

Chemical and physical studies of type 3 chondrites—V: The enstatite chondrites

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Abstract—We report instrumental neutron activation analysis determinations of 19 major, minor and trace elements in three enstatite chondrites. Based on these, and literature data on the bulk and mineral composition of enstatite chondrites, we discuss the history of the type 3 or unequilibrated enstatite chondrites, and their relationship with the other enstatite chondrites. The type 3 enstatite chondrites have E chondrite lithophile element abundances and their siderophile element abundances place them with the EH chondrites, well resolved from the EL chondrites. Moderately volatile chalcophile elements are at the low end of the EH range and Cr appears to be intermediate between EH and EL. We suggest that the type 3 enstatite chondrites are EH chondrites which have suffered small depletions of certain chalcophile elements through the loss of shock-produced sulfurous liquids. The oxygen isotope differences between type 3 and other enstatite chondrites is consistent with equilibration with the nebula gas $\sim 30^\circ$ higher than the others, or with the loss of a plagioclase-rich liquid. The mineral chemistry of the type 3 chondrites is consistent with either low temperature equilibration, or, in some instances, with shock effects.

INTRODUCTION

THE PARTICULAR INTEREST of the enstatite chondrites is that they formed in a uniquely reducing environment; they contain Si-bearing metal, very low FeO silicates and several minerals not found elsewhere (CaS, TiN, Si₂N₂O) and many normally lithophile elements are chalcophile. However, they do share many properties with the other chondrites: all but a few elements are within 20% of solar proportions, they are extremely old and they have not been involved in major planetary processing in the manner of lunar and terrestrial samples. Like the ordinary chondrites, they have experienced varying degrees of metamorphism—they are types 4 to 6 on the VAN SCHMUS and WOOD (1967) scheme—and they may be subdivided (into the EH and EL classes) on the basis of their siderophile element abundances (SEARS *et al.*, 1982a).

Recently, attention has focused on several enstatite chondrites that appear to have equilibrated less than the others; they have been referred to as type 3, or unequilibrated, enstatite chondrites (RAMBALDI *et al.*, 1983a; NEHRU *et al.*, 1984; PRINZ *et al.*, 1984a). They include Qingzhen, Parsa, Kota Kota, Allan Hills A77156, Yamato 69001, Galim and, based on the description by NAGAHARA and EL GORESY (1984), Yamato A74370. In addition to being less equilibrated than the others, three of them, Qingzhen, Yamato 69001 and Yamato 74370, have Mg/Si and Fe/Si values which appeared to be intermediate between the EH and EL classes (EL GORESY *et al.*, 1983, and PRINZ *et al.*, 1984a,b). In the present paper, we report the results of neutron activation analyses on two of these chondrites, Allan Hills A77156 and Qingzhen. We also report data for Reckling Peak A80259, a new enstatite chondrite from Antarctica which is the first known EL5 chondrite (SEARS *et al.*, 1984). We

discuss the relationship between the type 3 enstatite chondrites and the other enstatite chondrites.

EXPERIMENTAL

Two fragments of Allan Hills A77295 (which is paired with 77156, MCKINLEY *et al.*, 1984) and Reckling Peak A80259, and three of Qingzhen, were analyzed in five irradiations (Table 1). Any sawn surfaces were cleaned with carbide paper, the samples crushed and placed in high density polyethylene vials which were sealed with a hot quartz rod. Synthetic standards were prepared by micropipetting solutions, made by dissolving 3–5 n pure elements or oxides in HCl or HF, onto high purity, powdered SiO₂ glass. The Allende meteorite and USGS standard rock BCR-1 acted as secondary standards. Each sample was irradiated twice in row 1 of the University of Missouri Research Reactor, Columbia. A 5 second irradiation was followed by two 3-minute counts for Al, V, Mg and Mn, and a 15–30 minute irradiation was followed by 6–7 counts for 0.5 to 10 hours over 6–8 weeks for the remaining elements. High purity Ge detectors (29% efficient with respect to NaI(Tl), 1.68 keV resolution at 1.33 MeV) coupled to Nuclear Data ND66 analyzers were used for the counting. The data were recorded on magnetic tape and reduced using BAEDECKER's (1976) SPECTRA program. Potassium, As, Ga, Sb, Ca, La and Eu peaks were plotted, the baseline drawn by eye and SPECTRA's value adjusted accordingly.

Our data are listed in Table 1. The reproducibility of our six Allende analyses in six irradiations indicates 1σ uncertainties for duplicate analysis ($\sigma/\sqrt{2}$) are: $\leq 5\%$ for Na, Mg, Al, K, Sc, V, Cr, Mn, Fe, Co, Ni, Se, Sm, Eu; $< 8\%$ for Ca and La; $< 11\%$ for Ir; Zn, Ga, As and Au data have not yet been evaluated completely. The literature data for Allende and BCR-1 show that our data are free of systematic error.

RESULTS

Figures 1–3 show our data expressed as elemental abundance ratios to Mg and then normalized to the same quantity for CI chondrites. The siderophile, chalcophile and lithophile elements are plotted separately, and within each of these divisions appear in order of increasing nebular volatility. Also included

Table 1. Instrumental neutron activation analysis data for three enstatite chondrites and control samples, and literature data for Yamato 69001, Parsa, Allende and BCR-1.

