# Bleached chondrules: Evidence for widespread aqueous processes on the parent asteroids of ordinary chondrites

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**Abstract**–We present the first detailed study of a population of texturally distinct chondrules previously described by Kurat (1969), Christophe Michel-Lévy (1976), and Skinner *et al.* (1989) that are sharply depleted in alkalis and Al in their outer portions. These "bleached" chondrules, which are exclusively radial pyroxene and cryptocrystalline in texture, have porous outer zones where mesostasis has been lost. Bleached chondrules are present in all type 3 ordinary chondrites and are present in lower abundances in types 4–6. They are most abundant in the L and LL groups, apparently less common in H chondrites, and absent in enstatite chondrites. We used x-ray mapping and traditional electron microprobe techniques to characterize bleached chondrules in a cross section of ordinary chondrites. We studied bleached chondrules from Semarkona by ion microprobe for trace elements and H isotopes, and by transmission electron microscopy. Chondrule bleaching was the result of low-temperature alteration by aqueous fluids flowing through fine-grained chondrite matrix prior to thermal metamorphism. During aqueous alteration, interstitial glass dissolved and was partially replaced by phyllosilicates, troilite was altered to pentlandite, but pyroxene was completely unaffected. Calcium-rich zones formed at the inner margins of the bleached zones, either as the result of the early stages of metamorphism or because of fluid–chondrule reaction. The mineralogy of bleached chondrules is extremely sensitive to thermal metamorphism in type 3 ordinary chondrites, and bleached zones provide a favorable location for the growth of metamorphic minerals in higher petrologic types. The ubiquitous presence of bleached chondrules in ordinary chondrites implies that they all experienced aqueous alteration early in their asteroidal histories, but there is no relationship between the degree of alteration and metamorphic grade. A correlation between the oxidation state of chondrite groups and their degree of aqueous alteration is consistent with the source of water being either accreted ices or water released during oxidation of organic matter. Ordinary chondrites were probably open systems after accretion, and aqueous fluids may have carried volatile elements with them during dehydration. Individual radial pyroxene and cryptocrystalline chondrules were certainly open systems in all chondrites that experienced aqueous alteration leading to bleaching.

## INTRODUCTION

Chondrites are sedimentary rocks formed from primitive, nebular materials that accumulated into small planetesimals and asteroids in the earliest stages of the solar system's formation. They contain evidence of preaccretionary processes that occurred in the solar nebula (and earlier), as well as processes that happened on asteroids. One of the most difficult aspects of chondrite research has always been to differentiate those features recording nebular events from those recording asteroidal events.

At the time of their formation, most of the mass of every chondrite was present in one of two principal components: (1) chondrules, spheroidal silicate objects generally with igneous textures; and (2) matrix, fine-grained (micrometer-sized or smaller) material, interstitial to or rimming the much larger sized chondrules and other minor components. These components are widely believed to predate accretion of their parent asteroids. As the major components of chondrites, these materials can presumably give us the best information about how solids formed and were processed early in solar system history, and what chemical and physical conditions might have been prevalent at that time.

In order to study preaccretionary processes, one must either avoid studying chondrites that have been altered by secondary asteroidal processes such as thermal and shock metamorphism and

aqueous alteration, or understand these processes sufficiently to take into account their effects. This is fairly easy to do for the comparatively well-studied metamorphic processes, but we know much less about the extent to which aqueous alteration has affected many chondrites. The CI, CM, and CR meteorites contain a wide suite of secondary minerals formed by aqueous alteration (reviewed by Zolensky and McSween, 1988). There is evidence in some CV chondrites (Keller and Buseck, 1990; Tomeoka and Buseck, 1990; Weisberg *et al.*, 1993; Keller *et al.*, 1994; Brearley, 1997; Krot *et al.*, 1998a,b) and unequilibrated ordinary chondrites (*e.g.*, Hutchison *et al.*, 1987; Alexander *et al.*, 1989; Krot *et al.*, 1997) for light aqueous processing, usually in the form of hydrated phases or carbonates, either in the matrix or on the peripheries of chondrules, or in the form of the products left after dehydration has occurred.

In the unequilibrated ordinary chondrites, especially in the well-studied falls Semarkona, Bishunpur, Chainpur, and Tieschitz, most of the evidence for aqueous alteration has been found in matrix phases or in the mesostasis at the edges of chondrules, which suggests that the effects of aqueous alteration in chondrules has been minimal. Indeed, matrix and fine-grained chondrules must be sensitive recorders of secondary events, for their grain size renders them highly susceptible to mineralogical changes caused by thermal and chemical processing. There has been speculation that certain fine-grained chondrules have been leached by aqueous fluids. Kurat

(1969) noted that some "fibrous" pyroxene chondrules in Tieschitz were altered at their surfaces and along cracks and speculated that water may have leached Na, Al, and Si from these areas. Christophe Michel-Lévy (1976) made similar observations on Tieschitz, finding evidence that the glass in some chondrules may have been selectively dissolved by fluids and replaced in some cases by metal and troilite. Finally, Skinner *et al.* (1989) observed the same type of chondrules in all three groups of ordinary chondrites and dubbed them "bleached chondrules" for the light color of the affected zones. They too speculated that volatile-rich fluids were responsible for these observations.

In this paper, we present the results of the first detailed study of bleached chondrules in ordinary chondrites. The goals of this work were to describe the occurrence of these chondrules, measure in detail the chemical and isotopic effects of bleaching, and to test whether aqueous alteration is a viable alteration mechanism. In doing so, we will discuss the timing of the bleaching process relative to accretion, brecciation, and metamorphism. Finally, we will consider the consequences of this process relative to the distribution of elements in ordinary chondrites, and to interpreting the compositions of affected chondrules in terms of nebular processes.

## EXPERIMENTAL METHODS

### Electron Microprobe

This project was initiated after examination of a series of high-resolution x-ray maps of thin sections of the highly unequilibrated ordinary chondrites, Semarkona (LL3.0) and Bishunpur (L3.1), led to our "rediscovery" of bleached chondrules. For Semarkona section USNM 1805-7, a 4 × 5 grid of 20 maps, each containing 1000 × 1000 pixels with a 2 $\mu$m spacing was acquired on the JEOL 8900 electron microprobe at the U.S. Geological Survey, Reston, Virginia; this gave a total coverage of 0.8 cm². Data were collected simultaneously on five spectrometers for the K$\alpha$ x-rays of Na, Al, S, Mg, and Fe, using 65 nA beam current, 20 kV accelerating potential, and 20 ms dwell time per pixel, taking six days to complete. A 4 × 4 grid of similar maps was done for Bishunpur section USNM 1281-1. Bleached chondrules stand out on the Na and Al x-ray maps because their outer zones are extremely depleted in these elements. Once their existence became known, it was a simple matter of learning to recognize bleached chondrules with an optical microscope in other chondrites without resorting to thin-section-scale mapping (see below). High-resolution x-ray maps were acquired for each bleached chondrule that was identified, using 1 $\mu$m pixel spacing, and longer dwell times per pixel to increase count rates.

The second phase of this study involved searching for bleached chondrules in ordinary chondrites of higher metamorphic grade. This was done by optical microscopy at the National Museum of Natural History, Smithsonian Institution. The complete list of meteorites examined and thin sections used for electron probe microanalysis (EPMA) and ion probe analysis is given in Table 1.

The electron microprobe was used to make a series of line scans across each chondrule. The line scans consisted of a series of rastered-beam analyses ranging in size from 8 × 8 to 10 × 10 $\mu$m. Analytical conditions were 20 nA beam current and 15 kV accelerating voltage; conventional silicate mineral standards were used, and data were reduced using the CITZAF method of Armstrong (1995). Sodium loss due to the interaction of the electron beam with the sample is minimal under the experimental conditions used: Na was determined in the first 10 s after the beam was unblanked, and a low-current density is produced by rastering the beam over 64–100 $\mu$m².

TABLE 1. Meteorites searched for bleached chondrules.

| Name | Class | Found? | Sections analyzed |
|---|---|---|---|
| Sharps | H3.4 | Yes | USNM 640-9 |
| Dhajala | H3.8 | Yes | USNM 5832-3, 5832-5 |
| Ankober | H4 | No | — |
| Bath | H4 | No | — |
| Beaver Creek | H4 | No | — |
| Dimmit | H4 | No | — |
| Enigma | H4 | No | — |
| Farmville | H4 | No | — |
| Fayetteville | H4 | No | — |
| Menow | H4 | No | — |
| Miller | H4 | No | — |
| Ochansk | H4 | No | — |
| Quenggouk | H4 | No | — |
| Selma | H4 | No | — |
| Seminole | H4 | No | — |
| Tysnes Island | H4 | No | — |
| Weston | H4 | No | — |
| Allegan | H5 | No | — |
| Beardsley | H5 | No | — |
| Bonita Springs | H5 | No | — |
| Cangas de Onis | H5 | No | — |
| Faucett | H5 | No | — |
| Lost City | H5 | No | — |
| Jilin | H5 | No | — |
| Nuevo Mercurio | H5 | No | — |
| Pultusk | H5 | No | — |
| Richardton | H5 | No | — |
| Bjurböle | L/LL4 | Yes | USNM 610-8 |
| Barratta | L4 | No | — |
| Dalgety Downs | L4 | No | — |
| Rupota | L4 | No | — |
| Saratov | L4 | No | — |
| Arriba | L5 | No | — |
| Farmington | L5 | No | — |
| Honolulu | L5 | No | — |
| Knyahinya | L5 | No | — |
| Semarkona | LL3.0 | Yes | USNM 1805-7, 1805-8 |
| Krymka | LL3.0 | Yes | USNM 1729-5 |
| Bishunpur | LL3.1 | Yes | USNM 1281-1 |
| Chainpur | LL3.4 | Yes | USNM 1251-18 |
| Hamlet | LL4 | Yes | USNM 3455 |
| Kelly | LL4 | No | — |
| Soko-Banja | LL4 | Yes | USNM 3078-1 |
| Alta Ameen | LL5 | No | — |
| Oberlin | LL5 | No | — |
| Olivenza | LL5 | No | — |
| Paragould | LL5 | No | — |
| Siena | LL5 | No | — |

Because bleached chondrules are fine grained, typical areas analyzed by this EPMA method contain fairly representative mixtures of all silicate phases. Rastered-beam analyses such as these do require corrections for the differing densities, backscatter efficiencies, and excitation volumes of the various phases in the sample (*e.g.*, Warren, 1997; Lindstrom, 1999). These corrections are difficult to make with accuracy, requiring assumptions about the abundances and compositions of the phases present. In general terms, we calculate that the following levels of correction factors are applicable to those of our analyses that represent mixtures of pyroxene, feldspar or feldspathic glass, and troilite: Na, K, Al, Cl × 0.83; P, Si × 1.00 (no correction); Ca × 1.02; Mg, Cr, Mn, Fe × 1.03; S × 1.4. We have applied these correction factors uniformly to all of our data (Table 2) but caution the reader that uncorrected data, which might

TABLE 2. Analyses (wt%) of bleached chondrules in ordinary chondrites, and of smectite in a bleached chondrule and the matrix of Semarkona.*

