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Cobalt and nickel concentrations in the “komatiite component” of Apollo 16 polymict samples

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Some estimates for the concentrations of Co and Ni in the primitive mafic component of Apollo 16 breccias and soils are large, comparable to concentrations in terrestrial komatiites. These estimates may be erroneously high because the contribution from meteoritic contamination of the samples has been underestimated. However, even if the correction for meteoritic Co and Ni is valid and the calculated residual Ni is not of meteoritic origin, the Ni is presently carried by Fe-Ni metal while the Fe and Mg are carried by mafic silicates. If any large-scale separation of metal and silicate phases has occurred, the concentration ratio of Ni to Fe + Mg in the mafic silicates of the ancient crust in the vicinity of the Apollo 16 site has not been preserved by Apollo 16 rocks. Apollo 16 polymict breccias and soils contain much higher concentrations of siderophile elements and Fe-Ni metal than other nonmare samples from the Moon. Thus, it is likely that the Ni/(Mg + Fe) ratio estimated for the komatiite component from Apollo 16 samples is high compared to the actual ratio for the lunar crust.

1. Introduction

Nearly all samples returned by the Apollo 16 mission to the Moon are polymict breccias and soils. Compositional variation among these samples can be explained, to a first approximation, by the relative proportions in the mixtures of more-primitive constituents of two broad compositional types, namely (1) plagioclase-rich rocks, including anorthosite as well as troctolitic, noritic, and gabbroic anorthosites, and (2) norites in the form of impact melt breccias. The two most common compositional extremes found at Apollo 16 are represented by rocks of these types. As a result of this binary mixing, data for polymict samples are usually well correlated and plot along a line between anorthositic samples and noritic impact melt breccias in simple plots of lithophile element variation such as Fig. 1 [1–4].

The noritic impact melt breccias (“low-K Fra Mauro basalts”) are believed to have crystallized from melt produced by relatively large impacts [5–7]. They contain lithic and mineral clasts in a matrix often having an igneous texture. The matrices of different samples from a given site are

usually very uniform in composition, or fall into one of a few compositional groups each believed to represent melt from a different impact [7–9]. Noritic impact melt breccias are probably mixtures of more primitive igneous rocks as no rocks of this composition have been identified as unbrecciated.

Several efforts have been directed at identifying the nature of the primitive mafic component(s) of Apollo 16 materials [10–15]. In a recent paper, Ringwood et al. [16] readdress this issue and conclude that the primitive mafic component is a komatiite similar in composition to terrestrial komatiites. The concentrations of most elements in this komatiite component are estimated from mixing diagrams such as Fig. 1 by extrapolation of the mixing lines to high concentrations of elements associated with mafic mineral phases. This technique implicitly assumes that even the most mafic polymict samples in the Apollo 16 collection, the noritic impact melt breccias, contain a component of plagioclase that was acquired by mixing. It also requires a quantitative assumption about the proportion of such a plagioclase component in the mixtures in order to know how far to

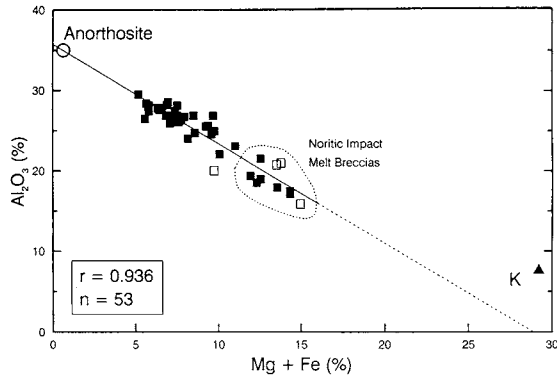


Fig. 1. Concentration of Al_2O_3 as a function of the concentration of $\text{Mg} + \text{Fe}$. The filled squares are for the 49 analyses in the data set of Delano and Ringwood [22]; the open squares are for 4 other analyses listed in the sources used by Delano and Ringwood [22], but apparently excluded from the data set. All samples are polymict breccias and soils from Apollo 16. The line is the best fit to these data (simple least squares). In the high Al_2O_3 direction, the line extrapolates toward anorthosite (circle). (If samples with $> 30\%$ Al_2O_3 had been included in the data set, they would fill the gap between 30 and 35% Al_2O_3 .) The polymict samples with high concentrations of $(\text{Mg} + \text{Fe})$ are (or have a large proportion of) noritic impact melt breccias. The composition of the "lunar komatiite" component of Ringwood et al. [16] is indicated by "K" and feldspathic ilherzolite 67767 [18] by the triangle.

