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Unequilibrated assemblages of sulphide, metal and oxide in the fusion crusts of the enstatite chondrite meteorites

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ABSTRACT

The fusion crusts of meteorites form due to heating during atmospheric entry and have mineralogies which are strongly influenced by changes in oxidation state. We have studied the fusion crusts of the most reduced primitive meteorite group, the enstatite chondrites, since they should demonstrate pronounced changes on oxidation. The fusion crusts are dominated by highly unequilibrated assemblages of sulphide, metal and oxide with compositions indicative of progressive oxidation by the reaction with atmospheric oxygen. Troilite becomes depleted in Ti, Cr and Mn, and enriched in Ni with increasing oxidation. Enrichments in the Ni-contents of kamacite and depletions in Si-content also occur with oxidation, although contemporaneous enrichments in Si within metal droplets occurs by partial melting. Assemblages dominated by Fe-oxide are found within fusion crusts as reaction rims on metal, as veins and within troilite-metal assemblages as droplets and formed by oxidation of metal during heating. Despite the evidence for large increases in redox state during heating, fusion crusts also contain lithophile sulphides indicating a high degree of disequilibrium during the atmospheric reprocessing of enstatite chondrite materials. Based on comparisons with experimental phase relations, ablation rates of 0.08–0.25 cm s^{-1} are predicted from the thermal gradients recorded in fusion crusts; these rates are broadly similar to those suggested for other meteorite groups.

Keywords: enstatite chondrites, fusion crust, oxidation, alteration.

Introduction

Fusion crusts are the thermally altered outermost layers of meteorites and form as a result of heating during passage through the Earth's atmosphere. The mineralogy and petrology of fusion crusts have been little studied, since the alteration that results from heating obscures the 'primary' characteristics that make meteorites useful as samples of ancient solar system materials. Pioneering studies of meteorite fusion crusts (Ramdohr, 1967, 1973; Krinov, 1960) provided many interesting insights into their mineralogy but are limited by the lack of micro-analysis. Studies of fusion crust, however, have provided estimates of the mass of meteoritic stones prior to their entry into the Earth's atmosphere (e.g. Sears and Mills, 1972) and the length of time they have resided on the Earth's surface (Sears and Mills, 1974; Benoit *et al.*, 1993). Meteorite fusion crusts also give valuable information on the style of ablation and the nature of processes that affect extraterrestrial materials during rapid heating (Genge and Grady, 1999).

In a recent survey of the fusion crusts of the stony meteorites (Genge and Grady, 1999), we have determined that the mineralogies and compositions of fusion crusts vary with meteorite type and are strongly affected by changes in the redox state imposed by heating in the atmosphere. In the current paper we focus in detail on the mineralogy of the fusion crusts of the enstatite chondrites (ECs) since these have much lower oxidation states than other primitive meteorites (Rubin *et al.*, 1988, and references therein) and are thus likely to exhibit the most pronounced changes on heating. Enstatite chondrites are characterized by unusual assemblages of highly reduced minerals including Si-bearing metal, low FeO silicates (principally enstatite) and many phases rarely found as natural compounds in other terrestrial or extraterrestrial rocks (e.g. sinoite

Si_2N_2O; e.g. Keil, 1968). The formation conditions of ECs were so reducing that normally lithophile elements exhibit chalcophile behaviour with the result that Mg-, Ca-, Mn-, Cr- and Ti-bearing sulphides occur (e.g. alabandite, MnS and oldhamite, CaS).

Two groups of enstatite chondrite, EH and EL chondrites, are recognized. The EH chondrites have siderophile and chalcophile element abundances ~1.5–2.0× higher than those of EL chondrites (Sears *et al.*, 1982; Weeks and Sears, 1985), but also differ in mineralogy and mineral compositions. The high Si-contents (>2.5 wt.%) of kamacite (α-iron with <8 wt.% Ni) and the occurrence of niningerite (MgS) in EH chondrites and the low Si-contents (<1.6 wt.%) of kamacite and the occurrence alabandite (MnS) in EL chondrites are the most characteristic mineralogical differences (Leitch and Smith, 1982; Rubin, 1997*a*). The sulphides, troilite (FeS), oldhamite, daubréelite (Cr_2FeS_4) and djerfisherite ($K_6Na_9(Fe,Cu)_{24}S_{26}Cl$) are found in both groups.

Enstatite chondrites also form a metamorphic sequence caused by differential heating on their parent asteroid(s). The least equilibrated meteorites contain abundant chondrules (spherical magmatic objects characteristic of chondritic meteorites) with sharp outlines. However, with increasing metamorphism these become obscured by recrystallization and in the most equilibrated meteorites, silicate minerals are predominantly coarse-grained (e.g. Keil, 1968). The extent of metamorphic equilibration varies from 3 to 6 with increasing equilibration (Van Schmus and Wood, 1967; Sears *et al.*, 1982). Most EH chondrites are petrologic grade 4 (i.e. EH4), the majority of EL chondrites are petrologic grade 6.

We report the mineral chemistries and textures of assemblages of sulphide, metal and oxide from EC fusion crusts in order to identify the nature of the oxidation reactions and allow phases formed during atmospheric entry heating to be distinguished from those present on the meteorite parent body.

Samples and techniques

Fusion crust was taken from seven ECs, covering both EH (Abee, Indarch and St Mark's) and EL (Daniel's Kuil, Hvittis, Khairpur and Pillistfer) groups (Table 1). All the meteorites studied were observed falls (i.e. recovered soon after they fell) and thus have been little affected by weathering resulting from exposure on the Earth's surface. Of the meteorites sampled for fusion crust, Abee and Indarch are EH4, St Mark's is EH5 and Daniel's Kuil, Hvittis, Khairpur and Pillisfter are EL6.

Fusion crusts were removed from meteorites under a binocular microscope using a scalpel blade and prepared as polished grain mounts. This sampling technique was adopted instead of using thin-sections in order to minimize the amount of material removed from the stones and has the advantage that numerous specimens may be obtained from different faces of the meteorite without causing significant damage. Fusion crust 'chips' are easily manipulated and can be orientated so that the external surface is approximately perpendicular to the plane of section (estimated at ±10°). The textures of fusion crust were characterized by reflected light microscopy (prior to carbon coating) and scanning electron microscopy (SEM). Mineral compositions were determined using a Hitachi S2500

TABLE 1. Enstatite chondrites sampled for fusion crust. The mass of stones and the year of fall are also given. All specimens are from the collections of the Natural History Museum, London

Meteorite	Class	Mass (kg)	Year	Specimen No
Abee	EH4	107	1952	BM1970,169
Indarch	EH4	27	1891	BM86948
St Mark's	EH5	13.9	1903	BM1916,59
Daniel's Kuil	EL6	5.5	1903	BM42502
Hvittis	EL6	14	1901	BM86754
Khairpur	EL6	2.5	1873	BM51366
Pillistfer	EL6	7.5	1868	BM1920,337

analytical SEM by energy dispersive spectroscopy (EDS), at an accelerating voltage of 15 kV and beam current of 1.0 nA, and using a Cameca SX50 electron microscope by wave dispersive spectroscopy (WDS) at 15 kV and 20 nA. Phases <5 μm in size were analysed by EDS because of the smaller effective spot size of the analytical SEM. Energy dispersive analyses were obtained against internal absorption coefficients and a vanadium gain calibration, and ZAF matrix corrections were also applied. Wave dispersive analyses were obtained against mineral standards and corrected by Cameca matrix correction procedures. Analytical errors are estimated as ~0.5 wt.% by EDS and ~0.05 wt.% by WDS.

