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Heavily-hydrated lithic clasts in CH chondrites and the related, metal-rich chondrites Queen Alexandra Range 94411 and Hammadah al Hamra 237

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Abstract–Fine-grained, heavily-hydrated lithic clasts in the metal-rich (CB) chondrites Queen Alexandra Range (QUE) 94411 and Hammadah al Hamra 237 and CH chondrites, such as Patuxent Range (PAT) 91546 and Allan Hills (ALH) 85085, are mineralogically similar suggesting genetic relationship between these meteorites. These clasts contain no anhydrous silicates and consist of framboidal and platelet magnetite, prismatic sulfides (pentlandite and pyrrhotite), and Fe-Mn-Mg-bearing Ca-carbonates set in a phyllosilicate-rich matrix. Two types of phyllosilicates were identified: serpentine, with basal spacing of ~0.73 nm, and saponite, with basal spacings of about 1.1–1.2 nm. Chondrules and FeNi-metal grains in CB and CH chondrites are believed to have formed at high temperature (>1300 K) by condensation in a solar nebula region that experienced complete vaporization. The absence of aqueous alteration of chondrules and metal grains in CB and CH chondrites indicates that the clasts experienced hydration in an asteroidal setting prior to incorporation into the CH and CB parent bodies. The hydrated clasts were either incorporated during regolith gardening or accreted together with chondrules and FeNi-metal grains after these high-temperature components had been transported from their hot formation region to a much colder region of the solar nebula.

INTRODUCTION

The metal-rich carbonaceous chondrites, Queen Alexandra Range (QUE) 94411 (paired with QUE 94627) and Hammadah al Hamra (HH) 237 have several important bulk chemical and isotopic properties in common with Bencubbin, Weatherford, Gujba, CR and CH chondrites. These properties include (1) a broad compositional range of FeNi-metal, which is characterized by an approximately solar Co/Ni ratio; (2) large depletions in moderately volatile elements, such as Mn, Na, K, Ga, Ge, and S; (3) bulk oxygen isotopic compositions plotting on or near the CR-mixing line on a three-isotope diagram; and (4) large positive anomalies in $\delta^{15}N$ (Herzog *et al.*, 2000; Weisberg *et al.*, 1993, 1995, 2001; Rubin *et al.*, 2001; Krot *et al.*, unpubl. data). Based on these observations, QUE 94411, HH 237, Bencubbin, Weatherford, and Gujba have recently been placed together in a new metal-rich chondritic grouplet called CB (carbonaceous Bencubbin-like) chondrites (Weisberg *et al.*, 2001). Due to their strong similarities to CR and CH chondrites they are considered as a part of the CR carbonaceous chondrite clan (Weisberg *et al.*, 1995, 2001). Weisberg *et al.* (2001), however, admitted that there are significant mineralogical and petrographic differences between QUE 94411, HH 237 and Bencubbin/Gujba/Weatherford and subdivided them into CB_a (Bencubbin, Gujba, and Weatherford) and CB_b (HH 237 and QUE 94411) subgroups. Other authors (*e.g.*, Krot *et al.*, 2001a) questioned this classification and suggested that HH 237 and QUE 94411 are more closely related to CH chondrites, rather than to Bencubbin/Gujba/Weatherford.

HH 237 and QUE 94411 consist of two major components: FeNi-metal grains (60–70 vol%) and chondrules with cryptocrystalline and barred olivine textures (Krot *et al.*, 2001b). It was recently suggested that these chondrules and FeNi-metal grains, which are also dominant components of CH chondrites (Krot *et al.*, 2000), formed at high temperature by condensation following complete vaporization of a solar nebula region with an initially high dust/gas ratio (10–50× solar) (Krot *et al.*, 2001b; Meibom *et al.*, 2000a; Petaev *et al.*, 2001; Campbell *et al.*,

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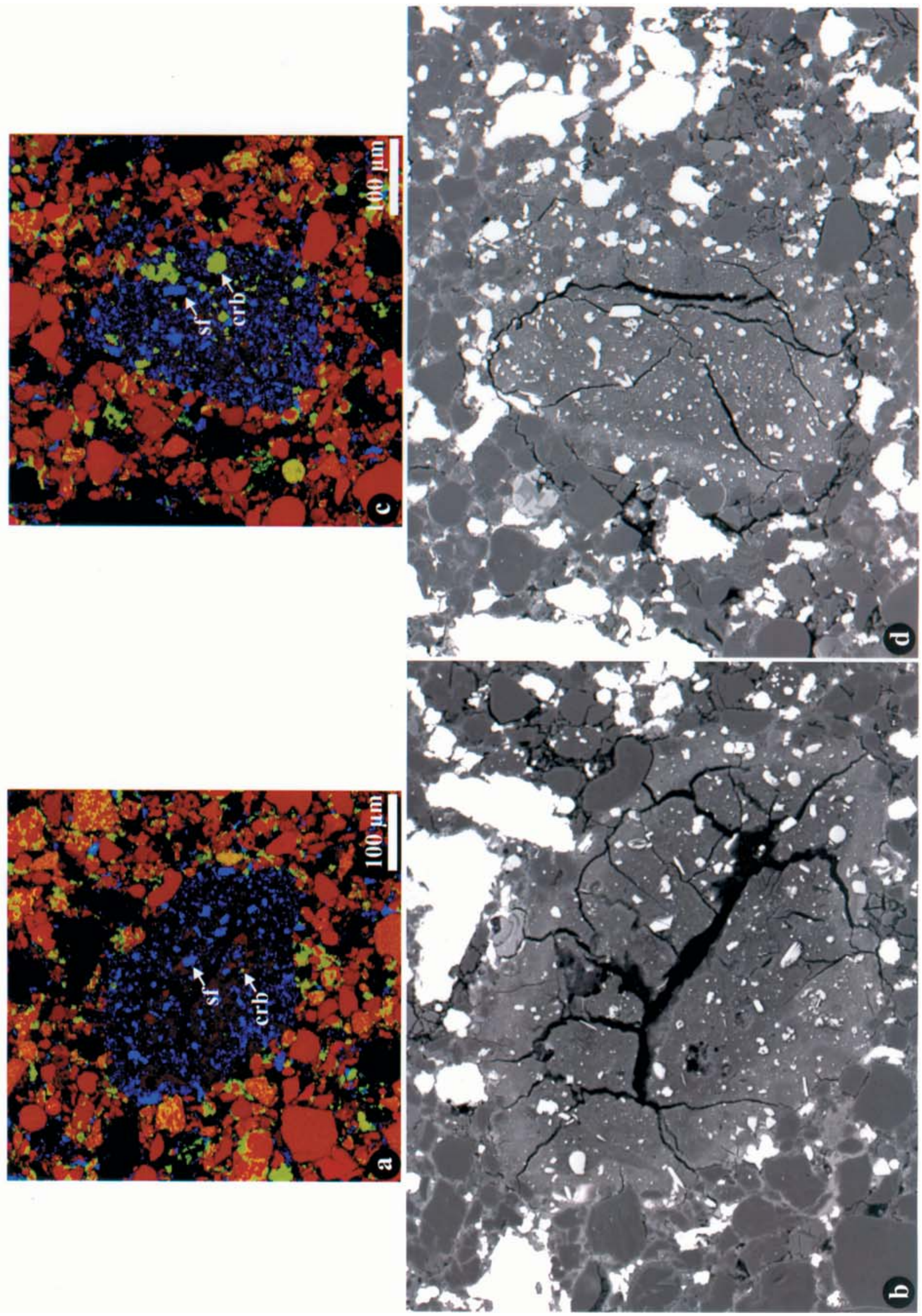

FIG. 1. Combined x-ray elemental maps in Mg (red), Ca (green), and S Kα (blue) (a, c) and BSE images (b, d) of the clasts #2 (a, b) and #4 (c, d) in the CH chondrite PAT 91546. The hydrated clasts contain abundant sulfides (sf); the abundance of carbonates (carb) varies; anhydrous silicates are absent. The outer portions of the clasts are brighter (b, d) and bulk analyses show they are enriched in FeO, probably due to heterogeneous distribution of Fe-bearing minerals (magnetite and sulfides).