extrapolate the mixing lines. Differences among estimates for the composition of the primitive mafic component of Apollo 16 materials arise primarily from differences in the magnitude of this assumption [10–16]. For example, Ringwood et al. [16] extrapolate their mixing lines to 6.6% Al_2O_3 , and obtain a concentration of 27.7% for $\text{Mg} + \text{Fe}$ in their primitive component. (The komatiite component does not plot exactly on the line of Fig. 1 because its composition was obtained by a best-fit technique involving mixing lines for several elements. Mixing lines for Al and Ca were extrapolated to the point where the Ca/Al ratio was chondritic, after Wänke et al. [13,14].)

Using a similar correlation technique, after subtracting an estimate of the Co and Ni concentrations derived from meteorites, Ringwood et al. [16] infer that the concentrations of Co and Ni in their komatiite component are very large (1327 $\mu\text{g}/\text{g}$ Ni and 78 $\mu\text{g}/\text{g}$ Co) compared to concentrations observed in those rocks from the lunar highlands that are generally believed to be unbrecciated relicts of the ancient lunar crust [17–19]. Korotev [20] and Warren et al. [21] have argued

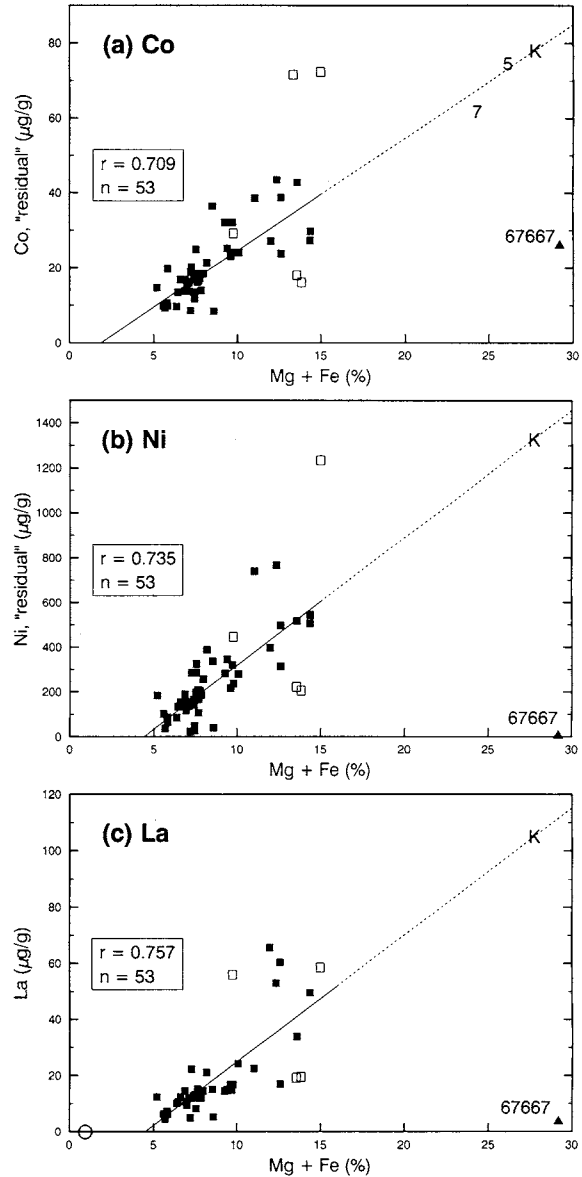


Fig. 2. (a) Concentration of Co, corrected for meteoritic contamination by the procedure of Ringwood et al. [16], as a function of $(\text{Mg} + \text{Fe})$ concentration in polymict breccias and soils from Apollo 16 (see Fig. 1). The line is the best-fit line to the filled squares, as read from fig. 4 of Ringwood et al. [16]. The Apollo 15 green glass plots at 5 and the Apollo 17 orange glass at 7. (b) Like (a), but for Ni. (c) Like (a) and (b), but for La. The line is the best-fit line (simple least squares) to the 53 data points (squares). In this plot the K represents the composition inferred here for the komatiite component using the same technique as used for Co and Ni, although a concentration for La was not reported by Ringwood et al. [16].

