EET 92052 Chondrule 1 is shown in Fig. 3.22 with the silicon terrestrial fractionation line. The corresponding probability density plot for $\delta^{29}\text{Si}$ in olivine and pyroxene phases is shown in Fig. 3.23. The magnesium three-isotope plot is show in Fig. 3.24 with the terrestrial fractionation line. Error ellipses represent one sigma analytical errors. Olivine data are shown in pink and pyroxene data are shown in black.

Fig. 3.22. Silicon three-isotope plot for EET 92052 Chondrule 1. Olivine analyses are shown in pink and pyroxene analyses are shown in black. Error ellipses represent 1- $\sigma$ analytical uncertainties.
Fig. 3.23. Probability density plot for $\delta^{29}\text{Si}$ measured in olivine (green, n=1) and pyroxene (red, n=3) in EET 92052 Chondrule 1.

Fig. 3.24. Magnesium three-isotope plot for EET 92052 Chondrule 1. Olivine analyses are shown in pink and pyroxene analyses are shown in black. Error ellipses represent 1-$\sigma$ analytical uncertainties.
3.5 Discussion

3.5.1 Allende Thin Section 458 Chondrule 1

At equilibrium, pyroxene would be isotopically lighter than olivine by ~0.01‰ at 1700 K (Méheut et al 2009). Based on the Raleigh-type condensation model, SiO condensing at equilibrium ($s_{\text{SiO}} = 1$) is a possible explanation for the fractionation between olivine and pyroxene as seen in Fig. 3.8. In this case approximately 75% of the SiO gas would have condensed from the gas. For $s_{\text{SiO}} = 1.1$, extraction of approximately 55% of the SiO gas is consistent with the data (Fig. 3.8). This level of undersaturation corresponds to an undercooling of -4.6 K or 4.6 K below the equilibrium temperature. As $s_{\text{SiO}}$ increases the degree of undercooling increases. A value $s_{\text{SiO}} = 1.5$ corresponds to an undercooling of -19.4 K. The experimentally determined isotope shift in the non-Raleigh-type condensation model implies that if SiO condensed into a partially or fully molten chondrule to react with olivine, then the reaction took place close to equilibrium conditions. If the gas were enriched in SiO relative to equilibrium ($s_{\text{SiO}} > 1.1$) then this model predicts an isotope shift in $\delta^{29}\text{Si}$ of at least -2‰. No isotope shifts of this magnitude were detected between pyroxene and olivine. The pyroxene in this chondrule rim appears to have formed under near equilibrium conditions with an undercooling of <2 K. The $\delta^{29}\text{Si}$ probability density plot shows overlapping, distinguishable $\delta^{29}\text{Si}$ values for pyroxene and olivine. It appears that the values for olivine and pyroxene are distinct.

3.5.2 EET 87747 Chondrules 2 and 3

The $\delta^{29}\text{Si}$ probability density plots show overlapping, yet distinguishable $\delta^{29}\text{Si}$ values for pyroxene and olivine in Chondrule 3, but not Chondrule 2. These values are
greater than the expected equilibrium fractionation and this implies that the difference in \(^{29}\text{Si}/^{28}\text{Si}\) between pyroxene and olivine is not an equilibrium fractionation between these phases. This in turn suggests that SiO may well have condensed into the melt of a molten or partially molten chondrule to form pyroxene with a partial pressure of SiO slightly greater than the equilibrium partial pressure of SiO.

This same trend is not observed in the \(\delta^{29}\text{Si}\) data for EET 87747 Chondrule 2. It is not entirely clear why Chondrule 2 does not show distinct values for \(\delta^{29}\text{Si}\) in olivine and pyroxene. There is a wider range of both olivine and pyroxene \(\delta^{29}\text{Si}\) values. It is possible that this chondrule experienced alteration after forming the pyroxene rim that could affect the isotopic values or it may have not have formed in the proposed process.

The proposed reaction requires silicon to condense into the melt and react with olivine. Large negative \(\delta^{29}\text{Si}\) in pyroxene relative to both \(\delta^{29}\text{Si}\) in olivine and relative to the magnesium isotope data suggests that we are seeing the isotopic consequences of reaction (1). The implied undercooling of between 1 and 2 K suggests that this process took place in near equilibrium conditions.

