

Siderophile-element anomalies in CK carbonaceous chondrites: Implications for parent-body aqueous alteration and terrestrial weathering of sulfides

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Abstract

CK chondrites constitute the most oxidized anhydrous carbonaceous chondrite group; most of the Fe occurs in magnetite and in FeO-rich mafic silicates. The two observed CK falls (Karoonda and Kobe), along with thirteen relatively unweathered CK finds, have unfractionated siderophile-element abundance patterns. In contrast, a sizable fraction of CK finds (9 of 24 investigated) shows fractionated siderophile abundance patterns including low abundances of Ni, Co, Se and Au; the most extreme depletions are in Ni (0.24 of normal CK) and Au (0.14 of normal CK). This depletion pattern has not been found in other chondrite groups. Out of the 74 CK chondrites listed in the Meteoritical Bulletin Database (2006; excluded considerably paired specimens; see <http://tin.er.usgs.gov/meteor/metbull.php>) we analyzed 24 and subclassified the CK chondrites in terms of their chemical composition and sulfide mineralogy: sL (siderophiles low; six samples) for large depletions in Ni, Co, Se and Au (>50% of sulfides lost); sM (siderophiles medium; two CKs) for moderately low Ni and Co abundances (sulfides are highly altered or partly lost); sH (siderophiles high; one specimen) for enrichments in Ni, Co, Se and Au; ‘normal’ for unfractionated samples (13 samples). The sole sH sample may have obtained additional sulfide from impact redistribution in the parent asteroid. We infer that these elements became incorporated into sulfides after asteroidal aqueous processes oxidized nebular metal; thermal metamorphism probably also played a role in their mineral siting. The siderophile losses in the sL and sM samples are mainly the result of oxidation of pentlandite, pyrite and violarite by terrestrial alteration followed by leaching of the resulting phases. Some Antarctic CK chondrites have lost most of their sulfides but retained Ni, Co, Se and Au, presumably as insoluble weathering products.

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1. Introduction

The Karoonda group (CK) is the most recently established group of carbonaceous chondrites (e.g., Geiger and Bischoff, 1991; Kallemeyn et al., 1991). The Meteoritical Bulletin Database reports 140 approved CK chondrite samples (on May 30, 2006). There are two falls, Karoonda and Kobe; most of the other CK chondrites are from the

Sahara or Antarctica, and a large fraction of these is probably paired.

CK chondrites are among the most oxidized anhydrous chondrite groups. They are essentially free of metallic Fe–Ni; only rare grains of micrometer size have been found. Most Fe is in olivine (Fa ~30) and magnetite. Some Fe and most of the other siderophile elements occur in sulfides; tiny amounts of Fe occur in arsenides and tellurides (no selenides have been reported) (Geiger and Bischoff, 1995). The major opaque phases in CK chondrites are magnetite (Fe₃O₄) and pentlandite (Fe,Ni)₉S₈; many magnetite grains contain exsolution lamellae of ilmenite (FeTiO₃).

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These phases occur as isolated grains in the chondrite groundmass, inclusions in coarse matrix silicate grains, micrometer-sized grains within shock veins, and nodules within silicate chondrules and in similarly sized (200–500 μm) nodules outside chondrules (Kallemeyn et al., 1991; Rubin, 1992, 1993). Magnetite and pentlandite were the only opaque phases reported in the Kobe fall (Tachibana et al., 2002).

In their neutron activation study of CK chondrites, Kallemeyn et al. (1991) classified several carbonaceous chondrites as either anomalous or probable CK chondrites. These include physically deteriorated samples (e.g., PCA 82500), as well as some meteorites that show anomalies in their siderophile-element patterns, i.e., low abundances of Ni, Co, Au and Se. These depletions were originally interpreted as having resulted from terrestrial weathering. Since the initial classification study by Kallemeyn et al. (1991), many more CK chondrites have been recovered from Northwest Africa and Antarctica. The expanded CK data set allows us to re-examine the question of whether the Ni and Co depletions result from terrestrial weathering or represent bulk compositional diversity of preterrestrial origin. In the petrographic part of the study, we focused on the composition of the opaque phases magnetite, pentlandite, pyrite and minor sulfide phases (monosulfide solid solution MSS, pyrrhotite and thiospinels) to determine whether whole-rock siderophile depletions correlate with changes in mineralogy.

2. Samples and analytical techniques

Table 1 lists the CK chondrites included in this study. The meteorites were chosen on the basis of size and availability. These meteorites were analyzed by instrumental neutron activation analysis (INAA) and studied petrologically. Table 2 lists the bulk compositions obtained by INAA of 14 CK chondrites, a clast from Tanezrouft 057, and a weathered zone in NWA 1563. The samples are classified as CK4 or CK5, with shock stages of S1 and S2, weathering grades from A to C, and weathering indices from wi-0 to wi-6 (Rubin and Huber, 2005). Because NWA 1563 has a ‘darkened weathering’ zone on the external surface, we analyzed both this material and an interior sample to examine the influence of obvious terrestrial weathering. Our Tanezrouft 057 sample contains a large (2.5 \times 4 cm) clast that was analyzed separately.

We ran duplicate INAA for all samples, both with short (1 min) and long (3 h) irradiations. Duplicating the INAA samples not only reduces the analytical uncertainties due to the sampling procedure, but also helps identifying unusual parts of the available sample. Samples were irradiated at the TRIGA Mark I reactor of the University of California, Irvine with a neutron flux of 1.8×10^{12} neutrons $\text{cm}^{-2} \text{s}^{-1}$. Sample masses were in the range of 200 ± 100 mg and, when possible, were cut into 3-mm-thick rectangular blocks or into 3-mm-thick slices of varying shapes. The samples were then mounted

Table 1
CK chondrites included in this study

	Petrologic type	Weathering grade	wi ^a	Shock stage	Comp. class. ^b	Source ^c
<i>Fractionated CK chondrites</i>						
Hot desert						
DaG 431	3	—	wi-6	S2	sL	NHML
Maralinga	4	—	wi-3	S2	sL	UCLA
NWA 060	5	—	wi-5	S2	sL	UCLA
NWA 1563	5	—	wi-5	S2	sL	MemT
NWA 1558	5	—	wi-5	S2	sL	MemT
Tanezrouft 057	5	—	wi-4	S2	sM	MetS
Cold desert						
LEW 86258	4	B	wi-4	S2	sL	MWG
QUE 93007	5	A/Be	wi-5	S2	sM	MWG
EET 99430	4	C	wi-4	S1	sH	MWG
<i>‘Normal’ CK chondrites</i>						
DAV 92300	4	A/B	—	—	Normal	MWG
LAP 03784	4	B	wi-0/1	S1	Normal	MWG
LAR 04318	4	A/B	wi-2	S1	Normal	MWG
LEW 87250	4	A/B	wi-4	S2	Normal	MWG
NWA 765	4/5	W1	wi-0	S2	Normal	MemT

Petrological type and weathering grades from Meteoritical Bulletin; shock stages from this study (by Rubin).

^a wi, weathering index based on the brown staining of silicates (Rubin and Huber, 2005). wi-0, <5 vol %; wi-1, 5–25 vol %; wi-2, 25–50 vol %; wi-3, 50–75 vol %; wi-4, 75–95 vol %; wi-5, >95 vol %; wi-6 significant replacement of mafic silicates by phyllosilicates.

^b Compositional classification based on Ni and Au content; sL depleted in Ni, Co, Au and Se; sM depleted in Ni and Co; sH enriched in Ni and Co.

^c Source abbreviations: NHML, Nat. Hist. Museum, London (S. Russell, C. Smith); MWG, Meteorite Working Group, NASA Johnson Space Center; MetS, Meteorite Show (F. Beroud); MemT, La Memoire de la Terre (B. Fectay, C. Bidaut).

Table 2

Whole-rock compositions of CK chondrites determined by INAA

	PT	Na	Mg	Al	K	Ca	Sc	V	Cr	Mn	Fe	Co	Ni	Zn	Ga	As	Se	Sb	La	Sm	Eu	Yb	Lu	Os	Ir	Au	
		(mg/g)	(mg/g)	(mg/g)	(μg/g)	(mg/g)	(μg/g)	(μg/g)	(mg/g)	(mg/g)	(mg/g)	(μg/g)	(mg/g)	(μg/g)	(μg/g)	(μg/g)	(μg/g)	(μg/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	
<i>Fractionated CK chondrites from hot deserts</i>																											
DaG 431	3	sL	2.90	131	15.1	402	37.0	9.3	96	3.18	1.39	228	291	3.10	77.0	4.92	2.10	3.07	81	464	310	110	309	50.3	736	706	15.0
Maralinga ^a	4	sL	2.98	144	17.9	342	23.5	10.6	92	3.47	1.43	223	382	4.17	57.1	5.06	1.49	2.39	55	431	266	104	290	43.3	878	844	48.4
NWA 060	5	sL	3.85	138	15.3	450	17.3	10.4	100	3.61	1.42	234	350	2.98	103	6.51	4.09	2.92	76	449	264	106	329	45.7	881	815	58.5
NWA 1563	5	sL	3.36	147	16.1	335	23.8	10.3	97	3.46	1.59	231	272	2.76	91.5	6.23	1.72	2.56	87	592	345	131	397	56.5	800	806	36.4
NWA 1563 wt ^b	5	sL	3.13	149	16.0	281	24.8	10.4	101	3.48	1.69	226	281	2.63	86.1	6.79	2.15	2.29	106	791	420	163	482	74.7	707	920	39.4
NWA1558	5	sL	3.58	147	16.3	312	21.3	9.88	95	3.43	1.57	233	267	2.84	97.9	5.81	2.62	1.70	58	407	271	114	362	42.8	764	739	15.3
Tanez 057	5	sM	3.32	138	16.6	359	26.8	9.80	100	2.95	1.41	231	313	4.20	116	5.93	1.13	5.30	51	439	277	108	284	46.0	693	672	76.1
Tanez 057 clast	5	sM	3.63	144	20.0	362	32.2	11.4	115	3.35	1.43	224	324	4.10	206	7.93	2.69	5.95	82	573	371	135	338	46.1	665	752	87.2
<i>Fractionated CK chondrites from cold deserts</i>																											
EET 99430	4	sH	3.54	132	19.8	304	15.0	11.0	103	3.53	1.26	212	1148	24.5	119	4.24	1.09	12.8	53	416	291	125	297	46.9	813	884	331
LEW 86258 ^c	4	sL	2.56	149	15.9	253	16.0	10.9	96	3.76	1.21	240	325	3.73	48.7	4.23	1.81	4.20	53	332	218	87.7	251	38.6	816	842	100
QUE 93007 ^b	5	sM	2.50	149	16.0	240	16.5	10.8	95	3.75	1.31	239	340	5.20	55.0	4.10	1.40	5.10	70	410	250	90.0	260	39.0	—	690	90.0
<i>Mean values for fractionated CK chondrites</i>																											
Mean sL			3.19	144	16.1	339	23.4	10.3	97	3.48	1.47	231	310	3.17	80.2	5.65	2.28	2.73	74	495	299	117	346	50.3	797	810	44.7
Mean sM			2.95	144	16.7	300	22.3	10.5	99	3.40	1.36	234	328	4.69	96.8	5.27	1.46	5.28	64	441	275	102	279	42.5	686	691	84.4
Mean sH			3.54	132	19.8	304	15.0	11.0	103	3.53	1.26	212	1148	24.5	119	4.24	1.09	12.8	53	416	291	125	297	46.9	813	884	331
<i>Unfractionated CK chondrites</i>																											
DAV 92300 ^b	4	n	3.10	150	16.1	290	17.3	11.4	97	3.69	1.45	240	600	11.5	100	5.60	1.70	6.90	—	500	310	110	300	45.1	—	745	121.
LAP 03784 ^b	4	n	3.36	150	18.3	299	12.2	10.3	102	3.50	1.45	229	652	13.7	82.4	5.36	1.69	6.70	46	443	288	110	284	43.2	999	799	145.
LAR 04318 ^b	4	n	3.37	150	18.8	287	13.8	9.9	98.5	3.38	1.52	223	945	22.9	91.4	7.12	1.54	7.73	57	394	251	105	279	36	1056	758	126.
LEW 87250	4	n	3.10	151	16.4	270	17.6	11.7	97	3.70	1.47	239	640	12.1	102	5.50	1.50	7.40	—	480	290	110	320	49.0	—	790	135.
NWA 765	4	n	2.97	153	16.7	274	14.9	9.72	92	3.39	1.46	232	583	13.3	80.9	6.67	1.49	6.24	115	494	288	119	361	45.0	896	728	94.1

sL, siderophile low; sM, siderophile medium low; sH, siderophile high; n, siderophile normal; Tanez, Tanezrouft. Except as marked, all data are averages of duplicate analyses.

