

Magnetite in the unequilibrated CK chondrites: Implications for metamorphism and new insights into the relationship between the CV and CK chondrites

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Abstract—Bulk isotopic and elemental compositions of CV and CK chondrites have led to the suggestion that both originate from the same asteroid. It has been argued that magnetite compositions also support this model; however, magnetite has been studied almost exclusively in the equilibrated (type 4–6) CKs. Magnetite in seven unequilibrated CKs analyzed here is enriched in MgO, TiO₂, and Al₂O₃ relative to the equilibrated CKs, suggesting that magnetite compositions are affected by metamorphism. Magnetite in CKs is compositionally distinct from CVs, particularly in abundances of Cr₂O₃, NiO, and TiO₂. Although there are minor similarities between CV and equilibrated CK chondrite magnetite, this is contrary to what we would expect if the CVs and CKs represent a single metamorphic sequence. CV magnetite should resemble CK3 magnetite, as both were metamorphosed to type 3 conditions. Oxygen fugacities and temperatures of CV_{ox} and CK chondrites are also difficult to reconcile using existing CV–CK parent body models. Mineral chemistries, which eliminate issues of bulk sample heterogeneity, provide a reliable alternative to techniques that involve a small amount of sample material. CV and CK chondrite magnetite has distinct compositional differences that cannot be explained by metamorphism.

INTRODUCTION

Carbonaceous chondrites represent some of the most pristine solar system material. They are distinguished from the ordinary and enstatite chondrites by their mostly unfractionated bulk chemical composition (relative to the Sun) and oxygen isotopic compositions that plot below the terrestrial fractionation line (Kallemeyn et al. 1991; Weisberg et al. 2006; Grady et al. 2014). All carbonaceous chondrites are comprised of three primary components: chondrules, refractory inclusions, and fine-grained matrix material. Olivine is the most ubiquitous phase present in these components. Opaque minerals (mostly oxides and sulfides) are also prominent in most

carbonaceous chondrite groups. The carbonaceous chondrite class is subdivided into eight groups, which are defined based on whole-rock compositions and abundances of chondrite components. Differences between the compositions of carbonaceous chondrite classes represent pre-solar conditions and effects of secondary processing, such as aqueous alteration or metamorphism. Meteorites within each group are commonly thought to originate from the same parent asteroid (Weisberg et al. 2006). Similarities between chemistry and mineralogy of certain carbonaceous chondrite groups have led to the establishment of carbonaceous chondrite clans. Groups within a clan are thought to be derived from similar regions of the solar nebula but still represent unique parent bodies

(Weisberg et al. 2006). One such well-established carbonaceous chondrite clan is the CV-CK clan (Weisberg et al. 2006).

The CV chondrites are a heterogeneous group of chondrites characterized by the presence of large chondrules (~45 vol%), refractory Ca-Al-rich inclusions, and amoeboid olivine aggregates (~10 vol%) (Rubin and Wasson 1987), relatively coarse-grained matrix with FeO-rich olivine, and high contents of dark matrix material (Rubin and Wasson 1987; Kimura and Ikeda 1995; Krot et al. 1995, 1998). The CV chondrites are divided into two general subgroups based on oxidation state. In the reduced subgroup (CV_{red}), Fe-Ni metal predominates over magnetite, sulfides (mostly troilite) are Ni-poor, and CAIs contain more unaltered melilite (McSween 1977; Choi et al. 2000). The reduced group (CV_{red}) has mostly escaped extensive aqueous alteration. The oxidized group (CV_{ox}) contains magnetite and Ni-rich sulfides (e.g., pentlandite), while Fe-Ni metal is rare. The oxidized CV chondrites are further divided into Allende-type (CV_{oxA}) and Bali-type (CV_{oxB}) subgroups, basely primarily on the type of secondary alteration (Weisberg et al. 1997). Bali-like CV_{ox} chondrites experienced aqueous alteration, as evidenced by the presence of phyllosilicates in their matrices and the abundance of secondary fayalite (Fa_{90-100}) (Krot et al. 1995, 1998; Choi et al. 2000). In contrast, Allende-like CV chondrites (CV_{oxA}) contain alteration minerals produced during Fe-alkali-halogen metasomatism (e.g., nepheline, sodalite, and andradite), lack abundant phyllosilicates, and contain more Mg-rich olivine (Fa_{40-60}) (Choi et al. 2000). Many CV chondrites are breccias containing clasts of both reduced and oxidized material. The Mokoia meteorite is a CV_{oxB} breccia containing clasts CV_{oxA} material that have undergone aqueous alteration (Krot et al. 2004). Vigarano (CV_{red}) contains clasts of both CV_{oxA} and CV_{oxB} materials that are inferred to have been mixed during regolith gardening (Krot et al. 1998, 2004).

The CK chondrites are one of the most oxidized groups of carbonaceous chondrites, as evidenced by the absence of Fe-Ni metal, high abundances of magnetite and Ni-rich sulfide minerals, and FeO-rich olivine (Kallemeyn et al. 1991; Geiger and Bischoff 1995). The CK chondrites are dominated by porphyritic (type II) olivine chondrules (Kallemeyn et al. 1991; Rubin 2010). Special attention has been paid by multiple authors (Rubin 1993; Geiger and Bischoff 1995) to rare (~0.1 vol%) magnetite-sulfide aggregates and chondrules in CK chondrites, which are commonly associated with hydroxyl- or Cl-apatite (Geiger and Bischoff 1995). Unlike chondrules in the CV chondrites, CK chondrite chondrules rarely have fayalitic rims, although many have sulfide rims (Rubin 2010). Sulfides minerals in CK

chondrites are dominated by monosulfide solid solution (MSS), pentlandite, and pyrite; minor pyrrhotite and chalcopyrite have also been reported (Geiger and Bischoff 1991). Magnetite is often found in large, rounded chondrules and commonly has apatite and sulfide inclusions. Magnetite in equilibrated (type 4–6) CK chondrites also exhibits lamellae of ilmenite and spinel (Kallemeyn et al. 1991), which are thought to form during exsolution and cooling (Geiger and Bischoff 1995). Both the sulfides and magnetite in CK chondrites often contain intergrowth of Os-Pt-Au-Ru-Is sulfides and tellurides, formed from subsolidus exsolution under highly oxidizing conditions (Geiger and Bischoff 1991). Unlike the CV chondrites, no CK breccias have been described.

One significant difference between the CV and CK chondrite groups is their thermal histories, or more specifically the degree of metamorphism each group experienced. The extent of metamorphism a chondrite experiences on the parent body is described using petrologic type (Van Schmus and Wood 1967; McSween et al. 1988). Chondrites that are relatively unmetamorphosed, or have experienced very slight heating, are designated as petrologic type 3 (unequilibrated), whereas chondrites that have undergone higher degrees of thermal metamorphism are designated as types 4–6 (equilibrated) (Van Schmus and Wood 1967; McSween et al. 1988). All CV chondrites are classified as petrologic type 3 (McSween 1977). The CK chondrites, however, are the only carbonaceous chondrite group to exhibit full range of thermal metamorphism from petrologic type 3 to type 6 (Kallemeyn et al. 1991; Geiger et al. 1993). Because metamorphic effects are particularly prominent in petrologic type 3 material, meteorites of this grade can be further divided into petrologic subtypes (i.e., type 3.0–3.9) (Sears et al. 1980, 1991; Chizmadia et al. 2002). Greenwood et al. (2010) suggested that the unequilibrated CKs are all petrologic type 3.7 or higher based on abundances and compositions of refractory inclusions. A few unequilibrated CK chondrites have been assigned petrologic type 3.8 or 3.9 (see Table 1 and references therein). Attempts to determine the petrologic subtypes of the CV chondrites have produced inconsistent results. Thermoluminescence sensitivity (e.g., Sears et al. 1980; Guimon et al. 1995) and Cr_2O_3 content of olivine (Grossman and Brearley 2005) indicate that CVs are petrologic subtype 3.3 or lower. However, Raman spectroscopy of organic materials suggests that some CVs are at least petrologic type 3.6 (Bonal et al. 2006). Despite the uncertainty, the general consensus is that CV chondrites have experienced lower degrees of metamorphism than the unequilibrated CK chondrites.

Table 1. List of CV and CK chondrites analyzed in this study.

Meteorite Name	Abbrev.	Type	Source	Weathering grade ^a	Weathering index ^b	Shock
Dar al Gani 431	DaG 431	CK 3-an	Colby		wi-6	S2
Dhofar 015	Dhofar 015	CK 3.9	Vernad.	W1		S3
Northwest Africa 1559	NWA 1559	CK 3.8	Colby		wi-3	
Northwest Africa 2043	NWA 2043	CK 3	UWS	W0		S1
Northwest Africa 4423	NWA 4423	CK 3.9	MNHN	W2		S1
Northwest Africa 4425	NWA 4425	CK 3.8	MNHN	W2		S1
Northwest Africa 5343	NWA 5343	CK 3	Colby	W2		S2
Northwest Africa 4422	NWA 4422	CK 4	MNHN	W2		S1
Bali		CV OxB	NMNH	Fall		Fall
Northwest Africa 2086	NWA 2086	CV OxB	Colby	W1		S1
Northwest Africa 4446	NWA 4446	CV OxB	Colby	W2		S2

^aWeathering grade from the Meteoritical Bulletin; based on Cassidy (1980) and Wlotzka (1993).

^bWeathering index for CK and R chondrites after Rubin and Huber (2005).

Weathering index for DaG 431 by Rubin and Huber (2005) and for NWA 1559 by Wasson et al. 2013

Colby = Colby College; Vernad. = Vernadsky Institute; UWS = University of Washington in Seattle; MNHN = Muséum national d'Histoire naturelle, Paris; NMNH = National Museum of Natural History, New York.

Prior to the discovery of Watson 002 in 1991 (Geiger et al. 1993), no type 3 CK chondrites had been identified. Since then, thirty CK chondrites have been classified as petrologic type 3, and three chondrites have been classified as anomalous CK3s. The surge in the number of unequilibrated CK chondrites and their similarities to the oxidized CV chondrites led researchers to postulate that the two groups may be genetically related. These similarities resulted in the establishment of the CV-CK clan (Weisberg et al. 2006). To further examine the relationship between the CV and CK chondrites, Greenwood et al. (2010) measured bulk elemental and isotopic abundances of fifteen CK chondrites and thirteen CV chondrites and compared these to previously published data on the same samples. They also measured magnetite compositions in two CV chondrites and four CK chondrites. Strong similarities in isotopic compositions, refractory lithophile element abundances, and in Cr₂O₃ content of magnetite between the two groups led Greenwood et al. (2010) to suggest that the CV and CK chondrites were derived from a single, thermally stratified parent body, much like the onion-shell model for the ordinary chondrites (Trieloff et al. 2003; Wood 2003). The single parent body model for the CV and CK chondrites has since gained support, although alternatives to the onion-shell model have been proposed. Chaumard et al. (2012) suggested that the CK chondrites formed as a result of metamorphism during radiative heating, while Wasson et al. (2013) proposed a model in which the CK chondrites were buried and aqueously altered on a shocked CV-like parent body.