that the concentrations estimated for indigenous Co and Ni are erroneously high and that the error derives from the assumption of Ringwood et al. [16] that the meteoritic component of the Apollo 16 breccias has ratios of Ir to Co and Ni like those in H chondrites. If the bulk of the extralunar Co and Ni in Apollo 16 samples is assumed, instead, to derive from meteorites with lower Ir/Co and Ir/Ni ratios, e.g., EH chondrites [21] or iron meteorites [20], then the concentration of "residual" (indigenous) Ni becomes much smaller and perhaps negligible. Others have also argued that the meteoritic component of Apollo 16 breccias is not like carbonaceous or H chondrites and that corrections based on chondritic ratios leads to an overestimation of the indigenous Ni [17,19]. This particular disagreement is not the subject of the present paper. The purpose here is to show that irrespective of the validity of the correction for meteoritic Co and Ni, the correlation technique used to estimate the composition of the komatiite component is likely to lead to a invalid result for siderophile elements in Apollo 16 samples.

2. Data set

I have attempted to duplicate the data set of Ringwood et al. [16]. This data set is that described [22] as "49 analyses for Co and Ni in Apollo 16 rocks and soils" that were obtained from several sources [13,14,23–27]. These sources contain data for 53 analyses in which concentrations for Al, Fe, Mg, Ni, Co, and Ir are reported and the Al_2O_3 concentration is less than 30%. The four analyses that do not appear to have been used are for two samples each of 60016 [13] and 62295 [14]. No explanation is given for why these four analyses were not included, but three of the four lie outside the range of the other samples in Fig. 2a and b. They are included here, however, and are given a different symbol in the figures (see Fig. 1).

3. Co and Ni correlations

Fig. 2a and b are plots of Co and Ni concentrations in Apollo 16 rocks and soils as a function of the sum of the Mg and Fe concentrations. In both plots, the Co and Ni concentrations have been corrected for "meteoritic contamination" by the

procedure of Ringwood et al. [16], i.e., the reported Co and Ni concentrations have been reduced by subtracting the quotient obtained by dividing the reported Ir concentration, which is assumed to derive entirely from the meteoritic component, by Ir/Co and Ir/Ni ratios in ordinary chondrites. For consistency, the same values for these ratios as used by Delano and Ringwood [22] are used here (Ir/Co = 1.1 mg/g and Ir/Ni = 51 $\mu\text{g/g}$). The corrected concentrations are called "residual" Co and Ni because they are intended to represent Co and Ni indigenous to the Moon. Following the precedent of Ringwood et al. [16], small "corrections" to the Fe concentrations have also been made following the same procedure. (Ringwood et al. [16] do not explain why similar corrections are not also made to Mg concentrations.) Fig. 2a and b are equivalent to figs. 4 and 5 of Ringwood et al. [16]. The distributions of points in the figures are not identical to those of Ringwood et al. [16], but are generally similar. The largest difference between the figures presented here and those of Ringwood et al. [16] is that Fig. 2a and b each appear to contain more points. In both figures, the lines are the best-fit lines of Ringwood et al. [16], as read from their corresponding figures; the correlation coefficients (r), however, are those obtained here for the 53 data pairs in each data set.

Ringwood et al. [16] argue on the basis of Fig. 2a and b that because Co and Ni concentrations correlate positively with Fe and Mg concentrations, Co and Ni must be associated with the ferromagnesian component of the breccias. They then extrapolate the best-fit lines to 27.7% Mg + Fe, the concentration in their primitive component (section 1, above), and conclude that the primitive component has 78 $\mu\text{g/g}$ Co and 1327 $\mu\text{g/g}$ Ni (Table 1). Although a procedure such as this would be valid with many systems, it can lead to unreasonable results in the particular case of lunar polymict samples. For example, in Fig. 2c the concentration of an incompatible trace element, La, is plotted against Mg + Fe concentration for the same data set as Fig. 2a and b. Although not strong, the correlation of La with Mg + Fe is slightly better than that for Co and Ni (Fig. 2a, b). By the same logic as used by Ringwood et al. [16], we would be obliged to conclude that the lunar komatiite component has a La con-

