ISOTOPIC STUDIES OF SHERGOTTITE CHRONOLOGY: II. POSSIBLE EFFECT OF CONTAMINATION ON THE Sm-Nd SYSTEM. L. Nyquist[1], B. Bansal[2], H. Wiesmann[2], C. Shih[2], and G. McKay[1] ([1]SN4, NASA Johnson Space Center, Houston, TX, 77058; [2]Lockheed, 2400 NASA Rd. 1, Houston, TX, 77058).

Small (~50 microns) spheres of iron and rare earth oxides have been found in samples of the Zagami and Murchison meteorites, apparently resulting from contamination from cigarette lighter flints (1). Lighter flints are an alloy of misch metal (mainly Ce, La, Nd, and Pr) and iron. Spheres from Zagami and a cigarette lighter were found to contain, respectively, 8% and 13% Nd (1). A misch metal oxide sphere was also found among 43 lunar mare volcanic glasses and similar spheres produced by striking cigarette and gas lighters were found to be extremely enriched in LREE, with chondrite normalized La/Sm and Nd/Sm ratios of ~ 5000 and 1200, respectively (2). Because a single 25 micron particle contains ~10 ng of Nd, comparable to the total amount required for isotopic analysis, lighter flint misch metal is a serious potential contaminant in Nd isotopic analyses.

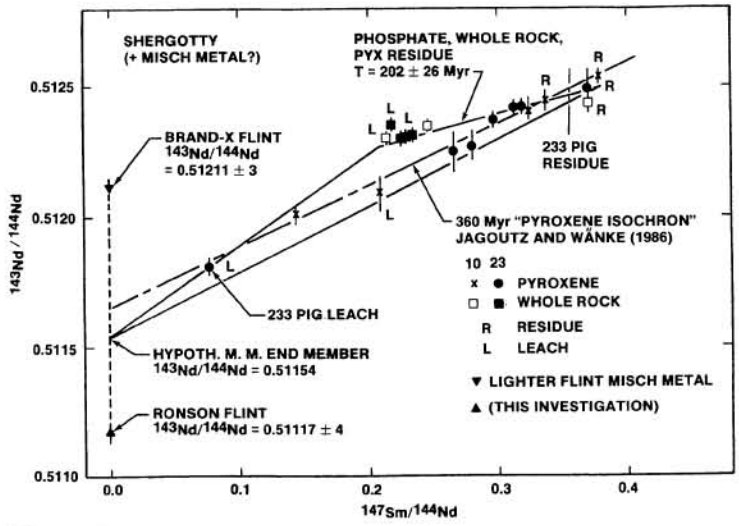

Figure 1.

Sm-Nd data for two lighter flints are shown in Figure 1. Brand-X had been used in a cigarette lighter; the Ronson flint was new. The Nd and Sm concentrations in the Brand-X flint were 12.3% and 45 ppm, respectively, and those in the Ronson flint were 9.2% and 3 ppm, respectively. A mixture of oxide and metal was produced by striking the Ronson flint in a gas lighter. The metal was dissolved in 1N HCl leaving the oxide as a residue. The Nd concentration of the oxide was measured to be 7.4%.

As shown in Figure 1, the Nd-isotopic composition of the two flints are quite different. This is perhaps expected since misch metal is obtained from the mineral monazite for which there are different sources, the principle ones being Brazil and India (3). Thus, it is impossible to identify misch metal contamination on the basis of a unique Nd isotopic composition. However, the exceptionally high Nd/Sm ratio of misch metal should provide a clue to contamination when it occurs. The two flints analysed here, like those analysed by (2), are severely depleted in Sm relative to Nd having chondrite normalized Nd/Sm ratios of 900 and 10,000, respectively. The assumption Sm/Nd = 0 in misch metal will be adequate when considering the role of misch metal as a contaminant in isotopic studies.

Jagoutz and Wanke (4) measured Sm/Nd ratios for some Shergotty pyroxene separates which are much lower than expected from partitioning of these elements between pyroxene and other mineral phases (5). No evidence of pyroxene with low Sm/Nd ratios had been found in the earlier work of Shih et al. (6) and subsequent electron and ion probe studies of pyroxene also showed no evidence of low Sm/Nd ratios (5,7). Jagoutz and Wanke (4) attributed the low Sm/Nd ratios to the presence of a soluble phosphate phase with different isotopic characteristics than the main phosphates in the meteorite. However, recent ion probe analyses of Shergotty phosphate by (7) have failed to find either whitlockite or apatite with the required low Sm/Nd ratio. Experimental partitioning studies also have shown that it is unlikely that such phosphates would have formed during crystallization of Shergotty (8). The unusually low Sm/Nd ratios found by (4) suggests consideration of misch metal as a possible contaminant. We thus performed an experiment to determine how hypothetical misch metal contamination might respond to the experimental procedures reported by (4).