Any potential model of a single CV-CK asteroid requires that both groups formed under similar parent

body conditions, such as temperatures and oxygen fugacities. Magnetite, which forms from oxidation of metal on a parent asteroid (Choi et al. 1997, 2000; Davidson et al. 2014), can be a useful indicator of the physical conditions under which an asteroid parent body formed. Because magnetite is the predominant oxide component of both CV and CK chondrites, it has been extensively studied in both meteorite groups (e.g., Haggerty and McMahon 1979; Rubin 1991; Murakami and Ikeda 1994; Geiger and Bischoff 1995; Simon et al. 1995). However, previous studies of magnetite in the CK chondrites have focused primarily on the equilibrated (type 4–6) CK chondrites. Magnetite in the unequilibrated CK chondrites has also been measured in previous studies, but only in two samples: Dhofar 015 (Ivanova et al. 2000) and Watson 002 (Greenwood et al. 2010; Chaumard et al. 2014; Davidson et al. 2014). Additional analyses of magnetite in the unequilibrated CK chondrites are necessary to effectively characterize the range of magnetite in the CK chondrites. In this study we present mineralogical analyses from seven unequilibrated CK chondrites and one equilibrated CK chondrite (Table 1) to better quantify the range of magnetite compositions in the CK chondrites. We also compare these compositions to magnetite from previously analyzed CV chondrites and three new CV_{oxB} chondrites in order to reevaluate the single parent body model for the CV and CK chondrites.

METHODOLOGY

Samples

We analyzed magnetite in seven unequilibrated CK chondrites — DaG 431, Dhofar 015, NWA 1559, NWA

2043, NWA 4423, NWA 4425, and NWA 5343—and one equilibrated CK chondrite, NWA 4422. We attempted to measure magnetite in CK3 chondrite NWA 5956, but the sample has experienced significant terrestrial weathering and unaltered magnetite could not be found. In addition to these CK chondrites, we also analyzed magnetite in three Bali-type oxidized CV chondrites: Bali, NWA 2086, and NWA 4446. We attempted to analyze magnetite in two additional CV_{oxB} chondrites, Kaba and Mokoia, but no suitable magnetite could be found. Although XRD-measured modal abundances indicate that magnetite is present in Kaba and Mokoia (Howard et al. 2010), magnetite in these chondrites was either too small for EPMA work (<5 μm) or contained significant FeS intergrowth, and thus resulted in mixed analyses (i.e., contained overlap of neighboring grains). Magnetite is present only at very low abundances (<2 vol%) in reduced CV chondrites (e.g., Howard et al. 2010), thus we did not attempt to analyze magnetite in the CV_{red} chondrites. Samples analyzed in this study are listed in Table 1.

Possible Weathering Effects

Of the three CV chondrites analyzed here, Bali is a fall, and thus represents pristine material. Based on the weathering scale of Wlotzka (1993), NWA 2086 has experienced minimal oxidation (W1) and NWA 4446 moderate oxidation (W2). All CK chondrites are desert finds, and thus have experienced some degree of terrestrial weathering (Table 1). All CK chondrites examined in this study except DaG 431 and NWA 1559 are slightly to moderately weathered. NWA 1559 is significantly weathered (wi-3) (Wasson et al. 2013) and DaG 431 is extremely weathered (wi-6) (Rubin and Huber 2005). Weathering in the CK chondrites is due to mobilization of oxidized iron derived from terrestrially weathered Ni-bearing sulfide grains (Rubin and Huber 2005; Huber et al. 2006). Although this results in depletion of bulk S, Se, Co, Au, and Ni abundances, magnetite is resistant to weathering (Huber et al. 2006), and thus we do not expect terrestrial weathering to substantially alter magnetite compositions.

Analytical Techniques

Chemical compositions of magnetite in the CV chondrites and all CK chondrites except DaG 431 and Dhofar 015 were obtained with the CAMECA SX-100 at the American Museum of Natural History, New York. Operating conditions were 15 keV accelerating voltage, 25 nA beam current, focused electron beam (1 μm in diameter), and peak and background counting times of 30–60 s per element. Analytical standards were

well-characterized synthetic oxides and natural minerals, including MgAl₂O₄ (Al, Mg), olivine (Si), hematite (Fe), troilite (Fe, S), Co-metal (Co), Ni-diopside (Ni), rutile (Ti), rhodinite (Mn), V₂O₃ (V), chromite (Cr), and diopside (Ca). The overlap correction of the CAMECA peak site software was used to correct for the peak overlap between Ti-V, Co-Fe, and Mn-Cr. Data quality was ensured by analyzing standard materials and secondary standards as unknowns. Magnetite in DaG 431 and NWA 1559 was analyzed using a JOEL JXA-2000 microprobe at Washington University in St. Louis, and Dhofar 015 was analyzed using a SX50 electron microprobe at the University of Tennessee and at the Vernadsky Institute using Camebax-microbeam electron microprobe operated at 15 kV and 15 nA. The minor difference in beam current between Dhofar 015 and the other samples should not result in any analytical inconsistencies between samples. A minimum of 15 grains were analyzed in each CK chondrite except NWA 5343, in which only 8 grains were analyzed. In most CK chondrites, at least 25 grains were analyzed. Between 6 and 14 grains were analyzed in each CV chondrite. The average composition and number of analyzed grains in the CK and CV chondrites are listed in Tables 2 and 3, respectively.

MAGNETITE IN THE CK CHONDRITES

Magnetite in unequilibrated CK chondrites occurs both as spheres in chondrules and as grains in the matrix. Magnetite in chondrules is sometimes oblate and ranges in size from 110 microns to < 5 microns (Figs. 1a, 1b, 1c, and 1e). In the matrix, most magnetite occurs as anhedral grains (Figs. 1d and 1f). Magnetite is often intergrown with FeS or Fe-Ni metal. Average compositions and standard deviations of magnetite in the eight CK chondrites analyzed in this study are shown in Table 2. Magnetite compositions in the seven unequilibrated (type 3) CK chondrites are rich in chromium, aluminum, and nickel. Average Cr₂O₃ content ranges from 2.56 to 2.95 wt%, average Al₂O₃ from 0.70 to 3.24 wt%, and average NiO from 0.30 to 0.37 wt%. Magnetite is also rich in TiO₂ and MgO, with average abundances ranging from 0.18 to 0.94 wt% and 0.10 to 0.88 wt%, respectively. Average Fe₂O₃ and FeO* abundances (calculated from stoichiometry) range from 58.27 to 62.73 wt% and 30.69 to 32.45 wt%, respectively. In all unequilibrated CK chondrites, MnO is present at abundances ≤ 0.10 wt% while CoO is below detectable limits (0.02 wt%). V₂O₃ was analyzed in five of the seven unequilibrated CK chondrites and is present at average abundances ranging from 0.11 to 0.16 wt%. Magnetite compositions in these CK3 chondrites are consistent with previous analyses of

Table 2. Average compositions (wt%) of magnetite in eight CK chondrites.

	DaG 431		Dhofar 015		NWA 1559		NWA 2043		NWA 4423		NWA 4425		NWA 5343		NWA 4422	
	CK3-an		CK3.9		CK3.8		CK3		CK3.9		CK3.8		CK3		CK4	
	N = 48		N = 52		N = 20		N = 26		N = 15		N = 21		N = 8		N = 40	
	Avg.	Stdev	Avg.	Stdev	Avg.	Stdev	Avg.	Stdev	Avg.	Stdev	Avg.	Stdev	Avg.	Stdev	Avg.	Stdev
MgO	0.68	0.06	0.10	0.04	0.74	0.08	0.75	0.09	0.59	0.07	0.88	0.01	0.83	0.24	0.14	0.13
Al ₂ O ₃	2.88	0.20	0.70	0.48	3.19	0.21	2.99	0.17	2.72	0.15	3.24	0.10	2.79	0.54	0.53	0.29
SiO ₂	0.16	0.11	0.03	0.03	0.16	0.16	0.10	0.13	0.02	0.01	0.02	0.02	0.05	0.03	0.04	0.10
CaO	0.29	0.34	0.06	0.07	0.17	0.21	0.12	0.26	0.05	0.04	0.10	0.13	0.27	0.36	0.02	0.03
TiO ₂	0.67	0.11	0.18	0.09	0.94	0.20	0.76	0.03	0.60	0.02	0.74	0.04	0.71	0.31	0.18	0.06
V ₂ O ₃	nm	nm	nm	nm	0.16	0.02	0.11	0.00	0.14	0.00	0.14	0.01	0.16	0.05	0.10	0.01
Cr ₂ O ₃	2.88	0.74	3.75	0.48	2.95	0.70	2.91	0.12	2.80	0.25	2.81	0.16	2.56	1.71	3.21	0.46
MnO	0.08	0.02	0.02	0.02	0.08	0.02	0.09	0.02	0.08	0.02	0.10	0.01	0.07	0.02	0.03	0.01
FeO	85.27	1.25	87.13	1.00	83.71	1.64	84.76	0.72	85.58	0.51	85.37	0.55	84.36	2.61	88.38	0.76
FeO*	31.94	0.77	30.69	0.28	31.28	0.93	31.04	0.74	32.45	0.15	30.86	0.23	30.94	0.96	30.85	0.38
Fe ₂ O ₃	59.28	1.95	62.73	1.21	58.27	2.04	59.70	1.51	59.05	0.57	60.57	0.71	59.37	3.17	63.93	1.06
CoO	nm	nm	nm	nm	0.01	0.01	0.02	0.02	0.00	0.00	0.02	0.01	0.02	0.01	0.00	0.00
NiO	0.33	0.03	0.35	0.08	0.33	0.04	0.34	0.05	0.30	0.02	0.37	0.02	0.32	0.06	0.25	0.03
Total	93.27	0.69	87.13	1.00	92.38	1.12	92.97	0.36	92.90	0.29	93.80	0.47	92.15	0.65	92.88	0.36
Total*	99.23	0.84	98.50	0.52	98.15	1.28	98.89	0.46	98.76	0.36	99.85	0.54	98.10	0.85	99.28	0.37

Petrologic subtypes: NWA 4423 and NWA 4425 (Chaumard et al. 2014), Dhofar 015 (Ivanova et al. 2000), and NWA 1559 (Rubin 2013).

