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Comparative ^{187}Re - ^{187}Os systematics of chondrites: Implications regarding early solar system processes

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Abstract—A suite of 47 carbonaceous, enstatite, and ordinary chondrites are examined for Re-Os isotopic systematics. There are significant differences in the $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios of carbonaceous chondrites compared with ordinary and enstatite chondrites. The average $^{187}\text{Re}/^{188}\text{Os}$ for carbonaceous chondrites is 0.392 ± 0.015 (excluding the CK chondrite, Karoonda), compared with 0.422 ± 0.025 and 0.421 ± 0.013 for ordinary and enstatite chondrites (1σ standard deviations). These ratios, recast into elemental Re/Os ratios, are as follows: 0.0814 ± 0.0031 , 0.0876 ± 0.0052 and 0.0874 ± 0.0027 , respectively. Correspondingly, the $^{187}\text{Os}/^{188}\text{Os}$ ratios of carbonaceous chondrites average 0.1262 ± 0.0006 (excluding Karoonda), and ordinary and enstatite chondrites average 0.1283 ± 0.0017 and 0.1281 ± 0.0004 , respectively (1σ standard deviations). The new results indicate that the Re/Os ratios of meteorites within each group are, in general, quite uniform. The minimal overlap between the isotopic compositions of ordinary and enstatite chondrites vs. carbonaceous chondrites indicates long-term differences in Re/Os for these materials, most likely reflecting chemical fractionation early in solar system history.

A majority of the chondrites do not plot within analytical uncertainties of a 4.56-Ga reference isochron. Most of the deviations from the isochron are consistent with minor, relatively recent redistribution of Re and/or Os on a scale of millimeters to centimeters. Some instances of the redistribution may be attributed to terrestrial weathering; others are most likely the result of aqueous alteration or shock events on the parent body within the past 2 Ga.

The $^{187}\text{Os}/^{188}\text{Os}$ ratio of Earth's primitive upper mantle has been estimated to be 0.1296 ± 8 . If this composition was set via addition of a late veneer of planetesimals after core formation, the composition suggests the veneer was dominated by materials that had Re/Os ratios most similar to ordinary and enstatite chondrites. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

The ^{187}Re - ^{187}Os system was the last of the major long-lived radiogenic isotope systems to be effectively applied to the study of early solar system materials. The paucity and imprecision of applications during the 1960s to the 1980s stemmed from both mass spectrometric and chemical processing difficulties. These difficulties were mostly resolved with the advent of negative thermal ionization mass spectrometry techniques for Re and Os (e.g., Creaser et al., 1991) and with the development of effective digestion techniques (Morgan and Walker, 1989; Shirey and Walker, 1995; Shen et al., 1996). As a result, the Re-Os isotopic systematics of iron meteorites, pallasites, mesosiderites, and some sulfides associated with irons are now well established (Shen et al., 1996; Smoliar et al., 1996; Chen et al., 1998, 2002; Horan et al., 1998).

In comparison to meteoritic metals and sulfides, relatively few Re-Os data for bulk chondrites or chondrite components have been published. Walker and Morgan (1989) reported whole-rock data for carbonaceous chondrites and one ordinary chondrite, which they determined by means of the relatively imprecise resonance ionization mass spectrometry technique. By use of much more precise techniques that were similar to

those used for the iron meteorite studies noted above, Meisel et al. (1996) reported data for a limited suite of whole-rock carbonaceous, enstatite, and ordinary chondrites. Similarly, Chen et al. (1998) reported high-precision whole-rock data for six ordinary chondrites. Most recently, Becker et al. (2001) reported data for several types of calcium-aluminum inclusions (CAIs) from the Allende and Leoville carbonaceous chondrites.