TABLE 1

Comparison of "lunar komatiite" [16] and Apollo 16 sample 67667,3 [18]

	Lunar komatiite	67667
SiO ₂ (%)	45.16	42.4
TiO ₂	0.54	1.0
Al ₂ O ₃	6.61	7.6
Cr ₂ O ₃	0.40	0.38
FeO	14.77	17.1
MnO	0.19	0.20
MgO	26.92	26.4
CaO	5.31	5.3
Na ₂ O	0.10	0.16
Ni (μg/g)	1327	4.4
Co	78	26
V	112	n.a.
Sc	23	24.4
La	105 ^a	3.6

^a Not reported by Ringwood et al. [16], but derived here by techniques similar to those used by Ringwood et al. to obtain the Ni and Co concentrations (Fig. 2).

centration of 105 μg/g, the value obtained by extrapolating the best fit line to 27.7% Mg + Fe. This is approximately the La concentration in lunar KREEP [28] and is considerably larger than that usually found in primitive mafic rocks, such as terrestrial komatiites.

The La concentration inferred from Fig. 2c is also much larger than the La concentration actually observed in primitive, mafic rocks from the Moon. Discounting fragments of exotic mare basalt, the most mafic Apollo 16 sample is 67667, described by Warren and Wasson [18] as a "feldspathic lherzolite". This 7.9 g rock is the only highly mafic sample from Apollo 16 for which compositional data are available to compare. As noted by Warren et al. [21], but not Ringwood et al. [16], the concentrations of compatible lithophile elements in 67667 are remarkably similar to those of the lunar komatiite (Table 1). However, the La concentration of 67667 is only 3.6 μg/g [18], considerably lower than the 105 μg/g obtained above by the extrapolation technique for the komatiite component (Fig. 2c). Similarly, the concentrations of Co (26 μg/g) and, particularly, Ni (4.4 μg/g) are much less in 67667 than the values for the komatiite component (Table 1). These observations suggest that there is some error associated with the correlation method used by

Ringwood et al. [16]. The reason why La concentrations correlate with those of Mg + Fe even though a primitive mafic component is not the carrier of the La is the subject of the next section.

4. Mixtures of mixtures

In general, polymict samples from the lunar highlands require four types of chemical components to account for four distinct "element associations" [29]: (1) a felsic component to account for Al and some Sr and Eu, (2) a mafic component to account for most of the Mg, Fe, Sc, Cr, etc., (3) a "residual liquid" (KREEP) component to account for incompatible trace elements, and (4) a meteoritic component to account for siderophile elements in excess of those supplied by the other three components. Each of these chemical components is probably represented by a variety of rock types with a range of compositions. In general, one would not necessarily expect binary mixing lines such as those in Figs. 1 and 2 in a four-component system. Apollo 16 polymict samples approximate simple binary mixtures because a single rock type, the noritic melt breccia, is the principal carrier of three of the four chemical components. Samples with the largest concentrations of Mg and Fe, such as breccias 61015 (melt rock portion [6]) and 65015, also have high concentrations of Ni and La; samples that contain high concentrations of elements from only one or two of these three element groupings are rare (e.g., 67667). Anorthositic samples from Apollo 16 seldom have high concentrations of either incompatible trace elements or siderophile elements.

Noritic melt breccias are the most mafic, common rock types in the lunar highlands. Samples of similar major element composition occur at nearly every landing site. As reviewed by Reid et al. in 1977 [5], it is unlikely that noritic impact melt breccias ("low-K Fra Mauro Basalts") are the direct product of some igneous process because although they are common, no samples with igneous textures have been found (an observation still true today). They were most likely produced by impacts large enough to penetrate the felsic surface material and incorporate mafic cumulates into the impact melt as well as material rich in the residual liquid of crust formation [5,7,18]. Thus, mathematical removal of the felsic component of

Apollo 16 breccias leaves a residuum dominated by a component of noritic melt breccia that itself may be a mixture of more primitive components. Mixing trends such as that in Fig. 2c indicate that the mafic component and the KREEP component of the breccias were intimately mixed before admixture of the felsic component which leads to the binary mixing trends.

