

Geochemical relationships between some pallasites and iron meteorites

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SUMMARY. Published analyses for 14 trace and minor siderophilic elements have been interpreted to indicate a close relationship between the IIIAB iron meteorites and the main group of pallasites. These two groups respectively account for about 32 and 75 % of all irons and pallasites. The composition of the metal in the main group pallasites is very close to that calculated for the liquid after 80 % of a IIIAB iron melt has fractionally crystallized. The pallasites probably formed by the intrusion of residual molten metal from the core into a surrounding olivine mantle.

PALLASITES are meteorites composed of roughly equal proportions by weight of metal and olivine (Mason, 1963). They are generally believed to have formed by the intrusion of molten metal into an olivine mantle that was produced by igneous differentiation of chondritic material (Ringwood, 1961; Lovering, 1962). Metal analyses by Buseck and Goldstein (1969) indicate that the pallasites cooled at about $1^{\circ}\text{K Myr}^{-1}$ through the temperature range 1000–700 °K. Calculations by Fricker *et al.* (1970) suggest that burial depths of around 200 km were necessary to achieve these cooling rates. The olivine–metal textures in pallasites appear to be consistent with a rapid intrusion of molten metal into an olivine aggregate. Scott (1977*b*) found that large sections of pallasites with angular olivines commonly show large olivine masses, which appear to have been disintegrating into smaller crystals, like those dispersed through the metal. If the metal was close to the liquidus temperature during its intrusion, incipient solidification of metal on olivine may have prevented the gravitational separation of these phases. Pallasites with rounded olivines probably formed during extensive annealing of olivines in partially molten metal (Scott, 1977*b*).

If pallasites formed by olivine–metal mixing, it would seem likely that some iron meteorites may represent unmixed metal from an adjacent location to the pallasites. The first authors to suggest that certain iron meteorites and pallasites were related were Lovering *et al.* (1957). They found that the Ni, Ga, and Ge contents of metal in 8 pallasites were almost indistinguishable from those in the third of their four groups of iron meteorites. Using greater precision and sensitivity, Wasson and co-workers have classified about 500 iron meteorites into 12 groups (Scott and Wasson, 1976, and earlier papers listed therein), and discovered two distinctive clusters amongst 34 pallasites, a main group and an Eagle station trio (Scott, 1977*a*).

Fig. 1 is a logarithmic Ga–Ni plot showing the outline of these meteorite groups with the pallasites distinguished by shading. The close proximity of group IIIAB, which is the largest iron meteorite group with 32 % of all irons (Scott and Wasson, 1975), and the main group of pallasites, which accounts for about 75 % of all pallasites, suggests that these two meteorite groups could be related. Although three other small groups of irons, IIE, IIIE, and IIICD also plot close to the main group pallasites, the unusual mineralogy of these irons would appear to rule out any close relationship with the pallasites (Scott, 1977*a*).

The fractionation of trace and minor elements within group IIIAB (and most other iron meteorite groups) was attributed by Scott (1972) to fractional crystallization of a molten iron

core. On logarithmic interelement plots, the IIIAB irons show strong correlations, and have gradients that are generally qualitatively consistent with element fractionations predicted from published phase diagrams for Fe alloy systems. Wasson and Wetherill (1967) also favoured a fractional crystallization origin for group IIIAB, and concluded that convective mixing, which is necessary for fractional crystallization, would occur if the core solidified from the centre to the edge.