2001). Both chondrules and FeNi-metal grains are believed to have been transported from their hot formation region before the temperature dropped below ~1200 K and accreted/stored in a much colder (<500 K) region of the solar nebula (Meibom *et al.*, 2000a; Krot *et al.*, 2001b). In addition to these pristine high-temperature components, QUE 94411 and HH 237 contain scattered, heavily-hydrated lithic clasts (Meibom *et al.*, 2000b; Greshake *et al.*, 2000). Such objects, also referred to as dark inclusions or dark clasts, have been previously described in CH and CR chondrites (Grossman *et al.*, 1988; Weisberg *et al.*, 1988; Zolensky *et al.*, 1992; Bischoff *et al.*, 1993; Endreß *et al.*, 1994; Meibom *et al.*, 2000b; Greshake *et al.*, 2000). The origin of these clasts remains controversial.

Weisberg *et al.* (1988) concluded that fine-grained lithic clasts in the Allan Hills (ALH) 85085 CH chondrite are petrologically similar to matrix and dark inclusions in the CR chondrites. Additionally, Weisberg *et al.* (1995) reported oxygen isotopic compositions of lithic clasts in the Patuxent Range (PAT) 91546 CH chondrite; one large clast plotted on the carbonaceous chondrite anhydrous mineral mixing line and a composite sample of five clasts plotted on the CR mixing line. The composite sample is isotopically similar to lithic clasts in the CR chondrites and to the anhydrous CH chondrules, but at somewhat heavier oxygen compositions. Endreß *et al.* (1994) concluded that dark inclusions in the CR chondrite El Djouf 001, similar to those described here, are aggregates of solar nebula condensates, which experienced nebular hydration. Sugiura (2000) suggested that heavily-hydrated clasts in the CH chondrite Pecora Escarpment (PCA) 91467 experienced *in situ* hydration. Greshake *et al.* (2000) inferred that heavily-hydrated lithic clasts in QUE 94411 and CH chondrites experienced aqueous alteration in a different asteroidal setting before incorporation into the meteorites where they are found today.

Here we present a scanning and transmission electron microscope (TEM) study of fine-grained heavily-hydrated clasts in QUE 94411, HH 237 and CH chondrite PAT 91546 as well as a study of chondrules in ALH 85085. Based on these data, we attempt to decipher the formation history of these objects and their relationship to chondrules and metal grains in their host meteorites.

ANALYTICAL PROCEDURES

Two polished thin sections prepared for TEM work, QUE 94411 (9) and PAT 91546 (22), and one polished thin section from ALH 85085 were kindly provided by the Meteorite Working Group. A thick polished section of HH 237 was kindly provided by Jutta Zipfel (Max-Plack-Institut für Chemie, Mainz). These samples were studied using optical microscopy, backscattered electron imaging (BSE), x-ray elemental mapping, electron microprobe analysis, and TEM. BSE images were obtained with a Zeiss DSM-962 scanning electron microscope using a 15 kV accelerating voltage and 1–2 nA beam current. Quantitative mineral analyses were performed with a Cameca SX-50 electron microprobe using a 15 kV accelerating voltage, 10–20 nA beam current, a beam size of 1–2 μm, and suitable mineral standards. For each element, counting times on both peak and background were 20 s (10 s for Na and K). Matrix effects were corrected using PAP procedures. The element detection limits with the Cameca SX-50 were (in wt%): SiO_2, Al_2O_3, MgO, 0.03; TiO_2, CaO, K_2O, 0.04; Na_2O, 0.05; Cr_2O_3, 0.06; MnO, 0.07; FeO, 0.08. The x-ray elemental maps were acquired on the same electron microprobe at 15 kV accelerating voltage, 50–100 nA beam current, and a beam size of approximately 1–2 μm.

Following detailed petrographic studies of the heavily-hydrated clasts in these samples, slotted Cu grids were glued on areas of interest of each thin section. The grids were then removed from the thin sections and thinned to perforation by argon ion-beam bombardment at 4.5 kV and an incidence angle of 12° using a GATAN 600 DIF duo ion mill. During thinning the samples were cooled by liquid nitrogen to avoid ion beam damage. After the first holes appeared, the samples were thinned at a very shallow angle (3°) for several minutes in order to remove any amorphous films from the sample surface. TEM studies were performed using a 200 kV PHILIPS CM 20 STEM equipped with a TRACOR Northern energy dispersive x-ray detector sensitive to elements with atomic numbers >5.

MINERALOGY AND PETROGRAPHY

Heavily-hydrated lithic clasts in PAT 91546, QUE 94411 and HH 237 are largely opaque in transmitted light and occur as distinct irregularly shaped objects of variable size. The clasts in CH chondrites are typically 30–500 μm in size (Figs. 1 and 2). An exceptionally large clast, measuring about 1.3 × 0.8 mm, was found in QUE 94411 (Fig. 3). A small (about 0.1 × 0.2 mm) clast was found in the HH 237 sample, but was studied only in backscattered electrons. All heavily-hydrated lithic clasts exhibit sharp boundaries to the host meteorites and are characterized by a high density of irregular fractures. The fractures do not extend into the host meteorites and are not filled with terrestrial weathering products, such as hydrous Fe-oxides and/or carbonates as reported from other CH and CR chondrites (Bischoff *et al.*, 1993; Endreß *et al.*, 1994).

The clasts in PAT 91546 show radial compositional zoning; the central portions of the clasts contain less Fe than their peripheries (Table 1, Figs. 1 and 2). Although the hydrated clast in QUE 94411 does not display radial zoning, it contains Fe-rich and Fe-poor portions that are clearly visible in BSE images (Figs. 3b and 4a).

Heavily-hydrated clasts in QUE 94411, HH 237, and PAT 91546 consist of magnetite, carbonates, and sulfides set in a hydrous phyllosilicate-rich matrix (Figs. 1–4). In contrast to hydrated clasts (dark inclusions) in CR chondrites (Endreß *et al.*, 1994), chondrules or chondrule fragments are not present in the objects studied here.

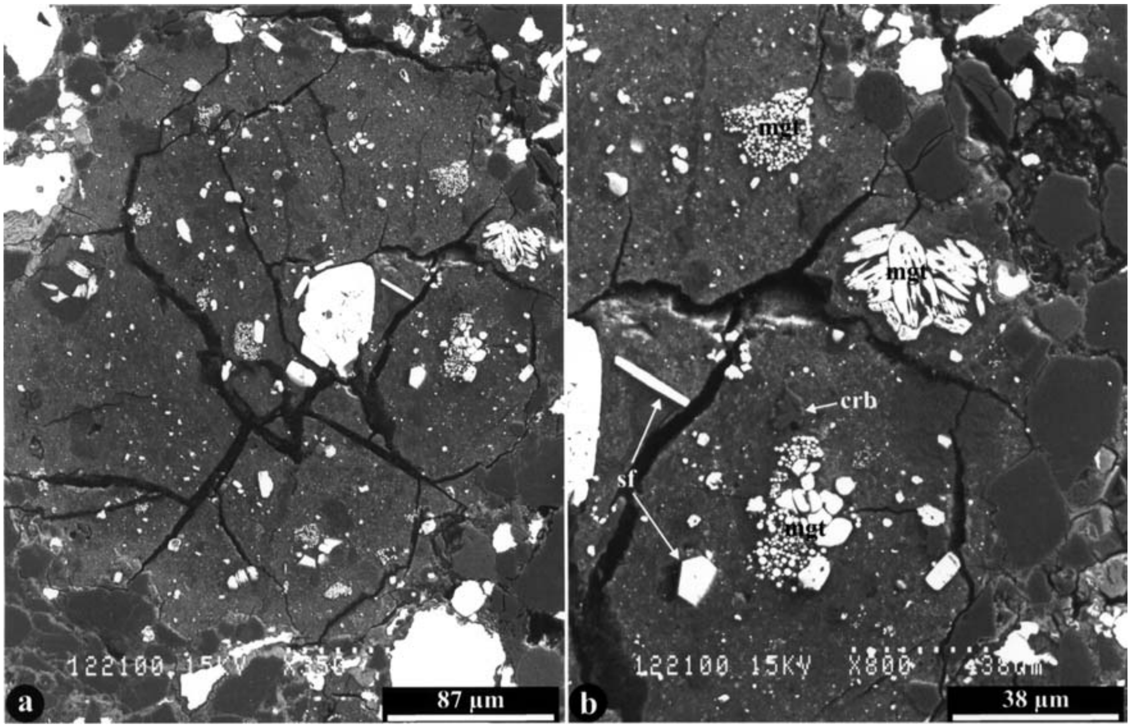

FIG. 2. BSE images of a clast #14 in PAT 91546. The clast contains framboidal and platelet magnetite (mgt), prismatic sulfides (sf) and anhedral carbonates (crb) embedded in phyllosilicate matrix.

