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Chemical classification of iron meteorites—IX. A new group (IIF), revision of IAB and IIICD, and data on 57 additional irons

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Abstract—Structural observations and concentrations of Ni, Ga, Ge and Ir allow the classification of 57 iron meteorites in addition to those described in the previous papers in this series; the number of classified independent iron meteorites is now 535. INAA for an additional six elements indicates that five previously studied irons having very high Ge/Ga ratios are compositionally closely related and can be gathered together as group IIF. A previously unstudied iron, Dehesa, has the highest Ge/Ga ratio known in an iron meteorite, a ratio 18 × higher than that in CI chondrites. Although such high Ge/Ga ratios are found in the metal grains of oxidized unequilibrated chondrites, their preservation during core formation requires disequilibrium melting or significant compositional and temperature effects on metal/silicate distribution constants and/or activity coefficients. In terms of Ge/Ga ratios and various other properties group IIF shows genetic links to the Eagle Station pallasites and CO/CV chondrites. Klamath Falls is a new high-Ni, low-Ir member of group IIIF that extends the concentration ranges in this group and makes these comparable to the ranges in large igneous groups such as IIIAB. Groups IAB and IIICD have been revised to extend the lower Ni boundary of group IIICD down to 62 mg/g. The iron having by far the highest known Ni concentration (585 mg/g), Oktibbeha County, is a member of group IAB and extends the concentration ranges of all elements in this nonmagmatic group. Morasko, a IAB iron associated with a crater field in Poland, is paired with the Seeläsgen iron discovered 100 km away. All explosion craters from which meteorites have been recovered were produced by IAB and IIIAB irons.

INTRODUCTION

THE ELEMENTS Ge and Ga have proven to be the most useful for the purpose of classifying iron meteorites. This results from the fact that they are (a) two of the three most volatile siderophiles and (b) little fractionated during fractional crystallization (WAI and WASSON, 1980). In previous papers of this series the concentrations of Ni, Ga, Ge, and Ir (the latter highly fractionated during fractional crystallization) have therefore been used to establish 12 independent iron meteorite groups (WASSON, 1967; 1969; 1970; WASSON and KIMBERLIN, 1967; WASSON and SCHAUDY, 1971; SCHAUDY *et al.*, 1972; SCOTT *et al.*, 1973; SCOTT and WASSON, 1976). It is thought that each of these groups originated in a single, discrete parent body. This paper establishes a new group, IIF, and discusses how the high Ge/Ga content of IIF may have originated. At the same time, the list of classified meteorites is updated to include 47 new members of established groups and 10 new ungrouped meteorites. We have now classified 535 independent and about 90 additional irons paired with these.

EXPERIMENTAL

One important change has been made to the procedures as outlined by WASSON and KIMBERLIN (1976) and KIMBERLIN *et al.* (1968). All radiochemical neutron activation analysis (RNAA) runs are now preceded by instrumental neutron activation analysis (INAA), which allows determination of up to eight additional elements (see SCOTT, 1977a, 1978; WILLIS, 1980). For meteorites containing more than 0.2 μg/g Ir, the INAA determination is more precise than the RNAA determination and the INAA value was therefore used exclusively. For Ir contents between 0.02 and 0.2 μg/g, an average of INAA and RNAA values weighted on the basis of analytical precision was used. Lower Ir concentrations were determined radiochemically. An outline of the INAA procedure and a discussion of its analytical precision, is given by WILLIS (1980). Determinations of Ni (atomic absorption) and Ge (RNAA) were performed the same way as described previously (WASSON and KIMBERLIN, 1967; KIMBERLIN *et al.*, 1968). If adequately precise Ga concentrations could be obtained by INAA, these were averaged with radiochemical data, using double statistical weight for the RNAA data. The 95% confidence limits for the means are about ±2% for Ni, ±4% for Ga and Ge, and ±10% for Ir. The Ge precision decreases below about 0.1 μg/g and the 95% confidence limits increase to about ±15% at concentrations of 0.04 μg/g.

As described by SCOTT and WASSON (1976), samples were mostly blocks sawed in roughly cubic shape and having masses of ~0.4 g; for meteorites with very coarse structures, the masses were increased to ~0.8 g. In all but a few cases (Yamato Y75105 and suspected paired meteorites), at least two replicates were run. Where these differ by more than the expected analytical uncertainty, or one value had

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Table 1. Ni, Ga, Ge and Ir concentrations in 57 iron meteorites

Meteorite	Chem. group	Struc. class	Width (mm)	Source†	Cat. No.	Ni (mg/g)	Ga (μg/g)	Ge (μg/g)	Ir (μg/g)
Allan Hills A76002	IA	Og		FMNH	-	70.0	92.4	423	2.4
Alt Bela	IID	Om	0.70	NMW		100.4	75.0	84	16
Armanty	IIIA	Om		KMAN	1231	91 ± 5	16.2	31.5	0.23
Barbacena	ungr	Opl	0.12‡	UNM	138.1	109	12.8	1.16	2.9
Bear Lodge	IIIA	Om	1.15	ASU	286ax	76.7	19.3	38.7	4.5
Benedict	IIIA	Om	1 ‡	AML	H113	86.2	21.4	45.4	0.18
Bluewater	IIIA	Om	1 ‡	UNM	15.1	81.2	19.8	40.6	2.6
Britstown	ungr	Opl	0.02	BM	1927.81	195	39.6	183	2.0
Buenaventura*	IIIB	Om	0.8‡	UCLA	947	99.2	17.4	34.5	0.011
Cabin Creek	IIIA	Om	1.10	NMW	F6342	82 ± 4	21.1	39.6	0.70
Carver	IIA	H		UNM	115.1	55.0	58.7	184	12
Cincinnati	IIA	H		AMNH	89	54.4	56	178	20
Colonia Obrerra	IIIE	Og	1.4‡	ASU	1032	86.2	17.4	37¶	0.055
Dehesa	ungr	D		MHNP	378	118	3.0	174¶	32
Denver City*	ungr	Of	0.20‡	UCLA	951	84.0	1.03	0.5¶	5.2
Duel Hill (1873)	IA	Og	2.40	AMNH	82	66 ± 2	84¶	426¶	4.3
El Mirage	IIA	H		ASU	1001	56.3	57.7	185	6.1
El Sampal	IIIA	Om	0.95‡	ASU	1014.4	88.0	20.0	39.6	0.58
Fort Pierre	IIIA	Om	1.05	AMNH	68	74.6	18.3	35.9	7.4
Harlowton	IA	Om	1.0	ASU	1045.9	88.2	61.5	222	2.5
Itapuranga	IA	Og	1.5	USP		67 ± 3	97	478	2.8
Itutinga	IIIA	Om	1.0	UNM	140.1	72	18.6	36.0	13
Jaralito	IIICD	Og	1.9‡	UCLA	1026	65.2	91.6	376	1.5
Jerslev	IIB	Ogg	10 ± 5	MMUC	977,540	56.6	58.0	168	0.19
Kaalijärv	IA	Og	2.0	KMAN	15158	73.6	74.9	293	2.8
Kinsella*	IIIB	Om	1.0‡	UCLA	948	87.8	20.3	42.0	0.12
Klamath Falls	IIIF	Of	0.5‡	UNM	17	85.0	6.79	0.701	0.0059
Linville	ungr	D-anom	0.03	NMW	···	158.0	7.5	16.1	0.012
Losttown	IID	Om	1.00	SI	1071	100	72.7	78.0	18
Millarville	IVA	anom		UClg	·	95.7	2.38	0.144	0.98
Morasko	IA	Og	2.5	PAC		65.6	98.9	496	1.0
Mt. Sir Charles	IVA	Of	0.3±1‡	SI	5669	83.0	2.32	0.126	1.5
Nantan	IIICD	Om	1 ‡	MPIH		68	77¶	293¶	1.7
Nenntmannsdorf	IIB	Ogg	10.0	YalU	P66	61.8	58.8	176	0.057
Oktibbeha County	IB	anom		AMNH	62	585	3.6¶	9.0¶	0.026
Old Woman	IIB	Ogg	10‡	·		57.1	58.5	190	0.80
Paracutu	IA	Og	2.6‡	MPIM		75.4	80.4	320	2.6
Patos de Minas (hex)	IIA	H		SI		53.6	59.8	170	43
Petropavlovsk	ungr	Om	1.3	KMAN	15208	81.0	21.7	48.6	0.57
Pirapora	IIA	H		MNB	23-Mr	54.3	57.8	189	30
Pooposo	IA	Og	2.60	NMW	···	69.8	78.8	325	2.8
Prambanan	ungr	Off	0.13	FMNH	Me1160	101.4	28.3	190	4.2
Quesa	ungr	Om	0.70	NMW	H443	110.4	37.3	101	0.080
Rancho Gomelia	IIIB	Om	0.8‡	ASU	1044.6	97 ± 6	16.4	28.8	0.013
Rica Aventura	IVA	Of	0.27§	FMNH	···	92.1	2.29	0.138	0.38
Sanclerlandia	IIIA	Om	1 ‡	UNM	144.1	74.7	18.6	36.4	7.1
Santa Clara	IVB	D	0.007‡	ASU	1060	179	0.22	0.054	18
São Joào Nepomuceno	IVA-An	Of	0.31‡	SI		80.0	2.16	0.118	2.6
Tacoma*	IA	Og	1.5‡	UCLA	950	72	73	272	2.4
Tishomingo	ungr	anom		SI	5862	325	0.25	0.088	17
Verissimo	IIIA	Om	0.9‡	MNB		75.4	18.3	34.9	14
Waingaromia	IIIA	Om	0.9	CMNZ	·	91.4	20.9	41.6	0.38
Winburg	IC-An	Om	1.3‡	MMUC	174,938	69.8	51.8	180	0.89
Yamato 75031	ungr	Opl	0.02‡	NIPR		142	31.2	232	0.34
Yamato 75105¶	IIA	H	--	NIPR		56.2	58.4	170	2.4
Yardea	IA	Og	2.00	UMel	5673	69.2	88.8	361	4.3
Zaffra	IIICD-An	Og	2.50	AMNH	2614	71.2	73.2	244	0.061

* Described by Scott *et al.* (1977).