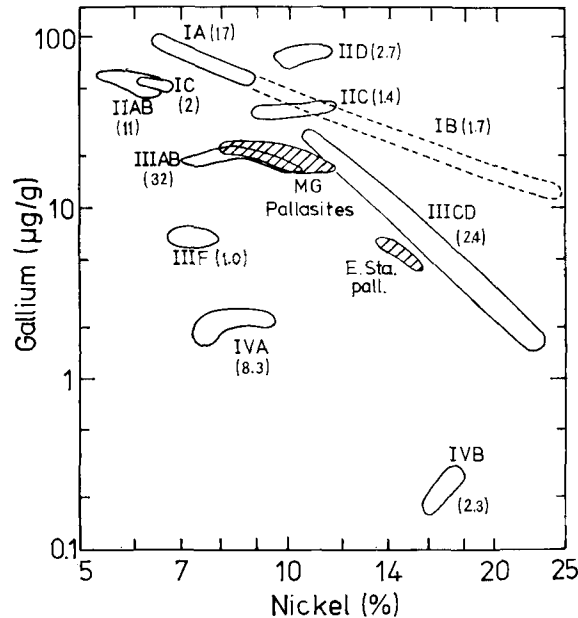


FIG. 1. Logarithmic plot of Ga against Ni showing analyses of metal in pallasites and iron meteorites. Meteorite groups are shown in outline, with the pallasites shaded and the percentage of irons in each group shown in parentheses. Most pallasites (~75%) belong to the main group, which overlaps the IIIAB irons. There is no obvious relationship between the Eagle station trio of pallasites and any of the recognized iron meteorite groups. (Data taken from Scott and Wasson, 1975; Scott 1977a.)

The purpose of this paper was to investigate whether the composition of metal in main group pallasites could be related to the liquid composition during fractional crystallization of a IIIAB core. Any relationship could provide useful clues to the origin of the pallasites, and support for Scott's (1972) explanation for the chemical trends in iron meteorite groups.

Fractional crystallization. The compositions of liquid C_L and solid C_S during fractional crystallization are given by the well-known Rayleigh (1896) fractionation law: $C_S = kC_L^0 (1-f)^{(k-1)}$, where k is the distribution coefficient, defined as the ratio of the solute concentration in the solid to that in the liquid, C_L^0 is the initial composition of the liquid, and f is the fraction of liquid remaining. It is assumed that k is constant during solidification, the liquid is thoroughly mixed, and there is no diffusion in the solid. In asteroidal cores, the third condition may be a good approximation as diffusion cannot homogenize metal over km distances. If analyses of core samples are subsequently plotted on two-element logarithmic graphs, the gradient is given by $(k^A - 1)/(k^B - 1)$, where k^A and k^B are the distribution coefficients for elements A and B (Scott, 1972). It is also easy to show that the path of the liquid composition during solidification defines a line with the same gradient (fig. 2).

Values for the distribution coefficients of the siderophilic elements between solid and liquid iron, and the bulk composition of the IIIAB core are not known with any certainty.

However, both parameters can be related to another that may be evaluated more easily. A histogram of Ni contents in group IIIAB shows a fairly sharp lower limit around 7.4 % Ni (Scott *et al.*, 1973), as would be expected for an element with $k < 1$ if the core is well sampled. The bulk composition can be obtained by dividing the concentration in group IIIAB at 7.4 % Ni by the appropriate distribution coefficient, thus reducing the number of unknown parameters in the fractionation equation.

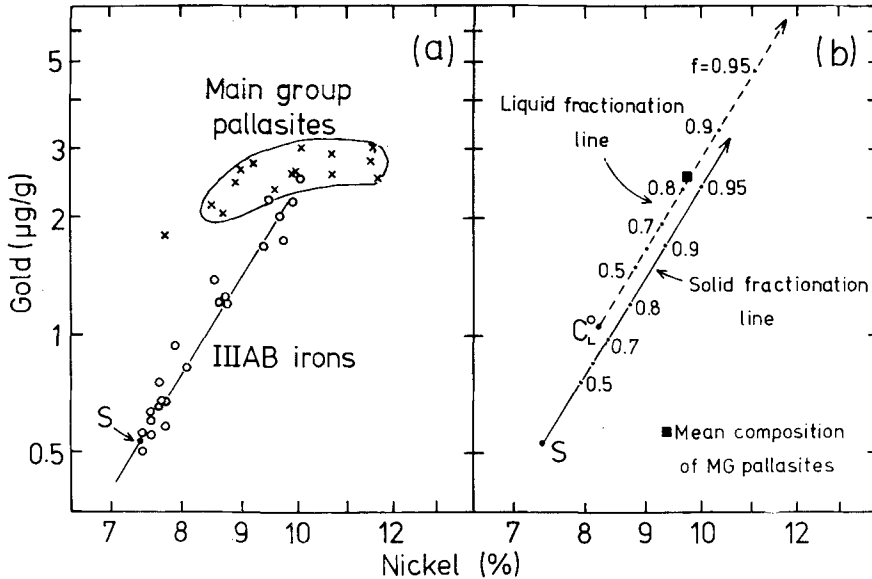


FIG. 2a (left). The logarithmic Au-Ni plot shows analyses for IIIAB irons (O) and metal in main group pallasites (X). FIG. 2b (right) shows the proposed path of the liquid composition during fractional crystallization when the IIIAB line in fig. 2a is taken to represent the solid fractionation line. C_L^0 is the bulk composition of the liquid core, and is derived from S, which is assumed to represent the composition of the first solid to form, and the relevant distribution coefficients (Table II). Values for f , the fraction solidified, are marked along liquid and solid fractionation lines. According to the proposed model, the mean composition of the metal in main group pallasites equals the liquid composition when $f = 0.82$.