The treatment of Ringwood et al. [16] implicitly assumes that Apollo 16 polymict samples are simple mixtures of two igneous rock types, a mafic rock type and an anorthositic rock type. When the mixing line in Fig. 1 is extrapolated to high Al_2O_3 concentrations, it does, in fact, intersect the field of a type of igneous rock common to Apollo 16, ferroan anorthosite. In similar plots for any pair of elements, the mixing lines trend toward anorthosite or noritic anorthosite (e.g., Fig. 2c). However, mixing lines extrapolated in the other direction past the field for noritic melt breccias do not intersect the field for any observed type of rock, igneous or otherwise. Although the line extrapolates toward sample 67667 in the Al_2O_3 vs. (Mg + Fe) plot of Fig. 1, the corresponding line in the Ni vs. (Mg + Fe) plot of Fig. 2b or the La vs. (Mg + Fe) plot of Fig. 2c does not. Thus, a rock type like 67667 is not the mafic, Ni-rich, La-rich component collectively implied by applying the method of Ringwood et al. [16] to the data of Fig. 2.

Given that the noritic melt breccias are themselves probably mixtures of two or more types of more primitive rock, we have no particular reason to suspect that such an extrapolation has any meaning with respect to actual rock types. This is demonstrated schematically in Fig. 3 (adapted from Korotev [30]). Polymict samples (circles) are binary mixtures of rock types A and B, both of which occur locally. Rock type B is itself a breccia that is a mixture of igneous rock types, I, M, and S (and, possibly, a small component of rock type A) that are not well represented at the site as discrete samples. As a consequence, the mixing trend defined by the polymict samples does not extrapolate toward rock types I, M, or S even though each is a chemical component of all the polymict samples. The extrapolation of the mixing line past point B has no meaning with respect to the component rock types of the polymict samples. If component M is the principal carrier of

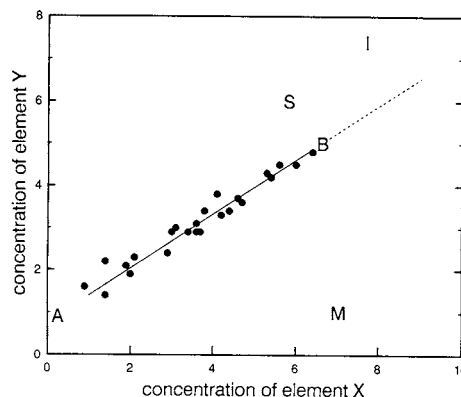


Fig. 3. Schematic mixing diagram for hypothetical components; see text. The circles represent polymict samples (breccias and soils); B is a breccia containing chemical components of igneous rocks A, S, I and M.

Mg and Fe, I is the principal carrier of the incompatible trace elements, and S the principal carrier of siderophile elements, then the extrapolation does not tell us anything about the siderophile element concentrations in component M. This example may appear extreme, but as shown below, most of the Ni and much of the Co in Apollo 16 polymict samples is, in fact, in a different phase (Fe-Ni metal) than most of the Mg and Fe (mafic silicates and oxides). Fig. 3 demonstrates the problem of inferring mixing relationships in systems with several generations or "levels" of mixing [30].

In the case of Apollo 16 samples, all we can conclude for certain from Fig. 2a and b is that residual Co and Ni are presently associated with Mg and Fe in the polymict samples with the greatest concentrations of these elements. In that sense, the statement of Ringwood et al. [16] that the correlations clearly show "that residual cobalt and nickel... are associated with the ferromagnesian component of the breccias" is indeed correct. The ferromagnesian component, however, is noritic impact melt rock, not necessarily a rock type that is more primitive and more mafic. Most of the Mg and Fe in mafic silicates of Apollo 16 samples have experienced at least one episode of crystallization from an impact melt. Thus, we cannot conclude for certain that the mafic igneous precursors of the noritic melt breccias (if there are precursors that are more mafic) have concentrations of Co and Ni as large as those derived by Ringwood et al. [16] because the primitive component that contributed the bulk of the Mg + Fe

tions, and (3) the sum of the concentrations of Fe, Co, and Ni in the metal is 100%, then we can calculate the composition of the metal [20]. These calculated metal compositions are listed in Table 2 along with the whole rock composition calculated from mass balance. The metal compositions obtained in this manner agree well with results of direct analysis of metal grains [33–37] and other previous estimates [20]. Each of the three samples in Table 2 has substantial concentrations of Fe-Ni metal, ranging from 0.51% to 1.14%. In sample 61015 (whole rock), 19% of the Fe, 90% of the Co, and virtually all of the Ni, Ir, and Au reside in the metal phase.