| | No.† | Na$_2$O | MgO | Al$_2$O$_3$ | SiO$_2$ | P$_2$O$_5$ | FeS‡ | Cl | K$_2$O | CaO | TiO$_2$ | Cr$_2$O$_3$ | MnO | FeO§ | Total | ffm# |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **ZONES IN BLEACHED CHONDRULES:** | | | | | | | | | | | | | | | | |
| **Semarkona (LL3.0) 1805-7-7 (C)** | | | | | | | | | | | | | | | | |
| Outer | 2 | 0.62 | 25.1 | 1.40 | 51.4 | 0.07 | n.a. | n.a. | 0.14 | 1.61 | 0.08 | 0.59 | 0.60 | 19.0 | 100.6 | 28.4 |
| Bleached | 17 | 0.32 | 26.1 | 0.95 | 52.3 | 0.08 | n.a. | n.a. | 0.05 | 1.73 | 0.10 | 0.66 | 0.73 | 17.2 | 100.3 | 25.6 |
| Core | 41 | 0.78 | 24.7 | 1.74 | 55.8 | 0.09 | n.a. | n.a. | 0.10 | 1.68 | 0.09 | 0.62 | 0.67 | 15.8 | 102.1 | 25.1 |
| **Semarkona (LL3.0) 1805-7-11 (C)** | | | | | | | | | | | | | | | | |
| Outer | 1 | 0.86 | 22.1 | 2.41 | 49.7 | 0.28 | n.a. | n.a. | 0.20 | 1.59 | 0.12 | 0.67 | 0.75 | 20.8 | 99.4 | 33.0 |
| Bleached | 9 | 0.38 | 23.4 | 0.93 | 50.1 | 0.09 | n.a. | n.a. | 0.05 | 1.42 | 0.08 | 0.64 | 0.91 | 22.6 | 100.6 | 33.6 |
| Core | 33 | 0.81 | 22.3 | 1.37 | 53.5 | 0.16 | n.a. | n.a. | 0.09 | 1.40 | 0.07 | 0.62 | 0.85 | 20.9 | 102.1 | 32.9 |
| **Chainpur (LL3.4) 1251-18-1 (C)** | | | | | | | | | | | | | | | | |
| Outer | 3 | 0.61 | 26.4 | 1.41 | 44.0 | 0.13 | 3.43 | 0.02 | 0.11 | 1.45 | 0.07 | 0.68 | 0.65 | 23.0 | 101.8 | 32.1 |
| Bleached | 6 | 0.39 | 27.4 | 1.26 | 45.6 | 0.06 | 0.48 | 0.10 | 0.10 | 1.61 | 0.06 | 0.79 | 0.69 | 18.7 | 97.2 | 26.5 |
| Ca-zone | 3 | 0.83 | 26.2 | 2.02 | 50.1 | 0.09 | 0.28 | 0.02 | 0.20 | 2.36 | 0.04 | 0.69 | 0.70 | 18.1 | 101.6 | 26.7 |
| Core | 26 | 0.97 | 25.4 | 1.57 | 55.5 | 0.05 | 0.53 | 0.01 | 0.29 | 1.56 | 0.09 | 0.70 | 0.77 | 14.8 | 102.3 | 23.5 |
| **Dhajala (H3.8) 5832-3-1 (C)** | | | | | | | | | | | | | | | | |
| Bleached | 6 | 0.61 | 28.5 | 1.03 | 56.2 | 0.40 | 0.64 | 0.01 | 0.05 | 2.42 | 0.10 | 0.31 | 0.54 | 10.9 | 101.7 | 17.0 |
| Ca-zone | 8 | 0.94 | 23.8 | 1.70 | 57.8 | 0.46 | 0.82 | 0.01 | 0.05 | 2.33 | 0.07 | 0.46 | 0.52 | 13.2 | 102.1 | 22.8 |
| Core | 32 | 0.92 | 21.0 | 1.68 | 57.3 | 0.39 | 1.02 | 0.01 | 0.05 | 1.76 | 0.07 | 0.53 | 0.57 | 16.4 | 101.8 | 29.4 |
| **Dhajala (H3.8) 5832-3-2 (C)** | | | | | | | | | | | | | | | | |
| Bleached | 4 | 0.32 | 28.4 | 0.70 | 55.2 | 0.03 | 0.47 | 0.00 | 0.19 | 1.85 | 0.02 | 0.49 | 0.57 | 12.7 | 100.9 | 19.1 |
| Ca-zone | 5 | 0.40 | 23.6 | 0.68 | 56.2 | 0.01 | 0.51 | 0.00 | 0.25 | 1.90 | 0.08 | 0.82 | 0.74 | 17.4 | 102.6 | 28.0 |
| Core | 14 | 0.39 | 22.8 | 0.69 | 56.1 | 0.00 | 0.46 | 0.01 | 0.26 | 1.56 | 0.05 | 0.84 | 0.78 | 18.5 | 102.4 | 30.0 |
| **Bjurböle (L/LL4) 610-8-1 (C)** | | | | | | | | | | | | | | | | |
| Bleached | 10 | 0.26 | 28.6 | 0.42 | 50.8 | 0.10 | 0.38 | 0.01 | 0.03 | 7.21 | 0.12 | 0.20 | 0.42 | 13.9 | 102.5 | 20.4 |
| Ca-zone | 8 | 0.45 | 28.8 | 0.91 | 52.8 | 0.09 | 0.57 | 0.01 | 0.06 | 3.21 | 0.12 | 0.35 | 0.44 | 14.0 | 101.8 | 20.5 |
| Core | 19 | 0.42 | 29.3 | 0.88 | 53.8 | 0.10 | 0.65 | 0.01 | 0.06 | 2.03 | 0.10 | 0.68 | 0.44 | 14.2 | 102.7 | 20.4 |
| **Soko-Banja (LL4) 3708-1-1 (RP)** | | | | | | | | | | | | | | | | |
| Bleached | 8 | 0.15 | 31.0 | 1.55 | 49.3 | 0.03 | 0.11 | 0.02 | 0.04 | 0.91 | 0.29 | 0.47 | 0.47 | 17.2 | 101.6 | 22.5 |
| Core | 29 | 1.08 | 28.3 | 2.83 | 51.7 | 0.01 | 0.49 | 0.01 | 0.08 | 0.94 | 0.18 | 0.68 | 0.42 | 15.3 | 102.0 | 22.2 |
| **Soko-Banja (LL4) 3708-1-2 (C)** | | | | | | | | | | | | | | | | |
| Bleached | 7 | 0.60 | 26.9 | 1.88 | 54.0 | 0.13 | 0.76 | 0.03 | 0.07 | 2.26 | 0.15 | 0.47 | 0.43 | 13.3 | 100.9 | 20.8 |
| Core | 47 | 0.86 | 26.8 | 1.85 | 55.5 | 0.09 | 0.92 | 0.01 | 0.10 | 1.89 | 0.12 | 0.62 | 0.46 | 13.5 | 102.7 | 21.2 |
| **SMECTITE:** | | | | | | | | | | | | | | | | |
| **Semarkona 1805-5x-2 (RP), bleached zone** | | | | | | | | | | | | | | | | |
| Point 1 | 1 | 4.6 | 10.8 | 9.0 | 44.5 | – | – | – | 1.1 | 0.7 | 0.7 | – | 0.4 | 28.2 | 100.0 | – |
| Point 2 | 1 | 3.0 | 10.9 | 7.6 | 43.7 | – | – | – | 0.8 | 0.1 | 1.0 | – | 0.3 | 32.6 | 100.0 | – |
| **SEMARKONA MATRIX:** | | | | | | | | | | | | | | | | |
| Point 1 | 1 | 7.7 | 6.9 | 6.1 | 37.2 | – | – | – | 1.2 | 1.9 | 0.3 | – | 0.5 | 38.2 | 100.0 | – |
| Point 2 | 1 | 5.8 | 9.2 | 6.1 | 49.3 | – | – | – | 0.9 | 0.7 | 0.0 | – | 0.5 | 27.5 | 100.0 | – |
| Lit.$ | – | 6.1 | 8.9 | 5.4 | 44.2 | – | – | – | 0.9 | 0.1 | – | – | – | 34.4 | 100.0 | – |

*Different zones in bleached chondrules were analyzed by rastered-beam EPMA as linear traverses across each chondrule. Smectite analyses were done by quantitative EDS using a TEM.
†Number of analyses that were averaged.
‡Total S, recalculated as FeS.
§Calculated from total Fe after subtraction of the amount needed to make FeS.
#Bulk FeO/(FeO + MgO) (mol%).
$Alexander *et al.* (1989).
n.a. = not analyzed, C = cryptocrystalline, RP = radial pyroxene.

be used for comparison, are common in the literature. None of the conclusions that we draw from our data would be significantly changed by errors in the correction factors that we applied.

### Ion Microprobe

Ion probe analyses of trace elements and H isotopes in bleached chondrules from Semarkona were carried out on the Department of Terrestrial Magnetism's Cameca 6f ion microprobe using a 12 kV O⁻ primary beam. Positive secondary ions were collected using a 10 kV secondary accelerating voltage. The trace element measurements were made with a ~5 nA primary beam, a secondary accelerating voltage offset of −75 V, and a 50 eV energy window. The ion intensities were corrected to elemental abundances using the method of Alexander (1994). The H-isotopic measurements were made with a 1–3 nA primary beam, a 50 eV energy window, and a mass-resolving power of at least 1600. The sample was sputtered with the primary ion beam for 5 min prior to analysis in order to remove any surface contamination.

### Transmission Electron Microscopy

Transmission electron microscopy (TEM) was used to look at the mineralogy of bleached chondrules in Semarkona. Unfortunately,

## (a) Semarkona 1805-7-7

## (b) Dhajala 5832-3-2

### 200 μm

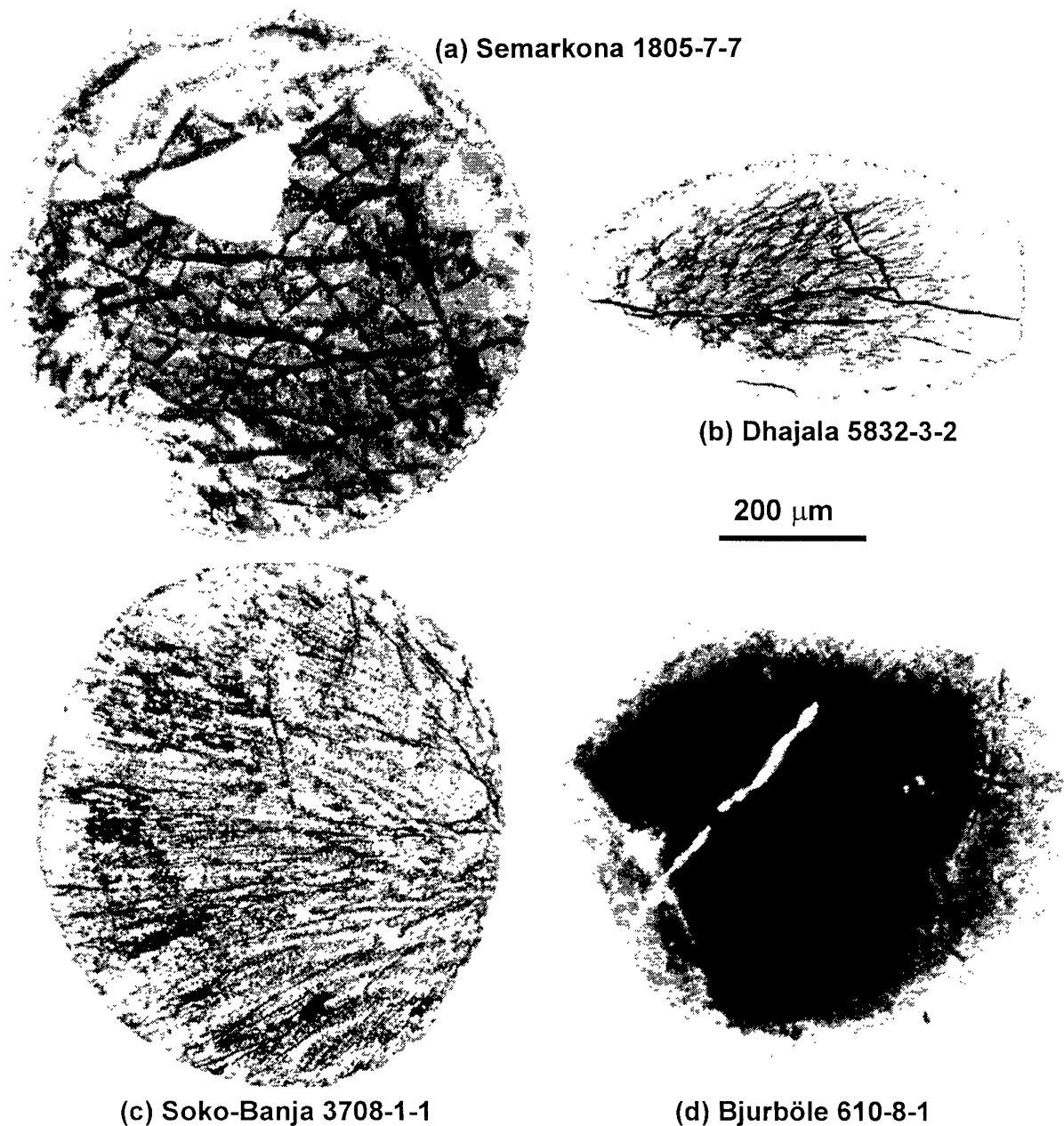## (c) Soko-Banja 3708-1-1                    ## (d) Bjurböle 610-8-1

FIG. 1. Transmitted light photomicrographs of bleached chondrules in ordinary chondrites of different groups and petrologic types. To maximize the contrast in each image, the chondrules were extracted digitally from surrounding matrix using commercial image-processing software. (a) A bleached cryptocrystalline chondrule from Semarkona (LL3.0). The large white area in the center of the chondrule was plucked during thin-section preparation and was filled with epoxy. The bleached zone is visible as a light gray area near the edge of the chondrule running counterclockwise from the "3 o'clock" to the "6 o'clock" positions. (b) An elliptical bleached chondrule from Dhajala (H3.8), with a light-colored bleached zone encircling the chondrule. (c) A bleached radial pyroxene chondrule from Soko-Banja (L4). The bleached zone is mainly visible at the top and left side of the image as a lighter gray area. (d) A bleached cryptocrystalline chondrule from Bjurböle (L/LL4), with an obvious bleached zone (gray) and outer zone (white) encircling the entire chondrule.

the chondrules in the Smithsonian thin sections that were analyzed by EPMA and ion probe methods were not available for TEM work. Demountable, doubly polished petrographic thin sections were prepared from eight small chips (~50 mg each) of Semarkona (USNM 1805). The sections were mounted using Superglue, an epoxy which is soluble in acetone. At each stage of preparation, the sections were impregnated with epoxy to prevent disintegration during polishing. One large bleached chondrule was found among these sections (Semarkona 1805-5x-2) and studied by optical

microscopy, scanning electron microscopy (SEM), EPMA, and finally TEM. Detailed x-ray maps were prepared using the U.S.G.S. electron microprobe. This procedure allowed characterization of the same region of the sample to be carried out at all scales.

The TEM was performed on JEOL 2000FX and JEOL 2010 instruments at the University of New Mexico, both operating at 200 kV. High-resolution TEM images were obtained on the JEOL 2010. The JEOL 2000FX, equipped with a Tracor Northern TN 5500 energy dispersive x-ray analysis system was used to obtain *in*

*situ* quantitative analytical data, using the Cliff-Lorimer thin-film approximation for data reduction (Cliff and Lorimer, 1975). Experimental *k*-factors, determined from a variety of mineral standards, were used throughout. The samples were prepared for TEM by conventional ion beam bombardment techniques using a Gatan ion beam thinner. Small areas in the bleached zone of Semarkona 1805-5x-2, near the original surface and in the core, were thinned in this way. Prior to TEM studies, the samples were coated with a light coat of C to prevent charging.

## RESULTS

### Petrography and Occurrence of Bleached Chondrules

Bleached cryptocrystalline chondrules are easily identified in thin sections: these chondrules are normally somewhat opaque to translucent in transmitted light because of their very fine grain size; however their bleached zones, if present, are much more transparent (Fig. 1a,b,d). Bleached radial pyroxene chondrules may be identified in the same way, but the contrast between bleached and unbleached zones in transmitted light may be more subtle because of the coarser grain size (Fig. 1c). Bleached zones, especially in highly unequilibrated chondrites, may also appear orange in transmitted light; their color resembles that of limonitic staining caused by the terrestrial weathering of metal, although the degree of coloration is not correlated with proximity to opaque assemblages. Part of the reason for the difference in optical properties between bleached and unbleached zones is that the bleached zones are porous. In bleached chondrules with coarse enough grain size, glassy areas are seen microscopically to be pitted, or entire regions are empty between pyroxene crystals where mesostasis would normally occur (*e.g.*, Fig. 2). In cryptocrystalline chondrules, tiny holes speckle the entire bleached region.

Bleached zones typically occur as annular regions in the outer 100 $\mu$m of chondrules, with sharp boundaries between them and the unbleached cores. The bleached zones tend to be of uniform thickness, following the contours of the chondrule surfaces. Where craters or blobs of metal–sulfide are present at the surface, bleached zones parallel the concave surfaces formed by chondrule silicates.

In some chondrules, bleached zones can also be seen following cracks into the interiors (Fig. 3). In many chondrules, the bleached zones are surrounded by outer zones that resemble the cores of the chondrules, but in which pyroxene is coarser grained (this zone is prominent in Fig. 2). These outer zones are probably the same features that have been described informally as "quenched margins" around some chondrules (in this paper, no evidence will be presented to contradict such an origin, and we will refer to them as "outer zones").

Bleached chondrules may also be recognized on the surfaces of hand samples and among separated chondrules from Semarkona. Broken open, they display solid black cores, white outer regions (bleached zones), and black surfaces (outer zones, grading into matrix; Fig. 3). When examined in this way, it is obvious how bleached zones follow cracks into chondrule interiors. (We did not attempt to search for bleached chondrules in bulk materials other than Semarkona.)