The presence of O and C within materials was determined qualitatively using the Cameca SX50 which can detect the light elements by virtue of its windowless detector. Oxygen abundances were determined quantitatively by WDS analyses through calibration to mineral standards. Repeat analyses of silicates suggest an analytical error of ~0.5 wt.%.

The textures and mineralogies of fusion crusts

The fusion crusts of the ECs are not homogeneous but consist of two distinct zones: (1) an outer melted crust, dominated by quench olivines in interstitial glass; and (2) a substrate, dominated by interconnected veins of sulphide and metal. The melted crust is vesicular and consists of euhedral-subhedral olivine phenocrysts (Fa_{12-30}), accessory dendritic magnetite and interstitial aluminosilicate glass. Ni-bearing (<2 wt.%) olivine and magnetite are restricted to the outermost layer of the melted crust. Sulphides occur as droplets and as menisci on vesicles within the melted crust. The substrate underlying the melted crust varies in structure depending on chemical group. EH chondrites have substrates dominated by networks of veins containing troilite and metal which connect small irregular metal grains. Irregular silicate glass veins occur occasionally adjacent to the melted crust (Fig. 1*a*). The substrates of EL chondrites have fewer veins and contain large irregular metal grains which extend to close to the melted crust (Fig. 1*b*). No veins of silicate glass were found within the substrates of EL chondrites.

The structure of EC fusion crusts differs from that of ordinary and carbonaceous chondrites. In the ordinary chondrites the fusion crust usually exhibits three well developed zones with a melted crust overlying an outer substrate dominated by silicate glass veins and an inner substrate containing metal and sulphide veins (Genge and Grady, 1999). Equivalent zones (1, 2 and 3) were also recognized by Ramdohr (1967) and by Krinov (1960). The outer substrate is present only in the EH chondrites and is poorly developed. The carbonaceous chondrites also lack an outer substrate in which silicates have partially melted except in individual chondrules (Genge and Grady, 1999) and also have a poorly developed inner substrate.

The most common veins in both EH and EL substrates contain subhedral troilite crystals with interstitial metal or symplectite-like intergrowths of sulphide and metal (Fig. 2*a*). These textures suggest crystallization from a sulphide liquid and exsolution at subsolidus temperatures from mesostasis. Larger metal grains are found in some troilite veins (most commonly at vein intersections) and vary from sub-spherical droplets to irregular grains with thin (<2 μm) overgrowths of metal with higher Ni contents than the host grain. Some irregular metal grains also have cores containing elongate dendrites within mesostasis. Although too fine-grained for quantitative analysis, the composition of this assemblage suggests these are metal dendrites within interstitial phosphide. Multiphase cores have convex outlines relative to the surrounding metal that suggest they formed from liquids within the core of the (solid) grain (Fig. 2*b*).

Large masses of metal also occur in substrates and have irregular outlines suggesting they have not melted. Irregular metal masses are usually surrounded by thin, complete rims of troilite that often extend into adjoining veins implying these were liquids that wetted or were formed along grain boundaries. Metal grains are also commonly embayed by an Fe-Ni-Co-S-rich oxide phase which can form complete, laminated rims on metal grains within the innermost regions of substrate and often contain thin troilite lamellae (Fig. 2*c*).

Towards the outer margin of the substrate adjacent to the melted crust, Fe-oxides occur as droplets within troilite veins and occasionally contain highly embayed metal grains. The droplet morphologies of these oxides suggest they were molten and immiscible with the surrounding sulphide liquid. Within the fusion crusts of Indarch and Abee, composite grains containing Fe-oxides, troilite, Si-bearing metal and P-bearing metal occur within troilite veins (Fig. 3*a*). Oxides within these grains commonly surround highly

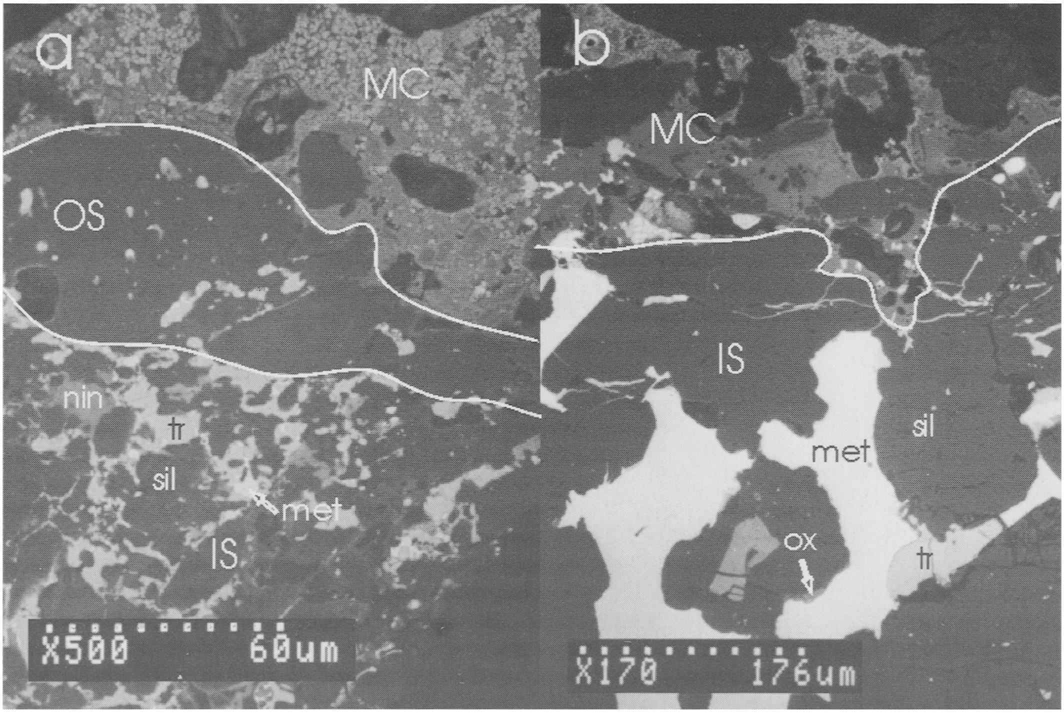

FIG. 1. Backscattered electron images illustrating the fusion crust structure. Fusion crusts comprise an outer completely melted crust (MC) consisting of olivine phenocrysts in a glassy mesostasis, and an underlying inner substrate (IS) dominated by veins of troilite and kamacite (separated by white line). The EH chondrites (*a*, Indarch EH4) have substrates containing networks of troilite veins linking small metal grains, niningerite veins (nin), and oxide veins. Adjacent to the melted crust, EH chondrites also exhibit irregular veins of silicate glass in the outer substrate (OS). The EL chondrites (*b*, Pillistfer EL6) also contain troilite-metal veins, but these do not form extensive networks. Kamacite forms large masses that extend to the substrate/melted crust boundary, reflecting the coarse-grained texture of the parent meteorite.

embayed Si-bearing metal and are themselves partially enclosed by P-bearing metal. Contacts between the oxides and vein troilite are curved, suggesting that these were coexisting liquids. The phosphide-bearing metal phase within composite grains in Abee has microporous rims (Fig. 2*d*).