### 3.5.3 Silicon Gas Isotopic Composition

The silicon isotopic composition of the hypothetical gas that condensed into the melt was calculated using the following equation:

\[
\left( \frac{R}{R_o} \right)_{\text{cond}} = x_{\text{Si,ol}} \left( \frac{R}{R_o} \right)_{\text{ol}} + x_{\text{Si,SiO}} \left( \frac{R}{R_o} \right)_{\text{SiO}} \tag{8}
\]
where $R/R_0$ is the measured $^{29}\text{Si}$ isotope ratio and $x_{\text{Si,ol}}$ and $x_{\text{Si,SO}}$ are the fractions of silicon obtained from the olivine and the silicon-rich gas, respectively. The calculated silicon isotopic composition of the gas is -0.34‰ for EET 87747 Chondrule 3 and -0.62‰ for Allende Chondrule 1.

The condensation model was used to calculate the fractionation for different supersaturations of SiO for temperatures ranging from 1200-1500 K. Fig. 3.25 shows the calculated fractionations based on supersaturation at 1200 and 1500 K for EET 87747 Chondrule 3. The experimentally determined silicon gas isotopic composition of -0.34‰ is plotted as a horizontal line that intersects both curves at a given value of $s$. If the process took place between 1200 and 1500 K then this corresponds to a supersaturation of between $s=1.05$ and $s=1.08$, or undercoolings of 1.5 to 2.2 degrees below the equilibrium temperature.

Fig. 3.26 shows a plot of the calculated $\delta^{29}\text{Si}$ fractionation based on the supersaturation for Chondrule 1 from Allende 458. The experimentally determined silicon gas isotopic composition of -0.62‰ is plotted a horizontal line. If this process took place between 1200 and 1500 K then the supersaturation is calculated to be between $s=1.07$ and $s=1.09$. This corresponds to an undercooling of 1.8 to 2.5 degrees below the equilibrium temperature.
Fig. 3.25. Expected fractionation of $\delta^{29}$Si versus the degree of supersaturation ($s$) for EET 87747 Chondrule 3. The top curve is for the process at 1200 K and the bottom curve is for the process at 1500K. The experimental silicon isotopic composition of the gas (-0.34‰) is shown as a horizontal line. The experimental isotopic composition corresponds to a value of the supersaturation between $s=1.05$ and $s=1.08$ and undercoolings of -1.5 to -2.2 K.
Fig. 3.26. Expected fractionation of $\delta^{29}\text{Si}$ versus the degree of supersaturation ($s$) for Allende 458 Chondrule 1. The top curve is for the process at 1200 K and the bottom curve is for the process at 1500K. The experimental silicon isotopic composition of the gas (-0.62‰) is shown as a horizontal line. The experimental isotopic composition corresponds to a value of the supersaturation between $s=1.07$ and $s=1.09$ and undercoolings of -1.8 to -2.5 K.

### 3.5.4 EET 87770 Chondrule 1

Seven analyses of olivine and ten analyses of pyroxene were made in EET 87770 Chondrule 1. The $\delta^{29}\text{Si}$ values measured in olivine and pyroxene in EET 87770 Chondrule 1 were overlapping and there was not a clear fractionation in $\delta^{29}\text{Si}$ values between olivine and pyroxene.
3.5.5 EET 92052 Chondrule 1

EET 92052 Chondrule 1 is fractured and there is a limited surface area available for analysis. There is a limited number of data points that may indicate a fractionation between olivine and pyroxene, but the fractionation is not clear without more data. Three pyroxene analyses were collected and show a bimodal distribution on the silicon three isotope plot. One olivine analysis was collected and plots near a pyroxene analysis. The olivine analysis plots near a pyroxene analysis that was adjacent to olivine and it is possible that the point is a mixture of olivine and pyroxene. However, the area appeared to be pyroxene at the surface and the bottom of the pit was confirmed to be pyroxene by EDS, so it is likely mostly pyroxene.

3.5.6 Metal composition of CR chondrites

Silicon is known to enter metal phases under reducing conditions (Gessman and Rubie 1998). Wasson and Rubin (2010) observed silicon in the metal of one chondrule in CR2.8 LAP 02342. However, after an extensive search for silicon in the metal of CR chondrules from LAP 02342 and other CR chondrites no other chondrules were found to contain greater than 0.1 wt% silicon. It is unlikely that silicon in metal would affect the measured silicon isotope ratios even if the metal was ablated.

