

## The Meteorite Component of Apollo 16 Noritic Impact Melt Breccias

RANDY L. KOROTEV

*Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, Missouri*

Noritic melt rocks (alias LKFM and VHA) from Apollo 16 have concentrations of Ni approximately three to five times those of impact melt rocks of similar composition from other lunar landing sites. The melt rock associated with Apollo 16 dimict breccias has the highest mean concentration of Ni of any lunar rock type (1150  $\mu\text{g/g}$  in 11 samples). The Ni is contained in Fe-Ni metal that is dissimilar in composition to metal from ordinary chondrites in having a lower Ni concentration (6%) and lower Ni/Co ratio (17). It also has Ir/Ni and Ir/Au ratios of about one-half and one-third those of chondrites. The metal in the noritic impact melts is the carrier of the siderophile element signature of ancient meteorite group 1H. The composition of the Fe-Ni metal is dissimilar to that of chondrites because it derives from metal-rich meteorites, probably irons, that created the impact melts 3.9 Ga ago. The metal from these iron meteorites dominates the siderophile element concentrations of polymict samples at Apollo 16. Models that attempt to estimate indigenous concentrations of Ni and Co in Apollo 16 materials overestimate their abundance by assuming that the meteoritic component has chondritic ratios of Ir to Ni and Co. The type-2 melt (VHA) associated with the dimict breccias and the type-1 melt (Apollo 16 LKFM) were most likely produced by impact of two related iron meteoroids that impacted near the Apollo 16 site. The type-2 melt found in samples from station 7 is probably from the same impact as that producing the dimict breccias, although it could represent the impact of a third, related iron.

### INTRODUCTION

Impact melt breccias (crystalline melt breccias) are the most common type of rock returned from the lunar highlands [Stöffler *et al.*, 1980]. These rocks are believed to have crystallized from melt produced during impact of meteoroids with the lunar surface during the late accretion of the moon about 3.9 Ga ago. Bulk compositions of impact melt breccias are highly variable, with  $\text{Al}_2\text{O}_3$  concentrations ranging from about 17% to over 30%. Melt rocks with  $\text{Al}_2\text{O}_3$  concentrations at the low end of this range, 17–22%, are particularly common and are often called LKFM (for “low-K Fra Mauro basalt”; see Reid *et al.*, [1977]). LKFM melt rocks occur at four of the Apollo landing sites (e.g., samples 14310, 15455, 60315, 77135; Reid *et al.* [1977]; Vaniman and Papike [1980], *Basaltic Volcanism Study Project* [1981]). Because the term LKFM has several different connotations [Korotev, 1987a], I will refer to melt breccias with 17–22%  $\text{Al}_2\text{O}_3$  as “noritic (impact) melt breccias” since the normative composition of such breccias overlaps the fields for norite, anorthositic norite, and olivine norite in the classification of Stöffler *et al.*, [1980].

Most noritic melt breccias contain high concentrations of siderophile elements such as Ni, Ir, and Au compared to lunar rocks thought to be uncontaminated with meteoritic material, and this is one argument against their volcanic origin [e.g., Vaniman and Papike, 1980]. In this paper I will show that (1) noritic impact melt breccias from Apollo 16 contain greater concentrations of siderophile elements than noritic melt breccias from other landing sites, (2) the high concentrations of siderophile elements result because the breccias contain a large amount of Fe-Ni metal, (3) the Fe-Ni metal is the carrier of the chemical signature of ancient meteorite group 1H of Hertogen *et al.* [1977], and (4) the bulk composition of the Fe-Ni metal is dissimilar to metal found in ordinary chondrites but is similar to that found in some iron meteorites. I also

argue that (5) the dissimilarity between the composition of the Fe-Ni metal in the noritic melt breccias and that in ordinary chondrites cannot result from reaction of chondritic metal with lunar silicates, (6) the similarity between the composition of the metal in the noritic melt breccias and in some iron meteorites along with the unusually large quantity of metal in the breccias suggests that the meteorites that produced the impact melts were irons, and (7) the erroneous assumption by Delano and Ringwood [1978a,b] and Wänke *et al.* [1978, 1979] that the meteorite component of the Apollo 16 breccias has chondritic ratios of Ni/Co and Ni/Ir leads to overestimation of the abundance of “indigenous” Ni in the lunar highlands.

### IDENTIFICATION OF THE METEORITIC COMPONENT

#### *Types of Apollo 16 Noritic Impact Melts*

Discussion of melt breccias from Apollo 16 is hampered by the variety of petrographic and textural names that have been applied to them. At Apollo 16, noritic melt breccias (17–22%  $\text{Al}_2\text{O}_3$ ) are usually assigned to one of two types. Type-1 melt breccias (i.e., the group-1 melt of Floran *et al.* [1976] and McKinley *et al.* [1984]) have the highest concentrations of incompatible trace elements (ITEs) among common Apollo rock types, approximately half as great as those in KREEP. They are usually poikilitic in texture and contain <20%  $\text{Al}_2\text{O}_3$ . Type-1 melt breccias are also known as “Apollo 16 KREEP” and “Apollo 16 LKFM.” Because samples assigned to this type are all so similar in composition, they are usually regarded as being samples of the same melt sheet [e.g., Floran *et al.*, 1976]. Type-2 melt breccias (i.e., the group-2 melt of Floran *et al.* [1976] and McKinley *et al.* [1984]) have a wide range in concentrations of ITEs and  $\text{Al}_2\text{O}_3$  (20–27%) suggesting that this type includes samples from several different melt sheets [Ryder, 1981; Ryder and Seymour, 1982; James *et al.*, 1984]. Type-2 melt breccias are also called “VHA” for very high alumina basalt [Hubbard *et al.*, 1973] or low- $\text{Al}_2\text{O}_3$  basaltic impact melts [Ryder, 1981]. (“Type 1” and “type 2” are used here instead of “group 1” and “group 2” to prevent confusion with meteorite groups to be discussed later.)

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TABLE 1. Data Set for Melt Rock Portions of Apollo 16 Dimict Breccias

Sample	<i>McKinley et al. (1984)</i>					<i>James et al. (1984)</i>					
	64559	64537	65757	64546	64475	61015	61015	61015	61015	61015	61015
Subsplit:	5	21	6	5	53	21M	21FM	28M	32M	100M	121FM
<i>Siderophile</i>											
FeO	9.4	9.5	11.2	8.3	8.0	8.94	7.87	6.90	7.93	7.98	6.89
Ni	1560	1725	2520	1140	1080	1420	877	342	860	750	330
Co	94	97	147	68	65	88.0	59.8	22.9	53.4	49.2	23.2
Ir	42	43	65	25	30	30	17	5.2	17	19	6.6
Au	36	38	52	25	30	n.r.	n.r.	n.r.	n.r.	11	5.7
<i>Lithophile</i>											
Al <sub>2</sub> O <sub>3</sub>	20.7	20.2	20.1	21.3	21.2	20.5	22.1	21.2	20.5	21.3	21.9
MgO	11.6	11.1	10.9	10.8	11.1	11.8	11.0	11.7	11.1	11.5	11.7
CaO	12.1	12.0	12.2	12.5	13.3	11.6	12.2	12.0	11.9	11.7	11.6
Sc	11.3	11.3	11.6	10.7	10.6	10.82	10.62	10.80	10.85	11.62	11.20
Cr	1185	1155	1210	1115	1115	1092	1056	1108	1094	1100	1070
Mn	660	645	650	665	635	667	666	661	658	716	678
Ba	300	325	310	300	290	290	285	290	290	270	260
La	29.2	29.0	29.2	27.8	27.8	26.6	26.3	26.9	27.4	28.9	27.1
Sm	13.8	13.7	13.8	12.8	13.2	13.01	12.52	12.86	12.91	12.87	12.53
Yb	8.96	8.87	8.83	8.40	8.37	8.68	8.40	8.65	8.73	8.75	8.50
Lu	1.31	1.29	1.30	1.23	1.21	1.30	1.24	1.29	1.31	1.38	1.31
Hf	9.3	9.4	9.7	8.9	8.6	10.05	9.60	9.98	10.10	10.4	10.1
mass	80.	91.	88.	88.	53.	65.	122.	125.	100.	72.	32.
(mg)											

n.r. = not reported. Oxides values are in weight %, Ir and Au values are in ng/g, and all other values are in  $\mu\text{g/g}$ . Cr and Mn values of *McKinley et al.* [1984] have been converted from percent oxide. Some values of *James et al.* [1984] have been changed: All MgO and Mn values have been multiplied by 0.921 and 0.959, respectively, to correct for a recent restandardization of the Mg and Mn standard, and all concentration values for 61015,21FM have been multiplied by 0.918 to correct for an error in sample mass (M. M. Lindstrom, personal communication, 1986).

However, among samples of type-2 melt are two subgroups, each composed of samples with very similar compositions. One of these is the melt rock associated with the dimict breccias (type-2 DB); the other is the melt rock found as rake samples and as clasts in feldspathic fragmental breccias from the North Ray Crater area (type-2 NRC). Both the type-2 DB and NRC melts are at the low-Al (i.e., noritic) extreme of the range of type-2 melt breccias and are very similar to each other in both bulk and trace element composition [*James et al.*, 1984]. Their major element compositions also nearly overlap with that of the type-1 melt breccias, although concentrations of ITEs are only about half as great. Nearly every sample of noritic impact melt breccia at Apollo 16 is of one of these three types (type-2 DB, type-2 NRC, and type-1 melt breccias). All three types share another important characteristic, namely, variable concentrations of siderophile elements among different small samples, but high mean concentrations. In this section I assume that the siderophile elements in these impact melt breccias derive primarily from the impactor that caused the melting and that their relative concentrations are not significantly different from those of the impactor. Other possibilities will be discussed later. The discussion will concentrate initially on the samples of melt rock from dimict breccias, because these samples are almost certainly samples of the same melt and because the data set is best for these samples. The variation in siderophile element abundances will be used to imply the nature of the meteoritic component of the dimict breccias. Later, the other two types of noritic impact melt breccias will be discussed and the similarities and differences noted.

#### *Dimict Breccia Melt*

The dimict breccias found at Apollo 16 are so named because they consist of two lithologies: ferroan anorthosite and impact

melt rock. The dimict breccias "were probably produced during formation of a large impact crater, by injection of VHA impact melt into anorthositic bedrock lining the walls and floor of the expanding crater cavity [*Stöffler et al.*, 1979; *James*, 1981]" [*James et al.*, 1984]. The crater is estimated to be 50–150 km in diameter and within a few hundred kilometers of the Apollo 16 site [*James et al.*, 1984]. Recent  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  age dating of the melt portion of dimict breccia 61015 yields an age of about 3.9 Ga [*Marvin et al.*, 1987]. This age is typical of other types of impact melt breccia from Apollo 16 as well as those from other landing sites [e.g., *Reimold et al.*, 1985].

Melt produced by a single impact usually has the average composition of that for the target materials and is relatively uniform in composition [e.g., *Dence*, 1971; *Grieve*, 1975; *Floran et al.*, 1978]. Two recent sets of compositional data on the melt portion of dimict breccias provide an excellent opportunity to examine compositional variation within the melt and to study effects not evident in data from a single sample. These are data on five rake samples from stations 4 and 5 by *McKinley et al.* [1984] and six subsplits of 61015 by *James et al.* [1984]. For reference, Table 1 contains selected data for these 11 samples.

Although concentrations of lithophile elements are very similar among the 11 samples in Table 1, concentrations of Ni and the other siderophile elements are highly variable from sample to sample; Ni concentrations range from 330 to 2520  $\mu\text{g/g}$  with a mean of 1150  $\mu\text{g/g}$ . This is the greatest average Ni concentration of any rock type returned from the moon. Figure 1 shows the variation in the concentrations of other siderophile elements (Fe, Co, Ir, and Au) with that of Ni for the 11 samples of dimict breccia melt. A strong positive correlation with Ni is obtained for each of the elements and the best-fit regression lines are indicated (solid lines). These best-fit lines represent mixing lines between two components of the melt, one of which is relatively poor in siderophile elements

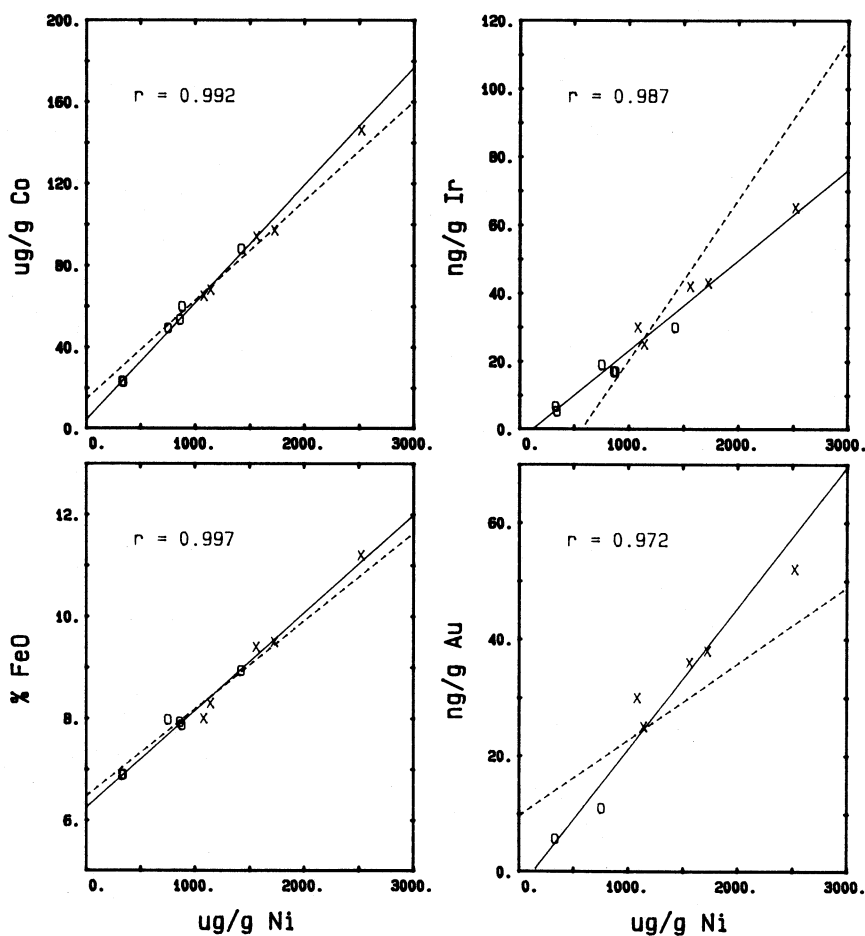


Fig. 1. Variation of siderophile elements with Ni in the melt rock portion of Apollo 16 dimict breccias. Data are from James *et al.* [1984] (o) and McKinley *et al.* [1984] (x) (see Table 1). The solid line is the best-fit line through all the data. The dashed line represents addition or subtraction of a chondritic meteorite (H-group) to or from the mean composition of the 11 samples; the corresponding line for a carbonaceous chondrite would be insignificantly different. All best-fit lines illustrated here were determined by the method of York [1969] using the square of the inverse of 10% of the concentration value as the weighting factor. (Identical results are obtained for any constant percentage.) In this way samples with small and large amounts of metal equally influence the slope of the line. The Ni intercepts of the Ir and Au variations are  $120 \pm 60 \mu\text{g/g}$  and  $130 \pm 150 \mu\text{g/g}$ , respectively, suggesting that the indigenous concentration of Ni does not exceed about  $120 \mu\text{g/g}$  in the melt. (All uncertainties stated in the text, tables, and figures are two standard deviations based on the regression analyses.)

and another, which I shall temporarily call the "Ni-rich" component, that is significantly richer. I will show, as others have [e.g., Palme, 1980; Morris *et al.*, 1986; Korotev, 1987b], that the Ni-rich end member is best explained by an extralunar component and will use the interelement variations to characterize it more specifically.