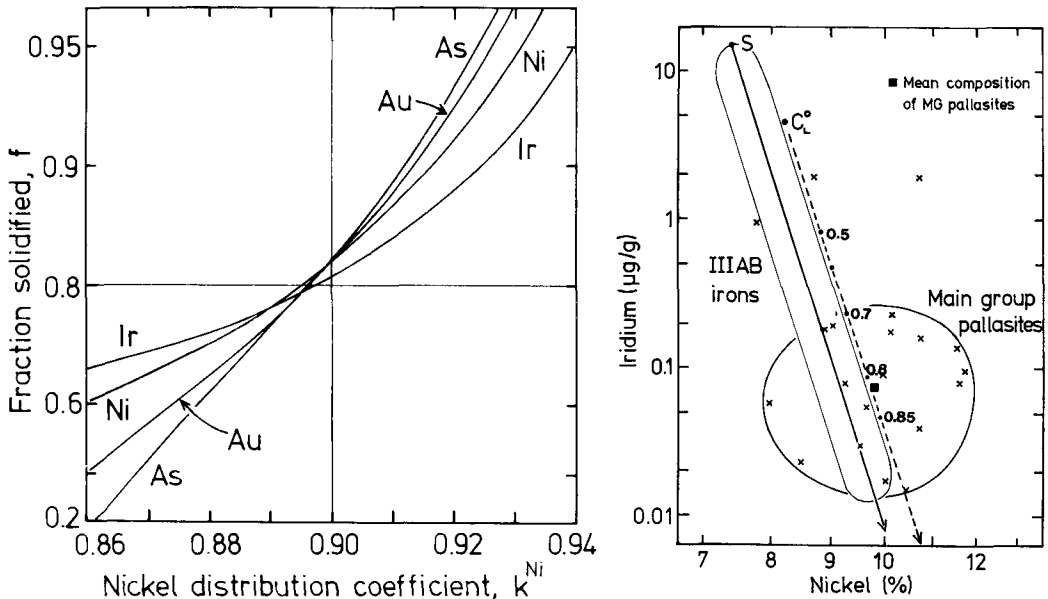
Since main group pallasites do not vary greatly in their metal composition (Scott, 1977a), we might consider the simplest mixing model in which all the liquid metal that is intruded into the olivine mantle has the same composition. If this is a reasonable approximation, the metal in main group pallasites should match that of the liquid in the IIIAB core at some stage of solidification.

Now if we measure the concentrations $[A]$ and $[B]$ of two elements in the IIIAB irons and the main group pallasites, and equate the latter with the concentrations in the liquid, $[A]_L$ and $[B]_L$, after a fraction of liquid f has solidified, we can write $[A]_L = [A]_L^0 (1-f)^{(k^A-1)}$ and $[B]_L = [B]_L^0 (1-f)^{(k^B-1)}$. We can then solve for f and k^A by substituting for $[A]_L^0$, $[B]_L^0$, and k^B from the initial IIIAB compositions and the gradient of the IIIAB analyses on a logarithmic A-B plot.

Fig. 3 shows graphical solutions for f and k^{Ni} obtained from interelement plots of Au, As, and Ir against Ni for IIIAB irons, and analyses for these elements in main group pallasites. These four elements provide the best estimates of these parameters as other elements like Co, which are as accurately known, show very little fractionation in group IIIAB. In fig. 3 the separation of the curves has been enhanced by plotting $\log(1-f)$ against k^{Ni} . The sources of

data and the number of analysed meteorites are listed in Table I. The pallasite analyses are mainly those of Scott (1977a), although two Ni analyses that differed significantly from other published values (see Scott, 1977a) were averaged with the published values.