Fe₂O₃ and FeO* were calculated from stoichiometry.

Table 3. Average compositions (wt%) of magnetite in CVoxB chondrites.

	NWA 2086		NWA 4446		Bali	
	N = 12		N = 14		N = 6	
	Avg.	Stdev	Avg.	Stdev	Avg.	Stdev
MgO	0.38	0.18	0.43	0.26	0.35	0.08
Al ₂ O ₃	0.94	0.16	0.39	0.16	0.06	0.05
SiO ₂	0.02	0.01	0.15	0.15	0.12	0.04
CaO	0.21	0.21	0.34	0.34	0.02	0.02
TiO ₂	0.05	0.02	0.06	0.03	0.02	0.01
V ₂ O ₃	0.02	0.02	0.03	0.01	0.01	0.00
Cr ₂ O ₃	1.12	0.29	1.78	0.62	1.87	0.79
MnO	0.03	0.02	0.02	0.02	0.03	0.02
FeO	89.38	0.71	89.43	1.22	89.35	0.80
FeO*	30.82	0.64	31.70	1.80	30.70	0.44
Fe ₂ O ₃	65.08	1.28	64.15	3.29	65.18	1.14
CoO	0.01	0.01	0.01	0.01	0.01	0.01
NiO	0.07	0.08	0.06	0.05	0.13	0.12
Total	92.24	0.50	92.82	0.47	92.05	0.23
Total*	98.76	0.60	99.13	0.68	98.56	0.16

Fe₂O₃ and FeO* were calculated from stoichiometry.

magnetite in Watson 002 (Greenwood et al. 2010; Davidson et al. 2014). Compared the CK3 chondrites, magnetite in CK4 chondrite NWA 4422 is depleted in all oxides except for Cr₂O₃ and Fe₂O₃. Average abundances of magnetite in NWA 4422 are listed in Table 2. Composition of magnetite in NWA 4422 is consistent with magnetite from 20 equilibrated CK chondrites measured in previous studies (Rubin 1993;

Geiger and Bischoff 1995; Greenwood et al. 2010; Chaumard et al. 2014). All magnetite analyses from our eight samples, along with magnetite compositions from previously analyzed CK chondrites (Rubin 1993; Geiger and Bischoff 1995; Greenwood et al. 2010; Chaumard et al. 2014), are plotted in terms of MgO versus oxide abundance on Fig. 2. Abundances are plotted relative to MgO because MgO versus Cr₂O₃ has historically been used to distinguish between the CK and CV chondrites (Ivanova et al. 2003; Greenwood et al. 2010).

As illustrated in Fig. 2, magnetite in the unequilibrated CK chondrites and the equilibrated CK chondrites always plot in two distinct compositional clusters. This is due in large part to a compositional gap between MgO abundances in the CK3 chondrites (<0.25 wt% MgO) and the equilibrated CK chondrites (>0.3 wt% MgO). The most obvious compositional differences between magnetite in the CK3 and equilibrated CK chondrites are in abundances of TiO₂ (Fig. 2b) and Al₂O₃ (Fig. 2d), which are higher in the unequilibrated CK chondrites. Although average abundances of NiO, MnO, and FeO* are higher in the CK3 chondrites, the overall range of each of these oxide abundances overlaps slightly between the unequilibrated and equilibrated CK chondrites (Figs. 2c, 2e, and 2g, respectively). Average abundances of Cr₂O₃ and Fe₂O₃ are higher in the equilibrated CK chondrites, although the range of abundances once again overlaps between the unequilibrated and equilibrated CKs (Figs. 2a and 2h, respectively). Abundances of Cr₂O₃ are most similar, with abundances ranging from 1.9 to 5.7 wt%

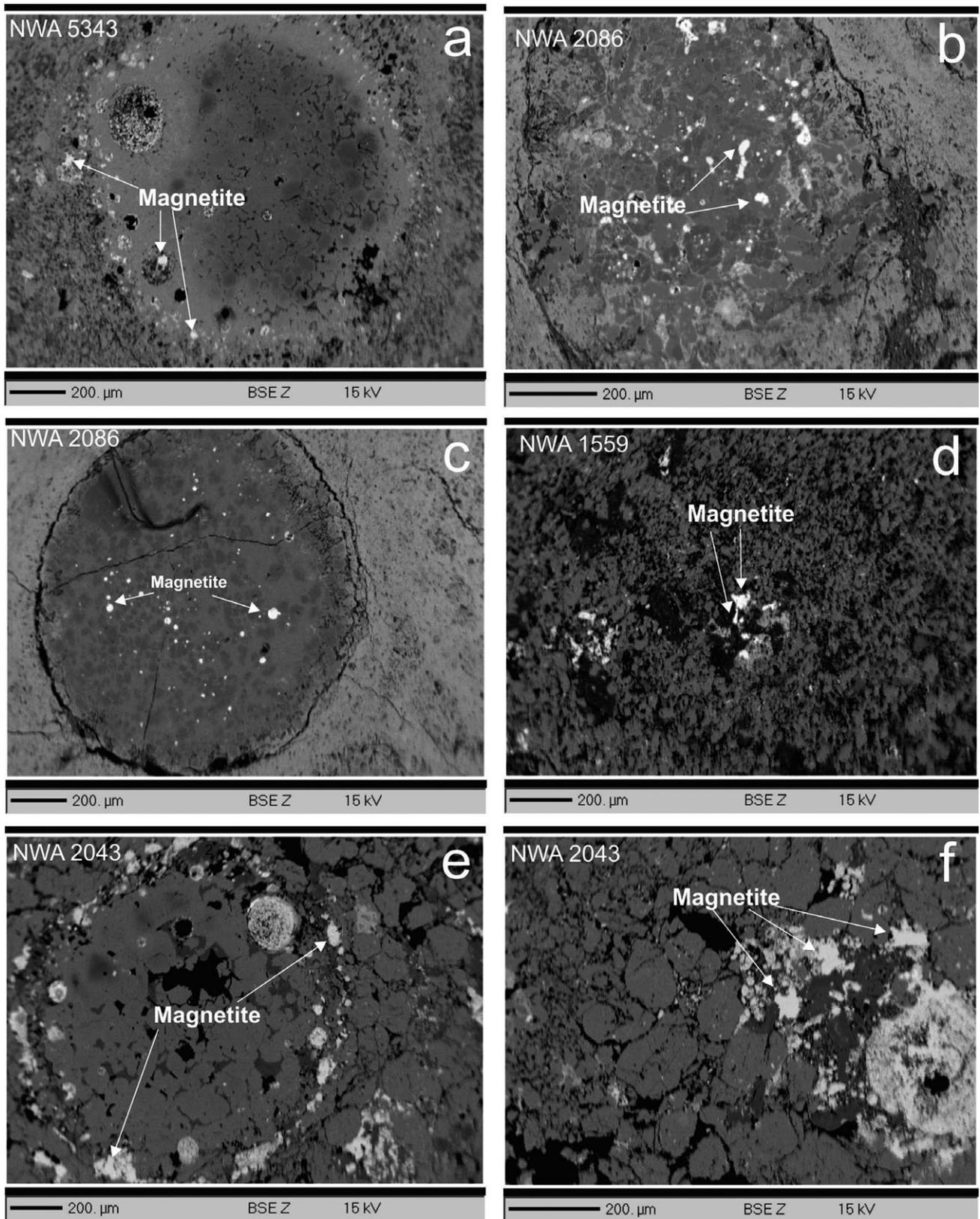


Fig. 1. Back scatter electron images of magnetite as spheres in chondrules (a, b, c, and e) and as subhedral grains in the matrix (d and f) of unequilibrated CK chondrites NWA 5343, NWA 1559, and NWA 2043 and CV_{oxB} chondrite NWA 2086.

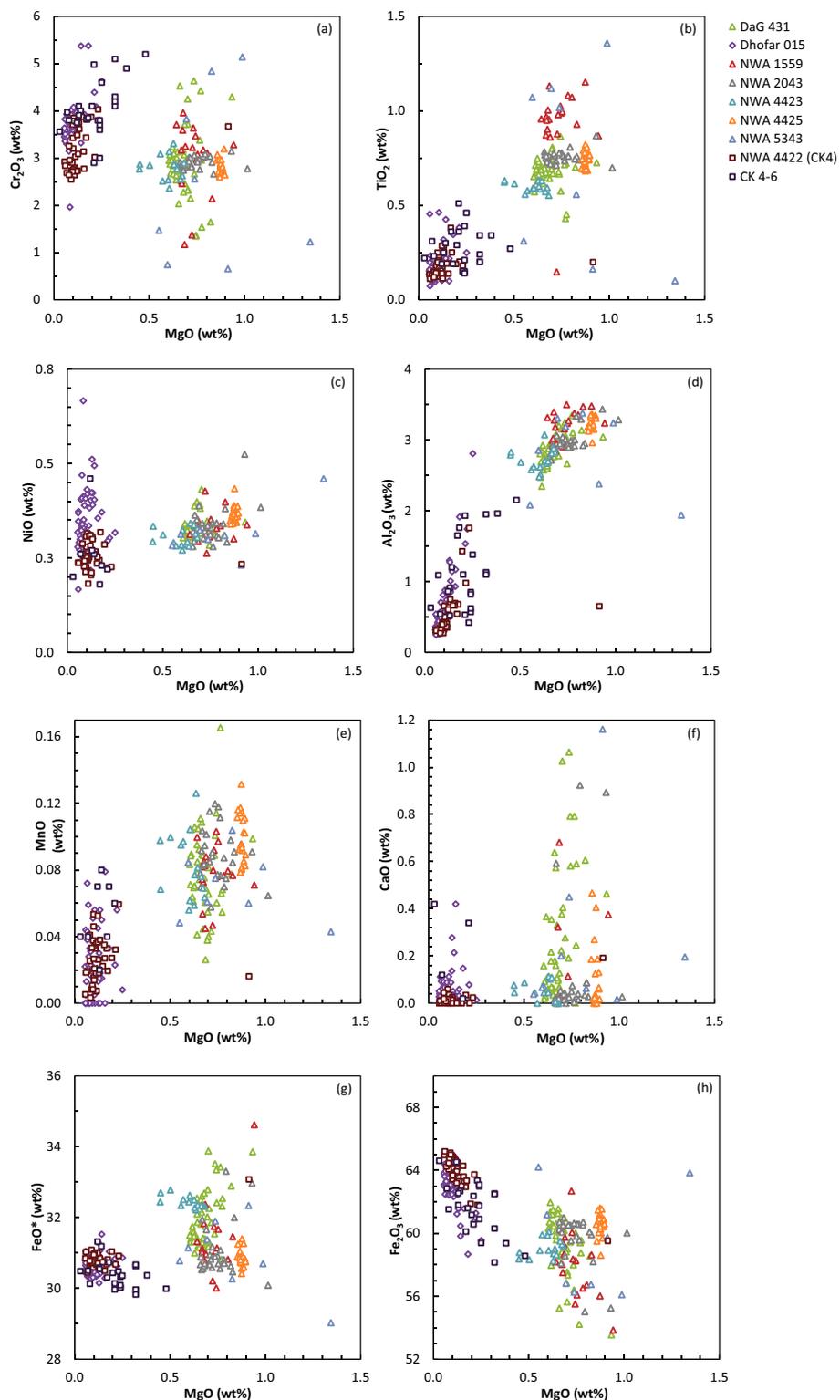


Fig. 2. Compositions of magnetite from seven unequilibrated CK chondrites and one CK4 chondrite (NWA 4422) analyzed in this study, plotted along with average compositions of magnetite in 20 equilibrated CK chondrites measured in previous studies (Rubin 1993; Geiger and Bischoff 1995; Greenwood et al. 2010; Chaumard et al. 2014; Davidson et al. 2014). Unequilibrated chondrites are represented by triangles, except for Dhofar 015, which is a diamond, and equilibrated CK chondrites are represented by squares. Compositions are plotted as MgO (wt%) versus (a) Cr_2O_3 , (b) TiO_2 , (c) NiO, (d) Al_2O_3 , (e) MnO, (f) CaO, (g) FeO^* , and (h) Fe_2O_3 . FeO^* and Fe_2O_3 were calculated from stoichiometry.