In addition to those containing troilite, veins dominated by other phases also occur. Veins containing Fe-oxides are widespread and are compositionally and spatially related to oxide alteration rims on large metal grains (Fig. 3*b*). Veins containing niningerite are observed in the fusion crusts of Indarch and St Mark's (Fig. 1*a*). Rounded blebs of troilite-metal assemblages within Fe-oxides in the substrate of Indarch (Fig. 3*c*) and droplets of niningerite within troilite veins in Abee (Fig. 3*d*) suggest liquid immiscibility between Fe-dominated sulphide liquids and both oxide and Mg-dominated sulphide liquids.

Relict unmelted oldhamite (CaS) commonly occurs as euhedral-subhedral grains and occasionally is embayed by troilite. Relict niningerites occur within troilite veins in St Mark's as rounded grains and have rims of Fe-Cr-rich niningerite.

Phase chemistry

Sulphides

Sulphides in EC fusion crusts are generally monosulphides and have a wide range of compositions (Table 2). Three types are recognized: (1) ferroan sulphides (troilites); (2) magnesian sulphides (Mg-Fe-S); and (3) calcium sulphides. No manganese sulphides (alabandite) were observed.

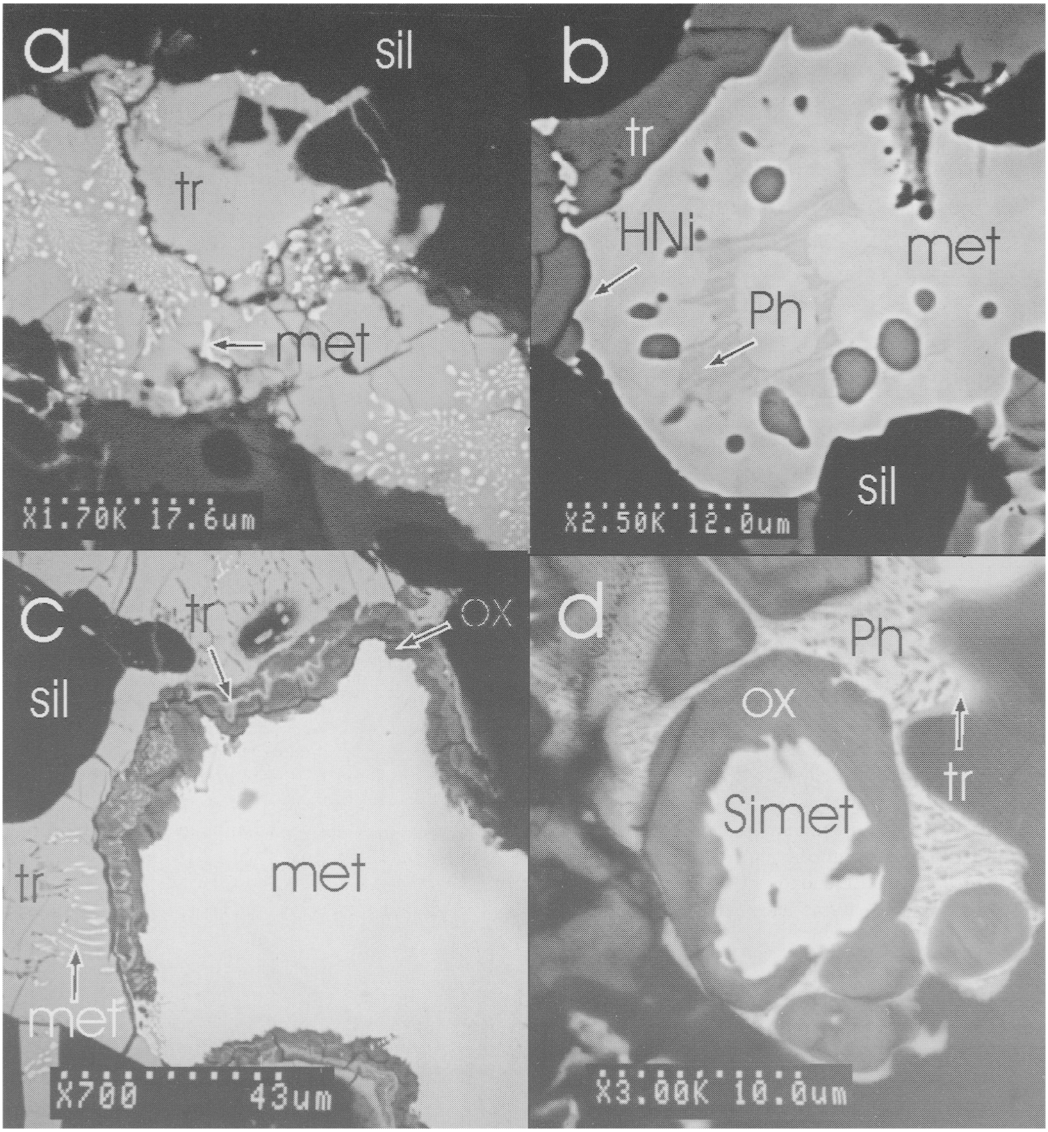

FIG. 2. Backscattered electron images of substrate. (*a*) Hvittis. Troilite-metal veins with subhedral troilite (tr) phenocrysts with interstitial areas filled with either high-Ni metal grains or symplectic intergrowths of metal and sulphide. (*b*) St Mark's. Metal grains (met) with overgrowths of high-Ni, low-Si metal (HNi). Some grains also have cores containing metal dendrites and interstitial Fe,Ni-phosphide (Ph). (*c*) Daniel's Kuil. Assemblages containing a significant component of Fe-oxide and troilite (tr) lamellae as reaction rims on highly embayed kamacite grains. Areas of the metal interstitial to troilite (met) are only found adjacent to metal grains. (*d*) Abee. Assemblages of Fe-oxide in complex grains associated with highly embayed Si-bearing metal (Simet), P-bearing metal (Pmet) and troilite.

Ferroan monosulphides

Iron-rich sulphides contain >47.2 wt.% Fe with minor Cr, Ni, Ti and Mn and are restricted to troilite-metal veins, irregular metal-poor polycrystalline troilite masses and rims around large irregular metal grains. Chromium is usually the most abundant minor element and comprises up to 14.9 wt.% although the majority of sulphides