In fig. 3 it can be seen that the curves intersect to give reasonably consistent values of 0.90 and 0.80 for k^{Ni} and f respectively. The values can be read from the graph with greater accuracy, but it is doubtful whether the simple model that was assumed for pallasite formation could give more precise numbers. Although other elements have not been measured in many pallasites, the available data can still provide a useful test of the model.



FIGS. 3 and 4: FIG. 3 (left). Data from interelement logarithmic plots of Au, As, and Ir against Ni for IIIAB and analyses of main group pallasites permit graphical solutions for k^{Ni} , the Ni distribution coefficient, and f , the fraction of liquid solidified when the liquid composition equals that of the metal in main group pallasites. The close intersections of the curves are consistent with the proposed fractional crystallization model for metal in these meteorites, and suggest $k^{\text{Ni}} = 0.90$ and $f = 0.80$. FIG. 4 (right). The logarithmic plot of Ir against Ni shows analyses for IIIAB irons (in outline only) and main group pallasites. As in fig. 2b, the heavy solid line is the IIIAB line, which is taken to represent the path of the solid composition during fractional crystallization of a IIIAB core, and the dashed line is the calculated liquid path. Possible explanations for the scatter in pallasite compositions from the mean Ir value are discussed in the text.

In Table II a value for the fraction of liquid solidified, f , at the time of pallasite formation is derived from each of 12 elements by using the value for k^{Ni} of 0.90, which was derived from fig. 3. The distribution coefficients (line 2 of Table II) are calculated from the gradients of the IIIAB lines on element-Ni plots (line 1), and are close to those deduced by Scott (1972). The bulk liquid composition (line 4) is estimated from these coefficients and the IIIAB compositions at 7.4 % Ni (line 3). Then the value for f is derived from the Rayleigh relationship using values for the mean compositions of metal in main group pallasites, given in line 5 (sources for data are listed in Table I).

Although some elements like Co, which is weakly fractionated in group IIIAB, and Pd and Pt, for which only one published pallasite analysis could be found, provide a rather weak test for the model, there are several such as Mo, Ru, Sb, and W that provide strong support. These four elements plus Au, As, and Ir each give a value for f that is within experimental

error of 0.82. These errors are calculated from the 95 % confidence limits of the means of analyses for metal in main group pallasites. It is worth noting that no elements give negative values for f . The final line in Table II gives the calculated composition for main group pallasitic metal using a value for f of 0.82.

The fit of the data to the model can also be usefully evaluated using logarithmic interelement plots. Fig. 2a is a Au–Ni plot showing analyses for both IIIAB irons and main group pallasites. Fig. 2b shows the path of liquid and solid compositions according to the fractional crystallization model for group IIIAB. The mean composition of the metal in main group pallasites would equal that of the liquid after 82 % of the IIIAB core had solidified. Fig. 4 is an Ir–Ni plot showing the outline of IIIAB iron analyses (Scott *et al.*, 1973, fig. 3), data for the main

TABLE I. Sources of analytical data for IIIAB irons and main group pallasites

	As	Au	Co	Cr	Ir	Mo	Ni	P	Pd	Pt	Ru	Sb	W
<i>IIIAB Irons</i>													
No. Meteorites	22	22	38	26	150	12	165	31	19	11	17	13	13
Reference*	8,11	8,11	6	6	9	6	9,10,12	6	6	1,6	1,6	11	8
<i>MG pallasites</i>													
No. Meteorites	15	15	15	4	16	3	19	–	1	1	3	5	12
Reference*	7	7	7	5	7	4	7	–	3	3	4	24,11	7

*References

1. Crocket. (1972).
2. Hamaguchi *et al.* (1961a).
3. Hamaguchi *et al.* (1961b).
4. Hermann and Wichl. (1974).
5. Lovering *et al.* (1957).
6. See Scott. (1972).
7. Scott. (1977a).
8. E. R. D. Scott. (Unpublished data).
9. Scott and Wasson. (1976).
10. Scott *et al.* (1973).
11. Smales *et al.* (1967).
12. J. T. Wasson. (Written communication).

group pallasites, and the path of liquid and solid compositions during fractional crystallization. Again, the bulk composition of the pallasites is close to that of the liquid after 82 % has solidified, but the spread of pallasite data is more marked than that in fig. 3. This spread cannot be explained by the simple model for pallasite formation; possible explanations are considered later.