3.5.7 Potential sources of SiO gas and evidence for silica enrichment in chondrites

Grossman (1972) performed equilibrium calculations to obtain condensation models for the solar nebula. One criticism of the model was that the olivine that is produced is end-member forsterite and not olivine with higher fayalite values as observed in chondrules. Another concern is that SiO₂ is not included in the condensation sequence
(Petaev and Wood 2004). It has been proposed that higher Fa values in olivine can be obtained if the formation environment contained a higher dust to gas ratio (Wood and Hashimoto 1993 and Palme and Fegley 1999). If an event vaporized the dust then the partial pressure of SiO in the nebular gas could increase and SiO may be incorporated into the chondrules. This may explain the source of SiO$_2$ in the silica-rich igneous rims observed in CR chondrites.

Brigham et al (1986) observed silica in chondrules and fragments in the ordinary chondrites Dhajala (H3.8), Bremervörde (H/L3.9), Sharps (H3.4), and Mező-Madaras (L3.7). They did not find silica in Khohar (L3.6), Tieschitz (H/L3.6), or Nadiabondi (H5). They noted that silica-rich rocks are common after igneous differentiation of planetary crusts, but that this is not likely to be how these chondrules and fragments formed. Such planetary igneous rocks are enriched in Ca, Al, and U, however the chondrules and fragments were depleted in Ca and Al and not enriched in U. They also excluded the chondrules and fragments as being enstatite chondrite inclusions. Enstatite chondrites are highly reduced and are known to contain silica polymorphs when there is an absence of MgO or FeO to produce enstatite or ferrosilite. They suggest some of the objects could have formed from a condensed gas that became enriched in silicon after having previously incompletely condensed and isolated from the condensate. Although reduction could produce silica it is also likely to produce Ni-free metal, but the metal present in these meteorites is nickel-rich.

Krot et al. (2004a) found that many type 1 chondrules in CR chondrites contain silica-rich igneous rims (SIR). These rims consist of low calcium pyroxene, mesostasis, FeNi metal, and crystalline silica. Krot et al. explored five mechanisms for the creation
of SIR. Reduction of ferromagnesian silicates was ruled out because it should produce magnesian olivine (not observed in SIR) and cannot explain why SIRs are enriched in moderately volatile elements. Partial melting may have occurred, but alone it does not account for pyroxene-rich igneous rims (PIR) that were observed outside SIR. Fractional crystallization was ruled out after computational modeling did not reproduce the observed mineralogy in the chondrules. This leaves two mechanisms for creating SIR, both of which involve adding Si-containing material to the chondrule. This could be dust that is accreted and then melted onto the chondrule or SiO gas condensing into the chondrule melt.

Noguchi (1995) reports nearly pure SiO$_2$ in the CR chondrite PCA 91082. Roughly half the chondrules (28 out of 64) studied in PCA 91082 contained silica patches that are described as “pod-like” and are up to 10 µm. These silica pods were limited to the peripheries of chondrules. Noguchi ruled out SiO$_2$-rich chondrule melts, fractional crystallization, and reduction as the source of the SiO$_2$ in the chondrule rims. The bulk compositions of chondrules do not show silica-rich chondrules. Fractional crystallization is not plausible because olivine and pyroxene in silica-containing chondrules has a similar composition to chondrules that do not contain silica patches and both types of chondrules likely had similar cooling histories. There are a few wt% of FeO in the olivine and pyroxene at the chondrule edges. Even if reduction occurred at chondrule peripheries (PCA 91082 does not show evidence of this) it is unlikely pure silica would form as a result. Silica-rich material adhering to the chondrule, possibly while it was partially molten, was found to be the most plausible mechanism for forming the SiO$_2$-rich areas.
Tissandier et al. (2002) studied interactions of chondrules and nebular gas experimentally. Their experimental set-up allowed partially molten synthetic chondrules to interact with SiO gas. These experiments reproduced petrographic features observed in chondrules including an increase in pyroxene/olivine closer to the chondrule rims, partially resorbed olivines, and in some cases crystalline SiO$_2$ phases like those observed in CR chondrules.

Krot et al. (2004a) note that pressure is a possible constraint on mechanisms for incorporating SiO$_{(g)}$ into chondrules. If SiO gas was incorporated into the chondrules it would require high dust/gas ratios and comparatively high pressures of approximately $10^{-3}$ bar. Galy et al. (2000) reported magnesium isotopic evidence for high pressures (100 Pa = $10^{-3}$ bar) during chondrule formation. Therefore, this mechanism is still feasible even though it does not take place at canonical pressure and dust/gas ratio.