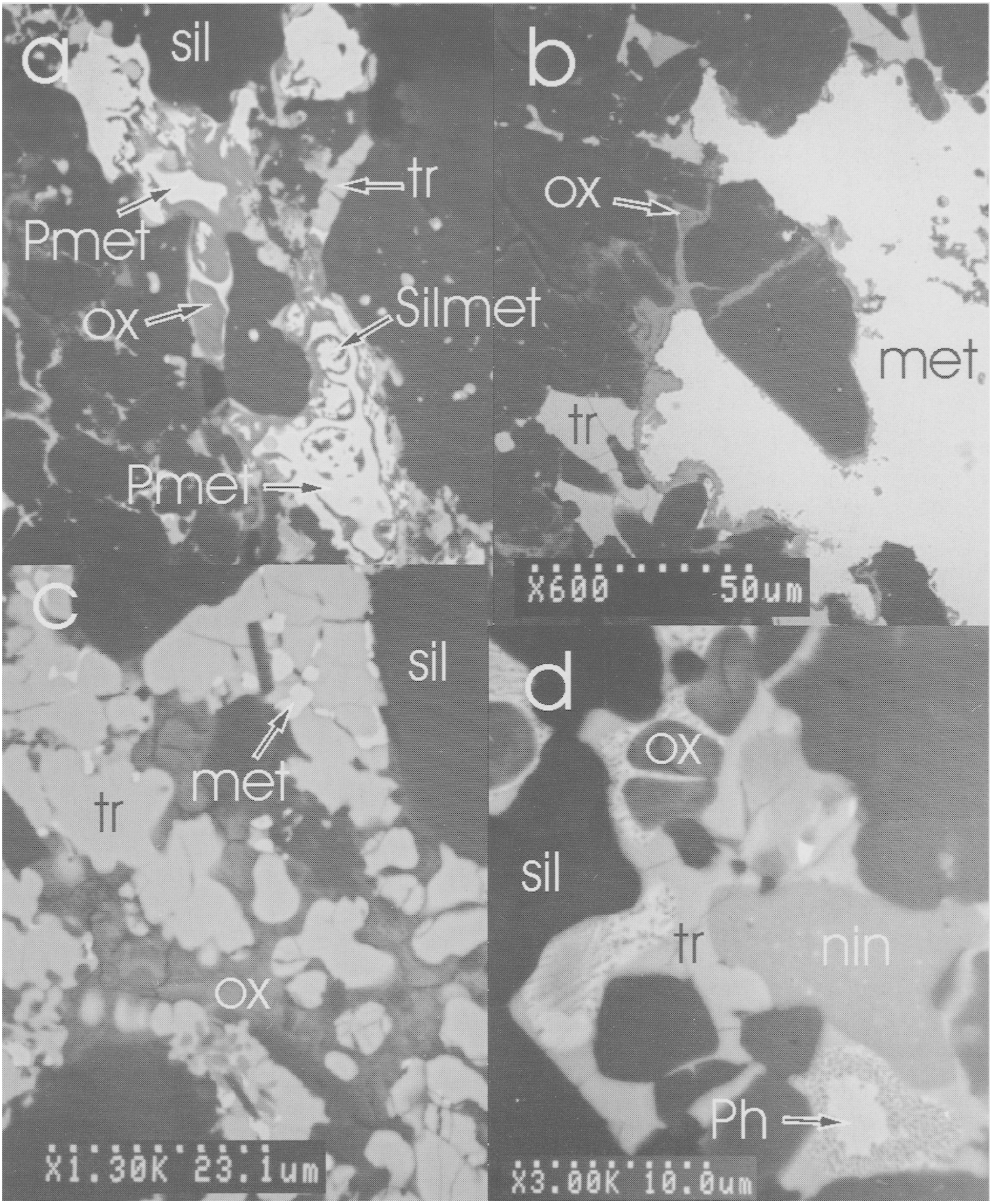

FIG. 3. Backscattered electron images of oxides in the substrates of the enstatite chondrites. (*a*) Indarch. Oxide droplets (Ox), some containing embayed Si-bearing metal (Simet), enclosed in phosphide-bearing metal (Pmet). These probably form by the partial melting of metal grains containing phosphide cores (e.g. Fig. 2*b*) and reaction of metal to oxide. (*f*) Daniel's Kuil. Fe-oxide veins spatially associated with the troilite-bearing (tr), oxide reaction rims on a kamacite grain (met). (*g*) St Mark's. Oxides containing irregular droplets of troilite. (*h*) Abee. Oxide assemblages and niningerite (nin) as blebs within troilite veins, associated with phosphide grains (Ph) with porous rims

TABLE 2. Compositions of sulphides in wt.%

	Troilite						Oldhamite			Niningerite			
	1	2	3	4	5	6	7	8	9	10	11	12	13
Mg	b.d.	b.d.	b.d.	b.d.	b.d.	0.05	0.39	0.78	0.82	8.17	23.06	20.18	11.34
S	36.41	35.92	36.02	36.58	36.99	38.28	43.65	44.08	43.53	41.40	47.92	45.36	40.79
Ca	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	51.33	52.31	51.26	4.38	0.51	1.00	2.50
Ti	0.15	b.d.	b.d.	b.d.	0.65	0.20	b.d.	b.d.	b.d.	0.21	b.d.	b.d.	b.d.
Cr	3.76	0.36	b.d.	4.86	7.79	14.68	0.07	b.d.	b.d.	3.11	0.25	1.04	2.25
Mn	0.51	0.18	b.d.	0.77	0.43	1.27	1.09	0.30	0.34	8.74	13.89	7.06	3.53
Fe	57.96	59.22	54.21	56.51	54.56	46.44	1.46	2.21	2.65	32.70	14.58	23.14	35.80
Co	0.09	0.19	0.52	b.d.	0.11	b.d.	b.d.	b.d.	b.d.	b.d.	0.05	b.d.	b.d.
Ni	0.80	2.78	9.28	0.90	b.d.	0.52	b.d.	0.06	0.14	0.13	0.06	b.d.	0.62
Totals	99.67	98.72	100.03	99.63	100.58	101.53	98.05	99.82	98.76	98.83	100.34	97.77	96.84

1–4 Daniel's Kuil
5 Khairpur
6,7 Pillistfer
8,12,13 Indarch
9, 11 cores of relict niningerites from St Mark's
10 rim on niningerite from St Mark's
b.d. – below detection limit

contain 0.5–5.0 wt.% Cr. Manganese within Fe-rich sulphides exhibits a general positive correlation with Cr content (Fig. 4) and is present at concentrations up to 1.3 wt.% although most contain ~0.5 wt.%. The Ti contents of most sulphides are low (<0.5 wt.%). However, rare examples containing up to 1.14 wt.% Ti were observed. The data suggest a general positive correlation between the Cr and Ti contents for the majority of Ti-rich Fe sulphides (Fig. 4). Iron-rich sulphides are generally Ni-bearing and contain up to 19.1 wt.% Ni. Those sulphides with the highest Ni-contents generally contain no detectable Cr or Mn and are located within or at the margins of the melted crust. Most iron-rich sulphides have Ni contents of 0.5–1.5 wt.%. A number of Fe-rich sulphides also contain detectable Zn (~0.5 wt.%).

Magnesian monosulphides

Niningerite (MgS) occurs in the crusts of EH chondrites as relict grains, rounded blebs in troilite-metal veins and within metal-free veins. The compositions of niningerites are shown in Fig. 5 and range from 37.2–13.6 wt.% Fe, 24.9–11.0 wt.% Mg and 14.3–3.43 wt.% Mn; in general Fe and Mn abundances decrease with increasing Mg content. Niningerites also contain 2.3–0.4 wt.% Ca, up to 3.4 wt.% Cr and up to 1.7 wt.% Na. The abundance of these minor elements generally increases with FeS content. Trace quantities of Ni and Ti were also detected. Reaction rims on relict niningerite grains in St Mark's have compositions which are more ferroan than the host grain and contain higher abundances of the minor elements.