If liquid is trapped during fractional crystallization, the fractionation equation can be rewritten by treating the trapped liquid as an additional phase with $k = 1$ (Greenland, 1970):

$$C_s = \bar{k} C_L^0 (1-f)^{(k-1)(1-\alpha)}$$

where α is the fraction of liquid trapped in the solid, and \bar{k} , the mean distribution coefficient, is given by

$$\bar{k} = k(1-\alpha) + \alpha.$$

It is easily shown that the gradients of solid and liquid fractionation lines on logarithmic interelement plots (like fig. 2b) are unchanged by liquid trapping. Nevertheless, the efficiency of element fractionation is reduced and the initial solid and liquid compositions are closer together.

Since the measured S contents of IIIAB irons, 0.1–2 % (Buchwald, 1975), exceed the solubility of S in solid iron, some liquid must have been trapped during the fractional crystallization of the IIIAB core. Without knowing the bulk S of the core we cannot estimate α precisely. If α had values between 0.05 and 0.15, the value of f at the time of pallasite formation might be about 3–10 % higher than the figure of 0.82, which was derived earlier.

TABLE II. Comparison of trace and minor element concentrations in IIIAB iron meteorites and metal in main group pallasites using a fractional-crystallization model. Values for the fraction of liquid solidified (line 6) when the liquid composition C_L was identical to that of pallasitic metal generally lie within experimental error of 0.82 for all 12 elements. Distribution coefficients k and initial bulk liquid composition C_L^0 are derived from IIIAB data in lines 1-4 using a value of 0.90 for k^{Ni} taken from fig. 1.

	As	Au	Co	Cr	Ir	Mo	Ni	P	Pd	Pt	Ru	Sb	W
1. IIIAB gradient g on el. *Ni plot	6.01	5.02	0.57	-11.25	-24.4	1.05	--	8.28	3.40	-7.38	-8.25	6.19	-5.62
2. Distribution coefficient, k	0.40	0.50	0.94	2.12	3.44	0.89	0.90	0.17	0.66	1.74	1.83	0.38	1.56
3. IIIAB comp. at 7.4% Ni	3.19	0.527	0.475	80	15.0	6.2	7.40	0.081	2.02	20.0	15.0	0.032	1.51
4. Bulk comp. of liquid, C_L^0	7.99	1.05	0.504	37.7	4.4	6.9	8.22	0.47	3.06	11.5	8.2	0.084	0.97
5. Mean comp. of Mg pallas. metal, Cp	23.2 ±2.5	2.54 ±0.20	0.53 ±0.02	(3) ±2	0.075 ^{††} +0.01 -0.04	8.8 ±0.8	9.8 ±0.5	--	4.1 ±1?	0.75 ±?	1.6 ±0.8	0.20 ±0.05	0.47 [†] ±0.10
6. Fraction solidified f when $C_L = C_p$	0.83 ±0.03	0.82 ±0.03	0.59 ±0.2 0.4	(0.90) ±0.06	0.81 ±0.07	0.89 +0.06 0.16	0.83 +0.07 -0.13	--	0.58 ±0.2 -0.5	0.97 ±?	0.86 ±0.08	0.75 +0.08 -0.14	0.73 +0.09 -0.12
7. Calc. Mg pallas. comp. at $f = 0.82$	22.4	2.47	0.56	5.5	0.067	8.3	9.76	2.0	5.48	3.2	2.0	0.243	0.37

* Abbreviations: C_L - liquid composition; calc. - calculated; comp. - composition; el. - element; **Mg pallas.** - main group pallasite.

† Geometric mean.

†† Excluding 3 pallasites with very high Ir contents.

Errata: Col. 1, entry 5, for Mg read M.G.; col. Co, entry 6, for 0.4 read -0.4; col. Pd, entry 6, for ±0.2 read +0.2.