in the equilibrated CKs and from 0.9 to 5.1 wt% in the unequilibrated CKs (Fig. 2a). Abundances of CaO (Fig. 2f) are quite variable in the unequilibrated CK chondrites (0 to 1.2 wt%) but are less so in the equilibrated CKs (>0.4 wt%). Clearly, there are distinct compositional differences between magnetite in the unequilibrated and equilibrated CK chondrites.

An unexpected observation from this study is that magnetite in Dhofar 015 (represented by a diamond on Fig. 2) plots firmly in the equilibrated chondrite clusters on all compositional diagrams. Dhofar 015 was initially assigned a petrologic subtype of 3.9 based on sharply defined chondrules, friable matrix, and a large range in feldspar compositions (Ivanova et al. 2000). In addition to magnetite compositions, the average fayalite content of Dhofar 015 (Fa₃₂) (Ivanova et al. 2000) is also consistent with that of the equilibrated chondrites. This suggests that Dhofar 015 is actually an equilibrated CK chondrite, despite its nebular features (Ivanova et al. 2000). Thus, henceforth we will refer to Dhofar 015 as an equilibrated CK chondrite. We will address this updated petrologic type more thoroughly in the section of the paper entitled, “Metamorphism and Thermal History of the CK Chondrites.

MAGNETITE IN THE CV CHONDRITES

Average compositions and standard deviations of magnetite in three CV_{oxB} chondrites analyzed in this study are shown in Table 3. All magnetite analyses from these samples are plotted in addition to the CK chondrites on Fig. 3. To supplement our analyses, compositions of magnetite measured in previous studies are also plotted on Fig. 3. This includes an average analysis of magnetite in Vigarano (CV_{red}) and Allende (CV_{oxA}) (Greenwood et al. 2010), four analyses of magnetite in opaque Allende chondrules (Rubin 1991), five analyses of magnetite in olivine-rich Allende chondrules (Haggerty and McMahon 1979), and four magnetite analyses from Yamato-86751 (CV_{oxA}) (Murakami and Ikeda 1994). It is important to note that the range of magnetite compositions from Greenwood et al. (2010) is much wider than what is represented by the average. For example, as illustrated on fig. 5 of Greenwood et al. (2010), the range of Cr₂O₃ content in Allende magnetite is ~1–4 wt%. However, with the exception of Cr₂O₃, only an average oxide abundance is available for each sample. CV chondrites are represented by closed circles on Fig 3.

Within the three CV_{oxB} chondrites analyzed in this study, Cr₂O₃ abundances range from 1.12 wt% (NWA 2086) to 1.87 wt% (Bali). Al₂O₃ and CaO are also variable, with abundances ranging from 0.05 to 1.4 wt% and 0.01 to 1.11 wt%, respectively. NiO ranges

from 0.02 to 0.40 wt%, though, a few analyses from NWA 2086 and Allende (Haggerty and McMahon 1979) are below detectable levels. FeO* is present at abundances ranging from 29.84 to 36.65 wt%, and Fe₂O₃ from 61.18 to 68.18 wt%. Magnetite compositions in the CV chondrites are characterized by low TiO₂ (≤0.15 wt%) and MnO (≤0.06 wt%). Compositions of magnetite in our CV_{oxB} chondrites are consistent with previously analyzed magnetite in CV_{oxB} chondrites, Kaba and Mokoia (Choi et al. 2000). Although we did not measure any Allende-type CV chondrites in this study, comparison of our data with CV_{oxA} chondrites Allende and Yamato-86571 (Figs. 3a–h) (Haggerty and McMahon 1979; Rubin 1991; Murakami and Ikeda 1994; Greenwood et al. 2010) suggest that there is no discernable difference between compositions of magnetite in the CV_{oxA} and CV_{oxB} chondrites. It is difficult to make any broad statements about magnetite in reduced CV chondrites because it is fine-grained, present in low abundances (McSween 1977; Howard et al. 2010), and thus difficult to analyze. However, Greenwood et al. (2010) analyzed 31 magnetite grains in Vigarano (CV_{red}). Averages and standard deviations of oxide abundances in Vigarano (Greenwood et al. 2010) suggest that magnetite in reduced CV chondrites differs compositionally from magnetite in the oxidized CV chondrites. In particular, abundances of MgO, Al₂O₃, NiO, and Cr₂O₃ are much lower in Vigarano than in the CV_{ox} chondrites.

ONE OR TWO PARENT BODIES?

Magnetite in the CV and CK Chondrites

If the CV and CK chondrites formed on a single parent body (Greenwood et al. 2010; Wasson et al. 2013; Chaumard et al. 2014) then they should represent a continuous metamorphic sequence. Based on observations about the degree of metamorphism experienced by each group (e.g., McSween 1977; Greenwood et al. 2010), the CV chondrites represent the most primitive material in this metamorphic sequence (≤3.3) and the CK3 chondrites represent the more metamorphosed material (>3.7). Although magnetite in the CV chondrites forms during low temperature aqueous alteration of metal (Choi et al. 2000), the CV and CK chondrites experienced higher temperatures associated with subsequent thermal metamorphism. Thus, we base our subsequent interpretations on the assumption that magnetite compositions have been affected by metamorphism and do not represent initial compositions associated with oxidation from metal.

As demonstrated in Fig. 3, there are considerable compositional differences between magnetite in the CV chondrites and magnetite in the CK chondrites, the

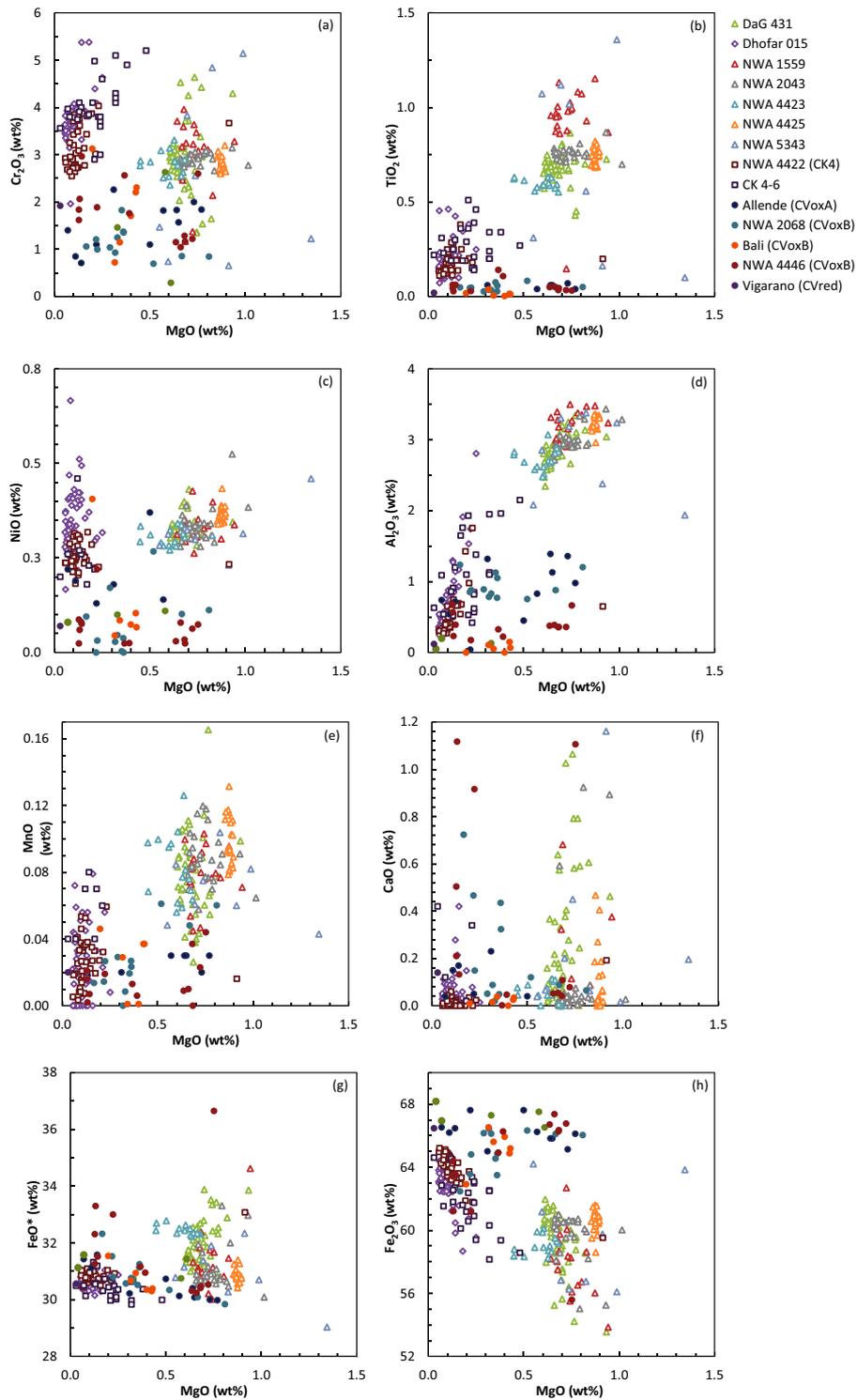


Fig. 3. Compositions of magnetite in CK chondrites from this and previous studies (see references for Fig. 2), three CV_{oxB} chondrites analyzed in this study, two previously analyzed CV_{oxA} chondrites, Allende (Haggerty and McMahon 1979; Rubin 1991; Greenwood et al. 2010) and Yamato-86751 (Murakami and Ikeda 1994), and reduced CV chondrite, Vigarano (average composition from Greenwood et al. 2010). Samples are plotted as MgO (wt%) versus (a) Cr₂O₃, (b) TiO₂, (c) NiO, (d) Al₂O₃, (e) MnO, (f) CaO, (g) FeO*, and (h) Fe₂O₃. CV chondrites are represented by solid circles, CK3 chondrites by open triangles (except Dhofar 015, which is an open diamond), equilibrated CK chondrites by open squares, and Dhofar 015 by an open diamond. FeO* and Fe₂O₃ were calculated from stoichiometry.