Irrad	Mass (mg)	Na (mg/g)	Mg (mg/g)	Al (mg/g)	K (mg/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)	Se (μg/g)	La (μg/g)	Sm (μg/g)	Eu (μg/g)	Ir (ng/g)	Au (ng/g)
QINGZHEN	FE 84 172.2	5.58	112	9.52	760	10.9	6.92	56	3.24	2.11	331	966	21.4	304	22.7	116	1.38	0.38	636	370
"	JA 82 146.6	5.68	114	7.7	859	7.2	6.04	54	3.13	1.90	309	917	19.6	318	25.5	395	1.49	--	526	345
"	MO 81 187.2	6.82	--	--	--	--	5.86	--	3.10	--	298	848	--	182	18.6	--	--	--	501	314
ALHA7795	DE 82 119.2	5.45	108	9.5	--	9.0	5.41	58	4.72	1.9	301	924	19.9	208	19.8	197	1.15	0.39	547	338
"	FE 83 143.0	5.53	101	7.5	406	10.1	6.41	59	3.66	1.7	342	1029	21.1	220	20.0	240	1.30	0.64	593	470
RKPA0259	DE 82 147.2	4.60	115	8.2	1090	8.1	5.83	59	3.33	2.1	224	673	13.8	<17	16.5	1.97	1.22	0.49	477	279
"	FE 03 147.2	4.04	110	5.5	386	--	6.13	60	3.10	2.0	229	673	14.3	<10	15.6	1.47	1.14	0.49	454	257
YAMATO69001†	6.41	116	8.2	703	7.22	--	--	--	2.86	1.91	298	890	18.6	--	--	--	--	--	638	286
PARSAT†	6.60	107	8.13	780	7.7	6.0	53	3.01	1.96	276	826	17.2	251	25.0	250	1.32	--	--	511	309
ALLENDE	FE 84 157.6	3.65	149	17.2	305	18.9	12.1	96	3.63	1.41	263	721	15.5	114	9.2	483	301	120	779	157
"	FE 83 120.8	3.11	140	19.8	274	21.5	12.2	105	3.43	1.39	239	662	14.3	116	8.6	437	304	122	963	172
"	DE 82 27.2	3.49	162	17.6	623	19.1	12.3	106	3.81	1.59	242	698	13.9	92	8.3	428	--	--	124	777
"	JA 82 141.7	3.19	157	17.1	--	16.0	10.8	99	3.37	1.53	211	611	12.5	92	7.8	--	--	--	630	145
ALLENDE Lit.*	3.41	148	17.3	272	19.1	10.9	115	3.68	1.47	233	629	14.0	116	7.95	475	276	116	791	163	
std. dev.		+13		+26		+60		+12	+08	+8.4	+27		+79	+026	+036	+027		+77	+40	
BCR-1	FE 84 140.7	23.4	--	73.5	15700	49.8	35.2	428	--	1.32	99.1	39.9	--	146	--	26.1	6.62	1.73	--	--
"	FE 83 150.3	23.4	21.7	63.0	14000	32.6	423	--	1.26	102	40	--	148	--	23.0	5.79	1.96	--	--	
"	DE 82 154.0	24.8	19.1	67.0	11800	49.9	30.9	368	19.0	1.31	96.8	39.1	--	159	--	--	--	--	--	
BCR-1 Lit.**	24.3	20.8	72.0	14100	49.5	33.0	399	17.6	1.4	93.7	38.0	15.8	120	--	26.0	6.6	1.94	--	--	

† Shima and Shima (1976). The literature values were 900 and 490 for Ir and Au, respectively. See text for details of adjustments.
 †† Sears et al. (1982a).
 * Bart et al. (1980); Chou et al. (1976); Clarke et al. (1970); Ebihara et al. (1982); Emery et al. (1969); Grossman (1973); Ikramuddin and Lipschutz (1975); Kallmeyer and Masson (1961); Malissa et al. (1972); Morgan et al. (1969); Neal et al. (1981); Ngo and Lipschutz (1980); Takahashi et al. (1978); Verkooren and Lipschutz (1983); Wakita and Schmitt (1970); Walsh and Lipschutz (1982); Warren (1972); Wolf et al. (1983). A complete compilation is available from authors on request. No standard deviations are quoted for elements with less than 4 determinations.
 ** Flanagan (1976).

in the plot are data for well analyzed EL and EH chondrites and data for two other members of the unequilibrated group identified by PRINZ *et al.* (1984a). From left to right in Figs. 1–3 the meteorites plotted, and references to the sources of data, are as follows: Pillistfer (SEARS *et al.*, 1982a), Daniel's Kuil, Khairpur, Hvittis, Jajh deh Kot Lalu (BAEDECKER and WASSON, 1975), Reckling Peak A80259 (this work), 69001 (SHIMA and SHIMA, 1976), Parsa (SEARS *et al.*, 1982a), Qingzhen and Allan Hills A77295 (this work), Indarch and St. Sauveur (SEARS *et al.*, 1982a), Adhi Kot and St. Marks (BAEDECKER and WASSON, 1975). Abee data were not used because of the particular heterogeneity of the meteorite (SEARS *et al.*, 1982b). Adjustments were made to SHIMA and SHIMA's (1976) values for Ir and Au in 69001 as their data for three elements in several samples seemed rather high. Their data for Yamato 69004, an equilibrated H chondrite, were divided by mean H group values (MASON, 1979) and this 'correction factor' applied to the 69001 data.

All of the siderophile elements plotted in Fig. 1 resolve the two groups of enstatite chondrites; the hiatus between the groups is especially well delineated for Ni, Co, Fe, Au and Ga. For Ir there is no hiatus, but the EH chondrites clearly lie above the values for the EL chondrites. Arsenic and Sb also resolve the two groups rather well, despite considerable scatter, even though these elements are heterogeneously distributed and are difficult to sample adequately. The type 3 chondrites plot along with the EH chondrites for all the siderophile elements, and are well resolved from the EL chondrites.

The moderately volatile chalcophile elements (Fig. 2) tend to scatter more than the siderophiles but generally the EH chondrites are a factor of about 2 higher in these elements than the EL chondrites. The hiatus between EH and EL chondrites varies from excellent to moderately good, with the type 3 chondrites tending to plot near the EH chondrites, but at the lower end of the EH range. In the case of Cr, where the EH-EL hiatus is not marked, the type 3 chondrites form a bridge between the two classes. Zinc is unusual in that the type 3 chondrites plot near the top of the EH range.

The refractory chalcophile elements Ca and, to some degree, the REE and V are about 25% more abundant in the EH than the EL chondrites and the type 3 chondrites appear to be intermediate between the two classes. The lithophile elements Al and Sc do not resolve the enstatite chondrite groups (Fig. 3).