† Source abbreviations are as follows: AML—American Meteorite Laboratory; AMNH—American Museum of Natural History; ASU—Arizona State University; BM—British Museum (Natural History); CMNZ—Christchurch Museum, New Zealand; FMNH—Field Museum of Natural History, Chicago; KMAN—Committee on Meteorites, Academy of Sciences, USSR; MHNP—Museum Histoire Naturelle, Paris; MMUC—Mineralogical Museum of the University, Copenhagen; MNB—Museu Nacional Brazil; MPIH—Max-Planck-Institut Heidelberg; MPIM—Max-Planck-Institut, Mainz; NIPR—National Institute of Polar Research, Japan; NMW—Naturhistorisches Museum, Vienna; PAC—Polish Academy of Sciences; SI—Smithsonian Institution, Washington D.C.; UCLA—University of California, Los Angeles; UClg—University of Calgary; UMel—University of Melbourne; UNM—University of New Mexico; USP—Universidad de São Paulo; YalU—Yale University.

‡ Bandwidths accurate to ±20%, remainder from Buchwald (1975 and personal communication) and accurate to ±10%.

§ Bandwidth from Olsen and Zeitschel (1979).

‖ Ungrouped is abbreviated ungr; these meteorites were designated anomalous in previous papers in this series.

¶ Estimated error is about twice the usual value.

to be discarded, increased error limits are given. Only turnings were available of Repeev Khutor which might have been contaminated with W and Cu and gave results of slightly lower analytical precision. In Table 1 the analyzed meteorites are listed alphabetically together with the group assignment, the structures, the sources of the samples, and the compositional data.

TAXONOMY

Group IIF

A relationship between the five members of this group has previously been suspected by SCOTT and WASSON (1976), on the basis of their uniquely high Ge/Ga ratio, their moderately high Ni contents, and their Ir:Ni correlation. We have determined additional trace elements by INAA, and our results support a common origin for the five members. Table 2 gives the results of both INAA and RNAA and Fig. 1 shows plots of trace element content vs Ni on a log–log scale for group IIF, the Eagle Station pallasites, and four ungrouped meteorites with high Ge/Ga ratios.

Least squares regression lines are drawn through the IIF data points in Fig. 1. With the exception of Ga and Ge, the slopes of these lines are very similar to those found in magmatic groups (all groups except IAB and IIICD); the Ga and Ge distributions are consistent with the convex upwards patterns found in the well-populated igneous groups IIAB, IIIAB and IVA. Table 3 gives a comparison of slope, intercept, and correlation coefficient of these regression lines for groups IIF, IIIAB and IVA. Although there is considerable scatter around the IIF regression lines on plots of As, Au, Ir, and Re vs Ni, it is scarcely greater than the expected scatter if regression lines were passed through the data for five IIIAB members picked at random. The Co contents of group IIF members are unusually high (average 7.0 mg/g) relative to other groups (typically ~5 mg/g). The Cu contents are also higher than typical. Phosphorus contents are quite low compared with other groups except IVA and IVB (data from BUCHWALD, 1975) and show a strong positive correlation with Ni, but the slope is less steep than in most igneous groups. This may indicate that the P solid/liquid distribution coefficient is greater at the higher Ni contents found in IIF. The compositional patterns thus seem to point at an origin by fractional crystallization of a core.

However, the structural properties do not seem consistent with origin in a single core. Kamacite bandwidth within the group increases with increasing Ni rather than decreasing as would be expected *a priori* if the cooling rates were the same for all members. Cooling rates calculated by the WASSON (1971) fit of the SHORT and GOLDSTEIN (1967) bandwidth-Ni relationships vary by over two orders of magnitude. Apparent differences in cooling rates between low-Ni and high-Ni members of other groups and their significance in terms of a core origin have repeatedly been discussed (WILLIS and WASSON, 1978a, b; MOREN and GOLDSTEIN, 1978), but in those cases the apparent variation is much smaller, typically less than one order of magnitude. SCOTT (1977b) discusses a core break-up model explaining the widely varying structures within group IC, but his model leads to random variation, not a positive relationship between bandwidth and Ni content as suggested by the IIF data.

We note that the bandwidth uncertainties (Table 4) are relatively large, such that the three low-Ni irons could have identical bandwidths near 0.07 mm and the two high-Ni irons identical bandwidths near 0.2 mm. Alternatively, the bandwidth based cooling rates of the three low-Ni members could all be about

Table 2. Composition of group IIF, four other irons, and the metal of the Eagle Station pallasites: Butler data from SCOTT (1978), pallasite data from SCOTT (1977a), other data from SCOTT and WASSON (1976) and this work

	Co (mg/g)	Ni (mg/g)	Cu (μg/g)	Ga (μg/g)	Ge (μg/g)	As (μg/g)	W (μg/g)	Re (μg/g)	Ir (μg/g)	Au (μg/g)	Ge/Ga‡
IIF											
Monahans	6.4	106.0	309	8.9	127	4.6	2.1	1.2	14	0.62	4.4
Dorofeevka	7.0	112.6	313	9.1	124	5.1	1.7	2.4	23	0.62	4.2
Del Rio	7.2	113.4	334	9.2	99	4.4	1.4	2.0	19	0.62	3.3
Corowa	7.0	131.3	291	10.1	159	17.3	0.53	0.11†	0.75	1.86	4.8
Repeev Khutor	7.0	143	*	11.6	193	12.4	*	0.26†	3.0	1.48	5.1
Ungrouped											
Butler	10.7	152.0	—	87.1	1970	43.0	5.0	<0.4	1.6	6.0	7.0
Dehesa	7.8	118	166	3.0	174†	10.4	1.01	3.2	32	1.25	17.8
Emsland	8.3	94.0	184	2.90	35.0	5.6	1.86	0.32	3.2	0.71	3.7
Mbosi	8.0	87.1	166	2.54	26.9	3.0	2.03	0.60	6.6	0.39	3.3
Eagle Station trio											
Cold Bay	5.4	136	—	6.2	113	6.4	0.16	—	5.8	0.87	5.6
Eagle Station	8.0	154	—	4.54	75	10.0	1.2	—	11.4†	0.98	5.1
Itzawisis	8.1†	147	—	5.73	86	6.2†	—	—	16 ± 3	1.04†	4.6

* Contamination suspected.
† Only one value, twice usual error.
‡ CI-chondrite normalized.