Whereas most bleached chondrules have approximately concentric outer bleached zones around unbleached cores, some do not. One cryptocrystalline chondrule in Semarkona (Fig. 4a, also shown in Fig. 1a) is bleached along ~80% of its circumference, but
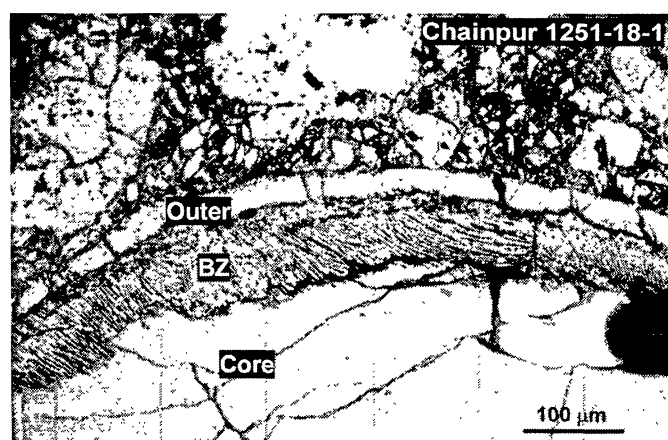


FIG. 2. Reflected light photomicrographs of a small part of a large bleached chondrule in Chainpur (LL3.4). The core of the chondrule is composed of elongated low-Ca pyroxene crystals (light gray) with interstitial glass (darker gray). The pyroxene continues into the bleached zone (BZ); however, most of the glass has been removed, leaving holes in the surface of the thin section. The outer zone is compositionally intermediate between the core and the bleached zone and contains more massive pyroxene than the core. It may represent the "quenched margin" of the original chondrule droplet.
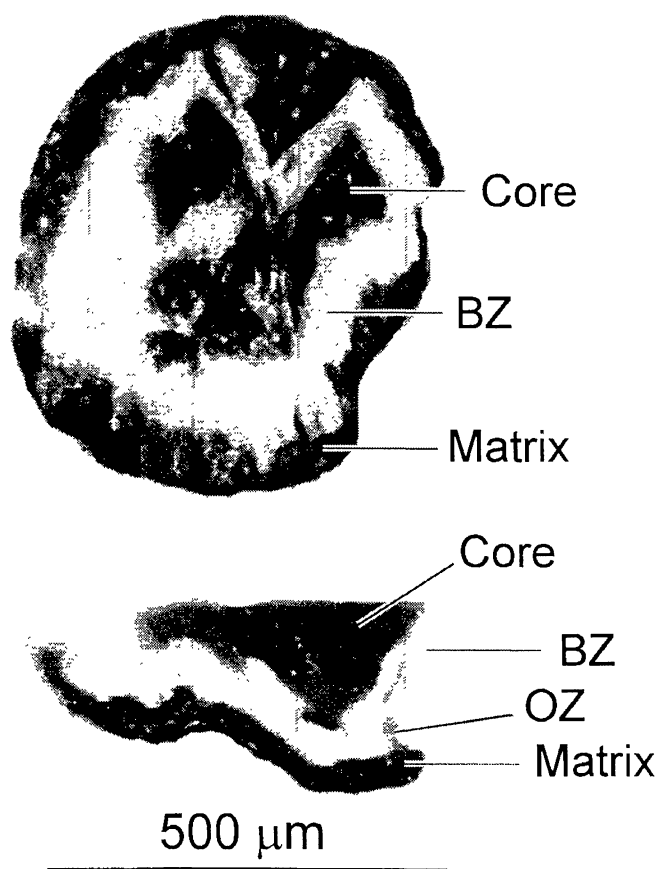


FIG. 3. Photographs of small lumps of material containing bleached chondrules that have been separated from Semarkona. Areas of the photographs that contained surrounding chondrule fragments and additional matrix have been digitally removed. The bleached zones (BZ) are clearly visible as white areas mantling very dark colored cores. Near the center of the lower image, the bleached zone can be clearly seen to follow a crack into the chondrule core. The outer zone (OZ) or "quenched margin" is barely visible in the lower image as a dark gray area just outside the bleached zone. The presence of bleached chondrules in hand-samples of Semarkona proves that they are not artifacts of the thin-section making process.
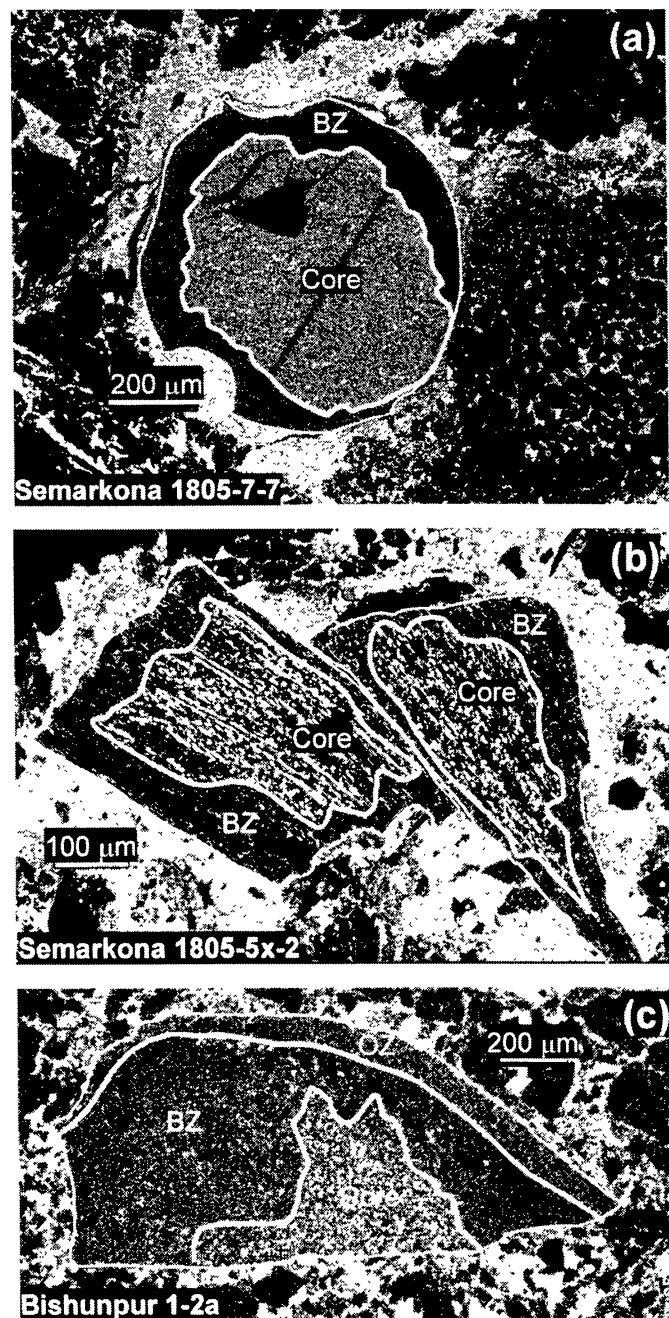
FIG. 4. Sodium x-ray maps of three bleached chondrules in unequilibrated ordinary chondrites. Higher concentrations of Na are indicated by lighter shades of gray. (a) The bleached zone (BZ) in this Semarkona chondrule (shown also in Fig. 1a) does not fully encircle the whole chondrule. It terminates where the chondrule is physically pressed up against an adjacent porphyritic chondrule in its lower-right quadrant. An aqueous fluid probably flowed freely through the opaque matrix (light gray) and bleached the chondrule only where it abuts matrix. (b) Fragments of a once-larger radial pyroxene chondrule in Semarkona. This chondrule broke, and two pieces were slightly offset during light brecciation on the parent body. Much of the chondrule is now missing. The bleached zone (BZ) is up to 100 $\mu$m thick along the outside of the chondrule, except along the plane of breakage where the bleached zone is ~20 $\mu$m thick. The bleaching process apparently occurred both before and after the brecciation event, giving rise to these features. (c) Fragment of a bleached cryptocrystalline chondrule from Bishunpur (LL3.1). This chondrule broke during a brecciation event that occurred after aqueous alteration ceased. The core, bleached zone (BZ), and outer zone (OZ) all terminate abruptly along the broken surface of the chondrule.

the unbleached core extends all the way to the surface in an area where the chondrule surface is in physical contact with another chondrule. Two fragments of a radial pyroxene chondrule in Semarkona (Fig. 4b) have cores surrounded by thick bleached zones along the original chondrule surface and thinner bleached zones where the two fragments detached from each other, presumably during light brecciation. Bishunpur, which has experienced a large degree of crushing and brecciation, has some bleached chondrules that were clearly broken after the bleached zone had already been established (Fig. 4c).

Bleached chondrules, defined operationally to be those with outer zones that show the optical and chemical properties described above, appear to comprise only nonporphyritic textural types. No porphyritic chondrules that we observed had light-colored outer zones, or regions visible on x-ray maps that were clearly depleted alkalis and Al. By this, we do not mean to imply that all porphyritic chondrules have homogeneous textures and compositions. None, however, could reasonably be termed "bleached chondrules."

Bleached chondrules were identified in each of the six unequilibrated ordinary chondrites that were examined (Table 1), although not necessarily in every thin section. In Semarkona, nearly all radial pyroxene and cryptocrystalline chondrules seem to be bleached. In the two H3 chondrites examined, Sharps and Dhajala, many cryptocrystalline chondrules are clearly *not* bleached, but some are. Other unequilibrated ordinary chondrites are intermediate. It seems likely from our limited survey that a smaller proportion of radial pyroxene and cryptocrystalline chondrules in H3 chondrites are bleached than is the case in L3 or LL3.

Thin sections of 23 type-4 and 19 type-5 ordinary chondrites were also searched (Table 1), but bleached chondrules were only identified in Bjurböle (L/LL4), Soko-Banja (LL4), and Hamlet (LL4). A thin section of an L6 chondrite, Elephant Moraine (EET) 96080, containing a very large bleached chondrule was brought to our attention by Alan Rubin. Thus, the abundance of bleached chondrules decreases sharply with metamorphic grade. And again, H chondrites seem to have lower abundances than L or LL chondrites. The petrographic and physical properties of bleached chondrules in metamorphosed ordinary chondrites are similar to those seen in unequilibrated ordinary chondrites, including optical contrast between bleached and unbleached zones, the geometry of the bleached zones, and porosity in areas between pyroxene crystals in bleached zones.

We searched for bleached chondrules in some carbonaceous and enstatite chondrites, although this work has not yet been done systematically. Approximately 10 low-petrologic type enstatite chondrites (EH3 and EL3) were searched, but no bleached chondrules were found despite a high abundance of radial pyroxene and cryptocrystalline chondrules. Bleached chondrules were found in low petrologic type CO3 chondrites (*e.g.*, Kainsaz, CO3.2), but not in those at or above metamorphic subtype 3.4 (*e.g.*, Felix, Lancé, Isna, Warrenton). The CM and CR chondrites were not examined, and the CV chondrites do not contain radial pyroxene or cryptocrystalline chondrules in sufficient abundance to search for bleached examples. No further work has been done on the bleached chondrules in CO3 chondrites.

## Chemical, Isotopic, and Mineralogical Properties of Bleached Chondrules in Semarkona

**Chemical Properties**–X-ray maps of bleached chondrules in Semarkona reveal a consistent set of features from one object to the next. Iron and Mg show little variation across bleached cryptocrys-
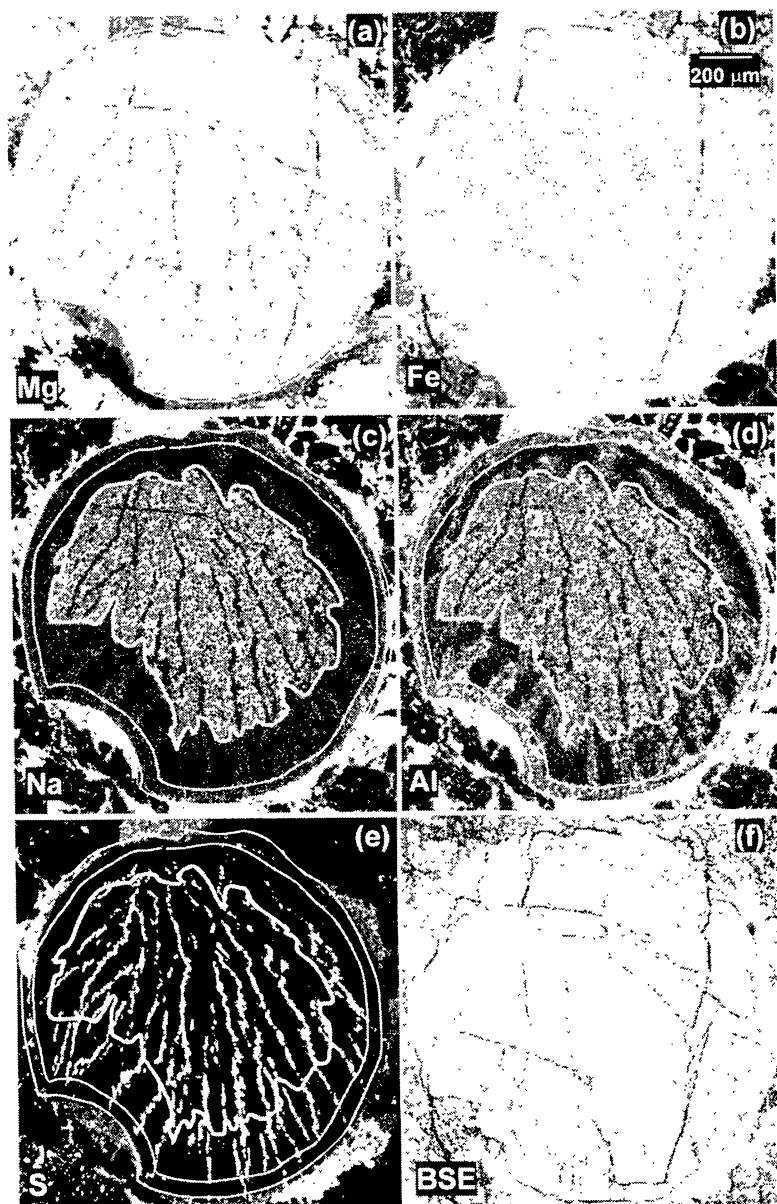
FIG. 5. X-ray maps of a complete bleached cryptocrystalline chondrule in Semarkona, number 1805-7-11. Outlines are shown in white for the core, bleached zone, and outer zone of the chondrule in each image. Magnesium (a) and Fe (b) show little variation from zone to zone in the chondrule, although a very small Fe enrichment is visible in the outer zone (slightly lighter gray). The bright white material visible in the Fe map is sulfide. Sodium (c) and Al (d) are strongly depleted in the bleached zone and along cracks in the core, but some real variation is visible in the extent of depletion in the bleached zone. The S map (e) shows that sulfide minerals are continuous from the core through the bleached zone but are much less abundant in the outer zone. The backscattered electron image (f) reveals the extreme porosity of this chondrule in its bleached zone.

unchanged and terminate just below or within the outer zones of chondrules. Some Fe, Na, and Al enrichment is visible in the bleached zones adjacent to sulfide stringers (Fig. 5b,c,d).