TABLE 1. Bulk compositions of the hydrated lithic clasts in the CH chondrite PAT 91546 and CB chondrite HH 237.

chondrite\oxides	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	NiO	S	Total
PAT 91546, clasts													
#2, core	33.3	0.06	2.5	0.43	18.6	0.11	22.5	0.50	0.23	0.10	2.1	1.5	81.9
#2, rim	23.9	0.05	1.7	0.38	36.5	0.17	17.2	0.45	0.25	0.06	2.2	1.9	84.7
#2, bulk	30.8	0.06	2.4	0.59	19.7	0.24	21.6	0.47	0.20	0.10	2.2	2.4	80.8
1σ $(n = 30)$	*4.2*	*0.05*	*0.21*	*0.55*	*3.3*	*0.37*	*3.2*	*0.09*	*0.05*	*0.03*	*1.5*	*2.2*	*4.5*
#4, core	31.7	0.05	2.6	0.46	22.2	0.06	22.4	0.17	0.32	0.08	1.5	2.3	83.8
#4, rim	26.0	<0.04	1.9	0.39	31.7	0.14	19.3	0.81	0.27	0.06	1.9	2.9	85.5
#4, bulk	25.0	<0.04	2.6	0.42	33.4	<0.07	17.9	0.22	0.26	0.07	1.6	3.8	85.3
1σ $(n = 30)$	*8.0*	–	*0.74*	*0.16*	*15.3*	*0.03*	*5.1*	*0.10*	*0.09*	*0.02*	*0.85*	*3.3*	*2.6*
#5, bulk	28.6	<0.04	2.1	0.39	30.2	0.09	18.8	0.09	0.25	<0.04	1.7	2.3	84.6
1σ $(n = 10)$	*2.1*	–	*0.24*	*0.04*	*4.0*	*0.03*	*1.0*	*0.04*	*0.10*	–	*0.40*	*0.34*	*1.1*
#6, bulk	22.1	0.05	1.5	0.43	33.5	0.16	17.4	0.31	0.16	<0.04	2.3	2.3	80.3
1σ $(n = 10)$	*1.0*	*0.12*	*0.08*	*0.05*	*1.5*	*0.05*	*0.94*	*0.09*	*0.02*	–	*0.45*	*0.77*	*1.2*
#10, core	30.1	<0.04	2.4	0.34	19.1	0.18	20.6	2.8	0.34	0.06	1.7	1.1	78.9
#10, rim	26.6	<0.04	1.9	0.35	28.0	0.29	19.7	0.40	0.50	0.07	1.5	1.7	81.0
#14, bulk	24.0	<0.04	1.8	0.36	32.8	0.10	17.7	0.37	0.36	0.07	2.4	2.4	82.4
1σ $(n = 30)$	*2.7*	–	*0.3*	*0.05*	*4.2*	*0.05*	*1.8*	*0.16*	*0.07*	*0.02*	*0.7*	*1.4*	*2.2*
HH 237													
clast	28.0	<0.04	2.0	0.40	38.0	n.a.	21.0	2.0	0.30	n.a.	n.a.	n.a.	91.7
1σ $(n = 10)$	*5.0*	–	*0.5*	*0.10*	*10.0*	–	*4.0*	*2.0*	*0.10*	–	–	–	*2.0*
silicate portion of impact melts	32.0	0.12	4.0	1.0	35.0	n.a.	24.0	2.0	0.40	n.a.	n.a.	n.a.	98.5
1σ $(n = 10)$	*4.0*	*0.02*	*2.0*	*0.20*	*5.0*	–	*3.0*	*0.5*	*0.05*	–	–	–	–

n.a. = not analyzed

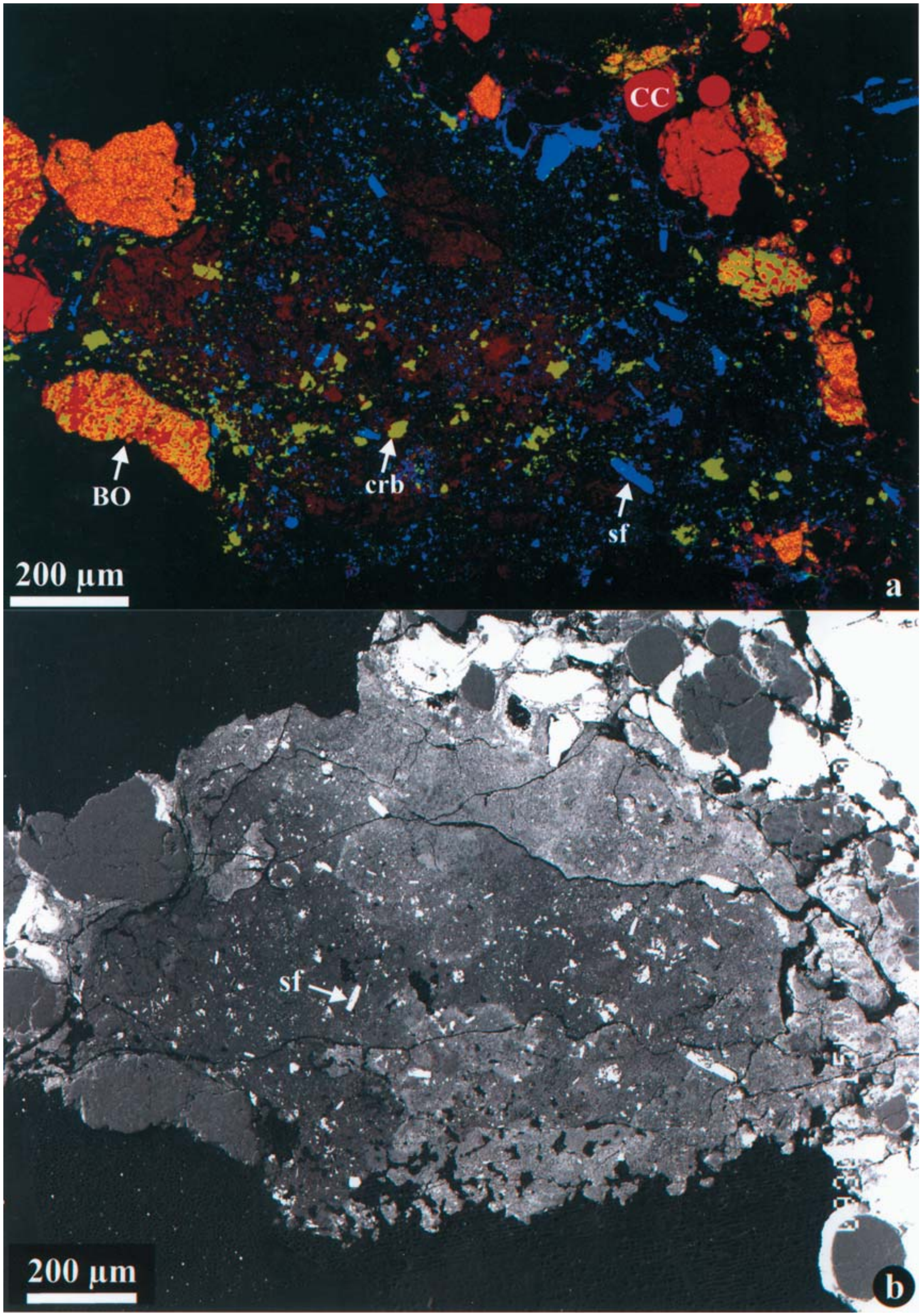

FIG. 3. Combined x-ray elemental map in Mg (red), Ca (green), and S Kα (blue) (a) and BSE image (b) of a hydrated clast in the metal-rich chondrite QUE 94411. The clast contains abundant Ca-carbonates (crb) and lath-shaped sulfides (sf) embedded in phyllosilicates; anhydrous silicates are absent. Variations in brightness in (b) are probably due to heterogeneous distribution of Fe-bearing minerals (magnetite and sulfides); coarse-grained carbonates are largely concentrated in the Fe-poor portion of the clast. There is a sharp boundary between the heavily-hydrated clast and host meteorite; cryptocrystalline (CC) and barred olivine (BO) chondrules in the latter show no evidence for hydration.