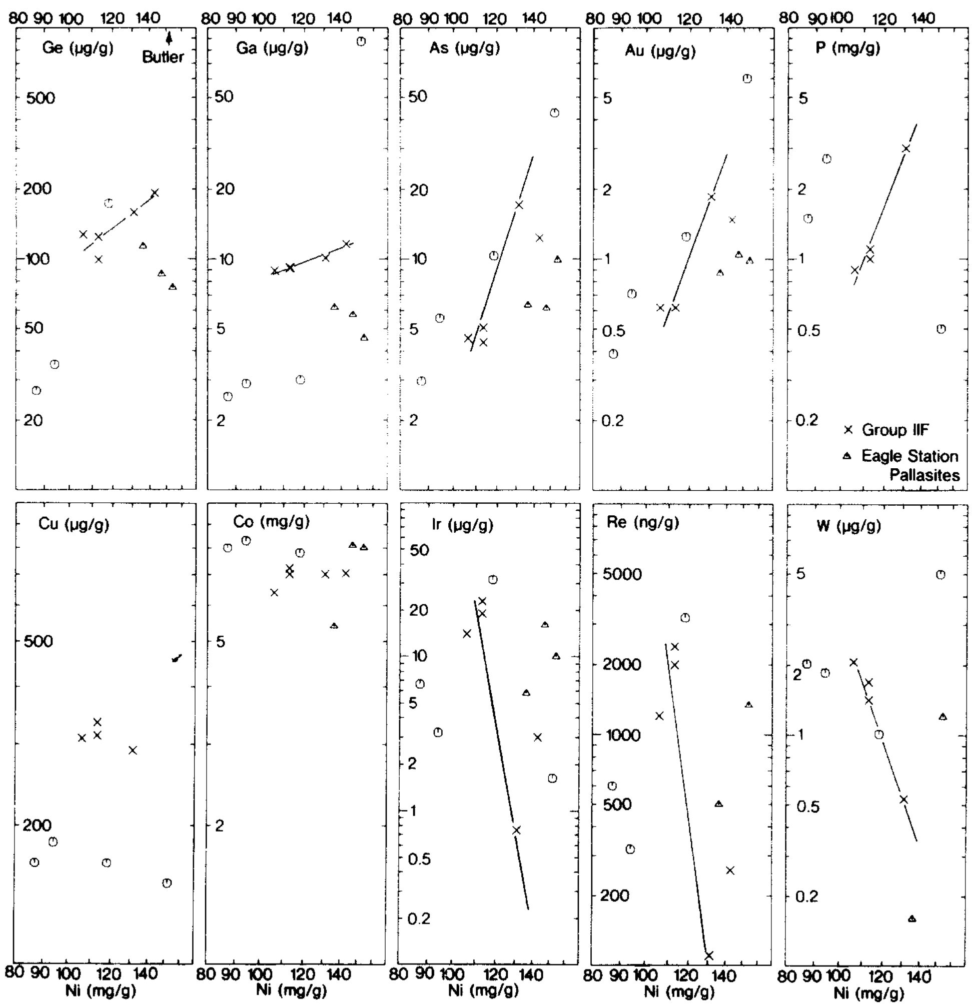

Fig. 1. Log–log plots of Ge, Ga, As, Au, P, Cu, Co, Ir, Re and W vs Ni for group IIF, the Eagle Station pallasites, and four ungrouped irons with high Ge/Ga ratios. Linear regression lines for group IIF, excluding Repeev Khutor are shown. Copper and W contamination is suspected in Repeev Khutor; this data is not shown. In addition, its high Ni value may also reflect contamination. The four ungrouped irons, plotted as circles, are Mbosi, Emsland, Dehesa and Butler in order of increasing Ni content.

Table 3. Slope (A), intercept (B), and correlation coefficient (R) of log X:log Ni correlations in group IIF and in igneous groups IIIAB and IVA; n = number of data points used for correlation

	IIF				IIIAB				IVA			
	n	A	B	R	n	A	B	R	n	A	B	R
P	4†	6.2	3.0	0.98	146	7.4	5.3	0.94	34	8.5	6.0	0.88
Co		‡			90	0.48	−1.8	0.64	25	0.50	−1.9	0.48
Cu		‡			36	−1.19	−5.1	−0.85	20	−1.58	5.6	−0.68
Ga	5	0.87	−4.2	0.96		*				*		
Ge	5	1.89	−2.1	0.86		*				*		
As	4†	7.5	1.82	0.94	37	6.0	1.31	0.97	18	7.9	3.2	0.95
W	4†	−6.8	−12	−0.99	18	−5.6	−12	−0.96	8	−2.0	−8.4	−0.82
Re	4†	−18	−23	−0.85	22	−28	−37	−0.94	12	−7.7	−15	−0.93
Ir	4†	−20	−24	−0.89	150	−25	−34	−0.95	39	−8.3	−15	−0.94
Au	4†	6.5	−0.01	0.94	50	5.3	−0.34	0.96	17	6.8	1.5	0.95

* Not linear.
† Repeev Khutor excluded.
‡ Co and Cu are uniform throughout the group.

Table 4. Kamacite bandwidth and calculated cooling rates for the irons of group IIF. Data from BUCHWALD (1975) and SCOTT and WASSON (1976)

	Ni (mg/g)	Bandwidth (mm)	Cooling rate ($K\ Myr^{-1}$) Min†	Mean	Max†
Monahans	106.0	0.05 ± 2	78	154	437
Dorofeevka	112.6	0.09 ± 3	15	27	62
Del Rio	113.4	0.07 ± 2	25	42	84
Corowa	131.3	0.20 ± 6*	0.8	1.3	2.8
Repeev Khutor	143	0.21 ± 5	0.4	0.6	1.0

* BUCHWALD (1975) gives "about 0.2 mm".

† Minimum and maximum cooling rates based only on the bandwidth uncertainty. Incorporation in Ni uncertainties would increase these ranges somewhat.

$70\ K\ Myr^{-1}$, those of the high-Ni irons about $0.9\ K\ Myr^{-1}$. These would in turn allow two possible scenarios: (1) Both sets of irons formed in the same parent core; after solidification, but before taenite decomposition, the core was disrupted, the fragment including the high-Ni irons ended up with more silicate insulation than the fragment including the low-Ni irons. (2) Two parent bodies nearly identical in composition but differing in size by nearly an order of magnitude were involved; the low-Ni samples happened to have originated in the smaller body, the high-Ni samples in the larger, the remaining parts of each core have not happened to fall as meteorites. The second scenario is inherently less plausible.

Still another scenario can be based on the observation that schreibersite is ubiquitous in the kamacite spindles of group members. This implies that the bulk of the bandwidth growth occurred before the phosphide exsolved. WILLIS and WASSON (1978a, b) note that P has a marked effect on the rate of Ni diffusion in kamacite, which would lead to an enhanced kamacite growth rate in the high-Ni, high-P irons relative to the low-Ni irons. Further, the schreibersite amounts to an appreciable fraction (~15%) of the volume of the large kamacite lamellae. These qualitative arguments suggest that there may be no difference in cooling rate between the low-Ni and high-Ni IIF irons. A detailed metallographic cooling rate study should be carried out.

Although the cooling rate evidence is ambiguous, we consider the chemical evidence for a common origin compelling for the following reasons: (a) the unusually high Ge/Ga ratios, found only in a total of 9 irons (group IIF, Emsland, Mbosi, Dehesa, and Butler) and three pallasites, (b) the very similar contents of Co and Cu, which are distinctly higher than in the majority of other groups, and (c) the similarity of regression line parameters (Table 3) to those observed in major groups of fractional crystallization origin. Although any one of these similarities by itself might be fortuitous, in combination they point at a chemical relationship between these five irons which is not less strong than between members of established groups separated by similar differences in Ni content. The relatively large compositional hiatus dividing the group into a low-Ni trio (Monahans, Dorofeevka, Del Rio) and high-Ni duo (Corowa, Repeev Khutor) caused SCOTT and WASSON (1976) to doubt the grouping. However, it would be a highly improbable coincidence if two clusters of anomalous meteorites would differ from one another in exactly such a way as to simulate an igneous fractionation trend. We therefore contend that in this case the criteria for group designation of WASSON and KIMBERLIN (1967), as amended by SCOTT and WASSON (1976), are fulfilled, and propose that these five irons form a new chemical group, IIF.

Relationship of group IIF to Eagle Station pallasites

Data on three Eagle Station pallasites from SCOTT (1977a), included in Fig. 1, show that the relationship between them and group IIF is not as close as that between main-group pallasites and group IIIAB. All three Eagle Station pallasites fall on the Ni-rich side of the regression lines on all of the plots; they are uniformly lower in Ge, and intermediate between low-Ni and high-Ni IIF-members in As, Au, Ir, and Re. Eagle Station and Itzawisis are resolvably higher in Co (8.0 mg/g) than group IIF: the low Co value of Cold Bay may be related to the heavy weathering effects in the metal (SCOTT, 1977a). Considering the large spread in Ni contents within the main-group pallasites compared to IIIAB irons the higher Ni contents of Eagle Station pallasites alone do not rule out a close relationship to group IIF. In fact, they support the idea that IIF and the Eagle Station trio originated in *similar* parent bodies. However, our best interpretation is that the significant differences in trace element content make it unlikely that they came from the *same* parent body, as proposed for IIIAB and the main-group pallasites by SCOTT (1977c).

Oktibbeha County—an IAB member containing 585 mg/g Ni

Oktibbeha County is the iron meteorite having the highest Ni concentration. The second highest concentration is 421 mg/g in the ungrouped Dermbach iron. Compositional evidence strongly favors the view that Oktibbeha County belongs to group IAB. As discussed in more detail by KRACHER and WILLIS (1980), trends on element/Ni diagrams for the elements Cu, Ga, Ge, As, Sb, Au, and Ir support this classification; one W (1.2 μg/g, 30× too high) value failed to follow the expected trend, but contamination is suspected since the replicate is <0.3 μg/g. As a result of this addition there is now a factor of at least 9 between the lowest (~64 mg/g) and highest Ni concentrations in normal members of IAB. This remarkable Ni range is to be compared with the factor of 4 range in IIICD, the other nonmagmatic group, and the factor of 1.4 range in IIIAB, the largest range in a magmatic group.

Table 5. New members of IIICD listed in order of decreasing Ni concentration

Meteorite	Group	Ni (mg/g)	Ga (μg/g)	Ge (μg/g)	As (μg/g)	Ir (μg/g)
Pittsburg	IIICD	61.6	83.0	339	13.3	2.0
Ballinger	IIICD	61.9	84.5	326	14.3	2.1
Carrizalillo†	IIICD	62.0	81.0	337	13.5	2.04
Jaralito	IIICD	65.2	91.6	376	12.6	1.54
Nantan	IIICD	68	77	293	12.9	1.73
Zaffra	IIICD-An	71.2	73.2	244	14.4	0.061

* As values are from SCOTT (1977) except Jaralito, Nantan and Zaffra (WASSON *et al.*, 1980).

† We use the corrected spelling of BUCHWALD (1975).