DISCUSSION

Classification of type 3 chondrites

As pointed out by UREY (1961) the ratio of two non-volatile elements, such as Mg/Si and Fe/Si, provides an insight into the formation of the material since these ratios cannot be upset by subsequent processes, such as metamorphism or shock heating,

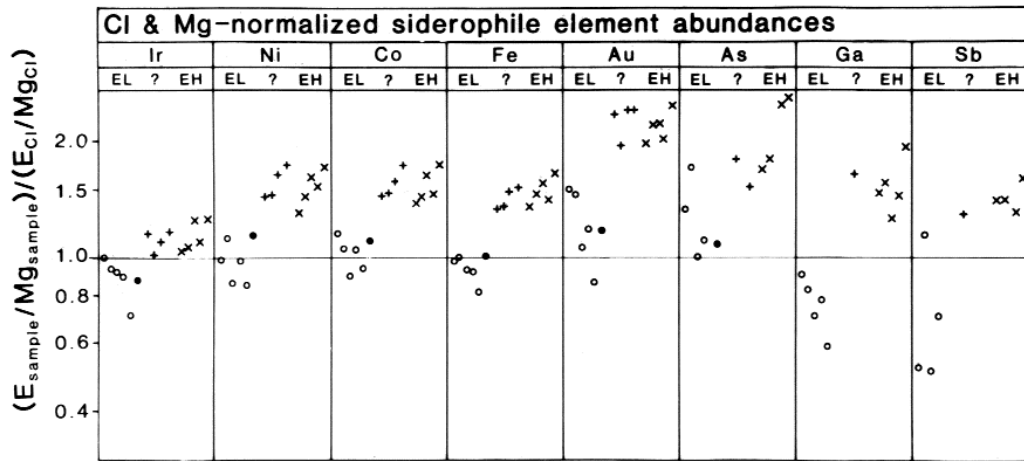


FIG. 1. CI and Mg-normalized plot of the siderophile element abundances in enstatite chondrites. Filled circles are Reckling Peak A80259; open circles are other EL chondrites; plus signs are the type 3 chondrites and crosses are the EH chondrites. From left to right the meteorites are Pillistfer, Daniel's Kuil, Khairpur, Hvittis, Jajh Kot Lalu, Reckling Peak A80259, Yamato 69001, Parsa, Qingzhen, Allan Hills A77295, Indarch, St. Sauveur, Adhi Kot and St. Marks. The 80259, 77295 and Qingzhen data are from this work, the others are from various literature sources (see text). The elements appear in order of decreasing nebular volatility.

which would cause diffusive loss. Especially important are the ratios of two cosmochemically diverse elements, such as a siderophile element/Mg, as the different physical properties of the two elements may provide further clues to the nebular process responsible for the ratio differences.

Figure 4 is a plot of the atomic ratios of Fe/Si against Mg/Si for enstatite chondrites based predominantly on wet-chemical analyses. The data have been taken from a variety of sources of varying quality, and the often considerable metal/silicate heterogeneity of this class compounds the usual difficulties in

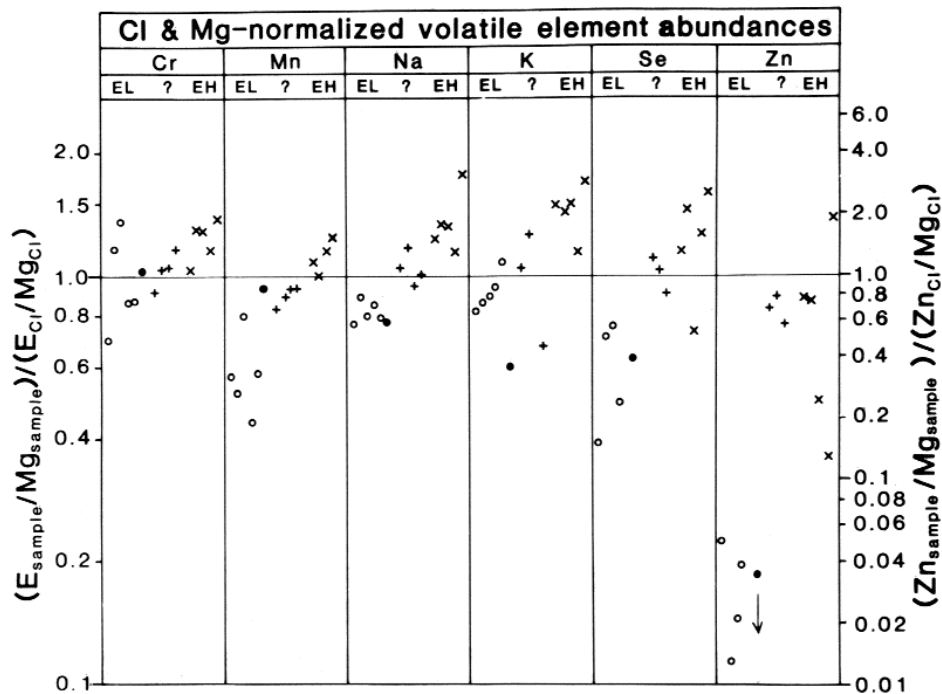


FIG. 2. CI and Mg-normalized plot of the abundance of moderately and highly volatile elements in enstatite chondrites. Details of the plot are as in Fig. 1.

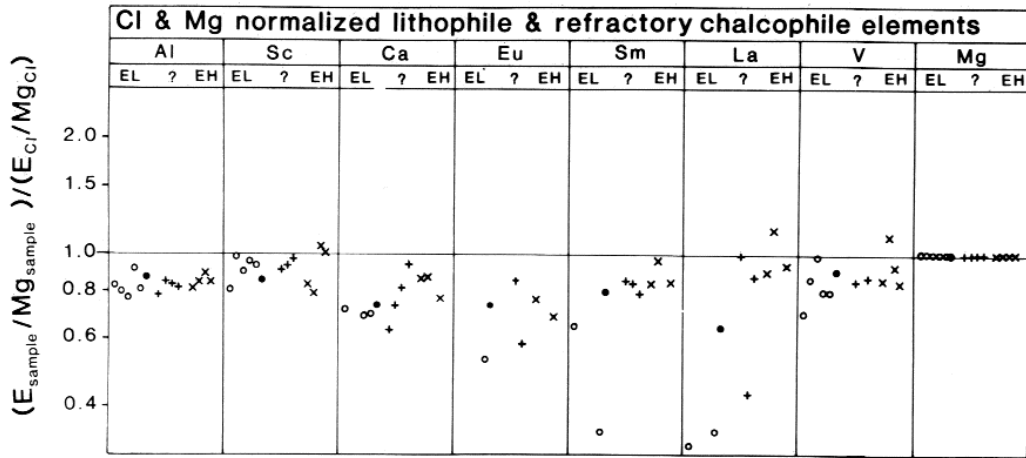


FIG. 3. CI and Mg-normalized plot of lithophile and refractory chalcophile element abundances in enstatite chondrites. Details of the plot are as in Fig. 1.