*Fe-Ni metal or carbonaceous chondrite?* During the sawing and processing of dimict breccia 61015 [James *et al.*, 1984], a large amount of metal "fell out" onto the floor of the processing cabinet (O. B. James, personal communication, 1986). Fe-Ni metal containing about 5–7% Ni is a common component of Apollo 16 breccias and soils [Brecher *et al.*, 1973; Nagata *et al.*, 1973; Pearce *et al.*, 1973; Goldstein and Axon, 1973; Reed and Taylor, 1974; Misra and Taylor, 1975; Hewins *et al.*, 1976]. Wänke *et al.* [1978] state that most of the siderophile elements in lunar highlands breccias reside in grains of metal. Hence the Ni-rich component might be Fe-Ni metal and the variation in siderophile element concentrations in Figure 1 may well represent "sampling error" resulting from variation among the small samples (32–122 mg, Table 1) in the number of grains of Fe-Ni metal rich in siderophile elements.

Alternatively, there is much evidence that the Apollo 16 regolith contains a significant (1–2%) component of carbonaceous chondrite derived from micrometeorites [Baedecker *et al.*, 1972; Anders *et al.*, 1973; Ganapathy *et al.*, 1973; Wasson *et al.*, 1975b; Korotev, 1987b]. Korotev [1983] reported on 1–2 mm particles from soil 65502 containing as much as 77% carbonaceous chondrite. Morris *et al.* [1986] show that the composition of the meteoritic component of impact melt splashes (glasses) from Apollo 16 is consistent with that of carbonaceous chondrite, but not with that of Fe-Ni metal. Hence the Ni-rich component implied by Figure 1 might also be carbonaceous chondrite. This is the implicit assumption in many chemical mixing and mass-balance models that use a component of carbonaceous chondrite to account for the high concentrations of Ni and other siderophile elements in the soils and rocks [Goles *et al.*, 1971; Schonfeld and Meyer, 1972; Fruchter *et al.*, 1973; Duncan *et al.*, 1975; Korotev, 1976; Delano and Ringwood, 1978a,b; Wänke *et al.*, 1978, 1979; Palme, 1980; Korotev *et al.*, 1980; Morris *et al.*, 1986]. As these two models are the ones most commonly invoked, we must first determine whether the Ni-rich component causing the variations in Figure 1 is

more consistent with being Fe-Ni metal or carbonaceous chondrite.

A strong argument against a chondritic component, carbonaceous or ordinary, is that the variations in Figure 1 cannot be caused by simple addition of a component with chondritic ratios of Ir and Au to Ni to a material poor in siderophile elements. In Figure 1, the dashed lines represent the mixing lines obtained by adding or subtracting a chondritic component to or from the mean composition of the dimict breccia melt. If the Ni-rich component were chondritic, then these lines would be coincident with the best fit lines. Figure 1 shows that the Ni-rich component of the dimict breccias has an Ir/Ni ratio that is significantly less than and an Au/Ni ratio that is significantly greater than the corresponding chondritic ratios, indicating that a chondritic component cannot cause the variation. This does not necessarily mean that the bulk meteoritic component of the breccias is not chondritic; it only means that the Ni-rich component causing the variations in Figure 1 is not a component with chondritic ratios of siderophile elements. That is, some process acting on a chondritic component would have to have produced a new component with the Ir/Ni and Au/Ni ratios significantly altered from their chondritic values, and only this new component is variable in the samples.

However, the dissimilarity of siderophile element ratios (particularly the Ir/Au ratio) in bulk analyses of Apollo 16 rocks and soil to those in carbonaceous chondrites has been noted many times and is usually attributed to an "ancient" or "short-lived" meteorite component that is not any type of chondrite [e.g., *Anders, 1973; Hertogen et al., 1977; Wasson et al., 1975a,b*]. These "ancient" meteorites are believed to be those associated with the late accretion of the moon, an idea that is consistent with the age of noritic impact melt breccias (3.9 Ga). In some mixing models for Apollo 16 rocks and soil, this ancient meteoritic component is assumed to have concentrations of lithophile elements and Ni like those of CI chondrites, but concentrations of trace siderophile elements like those implied for the ancient component [*Boynton et al., 1975; Chou et al., 1975; Wasson et al., 1977*]. However, even a component such as this cannot account for the dimict breccia data. As noted by *Morris et al. [1986]*, concentrations of some lithophile elements (e.g., Cr) are sufficiently large in carbonaceous chondrites (CC) compared to Apollo 16 material that variation in the amount of a CC component (or a component such as that used by *Boynton et al. [1975]* with a chondritic Cr/Ni ratio) would lead to a noticeable correlation of the element with Ni. Figure 2 is a plot of concentrations of various lithophile elements against those of Ni for the data in Table 1. If the variation in Ni concentration is entirely the consequence of variation in the amount of a CC-like component, then the 0–3000  $\mu\text{g/g}$  range in Ni concentration in Figure 2 represents a 0–25% range in the CC component (CI composition) and the correlation of, for example, Cr with Ni should be evident.

A complication in evaluating such correlations in the dimict breccia data is that there appears to be a slight interlaboratory bias between the two data sets for some elements. In addition, the mean Ni concentration of the five samples analyzed by *McKinley et al. [1984]* ( $1605 \pm 580 \mu\text{g/g}$ ) is greater than that of the six samples analyzed by *James et al. [1984]* ( $763 \pm 405 \mu\text{g/g}$ ). The difference (which is significant at the 95% confidence level, but not at 99%) is presumably the result of the extremely nonuniform distribution of the Ni-rich component among small samples of the melt. Because of the large difference in the means, the slope of any line using all 11 points may be determined

in part by the interlaboratory bias. If, for example, all five samples of *McKinley et al. [1984]* were determined to have exactly 10.0  $\mu\text{g/g}$  of element X and the six samples of *James et al. [1984]* were determined to have 10.1  $\mu\text{g/g}$ , and the 1% difference was entirely the result of interlaboratory bias, then the slope of the best-fit line through all 11 points would indicate a 1.7% decrease in the concentration of element X across the 3000  $\mu\text{g/g}$  range of Figure 2 when, in fact, there was no actual difference among the samples. Although 1.7% is a small error, it is approximately the magnitude of the effect of mixing of the Ni-rich component for some elements; thus the potential error from interlaboratory bias can significantly affect the interpretation of the data. In an attempt to make an objective correction for the effect of any interlaboratory bias, each of the two sets of data in Figure 2 was normalized by the procedure described in Table 2. The normalized data are replotted in Figure 3 and the solid line is the best-fit line to that data.

The dashed line in Figure 3 corresponds to addition or subtraction from the mean composition of the dimict breccias of a chondritic component. If the variation in Ni concentration results from variable amounts of a chondritic component, then the dashed line should be coincident with the solid line. The most useful elements should be Mg, Cr, and Mn, because concentrations of these elements are 2–3 times greater in chondrites than in dimict breccias and should increase with increasing Ni abundance if the Ni-rich component is chondritic. For Mg and Mn the concentrations do not increase and are, in fact, nearly invariant with increasing Ni concentration. Hence the data are not consistent with a component of carbonaceous chondrite or any other component with chondritic (Mg or Mn)/Ni ratios. The data are ambiguous for Cr because Cr concentrations are nearly invariant in the data set of *James et al. [1984]* (Figure 2) but increase with increasing Ni concentration in the data of *McKinley et al. [1984]*, although the increase is not enough to be caused by a chondritic component. This apparent increase is probably an analytical problem resulting from the proximity of the 320.3 keV gamma-ray peak of  $^{51}\text{Cr}$  to the 316.5 keV peak of  $^{192}\text{Ir}$ , i.e., increasing Ir concentration (Figure 1) leads to an apparent increase in Cr concentration. (For purposes of an argument to be made later, the chondrite mixing lines in Figure 3 are actually those for H-group chondrites, not CI chondrites, but the ratios of Mn, Cr, Mg, or any of the other elements to Ni are not significantly different between the two chondrite types.)

For comparison, a third line (dotted) is drawn on Figure 3 indicating the effect of variation in the amount of a component of Fe-Ni metal containing 6% Ni. The 0–3000  $\mu\text{g/g}$  range in Ni concentration of Figure 3 corresponds to a range of 0–5% in the abundance of the Fe-Ni metal component and the negative slope of the dotted lines represents the decrease in the concentration of lithophile elements resulting from the effect of 5% dilution. For elements primarily associated with major mineral phases (Al, Ca, Mg, Sc, Cr, and Mn), the metal-dilution model (dotted line) fits the data well (except for Cr, as already discussed). Hence from this analysis, the Ni-rich component inferred by Figures 1–3 is consistent with Fe-Ni metal but is not consistent with any component that has, for example, Al/Ni or Mg/Ni ratios as high as those in carbonaceous or ordinary chondrites.

However, trends for the ITEs are not consistent in a simple way with either model. The concentrations of the incompatible trace elements (Ba, La, Sm, Yb, Lu, and Hf) all increase slightly with increasing Ni concentration in Figure 3. This increase cannot

TABLE 2. Normalization Factors Applied to Data of Table 1 for Plotting in Figure 3

Element	F <sub>J</sub>	F <sub>M</sub>	Element	F <sub>J</sub>	F <sub>M</sub>
Al <sub>2</sub> O <sub>3</sub>	1.004	0.994	Ba	1.021	0.982
CaO	1.039	0.972	La	1.007	0.979
MgO	0.987	1.014	Sm	1.006	0.981
Sc	0.981	0.984	Yb	0.988	1.000
Cr	1.001	0.966	Lu	0.970	1.012
Mn	0.983	1.014	Hf	0.934	1.048

The following procedure was used to attempt to correct for the effect of any interlaboratory bias in the data of Table 1 (see text). Step 1: For each element X, regression lines were calculated from each of the two data sets independently (Figure 2). Ideally, these two lines should be parallel within their uncertainties and the offset in intercept would represent the interlaboratory bias. In reality there is also the effect of intralaboratory analytical uncertainty. Step 2: A new line was calculated by averaging the two slopes and intercepts of Step 1. Step 3: A value L was obtained by calculating the concentration of element X at the mean Ni concentration of the six samples of *James et al.* [1984] (763  $\mu\text{g/g}$ ) using the line obtained in Step 2. Step 4: The normalization factor F<sub>J</sub> was calculated by dividing L by the mean reported concentration of element X in the samples of *James et al.* [1984]. Step 5: All concentration values for element X from *James et al.* [1984] were multiplied by F<sub>J</sub>. Steps 3, 4, and 5 were then repeated for the data of *McKinley et al.* [1984] to yield factor F<sub>M</sub>. Step 6: The regression analysis was repeated on the normalized data. The normalized data from Step 5 and the lines obtained in Step 6 are plotted in Figure 3 as a solid line. (The line obtained in Step 5 is virtually identical to that obtained in Step 2). This procedure was applied only to the lithophile elements.

be caused by simple addition of any type of primitive meteoritic material because chondrites do not have higher concentrations of ITEs than do the dimict breccias. However, it does not necessarily eliminate the metal-dilution model, because each of these elements is associated with KREEP, which is highly variable as a component among lunar highlands breccias; i.e., the data can still be explained by variation in Fe-Ni metal if a third component is included. The increase in concentrations of ITEs with that of Ni is very slight and corresponds to an increase of only  $0.8 \pm 0.3\%$  KREEP per 1000  $\mu\text{g/g}$  Ni for the six elements. This explanation requires either that an unknown process cause the KREEP component of the melt to correlate weakly with the Fe-Ni metal component or that the correlation be accidental. Except for Ba, the increase in ITE concentrations with Ni is strongest in the rake samples of *McKinley et al.* [1984]; slopes obtained only from the subsamples of 61015 of *James et al.* [1984] for La, Yb, Lu, and Hf are within one standard deviation and those for Ba and Sm are within two standard deviations of being consistent with the metal-dilution model (Figure 2). (Uncertainties in the slopes of the data of *James et al.* [1984] are large, however, in part because of the narrow range in Ni concentrations.) Hence the six 61015 samples of *James et al.* [1984] are consistent with the metal-dilution model for both major and trace elements. Perhaps the most metal-rich samples of *McKinley et al.* [1984] come from a region of the melt with a slightly greater KREEP component.

The preceding discussion has shown that the variations in the concentration of Ni and other siderophile elements in the dimict breccia melt are not consistent with variation in the quantity of a component with the bulk composition of a chondritic meteorite, as is the case for glass samples of impact melt splashes at Apollo 16 [*Morris et al.*, 1986]. Instead, they are consistent with variation among the samples in the amount of an Fe-Ni metal component rich in siderophile elements. This is reasonable because, for impact melt like that in the dimict

breccias, it is difficult to imagine how the silicate target material could be so efficiently homogenized, yet a predominantly silicate projectile be distributed in the melt so nonuniformly if in fact the siderophile elements derive from the projectile causing the melt and the projectile were a carbonaceous chondrite. The large variation in siderophile element concentrations is much more easily explained by an immiscible metallic phase that is nonuniformly distributed in small subsamples of the melt. For the remaining discussion, it will be assumed that the variation in siderophile element abundances among the samples results only from variation in the amount of a metal phase and, consequently, that the impacting meteorite contained a large amount of Fe-Ni metal.

*Composition of the Fe-Ni metal.* The best-fit lines drawn in Figure 1 allow calculation of the mean composition of the Fe-Ni metal phase. The solid lines are mixing lines between the silicate and metal portions of the melt. Consequently, the composition of the metal phase responsible for the variation must lie on the extrapolation of the mixing lines to high Ni concentrations. If the metal is assumed to be composed entirely of Fe, Ni, and Co, then there is a unique composition such that the sum of the Fe, Ni, and Co concentrations equals 100% and the ratios of Co and Fe to Ni are such to account for the variation in Figure 1. This composition is listed in Table 3. The correlation technique used here is basically the same as that used by *Palme* [1980]. The advantage to the technique is that no assumption need be made about the concentrations of any element in the nonmetal (primarily silicate) phase. The composition in Table 3 is the only one that can account simultaneously for all the variations observed in Figure 1. The siderophile element concentrations in the silicate portion of the

TABLE 3. Concentrations and Element Ratios in the Metal Component

	DB		60601		65015 Emsland	
	mean	$\pm 2s$	a	b		
<i>Concentrations</i>						
Fe (%)	93.7	-	93.6	93.2	n.a.	n.a.
Ni (%)	6.0	-	6.1	6.0	5.67	9.40
Co (%)	0.34	-	0.36	0.40	n.a.	n.a.
Ga ( $\mu\text{g/g}$ )	n.a.	-	n.a.	n.a.	1.07	2.90
Ge ( $\mu\text{g/g}$ )	n.a.	-	n.a.	n.a.	37.8	35.0
Ir ( $\mu\text{g/g}$ )	1.57	-	1.64	1.45	0.99	2.9
Au ( $\mu\text{g/g}$ )	1.44	-	1.30	1.20	1.07	n.a.
<i>Ratios</i>						
Fe/Ni (g/g)	15.7	1.4	15.3	15.5	n.a.	n.a.
Ni/Co (g/g)	17.3	0.8	16.9	15.0	n.a.	n.a.
Ir/Ni ( $\mu\text{g/g}$ )	26.	3.	27.	24.	17.5	30.9
Au/Ni ( $\mu\text{g/g}$ )	24.	5.	21.	20.	18.9	n.a.
Ir/Au (g/g)	1.2	0.3	1.26	1.21	0.93	n.a.

n.a. = not analyzed. Concentrations and element ratios in the metal component causing siderophile element variations in the melt portion of Apollo 16 dimict breccias and comparison to metal grains from soil 60601 [*Wlotzka et al.*, 1973], a metal sphere from melt breccia 65015 [*Wasson et al.*, 1975a], and the anomalous iron meteorite Emsland [*Scott et al.*, 1973]. Concentrations of dimict breccia (DB) metal were calculated from the regression lines of Figure 1 assuming the sum of the Fe, Ni, and Co concentrations to be 100%. Uncertainties in the ratios are two standard deviations based on the slope obtained from the regression analysis. The Ir/Au ratio is not based on a regression, but is a mean of the ratios of concentrations in Table 1 weighted according to analytical uncertainty. Data of *Wlotzka et al.* [1973] are for (a) many fine grains weighing 0.2 mg, and (b) a single 1 mg grain. The metal sphere reported by *Wasson et al.* [1975a] weighed about 8 mg. Impact melt breccia 65015 is a type-1 breccia.