Electron microprobe traverses across two bleached chondrules in Semarkona confirm the observations made from x-ray maps and extend them to several other elements (Fig. 6a,b). All analyzed elements have essentially flat profiles across the cores of the chondrules. The bulk compositions of the cores (Table 2, Fig. 7a,b) are typical of radial pyroxene and cryptocrystalline chondrules: when normalized to Mg and to bulk CI chondrites, they are rich in Si, Cr, and especially Mn and modestly depleted in refractory elements (Al and Ca) and Fe. Core FeO/MgO ratios (0.64–0.94 g/g) are consistent with those found by Grossman and Wasson (1983) for bulk radial pyroxene chondrules in Semarkona (0.57–0.81 g/g). Points in the bleached zones have lower analytical totals and are very similar to the cores in their Ca, Ti, Mg, Cr, Mn, and Fe abundances. They are depleted relative to the cores by factors of up to 5 for Na, K, and Al; and the average compositions of the bleached zones are depleted by ~2× in these elements and by ~6% in Si. A calculation of normative compositions for the cores gives ~85 wt% pyroxene, ~7 wt% olivine, and ~8 wt% plagioclase; whereas bleached zone norms contain ~77 wt% pyroxene, ~19 wt% olivine, and only ~4 wt% plagioclase. The outer zones are intermediate between the cores and the bleached zones in their depletions of plagioclase components. They also show a small but probably significant increase in FeO compared to the cores and bleached zones.

Ion probe data for major and trace elements in bleached chondrule Semarkona 1805-7-7 (Table 3) are in good agreement with EPMA data for most elements. Hydrogen and Cl in bleached and outer zones (spots overlapped both zones) are at least 3–4× higher than in the core, with one Cl analysis ~100× the mean core value. Fluorine also appears elevated in the bleached and outer zones, with one analysis >10× the mean core value (not in the same spot that was rich in Cl). Rubidium appears to be higher in the bleached and outer zones by a small factor (a few tens of percent). Like Na, K, and Al, Sr is much lower in bleached and outer zones than in the core.

**Hydrogen Isotopes**–Semarkona chondrule 1805-7-7 was reanalyzed by ion microprobe to look for variations in water content and H-isotopic composition. Points were analyzed every 15–20 $\mu$m in a traverse from the core, across the bleached and outer zones, and into the surrounding matrix (points 0–9 in Table 4). In addition, three points were analyzed near the middle of the bleached zone and one more in the core (BZ1-3 and Core 1).

For points in the chondrule core, there is no relationship between H concentration (calculated as $H_2O$) or $\delta D$ and distance to the edge of the bleached zone (Table 4). However, $H_2O$ and $\delta D$ are strongly anticorrelated with each other in the core: in low-$H_2O$ areas (~550 ppm), $\delta D$ approaches +1200‰; whereas some areas have twice as much $H_2O$ with $\delta D$ of only +500‰ (Fig. 8). Given the very limited variation in all elements measured by EPMA in the

talline chondrules (Fig. 5a,b), although there is a small enhancement of Fe in the outer zones. Sodium and Al are strongly depleted in bleached zones (Fig. 5c,d). Some irregularities can be seen in the extent of Na and Al depletion from place to place in the bleached zones, partly controlled by the presence of cracks; the outer zones of the chondrules are somewhat less depleted in these elements. Sulfur mainly occurs as stringers of FeS between areas of pyroxene in these chondrules (Fig. 5e; also visible in the Fe map, Fig. 5b). These sulfide stringers pass through the bleached zones apparently
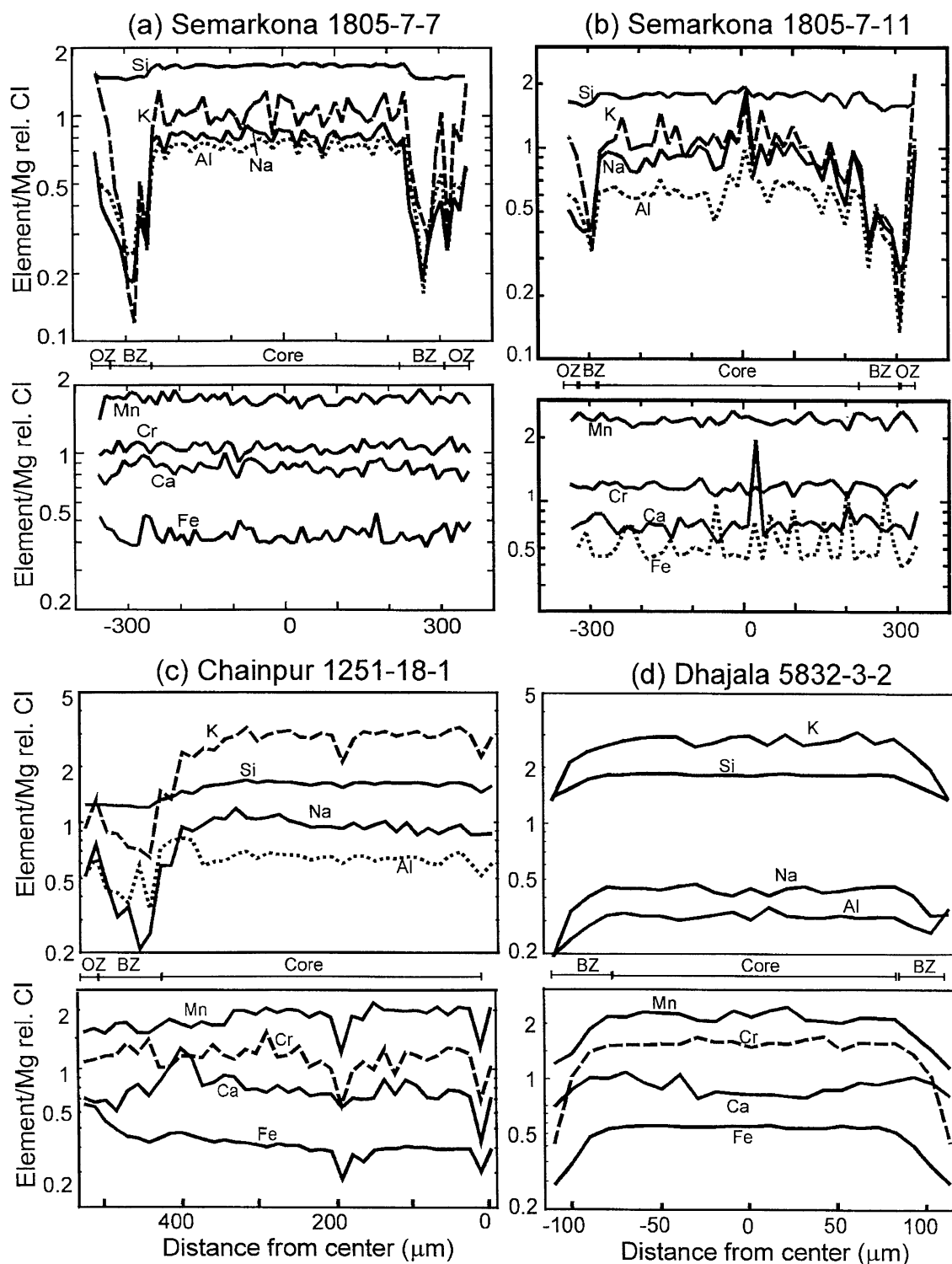
FIG. 6. Electron microprobe traverses across bleached chondrules in unequilibrated ordinary chondrites. Each point in the traverse represents a 64–100 μm² area, including pyroxene, mesostasis, and any other phases present in these extremely fine-grained chondrules. All elemental concentrations have been normalized to Mg, and to the same ratio in CI chondrites. The top of each part of the figure shows elements associated with alkali feldspar (Na, K, Al, and Si), and the bottom shows elements associated with mafic minerals (Ca, Cr, Mn, Fe). Locations of the various chondrule zones (OZ = outer zone, BZ = bleached zone) are indicated between the top and bottom parts of the figures. The two chondrules in Semarkona (a and b), the one in Chainpur (c, only a half-traverse), and the one in Dhajala (d) all show abrupt, parallel depletions in Na, K, and Al, with smaller depletions in Si in the bleached zones, which is consistent with the removal of feldspathic glass. The Semarkona and Chainpur chondrules have outer zones with compositions intermediate for these elements between cores and bleached zones. Calcium shows a distinct peak in the traverses at or just inside the bleached-zone–core boundary in Chainpur and Dhajala. Iron shows a broad core-to-rim zoning in Chainpur. In Dhajala, Fe and the minor elements associated with pyroxene are also depleted at the chondrule margin.
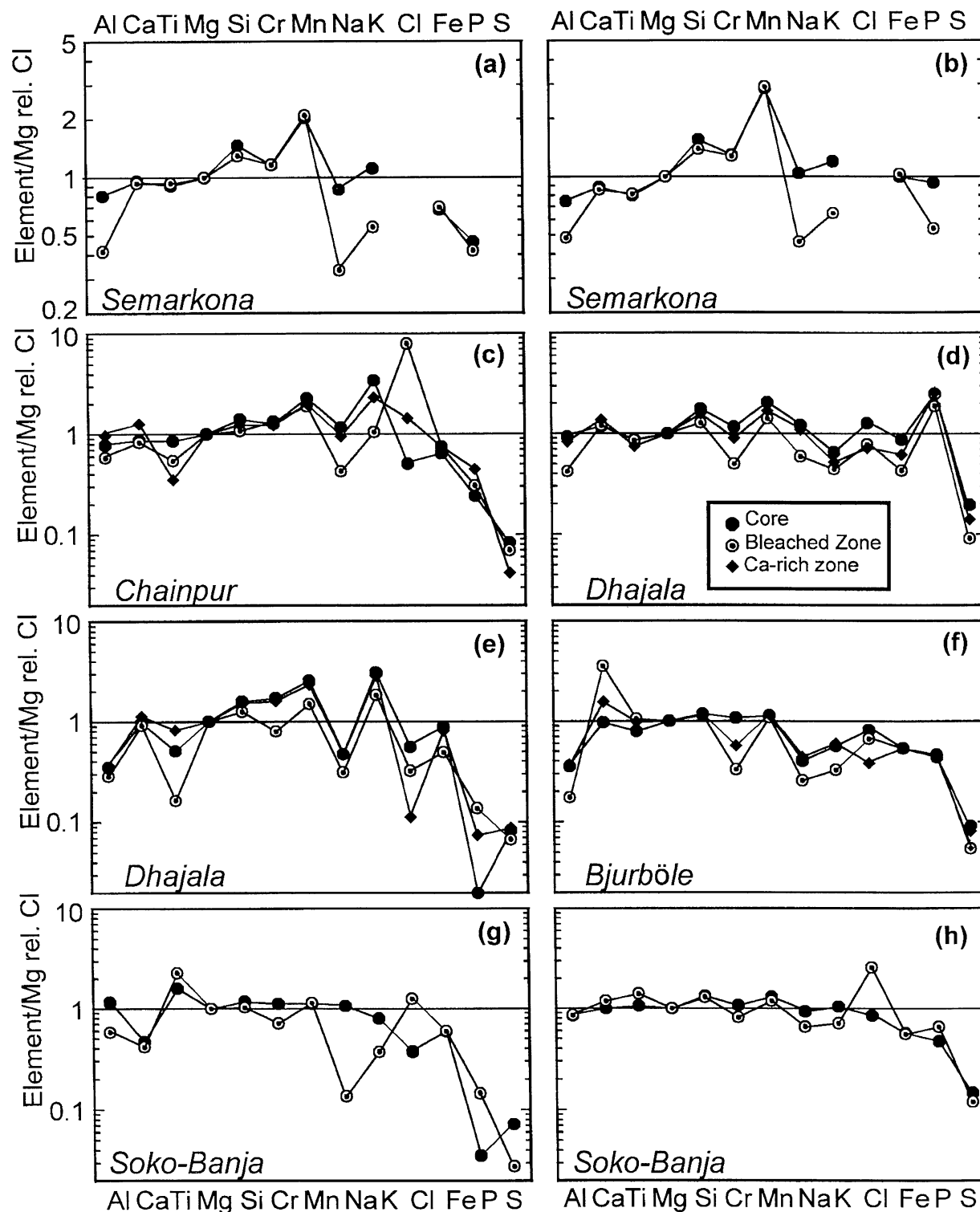
FIG. 7. Abundance diagrams normalized to Mg and to CI chondrites showing the mean compositions of the different zones in bleached chondrules from ordinary chondrites. Data are shown in Table 2. The cores of the Semarkona chondrules (a and b) have compositions that are typical of radial and cryptocrystalline chondrules, including a large Mn enrichment. The bleached zones have erratic patterns with non-solar Ca/Al and more fractionated Na/K ratios than the cores. The bleached Chainpur chondrule (c) is similar to the Semarkona chondrules and shows a large Cl enrichment in the bleached zone (Cl was not analyzed in Semarkona, but ion microprobe data confirm a similar enrichment). One of the Dhajala chondrules resembles Semarkona and Chainpur for many elements (d), and the other one has a fractionated composition even in its core (e). Bleached chondrules in the type 4 chondrites Bjurböle (f) and Soko-Banja (g, h) have variably fractionated Ca/Al ratios and abundance patterns that are more "chondritic" than Semarkona for elements of intermediate volatility but still show the same effects of bleaching (low alkalis and Al, high Cl) as are seen in the unequilibrated ordinary chondrites.

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TABLE 3. Ion microprobe results for major, minor, and trace elements in bleached chondrule Semarkona 1805-7-7.*

| | Zone[†] | Dist[‡] ($\mu$m) | $H_2O$ (ppm) | F (ppm) | $Na_2O$ (wt%) | MgO (wt%) | $Al_2O_3$ (wt%) | $SiO_2$[§] (wt%) | Cl (ppm) | $K_2O$ (wt%) | CaO (wt%) | $TiO_2$ (wt%) | $Cr_2O_3$ (wt%) | MnO (wt%) | FeO (wt%) | Rb (ppm) | Sr (ppm) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | Core | −130 | 948 | 11.2 | 0.94 | 22.1 | 1.68 | 56 | 25 | 0.10 | 1.78 | 0.005 | 0.76 | 0.68 | 18.6 | 2.5 | 8.4 |
| B | Core | −120 | 1002 | 16.5 | 0.78 | 21.4 | 1.83 | 56 | 67 | 0.13 | 1.68 | 0.10 | 0.76 | 0.67 | 14.9 | 3.3 | 8.7 |
| C | Core | −60 | 973 | 14.3 | 0.67 | 21.6 | 1.73 | 56 | 22 | 0.11 | 1.66 | 0.10 | 0.76 | 0.67 | 15.3 | 2.9 | 6.8 |
| D | Core | −40 | 853 | 9.1 | 0.65 | 21.5 | 1.80 | 56 | 20 | 0.11 | 1.63 | 0.10 | 0.74 | 0.67 | 14.4 | 3.0 | 5.9 |
| E | Core | −15 | 815 | 9.3 | 0.75 | 22.1 | 1.73 | 56 | 11 | 0.10 | 1.69 | 0.10 | 0.74 | 0.68 | 16.7 | 2.5 | 5.8 |
| F | BZ/OZ | 15 | 2802 | 18.0 | 1.55 | 20.3 | 1.61 | 53 | 2210 | 0.10 | 1.95 | 0.10 | 0.69 | 0.62 | 14.1 | 4.3 | 3.3 |
| G | BZ/OZ | 25 | 3199 | 148.6 | 0.69 | 23.5 | 1.51 | 53 | 120 | 0.07 | 1.84 | 0.11 | 0.78 | 0.70 | 16.4 | 3.6 | 2.6 |

*Spot diameter = ~20 $\mu$m.
[†]Abbreviations: BZ = bleached zone, OZ = outer zone. Slashes indicate overlap.
[‡]Approximate distance from core–bleached-zone boundary. Negative values are in core; positive values are in bleached zone.
[§]Value was taken from electron microprobe data and used for normalization of ion probe data.

chondrule core, it was surprising to find a factor of 2 variation in water content.