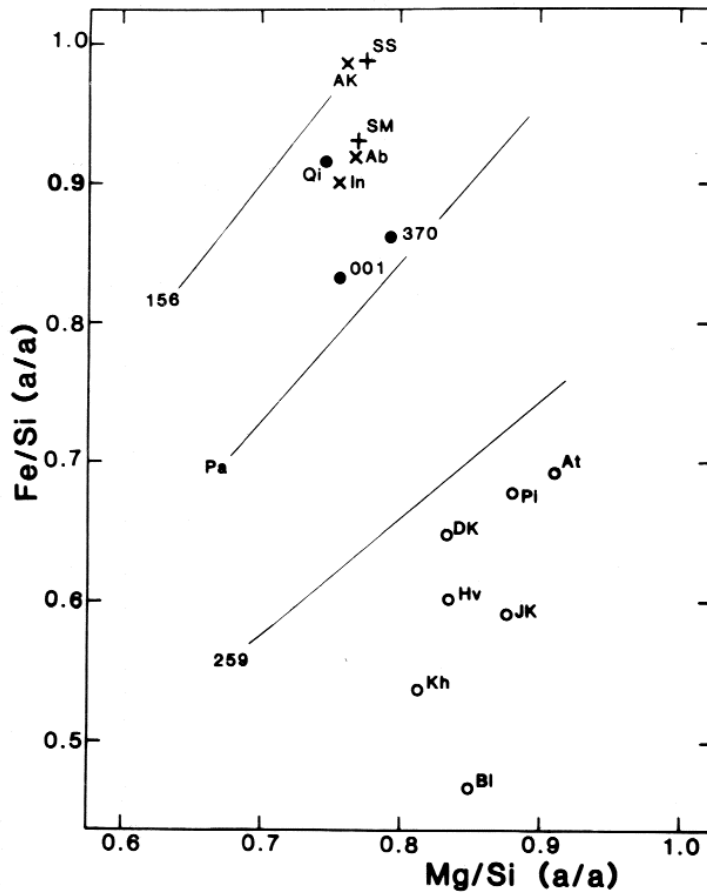


FIG. 4. Plot of atom ratios for Fe/Si against Mg/Si for enstatite chondrites. Data are from a compilation of literature sources (Appendix 1). Symbols as in Fig. 1. The abbreviations are as follows: SS, St. Sauveur; AK, Adhi Kot; SM, St. Marks; Ab, Abee; Qi, Qingzhen; In, Indarch; 370, Yamato 77370; 001, Yamato 69001; 156, Allan Hills A77156 (paired with Allan Hills A77295); Pa, Parsa; At, Atlanta; Pi, Pillistfer; 259, Reckling Peak A80259. The diagonals refer to meteorites for which Si values are not known.

analyzing for iron by wet-chemical means (MASON, 1962). The resolution of the two groups by Fe/Si is reasonable, with a hiatus between the two classes. There is no hiatus in Mg/Si, but the classes can be distinguished by this parameter since EL chondrites have Mg/Si greater than 0.8 while the EH chondrites have values below this. The type 3 chondrites plot in the EH cluster, and are not resolved from the more equilibrated members of the EH class. For Allan Hills A77156, Parsa and Reckling Peak A80259 there are no Si data in the literature, so their Fe/Mg ratio is indicated by diagonal lines. Parsa and Allan Hills A77156 have Fe/Mg ratios corresponding to the EH cluster, while 80259 diagonal passes through the EL cluster.

Although the Fe/Si *versus* Mg/Si plot has become popular for exploring relationships between chondritic classes, its main drawback is that even when high quality data are available, it provides only a "snapshot" of the chemical trends of the samples. The present data (Figs. 1–3) indicate that while the type 3 chondrites differ in some ways, they are compositionally very much like the EH chondrites. Virtually all of the elements examined are present in EH proportion (Mg-normalized), but many of the chalcophiles lie at the low end of the EH range. It is only for elements which poorly resolve the groups, that the type 3 chondrites form a bridge between the EH and EL classes. The question, then, is whether they are an entirely new type of chondritic material (*i.e.* a new class) or normal EH material which has compositional traits reflecting its low petrologic type or other effects. We suggest that the type 3 chondrites are EH chondrites since (1) elements which best resolve the two groups (namely the siderophiles), place them with the EH chondrites, and (2) the elements which are most genetically significant (again, the siderophiles) place them with the EH chondrites, well-resolved from the EL chondrites. The major question they pose, as with the type 3 ordinary chondrites, concerns their relationship with the other enstatite chondrites. The relationship between the unequilibrated ordinary chondrites and the equilibrated ordinary chondrites is not clear, even though the UOC are better studied than their enstatite chondrite counterparts. Perhaps a comparative study of both classes of type 3 chondrites will help in our understanding of both.

Relationships—mineralogical data

To a good approximation, the compositions of the minerals in enstatite chondrites vary with petrologic type in two ways. Magnesium in niningerite, Ca in oldhamite, Ti in troilite, Ni in metal and the FeO, MnO and CaO in the pyroxene vary systematically with petrologic type, with the type 3 chondrites at one end of the sequence and type 6 at the other. On the other hand, for Mn, Fe and Ca in niningerite/alabandite, Mg in oldhamite, Si in the metal and Ni

in the phosphides the compositional trend is 5–4–3–6. In the case of the sulfide minerals, this second trend was interpreted by SKINNER and LUCE (1971) as indicating that while the type 6 chondrites cooled slowly from their peak metamorphic temperatures, which were higher than the other types (as indicated by extensive recrystallization and the absence of chondrules), the type 4 and 5 chondrites cooled rapidly; perhaps they were released from their parent body by a shock event which resulted in quenching. Thus the type 6 chondrites equilibrated to low temperatures (400–300°C) while the type 4–5 chondrites equilibrated at 800–700°C.

Fig. 5 is a ternary diagram of the composition of niningerite/alabandite with Skinner and Luce's experimentally determined FeS solvus at 1000–700°C superimposed. We have also added the mineral compositions of the enstatite chondrites, including the type 3 chondrites, as determined from the sources listed in Appendix 1. The meteorites appear to form three clusters, corresponding essentially to the type 6, type 3 and types 4 + 5; the clustering is broken only by the type 5 chondrite St. Marks, which plots with the type 3 chondrites. Using the solvus curves of Skinner and Luce, the type 4 and 5 chondrites appear to have equilibrated at 700–600°C while the type 6 and type 3 chondrites equilibrated at <600°C, probably 400–300°C. The petrology of the type 3 chondrites is probably consistent with such low equilibration temperatures.