most distinct of which are in abundances of Cr_2O_3 , TiO_2 , NiO , and Fe_2O_3 (Figs. 3a, 3b, 3c, and 3h, respectively). TiO_2 , which is a principal constituent of magnetite in the CK chondrites (as high as 1.3 wt%), is present at abundances <0.15 wt% in the CV chondrites. Furthermore, in CK chondrite magnetite, TiO_2 decreases as MgO decreases, resulting in linear trend from the unequilibrated to the equilibrated CKs (Fig. 3b); this trend absent from the CV chondrites. The partition between NiO content in the CV and CK chondrites is at ~ 0.25 wt%, with the CV chondrites containing the lower abundances. Although a few magnetite analyses in the CV chondrites contain >0.25 wt% NiO (Fig. 3c), these appear to be anomalously high and not representative of CV chondrite magnetite. The same is true for Cr_2O_3 , although there is slightly more overlap in compositions between the CV and the equilibrated CK chondrites (Fig. 3a). This is due primarily to the heterogeneous nature of Cr_2O_3 in CK chondrites DaG 431 and NWA 5343. Fe_2O_3 is the only oxide that is present at higher abundances in the CV chondrites than in the CK chondrites, indicating that magnetite in the CV chondrites contains more Fe^{3+} than in the CKs (Fig. 3h). A few magnetite analyses in the CV_{oxB} chondrites contain abundances of Fe_2O_3 that are lower than the other CV chondrites, and thus overlap with compositions in the equilibrated CK chondrites. This is most prominent in NWA 4446, where half of the analyses contain <65 wt% Fe_2O_3 and the other contain >65 wt%. However, like TiO_2 , there is a linear trend in CK chondrite magnetite where Fe_2O_3 decreases as MgO increases. Once again, this trend is again absent from magnetite in the CVs, suggesting that the lower Fe_2O_3 magnetite in Bali is arbitrary rather than indicative of a genetic relationship between the two groups.

There is some compositional overlap between the Al_2O_3 content of magnetite in the CV and CK chondrites (Fig. 3d). However, this occurs over a limited range of compositions where MgO is <0.4 wt% and Al_2O_3 is <1.4 wt%. Abundances of Al_2O_3 in CK chondrite magnetite demonstrate the same linear trend with MgO as TiO_2 and Fe_2O_3 , and once again this trend is absent from magnetite in the CV chondrites. If the CK chondrites are metamorphosed CV chondrites (Greenwood et al. 2010; Chaumard et al. 2012; Wasson et al. 2013), we would expect the CV chondrites to fall on this trend as well. The absence of such a trend with the CV chondrites suggests that any similarities in oxide abundances between the two groups are arbitrary rather than the result of a genetic relationship. Furthermore, the observation that magnetite compositions in the CV chondrites are most similar to magnetite in the equilibrated CK chondrites (rather than the CK3

chondrites), also argues against a relationship between the two groups. Although the CK3 chondrites are slightly more metamorphosed ($>$ type 3.7) than the CV chondrites, they are still unequilibrated. Thus, compositionally the CV chondrites should be most similar to the CK3 chondrites, not the highly metamorphosed equilibrated CK chondrites. Although there are also some minor similarities in MnO and CaO abundances of magnetite between the CV and CK chondrites (Figs. 3e and 3f), both oxides are minor components of magnetite (<0.15 wt% MgO and <1 wt% CaO) and do not likely offer any information about petrogenesis. The observation that magnetite in the CV chondrites is most similar to magnetite in the equilibrated CK chondrites is contrary to what would be expected if the CK chondrites are metamorphosed CV chondrites.

Abundances of Fe_2O_3 , TiO_2 , and Al_2O_3 , in CK and CV chondrite magnetite are plotted relative to FeO on Fig. 4. In chondritic meteorites, FeO is sensitive to metamorphism (Dodd et al. 1967; Huss et al. 1978, 1981). FeO content of magnetite in the equilibrated CK chondrites is higher than in the unequilibrated CK chondrites, suggesting that FeO in magnetite increases during metamorphism (Figs. 4a–c). Figure 4a demonstrates that Fe_2O_3 content of magnetite in the CK chondrites also increases during metamorphism. If the CV and CK chondrites represent a single metamorphic sequence (Greenwood et al. 2010; Wasson et al. 2013), then the least metamorphosed CV chondrites should contain the lowest abundances of FeO and Fe_2O_3 . This is opposite of what is observed. Abundances of TiO_2 (Fig. 4b) decrease during metamorphism of the CK chondrites. However, magnetite in the CV chondrites is depleted in TiO_2 relative to the CK chondrites. Abundances of Al_2O_3 in CV and CK chondrite magnetite (Fig. 4c) demonstrate the same trend as TiO_2 , although there is some overlap between magnetite compositions in the CV and equilibrated CK chondrites. Again, both of these observations are contrary to what would be expected if the CK chondrites are metamorphosed CV chondrites. Regardless of whether compositions are plotted relative to MgO or FeO , magnetite compositions do not support the argument that CK chondrites are metamorphosed CV chondrites (Greenwood et al. 2010; Wasson et al. 2013).

While abundances of Cr_2O_3 , MgO , and TiO_2 in magnetite have historically been used to distinguish between the CV and CK chondrites (Ivanova et al. 2003; Greenwood et al. 2010), abundances of NiO also provide an additional method for differentiating between these two groups. This is illustrated in Fig. 5, in which all magnetite analyses from the samples in this

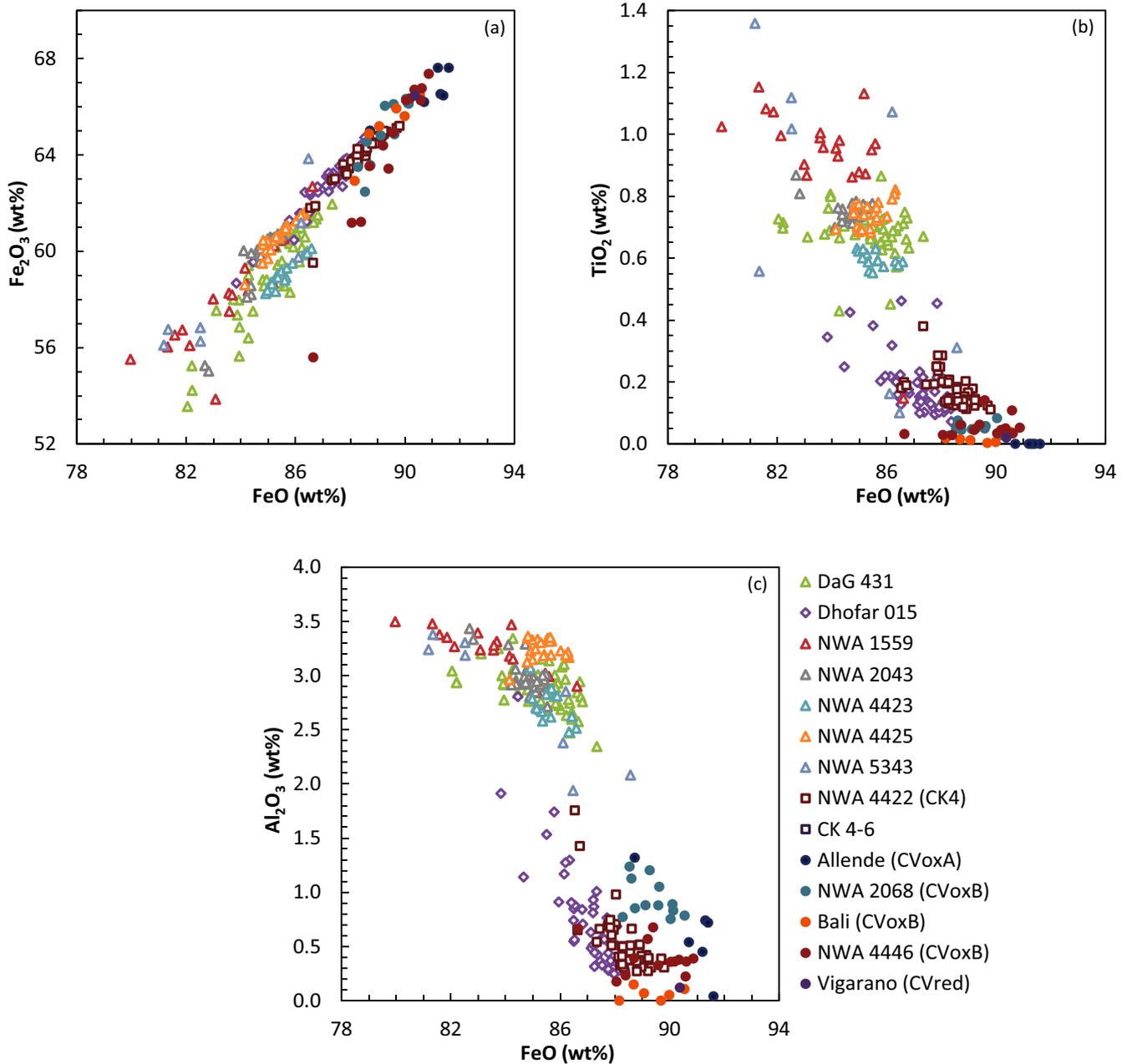


Fig. 4. Compositions of magnetite in CV and CK chondrites from this and previous studies (see references for Fig. 2) plotted as FeO (wt%) versus (a) Fe₂O₃, (b) TiO₂, and (c) Al₂O₃ (wt%). CV chondrites are represented by solid circles, CK3 chondrites by open triangles (except Dhofar 015, which is an open diamond), and equilibrated CK chondrites by open squares. Compositions of magnetite are contrary to what would be expected if the CK chondrites are metamorphosed CV chondrites.