All but one of the points analyzed in the bleached and outer zones of Semarkona 1805-7-7 show greatly elevated $H_2O$ contents, ranging from 3.6 to 13× core concentrations. The one exception to this, point 7, probably overlapped both bleached zone and core material. The $\delta$D varies greatly in the bleached and outer zones (+316 to +869‰), with the lowest value occurring in the point that overlapped matrix material outside the chondrule. In these points, there is no relationship between $\delta$D and $H_2O$ concentration, and $H_2O$ increases with distance from the core–bleached-zone boundary (Table 4). Both $\delta$D and $H_2O$ contents fall in or near the ranges measured for Semarkona matrix by Deloule and Robert (1995) (Fig. 8).

Our H-isotopic results on the Semarkona bleached chondrule are consistent with the bulk-chondrule H measurements reported by Sears *et al.* (1995a). Taking the average $H_2O$ and $\delta$D contents for the core and outer zones of Semarkona 1805-7-7 (Table 4) and weighting them 2:1 in favor of the core fraction gives a bulk $H_2O$ content of 2100 ppm and $\delta$D = +615‰. Sears *et al.* (1995a) measured two radial pyroxene or cryptocrystalline chondrules in Semarkona (their numbers 9 and 46), although it is not known whether they were bleached. For water released at high temperature,

they found $H_2O$ contents of <3800 and 2100 ppm, and $\delta$D of +740 and +2000‰ (with 70–100% uncertainties), respectively. These values overlap comfortably with our measurements and are significantly lower in $\delta$D than porphyritic chondrules also measured in the Sears study.

Deloule and Robert (1995) found that both $\delta$D and H concentration of Semarkona matrix increased as they made successive analyses of a single point, with $\delta$D rising from near-terrestrial values up to +3500‰ after the beam had penetrated a few micrometers into the sample. We made a similar measurement on Semarkona matrix. Our measurements also showed a gradual rise of $\delta$D from near +500 up to +1300‰, although the amount of H released stayed fairly constant.

**Mineralogy**– Transmission electron microscopic analyses were carried out on a bleached radial pyroxene chondrule from Semarkona, number 1805-5x-2 (the chondrule is shown in Fig. 4b). Although this object is a chondrule fragment, a portion of the original surface could be identified. The core of the chondrule has a fresh, igneous texture. The principal phases are low-Ca pyroxene and glass showing no signs of devitrification or chemical breakdown

TABLE 4. Ion microprobe results for H and H isotopes in Semarkona chondrule 1805-7-7.*

| Name | Zone[†] | Dist[‡] ($\mu$m) | $H_2O$ (ppm) | $\delta$D (‰) |
|---|---|---|---|---|
| Core1 | Core | −50 | 984 | 885 ± 76 |
| 0 | Core | −100 | 1125 | 797 ± 53 |
| 1 | Core | −85 | 823 | 983 ± 62 |
| 2 | Core | −70 | 660 | 1046 ± 77 |
| 3 | Core | −55 | 881 | 745 ± 72 |
| 4 | Core | −40 | 1221 | 506 ± 44 |
| 5 | Core | −25 | 557 | 1185 ± 116 |
| 6 | Core | −10 | 872 | 592 ± 66 |
| 7 | BZ/OZ | 10 | 1155 | 538 ± 58 |
| 8[§] | OZ | 25 | 3252 | 455 ± 28 |
| 9 | OZ/Mx | 45 | 9547 | 316 ± 16 |
| BZ1 | BZ | 40 | 6300 | 869 ± 22 |
| BZ2 | BZ/OZ | 70 | 11890 | 528 ± 18 |
| BZ3 | BZ | 40 | 4545 | 600 ± 28 |

*Spot diameter = ~20 $\mu$m.
[†]Abbreviations: BZ = bleached zone, OZ = outer zone, Mx = opaque matrix outside chondrule. Slashes indicate overlap.
[‡]Distance from core–bleached-zone boundary. Negative values are in core; positive values are in bleached zone.
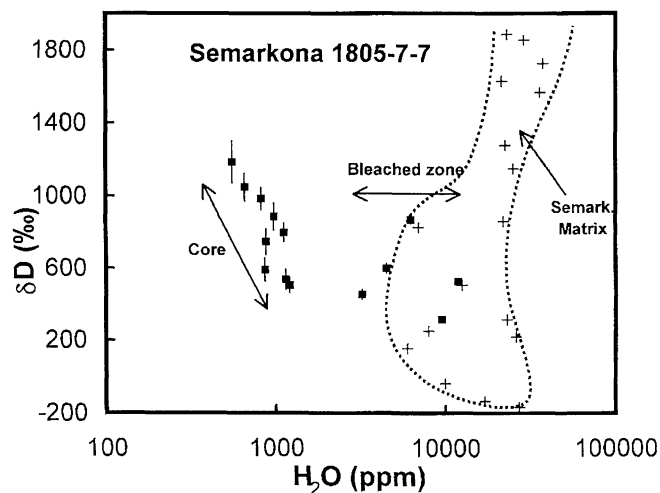[§]Same as point G in Table 3.



FIG. 8. Results for H measured by ion microprobe in a bleached Semarkona chondrule. The $\delta$D (in ‰ relative to SMOW) anticorrelates with the measured H concentration (expressed as $H_2O$) for analyses in the unbleached core of the chondrule. Analyses of the bleached zone have similar $H_2O$ contents and isotopic compositions as some measurements of Semarkona matrix by Deloule and Robert (1995) (shown as + symbols). The entire chondrule, including the core, was probably enriched in deuterium during aqueous alteration. Contamination by terrestrial water during thin-section preparation may be responsible for the low-$\delta$D–high-$H_2O$ values in the most porous, smectite rich areas of the chondrule (see text).
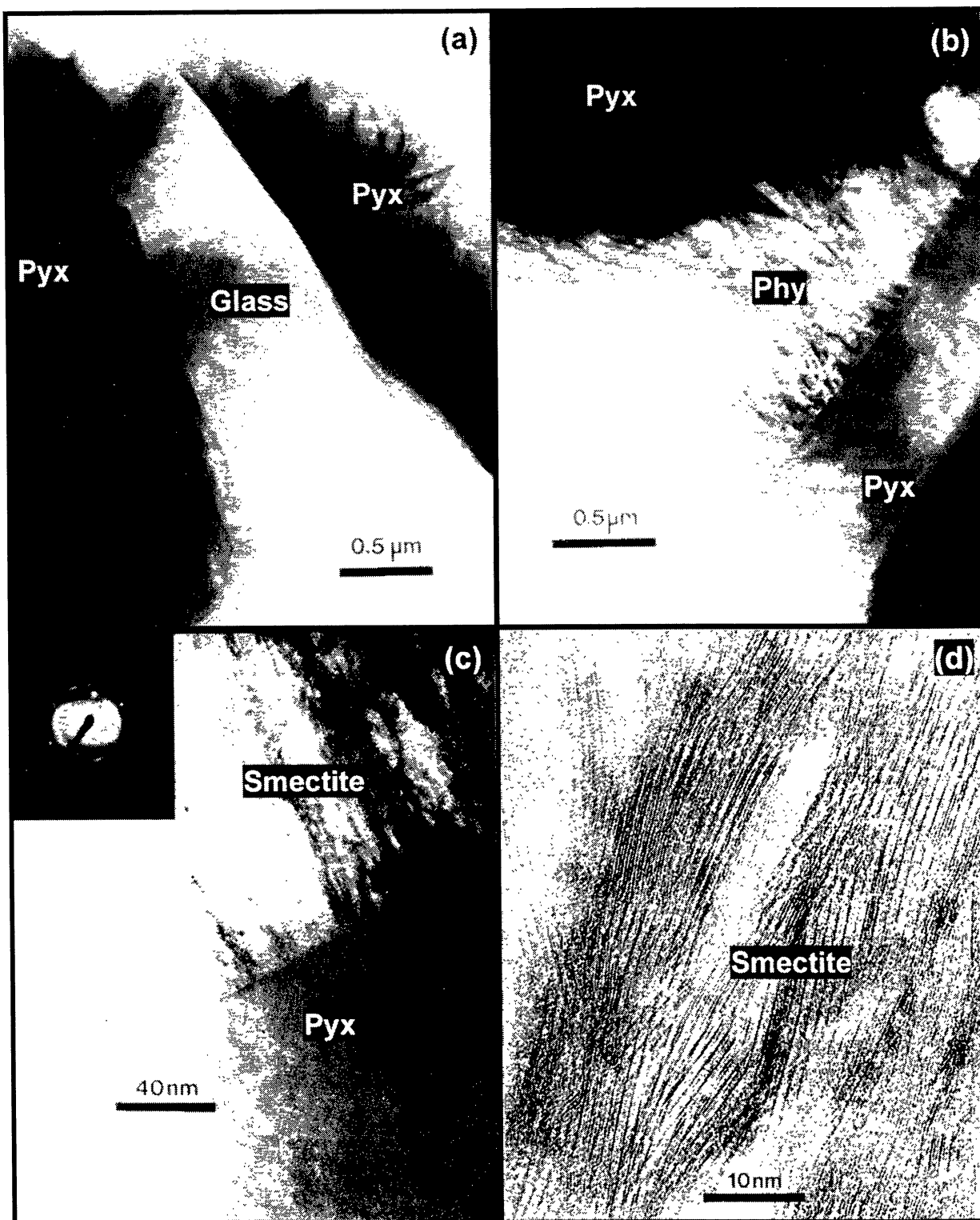
FIG. 9. Bright-field transmission electron micrographs of the microstructures present within the bleached, radial pyroxene chondrule in Semarkona. (a) Region in the interior of the chondrule showing pristine, unaltered, interstitial chondrule glass adjacent to two pyroxene grains (Pyx). (b) Region in the exterior, bleached zone of the chondrule consisting of fine-grained phyllosilicates (smectite) that has replaced glass. (c) Higher magnification image of the interface region between the pyroxene (Pyx) and the smectite. Individual smectite crystals appear to have nucleated and grown approximately normal to the original pyroxene–glass interface. This is also indicated in the inset electron diffraction pattern from across the interface that shows a strong diffraction arc from the (001) plane of the smectite that reflects the preferred orientation of the grains. Replacement of the pyroxene by the smectite appears to have been minimal. (d) High-resolution TEM image of smectite microcrystallites that have replaced the glass phase. The smectite crystallites have characteristic curved and straight morphologies and locally the lattice planes show undulations, probably indicative of loss of interlayer water in the vacuum of the TEM.

(Fig. 9a) as indicated by both high-resolution imaging and selected area electron diffraction (SAED) patterns. The SAED show broad diffuse rings typical of an amorphous material such as a glass, with no evidence of any sharp diffraction maxima that might be indicative of alteration phases or microcrystalline devitrification products. Small amounts of troilite are also present. Energy dispersive x-ray spectra confirm that most of the Na and Al in the chondrule are in the glass, as would normally be expected.

In contrast, the bleached zone of Semarkona 1805-5x-2 contains abundant phyllosilicates between the crystals of low-Ca pyroxene (Fig. 9b). No glass was found; although given the small area that was examined, we cannot rule out its presence. The phyllosilicates have a platy appearance and are extremely fine grained, averaging ~10 nm in thickness and 60–70 nm in length. The phyllosilicates appear to have grown in place, with their basal (001) planes oriented normal to the original pyroxene–glass grain boundary (Fig. 9c). This microstructure suggests that alteration commenced at the interface between glass and pyroxene, where the phyllosilicates nucleated. High-resolution TEM imaging shows that the phyllosilicates often show curved (001) lattice spacings and have somewhat variable basal spacings between ~0.98 nm and 1.1 nm, which is consistent with smectite. No evidence of interlayering of other layer lattice phases within the smectite was detected. The morphology and microstructure of this smectite appear to be essentially identical to the characteristics of smectite that has been described by Alexander *et al.* (1989) in Semarkona matrix (Fig. 9d). Quantitative energy dispersive spectrometric (EDS) analyses of the smectite that occurs within the bleached zones show that it is FeO-rich (28–32 wt% FeO) and contains ~4 wt% $Na_2O$ and ~8 wt% $Al_2O_3$. No Cl was detected in any of our analyses. Compositionally, it is remarkably similar to smectite in Semarkona matrix reported by Alexander *et al.* (1989) and measured in this study (Table 2). The main difference observed is that the $Al_2O_3$ content of the smectite in the bleached zones is higher (8–9 wt%) than matrix smectite (5–6 wt%). We attribute this difference to the fact that smectite in the bleached zone replaced chondrule glass which has a higher Al content than matrix.

In addition to the smectite, sulfide grains were detected in the bleached zones. In all cases, these grains were identified by electron diffraction and energy-dispersive x-ray spectra as pentlandite, not troilite, as was found in the chondrule core.

### Chemical and Mineralogical Properties of Bleached Chondrules in Metamorphosed Ordinary Chondrites

Detailed x-ray maps (1 $\mu$m pixel size) and microprobe traverses were prepared for bleached chondrules in a cross section of ordinary chondrites more metamorphosed than Semarkona, including Krymka (LL3.0), Bishunpur (LL3.1), Chainpur (LL3.4), Dhajala (H3.8), Bjurböle (L/LL4), Soko-Banja (LL4), and EET 96080 (L6) to see what effect thermal metamorphism had on the properties of these chondrules. The key features seen in bleached chondrules in Semarkona (*e.g.*, Fig. 5) are preserved across the entire metamorphic sequence (*i.e.*, there are always strong depletions in Na and Al in bleached zones).