Calcium monosulphides

Oldhamite (CaS) is found as relict grains in all the crusts examined and comprises >54.4 wt.%

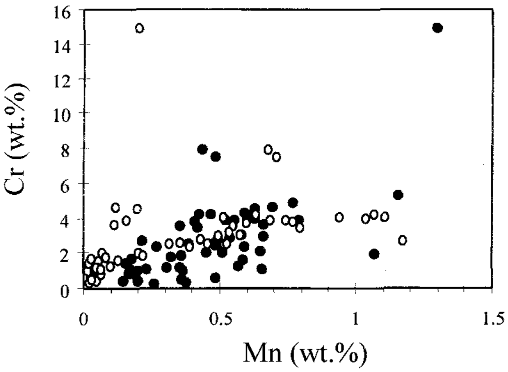

FIG. 4. Elemental correlations between minor elements in fusion crust vein troilites. Symbols: solid circles – Mn contents, open circles – Ti contents.

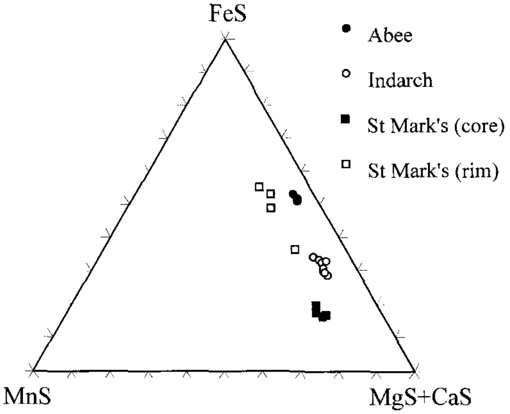

FIG. 5. The compositions of niningerites in fusion crusts in wt.%.

Ca. Iron and Mg are the most abundant minor elements having ranges of 2.8–0.9 wt.% (average 1.9 wt.%) and 2.39–0.4 wt.% (average 1.04 wt.%) respectively. The Mn contents are <1.2 wt.% and are mostly below EDS detection limits.

Fe,Ni metals

On the basis of its low Ni contents (<8 wt.% Ni), most metal within the fusion crusts of ECs is probably kamacite (body-centred cubic α-iron), although rare grains, usually occurring as small droplets in ferroan sulphide veins, have higher Ni contents of up to 12 wt.% Ni and may include taenite (face centred cubic γ-iron). The Ni-contents of rims on kamacites could not be accurately determined due to their small sizes but are higher than those of the host grains. The compositions of Fe,Ni metal are shown in Table 3 and vary considerably between and within individual meteorites. Large irregular metal grains generally have higher Si contents and lower Ni, Co and S abundances than small rounded droplets occurring within troilite veins, although there is considerable compositional overlap. Metal interstitial to sulphides and within symplectite-like intergrowths with sulphide in veins is in general too small for quantitative analysis, but appears to be Ni-rich and Si-poor. Phosphorous-rich areas of metal that form the cores to some kamacite grains contain 1.13–13.58 wt.% P, up to 3.5 wt.% S and can be enriched in Ni in comparison to the adjacent metal (up to 11 wt.% Ni). Microporous metal/phosphide in Abee (described above) approaches a schreibersite stoichometry ((Fe+Ni)/P = 3.36) and is possibly a cryptocrystalline assemblage dominated by Fe,Ni phosphide with minor kamacite and troilite.

Fe oxides

Iron-dominated materials with low totals (83.1–96.1 wt.%) occur as alteration rims on large metal grains, as rounded droplets within troilite veins and as veins throughout the fusion crusts of the ECs. These phases exhibit a wide range of compositions (Table 4) and can contain up to 16.9 wt.% S, up to 2.1 wt.% P and up to 9.7 wt.% Si and are thus probably cryptocrystalline assemblages of minerals. Qualitative wave dispersive spectra of these materials exhibit significant O-*K*α and no C- or N-*K*α emission lines and suggest that oxides are a significant component of these assemblages. Oxygen abundances (13.7–34.1 wt.%) determined by quantitative analysis are, however, insufficient to explain the low analytical totals. The presence of hydroxyl could explain the deficiency, implying that oxyhydroxides (e.g. ferrihydrite) are present, although low totals might alternatively result from the analytical difficulties posed by the poor polish of these materials and/or a sub-μm porosity/vesicularity. We conclude that these materials are cryptocrystalline assemblages of minerals dominated by oxides because their textural relations (discussed below) preclude an origin as a hydrous weathering product. One further possibility, that these represent artefacts of polishing can also be excluded since their low Al abundances indicate that the Al_2O_3 abrasives are not retained.

Systematic variations in the compositions of Fe-oxides are observed with textural setting. Oxides occurring as alteration rims on large metal grains demonstrate the widest range in compositions, with those occurring adjacent to the metal having lower Ni, Co, S and P and higher Si contents than those further away. Nickel and Co abundances in the outer rims can be up to 22.3 and 2.0 wt.% respectively. Oxides occurring as rounded droplets within troilite-metal veins show a similar range in composition to those within the outer parts of rims and some contain even higher Ni contents (up to 25.5 wt.% in Abee). Oxides occurring within metal-free veins generally have low S, Ni, Co and Si contents (<2 wt.%) but can contain appreciable Ca (<2 wt.%) and Mg

TABLE 3. The range in compositions of kamacite in fusion crusts in wt.%. Irregular, unmelted grains are denoted by I, droplets within troilite veins by D

	Daniel's Kuil		Khairpur	Pillistfer		Indarch		Abee		St Mark's	
	I	D	I	I	D	I	D	I	D	I	D
Fe	91.9–94.0	86.8	91.8–92.7	89.4–93.5	91.4	89.5–91.0	82.3–92.0	88.3–90.9	91.7	89.5–91.	85.9–93.7
Co	0.33–0.54	0.42	0.37–0.54	0.33–0.61	0.33	<0.4	<0.82	n.d.	n.d.	0.29–0.64	<0.53
Ni	4.53–6.33	12.39	6.0–6.60	5.4–79.64	5.04	4.07–6.90	4.21–10.56	5.30–8.19	6.3	4.98–5.9	5.52–8.85
Si	0.64–1.18	0.04	0.91–0.99	0.02–1.14	1.26	2.60–4.09	0.82–4.93	2.21–3.53	1.97	2.59–3.7	0.73–4.25
Cu	<0.25	b.d.	<0.16	b.d.–0.11	0.13	<0.06	<0.05	n.d.	n.d.	<0.09	<0.13
S	<0.05	0.12	<0.02	<0.21	1.63	<0.19	<2.16	<0.63	0.72	<0.04	<0.44

n.d. not detected
b.d. below detection level

TABLE 4. Compositions of oxide assemblages in wt.%. Oxygen abundances were determined quantitatively by calibration to mineral standards

	Rims on metal				Veins		
	1	2	3	4	5	6	7
O	26.04	25.59	15.25	29.40	30.03	28.51	25.62
Si	0.84	0.48	1.78	2.91	0.66	0.46	2.96
P	0.15	0.09	0.30	0.94	b.d.	b.d.	0.20
S	3.39	20.20	22.50	2.57	0.80	1.13	0.07
Ca	b.d.	0.11	0.10	b.d.	0.97	2.27	b.d.
Mn	0.05	0.13	0.03	b.d.	0.09	0.41	b.d.
Fe	46.51	26.69	28.02	41.15	54.28	50.80	55.89
Co	0.72	1.24	1.99	0.22	0.19	0.18	0.27
Ni	12.96	16.78	22.21	11.32	2.47	1.12	3.26
Total	90.69	91.31	92.17	88.57	89.52	84.90	88.32

1,2,5,6 Daniel's Kuil
3, 7 Pillistfer
4, Abee
b.d. below detection limit

(<2 wt.%). There are broad positive correlations between the Ni, Co and S abundances of oxides.