### 3.5.8 Formation of Pyroxene-Rich Chondrules

Lofgren and Russell (1986) made synthetic chondrules and heated them in an iron-saturated platinum crucible. Different temperatures and cooling rates were used throughout the experiment. Various experiments produced granular, barred, porphyritic olivine and pyroxene, and radial pyroxene textures. Pyroxene phenocrysts were observed when the temperature was below the liquidus temperature and olivine phenocrysts were observed above the liquidus temperature. The authors observed olivine crystals enclosed in pyroxene crystals. The olivine crystals were not relict crystals; they had grown that way in the experiment. The authors concluded that heterogeneous nucleation was needed to form porphyritic textures in chondrules and that the temperatures could not exceed the liquidus temperature for long periods of time without destroying nucleation sites.
Radomsky and Hewins (1990) performed similar experiments and their results agreed that chondrule texture depends on the number of nucleation sites.

3.6 Conclusions

Chondrules containing pyroxene-rich rims and silica patches are observed in chondrites. It seems likely that these silicon-rich areas could have formed from a silicon-rich gas that condensed into a molten or partially molten chondrule to produce silica patches or pyroxene formed from pre-existing olivine. This condensation process is expected to cause a detectable isotopic shift in the δ^{29}\text{Si} values of the olivine compared to the pyroxene, as the equilibrium δ^{29}\text{Si} values for olivine and pyroxene are almost indistinguishable. In this study silicon and magnesium isotopes were measured in olivine and pyroxene in five type 1AB chondrules with pyroxene rims. A difference in the average values of δ^{29}\text{Si} in olivine and pyroxene was measured in two of the five chondrules. These two chondrules do not have the equilibrium δ^{29}\text{Si} fractionation and the pyroxene in these chondrules may have formed from the incorporation of a nebular gas supersaturated in silicon. The same behavior was not observed for magnesium isotopes measured in both phases, indicating that it was silicon that may have condensed from the gas phase. The use of a condensation model indicated that if the pyroxene rims formed by the condensation of a silicon-rich gas then it happened at equilibrium or near-equilibrium conditions with a supersaturation of silicon between 1.0 and 1.1, corresponding to an undercooling of ~3 K or less. The silicon isotopic composition of the gas was estimated to be between -0.34‰ and -0.62‰ relative to typical chondritic values. These two chondrules provide evidence to support the hypothesis that SiO gas interacted with chondrules in the solar nebula. There is no clear evidence that the rims in
all type 1AB chondrules formed from incorporation of silicon-bearing gas, but this possibility is not ruled out. The chondrules most likely inhabited a gas-rich environment where they were able to exchange with a gaseous reservoir. Some chondrules may have exchanged gas under equilibrium or near equilibrium conditions that did not produce detectable isotopic shifts in silicon between olivine and pyroxene phases. Others may have resided in areas with slight undercooling that did produce isotopic shifts in $\delta^{29}\text{Si}$ between olivine and pyroxene after incorporation of a silicon-bearing gas.

3.7 References


Radomsky, P. M. and R. H. Hewins. Formation conditions of pyroxene-olivine and magnesian olivine chondrules. GCA, 54 (1990), 3475-3490.


Young, E. D. and E. A. Schauble. Isotopic consequences of CAI condensation. MAPS, 47 (2012), Abstract #4382.
Appendix A1

Descriptions of additional CR chondrites:

**Gao-Guenie (b)** is classified as type 2.8 and contains a few POP (porphyritic olivine-pyroxene) and PP (porphyritic pyroxene) chondrules that appear in transmitted light to contain clear, colorless or light-brown, isotropic glass. No chondrules have altered mafic silicate phenocrysts. The meteorite is very weathered (W4); more than 90% of the metal grains (in nodules, within chondrule interiors and at chondrule margins) have been altered to goethite. The interiors of the surviving metal grains are free of magnetite.