^a Average of this study and Kallemeyn et al. (1991).^b Only a single analysis.^c Data from Kallemeyn et al. (1991).

on cardboard slides in order to obtain the same measuring distance and 3D-distribution as the powdered material used as standards. Standards included the Allende meteorite (Jarosewich et al., 1987), the USGS international reference materials granite G-2 and BHVO-1 (Govindaraju, 1989), as well as elemental solutions pipetted onto MgO (for Os, Ir and Au). Analyses were performed at UCLA following a protocol similar to that of Kallemeyn et al. (1989). A subsequent short irradiation in the pneumatic irradiation facility at UC Irvine was performed to determine the abundances of elements with short-lived isotopes, such as, e.g., Al and Mg. Samples were irradiated for 60 s and counted for 200 s after a cooling period of 5–10 min. Standards used in this procedure included the USGS international reference materials BHVO-1, BIR-1 (Govindaraju, 1989) and the Allende meteorite (Jarosewich et al., 1987).

We used optical microscopy, SEM and microprobe analysis to characterize doubly polished thin sections of several samples: EET 99430,11, EET 99430,6, LAP03784,11 and LAR04318,12 from the Johnson Space Center (JSC); UCLA section S 851 and 852 of NWA-060; UCLA section 1800 of Tanezrouft 057 host; and an unnumbered Karoonda section from the Field Museum. These sections were studied microscopically in reflected and transmitted light. Because we used solid (unpowdered) samples for INAA, we could investigate the analyzed samples post facto under the binocular microscope to determine any unusual petrographic characteristics (e.g., large sulfide grains), an especially important possibility for samples with anomalous compositions. Back-scattered electron (BSE) images were made with the LEO 1430 VP scanning electron microscope (SEM) at UCLA using a 15 keV accelerating voltage and a working distance of ~26 mm. The compositions of minerals were determined with the JEOL electron microprobe at UCLA using natural and synthetic standards, an accelerating voltage of 15 keV, a 15 nA sample current, 20 s counting times per element, ZAF corrections and a focused beam.

The degree of weathering was determined using the weathering index developed by Rubin and Huber (2005). As CK chondrites are essentially devoid of metallic Fe–Ni, the criteria used in the traditional weathering scales of Wlotzka (1993) based on the degree of weathering of metallic Fe–Ni and sulfide and Cassidy (1980) (based on the degree of surface rustiness of Antarctic meteorite hand specimens) are inapplicable. The weathering index (wi) system of Rubin and Huber (2005), designed for the two highly oxidized chondrite groups (CK and R), is based on the modal abundance of crystalline material that is stained brown by oxidized iron. The scale ranges from wi-0 (<5 vol % brown-stained) to wi-6 (i.e., significant weathering replacement of mafic silicates by phyllosilicates); in Table 1 we list the inferred weathering indices (wi values) for the investigated samples for which we had thin sections.

3. Results

3.1. INAA

Combining our current results with previously published UCLA data (Kallemeyn et al., 1991), we can confirm the wide siderophile abundance variations within the CK group. Eight of the 14 samples in the combined data set show anomalously low Ni contents and two show anomalously high Ni contents, similar to the heterogeneities observed by Kallemeyn et al. (1991) and others (Zipfel et al., 2000; Ivanova et al., 2003).

The shaded region in Fig. 1 corresponds to one sample standard deviation on either side of the mean of the ‘normal’ CK chondrites; mean values (Table 3) and standard deviations are based on the combined data set of ‘normal’ CKs within this study and those of Kallemeyn et al. (1991). All abundances are Mg normalized except two for which the Mg abundance appeared to be systematically high (QUE 93007) or low (EET 99430); in these cases a combination of Sc, Cr and Mg was used for normalization. Abundances are also normalized to mean CK chondrites. All samples were analyzed at UCLA with the exception of Kobe, for which we used the published data of Hirota et al. (2002) and Oura et al. (2002).

In Fig. 1, the fractionated samples show Ni abundance ratios in the range of 0.22–0.44 and Co abundance ratios in the range of 0.43–0.62× (mean) CK. In contrast, Co and Ni in EET 99430 and LAR 04318 are ~2× higher than CK. Table 2 shows the means of duplicate analyses; individual analyses are given in Appendix A. Table 3 lists literature data on unfractionated CK chondrites. Although ALH 85002 and ALH 82135 were initially paired, it is now known that they have different cosmic-ray exposure ages of 17.3 Ma (Scherer and Schultz, 2000; although Eugster et al., 1998 reported 20.0 Ma) and 32.4 Ma (Sugiura and Zashu, 1995), respectively. Thus, they are clearly independent falls.

Based on the Se and siderophile fractionations shown in Figs. 1 and 2a–d, we defined three subgroups of the fractionated CK chondrites: sL (siderophiles low), with low abundances of Ni, Co, Au and Se; sM (siderophiles medium), with moderately depleted abundances of Ni and Co, but only slight depletions in Au and Se; and sH (siderophiles high), a subtype with high abundances of Ni, Co, Au and Se. These subgroups also have distinct differences in their sulfide mineralogy (see Figs. 3–6).

The sL samples are DaG 431, NWA 060, NWA 1558, NWA 1563, LEW 86258 and the CK-anomalous Maralinga. The sM samples are Tanezrouft 057 and QUE 93007. The sole sH sample is EET 99430 (high in Ni, Co, Au and Se). LAR 04318 has elevated contents of Ni and Co, but its mineralogy is similar to that in ‘normal’ CKs with abundant pentlandite, pyrite and some violarite (FeNi₂S₄); we therefore classify LAR 04318 as a ‘normal’ CK. In Figs. 2, 7, and 8, we use different symbols for the ‘normal’, sL, sM and sH subgroups of CK chondrites.

Table 3
Major and trace element compositions of CK chondrites (literature data)

PT	Na	Mg	Al	K	Ca	Sc	V	Cr	Mn	Fe	Co	Ni	Zn	Ga	As	Se	Sb	La	Sm	Eu	Yb	Lu	Os	Ir	Au	
	(mg/g)	(mg/g)	(mg/g)	(μg/g)	(mg/g)	(μg/g)	(μg/g)	(mg/g)	(mg/g)	(mg/g)	(μg/g)	(mg/g)	(μg/g)	(μg/g)	(μg/g)	(μg/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	
Karoonda ^b	4 f	3.10	151	16.6	302	17.4	11.1	99	3.75	1.42	240	682	13.6	91.7	5.23	1.23	7.23	67	450	281	109	312	45.6	907	853	138
Kobe ^c	4 f	2.89	150	—	267	15.0	—	3.65	1.40	235	628	15.1	75.3	—	—	—	—	495	282	103	289	43.1	—	—	—	
ALH 82135 ^{ab}	4 n	3.31	146	15.9	247	17.1	11.1	96	3.52	1.44	231	588	11.4	101	5.68	1.44	6.96	76	416	250	100	283	44.0	816	771	94.0
ALH 85002 ^b	4 n	3.06	148	16.0	298	17.0	10.6	96	3.76	1.46	244	661	13.9	89.8	5.14	1.41	6.72	63	471	274	109	316	42.0	821	796	95.0
EET 83311 ¹	5 n	3.27	147	16.1	259	18.0	11.1	96	3.54	1.45	221	620	11.1	95.0	5.71	1.53	6.30	76	408	285	109	289	40.0	760	721	73.0
EET 87860 ^b	5 n	3.23	147	16.2	294	16.4	12.0	94	3.63	1.50	239	681	14.1	109	5.50	1.55	7.25	68	485	299	109	325	47.0	875	798	133
EET 87507 ^{a,b}	5 n	3.21	148	15.2	285	16.4	10.8	95	3.72	1.45	239	542	10.6	104	5.50	1.58	7.37	75	441	266	99.9	278	40.1	837	764	148
LEW 87009 ^b	6 n	3.13	150	16.3	272	17.7	11.2	96	3.72	1.49	237	646	12.4	104	5.40	1.61	6.10	63	559	326	120	343	52.0	697	664	123
PCA 82500 ^b	4/5 n	3.11	139	15.1	234	15.1	8.24	94	3.21	1.34	218	504	10.5	71.5	5.40	1.04	7.50	51	349	219	89.0	242	35.5	715	620	138
Y-693 ^b	4 n	3.16	143	15.8	317	19.1	11.0	97	3.83	1.45	240	751	14.3	107	5.65	1.67	9.00	73	483	298	115	311	46.5	960	920	120
Av. normal ^d		3.12	148	16.2	280	16.5	10.8	96	3.63	1.44	235	631	12.9	93	5.54	1.40	7.06	70	464	282	108	304	44.2	849	773	121

f, fall; n, siderophile normal; PT, petrologic type; ALH 82135 paired with ALH 84038, ALH 85002; EET 87507 paired with EET 87514, EET 87519, EET 87526, EET 87529 and EET 90007.

^a Average of pairings.

^b Data from Kallemeyn et al. (1991).

^c Data from Hirota et al. (2002) and Oura et al. (2002).

^d Combined data with double weight on averaging for the falls Karoonda and K. boe.

Samples from cold deserts (i.e., Antarctica) are given open symbols; those from hot deserts (Australia, Sahara) are shown with filled symbols. The two observed falls are represented by asterisks.

Several siderophile elements show no resolvable anomalies in their distributions; these include Fe, the refractory siderophiles Ir and Os, and the volatile siderophiles Ga and Sb (see Fig. 2). The low concentrations of the common siderophiles Ni and Co, the volatile siderophile Au, and the chalcophile Se all correlate with the variations in the Ni/Co ratio. The mean Ni/Co ratio in the CK falls Karoonda and Kobe as well as in the sH sample is ~21; the mean in the low-Ni CK chondrites is ~11.

Concentrations of Ca, Na, K and As are uniformly high in samples from hot deserts (Figs. 1a and 2e); as discussed in more detail below, the extra Ca (as well as the enrichments of Na, K and As) seems to have been introduced by terrestrial weathering.

Abundances of the moderately volatile siderophile elements Ga and Sb are about the same in normal and fractionated samples (Figs. 1 and 2). Concentrations of Ga (and, to a lesser extent, Sb) are relatively low in Antarctic samples and slightly high (implying minor contamination) in samples from the Sahara (Fig. 2).

There are several reasons that the siderophile-element fractionations cannot be analytical artifacts. The analyses were performed in different time intervals (1990–1996 and 2003–2006) in a total of seven different irradiations by two different analysts (Huber and Kallemeyn). The relative sample standard deviations determined from the Allende reference material are less than 5% for most elements; Ca and K have ±6 and ±8 rel.% standard deviations, respectively. Chondrites belonging to other groups (CM, CO and H) were included in these runs and their Co and Ni values are within the normal ranges for these groups.

3.2. Optical microscopy/petrography

According to Krot et al. (2004), mean CK chondrites contain ~75 vol % matrix and 15% chondrules with rare CAIs (0.5%)—the only exception that is petrographically well described is Maralinga (~50% matrix, ~50% chondrules and 3% CAIs; Keller et al., 1992), suggesting that Maralinga is not a normal CK. All CK chondrites contain appreciable magnetite (1.2–8.1 vol %, with a mean of ~4 vol %), but the modal abundance of sulfides varies widely (from <0.1 vol % in some Ni-depleted finds such as Maralinga and LEW 86258 to 1.3 vol % or ~1.9 wt% in Karoonda) (Geiger and Bischoff, 1995).