Microprobe traverses across the bleached chondrules in Chainpur (LL3.4) and Dhajala (H3.8) show smooth, nearly monotonic changes of several elements with distance from the surface of the chondrule. In Chainpur, Fe is the only element that shows radial zonation: FeO content decreases from ~24 wt% at the chondrule rim to a uniform core value of ~14 wt% 350 $\mu$m into the chondrule (interior to the bleached zone) (Fig. 6c). In Dhajala, virtually every

element is radially zoned, with Mg decreasing, and Na, Al, Si, K, Ca, Cr, Mn, and FeO increasing from rim to core; but in this case, most of the changes take place across the bleached zone (Fig. 6d). There is no sign of this type of zoning in the chondrules from type-4 chondrites.

In bleached chondrules from unequilibrated ordinary chondrites, elemental abundance patterns are generally smoothest in chondrule cores, and most irregular in bleached zones (Fig. 7a–e). For example, Ca/Al ratios are nearly solar in all of the chondrule cores and significantly above solar in the bleached zones. Ratios of Na/K also tend to be closest to the solar value in cores but deviate the most from solar in bleached zones. Alkali abundances are closer to those of elements of similar volatility in the cores than in the bleached zones.

By petrologic type 4, all signs of the Mn enrichments seen in radial pyroxene and cryptocrystalline chondrules from unequilibrated ordinary chondrites are gone (Fig. 7f–h). Two of the three measured chondrules have nonsolar Ca/Al, even in their cores. Nevertheless, as was the case in the unequilibrated ordinary chondrites, the abundance patterns in the cores are overall much smoother than in the bleached zones.

There are other differences between bleached chondrules in Semarkona and in the more metamorphosed ordinary chondrites. Some of these are seen in x-ray maps of Ca (Fig. 10) and Na (Fig. 11). In Semarkona, Ca concentrations do not show much variation across bleached chondrules (Figs. 6a,b and 7a,b). However, very similar chondrules in Krymka, Chainpur, and Dhajala have a thin zone at or just inward of the core–bleached-zone contact where Ca is significantly enriched (Fig. 10a,b; Dhajala not shown). This zone appears wispy, with ill-defined edges in the x-ray maps. Microprobe traverses across the Chainpur and Dhajala chondrules show that Ca is enriched in this zone approximately 30–50% over core values (Fig. 6c,d; averages shown in Table 2). In the Chainpur chondrule, Al is also elevated by ~30% in the Ca-rich zone. No new phases could be identified in these Ca-rich zones using optical microscopy or backscattered electron imaging.

In bleached chondrules in type-4 chondrites (*e.g.*, Bjurböle, Fig. 10c) and in the one type-6 chondrite measured (EET 96080, Fig. 10d), Ca-rich zones can also be observed; but in these cases, abundant Ca-rich pyroxene grains are present. In these chondrites, the Ca-rich zones significantly overlap the bleached zone and are not as well defined as they are in type-3 chondrites.

The Na x-ray map of the bleached chondrule in Krymka (Fig. 11a) shows a wispy Na-rich zone very similar in position and morphology to the Ca-rich zone in the same chondrule, although on average it is somewhat closer to the core–bleached-zone boundary. This feature was not observed in any of the more metamorphosed ordinary chondrites (Fig. 11b–d), nor in Semarkona. However, in Bjurböle and EET 96080 (as well as Soko-Banja), small grains of plagioclase are abundant in the bleached zones (Fig. 11c,d), similar in size and distribution to the small grains of Ca-pyroxene.

### DISCUSSION

### The Origin of Bleached Chondrules in Highly Unequilibrated Chondrites

Our results on Semarkona support the ideas of Kurat (1969), Christophe Michel-Lévy (1976), and Skinner *et al.* (1989), who all concluded from petrographic observations of bleached chondrules that they formed when water dissolved some of the primary chondrule glass. The physical properties we observe are certainly
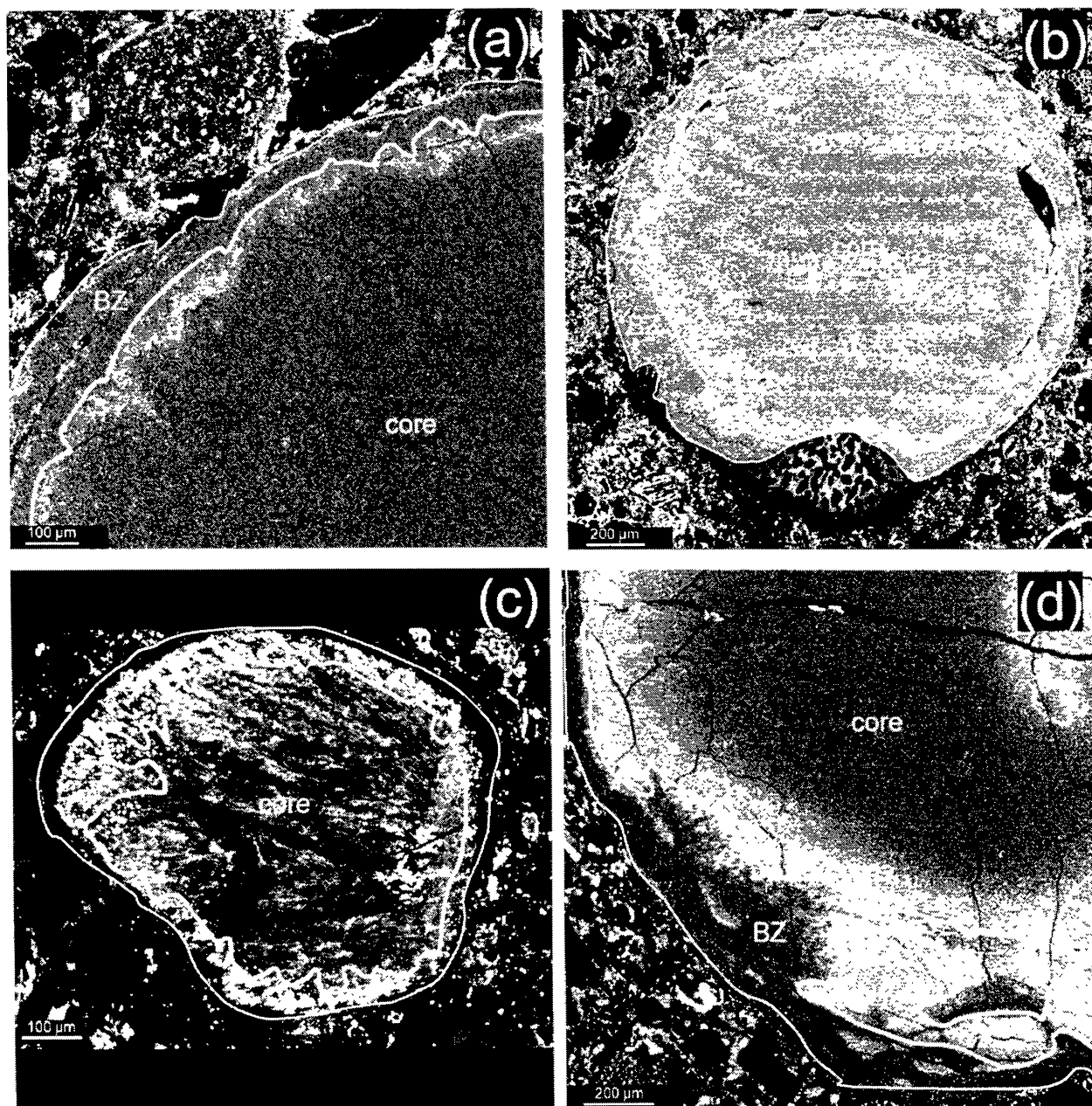
FIG. 10. Calcium x-ray maps of bleached chondrules showing Ca enrichments at or below the contact between the bleached zone (BZ) and core. (a) One quarter of a chondrule in Krymka (LL3.0). A wispy zone with a high concentration of Ca is developed in the unbleached core. No secondary minerals can be seen in this zone at the resolution of a scanning electron microscope. (b) A bleached chondrule in Chainpur (LL3.4), again showing a diffuse, Ca-rich zone in the outer part of the core. (c) A bleached cryptocrystalline chondrule in Bjurböle, with abundant secondary Ca-rich pyroxene grains developed in the outer part of the core and the inner part of the bleached zone. This chondrule may once have resembled the Krymka and Chainpur chondrules but now has a much more Ca-rich zone. (d) One-quarter of a bleached cryptocrystalline chondrule in EET 96080 (L6). The Ca-rich zone in this chondrule more closely resembles that seen in the unequilibrated ordinary chondrites than the type-4 chondrule in (c). Note that the Ca-enrichment effect in the core of this chondrule extends up to 300 $\mu$m below the bleached zone, which is much thicker than that seen in the unequilibrated ordinary chondrites.

consistent with chemical attack from outside the chondrules (*i.e.*, bleached zones occur exclusively at or near the chondrule surfaces and follow along cracks). We can rule out the possibility that the bleaching process happened after the meteorite's arrival on Earth. Bleached chondrules can be observed in hand specimens of fresh falls like Semarkona (Fig. 3); therefore, they cannot be artifacts of thin-section preparation in the laboratory. The occurrence of broken bleached chondrules in Bishunpur (*e.g.*, Fig. 4c) shows that, in some cases, bleaching predated the final lithification of the meteorite.

Indeed, the broken Semarkona chondrule shown in Fig. 4b appears to have experienced bleaching both before and after the event that caused the two halves to become slightly offset from each other. This is good evidence that bleaching was an asteroidal process that accompanied brecciation, perhaps in regoliths. Given all of this evidence, the best explanation for a case such as that shown in Fig. 4a, where the bleached zone is thick adjacent to the chondrule–matrix interface and thin-to-nonexistent where the chondrule impinges on a second chondrule, is that a fluid phase responsible for bleaching was
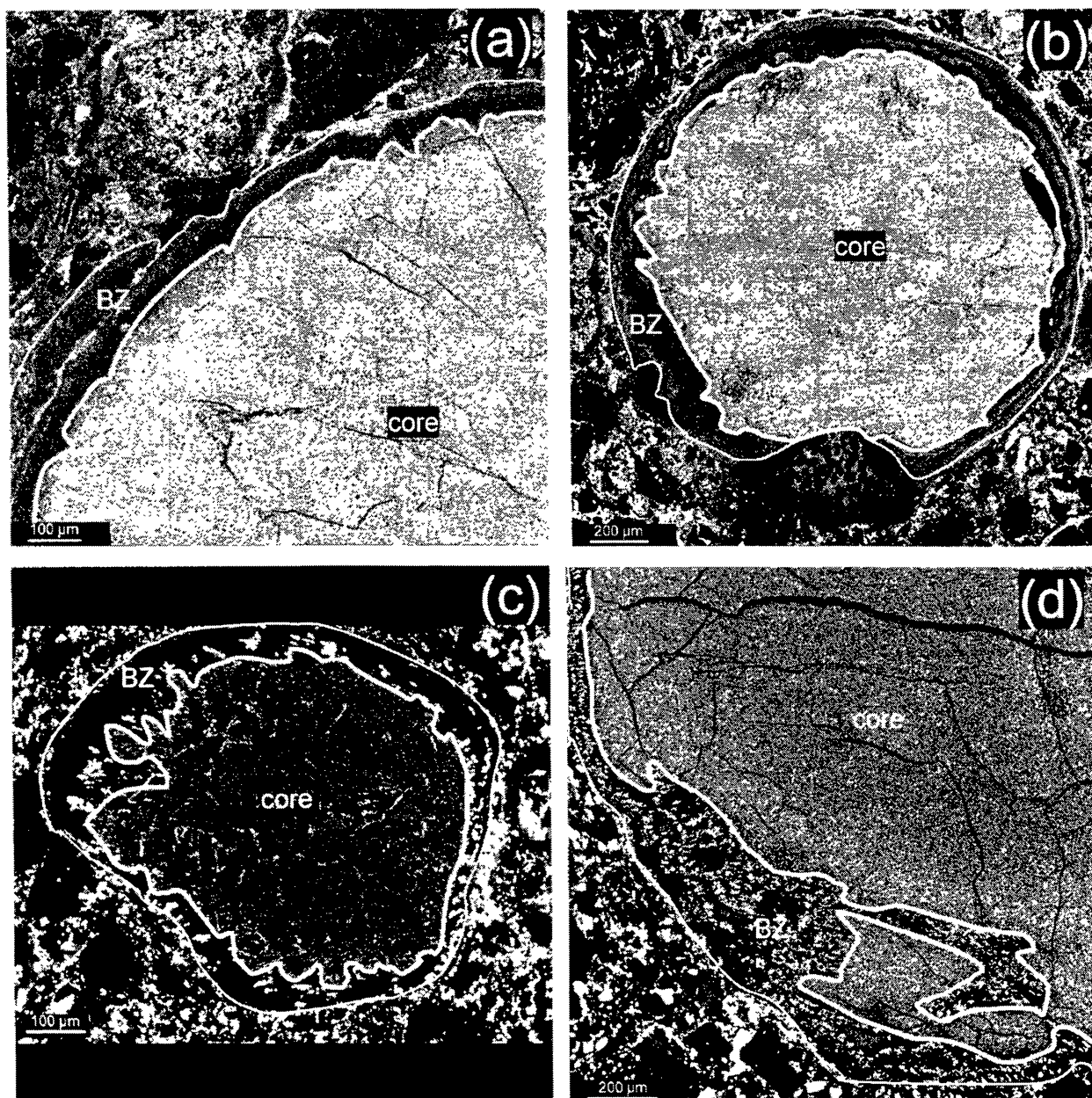
FIG. 11. Sodium x-ray maps of the same chondrules shown in Fig. 10. The Krymka chondrule (a) has a wispy Na-rich zone that approximately coincides with the Ca-rich zone shown in Fig. 10a. However, there is no sign of a Na-rich zone in the more metamorphosed bleached chondrules in Chainpur (b), Bjurböle (c), or EET 96080 (d). The types 4–6 chondrites show the development of metamorphic feldspar, growing preferentially in the bleached zones.

following pathways through the porous, fine-grained matrix at least up until the time that brecciation ceased.