**Acfer 394** and its paired specimens (Table 1) have well-defined chondrules that contain unaltered mafic-silicate phenocrysts. One of the chondrules we examined microscopically appears to contain clear, isotropic glass. Metallic Fe-Ni is moderately abundant; many chondrules are surrounded by discontinuous rims of metal blebs. Magnetite is absent. These specimens are classified as type 2.8 (Table 1). It is weathering stage W1-W2.
**MIL 090001** was classified initially as CV2 (Keller, 2011), but neutron-activation and O-isotope analyses showed that the rock is a CR2 chondrite (e.g., Isa et al., 2012; Keller et al., 2012). Chondrules lack glassy mesostases, but it is difficult to determine the level of phenocryst alteration due to the substantial terrestrial weathering (weathering stage W3). Magnetite occurs as plaquets, 1-2-µm-size spherulites and as grains adjacent to sulfide. It is similar in its degree of alteration to Renazzo and is classified here as type 2.4. Keller et al. (2012) reported 5-30-µm-size crystals of CaCO$_3$ (at least some of which is aragonite) throughout MIL 090001, indicative of substantial alteration. Matrix phyllosilicates comprise a mixture of serpentine and chlorite (Keller et al., 2012).
Appendix A2

Additional properties affected by aqueous alteration:

*O isotopes*

CR chondrites of lower subtypes (i.e., those with higher degrees of aqueous alteration) tend to have higher $\Delta^{17}O$ values; the lowest $\Delta^{17}O$ values are found in type 2.8 MET 00426, QUE 99177 and LAP 02342. If we give equal weight to all data for each individual meteorite in Table 10, we find that the mean $\Delta^{17}O$ values of the CR chondrites exhibit a significant negative correlation with CR subtype: $r = -0.664$, $n = 11$, $2\alpha = 0.03$, significant at the 97% confidence level. Similar trends occur in CM chondrites (Fig. 8 of Rubin et al., 2007) and CO chondrites (Rubin, 1998). The meteorites that underwent more-severe aqueous alteration presumably interacted to greater extents with $^{16}O$-poor fluids. One caveat, however, is that the pre-fluorination and acid wash may have partly removed asteroidal aqueous alteration products. Another is that the matrix of QUE 99177 appears to be enriched in $^{16}O$ relative to the whole rock (Schrader et al., 2014).

However, the position of an individual CR chondrite (particularly a find) on the standard three-isotope diagram is not sufficient to establish the degree of aqueous
alteration. Terrestrial weathering seems to have affected the O-isotopic compositions of the CR finds, moving them toward the terrestrial fractionation line.

Both our data set and that of Schrader et al. (2011) show that the more-altered samples have higher $\Delta^{17}$O, but the $\Delta^{17}$O values in the two data sets do not agree. This discrepancy is probably due to differences in sample preparation: Schrader et al. (2011) used unwashed samples; the samples in our plotted dataset were acid-washed. The discrepancy is greatest among the Saharan samples, i.e., the ones most in need of acid washing.

The large range in $\Delta^{17}$O among CR 2.8 chondrites shows that, for the least-altered CR samples, the O-isotopic composition in a single sample is not a particularly sensitive parameter. This may reflect inherent O-isotopic heterogeneity (caused mainly by refractory inclusions and chondrules) or significant contamination of some samples with terrestrial O.

$H$ isotopes

The correlation between O-isotopic composition and the degree of alteration in CR chondrites is due to the whole rocks incorporating high-$\Delta^{17}$O water. The other major component of water is H and it is worthwhile to determine if there is a correlation between $\delta^D$ and the degree of CR-chondrite alteration. The two principal H-rich components in chondrites are phyllosilicates (and other hydrated minerals) and organic matter. These two components might have experienced some isotopic exchange during aqueous alteration (Bonal et al., 2011).
Alexander et al. (2012a,b) found that the bulk H abundance correlates with δD values in CR chondrites and that CR2.0 GRO 95577 has the highest H abundance. However, several CR chondrites have δD values that do not follow the trend. The slightly altered samples, MET 00426 and QUE 99177, do not plot at the low-alteration extreme of the scale, suggesting variability in the H isotopic composition at centimeter-size scales (Alexander et al., 2012a,b). These results and the large variability in δD values in CR-chondrite matrices (Bonal et al., 2011) render δD measurements an inadequate tool for gauging the degree of CR-chondrite whole-rock aqueous alteration.