Expansion of group IIICD at the expense of group IAB

SCOTT and BILD (1974) reported that the fractionation trends in the small group IIICD were similar to those in group IAB, and inferred that IIICD was also formed non-magmatically. As defined by WASSON and SCHAUDY (1971), group IIICD consisted of irons having Ni contents in the range 110–230 mg/g; later the lower extreme was revised downward to 105 mg/g to include Hassi Jekna. SCOTT and BILD (1974) noted that an extrapolation of the IIICD field on Ga–Ni or Ge–Ni diagram intersected the IAB field, and suggested that the anomalous Mundrabilla and Waterville irons containing 77–78 mg/g Ni might be IIICD members. They presented no additional evidence to back up this suggestion, and SCOTT and WASSON

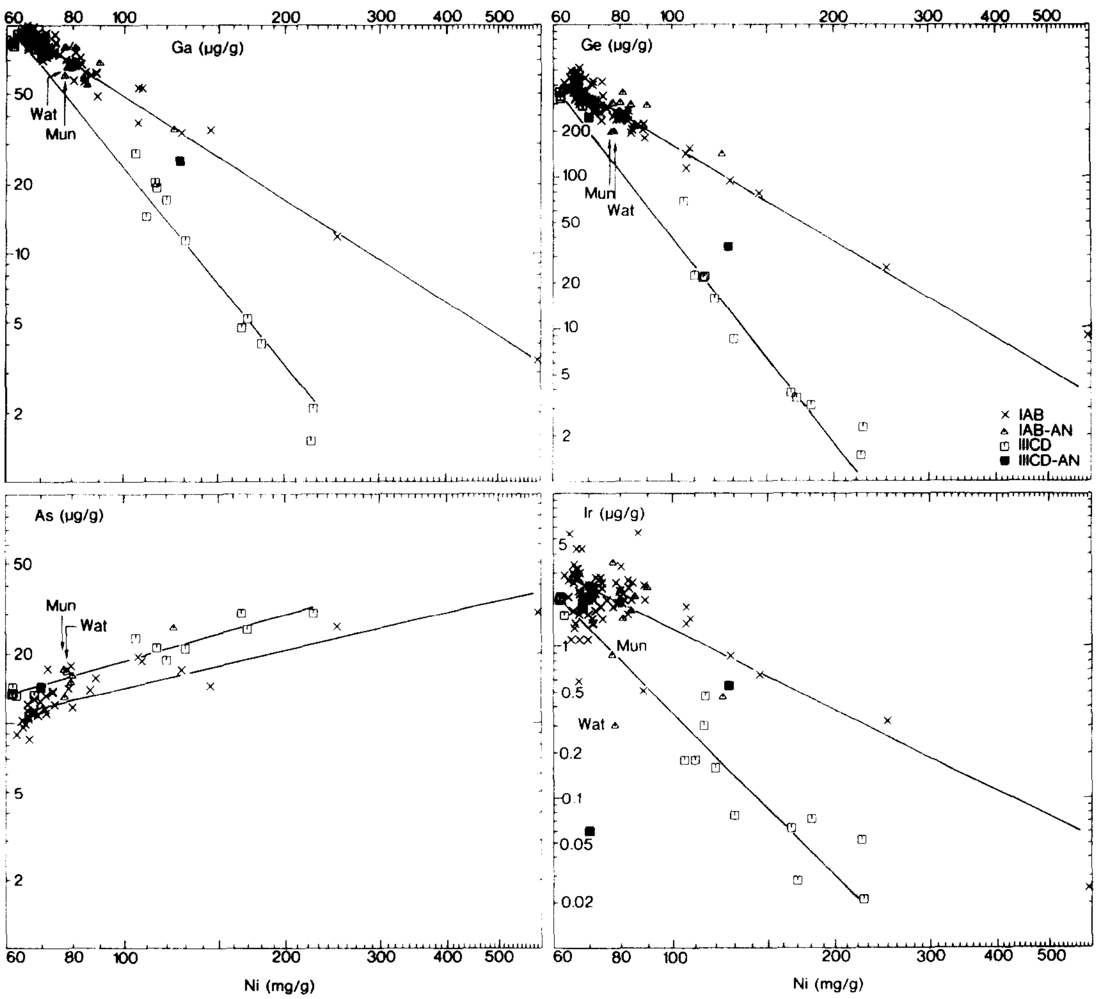

Fig. 2. Log–log plots of Ga, Ge, As and Ir vs Ni for groups IAB and IIICD. Mundrabilla (Mun) and Waterville (Wat), two anomalous members of group IAB, may be members of group IIICD. Other low Ni members of group IAB may be members of group IIICD but we lack sufficient data to reclassify them at the present time.

(1976) redesignated Mundrabilla and Waterville IAB-Anomalous.

WILLIS and WASSON (1980) compiled a large body of siderophile data purged of low-precision data and, as necessary, corrected for interlaboratory biases. Close examination of these data reveal that numerous IIICD trends can be extrapolated down to Ni concentrations of 62 mg/g to include some meteorites previously assigned to IAB. As documented by WASSON *et al.* (1980), the IIICD fields are lower than IAB fields on Ga, Ge, W, Re and Ir element–Ni log–log diagrams and higher on As–Ni diagrams. Accurate data on Ni, Ga or Ge, As and Ir are generally sufficient to allow the assignment of an iron to one or the other group. It appears that IIICD Au–Ni and P–Ni fields are also higher than IAB, but these are of marginal taxonomic value because the differences are small and comparable to the uncertainties in published data.

The new members of IIICD are listed in Table 5 together with their contents of Ni, Ga, Ge, As and Ir. The locations of these five irons and the remaining IIICD members relative to IAB are shown in Fig. 2. Zaffra is designated IIICD-An because of its anomalously low Ir content. Edmonton, Ky, previously considered to be a normal IIICD member, is redesignated IIICD-An because its Ni concentration of 127 mg/g is about 15 mg/g higher than that expected from its Ga, Ge and Ir concentrations.

Mundrabilla and Waterville continue to defy simple classification. Their low Re and Ir contents (particularly in Waterville) and high As content imply a close relationship to IIICD, but concentrations of Ga and Ge and other elements having some discriminatory power (Co, W) are intermediate between IAB and IIICD trends. Further, the Fe/(Fe + Mg) ratio in the orthopyroxene of Mundrabilla silicate inclusions is $\sim$6 mol%, within but near the upper limit of the IAB range, whereas those in IIICD members Carlton and Dayton are 9 and 12 mol%, respectively. We suspect that Mundrabilla and Waterville are more closely related to IIICD than IAB, but the evidence is so ambiguous that we propose to continue designating them IAB-An until a stronger case can be made for their reclassification to IIICD-An. Because of their unusual structures and ambiguous compositions it seems clear that they can never be considered normal members of either group.

We also propose to act conservatively regarding other reclassifications. We feel confident that some additional low-Ni irons associated with IAB will prove to be IIICD members when more extensive analytical data become available. Potential candidates include Casey County, Sardis, and Zacatecas (1792) which have Ga, Ge and Ir values lower than expected from their Ni contents and IAB trends.

Group IIAB: placement of the boundary between subgroups

WASSON (1969) found that the hexahedrites of subgroup IIA are distinguished from the chemically similar coarsest octahedrites which he designated subgroup IIB, by a hiatus in Ir contents, IIA having $\geq$2.1 ppm, IIB $\leq$0.46 ppm. Our data on Old Woman show that its Ir content falls in the hiatus. To permit unambiguous classification of future samples, it is useful to define a boundary between the two subgroups. This is analogous to the arbitrary boundaries between IA and IB, and IIIA and IIIB.

It might be argued that the difference between hexaahedrite and coarsest octahedrite establishes a natural boundary, but there are reasons against choosing such a definition: firstly, it is not obvious that there is a sharp discontinuity. If kamacite bandwidth increases to several centimeters near the IIA/B boundary, some small IIA 'hexahedrites' could be kamacite bars separated from a supercoarse octahedrite. Secondly, there are many cases where textural evidence is destroyed by later reheating (e.g. in Juromenha, Millarville). Thus, structural properties may not always allow unambiguous classification. Thirdly, although structure is highly correlated with composition (this is particularly apparent from BUCHWALD's 1975 descriptions), the classification scheme is basically compositional. For these reasons a compositional boundary between groups IIA and IIB seems best; we propose to use an Ir content of 1 μg/g as the boundary.

Group IIIF

Group IIIF was originally defined by SCOTT and WASSON (1976) with five members having a narrow range of Ni, Ga, Ge, and Ir contents. The data on a new IIIF member, Klamath Falls, considerably extend the Ni and Ir ranges. Klamath Falls bandwidth (0.5 mm) is near the lower extreme of the previous range (0.5–1.5 mm); the largest bandwidths are ascribed to assimilation. Few macroscopic inclusions are present in IIIF but microscopic daubreelite precipitates are abundant. The Ga and Ge contents for Klamath Falls fall in the range defined by the first five members of group IIIF. Although Ni and Ir fall considerably outside the previous ranges, they fall near a plausible extrapolation of the previously defined trend. Klamath Falls also lies along plausible extrapolations of IIIF Re–Ni, Au–Ni, W–Ni, and As–Ni trends (SCOTT, 1978) and has more schreibersite than other IIIF members, consistent with normal P–Ni trends (Fig. 3). There is little doubt that Klamath Falls belongs in group IIIF, whose ranges of Ni, Ir, W, Re, Cr, and Au are now comparable to those found in the large igneous groups IIAB and IIIAB.