The bleached zones in Semarkona chondrules consist mostly of unaltered low-Ca pyroxene with void space plus some alteration products between the crystals. Our normative compositional data support the idea that feldspathic mesostasis once filled these voids rather than some other phase such as metal, sulfide, or mafic silicates. About half of the mesostasis was removed from the bleached zones, resulting in ~50% losses of Na, K, Al, and Sr from the chondrule (Sr has been shown to be concentrated in chondrule glass by Alexander, 1994). The TEM data reveal the presence of hydrous alteration products (smectite) in the bleached zones that likely grew *in situ* during aqueous alteration of glass (Fig. 9). The

ubiquitous presence of phyllosilicates in bleached zones is supported by ion microprobe data indicating high concentrations of $H_2O$ (Fig. 8). Such relatively Fe-rich alteration products also probably cause the brownish color observed in many bleached zones. It is conceivable that some matrix material from outside preexisting bleached chondrules could have filled void spaces in bleached zones *via* mechanical processes during compaction. This is ruled out by the compositional difference between smectite in a bleached chondrule and in the matrix of Semarkona (Table 2) and would be unlikely anyway because of the fine-grained nature of radial pyroxene and cryptocrystalline chondrules. It is much more likely that the bleaching process involved the aqueous dissolution of part of the glass and the alteration of all or part of the remainder to form

phyllosilicates. The high-Al content of smectite in the bleached zone most likely resulted from its direct formation from Al-rich chondrule glass, in contrast to matrix smectite, which almost certainly formed in a lower Al environment. The conditions under which aqueous processing occurred were too mild to alter the low-Ca pyroxene adjacent to the glass that was affected by bleaching. Similar conditions existed in CM chondrites during their period of aqueous alteration (*e.g.*, Zolensky *et al.*, 1993). On the basis of the calculations of Alexander *et al.* (1989), the temperature of alteration did not exceed 260 °C and, based on comparisons with the mineral assemblages in altered carbonaceous chondrites, may well have been less than 100 °C (Zolensky *et al.*, 1993). Although low-Ca pyroxene remained unaltered, low-temperature sulfides (pentlandite) did form in the bleached zones, presumably by alteration of troilite, which in CM chondrites is clearly much more susceptible to alteration than low-Ca pyroxene. The unbleached cores of radial pyroxene and cryptocrystalline chondrules contain virtually no Ni-bearing phases, like metal. Therefore, the aqueous fluid must have transported Ni into the chondrules from elsewhere in the meteorite (we did not analyze for Ni by microprobe). The Fe in the smectite may also have been introduced during alteration, as chondrule glass is generally depleted in this element. Similarly, the excess halogens and Rb measured by ion microprobe in bleached zones (Table 3) may have been transported into chondrules by the fluid. Aqueous alteration in Semarkona thus modified chondrules both by removal of chemical components (Na, K, Al, Sr, and Si) and introduction of new ones ($H_2O$, halogens, Fe, Ni, and possibly Rb).

We had hoped to constrain the nature of the fluid phase that caused chondrule bleaching by using H-isotopic data; however, our results are ambiguous. Both Deloule and Robert (1995) and we found that sequential ion microprobe analyses of small areas of Semarkona matrix detected progressively higher $\delta D$ as the beam penetrated the sample. One explanation for this might be that a late-stage isotopically light fluid reacted with the matrix. But given the strong relationship between $\delta D$ and depth below the surface, a much better interpretation of these results is that terrestrial water has exchanged with phyllosilicates on the exposed surfaces of matrix, either during thin-section preparation or simply by exposure to the atmosphere. The true isotopic composition of smectite in Semarkona matrix may be near that of the latest released H in the sequential analyses (*i.e.*, over +3000‰), which would be in agreement with the measurement of +2670 ± 520‰ on separated matrix samples by Sears *et al.* (1995a). The bleached zones that we measured resemble matrix in that they are porous and rich in smectite (Alexander *et al.*, 1989). They too were probably contaminated by terrestrial water, and their true $\delta D$ is probably higher than that shown in Fig. 8. These results shed little light on the question of whether the water responsible for bleaching chondrules first flowed through and equilibrated with matrix, as we expect it would have done.

The inverse correlation observed between $\delta D$ and $H_2O$ content in the cores of bleached chondrules (Fig. 8) may also be explained by contamination by terrestrial water. Although the simplest explanation for this trend might appear to be two-component mixing between an isotopically heavy, low-$H_2O$ chondrule core and a late-stage isotopically light fluid, we think this is unlikely. Radial pyroxene and cryptocrystalline chondrules formed as completely molten droplets and are unlikely to retain even our minimum measured value of 600 ppm $H_2O$ after they crystallized. It is quite possible that glass in the chondrule core became hydrated during the aqueous alteration event that created the bleached zone, presumably giving it an isotopic composition resembling matrix (high $\delta D$). The

most porous, highly fractured areas of the chondrule core were probably more susceptible to exchange and reaction with terrestrial water than were the more compact areas. Additional experiments involving repeated analyses of single areas in bleached chondrules will have to be done to prove this explanation.

If bleached chondrules did form by aqueous alteration on the parent asteroid, then why do no porphyritic chondrules show this effect? The answer is probably that some do, but because porphyritic chondrules are so much coarser grained than radial pyroxene and especially cryptocrystalline chondrules, the alteration does not manifest itself as a uniformly bleached outer zone. We expect that fluids flowed through chondrites by moving along cracks and grain boundaries. These are most abundant in matrix, rims, and very fine-grained chondrules; so the effects of light aqueous alteration should be most prominent in these locations. Porphyritic chondrules, however, likely had fewer pathways leading into them, and areas of glass that were accessible to fluids tended to be much larger than in nonporphyritic chondrules. Thus alteration effects are likely to be more inhomogeneously distributed in porphyritic chondrules, albeit they would tend to be concentrated in the outer zones. It is also possible that alteration effects resembling bleaching would be less common in porphyritic chondrules because their glass compositions are different. Low-FeO porphyritic chondrules commonly have anorthitic glass, and high-FeO porphyritic chondrule mesostasis tends to have 60–80 wt% normative quartz in highly unequilibrated ordinary chondrites (Sears *et al.*, 1995b); whereas glass in radial pyroxene and cryptocrystalline chondrules generally contains >40 wt% normative albite (our normative compositions; Gooding, 1979; Rubin and Pernicka, 1989; Grossman *et al.*, 1985; see also discussion below). This contrast could lead to different degrees or styles of alteration in the various chondrule types.

There are several reports in the literature of alteration effects in porphyritic chondrules that could be equivalent to the bleaching effects we describe in radial pyroxene and cryptocrystalline chondrules. Hutchison *et al.* (1998) described areas of "blocky" mesostasis in Tieschitz (*e.g.*, their Fig. 3b), characterized by abundant voids and cracks between mafic dendrites that would otherwise be surrounded by glass. Perhaps not coincidentally, fresh glass in the two chondrules for which this alteration was described is rich in normative albite, similar to that in radial pyroxene and cryptocrystalline chondrules. They suggested that blocky mesostasis was formed at an inter-mediate stage in the leaching (bleaching) process described first by Kurat (1969). Bridges *et al.* (1997) reported on chondrules in Chainpur that contain evidence for entry of alkalis and Cl by metasomatic processes. A variety of textural types are represented in this study, including porphyritic and very coarse-grained radial pyroxene chondrules. Altered mesostases in these chondrules contain Na- and Cl-rich phases. (The authors did not report the composition of unaltered mesostasis, if it was present.) Although these chondrules are not concentrically zoned and appear to have undergone Na addition rather than removal, both they and bleached chondrules share in having experienced destruction of mesostasis (our interpretation), enrichment of Cl and, perhaps, Rb. Bridges *et al.* (1997) preferred to explain alkali and Cl enrichment as a high-temperature process accompanying crystallization. We think that a more plausible explanation might include aqueous processes similar to those that caused bleaching. Clearly, much additional petrologic and experimental work needs to be done to correlate mesostasis composition with alteration effects (especially in very low petrologic-type ordinary chondrites) in order to understand the relationships between alteration in the various chondrule types.

## The Origin of Bleached Chondrules in Metamorphosed Chondrites

**The Relative Timing of Bleaching and Metamorphism**—The bleached chondrules in metamorphosed ordinary chondrites are so similar to those in Semarkona in their textural properties and compositional zoning profiles that one must conclude they share a common origin by aqueous alteration. It seems very unlikely that a second, unrelated process affecting only more equilibrated meteorites could produce the same types of sharply delineated, Na- and Al-poor, porous zones, 100–200 $\mu$m thick that occur in Semarkona. If they did form by aqueous alteration, did this happen before, during, or after metamorphism?

There are several reasons to believe that the aqueous alteration that formed bleached chondrules happened before mineralogical and textural equilibration in metamorphosed chondrites. First, the bleached zones in high petrologic-type chondrites contain abundant, relatively coarse-grained secondary anhydrous minerals known to form during metamorphism. Plagioclase and pyroxene grains in bleached zones attain sizes comparable to those in the interchondrule material (which was once opaque matrix) of the same meteorites, whereas minerals in the chondrule cores remain more fine-grained after metamorphism. Abundant pore space present after bleaching would likely have provided a favorable location for the growth of new minerals and for the coarsening of existing minerals. If bleaching occurred after metamorphism, one would not expect to find the observed relationship between the depth to which feldspathic material was removed and the locations of metamorphic minerals, especially because one of the metamorphic minerals (plagioclase) contains the very components that are removed during bleaching. A second reason to believe that bleaching predated metamorphism has to do with the existence of the Ca-rich zones. These zones clearly become coarser during metamorphism (see below), and their location is controlled by the bleached-zone–core boundary (Fig. 10). For this to be true, bleaching had to predate metamorphism. Third, after metamorphism, all of the glass in chondrules has been converted to crystalline feldspar. Feldspar is more resistant to alteration than glass (*e.g.*, Banfield *et al.*, 1991; Bignall *et al.*, 1996), and the alteration conditions necessary to produce bleached chondrules in metamorphosed meteorites would need to be considerably harsher than in the unequilibrated ordinary chondrites. Indeed, one would expect that under the conditions needed to alter feldspar, olivine would also be greatly affected. However, metamorphosed ordinary chondrites contain much less $H_2O$ than do the unequilibrated ordinary chondrites (*e.g.*, LL3 chondrites contain 3× more $H_2O$ than LL4–6; Jarosewich, 1990) and are not known to contain phyllosilicates or other hydrated minerals. (We recognize that the discovery of aqueous fluid inclusions in easily destroyed salt crystals in some equilibrated chondrites by Zolensky *et al.*, 1999a,b, makes these measurements less certain, but it seems probable that the total amount of water in this form that might have been lost prior to Jarosewich's analyses would be quite small.) From this and the information presented in the preceding section, we conclude that aqueous alteration was a common process experienced by most ordinary chondrite material prior to the onset of metamorphism.

The low abundances of bleached chondrules in types 4–6 ordinary chondrites compared to those in unequilibrated ordinary chondrites are probably because of the obliteration of fine-grained chondrules during metamorphism. We observed that the abundance of cryptocrystalline chondrules becomes lower with increasing metamorphic grade. There is no reason to expect there to have been a different primary abundance of these chondrules among the materials that accreted to form the different metamorphic grades of ordinary chondrites. We assume that as grains coarsened and chondrule borders were obscured during metamorphism, fine-grained chondrules were preferentially integrated into the matrix, becoming less identifiable in thin sections. It is also possible that some of the properties that enable us to optically identify bleached chondrules are obscured by metamorphism. Although we did not attempt to quantify these effects (it would require searching thousands of thin sections), it seems plausible that the percentage of surviving, still-identifiable cryptocrystalline chondrules that are bleached is similar in types 4–6 ordinary chondrites and in unequilibrated ordinary chondrites, and therefore that the premetamorphic abundances were also similar.

**The Origin of Calcium-rich Zones**—Calcium-rich zones are absent in Semarkona, diffuse and fine-grained in Krymka and Chainpur, and become coarser with increasing metamorphic grade (Fig. 10). This sequence suggests that the formation of these zones is entirely a metamorphic effect. With increasing thermal metamorphism in unequilibrated ordinary chondrites, the compositions of chondrule mesostases gradually change as feldspar crystallizes from glass and equilibrates between different chondrules (*e.g.*, Sears *et al.*, 1995a). The normative compositions of the radial pyroxene and crypto-crystalline chondrules studied here show that they have albitic mesostases that would tend to gain Ca during thermal metamorphism and feldspar growth because of equilibration with more calcic feldspar in, for example, low-FeO porphyritic chondrules. The very finely disseminated glass in cryptocrystalline chondrules in highly unequilibrated ordinary chondrites would have been among the earliest nonmatrix materials to begin to equilibrate at the onset of metamorphism because of the presence of myriad grain boundaries with surrounding pyroxene. The fact that Dhajala has broader Ca-rich zones in its bleached chondrules is consistent with this metamorphic model because it was heated to higher temperatures. In contrast, Semarkona may not have experienced high enough metamorphic temperatures to produce these zones. One problem with this explanation is that bleached chondrules in types 4–6 chondrites still preserve Ca-rich zones in their outer regions, whereas the feldspar in these chondrules is certainly homogeneous by petrologic type 6. In metamorphosed meteorites, the Ca-rich zones can only reflect higher modal abundances of phases like Ca-rich pyroxene, not different compositions of phases.

Alternatively, the lack of Ca-rich zones in bleached Semarkona chondrules could be indicative of different alteration pathways in the various unequilibrated ordinary chondrites. For example, the smectite in Semarkona is Na-rich and Ca-poor (Alexander *et al.*, 1989); the Ca precipitated from the fluid as calcite in the fine-grained matrix (Hutchison *et al.*, 1987). Calcite has not been described in Krymka or Chainpur, and Bishunpur is known to contain a small amount of smectite that is Ca-rich (Alexander *et al.*, 1989). Calcium-rich zones may not have formed in Semarkona because calcite provided a good mineralogical sink for Ca liberated during alteration. In Krymka, Chainpur, and other meteorites that seemingly did not form appreciable calcite, excess Ca may have ultimately diffused into nearby chondrule mesostasis or even formed extremely fine-grained, Ca-rich pyroxene. With any dissipation of aqueous fluids during heating, this process of Ca diffusion could cease at relatively low metamorphic grades, allowing the preservation of Ca-rich zones in high-petrologic-type chondrites.

Neither one of these models for the formation of Ca-rich zones can easily explain all of our compositional observations. For example, the Krymka chondrule shown in Figs. 10 and 11 has a wispy Na-rich zone adjacent to and partly overlapping the Ca-rich zone, although the magnitude of the Na enrichment must be small compared to that of Ca. Metamorphism would not enrich both elements simultaneously during the equilibration of feldspar, and alteration products such as smectite can accommodate a large amount of Na. One way to explain the relationship between Na and Ca could be that the modal abundance of feldspar increases just below the bleached zone. But why this would happen in either of the above scenarios is not obvious.

**Other Metamorphic Effects**–Whether or not Ca-rich zones are products of the early stages of thermal metamorphism, some of the compositional properties of bleached chondrules clearly are. In Dhajala (H3.8), many elements, including Fe, are zoned in the outer portions of bleached chondrules (Fig. 6d). These chondrules show FeO depletions in their outer regions, with FeO/(FeO + MgO) molar ratios (*ffm*, expressed in percent) falling from ~30 to ~17 going from core to the extreme outer rim (Table 2 shows averages for each zone). Thus, pyroxene near the surfaces of these chondrules has reached the equilibrium *ffm* value for H-group chondrites of 16–18 (Brearley and Jones, 1998). Similarly, the core-to-rim zoning of MnO (falling from ~0.7 to 0.5 wt%) and $Cr_2O_3$ (falling from 0.6 to 0.2 wt%) in the Dhajala chondrules represents an approach to the equilibrium H-chondrite values of ~0.4 and 0.2 wt% for these oxides in low-Ca pyroxene, respectively (Brearley and Jones, 1998). The cores of cryptocrystalline chondrules in Dhajala are virtually identical to those in Semarkona (Table 2), whereas their rims have the composition of equilibrated H chondrites (minus components lost during bleaching such as Na and Al).