The Karoonda fall (wi-0, normal) contains 6.8 vol % magnetite with ilmenite exsolution lamellae and 1.3 vol % sulfide (Geiger and Bischoff, 1995); in addition to pentlandite, the sulfides include pyrite (FeS₂), chalcopyrite (CuFeS₂), pyrrhotite (Fe_{1-x}S) and Fe-rich MSS (Kallemeyn et al., 1991; Noguchi, 1993; Geiger and Bischoff, 1995). Also present in Karoonda are tiny grains of a

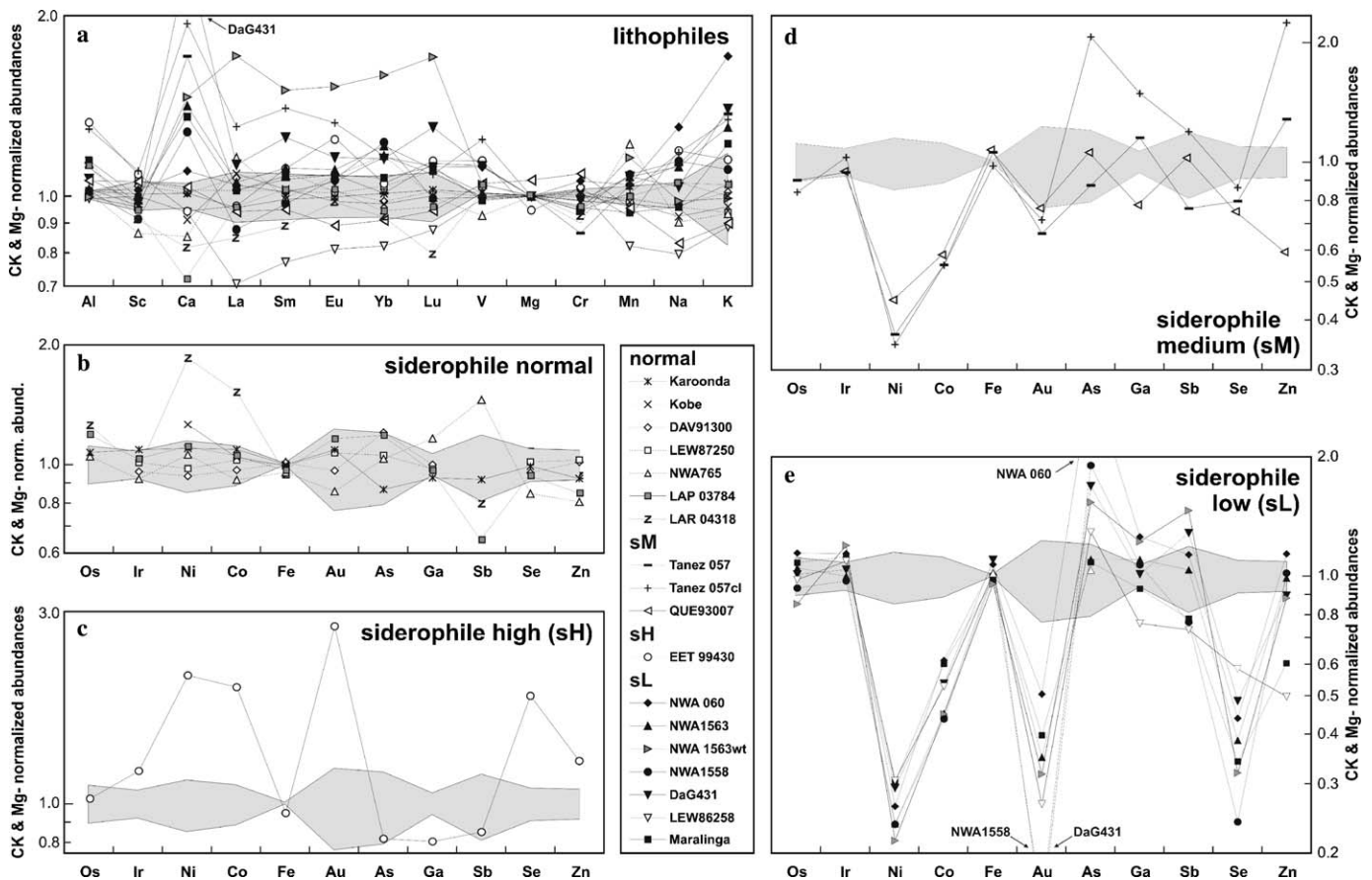


Fig. 1. Abundance ratios in CK chondrites normalized to mean CK chondrites (last row in Table 3) and Mg for lithophiles (a), siderophiles, chalcophiles and other non-lithophile elements (b–e). Data are averages of duplicate analyses and/or averages of paired samples. The grey shaded band shows mean CK $\pm 1\sigma$. See text for details on subgroups ‘normal’, sH (siderophile high), sM (siderophile medium), sL (siderophile low). Data on Karoonda from Kallemeyn et al. (1991); data on Kobe from Hirota et al. (2002) and Oura et al. (2002).

refractory-siderophile-rich telluride (i.e., chengbolite, PtTe_2) and refractory-rich sulfides (mainly Ir-bearing solid solutions of laurite, RuS_2 and erlichmanite, OsS_2 ; Geiger and Bischoff, 1995).

Although PCA 82500 (wi-3, normal) has unfractionated siderophile-element abundances (Kallemeyn et al., 1991), it is low in sulfide (~ 0.2 vol %). The whole rock contains millimeter to centimeter-size cavities caused by mechanical loss of weakly attached clasts during terrestrial weathering (Fig. 1 of Scott and Taylor, 1985). The mineralogical indications of terrestrial weathering (i.e., moderate sulfide loss and brown staining of silicate grains) are no more severe than those in other Antarctic CK chondrites.

EET 99430, (wi-4, sH) is the sole CK chondrite that is appreciably enriched in Ni, Co, Se and Au (Figs. 1 and 2). The replicated data for these elements differ by factors of 1.2–1.6; Fe is lower by 15% in the enriched sample. We examined the surfaces of irradiated samples but did not recognize any coarse sulfides that would account for the enrichments. Our two sections do not show high abundances of opaque phases; on the contrary, the textures resemble those of weathered CK chondrites in having a low sulfide abundance of ~ 0.1 – 0.2 vol % (see Figs. 3e and f) consistent with the very low bulk S content

(1.8 mg/g; Oura et al., 2004). The meteorite contains 1- to 30- μm -sized magnetite grains and 0.1–0.2 vol % sulfide (mainly MSS) as 0.5- to 4- μm -sized grains. Most of the MSS grains occur within olivine; one 40 μm olivine grain contains ~ 10 vol % 1- to 4- μm -sized MSS grains scattered throughout its interior. Some MSS grains occur in sulfide-magnetite assemblages and plagioclase and are surrounded by oxide haloes that appear red to orange in transmitted light. We could not find pentlandite in our EET 99430 sections. Instead, we found cavities that may have been occupied by sulfide veins (Figs. 4e and f), with only small blebs of pyrite now remaining.

A section through the NWA 1563 (wi-5, sL) stone contains a ~ 7 -mm-thick dark rind inferred to be a product of terrestrial weathering. Microscopic observation shows that the only significant difference between the rind and the interior of NWA 1563 is the presence of large (300–600 μm diameter) clumps of magnetite and associated limonite in the rind. Both the rind and interior contain small magnetite grains associated with limonite; both regions contain rare 2- μm -sized pentlandite grains.

Although the Tanezrouft 057 CK chondrite (wi-4, sM) was originally classified as type-4 (Russell et al., 2003), it has a relatively coarse groundmass with 100- to

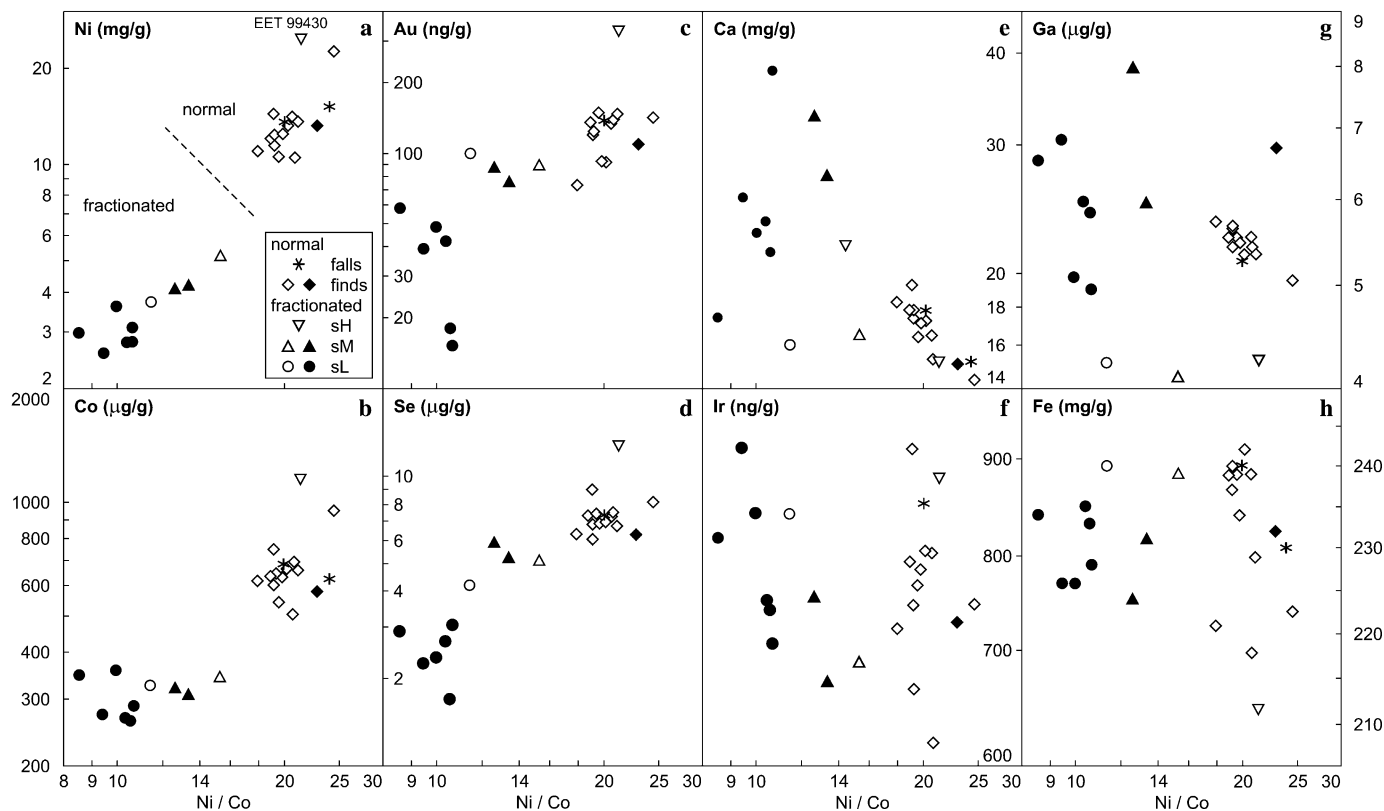


Fig. 2. Bulk Ni/Co ratios in CK chondrites are correlated with (a) Ni content, (b) Co content, (c) Au content and (d) Se content. The correlations are less significant between Ni/Co and (e) Ca, and not significant with (f) Ir, (g) Ga and (h) Fe contents. Low Ni/Co ratios are more common in samples from hot deserts than in those from cold deserts. Data from Tables 2 and 3.

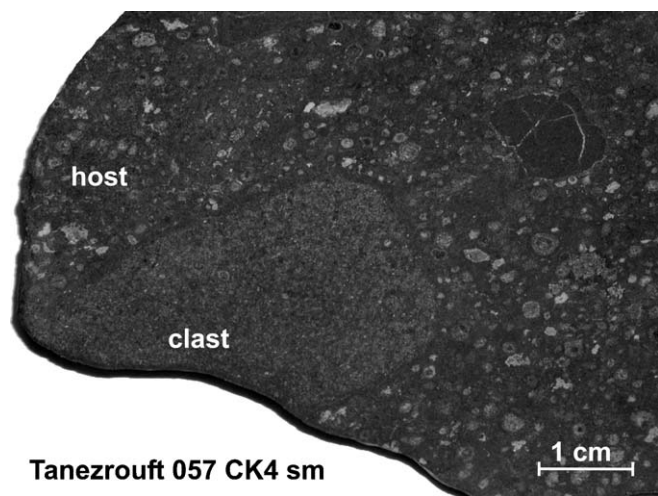


Fig. 3. The slab of Tanzrouft 057 used in this study. The clast (4×3 cm) of finer-grained material is located on the lower left. Both parts exhibit an equal depletion in Ni and Co, but only minor depletions in Au and Se (Fig. 1d). The highest discrepancies are found in As and Zn (4.5 \times and 3 \times enrichment for one replicate; Appendix A). For details on the petrography, see text.