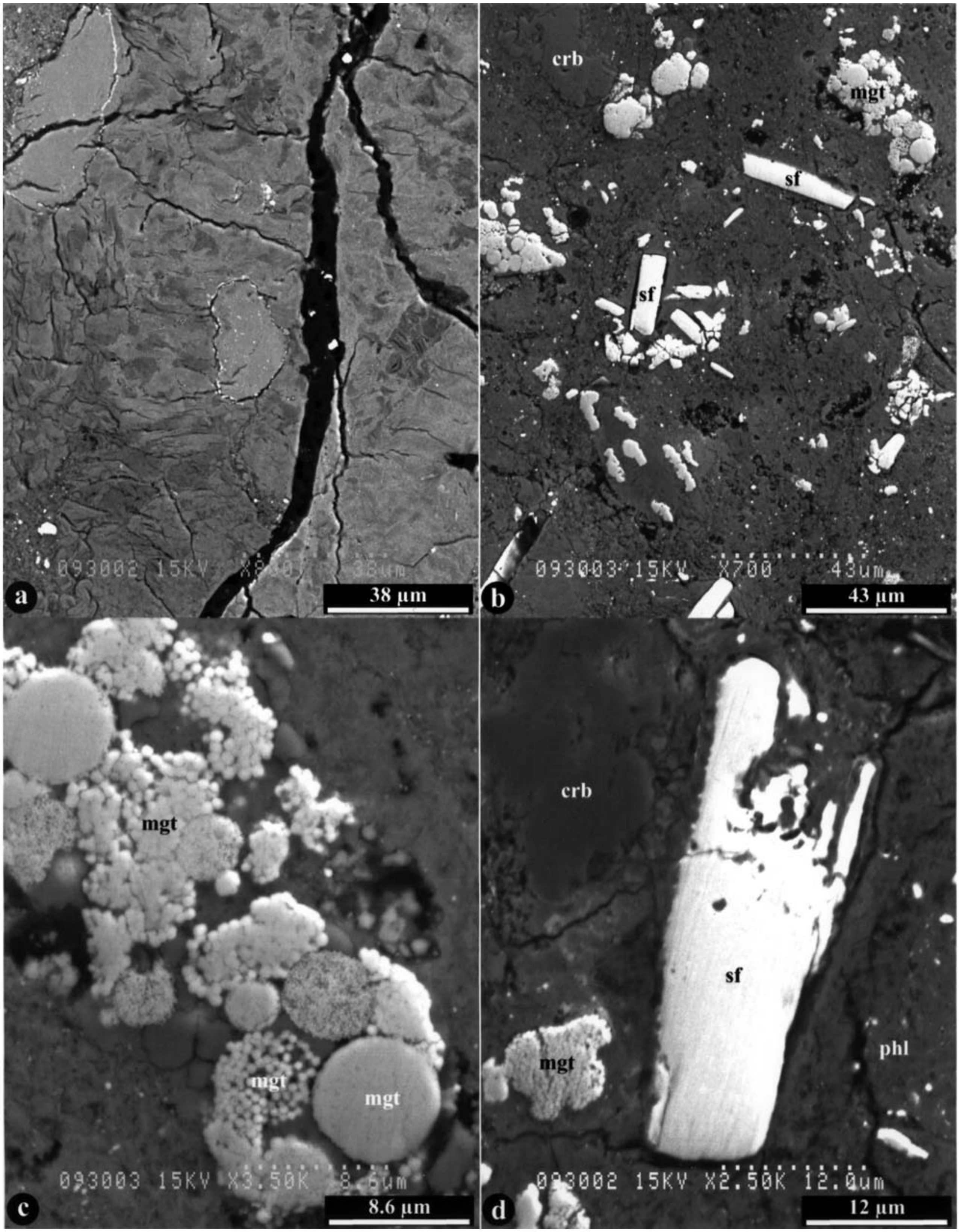

FIG. 4. BSE images of the hydrated clast in QUE 94411. (a) Mg-rich (dark) and Mg-poor (bright) regions in the clast. (b–d) It consists of lath-shaped sulfides (sf), framboidal magnetite (mgt) and anhedral carbonates (crb) surrounded by phyllosilicates (phl).

Magnetites occur as large spherules, clusters of tiny crystals, platelets, and as framboids (Figs. 2, 4b–d and 5a), morphologies that have been observed in various types of carbonaceous chondrites (*e.g.*, Jedwab, 1965; Hyman *et al.*, 1985; Hua and Buseck, 1998 and references therein). Compositionally, the magnetite is nearly pure Fe_3O_4 with minor amounts of Mg and Mn (<0.1 wt%). All morphological types of magnetite show a fine black spotty contrast in the TEM (Fig. 5b). Similar features have been previously described in extraterrestrial (*e.g.*, Müller, 1978) and terrestrial spinels of variable compositions (*e.g.*, Price, 1979, 1980) and are attributed to point defect clusters reflecting either a high local strain or chemical heterogeneity.

Carbonates occur as anhedral 10–30 μm sized fragments set in the phyllosilicate matrix (Fig. 4b,d). They are Ca-rich and contain significant concentrations (1–2 wt%) of Mg, Mn, and Fe.

The sulfides are predominantly euhedral, lath-shaped, and 5–50 μm in size (Figs. 2 and 4). They are pyrrhotite and pentlandite; we did not observe Ni-free troilite as reported previously in hydrated clasts in the CH chondrite ALH 85085 (Grossman *et al.*, 1988).

Magnetites, carbonates and sulfides are set in a fine-grained matrix whose grain size is below the resolution of the scanning electron microscope (SEM) (Figs. 2 and 4). Defocused beam electron microprobe analyses of the matrix reveal mean low totals of ~85 wt%, suggesting a hydrous nature for this mineral assemblage (Table 1). The low totals may also indicate some amount of porosity in the matrix, however.

The hydrous matrix consists of phyllosilicates exhibiting two different morphologies. Most phyllosilicates are poorly crystalline and occur as very small, sometimes only 1–2 layers thick, randomly orientated crystals (Fig. 6). They readily decompose under the electron beam and many areas appear to be almost totally amorphous. Ubiquitous 100–150 nm sized rounded inclusions of magnetite and sulfides and, rarely, angular carbonates were found in those regions (Fig. 7a). In several places more coarse-grained phyllosilicates occur in irregularly shaped clusters (Fig. 7b). High-resolution TEM and electron diffraction confirm the presence of two types of phyllosilicates (Figs. 8 and 9). (1) Blocky up to 0.3 μm wide and 1 μm long crystals of serpentine with characteristic (001) lattice spacing of 0.73 nm. These crystals exhibit either straight or gently curved morphologies and are of good crystallinity as proven by their single crystal electron diffraction patterns. In very few cases curled sheets of serpentine were found (Fig. 8b), a feature commonly observed in serpentines in CM chondrites (*e.g.*, Barber, 1981; Buseck and Hua, 1993; Brearley, 1995). However, no tubular chrysotile fibres, which dominate the matrix of CM chondrites, were encountered. (2) The second type of phyllosilicate occurs as 0.1 to 0.2 μm wide and up to 0.4 μm long flake-like grains with basal spacings of 1.1–1.2 nm, suggesting that they may be a smectite (probably saponite) that has suffered collapse of the interlayer site. Intergrowths of typically straight parallel serpentine layers and more curved wavy smectites frequently occur at the rim of the compact serpentine crystals. Both phyllosilicates contain numerous lattice defects (*i.e.*, terminated and discontinued layers).