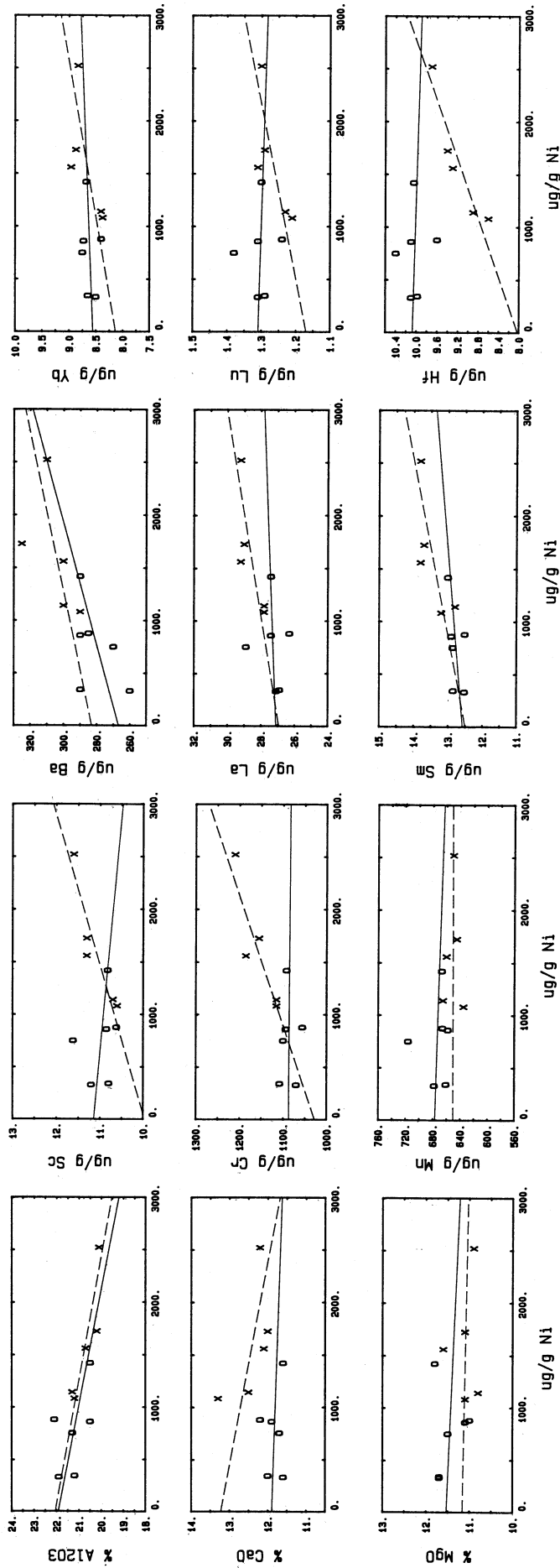


Fig. 2. Variation of some lithophile elements with Ni in the melt rock portion of Apollo 16 dimict breccias. The solid line is the best-fit line to the data of James *et al.* [1984] (o), and the broken line is the best-fit line to the data of McKinley *et al.* [1984] (x) (see Table I and Figure 3).

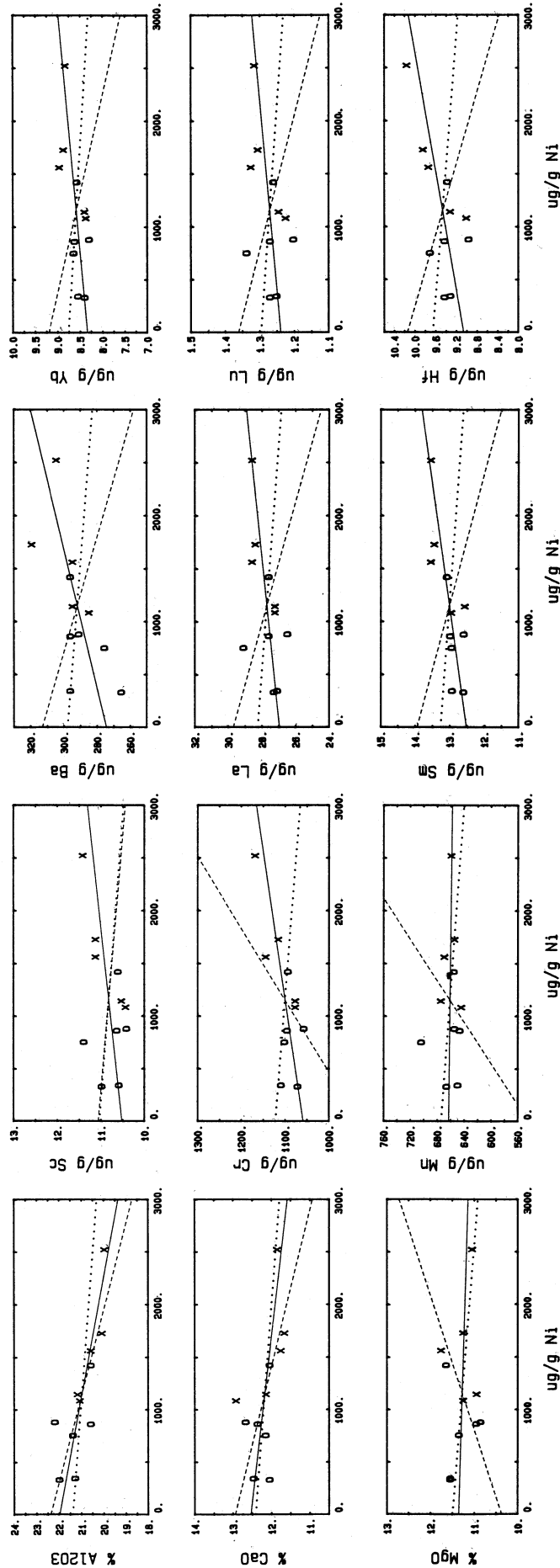


Fig. 3. Like Figure 2, but each of the two data sets have been normalized to attempt to cancel any effect of interlaboratory bias, using the normalization procedure described in Table 2. The solid line is the best-fit line through the 11 normalized data points. The dashed line represents addition or subtraction of chondritic meteorite (H-group) to or from the mean composition of the 11 samples. This line would not be significantly different in slope if any other type of ordinary chondrite were used. The dotted line represents the addition or subtraction of an Fe-Ni metal phase containing 6% Ni. The vertical axis of each plot is scaled such that the slope of the dotted line is the same with respect to the coordinates of this page.

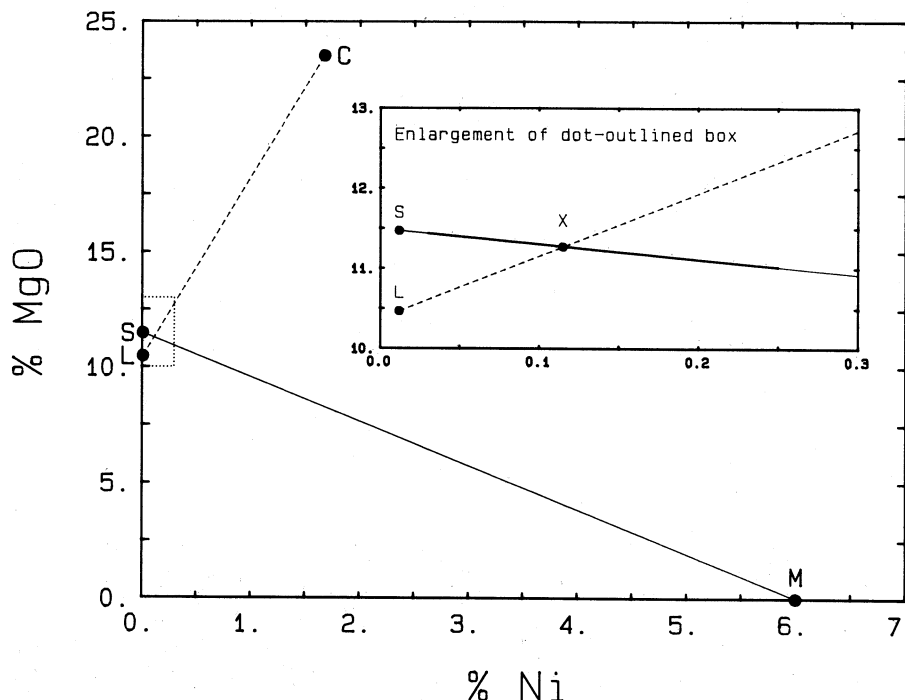


Fig. 4. Semischematic mixing diagram illustrating the decoupling of meteoritic lithophile and siderophile elements using MgO as an example. A silicate-iron meteorite with composition C (H-group chondrite) impacts lunar material with composition L resulting in a melt with bulk composition X. The melt consists of two immiscible phases, a metal phase derived entirely from the meteorite with composition M and a silicate phase of composition S consisting of well-mixed lunar and meteoritic silicates. The composition of small samples of the melt will vary about composition X along line SM, not LC, as long as no gross segregation of metal occurs. The thicker portion of line SM in the insert represents the range of Ni concentrations observed in the dimict breccias (Table 1).

melt must correspond to a point on the low-Ni end of the mixing lines at or below that of the sample with the lowest Ni concentration. We do not need to know exactly where in order to determine the composition of the metal.

The Ni and Co concentrations obtained by this technique for the dimict breccia metal (6% Ni and 0.34% Co) are typical of those found in metal grains from other Apollo 16 samples [Reed and Taylor, 1974; Goldstein and Axon, 1973; Hewins *et al.*, 1976; Misra and Taylor, 1975; Taylor *et al.*, 1976]. The concentrations of all elements estimated here are very similar to those obtained by direct analysis of metal grains separated from Apollo 16 soil 60601 [Wlotzka *et al.*, 1973] and for a single metal sphere from 65015, a type-1 noritic melt breccia [Wasson *et al.*, 1975a; Table 3]. The values obtained here are for the average composition of the metal in the dimict breccias. Individual metal grains may deviate from this mean, but the deviation is not expected to be large, considering the good correlations observed in Figure 1.

#### *Decoupling of meteoritic lithophile and siderophile elements.*

The simplest way to account for the data is that the impactor causing the dimict breccia melt was an iron meteorite and that the Fe-Ni metal grains found in the melt are fragments of it. In this case, no variation in lithophile element abundances would be expected except for the minor effect of dilution by the metal. This possibility will be explored in more detail later, but first we consider whether the compositional data for the dimict breccias are consistent with any type of silicate-bearing meteorite. The arguments made above do not require the impacting meteorite be devoid of silicates; they only require that the meteorite contain a substantial metal component and that the lithophile and siderophile elements were decoupled.

Figure 4 illustrates semischematically, using MgO as an example, how the observed variation could be accomplished by impact of, e.g., an ordinary chondrite. If a meteorite with composition C (a typical H-group chondrite composition) impacted lunar material with composition L to produce a volume of melt that is composed of about 6% meteorite and 94% lunar material, then the bulk composition of the system would plot at point X. This melt would consist of two immiscible phases, the metal portion of the meteorite, which would plot at point M, and a silicate portion, consisting of the meteorite and lunar material (presumably well mixed), which must plot at point S. Upon cooling, the minor metal phase (about 1.7% of the bulk melt) will not be uniformly distributed within the silicate portion. Assuming no large-scale segregation of metal, the composition of small samples would plot on the metal-silicate mixing line (SM) near the bulk composition (point X), not along the lunar-chondrite mixing line (LC). For comparison, the compositions L and X in this example were deliberately chosen so that Figure 4 resembles the MgO-Ni plot in Figure 3.

This model has several implications. First, it is sometimes assumed that extrapolation of lines such as those in Figure 2 to low Ni concentrations will predict the meteorite-free, indigenous lunar composition [e.g., Palme, 1980; Delano and Ringwood, 1978a,b]. If the meteoritic component is primarily a silicate-iron meteorite like an ordinary chondrite and if the decoupling model is applicable, then this assumption could lead to sizable errors. In Figure 1 both the Ir-Ni and Au-Ni regression lines intersect the Ni axis at about 120  $\mu\text{g/g}$  Ni. If all of the Ir and Au is assumed to be in the metal phase, then 120  $\mu\text{g/g}$  is the concentration of Ni in the nonmetal portion of the melt. Extrapolation of the regression lines in Figure 3 to 120

TABLE 4. Comparison of Bulk Composition and Metal-free Composition of Dimict Breccia Melt

		Bulk Mean n = 11	Metal-Free	
			mean	±2s
<i>Siderophile</i>				
Fe	%	6.57	5.03	0.16
Ni	μg/g	1150.	120.	60.
Co	μg/g	70.	10.9	2.0
Ir	ng/g	27.	0.	2.
Au	ng/g	25.	0.	4.
<i>Lithophile</i>				
Al <sub>2</sub> O <sub>3</sub>	%	21.0	21.9	0.6
MgO	%	11.3	11.3	0.4
CaO	%	12.1	12.5	0.4
Sc	μg/g	11.0	10.6	0.5
Cr	μg/g	1120.	1064.	31.
Mn	μg/g	664.	663.	22.
Ba	μg/g	292.	276.	14.
La	μg/g	27.8	27.0	0.9
Sm	μg/g	13.1	12.6	0.3
Yb	μg/g	8.65	8.37	0.23
Lu	μg/g	1.29	1.24	0.05
Hf	μg/g	9.65	9.1	0.4
<i>Ratios</i>				
mg'	%	70.5	75.7	
Fe/Mn		98.9	75.9	

"Bulk Mean" values are the average of the concentrations in Table 1, except for the Au concentration, which is the value of the regression line (Figure 3) at the mean Ni concentration. "Metal-free" values are the value of the regression lines (Figure 1, siderophile elements and Figure 3, lithophile elements) at 120 μg/g Ni.

