

## COMPARATIVE Re-Os ISOTOPE SYSTEMATICS in IIA and IIIA IRON METEORITES.

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The precise and accurate measurement of Re and Os concentrations and Os isotopic compositions in iron meteorites is important both from the standpoint of understanding the processes involved in asteroid core formation, and also in determining the chronology of those processes. Such studies of irons have been hampered by the problematic aspects of Re-Os measurement. To date, most Re-Os studies (terrestrial and extra-terrestrial materials) have utilized either acid or fusion digestion as the means of dissolving phases and equilibrating spikes with sample. The latter aspect is especially critical in Re-Os chemistry because of the numerous oxidation states and species possible for both elements. Each method has strengths and weaknesses. HCl+HF-based acid digestion techniques typically have low blanks, but are slow, and have limitations in the dissolution of resistant phases (including Os-Ir alloys). In addition, we have found that the Os released from some matrices is very difficult to equilibrate with spike using low-temperature, closed-system teflon digestions. Clearly, low-temperature, reduction-based equilibration is unsatisfactory for some matrices. Fusion techniques include traditional nickel-sulfide fire assays and sodium-peroxide digestion. In both instances the blank-to-sample ratio for Re can be disastrously high for samples with <1ppb Re. Previously, we have utilized the sodium-peroxide fusion technique for all of our meteorite studies. The fusion technique works reproducibly for high Re-Os abundance chondrites and irons, but, the Re blank contributed by the fusion becomes the limiting factor in the precise analysis of B-subgroup irons, with limited Re.

As a consequence of these problems, during the past year we have developed an acid-based, high-temperature oxidation, digestion and separation chemistry for silicates, sulfides and metals. Because of the need for closed-system digestion (Re and Os form volatile species when oxidized), reactions are accomplished in thick-walled pyrex tubes that are loaded with sample+reagents+spikes and subsequently sealed (first described by Carius in 1860). The reagent used for digestion/oxidation/equilibration is *aqua regia*. Similar sealed tube digestions for platinum-group elements were originally developed fifty years ago [1]. For our technique we add the sample to the approximately 25 cc volume tube, chill the tube with a mixture of dry-ice+ethanol, then sequentially add the spikes, concentrated HCl and concentrated HNO<sub>3</sub> (in the proportion 2:1 by volume). The tube is then sealed and heated to 230°C for approximately 12 hours. Such high temperature reaction digests refractory PGE minerals and alloys, iron-nickel alloys, sulfides and evidently sufficiently reacts with silicates to release all Re and Os [2]. The procedure has a relatively low blank (<50 pg Re and <10 pg Os; when sufficient reagent is used for 3-5 g sample).

In addition to the digestion improvements, we have also created a mixed Re-Os spike for meteorites. The new spike was calibrated against the same Re and Os standard solutions used in our previous studies. To check the reproducibility of the new procedure, we analyzed multiple pieces of the IIA iron Filomena (a very homogeneous iron). These samples were sawn from a single piece of the meteorite as adjacent chunks. Four chunks were leached in 0.8 M HNO<sub>3</sub>, removing approximately 5 wt. % of the iron. For these samples, Os concentration and isotopic composition data varied little. In contrast, Re abundances varied  $\pm 2\%$ , suggesting the Re was not consistently removed with the leachate. Four additional chunks were *not* leached. For these chunks, reproducibility was quite good, with total Re/Os uncertainty of  $\pm 0.2\%$  and <sup>187</sup>Os/<sup>188</sup>Os uncertainty of  $\pm 0.034\%$ . Because of the problems associated with leaching, we now recommend against leaching. These improvements have led to a factor of 2 reduction in Re/Os uncertainty relative to our previous techniques [3], and have enabled us to measure group IIA and IIIA irons to significantly higher precision than has yet been reported.

For this study we have analyzed 6 IIA irons (10 independent dissolutions, including replicates: samples are Filomena, Gressk, Coahuila, Negrillos, Lombard and Bennett County) and 6 IIIA irons (8 independent dissolutions, including duplicates: samples are Toubil River, Ssyromolotovo, Susuman, Henbury, Costilla Peak and Charcas). Results are shown in Figure 1. Both sets give well-defined lines (Model 1 regressions, 95% confidence). For IIA irons: slope is  $0.07851 \pm 0.00014$  (MSWD=1.2) and initial <sup>187</sup>Os/<sup>188</sup>Os is  $0.09544 \pm 0.00007$ . For IIIA irons: slope is  $0.07885 \pm 0.00028$  (MSWD=1.2) and initial <sup>187</sup>Os/<sup>188</sup>Os is  $0.09526 \pm 0.00013$ . The slope of the IIA isochron agrees within uncertainty of our previous results [3].