Discussion

Theory suggests that the fusion crusts retained on meteorites represent the very last products of heating and formed over the last few seconds of luminous flight (e.g. Öpik, 1958; Krinov, 1960). The rapid removal of molten materials from meteoroids (i.e. ablation) during surface heating produces high temperature gradients which migrate rapidly inwards, thus equilibrium conditions are unlikely to have been attained. Due to the temperature gradient, fusion crusts form a thin hot boundary layer on meteoroids and thus cool rapidly by thermal radiation once heating has ceased. Little re-equilibration will therefore occur during cooling.

Melted crust

The melted crusts of the ECs have evidently formed by large degrees of melting of the underlying substrate. The high Ni-contents of olivine phenocrysts in melted crust and the high Ni, low Cr and Ti contents of sulphide droplets suggest relatively high oxygen fugacities. The occurrence of magnetite as an accessory phase only within the outermost layer of the crust further suggests that oxygen fugacity decreases across the melted crust towards the substrate as discussed by Genge and Grady (1999).

Troilite-metal veins

The predominance of troilite veins within fusion crusts undoubtedly relates to the disparate melting temperatures of sulphides and the other main mineral phases in ECs. Troilite melts at temperatures of 1193°C, significantly lower than kamacite (~1534°C) or enstatite (~1543°C). During equilibrium melting of ECs, the first liquids will be formed at the Fe-FeS eutectic at ~988°C. Most veins contain troilite phenocrysts and interstitial Fe,Ni metal and thus have compositions which approach those of the Fe-FeS eutectic. Within the innermost substrate, assemblages of troilite and interstitial metal are restricted to the margins of large metal grains, thus the first melts produced on heating were probably eutectic Fe-FeS liquids formed at the boundaries of metal grains by reaction with pre-existing troilite.

Fusion crust troilites exhibit a wider range of Ti, Cr and Mn contents and significantly higher Ni contents than those of the parent meteorite. Preferential partitioning of Ti and Cr into Fe-FeS liquids at low degrees of partial melting might be responsible for high abundances of these elements, although the incorporation of daubréelite exsolution lamellae contained within pre-existing troilite probably explains the highest Cr abundances (the absence of daubréelite exsolution lamellae within fusion crust is probably a consequence of rapid cooling). Troilites containing less Ti, Cr and Mn than those in the parent meteorite probably result from increases in the oxidation state. This is supported by the observation that the maximum Ti and Cr contents of troilite decrease towards the 'oxidized' melted crust (Fig. 6). In contrast, the Mn contents of troilite increase towards the melted crust. However, these might result from the progressive reaction of Fe-FeS liquids with niningerite or alabandite. The high Ni contents of fusion crust troilite probably result from the reaction of Fe-FeS liquids with Ni-bearing metal. Nickel contents generally increase toward the melted crust.

The occurrence of sub-spherical droplets of kamacite within troilite veins suggests partial melting of metal and liquid immiscibility with sulphide liquids, contrary to Fe-FeS phase relations which indicate that metal and sulphide liquids are entirely miscible. These assemblages are thus not in equilibrium and probably originate from heterogeneous melting. Kamacite in fusion crust exhibits a wide range of compositions in comparison with the parent meteorite including grains with higher and lower Si and Ni abundances. Reductions in Si and increases in Ni content would occur as a result of oxidation. However, no correlations are observed between these elements to suggest coupled behaviour. Increases in the Si-content of metal on partial melting might complicate any relationships. The observation that kamacite with low-Si and high-Ni contents is most commonly observed as droplets within troilite veins close to the melted crust suggests increasing oxidation and equilibration with Fe-FeS liquids with progressive heating are responsible for the evolution of metal compositions.

Large unmelted metal grains occasionally have P-bearing cores with textures which suggest the crystallization of schreibersite (and kamacite) from a liquid. These cores probably form by partial melting of Si-bearing metal in the presence of pre-existing schreibersite grains. Small P-rich metal bodies within troilite veins close to the melted crust are usually associated with highly embayed Si-bearing metal and droplets of Ni- and Co-rich Fe-oxide. The morphology of these grains suggests they represent the partially melted P-rich cores of large metal grains surviving after the preferential alteration of Si-bearing metal to Fe-oxide.

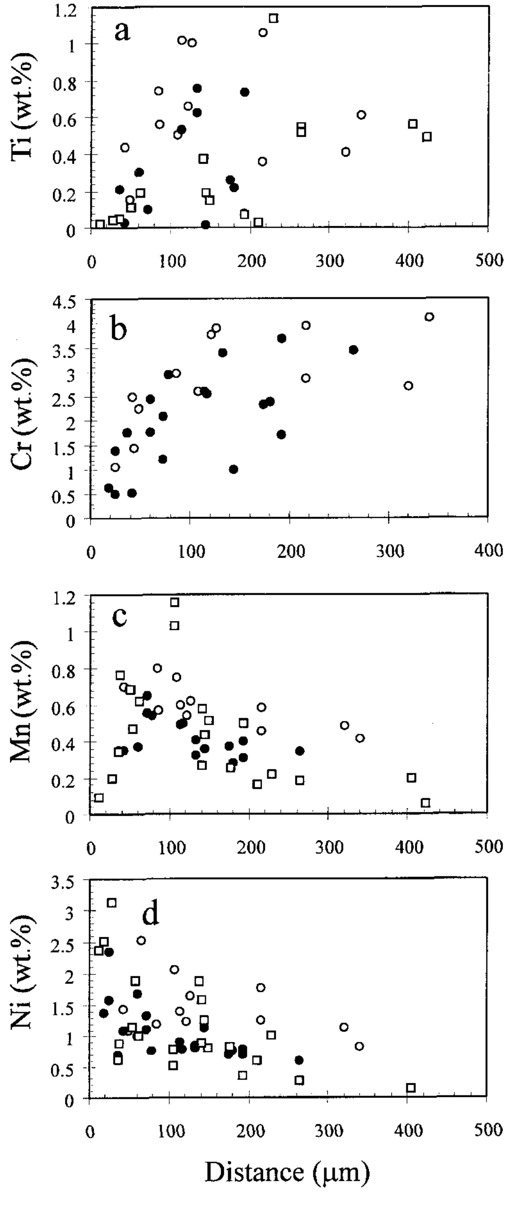

FIG. 6. Variations in the minor element abundance with distance from the melted crust/substrate boundary. Symbols: open circles – St Mark's, solid circles – Pillistfer, and open squares – Indarch.

Fe,Ni oxides

Iron-dominated oxides occur as rims on unmelted metal grains, as droplets within troilite veins and as veins throughout fusion crust. The chemical zoning of oxide rims from Si-rich Fe-oxides adjacent to metal to Ni, Co and S-rich Fe-oxides adjacent to sulphide, and the occurrence of troilite lamellae within the rims, suggests formation by reaction of metal with the surrounding sulphide liquid at high temperature. The presence of droplets of oxides with similar compositions to those within rims in troilite veins closer to the melted crusts implies that oxides melt with progressive heating. Consequently, oxide rims must have formed during atmospheric entry. Highly embayed Si-bearing metal grains within some oxide droplets also suggest that the alteration of metal by oxidation increases towards the melted crust. In light of its textural relations, oxide must therefore form during entry heating, the oxygen required presumably derived from the atmosphere. The presence of both oxide and reduced phases (e.g. Ti-bearing troilite, niningerite and Si-bearing metal) indicates that assemblages within fusion crust are highly unequilibrated.