The Ronson flint was placed in a gas lighter striker and struck 50 times to produce a mixture of metal shavings and oxide spheres. Following the procedures given by (4) the mixture was then "leached" successively in (i) 1 N HCl (5 min.); (ii) again in 1 N HCl (5 min.); (iii) 5% HF (2 min.). The metal phase dissolved nearly quantitatively during the first leach. More than 90% of the total Nd was contained in the first two leaches and is a measure of the proportion of metal in the original metal-oxide mixture. The oxide spheres were resistant to the HCl and 5% HF leaches but totally dissolved when our standard silicate dissolution procedures were used. Although the flints were "non-magnetic" to a hand magnet, the magnetic susceptibilities of the LREE are high relative to that of pyroxene. The prior magnetic separation employed by (4) thus would not have discriminated against misch metal

contamination if it were present adhering to pyroxene grains and may even have enriched any metal present in the most magnetic pyroxene fraction. Thus, if misch metal contamination were present in the analyses of (4), visual identification of its presence would have been the only effective discriminant against it. The probability that an individual sub-microgram particle might be overlooked in a several milligram sample seems significant. Thus, examination of the data for internal evidence of contamination seems justified.

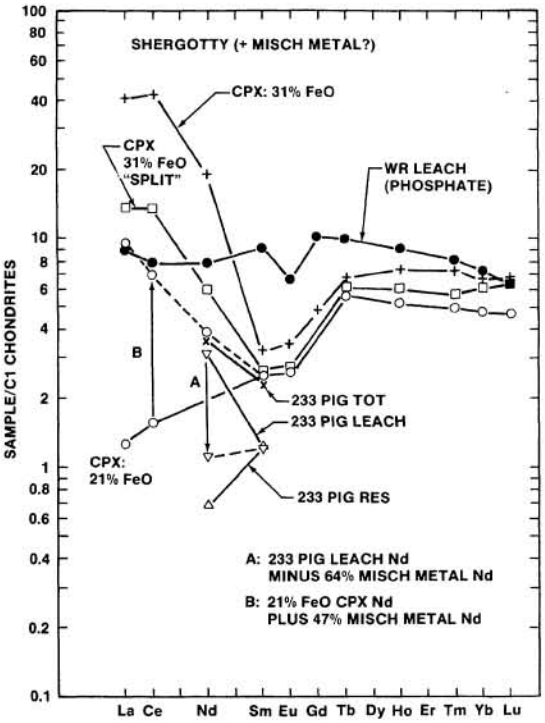

Figure 2.

Figure 1 shows the Nd isotopic data for the two flints in comparison to the Sm-Nd data of (4). A mixing line is shown which assumes that the Nd present in "233 Pig Leach" is a two component mix of a hypothetical misch metal contaminant and ordinarily leachable phosphates. Neither of the two flints actually analysed would be an acceptable end member in the mix, but it is reasonable to assume a quasi-continuum of isotopic compositions for randomly selected flints. With these assumptions, ~64% of the Nd in the analysis would be from misch metal. That is, 4.2 ng of the 6.5 ng analysed, equivalent to a metal particle ~18 microns in size. The triangle in the figure gives the approximate limits of data resulting from a 3-component mix of phosphates, pyroxenes, and "misch metal".

A related indication of possible misch metal contamination would be the occurrence of unusual enrichment of the LREE in trace element analyses. Figure 2 reproduces data from (9) and (4) and shows the effect of some possible mixing scenarios. Arrow A shows the effect on the chondrite normalized patterns of subtracting 64% of the Nd abundance measured by (4) for 233 Pig Leach. The resulting Nd-Sm pattern is similar to that of the whole rock leachate (phosphate), consistent with the assumption of the isotopic mixing calculation. Also shown is the effect of adding enough misch metal contamination to one of the uncontaminated pyroxene analyses reported by (9) to yield the Nd-Sm pattern of 233 Pig Tot (Arrow B). This calculation requires that 47% of the Nd in the mix be from the misch metal end member. The resultant pattern is similar to that of two other analyses of this sample reported by (9), although the LREE are less severely enriched. To obtain the La enrichment shown by the "31% FeO cpx" of (9) would require addition of ~0.2 micrograms of misch metal, equivalent to a single particle ~30 microns in size. The observed enrichment of La in the "split" of this sample could be produced by a particle only ~15 microns in size. The departure of other pyroxene and pyroxene leachate analyses (4) from a line through the data for whole rocks, whole rock leachates, and pyroxene residues also could be explained by the random addition of misch metal particles in the size range of ~ 14-26 microns. Thus, all the unusual LREE-enriched pyroxene analyses reported by (4) and (9) appear to be explainable by the random addition of individual misch metal particles in the size range of ~14-30 microns. As noted by (1) and (2) particles of this size and larger are produced in abundance when a cigarette lighter is struck.

We consider it premature to attach petrogenetic significance to the LREE-enriched pyroxene analyses of (9) or chronologic significance to the pyroxene "isochron" of (4) until a meteoritic phase with the extreme LREE enrichment required by their data is identified. Pending identification of such a phase, we consider the most probable age provided by the Sm-Nd isotopic data of (4) to be 202±26 Myr as obtained from regression of the data for the whole rocks, whole rock leachates, and pyroxene residues.

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