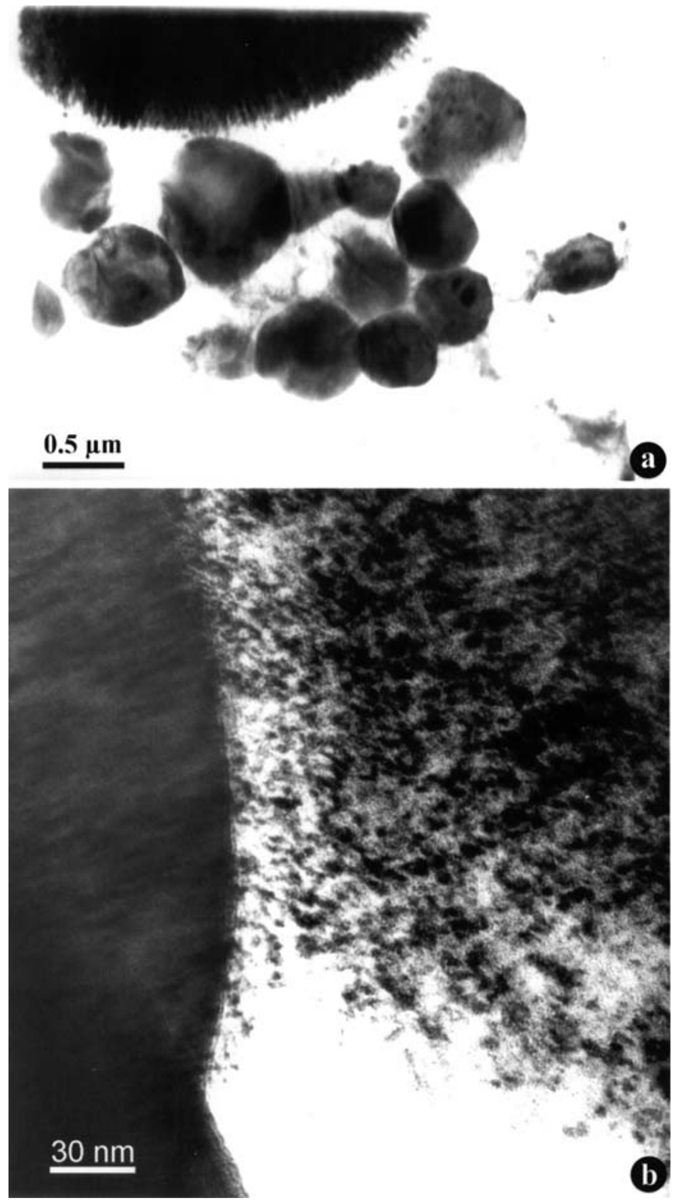

FIG. 5. (a) TEM micrograph of a magnetite cluster in a heavily-hydrated clast from PAT 91546. The cluster consists of larger spherules with a radiating internal structure (upper part of the image) and smaller spherules with smooth exteriors. (b) TEM micrograph of magnetite showing characteristic spotty contrast (on the right) probably caused by a high density of point defect clusters.

The Mg-rich and Fe-rich phyllosilicate clusters can be distinguished in the hydrated clasts. In a ternary (Si + Al)-Mg-Fe diagram, the compositions of phyllosilicates plot near the serpentine solid-solution line, which is in good agreement with the observation that the clusters are dominated by serpentine rather than by smectite (Fig. 10). The analyses also indicate that the fine phyllosilicates are more Fe- and S-rich, possibly

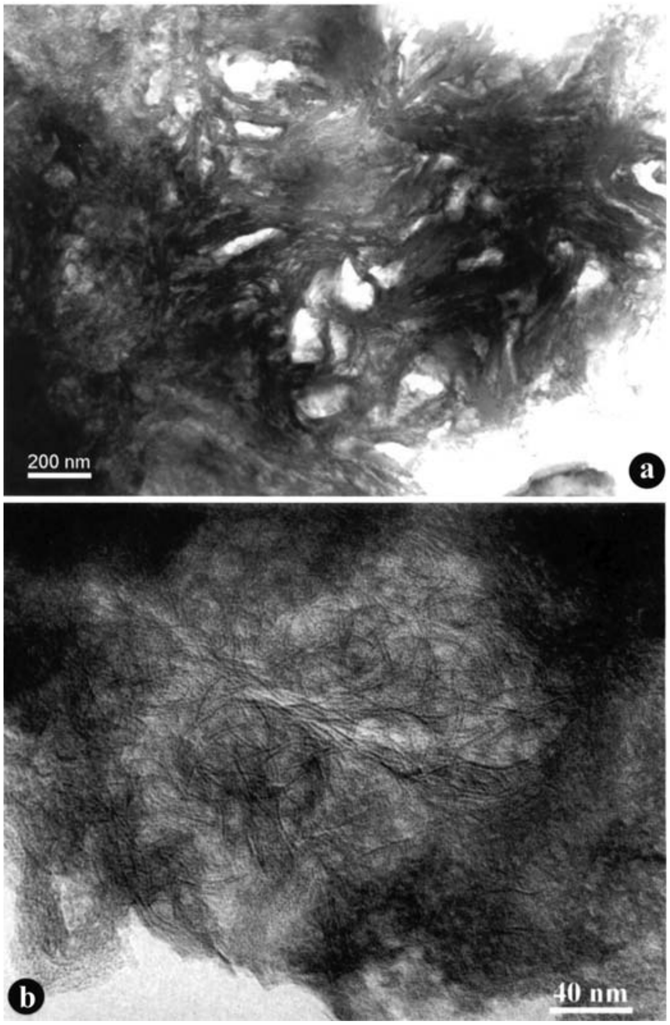

FIG. 6. (a) TEM micrograph of fine-grained and poorly crystalline phyllosilicates in clast from PAT 91546. (b) High-resolution TEM micrograph of extremely fine-grained (1–2 layers thick crystals) phyllosilicates set into an amorphous matrix.

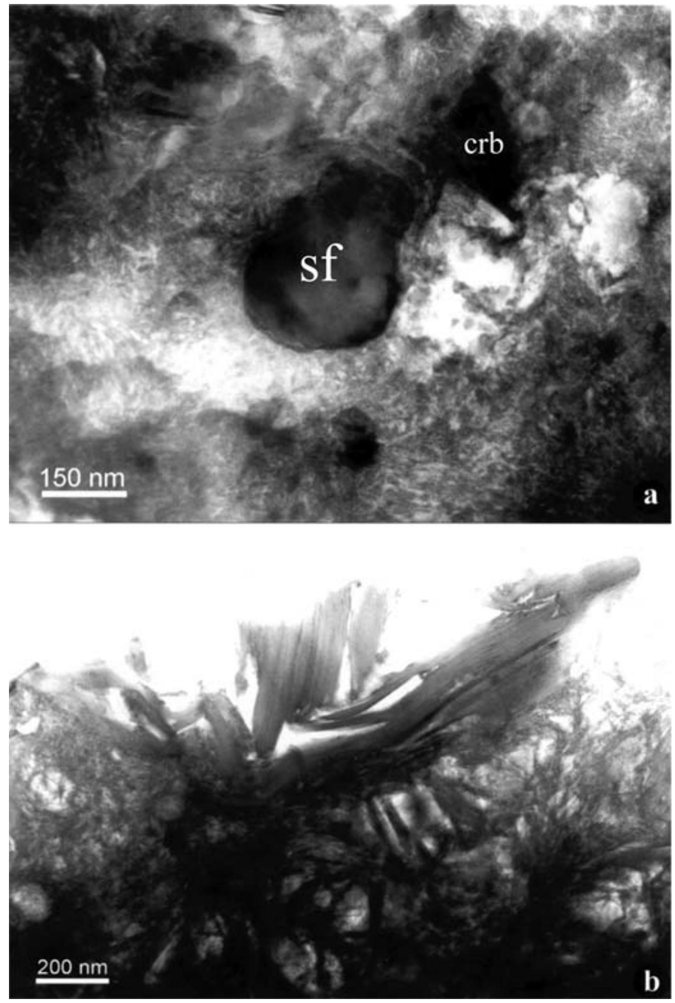

FIG. 7. (a) TEM micrograph of a small rounded sulfide and an angular carbonate in a matrix of poorly-crystalline phyllosilicates. (b) TEM micrograph of a cluster of coarse-grained phyllosilicates.

because they contain tiny magnetite and sulfide inclusions that cause the compositions to move towards the Fe apex in the diagram. The TEM studies do not reveal any evidence for the presence of tochilinite.