The correction for meteoritic Co and Ni of Ringwood et al. [16] is not intended to be a correction for metal. The "residual" Co and Ni concentrations of the samples in Fig. 2a and b (average: 21 $\mu\text{g/g}$ Co and 257 $\mu\text{g/g}$ Ni) are still much greater than the concentrations in the non-magnetic fractions of the samples in Table 2 (average: 6 $\mu\text{g/g}$ Co and 60 $\mu\text{g/g}$ Ni). Ringwood et al. ([16]; also [22,38]) assert that Co and Ni originally contained in lunar silicates (presumably, the komatiite component or a derivative) have been reduced by impact processes and partitioned into a metal phase derived primarily from metal-bearing meteorites. This hypothesis leads to some interesting, though seemingly improbable, corollaries. First, unless a large amount of iron was also reduced, the concentration of Ni found in Fe-Ni metal in Apollo 16 breccias must be greater than that of the impactors supplying the metal. However, the metal in the breccias has 5–7% Ni (Table 2), which is already at the low end of the range for metal in meteorites [20]. Second, the assumption requires that the reduction and extraction process was remarkably efficient. If the Co and Ni in the metal phase of the three rocks in Table 2 derive from impact reduction and the concentrations in the non-magnetic fractions represent the concentrations of Co and Ni in the non-metal phases, then 80% of the Co and 90% of the Ni in these rocks has been reduced. Any process this severe would likely lead to some unusual silicate mineralogy and composition, but the silicate portions of Apollo 16 impact melt rocks are the same as those which contain much less metal from other sites.

If we ignore these concerns and assume that the

contention of Ringwood et al. [16] is correct; i.e., that "residual" Co and Ni of Fig. 2a and b derives from lunar mafic silicates but is now contained in Fe-Ni metal through impact reduction, then it is still unlikely that the correlation technique can accurately predict the Co and Ni concentrations of the early lunar silicates. The problem is that of metal segregation. On a small scale, metal segregation has clearly occurred. Raw Co and Ni concentrations in the two samples of 60016 in the data set of Fig. 2a and 2b differ by a factor of 2.5 [13], and worse examples of non-uniform distribution of metal grains in Apollo 16 breccias have been observed [20]. This leads to most of the scatter in Fig. 2a and b. If any large-scale segregation has occurred, then systematic error will occur in the correlation technique. Only if Apollo 16 samples (silicate plus metal) have retained, on the average, Co/Mg and Ni/Mg ratios identical to those of the target material of the impacts will the correlation technique of Ringwood et al. [16] accurately predict the Co and Ni concentrations of the average preimpact material. If the Apollo 16 samples are enriched or depleted in Fe-Ni metal compared to the impactor–target system, however, then the method will overpredict or underpredict the Co and Ni concentrations of the preimpact silicates.

This oversight is curious, considering that Ringwood, Wänke and coworkers have been strong advocates of metal segregation in the lunar crust [16,22,31,38,39]. They have suggested that the reason that some rocks have such low concentrations of siderophile elements is that they derive from upper regions of impact melt pools from which siderophile elements were depleted by sinking of metal [16,31,38]. This suggestion requires that somewhere there are rocks which contain an excess of metal and, therefore, which contain Co and Ni scavenged from an entire melt pool. Perhaps Apollo 16 mafic impact melt rocks represent such samples. Among Apollo 16 samples, the melt-rock portions of the rock types known as dimict breccias, such as sample 61015 (Table 2), have, on the average, the highest Ni and metal concentrations of any returned lunar rock type [20]. From petrographic arguments, these samples are believed to be from the bottom of a large impact crater [6]. As noted by Ringwood et al. [16], when the correlation technique is applied to samples from other