The chemical zoning of Fe-oxide rims suggests the loss of Fe and the gain of S, presumably by reaction with Fe-FeS liquids. This might result from partial melting and the removal of eutectic FeO-FeS liquids, leaving residual solids enriched in Ni and Co. Nickel-poor Fe-oxide veins within substrates are spatially associated with oxide rims and extend further from melted crust than troilite veins indicating formation at lower temperatures than the Fe-FeS eutectic. These may have formed from the FeO-FeS liquids produced by partial melting of oxide rims which have eutectic temperatures of ~915°C (Naldrett, 1969). However, such eutectic liquids have much lower O contents (~8 wt.%) and higher S contents (15 wt.%) than the observed oxides. Thus, if these do form as eutectic liquids then their compositions must have been subsequently altered. The occurrence of droplets of troilite within Fe-oxides, and vice versa suggest that the Fe-FeS and oxide liquids were immiscible. Stable liquid immiscibility between S-bearing Fe-oxide and Fe-FeS liquids is predicted from the liquidus relations in the system Fe-S-O (Naldrett, 1969).

Lithophile sulphide relics and veins

Lithophile sulphides within the substrates of the ECs occur as both unmelted relicts and within veins. Relicts of oldhamite are common in both EL and EH chondrite crusts. Niningerite relicts are observed within the substrate of St Mark's (EH5) and have compositions close to those of the parent meteorite (Keil, 1968), although their rims are significantly enriched in Fe and depleted in Mg and Mn, presumably as a result of reaction with the surrounding Fe-FeS melt. The generation of Mg-Fe-Mn-S liquids during entry heating is supported by the presence of Fe-rich niningerite veins in fusion crust. These form networks separate from troilite veins suggesting that the Fe-FeS and Mg-Fe-Mn-S liquids were immiscible. Rounded droplets of niningerite within troilite veins in Abee further support liquid immiscibility between Mg-dominated and Fe-dominated sulphide liquids which is consistent with the phase relations of the system MgS-FeS (Skinner and Luce, 1971). No lithophile-dominated sulphides are observed within the melted crusts of any of the meteorites studied, supporting the evidence from troilite and olivine that melted crust has a higher redox state than the substrate.

Implications

Temperature gradients and ablation rate

The mineralogy of EC fusion crusts allows the temperature gradient developed at high temperatures and the mass ablation rate of stones to be estimated. Predicting peak temperatures from the phase assemblages within EC fusion crust is, however, complicated by uncertainties in both the phase relations of relevant analogue systems and the degree of equilibration between coexisting phases. Within these uncertainties, minimum estimates of temperature can be established from the compositions and 'first' occurrences of a number of phases.

Silicates

Partial melting of silicates is observed close to the melted crust of St Mark's and Indarch. The silicate fraction of ECs is a relatively simple assemblage dominated by enstatite with minor silica and forsterite. Thus its phase relations are adequately described by the binary system MgO-SiO_2. Partial melting occurs at the eutectic temperature 1543°C, and complete melting (producing the melted crust) probably occurs at temperatures of ~1660°C, based on a silicate portion containing 46 wt.% MgO (calculated from Jarosewich, 1990).

Ferroan sulphide veins and metal

Given the thermal regime, the innermost occurrence of troilite + interstitial metal within fusion crust, as discussed above, probably indicates a minimum temperature at the Fe-FeS eutectic (988°C). The presence of Ni will depress the eutectic, although at the low Ni abundances of the veins (<3 wt.%), reductions are likely to be minor.

Metal droplets within ferroan sulphide veins imply partial melting of kamacite and suggest minimum temperatures at the solidus of the Fe-Si binary. These vary between ~1500 and ~1400°C for the compositions range of EC kamacite (i.e. 1–5 wt.% Si). The Ni contents of <10 wt.% cause little depression of the solidus. Phosphorus- and S-bearing regions of unmelted metal grains have textures which suggest partial melting and have compositions which imply minimum melting temperatures of ~1050°C.

Lithophile monosulphides

The compositions of the lithophile monosulphides, oldhamite and niningerite, in equilibrium with troilite have been used as geothermometers within ECs (Skinner and Luce, 1971). Divergences from equilibrium in fusion crusts will, however, severely limit the accuracy of such estimates, but provide some constraints on the temperature profile. Niningerite compositions suggest ranges of temperatures lower than the eutectic temperature of the system MgS-FeS (~1070°C) with ranges of 800–825°C for Abee, 575–725°C Indarch and 800–1025°C for St Marks. These temperatures are, however, higher than those experienced by ECs during parent body metamorphism (Skinner and Luce, 1971). Rims on niningerites in St Mark's have compositions suggesting higher temperatures, up to 1025°C, close to the eutectic temperature which implies these are quenched liquids. Veins of niningerite in Indarch and rounded droplets in Abee both indicate temperatures greater than the eutectic at ~1070°C. Oldhamite compositions also suggest temperatures greater than those thought to have prevailed during metamorphism with ranges of 725–875°C for St Marks, 675°C for Pillistfer and 775–800°C for Indarch.

Fe,Ni oxides

Oxide rims and veins are problematic. If Fe-oxide veins originated as eutectic FeS-FeO liquids, as suggested above, then temperatures must have exceeded ~915°C.

Temperature gradients

Estimates of minimum temperatures with distance from the melted crust/substrate boundary for the fusion crust of Indarch are shown in Fig. 7 and are typical of those of the other studied ECs. The temperature profile is obtained by fitting the steady state solution of the thermal conductivity equation (1) to the minimum temperature profile. In equation (1), y is the distance from the melted crust/substrate boundary, and k is thermal diffusivity (8.4×10^{-3} cm^2 s^{-1}; Sears and Mills, 1972). The solution depends only on the temperature at the melted crust/substrate boundary (T_0), which is chosen from the liquidus temperature of the bulk meteorite silicate composition, and the ablation rate (a).

$$T(y) = T_0 exp(-\frac{ay}{k}) \tag{1}$$

The temperature gradient suggested by the innermost Fe-oxide veins (point 5 in Fig. 7) is lower than that suggested by the innermost occurrence of troilite-metal veins (point 4 in Fig. 7) for all studied crusts. This might result if heat transfer is higher than suggested by the conductivity equation due to (outward) fluid flow in veins. The ablation rates calculated by fitting to the estimated temperature profiles are shown in Table 5 and are in the range 0.08–0.25 cm s^{-1} and are broadly similar to those determined from the fusion crusts of other stony meteorites of ~0.2 cm s^{-1} (e.g. Sears and Mills, 1972, 1974 and references therein). The calculated mass ablation rates increase broadly with the mass of the meteoritic stone. However, since no attempt was made to identify the orientation of the face from which the crust was obtained, this may be fortuitous.