The new element–Ni trends are either similar to or steeper than those of group IIIAB indicative of a IIIF k_{Ni} value greater than that of IIIAB. The mean composition of the IIIF parent body, calculated using Scott's method and assuming an igneous core model (WILLIS and WASSON, 1980), reveals that volatile-element abundances decrease with decreasing condensation temperature, similar to those in groups IVA and IVB.

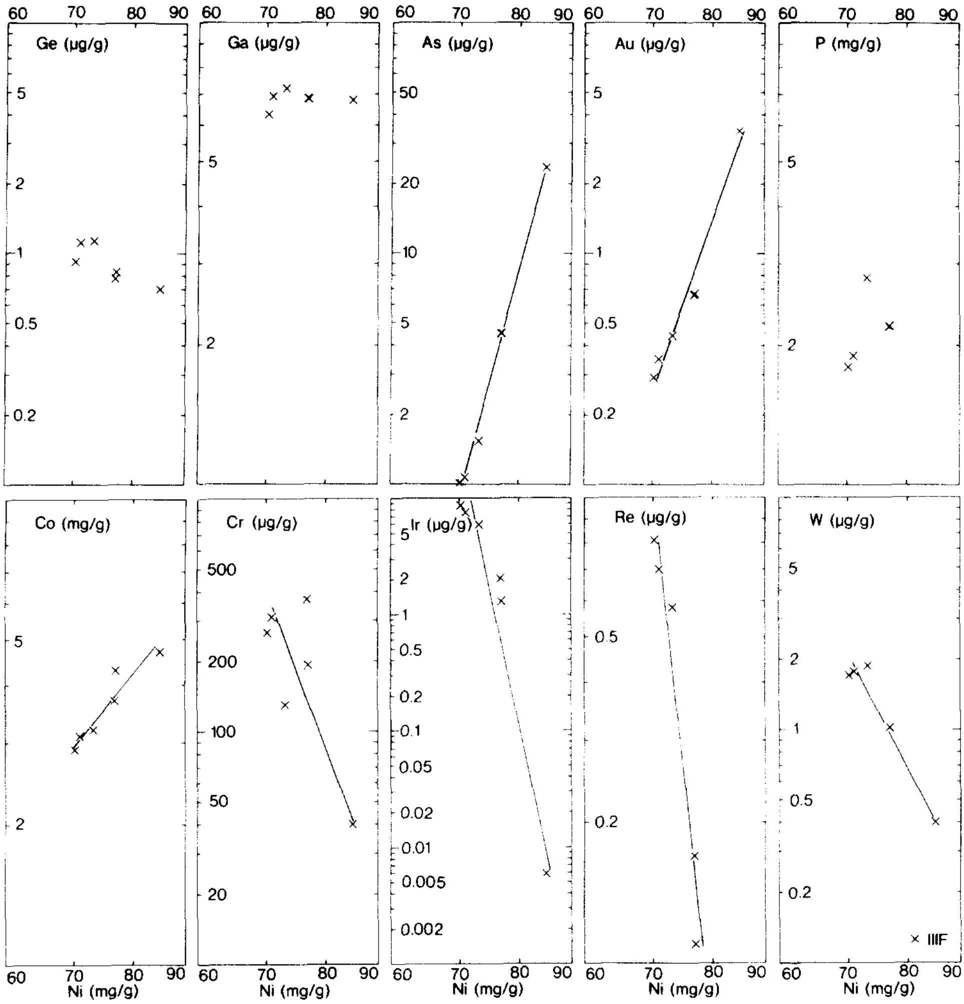

Fig. 3. Log–log plots of Ge, Ga, As, Au, P, Co, Cr, Ir, Re and W vs Ni for group IIIF. Linear regression lines based on the six members are shown for each plot. The new member, Klamath Falls, at 85 mg/g Ni, plots near extrapolations of linear regression lines calculated from data for the original five members.

Other groups

Of the meteorites listed in Table 1, 14 or 25% are members of group IIIAB, slightly fewer than the 33% expected from a random sample. Four belong to one of the established groups chemically, but are anomalous in one respect or another. IIICD-An Zaffra has an Ir content (61 ng/g) nearly 20× lower than that expected from the log Ir–log Ni correlation in the group; Co, Cu, Ga, Ge, As, Au, and W in Zaffra are in the typical IIICD range. Group IC is unusual: its members have large variations in structure, and three of the nine meteorites assigned to this group by SCOTT and WASSON (1976) have somewhat anomalous compositions requiring designation as IC-An. On element–Ni diagrams, two of the three IC-An irons have anomalously low Ge, and all three have anomalously high Ir contents. We now compound the confusion by our discovery of another IC-An iron; although Winburg's Ir content of 0.9 μg/g is lower than that of the other three, it is a factor of 10 higher than the value that would fit the Ir–Ni trend through the six normal members. IVA Millarville has a thoroughly reheated structure, reminiscent of IIIA Juromenha and IVA Smithland (BUCHWALD, 1975). IVA São João Nepomuceno contains silicates similar to Steinbach, and seems to be closely related to the latter (BILD, 1976).

Two meteorites, Mount Sir Charles and Yardea, were accidentally interchanged in the study by REED (1972), as acknowledged by a letter from Reed cited in BUCHWALD (1975). Yardea is a IAB coarse octahedrite, Mount Sir Charles is a IVA fine octahedrite whose structure has been nearly destroyed by reheating. Reed reported 8 μg/g Ga and Ge in Mount Sir Charles, much higher than our values. It appears that there can be serious blank or interference problems when the X-ray fluorescence technique that Reed used is pushed to such low Ga and Ge concentrations.

Ungrouped meteorites

Eleven meteorites in Table 1 do not belong to established groups. Such meteorites have previously been identified as anomalous, but since this term

Table 6. Composition of possibly related anomalous meteorites

	Cr (μg/g)	Co (mg/g)	Ni (mg/g)	Cu (μg/g)	Ga (μg/g)	Ge (μg/g)	As (μg/g)	W (μg/g)	Re (μg/g)	Ir (μg/g)	Au (μg/g)
Cruz del Aire*	84	5.6	90.0	264	38.2	187	10.9	2.2	0.68	5.9	1.15
Prambanan	50	7.0	101.4	236	28.3	190	7.5	0.61	0.38	4.2	0.95
Barbacena	56	6.0	109	198	12.8	1.16	11.5	2.84	0.48	2.9	1.92
Cambria*‡	†	5.7	101.7	177	11.1	1.52	19.0	†	†	0.88	2.33
Garden Head*‡	†	6.2	169.6	421	10.7	16.6	23.8	<0.25	†	0.12	2.61
Gay Gulch*‡	†	6.9	150.6	188	6.68	10.7	17.2	0.34	†	0.11	2.91
Kofa*‡	†	7.2	182.7	428	4.79	8.61	27.2	0.34	†	0.098	3.09
Linville	†	5.9	158.0	278	7.5	16.1	29.1	<0.12	†	0.012	2.90

* Ni, Ga, Ge and Ir from SCOTT and WASSON (1976) or WASSON (1974).
† Not determined.
‡ Only one value, twice usual error.

could be misinterpreted to infer that their history was somehow different from group members, we now prefer to call them ungrouped. Trace element content and origin of 7 of the ungrouped meteorites and of other iron meteorites with more than 10% Ni will be discussed more extensively by A. Kracher and others in a future manuscript; we limit our discussion here to classificational notes.

Petropavlovsk contains haxonite prompting BUCHWALD (1975) to guess that it belonged to group IAB. Our data show that it is very closely related to IIIAB and the minor, compositionally almost identical group IIIE. On element–Ni diagrams Petropavlovsk differs chiefly in terms of its Ge concentration, which is about 20% higher than expected in IIIAB, 25% higher than expected in IIIE. Since haxonite is not found in IIIAB members, we are tempted to designate Petropavlovsk IIIE-An. However, due to the discrepancy in Ge, we designate it ungrouped.

BILD (1977) has noted that Britstown contains IAB-type silicates, and concluded that it was a member of IB. Although it is almost certainly related, Ga, Ge, Sb, and Ir are too high for such an assignment. The problem cannot be solved by adjusting the Ni concentration, since Ga and Ge are negatively correlated with Ni, whereas Sb is positively correlated. The probability that the ataxite Yamato 75031 is related to IAB or IIICD is still smaller in our judgment, its Ge and W contents are about 2× higher than expected from element–Ni trends. Prambanan is closely related to Cruz del Aire (SCOTT and WASSON, 1976), forming a pair of ungrouped irons (Table 6). Another pair is Barbacena and Cambria, although the former does not share the high troilite content of the latter (Table 6). The low Ge/Ga ratios of both irons are unique among irons having Ge contents > 1 μg/g. Linville is in many respects related to the Garden Head–Gay Gulch–Kofa trio defined by WASSON and SCHAUDY (1971). However, our recent INAA data (Table 6) does not show the elemental correlations expected of either a magmatic or a nonmagmatic group. Not only do these four North American meteorites not form a quartet, it is not possible to pick out a closely related trio. The most closely related pair consists of Garden Head and Kofa, but their Ga and Ge contents differ by factors of 2.