μg/g Ni yields the concentrations of other elements in the nonmetal portion of the melt. These metal-free concentrations correspond to point S in Figure 4 and are listed in Table 4. This composition can be interpreted in two ways. If the meteorite is a silicate-iron, if the lithophile and siderophile elements are decoupled, and if the silicate portion of the melt is well mixed, then the metal-free composition listed in Table 4 is the composition of the mixture of lunar target material plus the silicate portion of the meteorite. Only if the meteorite is an iron meteorite does the metal-free composition in Table 4 represent the composition of the lunar target. For example, assume that the melt phase of the dimict breccias is the product of an impact of an object like an ordinary chondrite. Then for MgO, the solid line in Figure 3 represents the line SM and the dashed line represents the line LC in Figure 4. The MgO concentration of the lunar target lies on the dashed line at 120 μg/g Ni, a point that corresponds to 10.3% MgO (point L). This is significantly less than the 11.35% MgO predicted by extrapolating the regression line in Figure 3 to 120 μg/g Ni (point S). The difference between point S and point L is the MgO contributed by the meteorite. (The assumptions above implicitly require that point X, the intersection of the two lines, represents the bulk composition of the melt.)

Note that these arguments also apply to the 120 μg/g Ni obtained from the intercepts of the Au and Ir versus Ni plots (Figure 1). The value 120 μg/g is not necessarily the indigenous Ni concentration of the target. It only represents the portion of the Ni in the target-projectile system that is not correlated with Ir and Au. There may be a contribution of Ni from the nonmetal portion of the impactor. It is probably not a large proportion, however. *Rambaldi et al.* [1978] obtain an average of 614 μg/g Ni in the nonmagnetic fraction of 22 ordinary

chondrites. This value leads to a concentration of Ni in the target of about 80 μg/g, assuming that the melt consists of 6% ordinary chondrite and all Ir is in the metal phase. Even if the impactor were an iron meteorite, 120 μg/g Ni may still be an upper limit for the indigenous lunar concentration if the target contained meteoritic components from previous impacts.

A second implication of the decoupling model applies to the correction of the results of a single analysis of a sample for its meteoritic component and to mixing models that use Ni concentrations to determine the meteoritic component. If the meteoritic lithophile and siderophile elements are decoupled, then there is no assurance of the validity of any procedure that attempts to correct, for example, the MgO concentration of a sample for its meteoritic component based on the amount of Ni and the chondritic MgO/Ni ratio even if the meteoritic component is chondritic on the average. The procedure would be valid only if (1) the meteorite contained no metal, or (2) there is no gross separation of the metal and silicate portions of the meteorite and the particular sample happens to contain a typical concentration of Ni compared to other samples of its type (i.e., the Ni concentration of the sample plots close to point X in Figure 4). For a given sample, however, there is no way of knowing whether the meteoritic siderophile and lithophile elements are both present in their preimpact proportions, particularly if the sample is metal-rich. In a typical Apollo 16 soil, about half the Ni is contributed by a component of carbonaceous chondrite derived from micrometeorites (the concentration from this component is relatively constant from sample to sample) and half by Fe-Ni metal derived from impact melt rocks (the concentration of this source is highly variable in abundance from sample to sample, however) [*Korotev, 1987b*]. In this case, an accurate correction of any single analyzed sample for its meteoritic components is not possible unless the quantity of Fe-Ni metal is known.

*Does the silicate portion of the melt contain a meteoritic component?* The discussion above demonstrates how the dimict breccia impactor might be like an ordinary chondrite in having both a silicate and metal phase, but why we see no variation in the concentrations of lithophile elements. However, the dimict breccia impactor cannot be any known type of ordinary chondrite because the bulk composition of the metal is not like that of metal in chondrites. The metal in the dimict breccias contains 6% Ni whereas the Ni concentration in metal from ordinary chondrites is greater (% Ni = 8-12(H), 13-18(L), 16-30(LL) *Rambaldi* [1976, 1977]), except for rare E-group chondrites, in which the Ni concentration is usually less than 6%. Also, the Ni/Co ratio of the dimict breccia metal (17.3 ± 0.8, Table 3) is less than the chondritic ratio of 19-22 (Figure 1; see also *Korotev* [1987b]). Relative abundances of trace siderophile elements are also not consistent with those of metal in ordinary chondrites. The Ir/Ni ratio in the metal of the dimict breccias (26 ± 3 μg Ir/g Ni, Table 3) is low compared to chondritic metal (40 ± 16 μg/g, mean of 25 H-, L-, and LL-group chondrites [*Rambaldi, 1976, 1977*]) and the Au/Ni ratio (24 ± 5 μg/g) of the dimict breccia metal is about twice the value of metal in ordinary chondrites (12.6 ± 1.6 μg/g; *Rambaldi et al.* [1979]).

A compromise explanation is that the metal derives from some ancient, silicate-iron meteorite ("ancient" in the sense of *Anders et al.* [1973]) that differs from ordinary chondrites in having different relative concentrations of siderophile elements. The term silicate-iron meteorite is used here to mean any type of meteorite containing significant amounts of both a metal and nonmetal (primarily silicate) phase. Ordinary chondrites

are thus one form of silicate-iron meteorite. The term "stony-iron" is avoided because this term is usually restricted to achondrites, and we do not wish to exclude from consideration planetesimals in which the silicate portion is primitive in composition like that of ordinary chondrites. In fact, in the following discussion the consequence of making an assumption parallel to that of *Boynnton et al.* [1975] will be examined, namely, that our generic silicate-iron meteorite is generally like an ordinary chondrite but that it differs from known ordinary chondrites in having metal with an unusual bulk composition and nonchondritic concentrations of trace siderophile elements.

We have established thus far that the dimict breccia impactor must have had a substantial component of metal, that it might have been an iron meteorite, but that if it was a silicate-iron like an ordinary chondrite, then the silicate portion is well mixed with the target and only the metal portion is variable among the samples of the melt. One possible test between an iron and a silicate-iron might be the MgO concentration of the  $mg'$  value (mol % Mg/(Mg + Fe)) of the melt. However, the  $mg'$  of the lunar target is unknown and either model is consistent with likely values. If the meteorite is an iron, then the  $mg'$  of the metal-free portion of the melt (75.7, Table 4) is also the  $mg'$  of the lunar target and the difference between this value and the value for the bulk melt (70.5) results entirely from the contribution of Fe-Ni metal to the bulk. If the meteorite is a silicate-iron, then 75.7 is the average of the  $mg'$  of target and the silicate portion of the meteorite. The  $mg'$  value of the silicate portion of ordinary chondrites ( $mg' = 83(H), 78(L), 73(LL)$ ), *Wasson* [1985]) is not dissimilar enough from the lunar target for  $mg'$  value to be useful in distinguishing between an iron and silicate-iron impactor.

A more useful criterion is the Fe/Mn ratio. The Fe/Mn (or FeO/MnO) ratio in lunar samples is so constant [*Laul et al.*, 1972] that it has been one of the primary tests used to argue for the lunar origin of meteorite ALHA81005 [*Laul et al.*, 1983; *Palme et al.*, 1983; *Kallemeyn and Warren*, 1983]. This ratio is usually given as  $80 \pm 5$  [*Laul et al.*, 1983] but is reported as about 70 for highlands samples by *Palme et al.* [1983]. The bulk composition of the dimict breccia melt (metal plus silicate) has an Fe/Mn ratio of 99 (Table 4), which implies that the bulk Fe/Mn ratio of meteorite was high compared to the lunar value. The metal-free portion of the melt has an Fe/Mn ratio of 76 (Table 4), i.e., within the lunar range. If the meteorite was an iron meteorite, then 76 is the Fe/Mn ratio of the lunar target and the high Fe/Mn ratio of the bulk melt results from the meteoritic iron. Hence the Fe/Mn data are consistent with the iron-meteorite model.

The Fe/Mn data are not so easily explained by any component like an ordinary chondrite because the bulk Fe/Mn ratios of H-, L-, and LL-group chondrites are not great enough to raise the ratio of the bulk melt from 80 to the observed value of 99. Only the H-group of chondrites has a high enough value of Fe/Mn (Fe/Mn = 122(H), 89(L), 79(LL), data from *Mason* [1971]). Mixing of H-group chondrite (Fe = 27.6%, Mn = 2260  $\mu\text{g/g}$ ) and lunar material with a Fe/Mn ratio of 80 requires a 13% component of the meteorite and a lunar composition of 4.34% FeO and 420  $\mu\text{g/g}$  Mn in order to yield the bulk composition in Table 4. A meteoritic component as high as 13% is probably unreasonable, and a 13% component of H-group chondrite would provide about twice the Ni concentration actually observed in the dimict breccia melt. Thus no reasonable mixture of bulk ordinary chondrite and lunar material with

a Fe/Mn ratio of 80 can yield the bulk composition of the dimict breccia melt.

The dimict breccia data might still be explained by an impactor like an ordinary chondrite, however, if by some unknown mechanism the metal/silicate ratio of the meteoritic component of the melt is disproportionately high compared to the metal/silicate ratio of the impactor; i.e., in terms of the model discussed in Figure 4, the samples plot to the high-Ni side of the bulk composition, point X. The Fe/Mn ratio of 76 obtained for the metal-free melt (Table 4) represents that of the lunar plus meteoritic silicates. From the data of *Rambaldi* [1977] for the average Ni content of the metal (9%) and that of *Rambaldi et al.* [1979] for the average metal content (17.3%), an Fe concentration of 14.5% for the nonmetal portion of H-group chondrites can be estimated. Assuming that most of the Mn is in the nonmetal portion leads to a concentration of 2730  $\mu\text{g/g}$  Mn and a Fe/Mn ratio of 53 in the nonmetal portion of an H-group chondrite. Thus a 4% component of H-group silicate is required to lower the Fe/Mn ratio of the melt to 76 if the ratio for the target is assumed to be 80. The difference in Fe concentrations between the bulk and metal-free melt is 1.54% Fe (1.98% FeO, Table 4). Hence the metal/silicate ratio meteoritic component of the bulk melt would have to be about 0.4. This is still about twice the ratio in H-group chondrites [*Rambaldi et al.*, 1979], which have the highest metal/silicate ratio among ordinary chondrites.

In summary, the high metal content of the dimict breccia melt implies that the impactor contained a high proportion of metal. There is no evidence in the data that it also contained a silicate portion. If it did, and if that phase was similar in composition to the nonmetal portion of ordinary chondrites, then the metal/silicate ratio of the meteoritic component of the dimict breccia melt is at least twice as great as that of any type of ordinary chondrite. In this case, we can conclude that during formation of the dimict breccias, i.e., during the injection of the melt into the expanding crater cavity [e.g., *James et al.*, 1984], the metal phase was injected preferentially to the silicate phase. This conclusion requires, however, that there are other samples of the melt that are considerably poorer in metal than the dimict breccia samples in Table 1. As will be argued later, samples of the same melt with approximately half as much metal may exist in the type-2 melt associated with breccias from North Ray Crater. Alternatively, the composition of the metal is totally dissimilar to metal from ordinary chondrites. Hence the dimict breccia impactor might have been an iron or an achondritic stony iron. In the latter case, all we can say is that the silicate portion of the impactor did not significantly alter the Fe/Mn ratio of the melt from that of the lunar target; we can put no constraints on the composition or metal/silicate ratio of the impactor.

*Ancient iron meteorite.* The Ir/Au ratio of 1.2 for the dimict breccia metal corresponds to a chondrite normalized ratio of 0.36 and is at the low extreme of the wide range observed in lunar samples. The value is characteristic of "ancient meteorite groups" 1L and 1H [*Hertogen*, 1977; *Morgan and James*, 1981]. Most Apollo 16 samples studied by the Chicago group with similar Ir/Au ratios have been assigned to ancient meteorite group 1H, based on their higher Re concentration. Of the approximately 12 samples assigned to ancient meteorite group 1H by *Hertogen et al.* [1977], all but one are from Apollo 16. Each of the 12 Apollo 16 samples is (or has a large component of) impact melt rock with relatively high concentrations of ITEs

TABLE 5. Mean Ni and Fe-Ni Metal Concentrations of Some Lunar Impact Melts and Ni/Co Ratio in Metal or Meteorite Phase

	No. of Anal. (n)	Mean Concentration		Ni/Co $\pm 2s$	
		$\mu\text{g/g}$	%	%	
		Ni	Metal	Al <sub>2</sub> O <sub>3</sub>	
<i>Apollo 16 Noritic Impact Melt</i>					
A16 Type-2 DB (VHA)	11	1150	1.72	21	17.3 0.8
A16 Type-1 (A16 LKFM)	26	840	1.20	19	19.3 2.2
A16 Type-2 NRC (VHA)	17	590	0.78	21	14.9 0.9
<i>Other Apollo 16 Melt</i>					
A16 Glass Splashes (IMS)	50	780	-	28	19.4 1.7
<i>Other Noritic Impact Melt</i>					
A14 14310	14	170	?	20	
A15 15455/55 (A15 LKFM)	8	320	?	17	
A17 stations 2 and 3	34	200	?	21	

The mean metal concentrations of the melt rocks were calculated from the mean Ni concentration assuming that 120  $\mu\text{g/g}$  of the Ni was contained in the silicate phase and that the metal contained 6.0% Ni. Sources of data: Apollo 16 dimict breccias: Table 1. Apollo 16 type-1: Korotev [1987b] (clasts in 60016, 66035, 66075); Wänke et al. [1975] (clasts in 60016); Rose et al. [1973] (60315); Wänke et al. [1976] (60315, 62235, 65015); Laul et al. [1974] (60315, 62235, 60636, 65777); Brunfelt et al. [1973] (62235); Haskin et al. [1973] (65015); Wasson et al. [1977] (63556); Boynton et al. [1975]; Krühenbühl et al. [1973] (65015); and Ganapathy et al. [1974] (60315). Apollo 16 North Ray Crater VHA: Lindstrom and Salpas [1983] (67055, 67235, 67935); Marvin and Lindstrom [1983] (67015); Marvin et al. [1987] (67015); McKinley et al. [1984] (67944); Wänke et al. [1976] (67435). Ni data only from Hertogen et al. [1977] (67015, 67935) and Ganapathy et al. [1974] (63355). Apollo 16 impact melt splashes: Morris et al. [1986]. Apollo 14 14310: Hubbard et al. [1972]; Rose et al. [1972]; Taylor et al. [1972]; Helmke et al. [1972]; Baedecker et al. [1972]. Apollo 15 15445 and 15455: Taylor et al. [1973]; Blanchard et al. [1976a]; and M. Lindstrom (unpublished data, 1986). Apollo 17 noritic melt rock: Blanchard et al. [1975] (72215); James et al. [1975] (73215); Laul et al. [1974] (72315, 72355, 72375, 72395); Wänke et al. [1974] (73235); Laul and Schmitt [1975] (72535, 72355); and Blanchard et al. [1976b] (73215).

and each also has high absolute concentrations of siderophile elements (e.g., mean Ni = 559  $\mu\text{g/g}$ ).