The type 6 ordinary chondrites, which appear to have suffered comparable or less recrystallization than the type 6 enstatite chondrites, equilibrated at >1000°C (ONUMA *et al.*, 1972a; WASSON, 1972). On the basis essentially of the FeO in the silicates and Si in the metal, LARIMER and BUSECK (1974) found equilibration temperatures on the order of 1000°C for the type 6 enstatite chondrites. For different mineral systems to display different equilibration temperatures is not surprising since diffusion coefficients depend on the system as well as the temperature, but the difference between 400–300 and >1000°C may be a little large to be understood this way. An alternative idea is that the type 6 alabandites did equilibrate at >1000°C, but in the absence of FeS, so that mass-balance considerations prevented the minerals from following the FeS solvus in Fig. 4. This would occur either if the metamorphism was open system and all the FeS evaporated, in which case there would be no FeS currently in the meteorites, or if the equilibration of the sulfides occurred during accretion and before the formation of FeS. It is significant that the sulfides which indicate a very low equilibration temperature are refractory in a cooling solar gas of C/O twice cosmic (LARIMER and BARTHOLOMAY, 1979; LATTIMER and GROSSMAN, 1978). SEARS (1980) and LARIMER and BARTHOLOMAY (1979) suggested that the enstatite chondrites were a mixture of high-temperature, reduced components and low-temperature, volatile-rich components. They

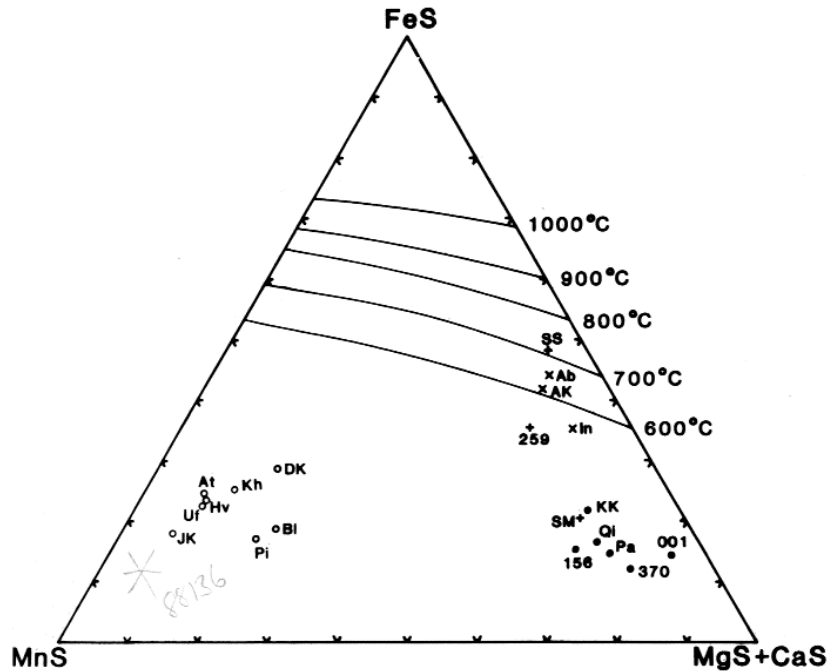


FIG. 5. Ternary diagram for the FeS-MnS-(MgS + CaS) system, as determined by SKINNER and LUCE (1971), with the enstatite, chondrites superimposed. Symbols as in Fig. 1, abbreviations as in Fig. 4. Data sources as follows: Abee, Adhi Kot, Indarch and Kota Kota—KEIL (1968) and LETCH and SMITH (1982); St. Marks, St. Sauveur, Atlanta, Blithfield, Daniel's Kuil, Hvittis, Jajh deh Kot Lalu, Pillistfer, Ufana and Khairpur—KEIL (1968); Yamata 69001—OKADA (1975) and PRINZ *et al.* (1984b); Qingzhen—RAMBALD-I *et al.* (1983a,b); Galim—CHRISTOPHE-MICHEL-LEVY and BOUROT-DENISE (1983); Allan Hills A77156—MCKINLEY *et al.* (1984); Yamato 74370—NAGAHARA and EL GORESY (1984); Reckling Peak A77259—SEARS *et al.* (1984) and A. E. RUBIN (unpublished); Parsa—NEHRU *et al.* (1984).

did not suggest however, that the mineral chemistries reflected equilibration established at the nebular stage.

The history of the metal phase is probably related to the history of the phosphides (Figs. 6, 7). The most notable feature of the metal composition is that the Ni/Fe ratio in the metal of type 3 chondrites is considerably less than the cosmic ratio (2.5% Ni instead of 5.5%). Several mechanisms are available for producing metal with higher than cosmic Ni/Fe, but processes which produce Ni-poor metal are few. SEARS (1978) showed that a gas of cosmic composition would produce metal with as low as 3% Ni at temperatures below 1000°K as the Ni transfers to the phosphide at low temperatures. No other phase preferentially attracts the Ni. The process would be unaffected by an atmosphere with higher than cosmic C/O ratio, except that phosphide stability might extend to lower temperatures since the formation of phosphates would be suppressed. One would expect therefore that systems that equilibrated over this temperature range would show an inverse correlation between Ni in the metal and Ni in the phosphides. The types 4, 5 and 3 meteorites show such a trend. The type 6 meteorites are not consistent with this behavior, since while their phosphides are Ni rich,

their metal is not Ni poor (Fig. 6). A resolution of this problem is the same as for the sulfides (Fig. 5), namely that the phosphides accreted and equilibrated at very high temperatures, *i.e.* before the metal formed. Before the condensation of metal, any phosphide formed would be Ni rich (Fig. 8).

The Si content of the metal (Fig. 7) is essentially fixed at the time of accretion of the major silicates and bulk redox state is fixed. Some variation will occur as a small quantity of CaSiO₃ gives up its O and the CaSiO₃ becomes CaS, as discussed by LARIMER and BUSECK (1974), but equilibration temperatures >1000°C are still indicated.