Tishomingo is quite unique among irons having Ni contents >230 mg/g in that it is high in refractories (Re, 1.64 μg/g), and very depleted in volatiles (As, 0.52 μg/g; Au, 0.14 μg/g). Although its Ni content is nearly twice as high, its Ni-normalized trace element pattern is quite similar to group IVB suggesting a related origin. In keeping with the nearly cosmic Co/Ni ratio typical of group IVB and similar irons, Tishomingo has the highest Co content (12.6 mg/g) known in an iron meteorite.

Paired and unpaired meteorites

Three of the irons in Table 1 and 11 additional meteorites are believed to be paired with previously studied meteorites. The compositional evidence for these pairings is presented in Table 7 along with analyses of the meteorites with which they are paired.

The most interesting case of pairing involves the Morasko, Poland, IA iron that is associated with a small crater field, the largest having a diameter of about 100 m. The identification of the Morasko projectile as a IAB maintains a strict tradition; all 9 explosion craters having recognizable meteoritic residues were made by IAB and IIIAB irons (WASSON, 1974; BUCHWALD, 1975). Among the iron meteorites analyzed by us are only three IA irons having Ge contents >450 μg/g and Ir contents <2 μg/g: Morasko, Burgavli and Seeläsgen all of which have 505 ± 14 μg/g Ge and 1.1 ± 0.1 μg/g Ir. Burgavli was found in Siberia about 800 km from Morasko, and is surely an independent fall; Seeläsgen was found buried in a peat bog at a depth of 4 m, 104 km WSW of Morasko, and is the iron meteorite discovered closest to the Morasko site. The 100 km distance of separation is unusual for a single shower, but other examples are known (e.g. the Gibeon IVA and the Campo del Cielo IA showers).

We have analyzed 535 independent iron meteorites. Thus, the probability that an iron chosen at random would have the same composition as Morasko is 0.4–0.6% depending on whether or not Seeläsgen is independent of Morasko. Given such a low probability, we conclude that Seeläsgen is part of the Morasko shower.

The Seeläsgen mass weighed 100 kg, an amount that prehistoric man could have transported for some distance. Thus human transport is not out of the question although it appears that Seeläsgen was not associated with artifacts and a peat bog (or shallow lake) seems an unlikely point for humans to deposit it.

The Morasko crater field covers a very small area, only about 0.3 × 0.4 km in extent if only the seven well-defined

Table 7. Compositions of 13 irons which are probably not independent and the meteorites with which they are paired; and of 2 independent irons incorrectly thought to be paired

	Source¶	Co (mg/g)	Ni (mg/g)	Cu (μg/g)	Ga (μg/g)	Ge (μg/g)	As (μg/g)	W (μg/g)	Re (μg/g)	Ir (μg/g)	Au (μg/g)
PAIRED											
IA Canyon Diablo†		4.4	69.8	*	81.8	324	12.4	1.0	0.26	2.4	1.54
Mamaroneck	AMNH	4.7	68	136	80.4	*	12.2	1.1	0.16	2.4	1.44
Oildale‡	UNM	4.6	70.6	*	79.2	339	12.3	1.9	0.26	2.2	1.66
IA Odessa§		*	72.0	*	74.7	285	*	*	*	2.2	*
Honey Creek	LACM	5.0	*	178	79.7	*	17.3	1.1	0.34	2.2	1.83
IA Morasko		4.6	66.5	130	102	500	11.5	1.7	*	1.0	1.47
Seeläsgen§	—	4.8	64.7	152	96.8	493	10.8	1.8	*	1.1	1.55
IC Bendego†		4.7	63.9	*	54.0	234	6.0	1.8	*	0.21	0.76
Adon	UNM	4.8	64.7	150	54.5	249	5.7	1.6	*	0.20	0.81
IIA Pirapora		4.4	53.1	134	59.5	190	3.5	3.4	2.8	28	0.51
Angra dos Reis§	—	4.5	54.8	134	57.2	188	3.5	3.4	2.7	31	0.48
IIA Tocopilla§		4.4	55.4	135	58.6	176	4.6	2.6†	0.20	3.5	0.63
Yungay	TUD	4.6	57.4	124	57.0	174	4.6	2.5	0.20	3.2	0.65
IIB Santa Luzia§		5.2	63	105	47.9	110	12.2	*	*	0.010	1.36
Minas Gerais	UNM	5.1	58	104	45.8	111	11.6	0.36	*	0.010	1.23
IIIA Carthage§		5.4	82.4	153	21.5	43.7	6.8	0.84	*	0.64	0.96
Jackson County	—	5.5	92	181	21.0	46.7	6.9	0.62	*	0.66	0.86
IIIB Rancho Gomelia		5.7	97	132	16.3	28.7	20.6	0.43	*	0.012	2.13
Poscente	ASU	5.6	102	134	16.6	29.0	20.6	0.43	*	0.014	2.20
IIIB Tieraco Creek§		*	105	*	16.2	28.0	*	*	*	0.041	*
W. Australia	TUD	5.8	106	115	16.1	29.6	23.4	0.20	*	0.036	2.50
IVA Gibeon§		3.9	78.2	160	1.97	0.111	3.4	0.69	0.29	2.24	0.89
Elandsburg	TUD	3.9	77.6	141	2.18	*	3.9	0.61	0.27	2.12	0.92
Fransfontein	TUD	3.8	72.5	136	1.94	*	2.8	0.53	0.23	2.14	0.78
UNPAIRED											
Bolivia		4.8	66	140	88.0	377	10.7	1.34	0.17	2.22	1.52
Pooposo		4.5	69.8	204	27.8	325	12.1	1.00	0.30	2.8	1.54

* Not determined.
† Data from SCOTT (1977b).
‡ E. R. D. SCOTT (unpublished data).
§ Ni, Ga, Ge, and Ir data from SCOTT and WASSON (1976) or WASSON (1974).
¶Sources listed for new samples not listed in Table 1; abbreviations: LACM—Los Angeles County Museum of Natural History; TUD—Technical University of Denmark; others as in Table 1.

craters are considered and 0.4 × 1.4 km if a poorly defined eighth crater is included (POKRZYWNICKI, 1964). Considering the small area, the suggestions of WNW–ESE (seven craters) or NNE–SSW (eight craters) trending axes are probably not significant.

If Seeläsgen fell at its discovery location together with the much larger masses that formed the Morasko craters, the direction of flight must have been along a roughly WSW–ENE line connecting the two locations. This suggests that additional, possibly quite large, iron meteorites may still be discovered in this region in Southwestern Poland. KORPIKIEWICA (1978) suggested that the direction of flight was NNE → SSW based on the distribution of magnetic grains, but it appears more likely that these grains formed during the cratering events, and that their distribution relates to meteorological conditions immediately following the impacts. If human transport of Seeläsgen was not involved, the direction of flight was WSW → ENE.

It seems impractical to use Seeläsgen as the name for the numerous meteorites recovered from the Morasko crater field. We therefore suggest that the proper name for this meteorite is Morasko, though we realize that this will cause considerable problems throughout the museum community since Seeläsgen is such a well-publicized and widely distributed find. The recent decision to substitute Camp del Cielo for Otumpa provides a useful precedent.

Two specimens, Oildale and Mamaroneck, were structurally very similar to Canyon Diablo even though they were reportedly found at considerable distances from the Canyon Diablo site (Oildale from central California and Mamaroneck from New York). However, small fragments from the Canyon Diablo site are now ubiquitous, and are often accidentally or deliberately reported as new meteorites. These meteorites show the shock-hardened IAB textures characteristic of 'shrapnel' collected from the rim of Meteor Crater. Mamaroneck was provided to us by M. Prinz after submission to him as a new meteorite. It was reputedly found as two independent masses in a vacant lot in Mamaroneck, Westchester County, New York. According to the owner, its blackened exterior resulted from storage in a house that burned. The combination of this rather remarkable story, the typical Canyon Diablo shock-hardened IAB texture, and the INAA data reported in Table 7 appear to confirm its attribution to Canyon Diablo. BUCHWALD (1975) reported that the structure of the small iron, Oildale, in the University of New Mexico collection was typical of shocked Canyon Diablo specimens. Our compositional data support his assignment of the material to Canyon Diablo.

The Honey Creek, Texas, specimen was allegedly found in the 1930's by Ed Hesse, a surveyor for the state highway department in the stream bed at the creek's intersection with highway 71 in Llano County. The small size and the unlikely setting prompted our suspicions that it might be Odessa material. The data reported in Table 7 provide circumstantial evidence that it should join McCamey and Thoreau as meteorites paired with Odessa.

Among several specimens from Brazil were two that appear to be mislabelled. The Adon specimen is from the Coffee Museum in Ribeiro Preto, SP, but no information about the source or the discovery location of Minas Gerais could be found for us. Adon is identical in structure and composition to Bendego and Minas Gerais is similarly related to Sant Luzia. As a result we consider it probable that Adon and Minas Gerais are mislabelled fragments of these widely distributed meteorites.