Anders et al. [1973] have argued that the ancient meteorites do not correspond to any known major meteorite class, including iron meteorites. The bulk composition of the dimict breccia metal does not exactly match that of any type of iron meteorite, although it is similar to that of some. The Ni concentration (6%, Table 3) is at the high end of the range for kamacite and at the low end of the range for iron meteorites, e.g., groups I and II. The Co concentration of the dimict breccia metal (0.34%) is also at the low extreme of the range for irons, but the Ni/Co ratio is well within the range [Mason, 1971; Buchwald, 1975]. (Note that the 6% Ni concentration for the dimict breccia metal is based almost entirely on the Ni-Fe regression of Figure 1 and the uncertainty on the Fe/Ni ratio is 9%. Hence the actual mean Ni content of the metal could be as high as 6.5%. In this case concentrations for all trace siderophile elements in Table 3 would be higher by the same relative amount, although the ratios would remain the same.)

A conclusive comparison of the dimict breccia metal with known groups of iron meteorites would require Ga and Ge concentrations for the dimict breccia metal [e.g., Wasson, 1985]. Although these are unavailable, approximate concentrations can be inferred from the analysis of a single metal sphere from 65015, a type-1 melt rock from Apollo 16 (Table 3). The Ni concentration of this sphere is very similar to that of the dimict

breccia metal, as is the Ir/Au ratio, although the absolute Ir and Au concentrations are only about two-thirds as great. The composition of the sphere does not fall exactly into the field of any group of iron meteorite, but the concentration of no element is outside the range of concentrations observed in irons. The most unusual feature of the composition of the 65015 sphere is that iron meteorites with Ga concentrations this low usually have higher Ni and lower Ge concentrations [Scott and Wasson, 1975; Wasson, 1985]. The lack of a specific match does not argue strongly against the idea that the sphere from 65015 is a fragment of an iron meteorite; 14% of analyzed iron meteorites are anomalous in that they do not fall in the compositional field of any recognized group [Scott and Wasson, 1975]. One of these, Emsland, is similar to the 65015 metal sphere with respect to the low Ga concentration (Table 3). As noted by Anders et al. [1973], known iron meteorite groups only populate a fraction of any classification plot (e.g., Ga versus Ni) and we have no reason to believe that some compositions are forbidden. The metal in the dimict breccias and the metal sphere from 65015 are certainly not from an ordinary chondrite and are probably not from any known group of iron meteorite. However, the composition is not dissimilar enough to known irons that the possibility can be discarded that they represent a group of iron meteorite that was common 3.9 Ga ago.

A somewhat more circumstantial argument in favor of an iron meteorite is simply the high metal content of the dimict breccia melt. As noted earlier, the mean Ni concentration of the dimict breccia melt (1150  $\mu\text{g/g}$ ) is the highest of any type of lunar sample and corresponds to 1.7% metal of the composition of Table 3 (range = 0.4–4% metal for the 11 samples of Table 1). If the projectile was an iron meteorite, then 1.7% is the fraction of projectile in the melt. Although this is a relatively large fraction compared to terrestrial impact melts [e.g., Palme et al., 1978], if the projectile also contained a silicate phase, then the melt must contain an even larger fraction of the projectile. Nickel concentrations in other types of noritic impact melt from Apollo 16 are also high, and are greater on the average by a factor of 3 to 5 than those of noritic impact melts of otherwise similar composition from other landing sites (Table 5). This suggests that something about the projectile(s) producing noritic impact melt at Apollo 16 was unusual.

In summary, the combined evidence points toward an iron meteorite as the ancient planetesimal that created the dimict breccia impact melt. None of the evidence is conclusive, but together the data are explained most easily by an iron impactor; any scenario involving a silicate-iron impactor requires more assumptions and the occurrence of less likely events. The evidence is as follows: (1) The Ni concentration of the melt is high compared to impact melt of similar composition from other landing sites. (2) If the impactor was an iron, then the melt contains an average of 1.7% projectile. If the impactor was a silicate-iron meteorite like an ordinary chondrite, then the melt must contain a severalfold greater component of the projectile and this may be an unreasonably large fraction. (3) The Fe/Mn ratio of the nonmetal portion of the melt is 76, which compares well with the typical value of 80 found in lunar rocks. The Fe/Mn ratio of the bulk melt is 99; no mixture of ordinary chondrite and lunar target with an Fe/Mn ratio of 80 can yield an Fe/Mn ratio as high as 99 in the bulk melt (silicate + iron) and still account for the Ni concentration of the bulk melt. (4) The bulk composition of the metal (6% Ni and 0.34% Co) is inconsistent with any ordinary chondrite, but is in the range

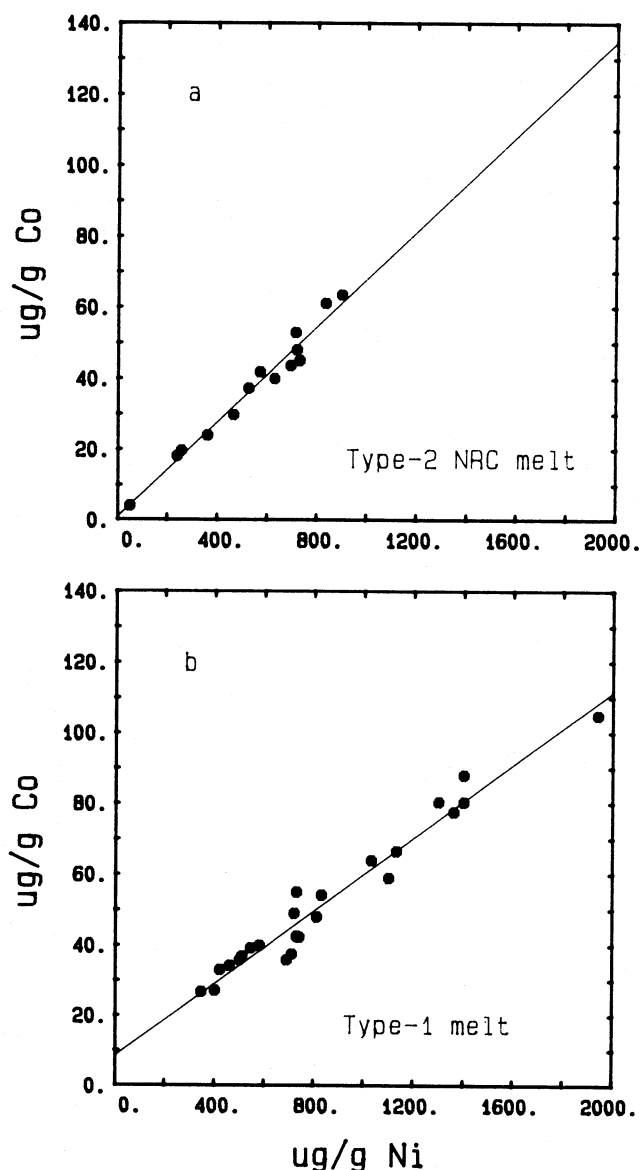


Fig. 5. Variation of Co with Ni in two other types of noritic impact melt from Apollo 16. (a) For samples of the type-2 (VHA) melt from North Ray Crater the correlation requires a metal with a Ni/Co ratio of  $14.9 \pm 0.9$ . (b) For samples of type-1 melt (Apollo 16 LKFM) the variation requires a metal with a Ni/Co ratio of  $19.3 \pm 2.2$ . Sources of the data are listed in Table 5.

of iron meteorites. (5) The Ir/Ni and Au/Ni ratios of the metal are inconsistent with any type of chondrite but are consistent with those of iron meteorites.

#### Other Noritic Impact Melt Breccias

For comparison, data for some other rock types thought to be impact melts are tabulated in Table 5. Values listed include the mean Ni and  $\text{Al}_2\text{O}_3$  concentrations of the samples and the Ni/Co ratio of the phase causing the variation in Ni and Co concentrations, as determined by the correlation technique. The calculated concentration of Ni in the metal phase (if metal is the cause of the variation) depends almost entirely upon the Fe-Ni correlation. This correlation is generally not as good for other melt rocks as it is for the dimict breccias, so the uncertainty is large. For example, the range for metal in type-1 melt rocks

(see below), based on the uncertainty of the slope of the Fe-Ni regression, is 3.7% to 6.8% Ni (two standard deviations). Also, it has only been demonstrated here that Fe-Ni metal is the cause of the variation in siderophile element concentrations for the dimict breccias; this may not be so for the other samples, although it almost certainly is for the other Apollo 16 noritic impact melts and almost certainly is not for the impact melt splashes of *Morris et al.* [1986]. Hence no estimate is made here for the Ni abundance in the metal phase of the samples from other sites. The variations in Ni concentrations among samples of Apollo 14, 15, and 17 melt rocks are not great enough for precise estimates of the Ni/Co ratios of the components causing the variation, hence this ratio is also not calculated here for the melt rocks from other sites. *Palme* [1980] argues that the Ni/Co ratio of the meteoritic component of Apollo 17 breccias is chondritic. However, the variation in Ni and Co concentrations in highlands soil from Apollo 17 requires a component with a Ni/Co ratio of  $15.5 \pm 1.6$ , just like the Apollo 16 soils [*Korotev, 1986; Korotev, 1987b*] and metal grains with 5–7% Ni and Ni/Co ratios of about 15 are common in Apollo 17 soil [*Goldstein et al., 1974*].

**Type-2 melt from North Ray Crater.** Another type of impact melt from Apollo 16 for which different samples have very similar concentrations of lithophile elements is the type-2 melt found as rake samples and as clasts in feldspathic fragmental breccias from North Ray Crater, e.g., 67055, 67235, and 67935 [*Lindstrom and Salpas, 1983*] and 67015 [*Marvin and Lindstrom, 1983*]. The lithophile element composition of this melt (type-2 NRC) is virtually identical to that of the dimict breccias (type-2 DB). (Compare, for example, 67055, f of *Lindstrom and Salpas* [1983] with 61015, 100m of *James et al.* [1984], both of which have the same Ni concentration, or 67944 in Table 2 of *McKinley et al.* [1984] with the five dimict breccias samples also listed there.) The crystallization age of one such sample, 67747 ( $3.94 \pm 0.5$  Ga [Rb-Sr, *Stöffler et al., 1985*];  $3.86 \pm 0.5$  Ga [Rb-Sr; *Reimold et al., 1985*]), is similar to that of the dimict breccia melt and other noritic impact melt rocks. All samples of type-2 NRC melt were found near North Ray Crater at the northern part of the Apollo 16 landing site, while the dimict breccias were found at the southern and central part. Hence it is worthwhile to compare the meteorite components of these two types of melt rock. (Samples of the type-2 NRC melt were excavated by the meteorite that formed North Ray Crater about 50 Ma ago, but the melt was not produced by the North Ray Crater event. I will call the melt "type-2 NRC melt" because of the location of the samples.)

The mean Ni concentration of 17 samples of the type-2 NRC melt,  $590 \mu\text{g/g}$ , is about half that of the type-2 DB melt (Table 5). Using the correlation technique described above, the mean Ni/Co ratio of the metal phase responsible for the variation in Ni and Co concentrations is  $14.9 \pm 0.9$  (Figure 5a). This is significantly different (99+% confidence) from the value of  $17.3 \pm 0.8$  obtained for the type-2 DB melt. There are too few data to obtain a good Ir/Au ratio by the correlation technique, but the mean Ir/Au ratio in five samples for which Ir and Au concentrations have been determined is  $1.1 \pm 0.5$ , the same as for the dimict breccias. Because of the low Ir/Au ratio, the three samples of type-2 NRC melt analyzed by *Ganapathy et al.* [1974] (63355) and *Hertogen et al.* [1977] (67015, 67935) have been assigned to ancient meteorite group 1H.

If the type-2 DB and type-2 NRC melts are the products of two different impacts, then it is easy to account for the different bulk Ni concentrations of the melt, different Ni/Co ratios of

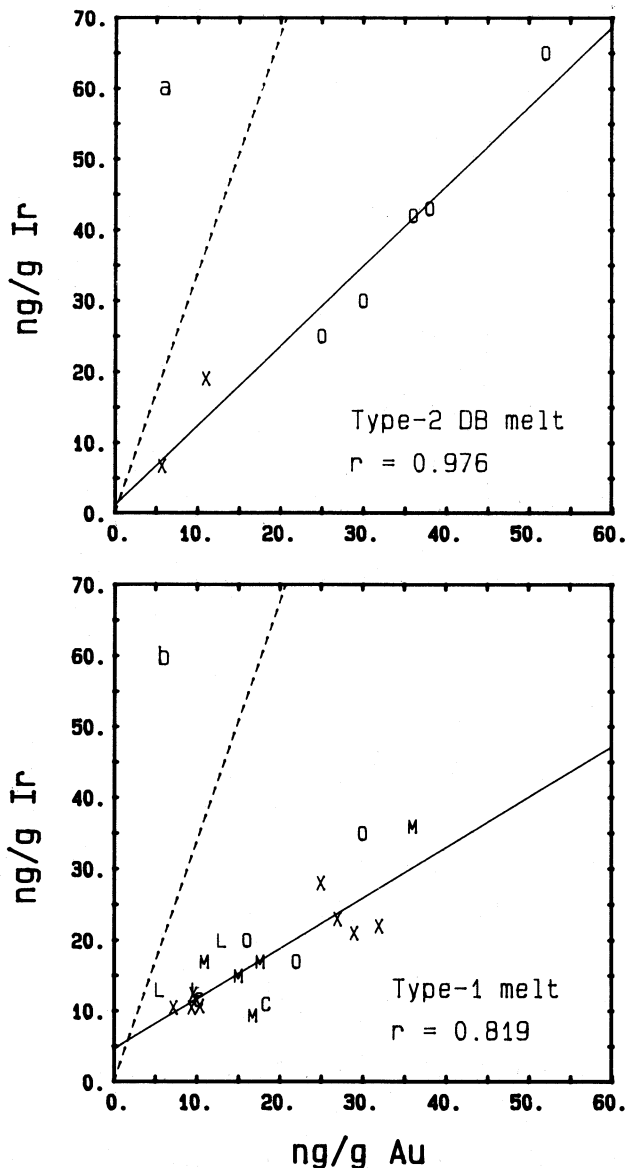


Fig. 6. Variation of Ir with Au in two types of Apollo 16 melt rocks. (a) For the dimict breccias the correlation requires a metal component with an Ir/Au ratio of  $1.2 \pm 0.3$  (Table 3). (b) For the type-1 melts the correlation requires metal with an Ir/Au ratio of  $0.7 \pm 0.3$ . If the line is forced through the origin, however, the Ir/Au ratio is 1.0, more nearly like that of the dimict breccias and of the metal sphere from type-1 melt breccia 65015 [Wasson *et al.*, 1975a; see Table 3]. The chondritic ratio, 3.38 [Hertogen *et al.*, 1977], is indicated by the dashed lines. Sources of data are listed in Table 5. Samples are keyed according to laboratory producing the data: C = University of Chicago (Anders); L = University of California, Los Angeles (Wasson); M = Max-Planck-Institut für Chemie, Mainz (Wänke); X = Washington University, St. Louis (Haskin); and O = Oregon State University (Schmitt). The M and C points with the lowest Ir/Au ratio at 15–20 ng/g Au are both samples of 60315.

the metal, and different geographic occurrence at the site. The two impactors would have to have been approximately equivalent in size and velocity and have impacted the same general area, however, to yield melts of such similar bulk composition. If, as argued earlier, the dimict breccia impactor was an iron meteorite, then the type-2 NRC impactor was probably also an iron meteorite because the Ni concentration of the melt is also high and the unusually low Ir/Au ratio is the same as that for the dimict breccias but different from that

of melt rock from other regions of the moon [e.g., Hertogen *et al.*, 1977]. In fact, the unusual Ir/Au ratio suggests that the two impactors must have been similar or related.