In summary, the mineral chemistry of the type 3 chondrites seems to imply equilibration at lower temperatures than the type 4 and 5. This is consistent with their heterogeneity and the abundance of glass, which is also observed in type 3 ordinary chondrites. Many mineral systems in the enstatite chondrites do not follow the type 6 to type 3 sequence, with the results that type 6 chondrites appear—contrary to petrologic properties and other palaeothermometers—to have equilibrated at temperatures below the others. However, it could be that for type 6 chondrites equilibration of niningerite/alabandite and phosphide

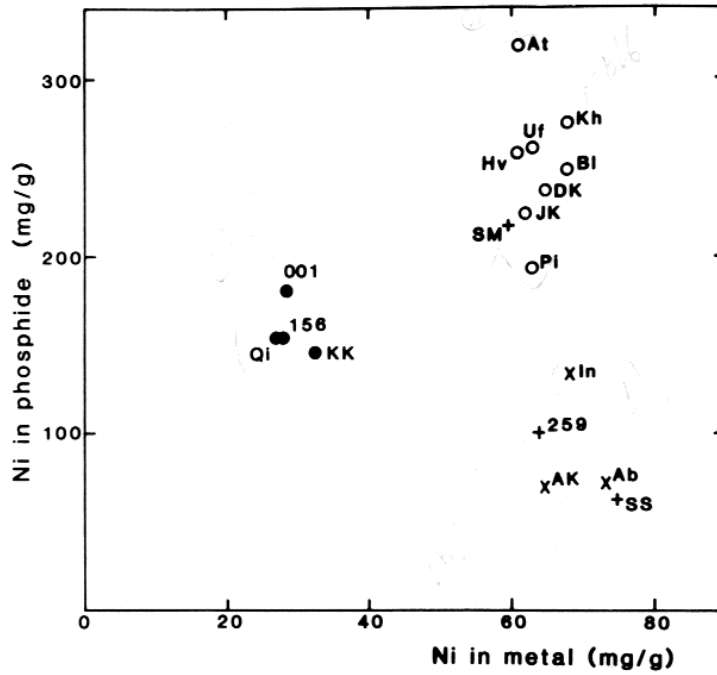


FIG. 6. Plot of the Ni content of the phosphide against the Ni content of the metal. Data sources as in Fig. 5.

occurred simultaneously with condensation and before the FeS and metal had condensed. In which case it would seem that the enstatite chondrites are a mixture

of materials that formed at a variety of temperatures during the nebular stage and subsequently suffered very limited or no re-equilibration.

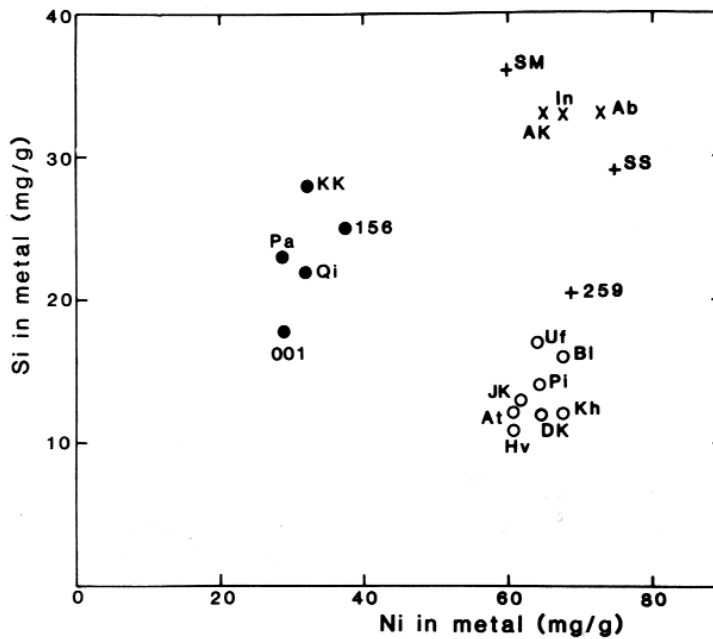


FIG. 7. Plot of Si content of the metal against Ni content of the metal. Data sources as in Fig. 5.

Relationships—bulk composition

The type 3 enstatite chondrites appear to be type 3 EH chondrites which are depleted in chalcophile elements. The depletion is not large, so that these meteorites lie at the low end of the EH spectrum. A possible cause for the depletions is weathering of the type 3 enstatite chondrites analyzed. Two are Antarctic finds, and Parsa and Qingzhen, while both were observed falls, appear to have suffered some terrestrial aqueous attack. Weathering may affect the composition of a meteorite by simple hydration or by selective dissolution and leaching. Simple hydration would affect all elements equally and, since the effect would be removed by normalization, it cannot explain the differences between the type 3 and the EH data observed in Figs. 1–3. In principle, leaching could produce the observed differences since several (perhaps all) of the sulfides in enstatite chondrites are soluble in water, especially when it is acidic. Such effects are erratic and complicated, and cannot be rejected entirely, but probably do not explain all the differences between the type 3 and EH chondrites. First, the type 3 chondrites are compositionally very similar and, since the degree of weathering varies widely, more scatter would be expected if their composition had been severely influenced by weathering. Second, the badly weathered non-type 3 enstatite chondrite analyzed here (80259), aside from an occasional individual element, plots with the EL class.

We suggest five possible extraterrestrial mechanisms by which such element depletion could occur. 1) Accretion at different temperatures, so that the missing proportion of the chalcophiles was left behind in the gas. 2) Differential accretion of fully condensed material, so that sulfide minerals were not as fully sampled by the type 3 chondrites as the other EH chondrites. This possibility is somewhat analogous to the metal-silicate fractionation suffered by the chondritic meteorites (LARIMER and ANDERS, 1970; WASSON, 1972). 3) Loss by diffusive processes following transient heating in the form of shock event. 4) Redistribution by processes involving sulfurous liquids or gases on the meteorite parent body. This process could be a shock event during which sulfurous veins would form. 5) Loss caused by redistribution associated with metamorphism (M. E. LIPSCHUTZ, per. commun.). This idea we do not discuss in depth because it implies greater loss from the type 3 than the more heavily metamorphosed type 4 chondrites, which we think very unlikely.

