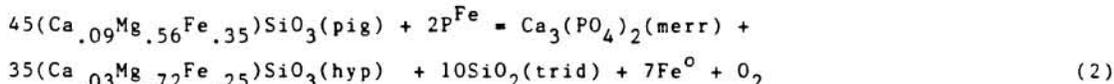
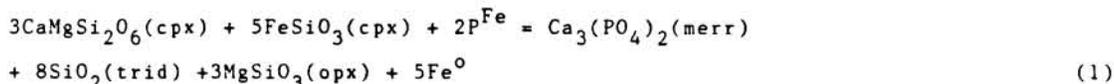


P - Fe⁰ SYSTEMATICS AS AN INDICATOR OF GENETIC ENVIRONMENT IN THE BASALTIC ACHONDRITE GROUP. William N. Agosto, Lunar Industries, Houston, TX 77259-0004

Questions about genetic relationships among the meteorite types of the basaltic achondrite group (BAG) which include the eucrites, cumulate eucrites, howardites, diogenites and mesosiderites persist 25 years after Mason proposed that they fractionally crystallized from an extensively melted planetesimal (1), 20 years after Duke and Silver elucidated their min-pet relations (2), and 10 years after Stolper characterized them as recrystallized partial melts (3).

Recently, Mittlefehldt studied whole rock volatiles/refractories (v/r) ratios culled from major, minor and trace element BAG data accumulated over the last 30 years (4) and found positive correlations between incompatible v/r ratios and volatile content in eucrites which he attributed to volatile loss during their surface solidification as basalts. In addition, he found incompatible v/r ratios in diogenites about an order of magnitude greater than in eucrites with cumulate eucrite v/r ratios between those of diogenites and eucrites. In particular, phosphorus/refractories ratios are especially high in diogenites. Further, unlike the basaltic eucrites, most of the diogenite and cumulate eucrite v/r ratios bear a negative correlation to their volatile content. Mittlefehldt also attributed this trend to (massive) volatile loss during fractional crystallization of the cumulate rocks. He concluded that the data are more consistent with Mason-style fractional crystallization for BAG genesis than Stolper-style partial melting which has been the favored BAG genetic scenario for over ten years.

v/r systematics in the BAG can be an important genetic indicator, and in that connection, Agosto (5,6,7,8,9) has shown that phosphorous diffusing from metal in mesosiderites can reduce iron out of clinopyroxene and form substantial silica and phosphate in those rocks according to reactions like:



In the above reactions, P^{Fe} refers to elemental P derived from metal; cpx and opx refer to mesosiderite clinopyroxenes and orthopyroxenes and their components; merr is merrillite (anhydrous whitlockite); trid is tridymite, pig pigeonite, hyp hypersthene and Fe⁰ pure metallic iron. In reaction (2) where oxygen is evolved as a product, pyroxene compositions are taken from probe data on ALHA77219, an Antarctic mesosiderite (5). In support of the above reactions, the average molar ratio [trid]/[merr] from the modes of 21 mesosiderites measured by Prinz et al. (10) is 9.8, between the predicted values of 8 and 10 in (1) and (2) respectively.

Agosto (6,7) has shown that the estimated f_{O₂} of formation of each of 15 mesosiderites bears a negative correlation to P₂O₅ contents of their silicates consistent with reaction (2) which predicts the evolution of oxygen with the formation of mesosiderite merrillite as well as the [trid]/[merr] ratio of approximately 10 calculated from the mesosiderite modes of Prinz et al. (10).

Free oxygen loss during P-Fe redox reactions in mesosiderite silicates is consistent with the idea that they are impact melts (11,12) because under those conditions reaction (2) could occur at or near a planetoid surface where generated oxygen can escape. Harlow et al. (13) and Delaney et al. (14) have argued that P-Fe redox reactions in mesosiderites are subsolidus because REE concentrations in mesosiderite merrillite are below ordinary EMPA detection limits while, for example, cerium (Ce) is at the 1 wt% level in some eucrite merrillites that presumably crystallized in late eucritic liquids. However, the modes of Prinz et al. (10) show that eucrite phosphate abundance is on the average 1/20 of mesosiderite phosphate abundance. Further, about half eucrite phosphate is F-apatite which takes up an order of magnitude less REE than merrillite at BAG f_{O₂}. In addition, Ce whole rock concentrations in mesosiderites are half that in eucrites (15). Accordingly, the average dilution of Ce in mesosiderite merrillite is expected to be 1/80 that of eucrite merrillite on the basis of relative Ce-