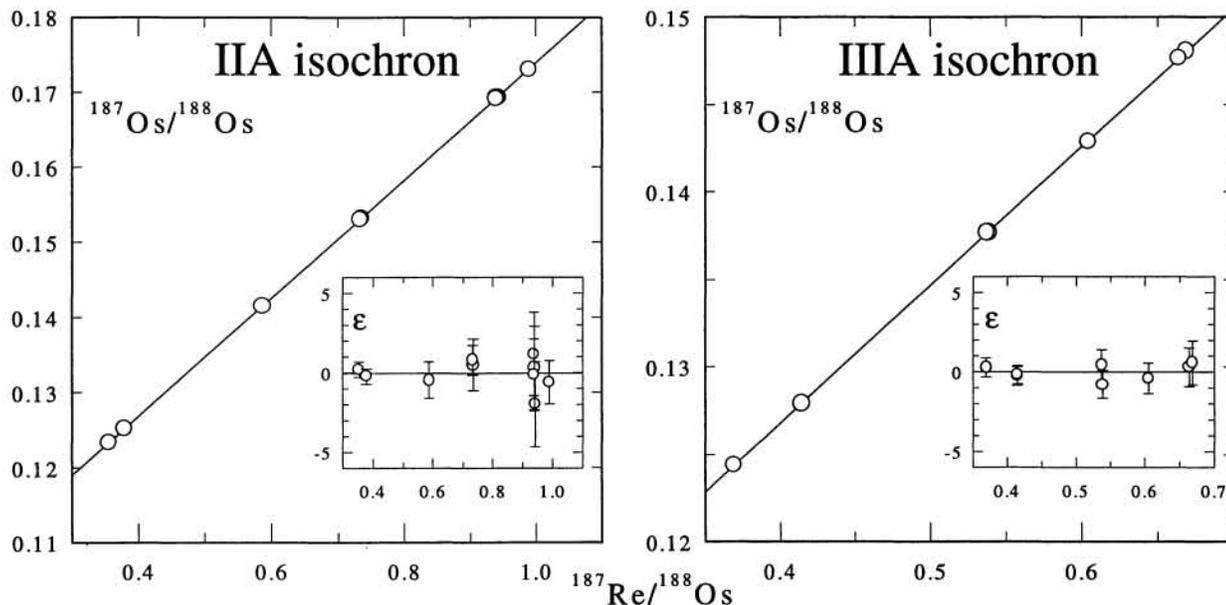
There are two problems that preclude a straightforward interpretation of these data. First, uncertainty in the decay constant of <sup>187</sup>Re is currently on the order of  $\pm 3\%$  [4]. Absolute age determinations using the Re-Os system are consequently hampered. Second, as discussed previously [5], there still exist no viable absolute standards for the calibration of Os spikes. The approximately  $\pm 1\%$  uncertainty in the absolute concentration of Os also hampers absolute age interpretations of isochrons. Despite these two limitations, the new data can be used in the comparison of different iron groups and variations within iron groups. Several conclusions can be made from

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these data. First, the good fit of the data to presumed isochrons suggests that the IIA and IIIA systems crystallized during a short time interval (<5 Ma). Slower crystallization would likely not have resulted in isochronous behavior. Our less precise data for B subgroups also indicate that they crystallized within the same general time interval [6]. Second, the high precision isochrons also indicate that at least the samples we examined have remained closed-systems with respect to Re and Os since their crystallization. Finally, although the slopes and initial ratios for the two iron groups overlap, the overlap is minimal (Figure 2). The results may indicate that the group IIAB system crystallized 5-20 Ma subsequent to the IIIAB system. The differences in the initial ratios therefore may have resulted from the ingrowth of radiogenic Os from a IIAB parent body with chondritic Re/Os prior to core formation.

We are currently developing an absolute Os standard. This is especially important because recent  $^{107}\text{Pd}$ - $^{107}\text{Ag}$  studies of group II and III irons [7,8], suggest that IIAB and IIIAB irons formed no more than 10 to 20 Ma following nucleosynthesis. With an absolute Os standard, our results should lead to the determination of the decay constant of  $^{187}\text{Re}$  to better than  $\pm 0.5\%$ .

**References.** [1] C.L. Gordon *et al.*, *J. Res. Nat'l Bur. Stand* **33**, 457, 1944. [2] S.B. Shirey and R.J. Walker, *EOS* **75**, 355, 1994. [3] M.F. Horan *et al.*, *Science* **255**, 1118, 1992. [4] Lindner *et al.*, *GCA* **53**, 1597, 1989. [5] D.A. Papanastassiou *et al.*, *LPSC XXV*, 1041, 1994.108, 191. [6] J.W. Morgan *et al.*, *GCA*, in review. [7] J.H. Chen and G.J. Wasserburg, *GCA* **54**, 1729, 1990. [8] J.H. Chen and G.J. Wasserburg, *EOS* **75**, 700, 1994.



**Figure 1 (above).** Re-Os isochrons for IIA and IIIA iron meteorites. The insets show the deviation of data points from the best-fit line in  $\epsilon$ -units:

$$\epsilon = ({}^{187}\text{Os}/{}^{188}\text{Os} - \text{slope} \cdot {}^{187}\text{Re}/{}^{188}\text{Os} - \text{initial}) \cdot 10^4$$

**Figure 2 (right).** Evolution plot for IIA and IIIA irons. Ellipses represent 95% confidence intervals for isochron results, dotted line shows a slope for evolution of object with CI-chondrite Re/Os ratio.