Although a few glassy chondrules partly replaced by phyllosilicates were found in the CH chondrite ALH 85085 (Table 2, Fig. 11), chondrules, CAIs and FeNi-metal grains in the QUE 94411, HH 237 and PAT 91546 show no evidence for aqueous alteration.

DISCUSSION

The observed similarity in mineralogy of hydrated lithic clasts from the CB chondrites QUE 94411 and HH 237 and those from CH chondrites, such as PAT 91546 and ALH 85085, support a genetic relationship between these chondrite groups and their classification as members of the CR clan (Weisberg *et al.*, 1995). Hydrated clasts have not yet been found in Bencubbin or Weatherford (Weisberg *et al.*, 2001). The apparent absence of hydrated clasts in Bencubbin and Weatherford was one of the reasons given for placing them in a separate subgroup from QUE 94411 and HH 237 (Weisberg *et al.*, 2001).

The overall mineralogical characteristics of all hydrated clasts in CB and CH chondrites studied here suggest a strong affinity of the objects to type 1 and type 2 carbonaceous chondrite matrix material. First evidence for a close relationship to such material comes from the different morphologies of magnetite observed in the clasts. The variety of distinct morphologies present in the hydrated clasts has been predominantly reported from CI, CM, CR chondrites and the Tagish Lake carbonaceous chondrite and was found to be characteristic for primitive type 1 and 2 chondrite material (*e.g.*, Jedwab, 1965; Hyman *et al.*, 1985, Endreß *et al.*, 1994; Hua and Buseck, 1998; Gounelle *et al.*, 2001).

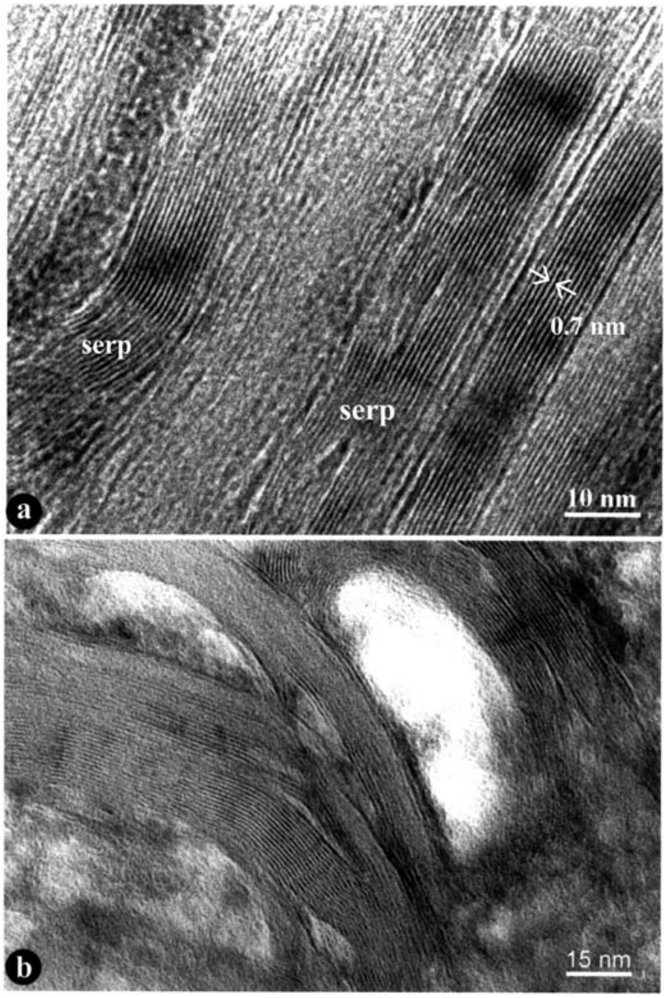

FIG. 8. (a) High-resolution TEM micrograph showing the typical morphologies of serpentine in the coarse-grained phyllosilicate clusters. While the grains on the right are of straight blocky appearance, the crystal on the left shows slight kinking and curvature. Serpentine of both morphologies displays lattice defects (*i.e.*, terminated layers). (b) High-resolution TEM micrograph of serpentine in coarse-grained phyllosilicate clusters. Serpentine occurs as straight blocky crystals, gently curved grains and curled sheets.

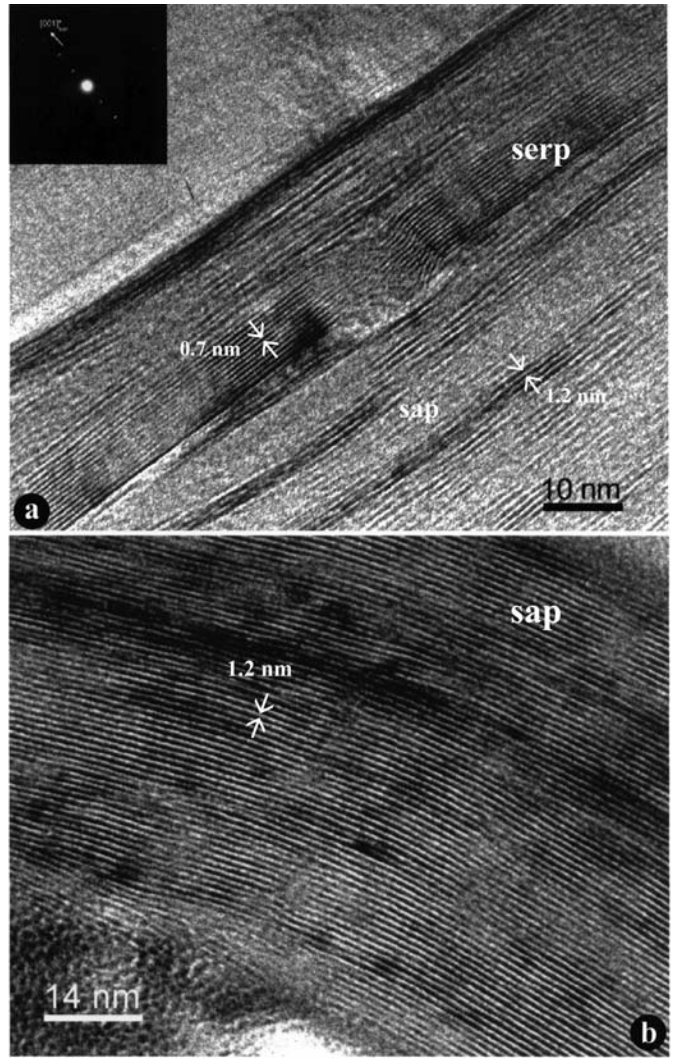

FIG. 9. (a) High-resolution TEM micrograph of serpentine and saponite intergrowths at the rim of coarse-grained phyllosilicate clusters. Note the lattice defects in serpentine. The inset shows a selected area electron diffraction pattern of serpentine proving its good crystallinity. (b) High-resolution TEM micrograph of saponite in coarse-grained phyllosilicate clusters. The crystals are typically bent or curved and contain numerous terminated and discontinued layers.

Second, the mineralogy of the phyllosilicate matrix of the hydrated clasts argues for a close relationship with type 1 and type 2 chondrite matrix material. In the clasts, carbonates, magnetite and sulfides are embedded in a phyllosilicate matrix composed of serpentine and a saponitic clay. Detailed TEM studies of the Orgueil and Alais CI chondrites revealed that these two phyllosilicates are also the dominating phases in their matrices (*e.g.*, Tomeoka and Buseck, 1988), while this assemblage is unlike that found in any CM chondrite. CM meteorites are dominated by the serpentine-type minerals cronstedtite, greenalite, ferroan antigorite, and chrysotile as well as by tochilinite and brucite (*e.g.*, Barber, 1981; Tomeoka and Buseck, 1985; Buseck and Hua, 1993). Especially chrysotile is present in a wide variety of complex forms including perfect cylindrical tubes (*e.g.*, Barber, 1981; Tomeoka and Buseck, 1985). Despite some observed curvature of serpentine in the lithic clasts no such characteristic forms were found. Additionally, the composition of the phyllosilicates in lithic clasts from PAT 91546 and QUE 94411 is different from those in CM chondrites. While the average composition of the clast phyllosilicates plots off the serpentine solid-solution line towards the Mg apex the main phases in CM chondrite matrices tochilinite and cronstedtite are much more Fe-rich (Fig. 10).