Presolar grain abundance

Although there are only limited data, the abundance of O-anomalous presolar grains in CR chondrites seems to decrease with increasing degree of aqueous alteration. The least-altered CR chondrites have high concentrations of O-anomalous presolar grains: CR2.8 QUE 99177 and MET 00426 have presolar grain concentrations of 220 ± 40 µg/g and 160 ± 30 µg/g, respectively (Floss and Stadermann, 2009); CR2.8 GRV 021710 has a concentration of 174 ± 30 µg/g (Zhao et al., 2011). However, there are much lower concentrations in those CR chondrites that are slightly more altered: CR2.7 GRA 95229 was found to have presolar-grain concentrations of 19 µg/g (Haenecour and Floss, 2011) and 48 µg/g (Leitner et al., 2012), CR2.5 GRA 06100 has 11 µg/g (Haenecour and Floss, 2011), and CR2.4 Renazzo has 18 µg/g (Leitner et al., 2012). This suggests that small amounts of aqueous alteration are highly destructive of O-anomalous presolar grains. A much larger data set is needed to examine whether this parameter provides a useful measure of aqueous alteration subtype.
Insoluble organic matter

Although the abundance of insoluble organic matter (IOM) does not correlate with the degree of alteration of CM or CR chondrites (Changela et al., 2012), the more-altered CR chondrites tend to have coarser IOM textures. The effect has not been quantified; at present there are too few data to use coarsening of IOM textures as a classificatory parameter.

Amino acids

Martins et al. (2007) used high-performance liquid chromatography with UV fluorescence detection to determine the abundance of amino acids in CR and CM chondrites. They reported that the abundances appear to be correlated with the degree of aqueous alteration. Combining their data with those of Botta et al. (2002) and Glavin et al. (2011), we find that less-altered CR chondrites tend to have higher abundances of amino acids than highly altered samples: type-2.8 QUE 99177 (81 µg/g), type-2.8 EET 92042 (180-320 µg/g), type-2.7 GRA 95229 (249 µg/g), type-2.4 Renazzo (4.8 µg/g), and type-2.0 GRO 95577 (~1 µg/g). The amino acid abundances in GRA 95229 and EET 92042 are the highest known among carbonaceous chondrites.

Although there are not many data, it appears that the destruction of amino acids occurs at relatively low levels of aqueous alteration (Martins et al., 2007). If that is in fact the case, then the amino-acid abundance would be useful only in assessing the subtypes of the least-altered chondrites. As with other parameters, heterogeneous distribution may require the analysis of several independent samples.
Water content

If the CR subtypes are valid, the fraction of hydrated minerals should increase between type-3.0 and -2.0 CR chondrites. In principle, the amount of water could be measured directly by, for example, thermogravimetric analysis (e.g., Horowitz and Metzger, 1963; Plante et al., 2009), but at this time there are insufficient data to evaluate the usefulness of this technique for CR classification.
Appendix A3

Potential complications to the aqueous alteration scale:

CR chondrites are regolith breccias containing solar-wind-implanted noble gases (Schultz and Kruse, 1989). A few types of clasts have been reported: (1) dark inclusions (e.g., Zolensky et al., 1992; Bischoff et al., 1993; Weisberg et al., 1993; Endress et al. 1994), (2) clastic portions of the matrices of some CR chondrites (Abreu and Brearley, 2004), and (3) unusual phyllosilicate clasts containing Ca-sulfate (Noguchi, 1995). It is not clear if some of these clasts and inclusions are xenolithic.

We report here a ~600-µm-size clast in MIL 07525 (CR2.8) that consists of Ca-carbonate containing small grains of iron oxide and phyllosilicate (Table 9; Fig. 10). (The clast differs from one in CI Orgueil that consists of a phyllosilicate matrix containing 35 vol.% Ca-carbonate grains; Fredriksson and Kerridge, 1988.) Because the phases in the MIL 07525 clast are characteristic of a highly altered assemblage and the host is slightly altered, we conclude that MIL 07525 is a breccia. This is analogous to the case for several CM chondrites (e.g., Murray and Cold Bokkeveld; Rubin and Wasson, 1986; Rubin et al., 2007) that contain millimeter-size clasts that differ appreciably from their hosts in the degree of aqueous alteration. Impact-gardening processes on the CM and CR parent bodies appear to have mixed together debris from different alteration zones. Those breccias containing more than one petrologic subtype should be classified by the predominant phase, i.e., the host.
If some CR chondrites such as MIL 07525 contain moderately large clasts, others may contain small clast fragments dispersed non-uniformly in the matrix. Unrepresentative sampling could potentially cause variations in the assessment of petrologic subtype for CR breccias. However, there appears to be little textural heterogeneity within individual CR chondrites on a scale of ~10 cm. We examined seven sections of samples believed to be paired with Acfer 394 (Table 1) and found them all texturally similar and free of discernable clasts. To the degree that Acfer 394 is typical, it seems likely that most individual CR chondrites do not differ substantially in petrologic subtype over distances of tens of centimeters.