200- μm -sized grains. Following the criteria of Kallemeyn et al. (1991), we reclassify this meteorite as CK5. Extending from the interior to the edge of the $\sim 7 \times 7$ cm slab of Tanzrouft 057 (Fig. 3) in the UCLA collection (LC 2143), is a

~ 2.5 -cm-wide clast that is at least 4 cm long. The boundary between the clast and host exhibits a 0.5-mm-thick weathering rind with a higher degree of brown staining of silicates than the clast or host (which are both wi-4; Rubin and Huber, 2005). Both clast and host have similarly coarse groundmasses; both contain magnetite and rare 2- μm -sized grains of pentlandite mainly occurring inside olivine. The principal difference between the clast and host is in the abundance of chondrules: the host contains 15–20 vol% millimeter-sized chondrules; the clast contains only ~ 0.1 –0.3 vol%. During oxidation and metamorphism, there has been appreciable growth of olivine grains and it is possible that the original abundance of small recognizable chondrule fragments in the clast was much higher.

NWA 060 (wi-5, sL) is a CK5 that contains ~ 15 vol% chondrules. Abundant magnetite is present as 2–25 μm size isolated grains in the matrix and as small grains forming curvilinear trails inside silicates. Magnetite also occurs in 200–500 μm -size clumps; these objects are probably magnetite–pentlandite nodules that lost pentlandite during terrestrial weathering. Only rare sulfide grains are present including small (4–15 μm size) grains of pentlandite, pyrite and a few grains of Os-bearing laurite. A few grains of barite (BaSO_4), probably products of terrestrial weathering (cf. Nyström and Wickman, 1991), also occur (see Fig. 4b).

LAP 03784 (wi-0, normal) is a CK4 sample that contains ~ 25 vol% well-defined chondrules and a few

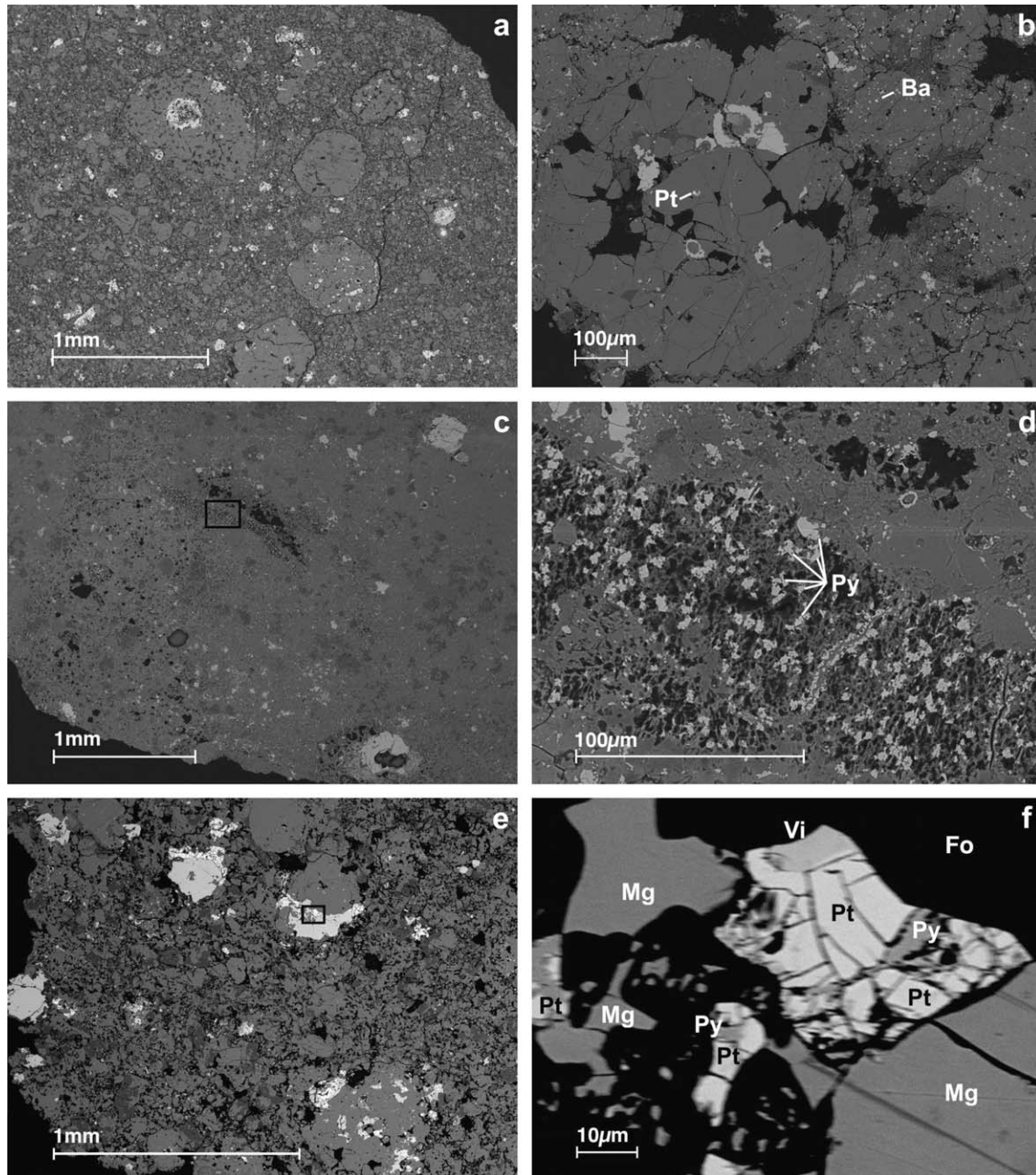


Fig. 4. Back-scattered electron images of sulfide assemblages from unfractionated and fractionated CK chondrites. Dark grey are silicates, light grey is magnetite, white are sulfides. Pt = pentlandite; Ba = barite; Py = pyrite; Mg = magnetite; Vi = violarite; Fo = forsterite. (a) Karoonda ('normal') contains fine-grained sulfides within the matrix and adjacent to magnetite. (b) NWA 060 (sL) has lost most of its sulfides with only a few grains of pentlandite and violarite remaining. Rare barite grains were found only in this particular CK chondrite. (c and d) In EET 99430 (sH-enriched in siderophiles) few sulfides are found; only pyrites of the (presumably) former pentlandite–pyrite assemblages remain in regions that resemble former sulfide veins. (d) A close-up of the black rectangular area in (c). (e) Overview of LAP 03784 ('normal'). The sulfides look unaltered and are, in contrast to Karoonda, blotchy with assemblages of pyrite, pentlandite and violarite. (f) Close-up of the black rectangle in (e) displaying the exsolution of violarite within the pyrite–pentlandite assemblages. These may be subsolidus exsolution features of MSS that formed after cooling below 225 °C (Craig, 1973). The contrast is enhanced compared to (e).

volume percent coarse, isolated mafic silicate grains. There are 200–500 µm size magnetite–pentlandite nodules and large clumps of magnetite–pentlandite at the margins of some chondrules (Figs. 4c and d). Pyrite grains occur associated with pentlandite. Image analysis of backscattered electron images revealed a ratio of 1:2 for pyrite

and pentlandite. Violarite occurs as a minor phase (<5 vol %).

LAR 04318 (wi-2, normal) is a CK chondrite with ~25 vol % well-defined chondrules. In addition to isolated magnetite grains and curvilinear trails of small magnetite grains, there are 150–200 µm size magnetite–pentlandite

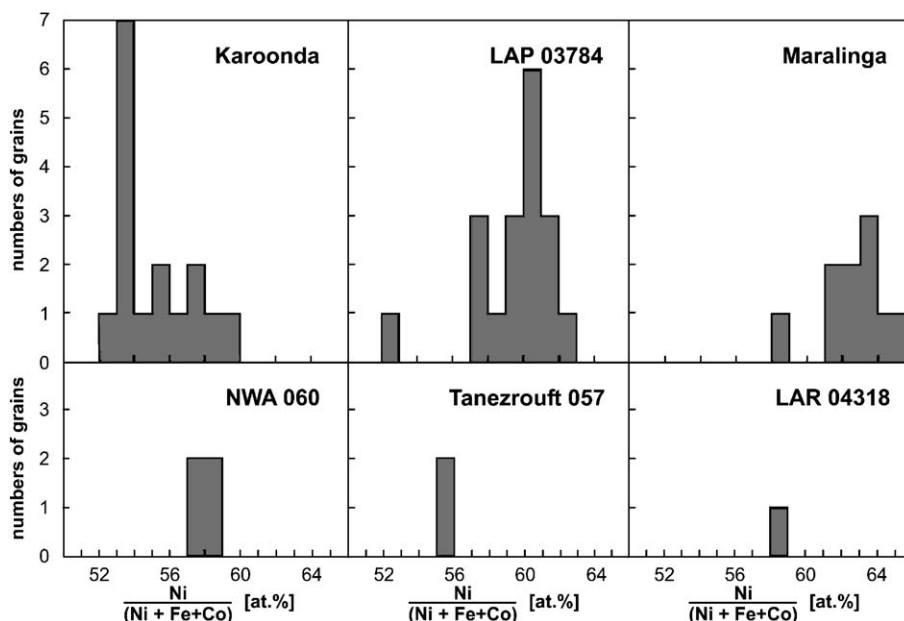


Fig. 5. Histograms of Ni/(Ni + Co + Fe) for pentlandites in CK chondrites for comparison with the alteration sequence for CM chondrites by Chokai et al. (2003). No conclusive trend of depletion in Ni with increasing alteration can be found for CKs. It seems that the differences in sizes of sulfides for Karoonda and LAP 03784 are pre-terrestrial since they correlate with an increase in overall Ni-content of the pentlandites. Most of the sulfides found in LAR 04318 are MSS with Ni/(Ni + Fe + Co) ratios of 40–50 at. % indicating under-abundant pentlandites.

nodules. Some nodules contain intergrown grains of pyrite. A few clumps of magnetite–pentlandite occur at the margins of some chondrules.

Maralinga (wi-3, sL) is not a normal CK chondrite. Its chondrule abundance (~50 vol %) is ~2–3× higher and the amount of CAIs (3 vol %) is ~6× higher than typical CK values. It also has high Ni contents in its mafic and opaque minerals compared to Karoonda and other normal CK chondrites (Noguchi, 1993; Geiger and Bischoff, 1995). Olivine, pentlandite, ilmenite, magnetite and pyroxene in Maralinga have the highest Ni contents within the CK chondrites studied by Noguchi (1993). Millerite (NiS) has been reported only in Maralinga (Noguchi, 1993; Geiger and Bischoff, 1995; Keller et al., 1992) and the paired CK-chondrite Cook 003 (Geiger et al., 1992).

The sulfides found in the ‘normal’ CK chondrites Karoonda and LAP 03784 show distinct differences in appearance and abundance (Figs. 4a and e). They could reflect terrestrial influences (fall vs. find) or resemble different formation conditions on the parent body. In Karoonda (and Kobe; Tachibana et al., 2002) pentlandite and pyrite are abundant; rare violarite and MSS are also present; The sulfides occur as finely dispersed phases within coarse-grained matrix olivines, chondrules and associated magnetite. In contrast, in LAP 03784, sulfides tend to occur as aggregates of 30–50 μm size associated with magnetite or within matrix olivines (Figs. 4e and f). The typical assemblage of pentlandite–pyrite is in some cases accompanied by Co-rich violarite exsolution as shown in Fig. 4f. The weathering index of LAP 03784 is wi-1 with ~10% brown staining of the silicates, typical for minor weathering. To determine whether there is a significant relationship between

petrologic type and size of sulfides we investigated samples exhibiting low to minor weathering of all petrographic types (CK3–CK6). There appears to be a slight tendency for sulfide grains to increase in size with increasing petrologic type of the whole-rock.