A third Brazilian iron is alleged to have been found near Pirapora, Minas Gerais; the date of find is unknown. It was acquired by the Technicological Institute in Belo Horizonte, then donated to the National Museum in Rio De Janeiro (BUCHWALD, 1975). Buchwald suggested, based on structural similarities, that it was possibly related to Angra dos Reis (iron), a hexahedrite from Brazil with an unknown origin. Our chemical data show these irons to be identical. Since the date of fall for the Angra Dos Reis achondrite was erroneously assigned to the 6 kg iron in the Vatican collection (BUCHWALD, 1975), we suspect that the name was also erroneously assigned, we suggest using Pirapora as the official name even though its mass is smaller (2.6 kg). This name indicates the find location of the meteorite and also eliminates the unnecessary confusion resulting from having two meteorites named Angra Dos Reis. A third Brazilian hexahedrite, Patos De Minas, was considered potentially paired with Pirapora and Angra Dos Reis, but trace element data, most notably Ir (44 μg/g for Patos De Minas as compared to 30 μg/g for Angra Dos Reis), disprove this pairing. Four other Brazilian meteorites, Itapuranga, Itutinga, Sanclerlandia, and Verissimo have distinct chemical compositions and do not appear to be paired with each other or with any other Brazilian irons.

BUCHWALD and GRAFF-PETERSEN (1976) suggested that Yungay was paired with Tocopilla and that Elandsburg and Fransfontein were paired with Gibeon. Our chemical analyses support these findings. BUCHWALD (1975) also suggested that Jackson County is paired with Carthage. Our investigation was hampered because two independent samples of 'Carthage' obtained for INAA studies proved to be mislabelled, but INAA data on genuine Carthage now obtained (Table 7) confirm the pairing.

V. F. Buchwald provided us a part slice of an iron meteorite obtained by H. H. Nininger from Western Australia. Details concerning its find location had been lost but it was almost certainly a fragment of some other Australian iron meteorite. Chemical analysis showed it to be a IIIB compositionally indistinguishable from Tieraco Creek. BUCHWALD (private communication) finds the structure to be identical to that of Tieraco Creek, thus this appears to be the correct identification.

A more difficult problem developed regarding two supposedly independent irons from Durango, Mexico: Rancho Gomelia and Poscente. Both meteorites were obtained by Arizona State University from a broker who stated that Rancho Gomelia was found about 80 m N. of Durango, Poscente about 90 m W. of Durango. Although C. F. LEWIS (personal communication) believes them to represent independent finds on the basis of differing degrees of weathering, their compositions are indistinguishable. The probability that one person would within a brief period of time obtain by chance two independent falls so similar in composition is $\ll 1\%$. Furthermore, the possibility exists that both may be specimens of Bella Roca or Chupaderos; Bella Roca was found within about 100 km of the reported discovery location of Rancho Gomelia. We tentatively propose to call Rancho Gomelia, the larger and the first obtained by ASU, a new iron and suggest that Poscente is paired with Rancho Gomelia, but future work may show that neither is an independent meteorite.

BUCHWALD (1975) suggested that the IA irons Pooposo and Bolivia are paired. Our analyses (Table 7) indicate that they are independent meteorites.

Three other meteorites listed in Table 1 were suspected of being paired with known meteorites. The Carver meteorite was discovered in the Tuskegee Institute, Alabama, by La Paz, but its exact origin is unknown. The southeastern portion of the United States has yielded numerous hexahedrites; five were found within 400 km of Tuskegee. However, all six irons are chemically distinct and there is no reason to consider any to be fragments of another. Rica Aventura, a IVA iron from the nitrate mining region of Northern Chile, was found near the discovery locations of two other IVA irons, Mantos Blancos and Maria Elena (OLSEN and ZEITSCHEL, 1979). Again, all three are compositionally distinct and represent independent meteorites. The Santa Clara IVB iron was initially suspected to be paired with Tlacotepec. However, its Ir concentration is resolvably lower, and it was reportedly found about 800 km NW of the Tlacotepec discovery site. Santa Clara is very similar in composition to Weaver Mountains. Since they were found approximately 1000 km apart, there appears to be no grounds for suspecting a pairing.

ORIGIN OF HIGH Ge/Ga RATIOS IN IRON METEORITES

Group IIF is characterized by unusually high Ge/Ga ratios (atom ratios ranging from 10 to 16); mean composition of the group, estimated by WILLIS and WASSON (1980), shows that Ga is the only moderately volatile siderophile having a low abundance; As, Cu, Sb, and Ge abundances are in the range 0.7–$1.4 \times$ CI values. During the course of this study we discovered a meteorite Dehesa, with a much higher Ge/Ga ratio of 56. Three other irons, Butler, Emsland, and Mbosi and three anomalous pallasites also have ratios > 10 (Table 2). Ge/Ga ratios in these 9 meteorites range from 3.2–$18 \times$ CI-chondrite ratios. It is of interest to examine the processes that could have produced such fractionations. The 3 processes we consider are (1) fractionation during nebula condensation and agglomeration; (2) fractionation during the high-temperature separation of metal and silicate phases in the parent body; (3) fractionations as a result of volatility-related transport in the parent body.

Nebula fractionation processes

Nebular fractionations can be investigated by studying unequilibrated chondrites and by equilibrium calculations for the conditions believed present in the solar nebula. The behavior of Ga and Ge during gas–solid equilibrium processes during the cooling of the solar nebula have recently been investigated by WASSON and WAI (1976), KELLY and LARIMER (1977), WAI and WASSON (1977, 1980) and SEARS (1978). Under all investigated sets of nebular conditions, Ga condenses before Ge; as a result it does not appear possible to produce a condensate having a Ge/Ga ratio higher than the CI ratio by a model in which equilibrium is maintained down to a specified minimum temperature. We also know of no simple non-equilibrium model (e.g. that of BLANDER and KATZ, 1967) that can produce a high Ge/Ga ratio in the bulk condensate.

It is possible to achieve high Ge/Ga ratios in nebular metal. CHOU and COHEN (1973) analyzed magnetic (chiefly Fe–Ni) fractions of 5 unequilibrated (type-3) ordinary chondrites and found Ge/Ga atom ratios ≥ 18 in all 5, and roughly 100 in the magnetic fraction of 2 (L3 Hallingeberg and LL3 Parnallee). CHOU *et al.* (1976) analyzed a magnetic fraction of Allende that contained 321 mg/g Fe, 225 mg/g Ni, 3.88 μg/g Ga, 131 μg/g Ge and 32 μg/g Ir. This separate was obviously contaminated with non-metallic material, since Fe and Ni do not sum to approximately 990 mg/g as expected of meteoritic Fe–Ni. If we assume that the contamination had whole-rock Allende composition, we obtain a metal concentration of ~450 mg/g Ni, ~0.9 μg/g Ga, ~300 μg/g Ge and ~80 μg/g Ir (slightly revised from CHOU *et al.*, 1976). This yields a Ge/Ga atom ratio of about 300, but the uncertainty is large because the calculated Ga content of the metal is highly dependent on the assumed concentration of the contamination material. Bulk Ge/Ga in Allende and Hallingeberg and Parnallee chondrites are in the range 2.4–2.9, slightly *lower* than the CI ratio.

The explanation of the high Ge/Ga ratios in the metal of these chondrites is to be found in calculations by WASSON and WAI (1976; see WAI and WASSON, 1980, for improved calculations which, however, are consistent with the following conclusions), who point out that, although under equilibrium condition, Ga condenses as a solute in Fe–Ni, but at slightly lower temperatures the stable solid is $GaO_{1.5}$, dissolved in silicates. The same shift in solid stability occurs for Ge but at substantially lower temperatures. The indicated explanation is that Ga reached the oxidized equilibrium state whereas at lower temperatures diffusion was too limited to allow Ge to oxidize.

To summarize this section, there is no simple mechanism to produce a bulk nebular condensate having a high Ge/Ga ratio, but high ratios are found in the metal separated from unequilibrated chondrites, and are understandable in terms of nebular processes. As noted by WASSON and WAI (1976) and discussed in more detail below, the iron meteorite problem is not solved since much of the Ga should reenter the Fe–Ni at the temperatures required to form cores.

Geochemical behavior of Ga during core formation

Gallium is also more lithophile than Ge under planetary conditions; it appears that the Ga silicate/metal distribution ratio is always higher than that for Ge under the conditions prevailing in meteorite parent bodies. However, both elements become more siderophile with increasing temperature. The primary redox buffer in meteoritic systems is the Fe^{2+} : Fe couple. At the time of core formation the concentrations of Ga in oxidized and reduced forms is given by the reaction:

$$\mathrm{Ga_{Fe-Ni-S}} + 1.5\,\mathrm{Fe^{2+}_{sil}} = 1.5\,\mathrm{Fe_{Fe-Ni-S}} + \mathrm{Ga^{3+}_{sil}} \quad (1)$$

where both the Fe–Ni–S and silicate phases are assumed to be liquids. The equilibrium relationship is:

$$K = \frac{a^{1.5}(\mathrm{Fe})\cdot a(\mathrm{Ga^{3+}})}{a^{1.5}(\mathrm{Fe^{2+}})\cdot a(\mathrm{Ga})} \quad (2)$$

where a stands for activity. The chief problem with using eqn (2) involves assessing activity coefficients for the species of interest in silicate and Fe–Ni–S melts; in particular, the presence of S could dramatically affect the activity coefficients in the metallic melt.