However, there are also some differences of the hydrated clasts to CI chondrites. Tomeoka and Buseck (1988) reported on the occurrence of coarse- and fine-grained phyllosilicates

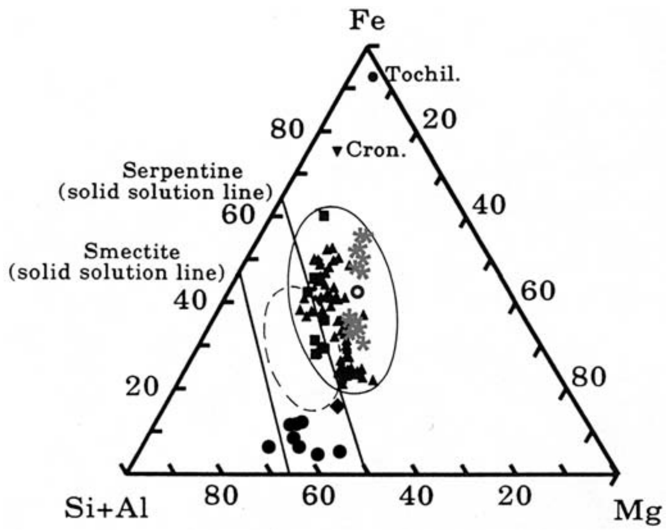

FIG. 10. Ternary Si + Al-Fe-Mg plot (wt%) comparing the composition of phyllosilicates in hydrated clasts from PAT 91546 (gray symbols) with other meteoritic phyllosilicates. Squares and triangles: Acfer 059 (Endreß *et al.*, 1994); dashed line: CR2 chondrites (Weisberg *et al.*, 1993); open circle: average hydrated clasts in PAT 91546; diamond: average Orgueil (Tomeoka and Buseck, 1988); filled circles: phyllosilicates replacing glassy chondrules in ALH 85085; cronstedtite and tochilinite: Murchison (Tomeoka and Buseck, 1985). Figure modified after Endreß *et al.* (1994).

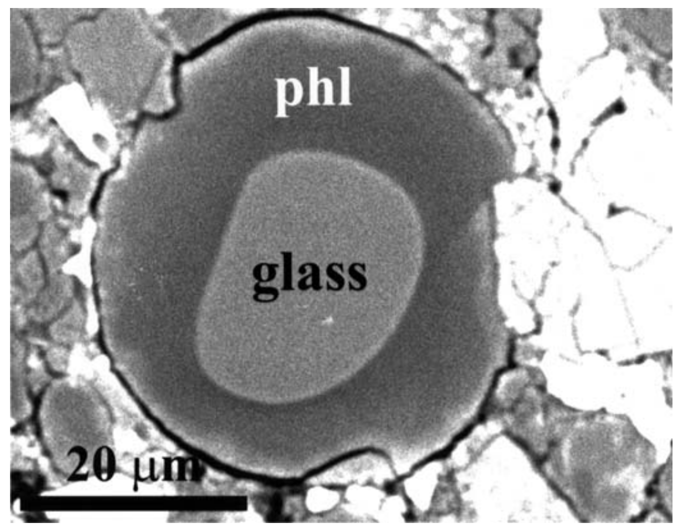

FIG. 11. BSE image of a glassy chondrule partly replaced by phyllosilicates (phl) in the CH chondrite ALH 85085.

in the Orgueil CI meteorite. Compositionally the coarse-grained aggregates plot on a coherent mixing line between the solid-solution lines of serpentine and smectite, whereas the more fine-grained phyllosilicates scatter off this line towards the Fe apex of the ternary diagram (Tomeoka and Buseck, 1988). The average composition of the matrix phyllosilicates in Orgueil lies very close to the serpentine solid-solution line with a Fe/(Fe + Mg) weight ratio of ~0.29 (Tomeoka and Buseck, 1988). Compared to these phyllosilicates, phyllosilicates in the lithic clasts from PAT 91546 and QUE 94411 are significantly more Fe-rich with an average composition characterized by a Fe/(Fe + Mg) ratio of ~0.62. The variability of Fe in the fine-grained phyllosilicates of Orgueil was attributed to the presence of ferryhydrite replacing pentlandite and magnetite in such matrix regions (Tomeoka and Buseck, 1988). Although pentlandite and magnetite were frequently found in the QUE 94411 and PAT 91546 clasts, none of the grains investigated so far showed any alteration to ferryhydrite. Finally, the phyllosilicate microstructures in the hydrated clasts differ slightly from those in CI chondrites: no intimate unit cell-scale interlayering of serpentine and saponite have been observed.

In summary, based on the magnetite morphologies, the matrix mineralogy, and the chemical composition of the constituent phases there seem to be a close relationship of the heavily hydrated lithic clasts in CB and CH chondrites to type 1 and type 2 carbonaceous chondrite matrix material. However, no unambiguous assignment to any certain group of carbonaceous chondrites can be established.

For several reasons it seems plausible to assume that the lithic clasts were hydrated outside their current host meteorites.

TABLE 2. Microprobe analysis (wt%) of glass (gl) and phyllosilicates (ph) in a partly altered glassy chondrule from ALH 85085.

ox/an.	gl#1	ph#1	gl#3	ph#3	gl#4	ph#4	gl#5	ph#5	gl#7	ph#7	gl#9	ph#9	gl#51	ph#51
SiO_2	53.7	50.3	55.2	47.9	55.3	47.7	55.5	50.2	53.0	49.8	54.3	49.1	54.9	48.8
TiO_2	<0.04	<0.10	<0.04	<0.04	0.07	0.13	0.05	<0.04	0.11	0.17	<0.04	<0.04	<0.04	0.07
Al_2O_3	0.33	0.45	0.64	0.86	1.1	1.4	0.18	0.24	2.8	3.5	0.19	0.26	0.61	0.75
Cr_2O_3	0.65	0.90	0.81	1.0	0.84	1.2	0.81	1.1	0.76	1.0	0.81	0.94	0.82	1.1
FeO	0.48	2.4	0.55	3.0	0.75	6.5	0.60	4.7	0.86	4.0	0.64	6.1	0.51	3.4
MnO	0.07	0.11	0.08	0.15	0.22	0.17	0.19	0.24	0.12	0.19	0.20	0.21	0.21	0.18
MgO	45.1	24.6	43.2	29.4	42.1	19.9	43.3	19.3	39.9	16.1	43.8	18.3	43.4	19.9
CaO	0.21	0.56	0.41	0.65	0.89	0.57	0.14	0.44	2.3	0.59	0.19	0.43	0.46	0.47
Na_2O	<0.05	<0.05	<0.05	0.06	0.06	<0.05	0.12	<0.05	<0.05	0.11	0.19	<0.05	0.57	0.09
Total	100.7	79.4	101	83.1	101.3	77.6	100.9	76.4	99.9	75.5	100.4	75.4	101.5	74.7

All hydrated clasts investigated in this study represent distinct objects with sharp boundaries to the surrounding material; they often contain sets of irregular fractures which do not extend into the host meteorite. No interaction between the meteorite matrix and the hydrated clasts was observed. Further, the clasts are clearly dominated by phyllosilicates and thus differ strongly from all other components which are totally anhydrous. A difference in alteration between clasts and host meteorite was also found for CR chondrites and interpreted as evidence for the alteration of these objects prior to incorporation into the host (Zolensky *et al.*, 1992; Weisberg *et al.*, 1993; Endreß *et al.*, 1994). Finally, the fact that magnetite with its great diversity of different morphologies is only present to the hydrated clasts and not found in the host meteorite supports the view that the clasts represent foreign material which did not form by *in situ* alteration of anhydrous CB or CH components.