In Tables 3 and 4 (and Figs. 5 and 6) we present the compositions of different sulfides within the normal samples Karoonda, LAP 03784 and LAR 04318, sL Maralinga and NWA 060, and sM Tanezrouft 057. These samples were chosen as representative of the different subgroups of siderophile depletions (‘normal’, sH, sM and sL). The data for Karoonda and averages for unfractionated (‘normal’) and depleted samples from Geiger and Bischoff (1995) and Noguchi (1993) are included and agree well with our study. Fig. 5 shows histograms depicting the variation in pentlandite composition among CK chondrites; Fig. 6 shows the different CK sulfides on a ternary Fe–Ni–Co diagram for normal and fractionated samples (Table 5).

Histograms of Ni/(Ni + Fe + Co) ratios for pentlandites show a range in atomic Ni/(Ni + Fe + Co) ratios from 0.52 to 0.64. We could not find pentlandite in EET 99430; in this weathered chondrite the remaining sulfides are pyrite and MSS. We considered various possible reasons for the differences in pentlandite composition. If all CKs originally had the pentlandite compositional distribution of Karoonda, it is conceivable that terrestrial weathering might have preferentially destroyed grains with lower Ni contents. This would be consistent with the data of Rubin (1993) who found that, in some magnetite–sulfide nodules in CK chondrites, the Ni content of pentlandite is systematically zoned from lower mean values for grains near the centers of nodules to higher means for grains near

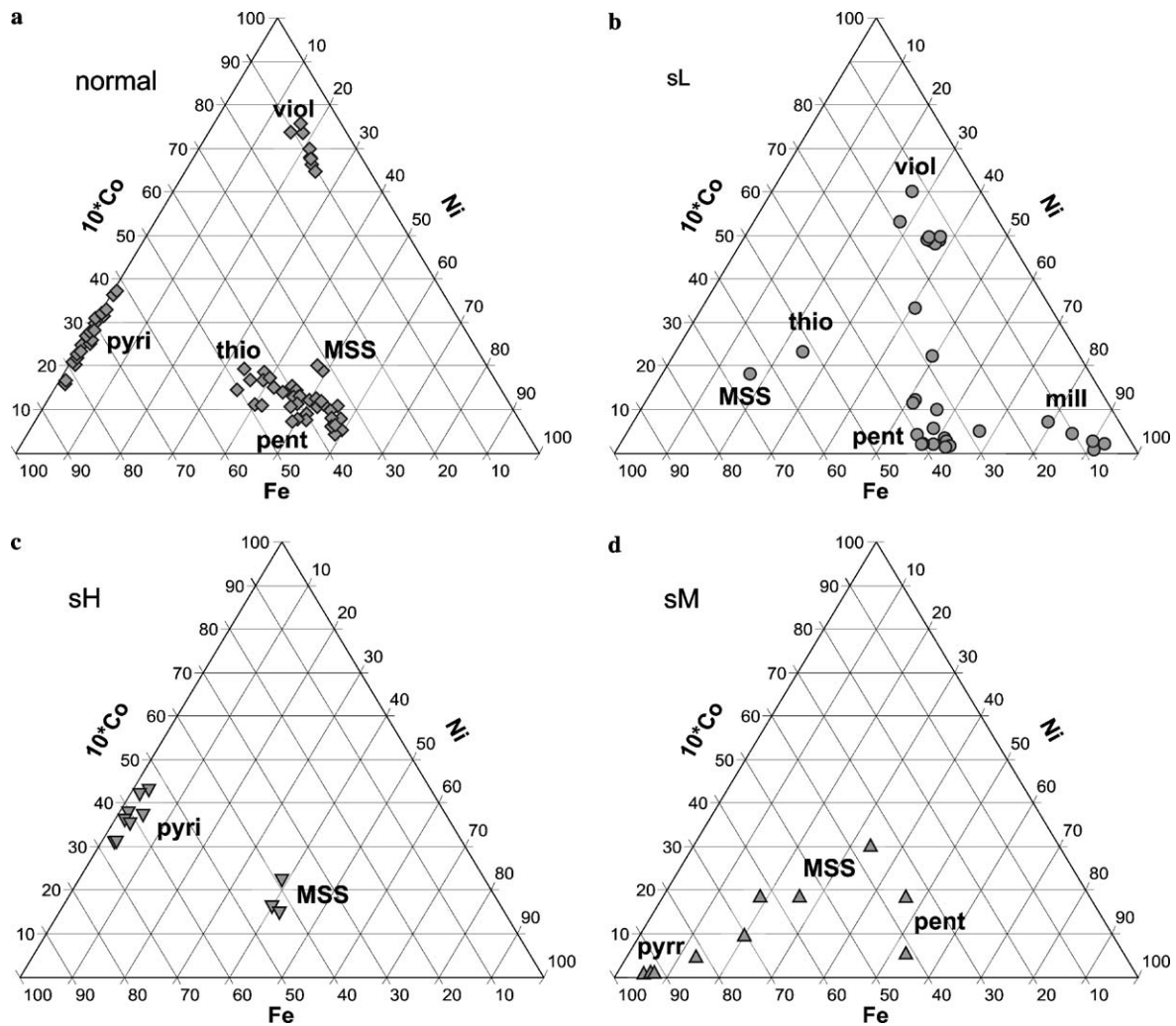


Fig. 6. Compositions of the observed sulfide phases for (a) ‘normal’ Karoonda, LAP 03487 and LAR 04318 (b) depleted sL (NWA 060 and Maralinga) and (c) enriched sH sample (EET 99430) in the Fe–Ni–Co system. (d) The sM subgroup (Tanzrouft 057) shows distinct differences due to replacement of pyrites and pentlandites by pyrrhotite and intermediate MSS phases. (py = pyrite; pyrr = pyrrhotite; MSS = monosulfide solid solution; pent = pentlandite; mill = millerite; viol = violarite; thio = (Fe,Ni)-thiospinels).

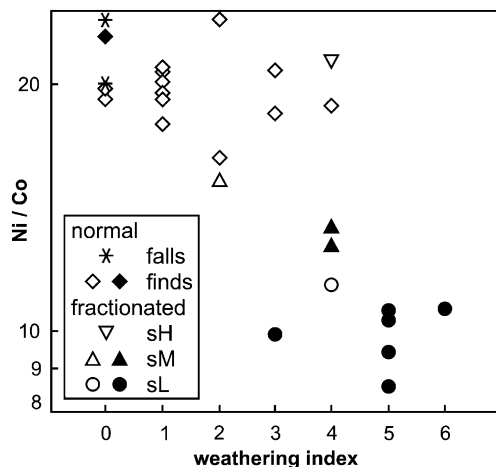


Fig. 7. The Ni/Co ratio correlates with the weathering index based on brown-staining of silicates proposed by Rubin and Huber (2005). The staining, caused by Fe-oxyhydroxides, was found also to correlate with Se and Cl (only for Antarctic samples), implying a Cl-bearing Fe-phase, such as akaganéite.

the rims, consistent with the preferential weathering of low-Ni pentlandite grains near the nodule rims. Another explanation could be that the lower Ni contents in Karoonda are analytical artifacts resulting from electron beam overlap between small pentlandite grains and intergrown Ni-free pyrite. Fluorescence of Fe in pyrite could also produce artificially low Ni/(Ni + Fe) ratios. This effect was also observed by Geiger and Bischoff (1995).

Thiospinels (sulfide minerals with a spinel structure) have previously been reported by Noguchi (1993) within Karoonda, EET 87507, Y-693 (all normal) and Maralinga (sL). Our studies show that Fe/Ni-thiospinels range from compositions with Fe/Ni > 1 and very low Co to near-stoichiometric violarite (FeNi_2S_4) with up to 10 wt% Co (replacing Ni). The Co-free thiospinels have varying Fe/Ni ratios with one ‘extreme’ example of the unnamed stoichiometric phase Fe_2NiS_4 present in highly weathered NWA 060. We will use the term violarite throughout this paper only for phases having compositions close to

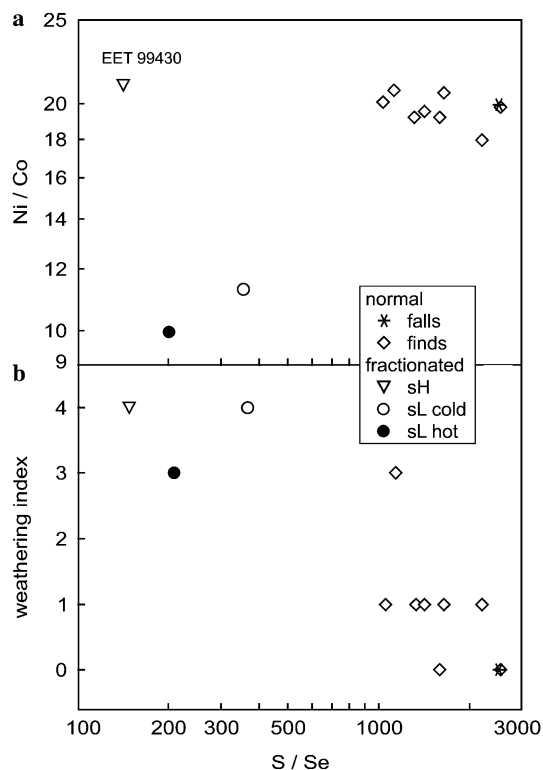


Fig. 8. The decoupling of Se and S during the alteration and metamorphism of CK chondrites is correlated with the loss of sulfide. Sulfur contents in Karoonda from Fitzgerald (1979) and Wiik (1969); Maralinga data from Dreibus et al. (1995) and Keller et al. (1992); EET 87526 and LEW 87009 data from Jarosewich (1990); data on all other CK chondrites from Oura et al. (2004). (a) Two different alteration processes are visible; on the one hand, the loss of Ni and Co-bearing sulfides such as pentlandite and pyrite result in the general trend from the top right to the lower left. EET 99430 seems to have experienced a complex history involving loss only of S, because the Se content and Ni/Co ratio correlate well (Fig. 2d). The low S content of EET 99430 is in good agreement with the near-complete loss of sulfides (Figs. 4c and d). (b) The weathering index (wi) of Rubin and Huber (2005) shows a weak correlation with the S/Se ratio. The group with wi-1 has unchanged Ni/Co ratios (a), but highly variable S/Se ratios (1.0–2.5). The population with highly decoupled S and Se has wi values of 3–4.

$\text{FeNi}_{1.5}\text{Co}_{0.5}\text{S}_4$. The slight sulfur depletion in violarites is consistent with secondary formation from pentlandite (Vaughan and Craig, 1985).

4. Discussion: CK composition and classification

The refractory lithophiles are key taxonomic elements for carbonaceous chondrites. Examination of the abundance ratio diagram (Fig. 1) shows that most of our samples have flat, chondritic patterns with abundance ratios close to mean CK chondrites.

Because these elements tend to fractionate during terrestrial weathering (e.g., Crozaz et al., 2003), it is important to consider how weathering may have affected elemental abundances and interelement patterns in CK chondrites. In weathered CKs mean Mg-normalized rare-earth element abundances are in the range of 0.85–1.15 relative to mean CK chondrites; their abundances do not correlate with

Ni anomalies. The weathered rim of NWA 1563 shows elevated REE abundances, while the unweathered sample of the interior plots within the normal range of CK chondrites. PCA 82500 and LEW 86258 have the lowest REE concentrations (low by ~30%) among all analyzed samples, but other REE abundances scatter around mean CK. Geiger et al. (1993) analyzed Watson 002 (CK3-an) crust and core separates by INAA. They found the core slightly depleted and the crust highly enriched (10×) in REE, especially the light REEs La–Sm (Bischoff, 2005, pers. comm.). These fractionations were accompanied by increases in Ca, Ba and As, a slight increase in Sb, and significant depletions in Ni, Co, Au and Se; the siderophile data indicate that Watson 002 is a member of the sL subgroup.