If we assume that the activity coefficients, though unknown, are relatively independent of the composition of the parent body, it is useful to write the equation in terms of concentration, designated by c:

$$K' = K\,\frac{\gamma^{1.5}(\mathrm{Fe^{2+}})\cdot\gamma(\mathrm{Ga})}{\gamma^{1.5}(\mathrm{Fe})\cdot\gamma(\mathrm{Ga^{3+}})} = \frac{c^{1.5}(\mathrm{Fe})\cdot c(\mathrm{Ga^{3+}})}{c^{1.5}(\mathrm{Fe^{2+}})\cdot c(\mathrm{Ga})} \quad (3)$$

The ratio involving Ga can be separated out:

$$\frac{c(\mathrm{Ga^{3+}})}{c(\mathrm{Ga})} = K'\left[\frac{c(\mathrm{Fe^{2+}})}{c(\mathrm{Fe})}\right]^{1.5} \quad (4)$$

If the activity coefficient term in eqn (3) is approximately constant, eqn (4) shows that the silicate/metal distribution ratio involving Ga increases as the Fe distribution ratio to the 1.5 power. If we can infer the Ga ratio for a system in which the Fe ratio is known, it is trivial to calculate the effect of changing the Fe ratio.

WASSON and WAI (1976), WAI and WASSON (1980) and WILLIS and WASSON (1980) have emphasized the similarity in abundance ratio patterns between the H chondrites and IIIAB irons. Relative to other, less oxyphile, moderately volatile elements (e.g. Cu, As, Ge) the CI-normalized abundance of Ga is normal in IIIAB. This allows us to estimate that no more than 20% of the originally accreted Ga remained with the mantle during IIIAB core formation. If the parent body had H-group composition and all metal and FeS was extracted into the core, the core contained about 25% of the total mass. The Ga distribution ratio must have been ≤ 0.083 if $\leq 20\%$ of the Ga remained in the mantle. We have assumed that it was exactly 0.083 in our reference model, line IIIAB in Table 7, since the higher the value, the greater the fractionation of Ga from the more noble siderophiles. CHOU *et al.* (1973) measured the distribution of Ga between magnetically separated silicate and metal in H-group chondrites and found silicate/metal distribution ratios as low as 0.161 (in Butsura). Since this ratio was established at metamorphic temperatures, and Ga becomes more siderophile with increasing temperature, an upper limit of 0.083 at the temperature of core segregation seems reasonable.

In Table 8 we show three models obtained by a

Table 8. Comparison of the Ga concentration of cores having H-group contents of bulk Fe (276 mg/g), Ni (19 mg/g) and S (19 mg/g) but differing in degree of oxidation

Model	Core Ni (mg/g)	Core* (mg/g)	Fe^{2+}/Fe†	Ga^{3+}/Ga†	Core Ga	Core sider.	Ga/sider.
IIIAB	82	252	0.098	0.083	≡1.00	≡1.00	1.00
IIF	123	184	0.216	0.271	0.78	1.37	0.57
High-Ni	190	134	0.266	0.372	0.69	1.88	0.37

* Fraction of parent body.
†Ratios of the mass fractioned in the mantle to that in the core.

ratio of 0.083 during core formation in the IIIAB body; the key parameter is given in the last column, which shows how the ratio of Ga to a completely siderophile element (distribution ratio → 0) changes as the degree of oxidation increases in a body that initially had an H-group chondrite composition. Since Ge has non-negligible lithophilic tendencies, this ratio gives an upper limit of the Ga/Ge fractionation that can be produced under the assumed conditions. The Ga/siderophile ratio decreases by only a factor of 2.7 even when enough Fe has been oxidized to increase the Ni content of the metal in the core from 82 to 190 mg/g; the Ni content of the IIF core is 123 mg/g Ni (WILLIS and WASSON, 1980), indicating that it is an intermediate case. The model is greatly oversimplified (e.g. temperatures need not have been constant, and K varies with temperature; the activity term may show a rather strong compositional dependence; some of the more refractory minerals may not have melted, affecting both K and activity coefficients), and as a result the uncertainty in this factor of 2.7 is large. However, we have no reason to believe that the model is biased in a way to decrease the factor, and we tentatively conclude that equilibrium partition of Ga between molten silicates and metal is at best marginally able to explain the high Ge/Ga ratio in IIF, and inadequate to explain the still higher ratios in Butler or Dehesa.

A possible alternative is disequilibrium melting of metal in which a high Ge/Ga ratio was produced by nebular processes, as described above. For example, a massive impact event might segregate metal and silicates too rapidly for equilibrium to be achieved. This is admittedly speculative, but shock segregation on a small scale is well known, e.g. in the Bencubbin meteorite (KALLEMEYN *et al.*, 1978; NEWSOM and DRAKE, 1979).

Pneumatolytic transport within the parent body

Germanium and Ga behave as dispersed elements in the Earth's crust, Ge commonly substituting for Si and Ga for Al in the various minerals of these elements. However, substantial enrichments of both Ga and Ge are found in connection with certain pegmatites. For example, Ge/Si ratios in 'granitic pegmatites' average $\sim 5\times$ higher than those in granites and basalts (HÖRMANN, 1970); Ga/Al ratios in 'alkaline pegmatites' appear to average $\sim 4\times$ higher than those in granites (BURTON and CULKIN, 1972). It appears that Ga and Ge data are not available for the same pegmatites, but there is enough evidence for differences in geochemical behavior to support the inference that large (order of magnitude) differences in Ge/Ga ratios are sometimes produced by such processes. Given the right plumbing and suitable major gaseous species, pneumatogenic deposits having high Ge/Ga ratios could be produced in a meteorite parent body.

It seems well possible that a pneumatolytic process could produce a local enrichment in Ge that might lead to enrichments in small pockets of metal. It is very doubtful that a significant enrichment could be produced in a metallic body big enough to undergo fractional crystallization, e.g. in the core of the IIF parent body. However, such processes might be involved in producing the enrichments of several volatiles in Butler (Table 2), which has Ni normalized meteorite/CI-chondrite abundance ratios of 4.2 for Ge, 2.8 for Au, 1.8 for As but only 0.6 for Ga. Butler also has relatively high contents of refractories (W, Ir), thus its volatile enrichments relative to CI chondrites cannot be attributed to fractional crystallization.

Summary of the fractionation discussion

The simplest acceptable scenario of iron meteorite formation consists of (1) condensation in a cooling nebula; (2) alteration of condensed grains as a result of the dependence of equilibria on temperature; (3) incomplete equilibration at low ($\lesssim 1000$ K) temperatures because of kinetic constraints; (4) agglomeration of grains to form chondritic rocks; (5) accretion of chondritic materials to parent bodies; and (6) melting and differentiation of the parent body. Our brief consideration of steps 1–4 indicated that the chondritic materials were likely to have Ge/Ga ratios at or below the CI-chondrite ratio. We cannot exclude the possibility that our model is too simple; perhaps agglomeration and accretion were occurring simultaneously with condensation, and bodies differing systematically in composition formed sequentially. Later formed bodies could certainly have enhanced Ge/Ga ratios, but they should also have Ge/Ni ratios higher than the CI value. Since this is not observed in IIF, there is no basis for this more complex model.

Our calculations show that melting and phase segregation, the sixth process, can fractionate Ga from more noble elements such as Ge, but that if the equilibrium constant and the activity expression remain constant, the anticipated enhancement of the Ge/Ga ratio in the core is about 2× less than that observed in group IIF. It seems marginally possible that changes in the equilibrium constant and activity coefficients could produce the observed IIF fractionation, but doubtful that still higher ratios in Butler and Dehesa originated in this fashion. We speculate that disequilibrium melting may have allowed the (partial) preservation of high Ge/Ga ratios known to be present in the metal of L, LL and CV chondrites. Disequilibrium melting without appreciable fractional crystallization is hypothesized to explain the formation of groups IAB and IIICD (WASSON *et al.*, 1980).

Volatilization and redeposition processes may have led to enhancements of one or several volatiles in localized areas. Perhaps this could produce volatile-enriched meteorites such as Butler, but we doubt that enough material could be transported to significantly enrich the larger magma body that was parental to group IIF.

GENETIC TIES BETWEEN IIF AND OTHER GROUPS

We noted above that the close compositional relationship between IIF and the pallasitic Eagle Station trio probably reflects formation at closely related locations (as a guess, within $\ll 1$ AU of each other), though not in the same parent body. In turn, the O-isotope data of CLAYTON *et al.* (1976; 1978) show that the Eagle Station trio is closely related to the CV and CO chondrites. The high Ge/Ga ratio in the metal of the Allende chondrite (CHOU *et al.*, 1976) suggests another link with the irons and pallasites having high Ge/Ga ratios, although the value of this clue is limited because of the possible alteration of this ratio during planetary differentiation, as discussed above. On balance, the evidence favors the idea that the IIF irons originated at about the same distance from the sun as the CV or CO chondrites and the Eagle Station pallasites. WASSON (1977) and WASSON and WETHERILL (1979) summarize evidence indicating that the CO–CV chondrites originated in the outer solar system, distinctly farther from the sun than the ordinary and enstatite chondrites and IAB, IIE and IIIAB irons.

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