study and previous studies are plotted as NiO versus TiO₂. Here, the CV chondrites are defined by a low-TiO₂ zone (<~0.15 wt%), while the CK chondrites form a trend from equilibrated (<0.3 wt% TiO₂) to unequilibrated (>0.3 wt% TiO₂). A similar trend is indicated by Cr₂O₃ (wt%) versus TiO₂ (wt%) (Fig. 6), which highlights the low Cr₂O₃ content of the CV chondrites relative to the CK chondrites. Here, the

unequilibrated and equilibrated CK chondrites are separated by a line with a slope of -0.34 . Compositions of magnetite in CK3-an chondrite Watson 002 (Greenwood et al. 2010; Davidson et al. 2014) are also plotted on Figs. 5 and 6. Watson 002 plots in the unequilibrated CK chondrite area, as expected. In addition to emphasizing the compositional differences between magnetite in the two groups, these figures

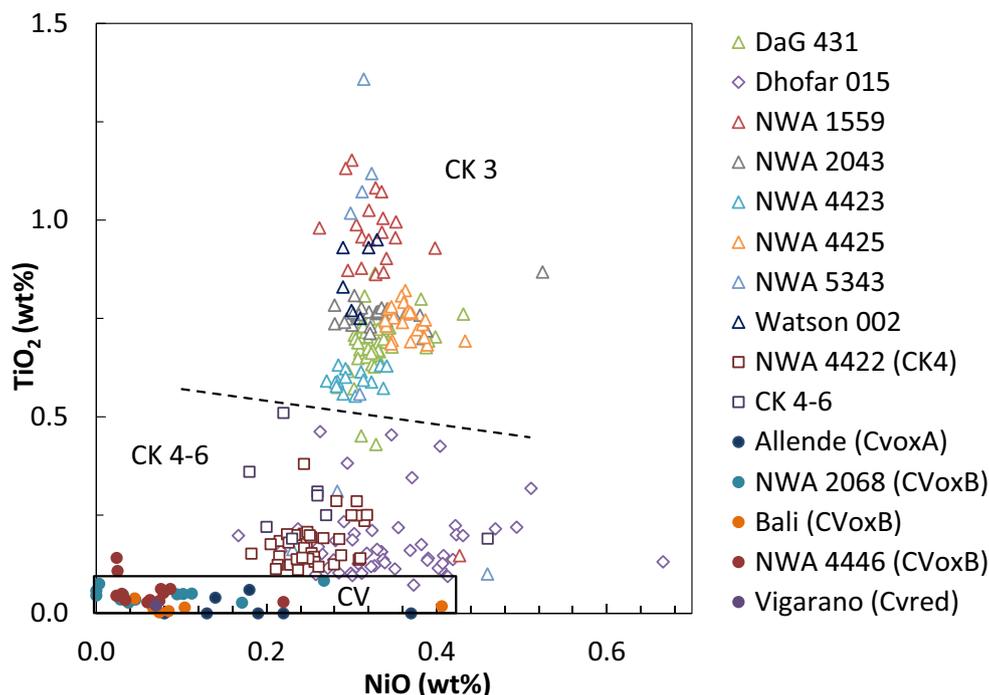


Fig. 5. Magnetite compositions from all CV and CK chondrites measured in this and in previous studies (see references in Fig. 3) shown as NiO (wt%) versus TiO₂ (wt%). Compositions of magnetite in CK3-an chondrite Watson 002 are also plotted (Greenwood et al. 2010; Davidson et al. 2014). CV chondrites are represented by solid circles, CK3 chondrites by open triangles (except Dhofar 015, which is an open diamond), and equilibrated CK chondrites by open squares. The CV chondrites are defined by a low TiO₂ zone (<~0.15 wt%), while the CK chondrites form a linear trend from equilibrated (<0.3 wt% TiO₂) to unequilibrated (>0.3 wt% TiO₂).

highlight the earlier observation that magnetite in the CV chondrites is most similar to the equilibrated CK chondrites rather than the unequilibrated CK chondrites, thus reinforcing the suggestion that the CV and CK chondrites do not appear to be genetically related.

Oxidation State of the CV-CK Parent Body(s)

If the CV and CK chondrites originated from the same parent body, we would expect both groups to have formed under similar conditions (e.g., temperatures and oxygen fugacities). We can use magnetite to further examine a possible genetic relationship between the CV and CK chondrites by considering the oxygen fugacity conditions under which magnetite must have formed. The presence of Ni-rich olivine in the CK chondrites suggests that they formed at an oxygen fugacity near the Ni-NiO buffer (Geiger and Bischoff 1995). Due to the absence of Ni-rich olivine in the CV_{ox} chondrites, they must form under a lower oxygen fugacity, likely near the wüstite-magnetite buffer (Geiger and Bischoff 1995). Righter and Neff (2007) used coexisting magnetite-ilmenite pairs to estimate oxygen fugacities in

the CK chondrites. These values ranged from 15 log f_{O_2} at 950K to -30 log f_{O_2} at 600K, or 2.0 to 5.1 log f_{O_2} units above the FMQ buffer. They also estimated oxygen fugacity of the CV chondrites using thermodynamic data (Robie and Hemingway 1995) and activity-composition relations for magnetite and metal (Sack and Ghiorso 1991). The oxygen fugacity of the CV chondrites was estimated to be 2.4 log f_{O_2} units below the FMQ buffer and ~ 1 log f_{O_2} unit above the IW buffer. Overall, the CK chondrites are 4 log f_{O_2} units more oxidized than CV chondrites (Righter and Neff 2007). Therefore, for a single parent body model to be correct, a mechanism must exist to produce an increase in oxygen fugacity prior to the formation of the CK chondrites. The more oxidized CK chondrites are also more metamorphosed (\geq type 3.7) than the CV chondrites (\leq type 3.3). Thus, an increase in oxygen fugacity would have to occur after metamorphism of the CV chondrites but prior to metamorphism of the CK chondrites, thus likely somewhere between petrologic type 3.4 and 3.6 conditions.

The most plausible agent responsible for an increase in oxidation is a fluid, such as O₂. Although the CV_{red} chondrites have mostly escaped extensive aqueous

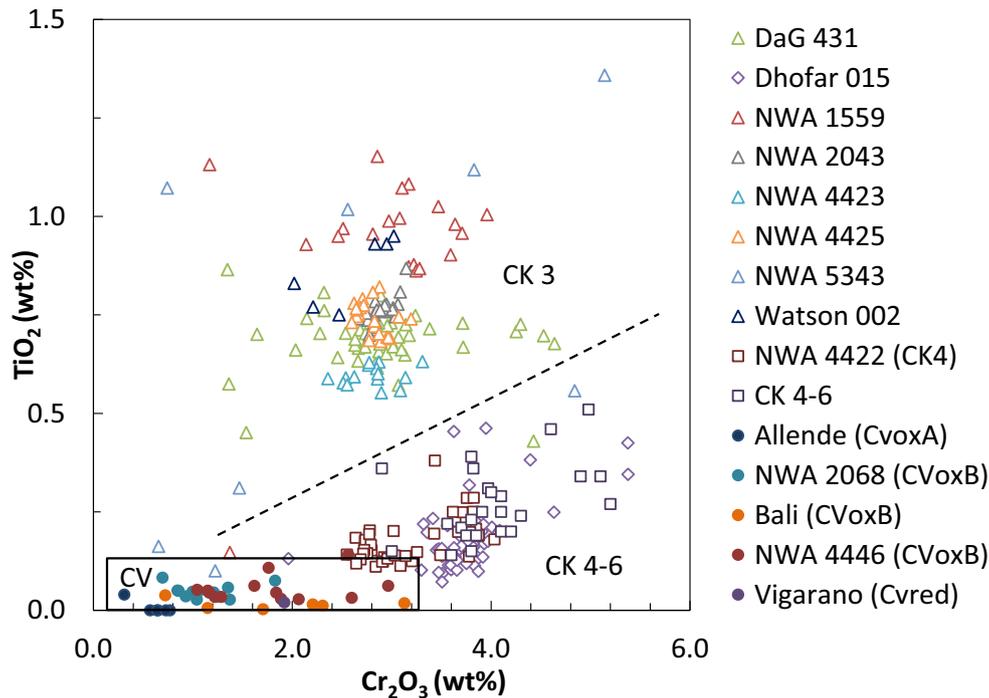


Fig. 6. Magnetite compositions from all CV and CK chondrites measured in this and in previous studies (see references in Fig. 3) shown as Cr_2O_3 (wt%) versus TiO_2 (wt%). Compositions of magnetite in CK3-an chondrite Watson 002 are also plotted (Greenwood et al. 2010; Davidson et al. 2014). CV chondrites are represented by solid circles, CK3 chondrites by open triangles (except Dhofar 015, which is an open diamond), and equilibrated CK chondrites by open squares. This figure highlights the low Cr_2O_3 content of the CV chondrites relative to the CK chondrites. Here, the unequilibrated and equilibrated CK chondrites are separated by a line with a slope of -0.34 .

alteration (Krot et al. 1995, 1998), the presence of phyllosilicates and alteration minerals produced during Fe-alkali-halogen metasomatism in the CV_{ox} chondrites leaves no doubt that a fluid was initially present on the CV parent body (Krot et al. 1995, 1998; Choi et al. 2000). This period of aqueous alteration is also significant because magnetite is thought to form during this time as a result of oxidation of metal (e.g., Choi et al. 1997, 2000; Davidson et al. 2014). Dehydration of phyllosilicates has been proposed as an internally derived source of fluid in asteroidal parent bodies (Wasson 2000), and phyllosilicates are abundant in the matrices of Bali-type CV_{ox} chondrites (Krot et al. 1995, 1998; Choi et al. 2000). However, the CV_{oxB} chondrites cannot be precursors to the CK chondrites because the dehydration of a phyllosilicate-bearing rock results in heavy isotope enrichment (Mayeda and Clayton 1998), and the CV_{oxB} chondrites are heavier than the CK chondrites (Greenwood et al. 2010). The Allende-type CV_{ox} chondrites, which are believed to be a more likely precursor for the CK chondrites (Greenwood et al. 2010), show evidence of aqueous alteration yet lack abundant phyllosilicates (Krot et al. 1995, 1998). Wasson et al. (2013) proposed that the CK chondrites

followed an independent oxidation path from the reduced CV chondrites; however, oxygen isotopes indicate that the CV_{red} chondrites formed under low water conditions (Greenwood et al. 2010). Because water is lost during metamorphism, it is unlikely that enough water would remain to increase oxygen fugacity after metamorphism of the CV_{red} chondrites. Isotopic compositions of the CK chondrites confirm that thermal metamorphism occurred under dry conditions (Greenwood et al. 2010; Davidson et al. 2014). Regardless of whether the CV_{red} or CV_{oxA} chondrites are direct precursors of the CK chondrites, it may be difficult to produce enough internally derived oxidizing fluid during dehydration of phyllosilicates to cause an increase in oxygen fugacity prior to metamorphism of the CK3 chondrites.