Chainpur and Semarkona, which are much less metamorphosed than Dhajala, have bleached chondrules showing a distinct enrichment of FeO in their outer and bleached zones (Fig. 6a,c). Semarkona chondrule 1805-7-7 and Chainpur chondrule 1251-18-1 have bulk *ffm* ratios that rise from ~25 in the cores to ~30 in the outer zones (Table 2). This zonation is in the direction that would be expected if all the FeO is in the pyroxene, and if this mineral began to equilibrate with the surrounding matrix (opaque matrix in Semarkona and Chainpur have bulk *ffm* of ~50; Huss *et al.*, 1981). Despite this, thermal metamorphism may not have caused these FeO increases. The porous bleached zones in the affected chondrules are brownish in transmitted light; in Semarkona and perhaps Chainpur, this is presumably because of the presence of secondary minerals formed by aqueous alteration involving the transport of Fe into the chondrules. Although it is unlikely that any excess Fe in the enriched areas of Semarkona chondrules has entered the fresh pyroxene examined by TEM, this may not be the case in Chainpur. Some coarse-grained olivine in Chainpur has experienced metamorphic entry of FeO (Ruzicka, 1986), and so too may have some of the extremely fine-grained pyroxene in cryptocrystalline chondrules.

It is not surprising that fine-grained chondrules, like the bleached cryptocrystalline chondrules studied here, are good recorders of thermal metamorphism. It has long been known that pyroxene equilibrates much more slowly than olivine during metamorphism in type-3 chondrites (*e.g.*, Dodd *et al.*, 1967). In Dhajala, most of the olivine is equilibrated whereas pyroxene is still highly unequilibrated (Noonan *et al.*, 1976). However, the properties of bleached chondrules in Dhajala are apparently just right to "freeze" metamorphic effects into the pyroxene at an intermediate stage. This partial equilibration has undoubtedly been aided in part by the porosity of the outer parts of these chondrules. By petrologic type 4, bleached chondrules have completely equilibrated and are unzoned for elements such as Fe, Cr, and Mn.

## IMPLICATIONS

It is well known that aqueous alteration played a major role in the formation of CI, CM, and CR chondrites, all of which have experienced little thermal metamorphism and contain abundant secondary minerals (*e.g.*, Zolensky and McSween, 1988). There is evidence for similar processes having affected CV3 chondrites (*e.g.*, Krot *et al.*, 1998a,b). Until now, evidence for aqueous alteration in ordinary chondrites has been limited to a few highly unequilibrated meteorites such as Semarkona, Bishunpur, and Tieschitz (*e.g.*, Hutchison *et al.*, 1987, 1998; Alexander *et al.*, 1989; Krot *et al.*, 1997). However, the presence of bleached chondrules in ordinary chondrites of all metamorphic grades shows that aqueous alteration was a ubiquitous process on their parent asteroids. As is the case in CV chondrites, most of the direct mineralogical evidence for aqueous alteration has been erased by subsequent metamorphism in the vast majority of ordinary chondrites.

Sears and Dodd (1988) suggested that the traditional Van Schmus and Wood (1967) chemical–petrologic classification scheme for ordinary chondrites, as modified by Sears *et al.* (1980), was oversimplified because it implied there was a simple, prograde metamorphic sequence from type $3.0 \rightarrow 3.9 \rightarrow 4 \rightarrow 5 \rightarrow 6$. They suggested instead that the sequence $3.3 \rightarrow 6$ was due to dry thermal metamorphism, whereas the sequence $3.3 \rightarrow 3.2 \rightarrow 3.1 \rightarrow 3.0$ represented increasing degrees of aqueous alteration (although Sears *et al.*, 1995b, point out that this too may be overly simplified). In light of the present work, we now know that aqueous alteration was important across the entire range of petrologic types and may have been decoupled from thermal metamorphism.

It is difficult to quantify the relative extents to which aqueous alteration affected different ordinary chondrites in the sequence from type 3.0 to 6. Evidence such as the presence of altered glass in chondrules (*e.g.*, Hutchison *et al.*, 1998) will certainly be destroyed as glass devitrifies above type 3.4, and any phyllosilicates in chondrite matrix will be destroyed or greatly modified as the matrix thoroughly recrystallizes by type 3.6 (Huss *et al.*, 1981; Sears *et al.*, 1980). We do not know if chondrule bleaching happens at the very earliest stages of aqueous alteration (either at low fluid–rock ratios, low temperature, short times, or all three), or if every meteorite that contains bleached chondrules was once as altered as Semarkona. We suspect that the alteration of the finely disseminated glass in cryptocrystalline chondrules would be a relatively rapid process in the presence of liquid water and temperatures of up to few hundred degrees Celsius. This is supported by the fact that studies of CM chondrites demonstrate that chondrule glasses are among the first phases to be replaced during aqueous alteration (*e.g.*, Fuchs *et al.*, 1973; Zolensky *et al.*, 1993). Because bleached zones have about the same thickness in Semarkona as they do in type 4–6 chondrites, it does not appear that there is any correlation between the extent of early aqueous alteration and later thermal metamorphism.

It might be expected that if other ordinary chondrites once experienced the same degree of hydration as Semarkona, then their matrices would contain significant quantities of minerals such as micas, formed during metamorphism. However, this is probably not very likely. First, matrix concentrations of $Na_2O$ and $K_2O$ are fairly low (~2 and 0.5 wt%, respectively), so formation of a mica is

unlikely simply on compositional grounds. Second, thermally metamorphosed carbonaceous chondrites (*e.g.*, Yamato 86720) that originally contained smectite with serpentine in their matrices consist of olivine and an amorphous phase after metamorphism at temperatures of ~500 °C (Tomeoka *et al.*, 1989). Akai (1992) found that smectite (Fe-saponite) is more stable than Fe-serpentine during thermal metamorphism and will apparently survive longer and to higher temperatures. The short duration of the dehydration experiments (hours) performed by Akai (1992) cannot be readily extrapolated to metamorphic timescales for ordinary chondrites. However, it is clear that micaceous phases have not been observed in any metamorphosed carbonaceous chondrites, so that their absence in metamorphosed ordinary chondrites that contain bleached chondrules does not appear to be problematic.

In contrast, it may be possible to compare the relative extents of aqueous alteration in different chondrite groups based on the occurrence of bleached chondrules. Radial pyroxene and cryptocrystalline chondrules are relatively abundant in H, L, and LL chondrites (~12% of chondrules), and they are even more common in enstatite chondrites (~17%) (Gooding and Keil, 1981; Grossman *et al.*, 1988). From our observations, it appears that the fractions of these chondrules which are bleached decrease in the order L + LL > H > EH + EL (= 0). (We have not made sufficient observations to fit any carbonaceous chondrite groups into this sequence.) This sequence may either reflect decreasing amounts of aqueous alteration or increasing resistance of chondrules to such alteration. The latter possibility could result if there were some change in the composition of radial pyroxene and cryptocrystalline chondrule mesostasis across the chondrite groups. There is little evidence, however, to support such a change. Radial pyroxene chondrules from Qingzhen (EH3) studied by Grossman *et al.* (1985) have albitic mesostasis similar to those found in radial pyroxene chondrules in Chainpur measured by Gooding (1979). Normative mineralogy in all of these mesostases is dominated by albite (40–50 wt%) and quartz (20–40 wt%), with small amounts of pyroxene (<20 wt%). Rubin and Pernicka (1989) also report albitic mesostasis in many radial pyroxene chondrules from Sharps (H3.4), but they found some with highly quartz-normative mesostasis as well. The FeO content of mesostasis is lower in the EH3 chondrules (~2 wt%, range 0.2–4.9 wt%, N = 4) than in Sharps (3.3 wt%, range 0.7–7.3 wt%, N = 7) and Chainpur (3.2% in each of two chondrules); but it seems unlikely that this small difference would render the glass impervious to aqueous alteration. Extremely silica-rich glass, such as was found in some radial pyroxene chondrules in Sharps, would almost certainly alter differently than albitic glass, if for no other reason than it has little alkalis and Al to be leached out. X-ray mapping of a 3 × 5 mm area of Sharps (J. N. Grossman, unpubl. data) suggests that the albitic radial pyroxene chondrules in H chondrites are the dominant type. We therefore can conclude that only differing degrees of aqueous alteration adequately explains the observed sequence among the chondrite groups.

It is probably no coincidence that the most reduced groups of chondrites experienced the least aqueous alteration. Two possible sources of $H_2O$ would both be more abundant in oxidized materials: $H_2O$ that accreted to the parent asteroids as ice and $H_2O$ produced during either the pyrolysis or oxidation of accreted organic material or both. In the more oxidized nebular settings in which L and LL chondrites probably formed, the higher $fO_2$ of the gas would result in a higher $H_2O/H_2$ ratio (Rubin *et al.*, 1988) and at low temperatures could result in a larger amount of water-ice accreting onto planetesimals than would be the case in the H or EH formation regions. This $H_2O$ would be released at the onset of metamorphism (causing bleaching) and ultimately be lost from any high-grade material produced. Alexander *et al.* (1998) suggest that pyrolysis and oxidation of organic matter during metamorphism could result in the release of $H_2O$ vapor. In L and LL chondrites, where there are abundant sources of oxidizing agents such as iron oxides (*e.g.*, FeO in rims and matrix), any organic material that decomposed during metamorphism would oxidize, producing $H_2O$. In highly reduced meteorites such as enstatite chondrites, the amount of $H_2O$ released by the same process would be limited by the amount of O in the organic matter. In this scenario, $H_2O$ vapor would be released deep in an internally heated parent body and move upward through the asteroid (a scenario similar to that envisioned by Krot *et al.*, 1997). This would result in a $H_2O$-rich "front" moving upward just ahead of material that has been heated sufficiently to decompose the organic matter. In this zone in oxidized parent bodies, the partial pressure of $H_2O$ might be sufficient to cause bleaching of chondrules.

Recently, Zolensky *et al.* (1999a,b) reported the presence of aqueous fluid inclusions in alkali chloride crystals in two ordinary chondrite regolith breccias, Monahans (1998) (H5) and Zag (H3–6). In contrast to our study, which provides evidence for premetamorphic aqueous activity on ordinary chondrite asteroids, Zolensky's work indicates that water was present after metamorphism, but prior to final lithification. Zolensky *et al.* (1999a,b) speculate that the water found in Monahans (1998) and Zag may either be indigenous fluids from elsewhere in the H-chondrite asteroid or fluids introduced by late-stage impacts of icy bodies. Without knowing more about the isotopic composition of water in the fluid inclusions, it is difficult to decide between these two possible sources. However, our results do verify the existence of pervasive aqueous fluids on ordinary chondrite asteroids, and so increase the likelihood that the fluid inclusions are indeed filled with indigenous water. Clearly, for this to be true, the parent body would have to be disrupted and reassembled in order to bring metamorphosed and, presumably, dehydrated type 5 or 6 material to the asteroidal surface where it could incorporate water released from later metamorphic dehydration within the body.

The fact that bleached chondrules occur in all metamorphic grades of ordinary chondrites is clear evidence that these meteorites behaved as open systems during thermal metamorphism: the $H_2O$ responsible for bleaching has been lost from the higher petrologic types. This has implications in the ancient debate over whether volatile depletions in types 4–6 chondrites are due to their higher temperature accretion or to loss of volatiles during metamorphism (*i.e.*, hot accretion *vs.* cold accretion; arguments summarized in Lipschutz and Woolum, 1988, and Rubin and Brearley, 1996). A relatively abundant metamorphic fluid like $H_2O$ vapor could act as a "carrier gas," and its loss would facilitate the loss of volatile trace elements. If temperatures were low enough that water-ice or organic matter accreted, this basically settles the controversy: clearly, the presence of bleached chondrules formed by premetamorphic aqueous alteration rules out traditional models for volatile depletion involving hot accretion of ordinary chondrites.

Another implication of our observations on bleached chondrules is that one must be careful in interpreting bulk chondrule compositions in cases where there is a possibility that aqueous alteration occurred. The open-system behavior that accompanies bleaching results in the loss of alkalis, Al, and some Si from these chondrules (bulk compositional effects are shown in Fig. 7). Statistical studies of these chondrules might mistakenly conclude that there was an

albite component among the chondrule precursors or that an unusual mechanism is required to form the chondrules by igneous processes. For example, it is quite plausible that the tiny, Na-, Al-, Ca-poor cryptocrystalline chondrules in Allan Hills 85085 that Scott (1988) called "a very extreme product of the nebular chondrule-forming process" were simply bleached (assuming that Ca is in the glass and could therefore be lost this way). Indeed, one must use extreme caution in interpreting data from all of the chondrite groups with tiny chondrules (*i.e.*, CM, CO, and CH), because a similar degree of aqueous alteration that produced 100 $\mu$m thick bleached zones in ordinary chondrites would not leave any unaltered cores in crypto-crystalline and radial pyroxene chondrules in these meteorites.

## CONCLUSIONS

Bleached chondrules occur in ordinary chondrites of all meta-morphic grades. They formed when fluids interacted with mesostasis in the outer portions of radial pyroxene and cryptocrystalline chondrules during aqueous alteration. The process resulted in outer zones containing unaltered pyroxene, secondary alteration products, and abundant pore space where mesostasis was removed. This alteration took place prior to or at the earliest stages of thermal metamorphism and was ongoing during the period of light parent-body brecciation in some chondrites. The water that caused bleaching probably circulated through the chondrites' fine-grained matrix.

Calcium-rich zones are present in the outer portions of the cores of many bleached chondrules. They are absent in Semarkona but are present in bleached chondrules in chondrites ranging from petrologic type 3.1 up to 6. They may have formed as the result of the earliest stages of thermal metamorphism. Alternatively, they may be indicators of different fluid–rock interactions in different chondrites.

Bleached chondrules are sensitive indicators of thermal meta-morphism in ordinary chondrites because of their very fine-grain size. Traverses across individual bleached chondrules in Dhajala preserve the complete range of bulk compositions ranging from "primitive" (perhaps nebular) in their cores to thoroughly equilibrated in the porous outer zones. In types 4–6 ordinary chondrites, secondary metamorphic minerals crystallize abundantly in the bleached zones produced at lower temperatures during aqueous alteration.

There is no obvious correlation between metamorphic grade and degree of aqueous alteration in ordinary chondrites. Aside from bleached chondrules, most of the effects of aqueous alteration must be lost during thermal metamorphism. The degree of aqueous alteration is probably correlated with the oxidation state of the chondrite. This would imply that the water responsible for bleaching either accreted as ices, most abundantly in L and LL chondrites, or had another source such as water released during the pyrolysis of organic matter.

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