TABLE 5. Ablation rates estimated from fitted temperature profiles. Ranges denote the degree of uncertainty

Meteorite	Ablation rate (cm s^{-1})	Mass of stone (kg)
Abee	0.225–0.175	107
Indarch	0.100–0.150	27
St Mark's	0.125–0.175	14
Daniel's Kuil	0.075–0.125	5.5
Pillistfer	0.100–0.150	7.5

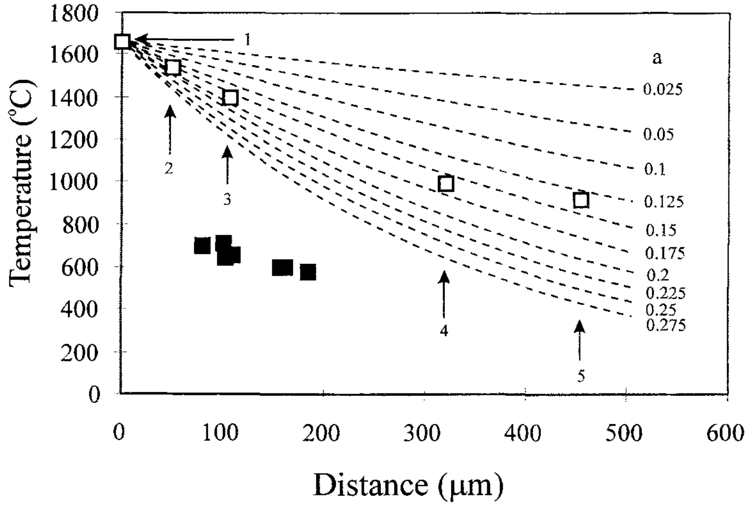

FIG. 7. Temperature gradient curves (dashed lines) calculated using the one dimensional thermal conductivity equation (eqn 1) for Indarch fusion crust. Curves are labelled with the mass ablation rate. The distance is measured from the melted crust/substrate boundary. Open symbols represent the data points used to estimate peak temperature gradient and represent: (1) melted crust/substrate boundary; (2) innermost silicate glass veins; (3) innermost metal droplets; (4) innermost troilite-metal assemblages; and (5) innermost Fe-oxide veins. Solid symbols represent the temperature estimates from niningerite veins. These are consistent with the overall temperature profile, but fall at much lower temperatures due to the low degree of equilibration with troilite. The mass ablation rate is estimated to be between ~0.13 and ~0.18 cm s^{-1}.

Polymict impact melt breccias

Several ECs have recently been recognized as impact melt breccias (Rubin and Scott, 1997), formed by melting during large impacts on their parent asteroids. Those formed within regolith (i.e. the soil/debris layers of asteroids) experienced rapid heating and cooling rates by the passage of a shock front through the target rocks (e.g. Bunch and Rajan, 1988). Other impact melt breccias, formed as ejecta blankets of solid and molten debris emplaced on the surface of the parent asteroid, would likewise have cooled rapidly. Given that meteorites formed as impact melt breccias, experienced rapid heating and cooling, difficulties may arise in distinguishing their 'primary' textures and minerals in these rocks from those formed during atmospheric heating, particularly in small stones.

Abee and related EH chondrites are monomict impact melt breccias (i.e. they contain only clasts derived from EH chondrites) that contain metal-rimmed clasts, kamacite globules and matrix with igneous textures (Rubin and Scott, 1997) indicating that silicates have partially melted. These meteorites have experienced higher temperatures during their formation by impact than most of the fusion crust during atmospheric entry heating. Due to their monomict nature, Abee and other related EH melt breccias also retain the highly reduced mineralogies characteristic of EH chondrites and thus any oxidized phases found within such meteorites are likely to have formed during entry heating.

In contrast, polymict impact-melt breccias incorporate both oxidized chondrite (e.g. LL ordinary chondrite) and reduced EH chondrite clasts and thus have higher oxidation states more akin to those of fusion crusts. The Galim (LL/EH) polymict impact-melt breccia is one such example (Rubin, 1997*b*). However, Galim lacks the reduced phases typical of EH chondrites (Si-bearing metal, Ti-bearing troilite, niningerite and oldhamite) and thus appears to be more oxidized than fusion crust. Rubin (1997*b*) suggests that Galim formed on the LL chondrite parent by impact melting of a pre-existing regolith breccia containing EH chondrite clasts. The redox state of Galim thus results from the predominance of highly oxidized LL chondrite materials within the regolith.

EC-bearing polymict impact-melt breccias with oxidation states intermediate between Galim and Abee could be reasonably expected to form if higher abundances of EC clasts exist locally within regolith, or alternatively if the predominant material is less oxidized (L or H chondrite). The occurrence of ordinary chondrite clasts within the regoliths of EC parent bodies might also exhibit similar effects, but have yet to be observed in meteorites. The mineralogy of EC fusion crusts may be similar to polymict impact-melt breccias that form under relatively low degrees of melting (such that silicates are not extensively melted). Troilite in such breccias will probably contain less Ti and Cr than those of EH chondrites and might include significant abundances of Ni. Niningerite may become depleted in Mn and enriched in Ca, Fe and contain significant Cr. Oldhamite likewise should contain higher Fe and Mg contents indicating higher temperatures of formation. Kamacite is likely to become depleted in Si and enriched in Ni and Co. The formation of Fe-Ni-Co-oxides in polymict impact melt breccias is difficult to predict, SiO_2-rich rims on kamacite from Galim are suggested to form because of the oxidation and reaction of Si released from the metal, and indicate that oxidized rims can form on metal after shock heating.

Variations in redox state during shock melting due to local differences in clast abundances might be preserved as unequilibrated mineral assemblages in unmetamorphosed polymict melt breccias. However, larger scale variations in clast abundance (e.g. by the reassembly of bodies catastrophically disrupted by collision) might be necessary to preserve redox effects after metamorphism in equilibrated meteorites. The survival of reduced lithophile sulphides in polymict impact-melt breccias of intermediate oxidation states would however result in the equilibration of troilite, niningerite, alabandite and oldhamite compositions during metamorphism. Subsequent annealing (by metamorphism or less intense shock events) might also cause the exsolution of daubréelite from troilite resulting in Cr abundances similar to or lower than other ECs. Thus in equilibrated polymict impact-melt breccias only the lower Si and higher Ni and Co abundances of kamacite, oxidized reaction rims on metal and the high Ni-contents of troilite might be preserved to indicate that oxygen fugacity was higher than in monomict EC impact melt-breccias.

Conclusions

The fusion crusts of ECs, formed during atmospheric entry heating, contain highly unequilibrated assemblages of sulphide, metal and oxide which testify to increases in redox state. The mineral compositions of sulphides and metal show decreases in the abundances of the lithophile elements and increases in Ni contents due to oxidation. Assemblages dominated by Fe-oxide occur within fusion crust and have textures which indicate that these formed as the products of atmospheric heating. The occurrence of both highly-reduced phases such as oldhamite and oxide assemblages in fusion crusts indicates a large degree of disequilibrium during heating, possibly resulting from the kinetics of oxidation reactions. Mass ablation rates derived from estimated temperature gradients are in the range $0.075-0.250\ cm^2s^{-1}$ and are similar to those of other stony meteorites. The textures and mineralogy of the fusion crusts of the ECs might provide an analogue to impact-melt breccias formed within regoliths containing reduced and oxidized lithic materials.

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