On the other hand, if the type-2 DB and NRC melts are products of the same impact, then the different Ni/Co ratios of the metal and the factor of two difference in Ni concentration must be explained. The two melt rocks have different petrographic settings, one in association with anorthosite, the other as rake samples and clasts in feldspathic fragmental breccias. A likely possibility is that the type-2 DB melt is from the bottom of the crater cavity, as postulated by Stöffler *et al.* [1979], whereas the type-2 NRC melt was ejected from the crater at impact. This would explain the higher metal content of the dimict breccias because the projectile metal preferentially remains in the crater. Palme *et al.* [1978] argue that meteoritic material is not distributed uniformly within the melt of some terrestrial craters and review evidence that the largest concentration of meteoritic material is expected beneath the crater floor. The only remaining problem with this scenario is the difference in the Ni/Co ratios of the Fe/Ni metal,  $17.3 \pm 0.8$  versus  $14.9 \pm 0.9$ . This difference may only indicate that the projectile itself was heterogeneous in this regard.

*Type-1 melt.* Compositions of samples regarded as type-1 melts are somewhat more variable than those of the dimict breccia melt; even subsamples of the same rock show more variation [Haskin *et al.*, 1973] than the dimict breccia samples of Table 1. In this analysis, only those samples with Sm concentrations between 20 and 27  $\mu\text{g/g}$  and Sc concentrations between 13 and 17  $\mu\text{g/g}$  are included. McKinley *et al.* [1984] conclude that different samples of type-1 melt rock "do not represent a single impact event" based on the spread of Ir/Au ratios and reported ages. However, it is not clear from their analysis whether all the samples they considered fall within the restricted compositional range defined above. Clasts of melt rock of this composition are common in ancient regolith breccias 60016 and 66075 [McKay *et al.*, 1986; Korotev, 1987b; Wänke *et al.*, 1975] and data for 11 such clasts are used in the analysis discussed here. It is likely that most of the samples of impact melt with the type-1 composition found at Apollo 16 are related by a single impact, although all may not be.

The mean Ni concentration in 26 samples of type-1 melt is 840  $\mu\text{g/g}$  (Table 5). Except for the melt rock of the dimict breccias, this is the largest mean Ni concentration of any type of melt rock returned from the moon. Fe-Ni metal containing about 6% Ni is a common component of type-1 melt rocks such as 60315 and 65015 [Reed and Taylor, 1974; Taylor *et al.*, 1976]. Hence it is reasonable to assume that the high Ni concentrations are the result of high content of Fe-Ni metal. Figure 5b is a Co-Ni plot for samples of type-1 melt. As for the dimict breccias, the Ni and Co concentrations among different samples are highly variable. The mean Ni/Co ratio of the metal phase causing this variation is  $19.3 \pm 2.2$ , a value that is intermediate between that of the dimict breccias and that of chondrites and within uncertainty of both (Table 5).

Also, like the type-2 DB and NRC melt rocks, the Ir/Au ratios in the type-1 melt rocks are distinct among lunar samples in being low. The correlation of Ir with Au in the type-1 melt and type-2 DB melt is plotted in Figure 6. A component with an Ir/Au ratio of  $0.7 \pm 0.3$  is required to explain the correlation for the type-1 melt rocks. If the correlation line is forced through the origin, a ratio of 1.0 is obtained. The latter value is more similar to the ratio of 0.93 obtained by Wasson *et al.* [1975a] on a single metal grain separated from type-1 breccia 65015

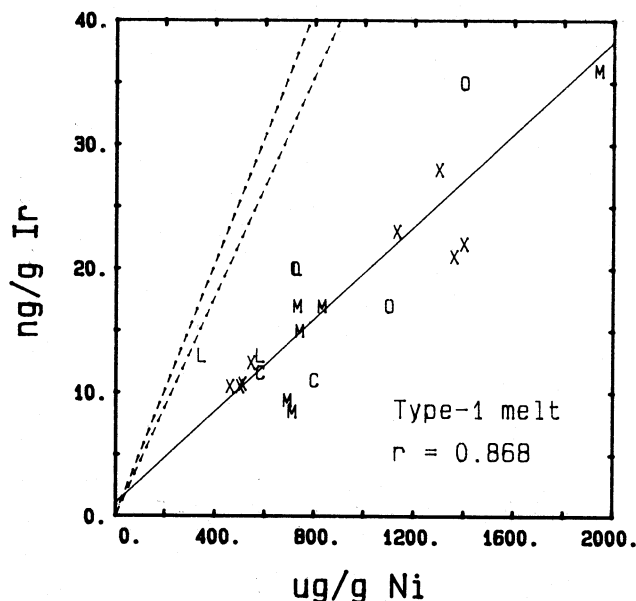


Fig. 7. Variation of Ir with Ni in type-1 melt breccias. The correlation requires a metal with an Ir/Ni ratio of  $19 \pm 6 \mu\text{g/g}$ . This compares with 17.5 obtained from a single metal sphere from type-1 melt breccia 65105 [Wasson *et al.*, 1975a] and  $26 \pm 3 \mu\text{g/g}$  obtained for the dimict breccias (Figure 1; Table 3). The chondritic ratio ( $51 \mu\text{g/g}$  [Delano and Ringwood, 1978b] or  $44.4 \mu\text{g/g}$  [Wänke *et al.*, 1979]) is indicated by the dashed lines. The Ni intercept of the best-fit line is  $-60 \pm 240 \mu\text{g/g}$ , a value that is of little use for establishing the indigenous Ni concentration. A similar plot for Au, however, intersects at  $120 \pm 60 \mu\text{g/g}$  Ni. This value agrees very well with the values obtained from the dimict breccias (see Figure 1). Sources of data are listed in Table 5. Sample key is the same as Figure 6.

(see Table 3). An Ir/Au ratio of unity leads to a chondrite-normalized ratio of 0.30, a value corresponding to ancient meteorite group 1H of Hertogen *et al.* [1977]. Bulk Ir/Au ratios in two samples of 60315 are lower than for most other samples of type-1 melt and are among the lowest observed in Ni-rich lunar rocks (Ir/Au = 0.60 [Ganapathy *et al.*, 1974] and 0.56 [Wänke *et al.*, 1974] and 0.56 [Wänke *et al.*, 1976]). Hertogen *et al.* [1977] suggest that this low ratio may indicate a different ancient meteorite group (1LL). However, a third sample of 60315 has a bulk Ir/Au ratio of 1.17 [Laul *et al.*, 1974]. Korotev [1987b] shows that the Au/Ni ratios in the Fe-Ni metal from type-1 melt and type-2 DB melt are identical ( $24 \mu\text{g Au/g Ni}$ ) but that the Ir/Ni ratios differ (type-1:  $19 \pm 6 \mu\text{g/g}$ , see Figure 7; type-2 DB:  $26 \pm 3 \mu\text{g/g}$ , Table 3), indicating that the variation in Ir/Au ratios among different samples results primarily from variation in the absolute Ir concentration of the metal. This is consistent with the wide range in Ir concentrations observed in iron meteorites, even among samples assigned to the same group (e.g., Figure II-11 of Wasson [1985]).

**Relationship among Apollo 16 noritic impact melts.** In a recent review of all siderophile and volatile element concentrations reported for Apollo 16 melt rocks, James [1986] concludes that type-1 melt rocks ("poikilitic LKFM," samples 65015 and 60315) are dissimilar to any other type of lunar melt rock. It is almost certain that the dimict breccia melt rock and type-1 melt rock represent at least two different impacts because of the difference in bulk compositions of the melts. From the similarity in both the bulk and trace element composition of the metal phase in the two types of rocks (Table 3) and the dissimilarity of the Ir/Au ratio in these two melt rocks to that

of melt rocks from other sites, the most likely scenario is that these two melts were produced by related meteoroids, possibly fragments of the same body. It follows from the arguments presented earlier for the dimict breccia melt rock that the impactor producing the type-1 melt rocks was also a metal-rich, probably iron, meteorite. The type-2 NRC melt represents either a third impact of a related iron projectile or, as discussed earlier, is melt from a different portion of the melt sheet produced during formation of the dimict breccias. James *et al.* [1984] argue on the basis of siderophile elements, bulk composition, and cratering mechanics that the dimict breccias were formed in an intermediate-sized (50–150 km diameter) crater local to the Apollo 16 site. Hertogen *et al.* [1977] argue that because samples with the signature of ancient meteorite group 1H (i.e., approximately equal Ir and Au concentrations) are restricted to the Apollo 16 area, the 1H crater (actually, two or three related craters, as suggested here) must be local to Apollo 16. They suggest either the Nectaris Basin or Unnamed Crater B, a 60-km diameter crater whose rim is believed to form Stone and Smokey Mountains at the Apollo 16 site [Head, 1974]. Although the lithophile element composition of the type-1 rocks is similar to that of noritic melt rocks from Apollos 14 and 15, the siderophile element signature is distinctly different. Hence it is unlikely that the type-1 melt rocks at Apollo 16 are melt from the Imbrium event, as suggested by Spudis [1984]. Type-1 melt rocks must also have been formed during excavation of a crater local to the Apollo 16 area (possibly Nectaris). The fact that noritic melt rocks (LKFM) from various locations have similar bulk compositions suggests that the nearside lunar crust is relatively uniform in composition on the scale of the quantity of material excavated by impacts such as the one that formed the type-1 melt rocks.

**Other Apollo 16 meteorite components.** Not all Apollo 16 samples have low Ir/Au ratios. Some have ratios 10 times greater than those of the noritic melt rocks, i.e., 3–5 times the CI ratio. These samples, which are assigned to ancient meteorite group 7, are primarily found near North Ray Crater [Hertogen *et al.*, 1977]. However, none of the group-7 samples are melt rocks and all have very low concentrations of Au compared to the low-Ir/Au (group 1H) melt rocks. Most other Apollo 16 rocks have chondritic Ir/Au ratios. Although these have been assigned to "ancient" meteorite group 5H [Hertogen *et al.*, 1977], at least some derive their siderophile elements from recent impacts. The three group 5H samples of Hertogen *et al.* [1977] that have particularly large concentrations of siderophile elements are all glasses. Morris *et al.* [1986] have shown that the high Ni concentrations in these three samples derive from a component of bulk chondrite, not metal, because Cr correlates with Ni. They argue that these samples were produced during formation of South Ray Crater about 2 Ma ago. Glass with a chondritic Ir/Au ratio actually coats dimict breccia sample 61015 (sample 61015,90G; James *et al.* [1984]). Hence the meteorite component of these glasses is not "ancient" in the sense of Hertogen *et al.* [1977]. Other breccias with the signature of ancient meteorite group 5H have considerably lower concentrations of siderophile elements. The soils, which contain a 1–2% component of carbonaceous chondrite from micrometeorites accumulated since formation of the lunar crust, still have subchondritic Ir/Au ratios from the 0.5 component of Fe-Ni metal derived from ancient, noritic melt rocks [Korotev, 1987b]. For example, the mean Ir/Au ratio of 67 soil samples from the 64001 core is 1.4 [Korotev *et al.*, 1984], a value intermediate to that of the noritic melt rocks (about 1.0) and chondrites (3.3). Hence,

although several different kinds of meteorites are represented in Apollo 16 polymict material, the low-Ir/Au metal derived from noritic impact melt rocks dominates the siderophile element signature because of its high abundance and high absolute concentrations of siderophile elements.

#### NONCHONDRITIC METAL AND REACTION WITH LUNAR SILICATES

Thus far I have assumed that the concentrations of siderophile elements in the metal associated with some impact melt rocks are not significantly different from the concentrations in the metal phase of the meteorites that formed the melts. If this assumption is incorrect, then many of the arguments made above are moot. In this section I argue that it is unlikely that the nonchondritic composition of the metal found in noritic impact melt breccias from Apollo 16 results primarily from processes that have occurred on the lunar surface.

There are many suggestions in the literature that siderophile element ratios in lunar rocks and Fe-Ni metal in the rocks differ from the chondritic values because the metal was produced by reduction upon impact or because metal in the meteorites reacted with lunar silicates and extracted siderophile elements in a way that changed the ratios. *Wlotzka et al.* [1973] account for the low Ni/Co ratio of Apollo 16 metal by uptake of Co from lunar rocks while *Palme* [1980] attribute the low Ir/Ni ratio of Apollo 16 VHA melt rocks to assimilation of indigenous Ni by the metal in the rocks. *Reed and Taylor* [1974] suggest that the low Ni concentration (6%) in metal from Apollo 16 rocks and soils may be derived from iron meteorites, but might also be the result of dilution by native lunar iron or preferential volatilization of Ni. *Delano and Ringwood* [1978a] argue that although most Ni and Co in highlands samples is present today in metal phases, some of this metal was produced by reduction during impact events. Similarly, *Wänke et al.* [1979] contend that the Ni content of lunar igneous rocks is low in part because of extraction of Ni into iron metal phases. *Delano and Ringwood* [1978a,b] and *Wänke et al.* [1978] argue that fumarolic volcanism has caused Au to be fractionated from Ir.

Others have argued, however, that the siderophile element signature of the lunar samples is essentially that of the impacting meteorites. *Anders* [1978] shows that most of the Au is meteoritic, not fumarolic, because Au correlates roughly with Ir, but not with Tl. *Goldstein and Axon* [1973] conclude that the Fe-Ni metal grains in Apollo 16 soils were fragments of meteorites. *Hewins et al.* [1976] present a detailed review of various petrologic arguments for why the Ni and Co concentrations observed in metal from Apollo 16 materials are probably not significantly different from that of the impacting meteorites. They note that although the metal in melt rocks has fractionated during cooling along with the silicate material and phosphorous concentrations have sometimes increased, Ni and Co concentrations are not likely to have changed much. They also note that the metal in lunar breccias "consistently" contains 6% Ni, and that this is different from the composition of metal in rocks generally regarded as uncontaminated by meteoritic material (mare basalts, anorthosites) and metal in ordinary chondrites. They concluded that the concentration of 6% Ni in the metal is characteristic of the ancient meteorites, not the result of processes occurring on the moon.

Most of the explanations for why highlands samples contain metal with nonchondritic ratios of Ni, Co, Ir, and Au are hypothetical in that there is little direct evidence in the samples

themselves that the processes proposed actually occurred or that they occurred to the extent necessary to produce such a large amount of metal. *Taylor et al.* [1976] have demonstrated experimentally that Fe metal containing <1% Ni can be produced from glass-bearing samples through subsolidus reduction. However, their experiments on type-I melt rock 65015 showed that the effect of subsolidus annealing on the composition of the metal grains was minimal; there was only a slight decrease in the mean Ni concentration of the metal. It is well documented that lunar Fe-Ni metal often does contain an excess of P and W that is believed to derive from the silicate melt by equilibration during cooling [*Wlotzka et al.*, 1973; *Goldstein and Axon*, 1973; *Reed and Taylor*, 1974; *Gooley et al.*, 1973; *Misra and Taylor*, 1975; *Hewins et al.*, 1976; *Wänke et al.*, 1979; *Palme et al.*, 1982]. However, both P and W are lithophile as well as siderophile. Unlike Ni and Co, neither element partitions into major mineral phases during crystallization of the melt. *Palme et al.* [1982] suggest that metal with high P and W contents may be a late-stage crystallization product in melt rocks because of the combined effect of concentration of these elements into the liquid during cooling and depression of the melting point of the metal by P. Although this explanation accounts for W and P, it does not account for fractionation of Ir from Ni and Au.