The shock loss process can be discussed in the least speculative manner. Qingzhen and Yamato 69001 both have very low K-Ar ages, 3.2 Ga and 1.1 Ga, respectively (CRABB and ANDERS, 1982; SHIMA *et al.*, 1973). CRABB and ANDERS (1982) argued that the low K-Ar age was not due to shock heating since Qingzhen's low $^3\text{He}/^{21}\text{Ne}$ (1.1) implied solar heating. However, this argument cannot be invoked by Yamato 69001, whose $^3\text{He}/^{21}\text{Ne}$ is normal (3.3). In the

case of ordinary chondrites, low K-Ar ages are always associated with violently shocked meteorites (HEY-MANN, 1967). Shock heating in an oxidizing atmosphere would also account for heterogeneous oxidation of the silicates, the production of glass (although it may look petrographically distinct from igneous primary glass), and the sulfurous veins described by EL GORESY *et al.* (1983). WANG and XIE (1981) described shock-blackened enstatite grains in Qingzhen. WALSH and LIPSCHUTZ (1982) have shown that the pattern of trace element loss following laboratory heating for 1 week at 1000°C closely resembles the pattern of element depletion in heavily shocked L chondrites. The presence of sulfurous and low K-Ar ages probably suggests that, at least locally, post-shock residual temperatures were 800–1000°C, so the annealing data for Abee therefore provides an indication of the expected trace element loss for a shocked EH chondrite. Even if shock temperatures were not so high, the pattern of element release at lower temperatures is very similar to that at 1000°C. Fig. 9 compares the annealing data of IKRAMUDDIN *et al.* (1976) with the composition of the type 3 EH chondrites. It can be seen that the two patterns are very different, the laboratory heating causes a much greater loss of Zn than has been the case for the type 3 chondrites. We think this is strong evidence against the idea that the type 3 chondrites suffered element loss by evaporation. However, it does not rule out shock-induced loss by the production by sulfurous veins, as this would be governed by the formation of miscible liquids.

Also shown in Fig. 9 is an attempt to eliminate either the condensation or the accretionary mechanisms mentioned above (possibilities 1 and 2). If the cause of the "depletion" of chalcophile elements in type 3 chondrites were associated with the loss of nebular gas, simultaneous with accretion ("gas-dust fractionation"), then one would expect to see a relationship between the extent of depletion and the volatility of the element. On the other hand, if the depletion were associated with the removal of sulfides after total condensation, then one would expect to see a plateau (a constant level of depletion) with the level of the depletion indicating the amount of material removed. We suggest that the data essentially eliminates possibility (1), and are more consistent with the mechanical removal of a sulfide-rich material containing about 20% of the chalcophile elements. Perhaps their density, being intermediate between silicates and metal, was involved.

The fourth possibility was favored by EL GORESY *et al.* (1983) on the basis of the separation of Na and K into different "lithologies", their association with very different mineral assemblages and the presence of certain alkali metal sulfides in veins. The evidence for parent body processes of some sort seems very strong, but whether they produce element depletions is unclear. It seems doubtful that they would result in a plateau in Fig. 9. If the medium which produced the veins were gaseous, then presumably the loss

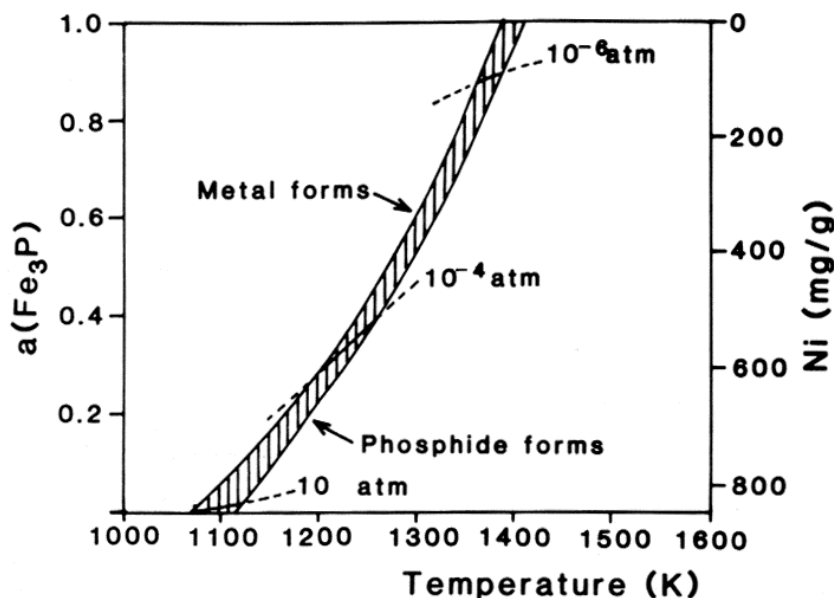


FIG. 8. Plot of the calculated Ni content of the metal as a function of the Ni content of the phosphide from the calculations of SEARS (1978). The limits of the band are indicated by the condensation of (Fe, Ni)₃P and metal. The applicable pressures are indicated.

would depend on volatility. If the medium were fluid, then the extent of loss would depend on the liquid-solid distribution coefficients for the elements and systems involved and the miscibilities of the liquid sulfides. In view of the evidence for shock, and EL GORESY *et al.*'s (1983) observation of sulfurous veins, we are inclined to suspect that shock-produced sulfur-rich veins were responsible for the depletions of volatile chalcophiles observed in the type 3 enstatite chondrites.

Relationships—oxygen isotopes

The oxygen isotope ratios of ten enstatite chondrites, including four type 3 enstatite chondrites, were reported by CLAYTON *et al.* (1984). The EL chondrites form a tight cluster on the terrestrial fractionation line with $\delta^{18}\text{O} = 5.57 \pm 0.13$. The EH chondrites, without the four type 3 chondrites, plot along the line with a mean $\delta^{18}\text{O}$ identical to that of the EL chondrites (5.59 ± 0.27). The type 3 EH chondrites