It is possible that the fluid necessary to increase the oxidation state on the CV-CK chondrite parent was derived from an external source. The most plausible source of such a fluid is accreted ice, which melts during heating (McSween and Labotka 1993). Although the parent asteroids of the CV and CK chondrites have not been identified, spectral similarities suggest that carbonaceous chondrites are derived from C-type

asteroids (e.g., McCord and Gaffey 1974; Chapman 1976), and C-type asteroids are generally thought to have formed beyond the snow line (Demeo and Carey 2012). Thus, it is conceivable that ice may have accreted on a hypothetical CV-CK chondrite parent body. Melted ice could behave as an oxidizing agent in the CV-CK parent body model suggested by Chaumard et al. (2012), where fragments of a CV-like parent body (disrupted by an impact) experience radiative heating close the sun. However, this scenario would require that disruption of the initial parent body occurred beyond the snow line as well, allowing the fragments to accrete ice before approaching the sun. Additionally, Chaumard et al. (2014) acknowledge that the probability that the conditions (e.g., parent body size and orbit) necessary for radiative heating to occur and reach the temperatures necessary for metamorphism is low. Melted ice as an oxidizing agent is not easily reconciled with the onion skin model (Greenwood et al. 2010), where the CV chondrite material resides near the surface and the CK chondrite materials exists deeper in the parent body. Ice on the surface would be required to melt and percolate through the parent body, possibly along a system of fractures, in order to reach the buried CK material. It seems likely that this water supply would have been exhausted during metamorphism of the CV chondrites, leaving no oxidizing agent remaining for metamorphism of the CK chondrites. In this scenario, we might also expect the CV_{ox} chondrites to be more oxidized than the CK chondrites, as they would have remained in contact with the fluid for a longer duration than the CK chondrites. However, this is contrary to what is observed (Righter and Neff 2007).

Temperature also plays a significant role in oxidation, as higher temperatures favor a more rapid and extensive reaction. It is possible that the increase in oxygen fugacity from the CV_{ox} to the CK3 chondrites could reflect more advanced oxidation at higher temperatures. In a series of heating experiments, Geiger and Bischoff (1991) observed that CK chondrite mineralogies could be produced by heating oxidized CV chondrite material at oxygen fugacities near the Ni-NiO buffer. However, temperatures under which the Geiger and Bischoff (1991) experiments were conducted (1320K and 1370K) are higher than peak temperatures estimated for the CK chondrites (Clayton et al. 1977; Geiger and Bischoff 1991; Noguchi 1993; Clayton and Meyada 1999; Nakamuta et al. 2001; Chaumard et al. 2014). Because the CK3 chondrites and CV_{ox} chondrites are both unequilibrated, any increase in oxygen fugacity would have to occur at temperatures associated with petrologic type 3 conditions. Metamorphic temperatures in the CV chondrites are uncertain due to their complicated alteration histories; however, numerous

authors have estimated peak metamorphic temperatures from 500 to 900K (e.g., Blum et al. 1989; Huss and Lewis 1994; Weinbrunch et al. 1994; Krot et al. 1995; Weisberg et al. 2006). Although peak temperatures have not been calculated for unequilibrated CK chondrites, peak temperatures for type 4 CK chondrites, calculated using a variety of geothermometers, range from 800 to 1070 K (Clayton et al. 1977; Geiger and Bischoff 1991; Noguchi 1993; Clayton and Mayeda 1999; Nakamuta et al. 2001; Chaumard et al. 2014). Thus, maximum temperatures reached during metamorphism of the CV_{ox} and CK3 chondrites (~1070K) are below the temperatures associated with the Geiger and Bischoff (1991) heating experiments. Additional experiments would be required to determine if CK material could be produced from CV_{ox} material at lower temperatures.

Wasson et al. (2013) proposed an alternative CV-CK parent body model in which the CK chondrites were derived from impact heating, rather than internally driven thermal metamorphism, followed by burial and aqueous alteration. They argued that the fluid necessary for oxidation, in this case H₂O gas, was produced as a result of these impact events. There is ample evidence that the CK chondrites experienced shock (Rubin 1992; Scott et al. 1992; Tomeoka et al. 2001). However, temperatures estimated for shock metamorphism of the CK4 chondrite Kobe (~873 K) are below the temperatures at which CV material was converted into CK material in the Geiger and Bischoff (1991) experiments. The lower abundances of volatile elements in the CK chondrites compared to the CV chondrites, which Wasson et al. (2013) attributed to impact heating, can also result from thermal metamorphism. We contend that the presence of a well-defined metamorphic sequence in the CK chondrites from petrologic types 3–6 supports radiogenic decay of ²⁶Al as a more likely primary heat source than impact heating. However, we acknowledge that any model of a CK chondrite parent body should account for impact and shock heating.

Observations from Petrography, Isotopes, and Elemental Compositions

Petrographic Characteristics

The CK chondrites were initially distinguished from the CV chondrites based on refractory lithophile abundances, oxygen isotopes, and abundances of chondrite components (e.g., chondrules, CAIs, and matrix) (Kallemeyn et al. 1991). However, at that time only equilibrated CK chondrites had been recognized; unequilibrated CK chondrites have been examined only recently (e.g., Greenwood et al. 2010; Wasson et al. 2013; Chaumard et al. 2014; Chaumard and Devouard

Table 4. CV and CK chondrite petrographies from previous studies.

	CAI abundance ^a (area%)			Chondrule diameter ^b (mm)			Chondrule abundance ^b (area%)		
	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
CV	3.0	13.0	9.4	0.0	4.3	0.6	18.5	55.7	39.1
CK3	4.0	16.0	9.6	0.1	3.9	0.8	17.1	25.7	22.1
CK4-6	0.0	9.1	1.5	0.5	1.1	0.6	0.0	50.5	22.6

^aChaumard et al. (2014).

^bChaumard and Devouard (2016).

2016). Kallemeyn et al. (1991)'s initial observations about chondrite components indicated the CKs had higher matrix:chondrule ratios, lower abundances of CAIs, and smaller chondrules than the CV chondrites. Kallemeyn et al. (1991) also noted that chondrule rims, which are common in the CV chondrites, were absent from the CKs. Recently, Chaumard et al. (2014) and Chaumard and Devouard (2016) examined the petrography of CK and CV chondrites to qualify the similarities and differences between the two groups. They measured abundances and sizes of CAIs (Chaumard et al. 2014) and chondrules (Chaumard and Devouard 2016) in five CV, five unequilibrated CK, and thirteen equilibrated CK chondrites. Analysis of the data presented by Chaumard et al. (2014) and Chaumard and Devouard (2016) suggests that there are some discernable petrographic differences between equilibrated CK chondrites and the CV chondrites, as recognized by Kallemeyn et al. (1991). A summary of petrographic data measured by Chaumard et al. (2014) and Chaumard and Devouard (2016) is presented in Table 4. Abundances of both CAIs and chondrules are higher in the CV chondrites (9.4 area% and 39.1 area %, respectively) than in the equilibrated CK chondrites (1.5 area% and 22.6 area%, respectively) (Chaumard et al. 2014; Chaumard and Devouard 2016). There does not appear to be an appreciable difference in chondrule size, as the average chondrule diameter is 0.60 mm in the CVs and 0.64 mm in the equilibrated CKs. It is not surprising that the CV chondrites contain higher abundances of CAIs and chondrules than the more metamorphosed equilibrated CK chondrites, as these components would recrystallize during metamorphism.

The more pressing question is whether the CV chondrites have comparable petrographies to the unequilibrated CK chondrites, as they should be more representative of unaltered (pre-metamorphosed) CK chondrite material than the equilibrated CK chondrites. The range of CAI abundances in the two groups is similar, with CAI's comprising 3–13 area% of the CV chondrites and 4–16 area% of the unequilibrated CK chondrites (Chaumard et al. 2014). Average abundances

are 9.4 area% in CVs and 9.6 area% in the unequilibrated CKs (Chaumard et al. 2014). However, the authors acknowledged that these abundances may be biased due to the small surface areas (0.75–25.3 cm²) examined (Chaumard et al. 2014). Unlike CAIs, chondrule abundances do differ between the CV and CK3 chondrites. Chondrules are less abundant in the unequilibrated CK chondrites (22.1 area%) than in the CV chondrites (39.1 area%). The CV chondrites also exhibit a wider range of chondrule abundances (18.5–55.7 area%) than the CK3s (17.1–25.7 area%) (Chaumard and Devouard 2016). Chaumard and Devouard (2016) suggested that the difference between chondrule abundances in the CV and CK3 chondrites can be explained by metamorphic recrystallization. Although the unequilibrated CK chondrites are slightly more metamorphosed than the CV chondrites, textural changes due to recrystallization are not prominent until petrologic type 4 (Huss et al. 1978, 1981). Therefore, it is unlikely that differences in chondrule abundances in the CVs and CK3s would be the result of metamorphism. Average chondrule size, which was the same in the CV chondrites and equilibrated CK chondrites, is noticeably larger in the unequilibrated CK chondrites (0.82 mm) than in the CV chondrites (0.60 mm). Chaumard and Devouard (2016) argue that chondrule diameters are not the best criterion for distinguishing between chondrite groups due to bias resulting from nonequatorial sectioning of samples (Eisenhour 1996). We agree that average sizes may not be the best measure of a chondrule population due to this inherent bias. However, the range of chondrule sizes is a useful criterion because it defines the entire chondrule population. Chondrule sizes in the CV chondrites range from 0.04 to 4.28 mm, while chondrules in the CK3 chondrites define a more narrow range from 0.12 to 3.86 mm. Although it is possible that measured chondrule sizes may not accurately reflect the entire population of a sample (Chaumard and Devouard 2016), the inconsistencies between chondrule size and abundance in the CV and CK3 chondrites suggest that there are observable, although minor, petrographic differences between the two groups that are not a result of metamorphism.