None of the suggested mechanisms involving reduction of lunar silicates and/or extraction of siderophile elements from lunar silicates attempts to account even qualitatively for (1) the large amount of metal present in the noritic melt rocks, (2) the recurring value of 6% Ni in the metal, and (3) the low Ir/Ni ratio of the metal. Any such process would have to be extremely efficient to yield metal with 6% Ni from metal typical of that in ordinary chondrites. The metal would have to react with a large excess of silicate. The mean concentration of Fe-Ni metal in the dimict breccia melt is 1.72%, of which 1.61% is Fe (Table 5). If all of the Ni in the metal phase (1150–120  $\mu\text{g/g}$  = 1030  $\mu\text{g Ni/g}$  melt, Table 4) derives from the meteorite and the metal in the meteorite is 12% Ni (mean of H- and L-group chondrites), then the Fe metal contributed by the meteorite is  $1030(88/12) = 7600 \mu\text{g/g}$ , i.e., 7600 micrograms of Fe metal derived from the meteorite per gram melt (0.76%). The difference (1.61–0.76% = 0.85%) must be the percentage of Fe metal reduced from the silicate melt. The present Fe content of the metal-free portion of the melt is 5.0% (Table 4). Hence  $0.85/(5.0 + 0.85) = 17\%$  of the iron originally in the silicate phase of the melt would have to have been reduced and incorporated into the metal phase to dilute the Ni content of the metal from 12% to 6%. This is a large fraction; What is the reducing agent? Any process this efficient would also have reduced Ni and extracted it into the metal phase, yet the metal-free portion of the melt still contains at least 120  $\mu\text{g/g}$  Ni (Table 4, based on the Ir and Au correlations with Ni, Figure 1). If the dimict breccia projectile did not contain any appreciable quantity of metal, e.g., it was a CI chondrite, then all of the observed metallic iron would have to have been produced by reduction, i.e., 25% of the Fe and nearly all the Ni in the target-projectile system must have been reduced. There is no evidence that impact-induced reduction is this efficient.

The Ir/Ni ratios in metal from the dimict breccia melt and type-I melt are about a factor of two less than the chondritic ratio (see discussion above and Figure 7). *Palme* [1980] suggested that meteoritic metal with a chondritic Ir/Ni ratio assimilated Ni from the lunar silicates to lower the ratio. However, this would require meteoritic metal with a chondritic Ir/Ni ratio,

TABLE 6. Hypothetical Data Set Illustrating How an Apparently Nearly Chondritic Ni/Co Ratio Might Be Obtained from Two Melt Rocks with Subchondritic Ni/Co Ratios in the Metal Phase

	Input Data		Regression Results, Co Against Ni		
	μg/g Ni	μg/g Co	slope Co/Ni	intercept μg/g Co	metal Ni/Co
<i>Data Set 1</i> (n = 5)	200. 300. 400. 500. 600.	18.3 25.0 31.7 38.3 45.0	0.06676	4.96	14.96 ± 0.04
<i>Data Set 2</i> (n = 5)	800. 900. 1000. 1100. 1200.	47.1 52.9 58.8 64.7 70.6	0.05876	0.06	17.02 ± 0.07
<i>Both Data Sets</i> (n = 10)			0.05202	9.05	19.17 ± 2.01

Regressions obtained for Co against Ni by method of York [1969] using the inverse squared of 10% of the concentration value as the weight for each datum (see text). The metal ratio is the Ni/Co ratio of a point on the regression line at 6% Ni with two standard deviations uncertainty.

but containing initially only about 3% Ni. No such composition is known among meteorites. Any mechanism invoked to explain why the Ir/Ni ratio of the metal is low compared to the chondritic ratio must also explain why the Au/Ni ratio is high (Figure 1). Also, if the metal extracts Ni from the lunar silicates, we would expect the Ni/Co ratio of the metal to be greater than the chondritic ratio because Ni is more siderophile than is Co. Instead, the Ni/Co ratio of the Fe-Ni metal in Apollo 16 rocks and soils is always less than the chondritic ratio.

Mixing of meteoritic metal with native lunar metal could account for the low Ni/Co ratios found in polymict samples because metal associated with samples uncontaminated with meteorites is poor in Ni (<1%) but contains up to several percent Co [e.g., Ryder *et al.*, 1980]. However, this explanation would require about 1:1 mixing of native Fe metal containing about 0% Ni with metal typical of that in ordinary chondrites (e.g., 12% Ni) to account for the metal with 6% Ni observed in the rocks and soils. It is unlikely that the totally melted portion of the target rocks of, e.g., the dimict breccia impactor, contained a quantity of metal equivalent to that of the impactor, considering that the present average metal content of the melt is so high.

I conclude that although some fractionation associated with reaction of meteoritic metal and lunar target material may have occurred, this is not the major reason that siderophile element abundances and ratios in metal from Apollo 16 materials are not chondritic. The major reason, as noted by Hewins *et al.* [1977], is that the Apollo 16 rocks and soils obtained a large fraction of their siderophile elements about 4 Ga ago from a few metal-rich meteorites and these meteorites were not chondrites. The wide variation in Ir/Au ratios observed in lunar samples [e.g., Hertogen, 1977] is in itself reason enough to doubt that all bodies impacting the lunar surface were chondrites. The invocation of a type of meteorite not exactly like any known type of meteorite might be regarded as an ad hoc explanation of the data. However, most of the other explanations discussed above for the nonchondritic composition of the metal in Apollo

16 rocks and soils are no less ad hoc as there is no evidence that such a large quantity of metal of the observed composition can actually be produced by the various mechanisms suggested. The only direct evidence that any chemical fractionation of siderophile elements has occurred is the high concentrations of P and W from the lunar silicates. If models are to assume that the meteoritic component of the breccias is chondritic when the carrier of the siderophile elements, the Fe-Ni metal, is clearly not, then the assumption should be justified with a model for how such a large amount of metal of the observed composition can be produced from a chondritic source.

#### SOME IMPLICATIONS

##### *Model of Palme*

Palme [1980] has used a regression technique similar to that used here on a number of Apollo 16 breccias. He obtains a mean Ni/Co ratio of  $20.0 \pm 1.9$  (one standard deviation?) for a set of nine VHA impact melts and concludes that the projectile responsible for the VHA melt was chondritic with respect to these two elements. However, by the same technique, Ni/Co ratios of 15 and 17 are obtained for two types of VHA melt (Table 5). In this section some reasons for this apparent contradicting conclusion will be examined. Applying the regression technique used here to the data set used by Palme yields essentially the same result:  $20.1 \pm 3.2$  (two standard deviations). One of the samples was a dimict breccia (61015) and another was a sample of type-2 NRC melt (67435). However, the other seven samples are much more variable in composition than are the samples of type-2 DB and NRC melt discussed above. Samples regarded as type-2 melt have a wide range of composition, with Al<sub>2</sub>O<sub>3</sub> concentrations ranging from roughly 20% to 25%. The samples considered by Palme cover this range. Because of the wide and continuous range in compositions with only a few tight clusters (e.g., the dimict breccias), Ryder and Seymour [1982] conclude that "a very large number of melt sheets" were represented among samples of type-2 impact melt rocks. The apparent discrepancy in the Ni/Co ratio of type-2 melts results because Palme [1980] includes some samples that do not necessarily contain the same meteoritic component as the type-2 melts studied here. Two of the samples used by Palme (61156 and 60335) have bulk Ni/Co ratios of about 20. None of the dimict breccias (Table 1) exceeds 18 in bulk Ni/Co ratio.

For reasons already discussed, I disagree with the conclusion of Palme that "... all projectiles, which contributed to the siderophile inventory of Apollo 16 rocks, must have had chondritic Ni/Co ratios..." His conclusion is based on the regression of Co against Ni for a large number of Apollo 16 breccias of a variety of petrographic and compositional types. The Ni/Co ratio obtained is 19. Although this may, in fact, be the mean value, it does not necessarily have the significance Palme states and might be meaningless. Table 6 illustrates why this might be, using hypothetical data. Data set 1 represents different samples from melt rock 1. The metal component of the melt has a Ni/Co ratio of 15 and Ni and Co concentrations in the samples are well correlated. Melt rock 2 has a metal component with a Ni/Co ratio of 17 and Ni and Co concentrations in the five samples are well correlated. Samples of melt rock 2 contain more metal on the average than samples from melt rock 1. The regression analysis based on the data for all 10 samples indicates that the average metal component has a Ni/Co ratio of  $19 \pm 2$ . This value is within the range

for chondrites, whereas the Ni/Co ratio of the metal in neither type of melt rock is. Mathematically, this discrepancy occurs because the Co intercepts and average metal contents are not the same for both data sets. Except for the precision of the data, this hypothetical example is not greatly exaggerated compared to data for Apollo 16 melt rocks. Note that it is not necessary for the targets to have vastly different indigenous concentrations of Co and Ni for this effect to be operative. If for data set 1 the target has 50  $\mu\text{g/g}$  indigenous Ni, then the indigenous Co concentration is 8.3  $\mu\text{g/g}$ . If the target for data set 2 has the same indigenous Co concentration, then the indigenous Ni concentration is 140  $\mu\text{g/g}$ . This is not a large difference considering that the Co intercepts of the two regression lines differ by a factor of 80. If the variation in siderophile abundance among different samples is to be used to infer the composition of the meteoritic component, then it is necessary to use some independent criteria to assure that all samples, in fact, have the same meteoritic component.

Palme [1980] also notes that Ir and Ni concentrations are not tightly correlated in the nine VHA samples and that the implied Ir/Ni ratio of the meteoritic component (25  $\mu\text{g Ir/g Ni}$ ) was substantially different from the chondritic ratio (about 45  $\mu\text{g/g}$ ). After eliminating the three samples with Ni concentrations exceeding 1000  $\mu\text{g/g}$ , a more nearly chondritic Ir/Ni ratio was obtained. Elimination of these samples was rationalized by assuming that the high-Ni samples contained large metal grains that were originally many small grains and that these small grains had efficiently extracted indigenous lunar Ni to lower the Ir/Ni ratio of the metal. If this mechanism were operative, then it would be applicable to the low Ni samples as well, which differ from the high-Ni samples only in containing less (fewer grains of) metal. In this case, no dependence of the Ir/Ni ratio with Ni concentration would be expected. The Ir/Ni ratio obtained by Palme for all nine VHA samples (25  $\mu\text{g Ir/g Ni}$ ) is the same as the value obtained from the dimict breccias (26  $\pm$  3, Table 3). Unlike the data set of Palme [1980], there is no indication of a change in Ir/Ni ratio with Ni concentration in the dimict breccias (Figure 1).

In summary, if samples of the same melt are used, the regression technique can indicate much about the composition of the projectile. If the samples are products of different melting events, then the results of the regression technique do not necessarily relate even to the average composition of the different projectiles.

#### *Indigenous Ni Concentrations and the Models of Wänke et al. and Delano and Ringwood*

Siderophile elements in Apollo 16 polymict samples are contained primarily in metal with nonchondritic concentrations and ratios of these elements. If the metal is essentially similar in composition to that of the meteorite from which it derives, then several models that have assumed a chondrite-like meteoritic component for the samples must be reexamined. Most of these models involve estimating the indigenous abundances of siderophile elements in lunar samples. Two models will be discussed here, both of which attempt to correct for meteoritic Ni and Co in highlands breccias by assuming that all Ir in the breccias is meteoritic and that the Ir/Ni and Ir/Co ratios of the meteoritic component are chondritic. Compared to its concentration in chondrites, Ir is depleted with respect to Ni, Co, and Au in the ancient meteorites that produced the Ni- and Co-rich melt rocks at Apollo 16, and the siderophile elements

from these melt rocks dominate over other meteorite components in the breccias. Consequently, models that assume chondritic Ir/Ni and Ir/Co ratios for the meteorite component undercorrect for the meteoritic contribution to Ni and Co in the breccias and predict large and incorrect concentrations of indigenous Ni and Co. This point is essentially that made by Anders [1978] with respect to Au and the Ir/Au ratio. In this section the effects of assuming chondritic ratios for the meteoritic component of Apollo 16 breccias will be demonstrated for Ni and Co.

*Models of Wänke et al.* In a series of papers from the Mainz group culminating with those of Wänke et al. [1978, 1979] and Palme [1980], it is argued that a large portion of the Ni and Co in the lunar highlands is not of meteoritic origin. The arguments depend to some extent on data for pristine rocks but in large part from data on Ni-rich Apollo 16 breccias. In Table 1 of Wänke et al. [1979], the bulk Ni and Co concentrations in 14 Apollo 16 breccia samples and Apollo 14 sample 14321 are listed along with the fraction of each element contributed by meteorites, based on the assumption that all Ir is meteoritic and that the meteoritic component has chondritic Ir/Ni and Ir/Co ratios. Figure 8 is a plot of the indigenous concentrations against the meteoritic concentrations (the sum of the two is the reported bulk value) as presented in Table 1 of Wänke et al. [1979]. Implications of the results of this "correction" procedure are (1) that indigenous concentrations of Ni as high as 500  $\mu\text{g/g}$  occur in some samples, (2) that indigenous concentrations of Ni and Co vary by an order-of-magnitude among breccia samples that are quite similar in bulk composition and mafic mineral abundance, and (3) that as the concentrations of indigenous Ni and Co increase, so does the abundance of Ni and Co from meteoritic contamination. Each of the last two implications would have important significance if true. However, it is reasonable to expect that the distribution of points should define an approximately vertical line at some indigenous concentration of Ni and Co. The positive correlation and high indigenous concentrations are obtained because the correction procedure underestimates the amount of meteoritic Ni and Co.

Wänke et al. [1979] observe that data for a suite of polymict breccias corrected in this manner yield a Co/(Mg + Fe) ratio averaging 1.37 times the mean value observed for pristine rocks (i.e., rocks thought to be uncontaminated by meteorites, e.g., [Warren and Wasson, 1979]). The high value is in part a manifestation of undercorrection for meteoritic Co. The mean ratio for this suite of breccias would agree with that for pristine rocks if the chondritic constraint were removed and a smaller Ir/Co ratio, i.e., 1/1.37 of the chondritic ratio, were used to apply the correction. If the procedure of Wänke et al. [1979] is applied to the dimict breccias of this work, the mean composition (Table 4) leads to a Co/(Mg + Fe) ratio of 1.81 times the ratio for pristine rocks because of the high content of meteoritic metal. The Ir/Co ratio in the dimict breccia metal, however, is only 0.46 mg Ir/g Co (Table 3), about 50% of the chondritic ratio. As a result, correcting the dimict breccia data by the Co/Ir ratio of the dimict breccia metal yields a Co/(Mg + Fe) ratio lower than the pristine rock ratio, by about 0.51 times. (This is equivalent to calculating the Co/(Mg + Fe) ratio of the metal-free melt composition of Table 4.) Thus neither correction procedure yields a Co/(Mg + Fe) ratio for the dimict breccias similar to the pristine rock ratio; one is low and one is high, each by about a factor of two.