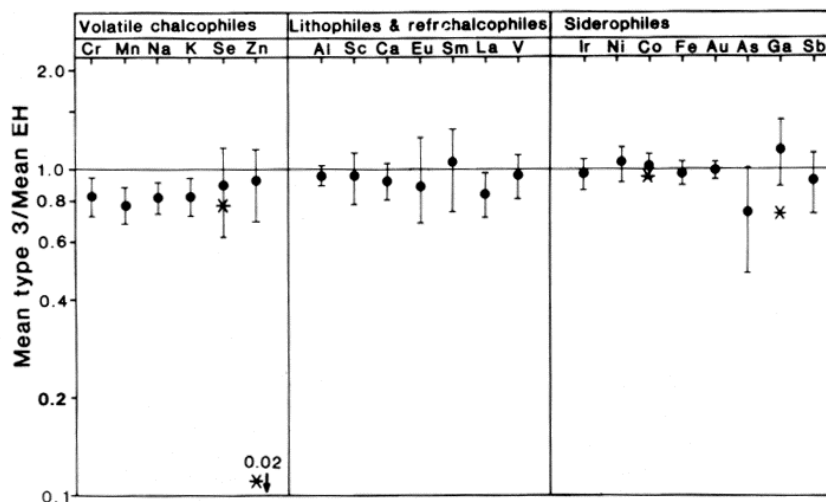


FIG. 9. Plot of the depletion of chalcophile elements in type 3 chondrites against order of increasing volatility. Also indicated with an asterisk are data for Abee samples which have been annealed for 1 week at 1000°C (data from IKRAMUDDIN *et al.*, 1976).

have $\delta^{18}\text{O}$ 0.5–1.0‰ lighter than the other EH chondrites (4.91 ± 0.32). This is in contrast to the type 3 ordinary chondrites which tend to have oxygen isotopes $\sim 1\%$ heavier in $\delta^{18}\text{O}$ than their equilibrated counterparts (CLAYTON *et al.*, 1981). If these $\delta^{18}\text{O}$ values reflect equilibration temperatures between silicates in the meteorite and the nebular gases, then the UOC equilibrated $\sim 30^\circ$ lower than their equilibrated counterparts, while the type 3 enstatite chondrites equilibrated $\sim 30^\circ$ higher than the EH and EL chondrites.

In view of the small chemical differences between the type 3 chondrites and the EH chondrites, it is worthwhile to consider the influences on oxygen isotopes of the processes discussed above. Weathering would move the samples up along the terrestrial fractionation line since it would add heavy tropospheric oxygen ($\delta^{18}\text{O} = 23.6$). Although it might explain the difference in oxygen isotopic composition between the two Parsa fragments examined by CLAYTON *et al.* (1981), it is totally incapable of explaining the differences between the type 3 enstatite chondrites and the others. Loss of a plagioclase-rich liquid would produce a residue with lighter isotopes, since heavy oxygen tends to partition itself in the plagioclase (CLAYTON *et al.*, 1976). ONUMA *et al.* (1972b) state that the relationship between the plagioclase-pyroxene fractionation (Δ) and temperature (T , K) is $\Delta = 1.17(10^6 T^{-2})$ in which case $\Delta = 2.3$ and 3.6 at 400 and 300°C , respectively. Thus if all the plagioclase were lost, the bulk $\delta^{18}\text{O}$ would decrease by 0.3 and 0.6% , respectively, while if half were lost, the decreases would be 0.2 and 0.3% . These values are similar to the observed differences between $\delta^{18}\text{O}$ for type 3 and the other enstatite chondrites. The alternative is that instead of removal of plagioclase containing heavy oxygen isotopes, light oxygen-bearing olivine could have been added. However, it is difficult to conceive of a physical scenario to accomplish this. We speculate, therefore, that the oxygen isotopes may reflect a loss of a shock-produced, plagioclase-rich melt and could be a further consequence of shock processes playing a major part in the history of the type 3 enstatite chondrites.

CONCLUSIONS

The meteorites identified by PRINZ *et al.* (1984a) are EH chondrites that equilibrated at lower temperatures than the type 4–6 enstatite chondrites. These are depleted in chalcophile elements by an amount which is independent of volatility; their abundance lies at the low end of the EH range. It is thought unlikely that the depletions are caused by weathering since more extensively weathered non-type 3 enstatite chondrites do not show such depletions. Rather it is suggested that the chalcophile element depletions are the result of shock events suffered by the parent body which removed certain chalcophiles by the formation of sulfurous veins. If the shock also produced plagioclase-rich liquids, then the oxygen isotope differences

between type 3 and equilibrated chondrites could also be explained. The complex mineral chemistry of enstatite chondrites may be best understood in terms of simultaneous condensation, accretion and equilibration of components that formed at a variety of temperatures and were subsequently mixed and suffered little or no subsequent reequilibration. Thus the type 6 chondrites contain a large portion of material that formed and agglomerated at the highest temperatures ($>1000^\circ\text{C}$), the type 4–5 at intermediate temperatures ($600\text{--}700^\circ\text{C}$) and the type 3 at the lowest temperatures ($300\text{--}400^\circ\text{C}$).

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Appendix 1. Mg/Si and Fe/Si data used in Fig. 4 and their literature sources.*

	Mg (mg/g)	Fe (mg/g)	Si (mg/g)	References†
Abee	115,111	326,304	163,175	1,11
Adhi Kot	111	333	168	2
Indarch	113,110, 104	304,269, 332	167,165	1,3,4
St. Marks	111,116	314,324	170,171	1,4
St. Sauveur	106,103	295,350	156	3,7
Parsa	113	276		3
Yamato 69001	116	298	177	8
Qingzhen	110,113	314,312	170	9,14
Allan Hills A77156	105	314		14
Yamato 74370				10
Atlanta	127,153	248,[290]	176,177	1,4
Blythfield	160,149	197,207	222,199	1,13
Daniels' Kuil	130	[290],237	180	2,6
Hvittis	127,147, 140	235,226, 249	173,194, 198	1,4,12
Jajh deh Kot Lalu	140	222	184	4
Pillistfer	136,156	278,267, 270,233	191	1,2,3
Khairpur Reckling Peak A80259	148,139 113	235,211 218	204	5,6 14

* Values in square brackets were rejected as being out of line with other data.

† 1. Von Michaelis et al. (1969); 2. Mason (1966); 3. Sears et al. (1982a); 4. Wiik (1969); 5. Moss et al. (1967); 6. Prior (1916); 7. La Croix (1923); 8. Shima and Shima (1976); 9. Wang and Xie (1981); 10. Nagahara and El Goresy (1984), ratios only quoted; 11. Dawson et al. (1960); 12. Borgstrom (1903); 13. Johnston and Connor (1922); 14. Present work.