Discussion. The validity and implications of the simple fractionation model, described above, cannot be fully evaluated without some discussion of the possible causes for the mixing of olivine and metal. If the simple model is a good approximation, it provides some clues to the timing and cause of the olivine-metal mixing. One mechanism that would be compatible with mixing during the final stages of solidification is that of Wasson and Wetherill (1967). They suggested that contraction during solidification of the metal core may have caused the fracture of the olivine shell. Other possible mechanisms are discussed by Scott and Wasson (in preparation). The latter authors also examine other implications, for example the absence of pure olivine meteorites and the apparent lack of pallasites that are related to the other iron meteorite groups. In this section some of the possible objections to the proposed relationship between main group pallasites and IIIAB irons are examined:

Heterogeneity of pallasitic metal. Some of the apparent spread in composition of metal in main group pallasites (figs. 2 and 4) may be a result of non-representative kamacite-taenite ratios and olivine inclusions in the analytical samples (generally 1 g or less in weight). Scott (1976a) found that agreement between duplicate Ni analyses was much poorer for pallasitic metal than for iron meteorites, although the analytical procedures were identical. Some scatter in the Ni and Au values may be caused by sampling difficulties, but this cannot be the explanation for the high Ir contents in three main group pallasites (fig. 4). One possible explanation might be contamination of pallasitic metal with early-formed metal that solidified locally on the core-mantle interface. An addition of 5 to 10% of such metal could produce the high Ir contents of these three pallasites, without significantly affecting the concentration of elements like Au, which are depleted in the early-formed solid. Some of the spread in the composition of pallasitic metal parallel to the solid fractionation line (figs. 2 and 4) could be explained by limited local fractional crystallization of pallasitic metal prior to olivine-metal mixing. The positive Au-Ni correlation in main group metal, however, does not lie along this line (fig. 2) and requires a different explanation. If Au, like Ni, concentrated preferentially in taenite, the correlation might be produced by poor sampling. But this cannot be the explanation for the negative Ni-Ga and Ni-Ge correlations that are observed in the main group (Scott, 1976a), as Ni, Ga, and Ge are all concentrated in the taenite. However, the distributions of Ga and Ge in group IIIAB are also difficult to explain by the fractional crystallization model (Scott *et al.*, 1973). These problems are discussed further by Scott and Wasson (in preparation).

Cooling rates. If the cooling rates of main group pallasites, $0.5-1.5$ °K Myr⁻¹, are compared with the total range shown by all iron meteorites, $500-0.2$ °K Myr⁻¹ (Goldstein and Short, 1967), the IIIAB range of $1-10$ °K Myr⁻¹ looks fairly similar to that shown by the pallasites (Buseck and Goldstein, 1969). Some of the variation in group IIIAB may be an artefact (Scott *et al.*, 1973), but group IIIB alone appears to have a small variation of $1.5-2$ °K Myr⁻¹ (Goldstein and Short, 1967), which is close to, but still apparently different from the pallasite range of $0.5-1.5$ °K Myr⁻¹. Clearly the model requires that pallasites should have very similar cooling rates to the IIIAB irons because of the high thermal conductivity of iron, but any differences should be in the opposite direction to those which are observed. Future investigations of the effects of minor elements like P on cooling-rate estimates may allow the importance of this discrepancy to be evaluated. At present it does not seem sufficient reason for rejecting the proposed relationship between main group pallasites and IIIAB irons.

Mineralogical differences. Some pallasitic minerals, like farringtonite, Mg₃(PO₄)₂ (Fuchs, 1969) might form as a result of olivine-metal mixing, so their absence in IIIAB irons is not a problem for the proposed relationship. Traces of cohenite Fe₃C and carlsbergite, CrN, are found at the low-Ni end of IIIAB but not at the high-Ni end (Scott and Wasson, 1975). Thus their absence in pallasites is easily explained. Chromite is much more abundant in pallasites

than in IIIAB irons but chromite was probably a common mineral in the olivine-rich aggregate prior to olivine-metal mixing. Signs of shock, e.g. shock-melted troilite, are common in both iron and stony-iron groups, but shock-hatched kamacite is curiously absent in pallasites although abundant in IIIAB irons. The explanation for this is not clear, but the pallasitic layer would be much more easily fragmented than the iron core, and may have been removed before the core was fractured.

It is concluded that, on balance, there is good evidence for a genetic relationship between IIIAB irons and main group pallasites, and reasonable evidence to suggest that the pallasites formed during the final stages of fractional crystallization of a IIIAB core. Any conclusive proof, however, cannot be obtained until more precise values of the distribution coefficients are obtained for comparison with those derived from the meteorites.

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