Hirota et al. (2002) focused on REE distributions and reported resolvable negative Eu-anomalies for most of the samples, but a positive anomaly for Maralinga. In our data set, no negative Eu anomalies were resolvable for any of the samples. EET 99430 shows a relatively flat refractory lithophile pattern; it has concentration ratios about 1.6× mean CK abundances and a positive Eu anomaly.

Six of our samples, all from hot-desert environments, have Ca abundance ratios in the range of 1.3–2.6× mean CK (Fig. 2e). We strongly suspect that these samples are enriched in a calcite-like weathering product, as proposed by Keller et al. (1992) for Maralinga and found by Al-Kathiri et al. (2005) for OCs. Although Noguchi (1993) suggested that higher Ca abundances in Maralinga might be due to the higher abundance of CAIs, high Ca is common in meteorite finds from hot deserts, and particularly in those from dry deserts. Geiger et al. (1993) noted that Watson 002 has abundant CAIs and presented similar arguments about these inclusions being responsible for the high (>4×) Ca enrichment in a separated core sample. Most of the Ni-poor CK chondrite samples have much higher Ca abundances than bulk Maralinga, but they do not have the relatively high abundances of CAIs as found in Maralinga. In addition, high Ca is not accompanied by high Al as would be expected in a rock with a high modal abundance of CAIs. We thus favor the view of Keller et al. (1992) that high Ca contents in most CK hot-desert finds are due to terrestrial contamination. For Antarctic meteorites, Velbel et al. (1991) found that efflorescences on stony meteorites contain Mg-carbonates rather than Ca-salts due to leaching of olivine and reprecipitation of Mg-rich phases on the meteorite surface. Tiny (10 μm) barite crystals were found in our study in the highly weathered NWA 060 (Fig. 4b), an analog to barites found in ordinary chondrites from Oman (Al-Kathiri et al., 2005).

5. Discussion: Ni, Co, Au and Se fractionations in CK chondrites

As described earlier, some CK chondrites from desert environments have very low abundances of Ni, Co, Au and Se. Depletions of siderophile elements (particularly

Table 4
Sulfide mineral compositions (wt.%) of CK chondrites determined by EMPA

Pentlandite									
Group	Karoonda normal	LAP 03784 normal	LAR 04318 normal	Tanez 057 sM	NWA 060 SL	Maralinga sL	Lit mean sL	Lit mean sL	Karoonda normal
<i>n</i>	17	18	5	2	4	10			
Fe	28.7 ± 1.4	26.4 ± 1.1	26.5 ± 1.0	28.6 ± 0.9	27.5 ± 0.2	24.4 ± 1.9	29.3 ± 1.3	27.9 ± 1.2	28.1 ± 1.2
Ni	36.2 ± 1.4	40.2 ± 1.7	40.3 ± 1.3	37.6 ± 0.1	39.3 ± 0.5	42.6 ± 2.5	35.6 ± 1.3	37.2 ± 1.3	37.2 ± 1.3
Co	0.6 ± 0.2	0.6 ± 0.2	0.6 ± 0.2	0.9 ± 0.8	0.3 ± 0.4	0.3 ± 0.5	0.74 ± 0.27	0.88 ± 0.26	0.84 ± 0.26
Cr	0.09 ± 0.08	0.03 ± 0.03	0.12 ± 0.08	0.07 ± 0	0.08 ± 0.03	0.32 ± 0.22	0.07 ± 0.08	0.3 ± 0.07	0.08 ± 0.07
S	32.7 ± 0.6	32.8 ± 0.7	30.7 ± 1.1	32.8 ± 0.3	32.4 ± 0.4	32.9 ± 1.1	33.9 ± 0.7	34 ± 0.7	33.1 ± 0.7
Total	98.3	100.0	98.3	99.9	99.6	100.5	99.6	100.3	99.3
Pyrite							Pyrrhotite		
Group	Karoonda normal	LAP 03784 normal	LAR 04318 normal	EET 99430 sH	Lit falls ^a normal	Karoonda normal	Tanez 057 sM		
<i>n</i>	10	15	3	8			4		
Fe	45.1 ± 0.9	45.1 ± 0.5	44.8 ± 3.3	42.8 ± 1	43.0 ± 1.7	45.0 ± 0.3	55.7 ± 2.5		
Ni	0.7 ± 0.4	0.4 ± 0.2	0.6 ± 0.4	2.2 ± 0.8	1.8 ± 1.0	1.5 ± 0.0	5.1 ± 2.4		
Co	1.5 ± 0.4	1.8 ± 0.5	1.2 ± 0.5	2.6 ± 0.5	1.76 ± 1.43	0.8 ± 0.7	0.1 ± 0.1		
Cr	0.07 ± 0.03	0.03 ± 0.02	0.11 ± 0.10	0.02 ± 0.02	0.04 ± 0.04	0.05 ± 0.05	0.05 ± 0.05		
S	52.7 ± 0.7	52.7 ± 0.3	50.9 ± 3.6	52.4 ± 0.7	52.1 ± 1.5	52.7 ± 0.8	39 ± 0.1		
Total	100.1	100.0	97.6	100.0	98.7	100.1	99.9		
MSS							Millerite		
Group	LAR 04318 normal	EET 99430 sH	Tanez 057 sM	Maralinga sL	Lit mean normal		Maralinga sL		
<i>n</i>	9	3	3	1			4		
Fe	30.4 ± 3.8	31.3 ± 1.3	38.7 ± 8.2	32.1	29.9 ± 2.2		6.1 ± 2.1		
Ni	30.6 ± 4.7	29.7 ± 0.7	20.7 ± 7.3	30.2	29.6 ± 2.1		60.4 ± 4.3		
Co	0.9 ± 0.3	1.3 ± 0.3	1.7 ± 0.7	0.7	1.6 ± 1.2		0.1 ± 0.2		
Cr	0.13 ± 0.07	0.06 ± 0.03	0.22 ± 0.03	0.29	0.05 ± 0.06		0.28 ± 0.08		
S	36.4 ± 0.9	37.6 ± 0.4	38.7 ± 0.9	36.6	38.7 ± 1.3		35.6 ± 0.9		
Total	98.4	99.9	100.0	99.6	99.8		102.4		
Violarite					Thiospinel				
Group	LAP 03784 normal	LAR 04318-1 normal	Maralinga sL	Lit Karoonda normal	LAR 04318-2 normal	NWA 060 sL	Lit Ant. Falls ^b normal		
<i>n</i>	7	1	10		3	1			
Fe	14.7 ± 0.8	13.9	16.8 ± 2.7	15.7 ± 1.9	30.2 ± 1.3	35.7	25.0 ± 0.4		
Ni	32.5 ± 3.3	31.1	36.9 ± 3	30.3 ± 2.7	26.2 ± 1.1	19.8	28.6 ± 0.5		
Co	10.4 ± 1.2	13.9	5.0 ± 1.1	10.4 ± 1.3	1.0 ± 0.1	1.4	3.40 ± 0.2		
Cr	0.02 ± 0.01	0.1	0.26 ± 0.12	n.d.	0.09 ± 0.03	0.06	n.d.		
S	42.3 ± 2	40.4	40.7 ± 1.7	42.5 ± 0.7	40.5 ± 0.7	40.8	42.7 ± 0.8		
Total	99.9	98.0	99.7	98.1	99.4	97.7	99.7		

^a Mean of Y-693, ALH 82135, ALH 84038, ALH 85002, EET 87514, EET 87519, EET 87526, LEW 87009, EET 87507 from Geiger and Bischoff (1995) and Noguchi (1993).

^b Antarctic falls: mean of Y-693 and EET 87507 from Noguchi (1993). Lit: averages of data from Geiger and Bischoff (1995) and Noguchi (1993).

Ni and Co) in meteorite groups other than CK chondrites have been previously reported (e.g., Presper et al., 1993; Bischoff et al., 1994; Krot et al., 2000). The proposed explanations for these anomalies involved either parent-body hydrothermal alteration or terrestrial weathering. The depletions in Ni and Co in micrometeorites from Antarctica may have resulted from the leaching of Ni-rich sulfates (Presper et al., 1993). Krot et al. (2000) discussed siderophile fractionations in the ungrouped carbonaceous (CM–CO) chondrite MacAlpine Hills 88107; its low Ni and Co abundances were inferred to have resulted from weathering of metal; no loss of Au or Se was observed. In the Acfer 217 R-chondrite,

Bischoff et al. (1994) found depletions in Ni and Co, undepleted Se and enriched Au.

We have considered several mechanisms by which the CK siderophile depletions could have arisen: nebular processes, parent-body processes (aqueous or thermal alteration or impact mobilization) and terrestrial weathering.

5.1. Nebular processes

It is likely that CK and CV chondrites formed under similar nebular conditions (Kallemeyn et al., 1991). Both groups have similarly large chondrules (~800 and ~1000 μm, respectively), similar bulk O-isotopic compositions (the

Table 5
EMPA analysis (wt.%) of oxides from CK chondrites

Group	LAP 03784 normal	LAR 04318 normal	EET 99430 sH	Tanez 057 sM	NWA 060 sL
Olivine					
<i>n</i>	8	13	24	12	7
SiO ₂	36.8 ± 0.3	37.5 ± 0.4	37.2 ± 0.2	37.2 ± 1.6	36.8 ± 0.4
TiO ₂	0.04 ± 0.03	0.04 ± 0.05	0.05 ± 0.04	0.06 ± 0.03	0.01 ± 0.01
Al ₂ O ₃	0.15 ± 0.34	0.02 ± 0.03	0.20 ± 0.32	0.56 ± 0.97	0.02 ± 0.01
Cr ₂ O ₃	0.04 ± 0.02	0.06 ± 0.03	0.08 ± 0.04	0.13 ± 0.17	0.09 ± 0.06
FeO	29.3 ± 0.6	25.6 ± 0.4	28.9 ± 0.4	26.0 ± 2.2	26.0 ± 0.7
NiO	0.58 ± 0.04	0.49 ± 0.1	0.25 ± 0.03	0.37 ± 0.04	0.41 ± 0.08
MnO	0.23 ± 0.02	0.25 ± 0.02	0.24 ± 0.03	0.22 ± 0.04	0.24 ± 0.02
MgO	33.9 ± 0.4	36.3 ± 0.4	34.1 ± 0.8	35.9 ± 1.2	35.6 ± 1.1
CaO	0.07 ± 0.12	0.14 ± 0.39	0.19 ± 0.32	0.08 ± 0.07	0.09 ± 0.19
Na ₂ O	0.03 ± 0.03	0.01 ± 0.01	0.02 ± 0.02	0.01 ± 0.01	0.01 ± 0.01
Fa	32.5 ± 0.3	28.3 ± 0.2	32.6 ± 0.9	29.9 ± 0.7	29.1 ± 0.4
Magnetite					
	LAP 03784	LAR 04318	EET 99430	Tanez 057	NWA 060
<i>n</i>	10	19	8	12	5
FeO	84.8 ± 0.5	84.9 ± 3.2	85.3 ± 2.4	84.0 ± 1.1	85.2 ± 1.4
Cr ₂ O ₃	5.03 ± 0.32	3.62 ± 0.81	3.70 ± 0.81	3.33 ± 0.54	4.17 ± 0.26
Al ₂ O ₃	2.22 ± 0.31	0.97 ± 0.76	1.23 ± 0.72	3.36 ± 0.20	0.83 ± 0.50
TiO ₂	0.38 ± 0.13	0.17 ± 0.22	0.19 ± 0.05	0.78 ± 0.18	0.19 ± 0.13
NiO	0.25 ± 0.11	0.20 ± 0.11	0.16 ± 0.04	0.27 ± 0.09	0.16 ± 0.08
MnO	0.04 ± 0.02	0.04 ± 0.03	—	0.10 ± 0.02	0.03 ± 0.03
MgO	0.29 ± 0.06	0.18 ± 0.19	0.14 ± 0.09	0.97 ± 0.03	0.12 ± 0.04
CaO	0.02 ± 0.01	0.09 ± 0.10	0.04 ± 0.03	0.22 ± 0.52	0.05 ± 0.05
Na ₂ O	0.03 ± 0.02	0.03 ± 0.02	—	0.02 ± 0.03	0.02 ± 0.01
Co	0.02	0.0	—	—	0.0

Co contents are averages of WDS analysis for two magnetite grains per sample.

ranges overlap on the CCAM line on the standard three-isotope diagram, although most CV chondrites have somewhat higher $\delta^{18}\text{O}$ values) and similar refractory lithophile abundances (1.21 and $1.33 \times \text{CI}$, respectively). However, none of the CV chondrites shows siderophile-element fractionations comparable to those in the anomalous CK chondrites.