We thus infer that the presence of completely hydrated, type 1/2-like clasts associated with unaltered, coarse-grained, high-temperature components, such as CAIs, chondrules, and FeNi-metal grains, indicates that the clast materials experienced hydration before they were incorporated into their host meteorite parent bodies. They either accreted together with the high-temperature components or were added later, during regolith gardening.

There is, however, evidence that the lithic clasts also experienced some degree of aqueous alteration on the meteorite parent body which mainly affected highly mobile elements and changed the original bulk composition of the clast. The enrichment in FeO of the peripheral portions of the hydrated clasts in PAT 91546 must have resulted from such a subsequent alteration in the host; it can be due to incipient alteration of the surrounding metal grains, but terrestrial weathering cannot be entirely excluded. Also the depletion of Ca in the lithic clasts is probably attributed to parent body alteration (Fig. 12).

The slow kinetics of hydration reactions in the solar nebula (Prinn and Fegley, 1989) and mineralogical similarities between the clasts and type 1/2 chondritic material suggest that the former experienced alteration in an asteroidal setting. Based on O-isotope data for carbonates, magnetite and phyllosilicates in CI chondrites, Clayton and Mayeda (1999) argued that their aqueous alteration occurred at relatively high temperature (about 100–150 °C) and high water/rock ratios. Similar conditions of alteration may be postulated for hydrated clasts in the metal-rich chondrites, but oxygen isotopic analysis will be required to confirm this similarity.

Meibom *et al.* (2000b) concluded that the QUE 94411 clast described above is compositionally similar to the FeNi-metal-sulfide-ferrous silicate impact melts between chondrules and FeNi-metal grains that seem to glue the QUE 94411 and HH 237 assemblages together (Table 1, Fig. 12). These authors suggested that fine-grained, porous material compositionally

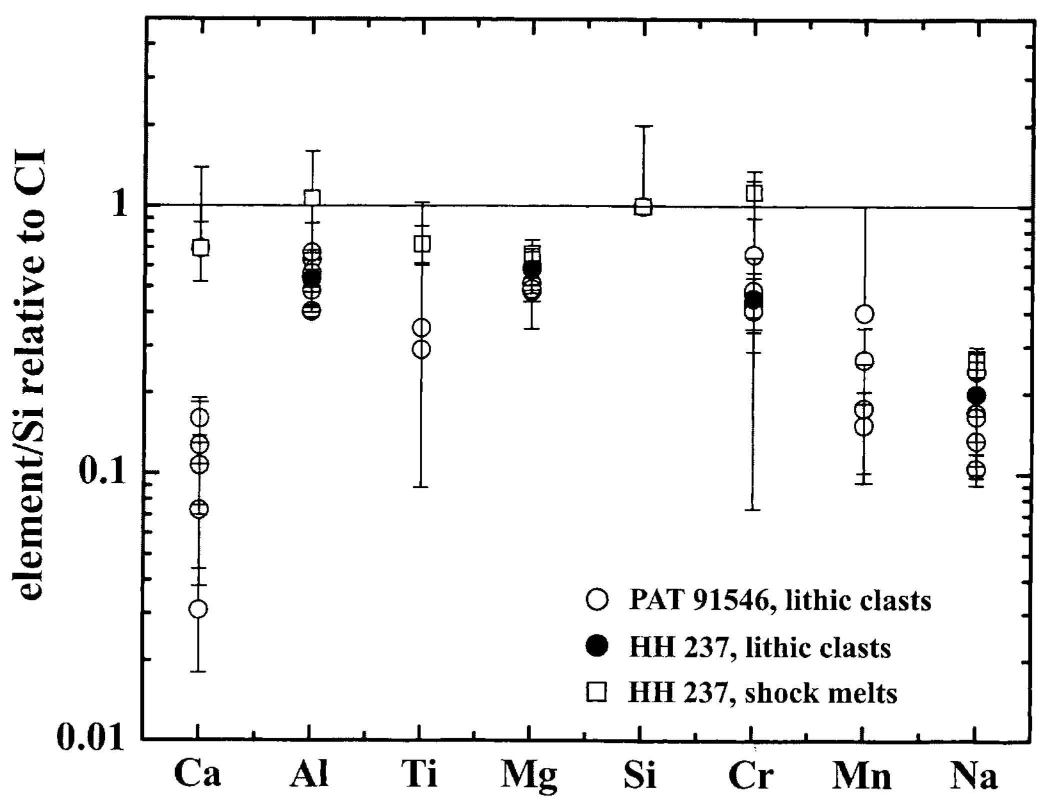

FIG. 12. Bulk contents of lithophile elements normalized to Si and CI chondrite abundances in the hydrated clasts and silicate portions of impact melts in HH 237 and PAT 91546.

similar to the clast was present between the chondrules and FeNi-metal grains, but was heated preferentially and melted in a shock event. Although preliminary studies of shock melts revealed the presence of rare phyllosilicates in the impact melt regions (Zolensky, pers. comm.), we cannot exclude the possibility that these phyllosilicates resulted from aqueous alteration of impact melts, rather than being relic phases.

It was recently suggested that chondrules and FeNi-metal grains in QUE 94411 and HH 237 formed by condensation following a large-scale thermal event that resulted in complete vaporization of a solar nebula region with initially enhanced dust/gas ratio (Meibom *et al.*, 2000a; Krot *et al.*, unpubl. data). According to this model, chondrules condensed as liquids prior to gas-solid condensation of FeNi-metal grains; fine-grained matrix materials were absent from the chondrule-forming region. The absence of complementarity observed for elements which are geochemically highly immobile during aqueous alteration (*i.e.*, Al and Ti) in HH 237 and QUE 94411 chondrules (see Fig. 3a in Krot *et al.*, unpubl. data) and hydrated clast in QUE 94411 (Fig. 12), is consistent with this scenario.

Based on the depletion of moderately volatile elements, such as Mn, Na, K, Ga, Ge, and S, in chondrules and metal, we have argued that, following condensation, these components were isolated from the hot nebular gas prior to condensation of these elements (Meibom *et al.*, 2000a; Krot *et al.*, 2000). This could have been accomplished if the chondrules were formed in the inner parts of the solar nebula and were rapidly transported radially outward to the much colder asteroid belt regions (*e.g.*, by the strong winds that are observed in young stellar systems and believed to originate close to the inner edge of the protoplanetary disk) (*e.g.*, Shu *et al.*, 1996; Meibom *et al.*, 2000a). Along the lines of this model, QUE 94411 and HH 237 could be accretionary breccias if the chondrules and FeNi-metal grains after their removal from the inner parts of the solar nebula accreted with the heavily-hydrated clasts in the asteroid belt. However, any such astrophysical model must also be able to explain the extreme metal/silicate ratios in QUE and HH 237 and the apparent lack of size-sorting between metal particles and chondrules. This has yet to be attempted.

All meteorites of the CR clan show large positive anomalies in $\delta^{15}N$; the origin of these anomalies remains poorly understood (*e.g.*, Franchi *et al.*, 1986; Grady and Pillinger, 1990; Ash and Pillinger, 1992; Sugiura *et al.*, 2000). Sugiura *et al.* (2000) showed that enrichment in heavy N of QUE 94411 and HH 237 appears to be associated with the shock melts. Marty *et al.* (2000) reported evidence for shock-induced mobilization of heavy nitrogen in the Bencubbin meteorite. Mostefaoui *et al.* (2001) discovered large ^{15}N excesses in SiC and carbon grains found in acid-resistant residues of the Bencubbin meteorite, but found that these grains were thermally processed. Campbell *et al.* (2001) recently showed that in the region where Fe-Ni-metal grains in HH 237 and QUE 94411 formed even platinum elements with condensation temperatures >1750 K were completely vaporized. Since the condensation temperature of SiC is <1650 K it is unlikely that the nitrogen anomaly would survive the vaporization-condensation process that resulted in the formation of chondrules and FeNi-metal grains in QUE 94411 and HH 237. We thus suggest that the unshocked and thermally unprocessed type1/2-like clasts in these meteorites could be the source of the ^{15}N-rich grains. An ion microprobe study of acid-resistant residues of these meteorites is in progress.

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