Oxygen Isotopes and Bulk Elemental Compositions

Oxygen isotopes and bulk rock compositions, which were also initially used to distinguish the CK chondrites from other chondrite groups, have more recently been used to argue in favor of a single CV-CK chondrite group (Greenwood et al. 2010; Wasson et al. 2013). Greenwood et al. (2010) measured oxygen isotopic compositions and refractory lithophile element abundances of fifteen CK chondrites and thirteen CV chondrites, and they observed strong similarities between the two groups. Although there is certainly overlap between bulk oxygen isotope abundances in the CV and CK chondrites (see fig. 3 in Greenwood et al. 2010), it is possible that this is, in part, a function of sample heterogeneity and volume of material analyzed. CV chondrites are characterized by their heterogeneity (e.g., Krot et al. 1995), and several CV chondrites are breccias containing clasts of both reduced and oxidized material (McSween 1977; Johnson et al. 1990; Krot et al. 2004). Therefore, analyses of multiple aliquots from a single sample can vary. For example, Clayton and Mayeda (1999) reported a 6‰ difference between two measurements in Bali (CV_{oxB}) and a 7‰ difference between two measurements in Leoville (CV_{red}). Analyses of Leoville (CV_{red}) and Bali (CV_{oxB}) by Greenwood et al. (2010) also differed from these previously published results. Heterogeneity may also be an issue in the unequilibrated CK chondrites. Average isotopic compositions of Watson 002 (CK3) measured by Greenwood et al. (2010) are +0.26 $\delta^{18}\text{O}$ ($\sigma = 0.19$) and $-3.42 \delta^{17}\text{O}$ ($\sigma = 0.08$), while compositions measured by Geiger et al. (1993) are +5.12 $\delta^{18}\text{O}$ and $-0.55 \delta^{17}\text{O}$. Greenwood et al. (2010) reported reasonable agreement with previous isotopic analyses in the equilibrated CKs and the oxidized CVs but poorer agreement in the unequilibrated CKs and reduced CVs. Bulk refractory elemental abundances, which have also been used as a criterion for establishing a relationship between the CV and CK chondrites (Greenwood et al. 2010; Wasson et al. 2013), could also easily be affected by sample heterogeneity.

The effects of sample heterogeneity may be amplified when small volumes of material are used in an analysis. This is the case in both oxygen isotopic and bulk elemental analyses, which require 0.5-2 mg and 5-20 mg of material, respectively (e.g., Greenwood et al. 2010). Techniques such as X-ray diffraction, which study larger volumes of bulk sample (e.g., 100-200 mg aliquots or larger bulk powders) typically do not reveal such heterogeneities (Howard et al. 2010). Thus, elemental and isotopic compositions measured from small volumes of material may not accurately represent heterogeneous samples, such as the CV and CK chondrites. We suggest instead that individual mineral chemistries, which eliminate the issue of bulk sample heterogeneity, provide

a reliable alternative to techniques that require small volumes of sample material.

METAMORPHISM AND THERMAL HISTORY OF THE CK CHONDRITES

The most obvious compositional differences between magnetite in the unequilibrated and equilibrated CK chondrites are abundances of TiO₂ (Fig. 2b) and Al₂O₃ (Fig. 2d). Magnetite compositions, therefore, can certainly be used to determine if a sample is unequilibrated (type 3) or equilibrated (types 4–6). Although texture is also indicative of whether a sample is equilibrated or not, sometimes textural evidence of equilibration may be difficult to decipher. This is illustrated by Dhofar 015, which was initially assigned a petrologic subtype of 3.9 based on sharply defined chondrules, friable matrix, and a large range in feldspar compositions (Ivanova et al. 2000). However, Dhofar 015 plots firmly in the equilibrated chondrite clusters on all compositional diagrams. The fayalite content of Dhofar 015 (Fa₃₂; Ivanova et al. 2000) is also consistent with that of the equilibrated chondrites. This suggests that Dhofar 015 is actually an equilibrated CK chondrite despite its nebular features (Ivanova et al. 2000). Magnetite compositions do not appear to be useful in distinguishing between petrologic types 4, 5, and 6, as we have not observed any relationship between magnetite composition and petrologic type once equilibration is reached. However, petrologic type can be determined instead using other variables, such as the extent of matrix and chondrule recrystallization (Wood 1967; Dodd 1969). Although based on texture, Dhofar 015 is petrologic type 3–4, its magnetite compositions suggest that it is petrologic type 4.

The compositional differences between the unequilibrated and equilibrated CK chondrites also provide information about the thermal history of the CK chondrite parent body. As illustrated in Fig. 2, magnetite in the unequilibrated CK chondrites is enriched in oxide abundances relative to the equilibrated CK chondrites, with the exception of Cr₂O₃, indicating that there is a compositional change in CK chondrite magnetite either during progressive metamorphism (petrologic types 4–6) or during cooling. Geiger and Bischoff (1995) observed that large magnetite grains (up to ~1 mm diameter) in the equilibrated CK chondrites typically exhibit exsolution lamellae of ilmenite (FeTiO₃) and spinel (MgAl₂O₄), but did not observe any lamellae in unequilibrated CK chondrite, Watson 002. This study has confirmed the absence of lamellae in the unequilibrated CK chondrites. Geiger and Bischoff (1995) suggested that the chemical constituents that comprise spinel and

ilmenite (MgO , Al_2O_3 , and TiO_2) were initially dissolved in unequilibrated CK chondrite magnetite and then exsolved into ilmenite and spinel during cooling. Our analyses confirm that abundances of MgO , Al_2O_3 , and TiO_2 in magnetite are higher in the unequilibrated CK chondrites than in the equilibrated CK chondrites. In fact, both Al_2O_3 and TiO_2 decrease as MgO decreases, forming well-defined linear trends from the unequilibrated CK chondrites to the equilibrated CK chondrites (Figs. 3c and 3d). This would appear to confirm the hypothesis ilmenite and spinel exsolve from magnetite during cooling of the parent body. We suggest that the decrease in MnO , which often substitutes for MgO , and Fe_2O_3 may also be attributed to exsolution of ilmenite and spinel.

Not all of the compositional changes in magnetite are the result of cooling. The slight decrease in NiO from the unequilibrated to the equilibrated CKs is not likely to be a result of cooling, as neither spinel nor ilmenite are Ni-rich. Geiger and Bischoff (1995) suggested that nickel diffuses into olivine during metamorphism because there are not enough sulfide phases to incorporate all the nickel. Our preliminary work also demonstrates that NiO in olivine is higher in the equilibrated CK chondrites than the unequilibrated chondrites (Dunn 2011). Thus, these trends support the hypothesis that NiO diffuses from magnetite into olivine during metamorphism. Because spinel in the CK chondrites is Cr-rich, we may also expect to see a decrease in Cr_2O_3 content of magnetite as a result of exsolution of spinel. Instead, abundances of Cr_2O_3 in magnetite increase slightly from the unequilibrated to equilibrated CK chondrites. Therefore, magnetite must become enriched in Cr_2O_3 during metamorphism. Kallemeyn et al. (1991) and Noguchi (1993) suggested that Cr_2O_3 diffuses from olivine into magnetite during metamorphism. If this is the case, then Cr_2O_3 abundances in olivine should be higher in the unequilibrated CK chondrites than the equilibrated CK chondrites. Our previous work (Runyon and Dunn 2011) confirms this trend, suggesting that diffusion of Cr_2O_3 from olivine into magnetite during metamorphism is possible. Although Cr_2O_3 could also be diffusing into magnetite from a different source, the Cr-rich nature of olivine in the CK chondrites makes it a probable candidate. We are completing an in-depth analysis of olivine in the CK chondrites, which will be presented elsewhere, to determine if diffusion of NiO and Cr_2O_3 between magnetite and olivine can be confirmed.

SUMMARY

More than 30 CK chondrites have been classified as petrologic type 3 since the discovery of the first CK3

chondrite, Waston 002 (Geiger et al. 1993). Since then, several studies have attempted to fully characterize the compositions and thermal histories of the unequilibrated CK chondrites (Rubin 2013; Wasson et al. 2013; Chaumard et al. 2014; Chaumard and Devouard 2016). In this study we analyzed magnetite in seven meteorites classified as type 3 CK and one equilibrated CK chondrite to more completely describe the range of magnetite compositions in the CK chondrites. Because magnetite compositions in the CK chondrites have also been used to argue for a shared thermal history with the CV chondrites (Greenwood et al. 2010), we compared magnetite in the CK chondrites to magnetite in the CV chondrites in order to better address to question of whether or not the CV chondrites and the CK chondrites are derived from the same parent body. Our analysis yields the following conclusions.

1. Magnetite in the CV chondrites is compositionally distinct from magnetite in the CK chondrites. The most apparent compositional differences between the groups are in abundances of Cr_2O_3 , NiO , and TiO_2 . While abundances of Cr_2O_3 , MgO , and TiO_2 have historically been used to distinguish between the CV and CK chondrites (Ivanova et al. 2003; Greenwood et al. 2010), abundances of NiO provide an additional method of distinguishing these two groups.
2. Minor compositional similarities between magnetite in the CV and equilibrated CK chondrites, particularly in abundances of Al_2O_3 , do not preclude the two parent body model. In CK chondrite magnetite, abundances of Al_2O_3 decrease as MgO abundances decrease; however, this trend is absent from magnetite in the CV chondrites. Additionally, the observation that magnetite in the CV chondrites is most similar to magnetite in the equilibrated CK chondrites (rather than the unequilibrated CKs) is contrary to what would be expected if the CK chondrites are metamorphosed CV chondrites.
3. Magnetite compositions can be used to determine if a CK chondrite is unequilibrated or equilibrated. This is particularly useful for samples on the unequilibrated/equilibrated boundary (i.e., type 3.9 or type 4), where textural evidence of equilibration may be difficult to decipher. The most obvious compositional difference between magnetite in the unequilibrated and equilibrated CK chondrites are abundances of TiO_2 and Al_2O_3 . Magnetite in unequilibrated CK chondrites contains >0.5 wt% TiO_2 and >2.2 wt% Al_2O_3 , while equilibrated CK chondrite magnetite contain <0.5 wt% TiO_2 and <2.2 wt% Al_2O_3 .
4. The CK chondrites formed under higher oxygen fugacity conditions than the CV_{ox} chondrites. If the CV and CK chondrites are derived from the same

parent body, then oxygen fugacity on the parent asteroid must have increased prior to the metamorphism of the CK chondrites. This increase in oxygen fugacity could be driven by the introduction of an externally derived fluid or an increase in temperature. However, externally derived water as oxidizing agent is not easily reconciled with the various models for a single CV-CK chondrite parent body, and maximum temperatures reached during metamorphism of the CV_{ox} and CK3 chondrites (~1070 K) are below the experimental temperatures necessary to convert CV chondrites to CK chondrite-like material.

5. Differences between size and abundance of chondrules in the CV and CK3 chondrites cannot be explained by thermal metamorphism, as recrystallization effects due to metamorphism are not prominent until petrologic type 4. This suggests that there are observable petrographic differences between the two groups.
6. The heterogeneous nature of the CVs and unequilibrated CKs, and the small volume of material used in isotopic and elemental analyses, suggest that individual mineral chemistries may provide a reliable alternative to bulk analyses.

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