Kurat et al. (1991) suggested that the siderophile anomalies in CK-sL Maralinga resulted from a heating event under highly oxidizing nebular conditions; they inferred that the missing siderophile elements were never incorporated into the agglomerated chondritic materials. This suggestion was based on preliminary data (mainly Re and Mo) provided from a study of heating experiments on Allende samples (Wulf et al., 1995). A problem for the model is that the Mo concentration in normal Karoonda is within the same range (380 $\mu\text{g/g}$, Palme and Rammensee, 1981) observed in Maralinga. Additionally, the Mo determinations of Wulf et al., 1995, are of low precision, so the suggestion for nebular oxidation was mainly based only on Re for which the data are only slightly more precise but still ambiguous. The Karoonda fall has Re concentrations ranging from 45 to 64 ng/g, DaG 431 (a CK-sL) has 40 ng/g and Y-693 (a 'normal' CK) averages 65 ng/g. The Maralinga sample investigated by Kurat et al. (1991) plots with the heated Allende sample for most siderophile refractory elements. In any case, the depletions in Ni and Co cannot be

explained by this process because the heating experiments showed no indications of volatility-related losses of Ni and Co.

Some information about possible differences in nebular materials can be obtained by comparing the host material and a chondritic clast in Tanezrouft 057 (Table 1 and Fig. 3). Although the textures are quite different (the clast has a much lower abundance of chondrules than the host and seems to have a lower sulfide content), the two lithologies show similar siderophile fractionations (Fig. 1d). They both belong to the sM group with minor Au and Se depletions and major depletions of Ni and Co. A caveat is that we are not sure that the clast obtained its low chondrule abundance in the nebula; crushing on the asteroid followed by grain coarsening during alteration processes may be a plausible alternative. Only one analysis of the clast material reveals high abundances for REEs, As, Ga and Zn (see Appendix A), reflecting differences in degree of terrestrial contamination.

The chief argument that the siderophile anomalies in the CK sL subgroup were not produced in the nebula is that they are not found in the two observed CK falls. Indirect evidence for a non-nebular origin for the siderophile depletions is that large fractionations between elements having similar nebular volatilities (e.g., Fe, Ni and Co) have not been documented in any chondrite group. It thus seems unlikely that nebular processes can account for the anomalous siderophile fractionations in CK chondrites.

5.2. Parent-body processes

As first discussed for the Tanezrouft 057 breccia, it is conceivable that different regions of the CK parent asteroid experienced different degrees of alteration. These regions might be recognized if they form clusters in cosmic-ray-exposure ages. The ^{21}Ne ages for CK chondrites vary between 2 and 50.4 Ma (Sugiura and Zashu, 1995; Scherer and Schultz, 2000; Matsumoto et al., 2002). The four CK sL samples included in these studies (LEW 86258, Maralinga, Cook 003, Camel Donga 003, and Watson 002) have ages of 2, 5 and 6 and 9 and 10 Ma. Samples with unfractionated siderophile-element patterns all have ^{21}T ages of 9.5 Ma and higher; due to the overlap in ages with CK sL samples regional siderophile variations on the parent body cannot be reasonably assumed.

Another notion, that the CK compositional anomalies are products of thermal metamorphism, can be readily dismissed. The siderophile fractionations are not closely related to the petrologic type; the CK-sL set includes CK3 (e.g., Dar al Gani 431) to CK5 (e.g., NWA 060, QUE 93007) chondrites, while the normal CKs range from type 4 (e.g., Karoonda) to type 6 (e.g., LEW 87009). It seems that all hot-desert CK3 chondrites belong to the depleted subgroups; these include Dhofar 015 (M. Ivanova, 2005, pers. commun.), Dar al Gani 431 (Zipfel et al., 2000; Smith and Russell, 2003), Watson 002 (Geiger et al., 1993), and Camel Donga 003 (Spettel et al., 1992).

One possibility is that asteroidal aqueous alteration caused the CK siderophile depletions. Together with R chondrites, the CK chondrites are the most oxidized, generally anhydrous, meteorites known (with oxidized CV chondrites being only slightly more reduced; e.g., Neff and Righter, 2006). Based on the general patterns observed in less-metamorphosed carbonaceous chondrites, it seems probable that asteroidal aqueous alteration was responsible for the oxidation of the CK chondrites.

Another possibility is the influence of shock metamorphism. Siderophile/chalcophile anomalies can be produced by the flow of a metal-sulfide liquid depleting these elements in one micro-region while enhancing them in another. This appears to be the best scenario to explain the enhancements of siderophiles in EET 99430. Some micro-regions must have been depleted by this mechanism but the fact that there is no petrological evidence for impact-induced depletions in the CK sL subgroup indicates that shock waves are not the correct model for the siderophile fractionations.

Smith and Russell (2003) inferred that Dar al Gani 431 (CK3, sL) experienced a complex parent-body alteration history involving changing fluid compositions. Similar processes were inferred to be responsible for the Ni dissolution and redeposition in the matrix of CI chondrites (Bullock et al., 2005). These authors suggested that Ni was dissolved from magnetite and sulfide and redeposited in the matrix; some Ni partitioned into Ni-sulfates (bloedites). Similar Ni-sulfates were described by Romanek et al. (1994) in

efflorescences on Antarctic samples (e.g., EET 9007, 'normal'). They found hydrated Ni-sulfates and Ni-hexahydrate using X-ray diffraction and differential scanning calorimetry (DSC).

However, in the hydrated carbonaceous chondrites (CI, CM, and CR), there is no evidence of elemental fractionations associated with leaching. The fraction of water present during aqueous alteration in the anhydrous CK chondrites seems to have been small, (e.g., marginally pore filling) consistent with the fact that there are no documented fractionations attributable to the transport of soluble elements. We conclude that parent-body aqueous alteration is unlikely to be solely responsible for the observed losses in CK siderophiles.

5.3. Terrestrial weathering of sulfides

There is much evidence suggesting that the compositional anomalies in CK chondrites are due to terrestrial weathering and are functions mainly of terrestrial residence time and location. Most of the fractionated samples are from the Sahara, suggesting that the origin of these compositional anomalies is related to the terrestrial environment. Unfortunately, terrestrial ages are not available for any of the hot desert samples; the Antarctic samples PCA 82500 and ALH 85002 have terrestrial ages of ~ 280 ka and ~ 8 ka, respectively (Nishiizumi et al., 1989; Jull et al., 1998). Consistent with those differences, PCA 82500 is a highly weathered sample with weathering index wi-3 whereas ALH 85002 is only slightly weathered (wi-1). Nevertheless, both samples plot within the range of unfractionated samples in Fig. 1. Although terrestrial residence time must be partly responsible for CK siderophile-element depletions, environmental differences seem to be much more important.

In CK-sL chondrites, Se is, on average, less depleted than Ni and Au. This implies either that Se was enriched in phases less affected by weathering or that Se efficiently formed insoluble weathering products. The detailed study of S and Se in hot-desert chondrite samples by Dreibus et al. (1995) showed that oxidized to highly oxidized anhydrous chondrite groups such as CK, CV and R have lost large fractions of their S, but that Se is depleted by smaller factors. Typical S/Se ratios in these samples are 5–10 \times lower than those in falls from the same chondrite groups.

Loss of S is consistent with the observation of increased S contents in weathering products around sulfide grains in Antarctic OC (Gooding, 1981) and in soils retrieved below OC finds from the hot desert in Oman (Al-Kathiri et al., 2005). Sulfate phases were not identified in the Karoonda fall either microscopically or by DSC (Gooding, 1986), but have been reported in the weathered 'normal' find PCA 82500 and the CK-sL NWA 060. In Fig. 8 we examine the relationship between the S/Se ratio, the Ni/Co ratio, and the Rubin–Huber weathering index. S/Se ratios are available for only three

fractionated CK meteorites, i.e., EET 99430, LEW 86258 and Maralinga; their ratios are <400, whereas those in normal CK chondrites are >1000. CK-sH EET 99430 has a normal Ni/Co ratio and the two sL samples LEW 86258 and Maralinga have Ni/Co ratios about 2× lower than the normal range.

In the CK chondrites, the most abundant sulfide is pentlandite (~65 vol %) followed by pyrite (~33 vol %). The remaining sulfides are the minor phases of thiospinels, pyrrhotite or MSS. Hence, most of the S that was lost during the alteration came from pentlandite or pyrite (Fig. 7). Because Se is a chalcophile element and because the most common Se compounds are analogs of common S compounds, it is generally held that Se is an excellent proxy for chondritic S. However, this may not be the case for the fractionated CK chondrites.

The decoupling of S and Se could have resulted if most of the Se resided in sulfide phases other than pentlandite (e.g., violarite or MSS), or if Se reprecipitated as insoluble compounds after the breakup of the original sulfides. Dreibus et al. (1995) mentioned the latter possibility and pointed out that SeO₂ is a solid (e.g., the stable phase downeyite), whereas SO₂ and SO₃ are gaseous. Lorand et al. (2003) explained the variations in S/Se ratios for peridotite xenoliths by differences in the partitioning of Se into pentlandite and MSS, especially attributing low S/Se ratios to supergene weathered sulfides. Our working model is that pentlandite, pyrite and violarite were largely converted to other phases in the sL subgroup by aqueous alteration. Dreibus et al. (1995) reported only 0.5 mg/g S in Maralinga; Oura et al. (2004) reported 1.5 mg/g S for LEW 86258. The S content of Kobe is 18.8 mg/g; while there is some scatter among the three S analyses of Karoonda, we will use the mean value of 18.2 mg/g. By combining the values we find the S content of normal CKs to be 18.5 mg/g, about 37× higher than in Maralinga. Thus, if Maralinga and LEW 86258 are representatives of the CK-sL chondrites, these rocks have lost >90% of their S and, thus, probably similar proportions of the main sulfides pentlandite and pyrite.

An appreciable fraction (15–20%) of the Ni in CK chondrites is in olivine (0.3–0.6 wt% NiO). Geiger and Bischoff (1995) suggested that diffusion of Ni into olivine occurred during the thermal breakdown of sulfides in the metamorphic event. The remaining Ni formed sulfides, mainly pentlandite, MSS, and violarite. The fraction of the Ni lost in the CK-sL group is a good proxy of the fraction of sulfide loss.

The concentration of Ni in pentlandite is somewhat greater than that of Fe. Modal abundances show roughly a 1:0.7 distribution of Ni and Fe in pentlandites (in MSS the Fe/Ni ~ 1). The Fe/Ni ratio in the pentlandites and other phases is not dependent on whether the CK chondrites are 'normal' or fractionated. It is therefore important to examine possible Fe loss during the weathering of pentlandite and other sulfides. If we assume

that all S is lost by destruction of pentlandite, the expected S loss is ~22 mg/g for Maralinga and ~12 mg/g for LEW 86258; the loss of Fe would be ~15 mg/g in Maralinga and ~8 mg/g in LEW 86258 or <10% of total Fe. From Table 2 we infer that half of this Fe remained in the stones as the brown-staining Fe-oxyhydroxides of silicates (for wi-2 and higher). Because Maralinga generally has the highest Ni contents of each individual mineral studied (Table 2; Noguchi, 1993), it seems likely that its original bulk Ni/S ratio was also higher than for mean CKs.

The situation for Co is less clear. The Co contents of the pentlandite in the fractionated samples show a wide range from <0.3 to 1.54 wt%. Loss of pentlandite alone could account for the small depletion Co in Maralinga, but it could not account for the larger depletion in LEW 86258. The distribution of sulfides in the different subgroups of fractionated CK chondrites shown in Fig. 6 can be used to help assess depletion mechanisms. Pyrites that contain up to 2 wt% Co but essentially no Ni are missing from the fractionated samples. Since roughly 33 vol % of the sulfides are pyrite, complete loss of this phase would be equivalent to a loss of 41 µg/g Co, i.e., 13% of the removed Co.