P - Fe⁰ SYSTEMATICS IN BASALTIC ACHONDRITES

AGOSTO, W. N.

merrillite abundances alone. Crozaz (16) has reported Ce in the Emery and Vaca Meurta mesosiderites at approximately 100 x OC. That translates to >10,000 X Cl for average eucritic merrillite which is the level Delaney (14) reports. Accordingly, the lower REE concentrations in mesosiderite phosphate do not discriminate between liquid and solid state P-Fe redox reactions and are perfectly consistent with the interpretation of mesosiderites as impact melts.

In interesting contrast to the mesosiderites, the only Fe³⁺-P₂O₅ data I have seen for diogenites is the whole rock analysis of Antarctic diogenite ALHA77256 by Haramura in Takeda (17). In the Haramura data, P₂O₅ is 0.21 wt % corresponding to over 900 ppm P, more than an order of magnitude greater than average diogenite whole rock P of 59 ppm in Mittlefehldt's 1986 data compilation (4). Further, [Fe³⁺]/[P₂O₅] in the Haramura data is precisely 5 (to two places) as predicted by reaction (1) if it is assumed the Fe³⁺ was pure diogenitic iron reduced by phosphorus in the BAG planetoid and later terrestrially oxidized.

The fit of the Haramura data to reaction (1) in which free oxygen is not generated is consistent with the interpretation of diogenite genesis as cumulates from an abyssal partial ultrabasic melt where free oxygen or other volatiles could not easily escape from redox reactions and supports the Stolper BAG genetic model over the Mason model. Accordingly, reactions (1) and (2) can serve as tests of genetic venue for BAG rock types.

My interpretation of the Haramura ALHA77256 data is in conflict with Mittlefehldt's account of v/r systematics in diogenites as due to massive outgassing since reaction (1) presumes no outgassing. In my view, the data Mittlefehldt has so carefully compiled is much more readily explained by diogenite accumulation at depth in the parent planetoid during core formation. As the core forms, large quantities of volatile and refractory incompatibles are displaced radially upward in exponentially decreasing gradients. Volatiles decrease upward more rapidly than refractories near the crust because they are more mobile and, by definition, can outgas in basaltic flows through the crust. Hence basaltic v/r ratios are significantly lower in surficial eucrites than in deep diogenites. Conversely, both volatiles and refractories increase downward in the planetoid interior as the core is approached, but refractories increase more rapidly with increasing depth near the core because they are less mobile than the volatiles and describe a steeper exponential concentration gradient (Fig 1). Consequently, as volatiles increase at depth, v/r ratios decrease. Accordingly, the negative correlation of volatiles/refractories with total volatiles in both the diogenites and the cumulate eucrites may be an indicator of the depth where each rock accumulated (e.g., v/r ratios in the cumulate eucrites lie between those in diogenites and eucrites placing them closer to the surface than the diogenites). The very high P/refractories ratios for diogenites are also consistent with their accumulation near the core which is presumably the chief source of P in the planetoid (5). It is true that diogenites have substantially less total incompatibles than the eucrites (4) but that can be explained by their very low late liquid content compared with surface rocks. More whole-rock P-Fe⁰ data will be required from all BAG rock types to elucidate this model.

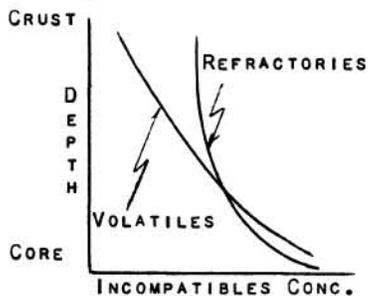


FIG. 1. INCOMPATIBLES VS DEPTH IN THE BAG PLANETOID

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