The relative constancy of the Co/(Mg + Fe) ratio for the pristine norites and troctolites plotted by Wänke et al. [1979]

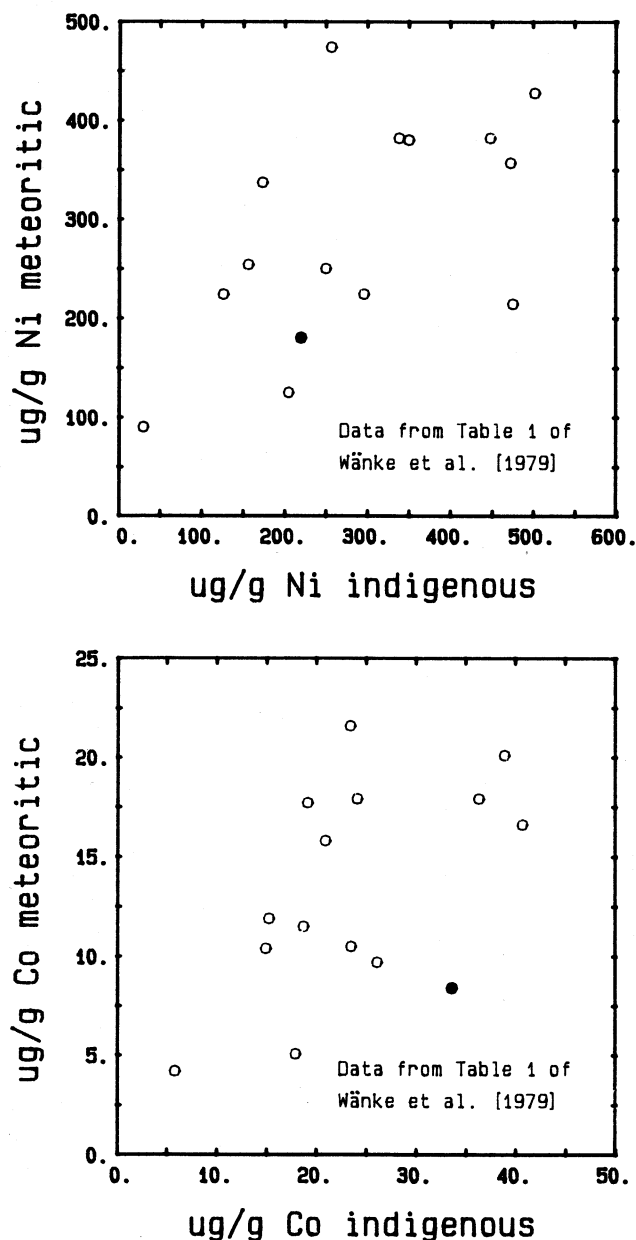


Fig. 8. Data from Table 1 of Wänke *et al.* [1979] in which the bulk concentrations of Ni and Co have been apportioned between a meteoritic and nonmeteoritic (presumably indigenous) component based on a model that assumes all Ir is meteoritic and that the meteoritic component has chondritic Ir/Ni and Ir/Co ratios. All samples are Apollo 16 breccias except one, which is Apollo 14 sample 14321 (filled symbol). The model implies that the Ni and Co contributed by meteorites is somehow correlated with the indigenous concentrations in the target rocks. The correlation results because the assumption of chondritic Ir/(Ni,Co) ratios for the meteoritic component is incorrect and undercorrects for the meteoritic contribution of Ni and Co.

is impressive. However, there is no particular reason to conclude that simply because the meteorite-corrected ratio for a polymict breccia does not agree with the pristine ratio that the correction procedure was in error. *Palme et al.* [1984] note that Co/(Mg + Fe) ratios for Apollo 16 anorthosites are much lower than those for pristine norites and troctolites. These anorthosites are clearly more closely related to Apollo 16 breccias than to the norites and troctolites from Apollos 15 and 17. Hence the Co/(Mg + Fe) ratio obtained above from the metal-free composition

of the dimict breccia melt, although low, may be the correct indigenous ratio for these samples. The low Co/(Mg + Fe) ratio for ferroan anorthosites may be another chemical difference between the ferroan and magnesian suite of pristine rocks. Note that the Co/(Mg + Fe) ratio for 67215 (67215,8A of *Lindstrom and Lindstrom* [1986]), one of the most mafic ferroan rocks collected at Apollo 16, is also less than the ratio for pristine (magnesian) norites and troctolites. This rock has only about 1 ng/g of Ir, so the meteoritic correction is small and leads to a Co/(Mg + Fe) ratio 0.74 times the pristine value (using the chondritic Ir/Co ratio) or 0.64 times (using the dimict breccia Co/Ir ratio). The latter value is similar to that obtained for the dimict breccias.

*Model of Delano and Ringwood.* *Delano and Ringwood* [1978a,b] also argue that the indigenous concentration of Ni in lunar rocks is high. These arguments are repeated in later works and are the basis of models regarding the origin of the moon and differentiation of the lunar crust [*Ringwood*, 1979, 1986; *Ringwood and Seifert*, 1986; *Ringwood et al.*, 1987]. The arguments are based on plots of Ni/Co ratio against Ni concentration for a suite of Apollo 16 rocks and soils [Figures 2, 4, and 5, *Delano and Ringwood*, 1978a; Figures 2 and 3, *Delano and Ringwood*, 1978b]. A plot similar to that of *Delano and Ringwood* [1978a,b] is presented in Figure 9. The data set plotted here (Figure 9a) is not the same as that used by *Delano and Ringwood* [1978a,b]. Instead the data in Figure 9a are for samples of the dimict breccia melt and type-1 melt of Figures 1 and 5b for which Ir concentrations are available. The distribution of points is similar, however, because there are some data in common and all samples plotted by *Delano and Ringwood* [1978a,b] are Ni-rich polymict breccias (and some soils) that contain a large component of noritic melt rock. *Delano and Ringwood* [1978a,b] argue that the trend in the data results from mixing of two components, a high Ni, meteoritic component with a primordial Ni/Co ratio and a low-Ni, indigenous component with a low Ni/Co ratio. Except for the primordial Ni/Co ratio of the high-Ni component, this conclusion is the same as that made early in this paper based on Figure 1 in which mixing relationships are more obvious than they are in the ratio plots of *Delano and Ringwood* [1978a,b]. The best-fit lines from Figures 1 and 5b are curved lines in Figure 9 and represent the mixing relationship between the low-Ni (indigenous) component and the high-Ni (meteoritic) component.

*Delano and Ringwood* [1978a,b] attempt to derive the Ni and Co concentrations of the indigenous component by subtracting from the bulk compositions the meteoritic contribution based on the chondritic (H-group) ratio of Ir to Ni and Co and the assumption that all Ir is meteoritic. The result of applying the Delano-Ringwood correction to the data of Figure 9a is shown in Figure 9b. (As I am only addressing the appropriateness of the meteoritic correction, I have not applied the "plagioclase-dilution" adjustment of *Delano and Ringwood* [1978a,b]. This adjustment would yield points plotting at even higher Ni concentrations than those of Figure 9b, but at the same Ni/Co ratio.) Taken at face value Figure 9b implies that (1) indigenous Ni concentrations as high as 1200  $\mu\text{g/g}$  occur in some samples, (2) other samples of the same melt (which have nearly identical lithophile element concentrations and some of which are pieces of the same rock) have indigenous Ni concentrations as low as 100 to 200  $\mu\text{g/g}$ , and (3) indigenous Ni/Co ratios in the samples range over a factor of three and increase with increasing indigenous Ni concentration. *Delano*

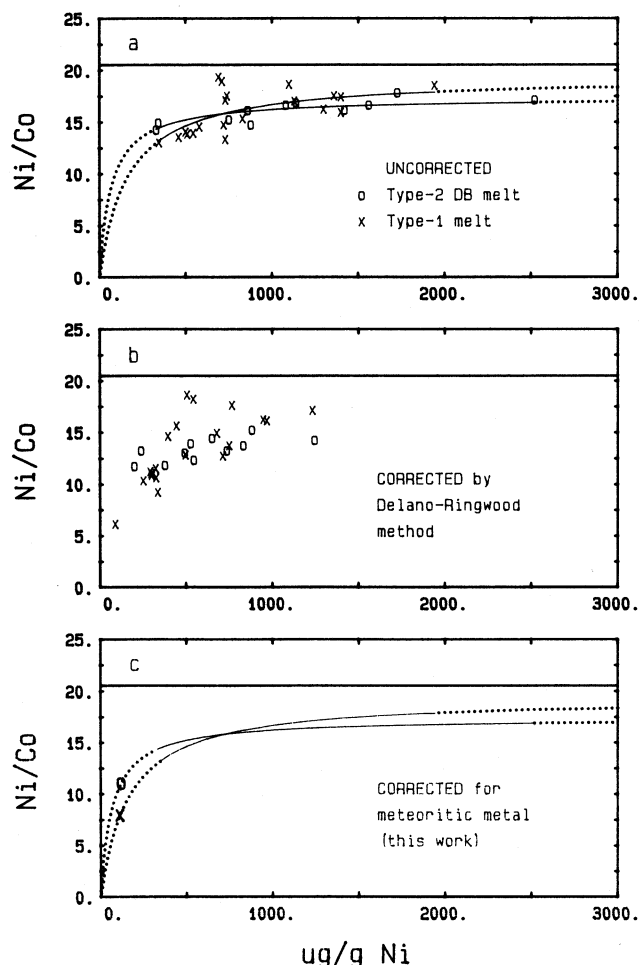


Fig. 9. Ni/Co versus Ni, after *Delano and Ringwood* [1978a,b]. (a) Same data as Figures 1 (dimict breccia melt) and 6a (type-1 melt), but only for those samples for which Ir data are available. The horizontal line is the chondritic Ni/Co ratio of 20.5. The curved lines are the best-fit (solid) lines from Figures 1 and 5b; the dotted portion represents extrapolation past the extreme data points. (b) Data corrected for the meteoritic component by the method of *Delano and Ringwood* [1978a,b], which uses the chondritic Ir/Ni and Ir/Co ratio (51  $\mu\text{g/g}$  and 1.1 mg/g, respectively) and assumes all Ir is meteoritic. (c) Data corrected for meteoritic metal using the same technique as used by *Delano and Ringwood* [1978a,b], but using the ratios of Ir/(Ni,Co) in the metal (Table 3; Figure 7) instead of the chondritic ratios. The  $\circ$  and  $\times$  at 120  $\mu\text{g/g}$  Ni represent the mean of all samples of each type. As the corrections in this case are nearly 100% corrections, the individual data points scatter greatly and include negative values.

and Ringwood interpret this last observation as a fractionation trend such as is observed in terrestrial tholeiitic basalts. It seems unlikely that any such a trend would be observed within samples from a single hand specimen (61015, Table 1).

These implications are simply unreasonable. They are basically the same as those obtained above from the model of *Wänke et al.* [1979] and result from the same incorrect assumption, namely, that the Ir/Ni and Ir/Co ratios of the meteoritic component are primordial. Correcting the data in Figure 9a by using the Ir/Ni and Ir/Co ratios of the metal phase obtained from the regression technique (see Figure 7) yields the results illustrated in Figure 9c, i.e., a very much lower indigenous Ni concentration. Only the mean values for the two types of rocks are plotted. The scatter in values for individual samples is great because the correction is typically >90% for Ni, and both positive

and negative Ni concentrations are obtained for individual samples when the mean Ir/Ni ratios calculated from the regressions in Figures 1 and 7 are used.

Note also that even if *Wänke et al.* [1979] and *Delano and Ringwood* [1978a,b] are correct that the Ir/Ni and Ir/Co ratios of the meteoritic component of Apollo 16 rocks and soils is chondritic, their correction procedures are not applicable to individual samples. By their models, the Ir, most of the Ni, and some of the Co are presently carried by metal grains. They argue that a fraction of the Ni in the metal (this would be a large fraction in the case of Apollo 16 rocks) is Ni that has been extracted into the metal but that was originally associated with lunar silicates, and they implicitly or explicitly argue that this is the cause of the subchondritic Ir/Ni ratio of the metal. The concentration of metal is highly variable even among samples from the same rock (Table 1). Hence the Ir concentration of a given sample tells us at best only about the quantity of metal in that particular sample (which may be high or low compared to other samples of its type if we assume constancy of Ir concentration in the metal). Because the Ni that remains after correcting for the meteoritic contribution resides primarily in an immiscible metal phase, the concentration obtained does not necessarily reflect the indigenous concentration in that particular sample. The "fractionation" trends in Figures 8 and 9b simply represent sampling error associated with nonuniform distribution of the metal grains among small samples. Hence even if the Ir/Ni and Ir/Co ratios of the meteoritic component are chondritic, the corrected data of Figure 9b do not have the significance stated by *Delano and Ringwood*.

Another reason that such high concentrations of indigenous Ni are calculated by *Wänke et al.* [1979] and *Delano and Ringwood* [1978a,b] is that the estimates are made from those samples most severely contaminated by meteoritic Ni. If they had used samples with lower Ir concentrations, they would have obtained lower estimates for the indigenous concentrations of Ni and Co. To minimize the uncertainty associated with any correction for meteoritic siderophiles, the best estimates of the indigenous Ni concentrations in the lunar highlands should be obtained from the samples least contaminated by meteorites such as the "pristine rocks" [e.g., *Anders, 1978; Warren and Wasson, 1979*]. *Anders* [1978] estimates 6  $\mu\text{g/g}$  indigenous Ni for the highlands crust based on data for pristine rocks. On the other hand, this estimate is almost certainly too low for the types of breccias considered by *Wänke et al.* [1979] and *Delano and Ringwood* [1978a,b]. The Apollo 16 samples upon which *Anders* [1978] based his estimate are mostly anorthositic rocks with very low contents of mafic minerals, the primary carriers of indigenous Ni. We would expect the indigenous Ni concentrations of the noritic melt rocks from Apollo 16 to be greater because the Fe concentrations are probably much greater than the pristine rocks considered by *Anders* [1978]. (We can only infer the Fe content of the rocks plotted in Figure 3 of *Anders* [1978] by the sample descriptions in *Hertogen et al.* [1977] and their low Rb contents.)

*Delano and Ringwood* [1978a] argue that the pristine rocks do not offer a true estimate of the indigenous concentration of Ni in the lunar crust because they are not primary igneous rocks, but impact melts from which the siderophile elements have been nearly totally extracted by metal that sunk to the bottom of the melt pool and was unsampled. *Warren and Wasson* [1979] have argued strongly against this scenario. To their arguments I add the following. We would expect that the settling of the metal would not be 100% efficient. The rocks discussed

earlier in this work are impact melt rocks containing 1–2% metal that apparently did not settle so deeply that it was unsampled. Hence we would expect that any metal found in the pristine rocks would be similar to the metal found in noritic melt rocks if, as *Delano and Ringwood* [1978a,b] suggest, the pristine rocks are also impact melts. However, *Ryder et al.* [1980] have shown that metal from pristine norites and troctolites, although rare, has a distinctly different composition than that from polymict rocks; it usually has much lower Ni concentrations and higher Co concentrations than any metal of meteoritic origin. Although most of the pristine samples studied by *Ryder et al.* [1980] are from Apollo 17, the bulk composition of Fe-Ni metal in polymict samples from Apollo 17 is generally similar to that in polymict samples from Apollo 16. Again, the best estimate of the indigenous concentration of siderophile elements in the lunar crust should be made from the samples least contaminated by meteorites, e.g., the pristine rocks, not from samples containing the largest component of extralunar siderophile elements.

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R. L. Korotev, Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130.

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