There is also a distinct difference between 'normal' CKs and weathered specimens in terms of the Co-content of the thiospinel violarite. Our electron-probe data (Table 4) confirm the trend visible in the data set of Noguchi (1993) with Karoonda having 10.4 wt% Co in violarite whereas the thiospinels in the more-altered finds (Y-693, EET 87507) are lower in Co (3–4 wt%). The slightly weathered specimens LAP 03784 and LAR 04318 have subequal and high (10–14 wt%) Co contents in the violarites, with LAR 04318 being the only sample containing both the low- and high-Co-bearing thiospinels. Although the small amount of thiospinels present in CK chondrites (<1 vol % of sulfide phases) makes a reliable estimate quite difficult, the fraction of Co retained of lost with this phase is minor.

Again, Maralinga is an outstanding case with an increase in Ni, but a decrease in Co in the violarite, consistent with the formation of millerite. One highly Co-enriched violarite grain (13 wt%) was found in Maralinga, whereas most grains contain 2–4 wt% Co. This, and the fact that Maralinga has consistently the highest Ni contents in all sulfide and oxide phases determined by Geiger and Bischoff (1995), Noguchi (1993) and this study, leads us to the interpretation that it formed under different asteroidal conditions than the other siderophile-fractionated meteorites. On the other hand, a lower degree of thermal metamorphism of Maralinga might account for the overall higher Ni contents of many minerals in this meteorite if these species did not equilibrate with fine-grained phases in the matrix. A smaller degree of comminution on the parent asteroid could account for higher abundances of intact chondrules.

Overall, the fractionation pattern for the sL subgroup (Fig. 1e) can be explained by complete removal of pentlandite and pyrite. Different weathering conditions (hot or cold desert) could explain the differences within the subgroup.

The depletion in Au in the CK-sL subgroup is similar to or greater than that of Ni. We note that the mean abundance of Au in DaG 431 and NWA 1558 is only about 0.14× mean CK, implying that 86% of the original Au was lost during weathering. This could be attributed to a loss of trace amounts of Au present in the weathered pentlandite, but also to loss of Au-bearing sulfide phases like those described in detail by Geiger and Bischoff (1995). Because we do not know the Au content of pyrite or pentlandite, we cannot assess what fraction of the lost Au originated in each of these phases.

Our explanation of the patterns in the CK-sM samples is similar to that for the CK-sL samples. The chief difference results from the need to retain most of the Au and Se and more of the Ni than Co within the weathering stone. This may reflect one or both of the following mechanisms: (1) formation of insoluble weathering products that were retained within the meteorite and/or (2) selective weathering of sulfides having Ni, Au and Se contents lower than the dominant phases that were lost from the sL chondrites. In any case, the differences in sulfide mineralogy between sL and sM samples are significant and will need further investigation. The role of cold vs. hot deserts cannot yet be definitively resolved because Tanezrouft 057 and QUE 97009 show similar patterns despite experiencing distinctively different terrestrial environmental conditions.

5.4. sH EET 99430

As noted above, the sH-subgroup sample EET 99430 has high concentrations of Ni, Co, Au and Se, although Fig. 1c shows a rather chondritic Ni and Co pattern. If we assume that the S-bearing component that was lost during weathering was pure pentlandite (Figs. 4c,d and 7c), this would add, on average, another 20.4 mg/g Ni and 286 µg/g Co, leading to a whole-rock Ni/Co ratio of ~31. The resulting siderophile-element pattern looks like the inverse of those in the CK-sL chondrites.

The probable mechanism for generating an enhancement of sulfides would be impact mobilization on the parent asteroid. Impact-altered chondrites of other classes tend to show scatter between replicate analyses, and this is also the case for EET 99430 (see Appendix A). The former occurrence of sulfide veins of pentlandite–pyrite (Figs. 4b and c) with only pyrites remaining suggests that this sample was altered somewhat differently than the CK chondrites from hot deserts. As has been discussed above, the low S/Se ratio (see Fig. 7) could reflect weathering of the original sulfide aggregates, leaving behind Se that reprecipitated within the chondrite.

6. Summary

The CK chondrites constitute the most oxidized anhydrous carbonaceous chondrite group. They contain abundant magnetite and only very rare micrometer-sized grains of metallic Fe–Ni. The most abundant sulfide is pentlandite, followed by MSS, pyrite, Fe/Ni-thiospinels and pyrrhotite. Kobe and Karoonda (the only two observed CK falls) and some unweathered CK finds have unfractionated siderophile-element abundance patterns. The CK sulfide mineralogy is quite distinctive.

Many CK finds (e.g., DaG 431; NWA 060; LEW 86258) show major depletions in Ni, Au, Co and Se; they were placed in a low-siderophile (sL) subgroup. The CK chondrites with the most extreme depletions of Ni, Co, Se and Au have Ni contents equivalent to 0.24 of normal CK and Au contents equivalent to 0.14 of normal CK. It appears that following the asteroidal oxidation of nearly all the original metal, the depleted Se and siderophiles were incorporated into sulfides; we thus infer that these rocks lost about 90% of their sulfides. This depletion pattern has not been found in other chondrite groups.

A few other samples (e.g., Tanezrouft 057; QUE 93007) were placed in a medium-fractionated (sM) subgroup; these rocks have low Ni and Co abundances but unfractionated Au and Se contents. In addition, one CK chondrite (EET 99430) that has enhanced abundances of Ni, Co, Se and Au was placed in a sH subgroup. It is possible that this sample obtained additional sulfide from impact redistribution in the parent asteroid, coupled with subsequent loss of pentlandite during terrestrial weathering.

It appears that the CK chondrites with siderophile-element depletions obtained their fractionated patterns mainly from the terrestrial weathering of sulfides (primarily pentlandite) that occurred in two steps: (1) oxidation of pentlandite and possibly violarite and pyrite to sulfates or other oxides, and (2) in some cases (particularly in samples from hot deserts), removal of the weathering products by leaching. In any case, samples of the fractionated CK chondrites lost significant amounts of Ni, Co, Au and Se released by the oxidation of original sulfide phases.

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Appendix A

Individual analyses of CK chondrites determined by INAA

	Na (mg/g)	Mg (mg/g)	Al (mg/g)	K (μg/g)	Ca (mg/g)	Sc (μg/g)	V (μg/g)	Cr (mg/g)	Mn (mg/g)	Fe (mg/g)	Co (μg/g)	Ni (mg/g)	Zn (μg/g)	Ga (μg/g)	As (μg/g)	Se (μg/g)	Sb (ng/g)	La (ng/g)	Sm (ng/g)	Eu (ng/g)	Yb (ng/g)	Lu (ng/g)	Os (ng/g)	Ir (ng/g)	Au (ng/g)	Ni/Co
DAV 92300 ^a	3.10	150	16.1	290	17.3	11.4	97.0	3.69	1.45	240	600	11.5	100	5.60	1.70	6.90	—	500	310	110	300	45.0	—	745	121	19.2
LEW 87250 ^a	3.10	151	16.4	270	17.6	11.7	97.0	3.70	1.47	239	640	12.1	102	5.50	1.50	7.40	—	480	290	110	320	49.0	—	790	135	18.9
LAP 03784 ^a	3.36	150	18.3	299	12.2	10.3	102	3.50	1.45	229	652	13.7	82.4	5.36	1.69	6.70	46	443	288	110	284	43.2	999	799	145.	21.0
NWA 765	3.04	155	18.0	405	14.0	10.2	95.2	3.34	1.57	229	653	14.4	78.9	7.65	1.30	6.46	111	534	332	134	358	56.4	928	749	114	22.1
NWA 765	2.89	151	15.4	144	15.8	9.26	88.9	3.44	1.36	234	506	12.2	82.9	5.68	1.67	6.02	106	569	242	105	371	33.8	865	707	105	24.2
EET 99430	3.65	131	18.9	356	16.3	11.2	101.	3.64	1.33	226	1055	20.9	115	3.87	0.92	9.85	58.2	472	275	121	283	35.7	719	962	294	19.8
EET 99430	3.42	132	20.7	253	13.5	10.9	104.	3.42	1.18	198	1242	28.0	123	4.61	1.26	15.7	48.1	361	306	130	311	58.2	907	806	369	22.6
LAR 04318 ^a	3.37	150	18.8	287	13.8	9.9	98.5	3.38	1.52	223	945	22.9	91.4	7.12	1.54	7.73	57	394	251	105	279	36	1056	758	126.	24.3
QUE 93007 ^a	2.50	149	16.0	240	16.5	10.8	95.0	3.75	1.31	239	340	5.20	55	4.10	1.40	5.10	70.0	410	250	90	260	39.0	—	690	90	15.3
Maralinga	2.75	147	15.6	365	23.6	10.3	92.0	3.62	1.34	232	367	3.50	57	5.00	1.48	1.70	60.0	428	259	100	299	42.0	710	694	51	9.5
Maralinga	3.24	145	20.4	314	21.4	10.9	93.9	3.25	1.35	219	357	3.72	58	5.12	1.50	3.08	50.7	499	333	128	338	54.2	1048	994	46	10.4
NWA 060	3.88	135	14.5	439	19.7	10.6	98.9	3.77	1.38	241	361	3.20	113	5.89	4.64	3.19	88.5	457	278	93	300	45.7	941	835	47	8.9
NWA 060	3.83	142	16.1	461	14.9	10.1	102.	3.44	1.46	228	339	2.75	93	7.13	3.53	2.65	63.1	442	250	118	357	45.8	823	795	70	8.1
NWA 1563	3.41	149	16.5	419	19.0	10.2	101.	3.49	1.62	231	286	2.66	91	5.07	1.34	2.59	84.1	420	352	116	352	49.1	785	721	35	9.3
NWA 1563	3.54	141	15.7	303	27.4	10.3	89.6	3.41	1.45	239	254	2.99	97	6.82	1.66	2.81	62.6	529	259	115	365	46.0	909	778	49	11.8
NWA 1563 wt ^a	3.13	149	16.0	281	24.8	10.4	101	3.48	1.69	226	276	2.63	86	6.79	2.15	2.29	106.	792	420	163	482	74.7	708	921	39	9.5
NWA 1558	3.45	155	17.9	351	20.0	10.7	105.	3.50	1.70	233	281	2.62	91	5.03	2.39	1.67	54.0	420	292	130	324	41.9	756	739	17	9.3
NWA 1558	3.72	139	14.7	273	22.6	9.04	85.5	3.35	1.44	233	250	3.06	104	6.59	2.84	1.73	55.1	386	248	98	408	43.9	773	739	19	12.3
Tanez 057	3.44	138	16.8	352	25.2	9.60	101.	3.05	1.32	222	298	4.60	121	5.27	1.51	5.21	59.5	497	287	109	285	46.1	770	695	79	15.4
Tanez 057	3.20	137	16.1	366	28.5	10.0	99.8	2.84	1.47	240	328	3.71	111	6.13	0.67	5.38	42.8	365	261	106	281	45.9	593	637	73	11.3
Tanez 057 cl	3.49	153	18.6	264	41.5	8.41	110.	3.34	1.51	241	273	3.67	106	6.63	0.81	5.23	66.5	381	234	98	263	45.7	492	530	108	13.5
Tanez 057 cl	3.77	136	21.3	459	22.9	14.4	121.	3.37	1.35	207	374	4.46	307	9.23	4.57	6.66	98.3	765	508	172	413	46.5	837	975	66	11.9
DaG 431	3.09	127	14.0	351	36.5	8.79	79.0	3.01	1.29	225	262	3.18	69	5.61	1.52	2.78	88.8	352	285	92	292	49.5	790	632	15	12.1
DaG 431	2.70	136	16.2	453	37.5	9.90	113.	3.35	1.48	231	319	3.09	86	4.24	2.68	3.37	74.2	575	334	129	325	51.0	683	781	16	9.7

Data in Table 1 are averages of duplicates.

^a Only single analysis; NWA 1563 wt.—weathered crust; Tanez 057 cl—clast within Tanezrouft 057 (see Fig. 3).

Sulfide alterations in CK chondrites

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