Elucidation of the Re-Os isotopic systematics of chondrites is important for several reasons. First, data for bulk chondrites and their components are necessary to place constraints on the initial Os isotopic composition of the solar system. Although precise initial isotopic composition data for the early solar system exist from studies of iron meteorites, chondrites and chondrite components largely predate the formation of irons. Precisely determining the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of the solar system may prove critical for ultimately utilizing the system to date refractory components in chondrites. Second, differences in the modern Re/Os and the time-integrated $^{187}\text{Os}/^{188}\text{Os}$ of whole-rock chondrites may reflect fractionations resulting from high-temperature nebular condensation processes in precursor materials (e.g., Grossman, 1973; Sylvester et al., 1990). Thus, Os isotopes may provide a robust method for comparing the nebular histories of refractory phases within chondrite components and among chondrite groups. Finally, Os isotopic compositions may prove useful for "fingerprinting" the provenance

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of the planetesimals that dominated the late veneers to planetary mantles (e.g., Morgan, 1985).

Here we present Re-Os concentration and isotopic data for 14 carbonaceous, 14 enstatite, and 19 ordinary chondrites. Many of the samples were analyzed multiple times, and several were analyzed by means of different digestion techniques to assess the efficiency of the digestion techniques and the homogeneity of samples. In addition, we report data for separated chondrules, matrix, and sulfide from the Allende carbonaceous chondrite, and also for metal from the lodranite Graves Nunataks (GRA) 95209. Horan et al. (in press), also report Pt, Pd, Ru, and Ir concentrations for many of the same chondrites as a means of further characterizing the relative abundances of other highly siderophile elements (HSE) in chondrites. For that work, the corresponding Re-Os isotopic data permit insights to the effects of open-system behavior on the relative abundances of the other HSE within chondrites.

2. SAMPLES

A broad range of composition types and metamorphic grades within the general category of chondrites was analyzed. The suite of carbonaceous chondrites consists of two CI, one CK, three CM, two CO, and one Bencubbin-like meteorite (Hammad al Hamra (HaH) 237; Weisberg et al., 2001), as well as three CR and two CV chondrites. The enstatite chondrite suite includes five EH4, two EH5, and eight EL6 chondrites. The suite of ordinary chondrites includes four H3, three H4, five H5, two H6, one H3-6 breccia (Zag), one L5, one L6, and two LL3 chondrites.

Four of the ordinary chondrites (Chico, Zag, Farmington, Rose City) were specifically chosen to examine the effects of relatively late-stage shock metamorphism on the Re-Os system. Chico (L6) consists of ~60 vol% impact melt and ~40 vol% shocked chondritic host material (Bogard et al., 1995). Chico appears to have formed in a relatively recent impact event on its parent body, ~0.5 to 0.6 Ga before the present (Nakamura et al., 1990; Fujiwara and Nakamura, 1992; Garrison and Bogard, 1992). Rose City is an impact melt breccia (shock stage S6) containing H5 clasts and bands of silicate interpreted as originally melt (Rubin, 1985, 1995). Like Chico, Rose City also shows evidence for recent impact, 0.2 to 0.5 Ga ago (Kunz et al., 1997). Farmington (L5) exhibits extensive silicate darkening and is considered the prototypical black chondrite (Britt and Pieters, 1991). Farmington also contains numerous localized patches of feldspathic melt. Mafic silicates exhibit strong mosaic extinction. Some glassy shock veins are present, but there are no thick veins of silicate melt. There are 1- to 5-mm rounded to elongated metal nodules and thin metal veins several millimeters in length. Zag (H3-6) is a regolith breccia containing solar wind-implanted rare gases and blue-purple crystals of halite and sylvite with aqueous fluid inclusions (Rubin et al., 2002). Zag also contains dark clasts, some with maskelynite, indicative of shock stage S5 (Stöffler et al., 1991). Shock veins occur in many of the clasts. The parent asteroid of Zag appears to have experienced a series of superposed shock, heating, and alteration events before 4.25 Ga ago (Whitby et al., 2000; Rubin et al., 2002). Shock heating may have resulted in dehydration of phyllosilicates, release of aqueous fluids that

leached some silicates, and eventual deposition of salts in the matrix (Rubin et al., 2002).

3. ANALYTICAL METHODS

Pieces of chondrite were obtained from the Smithsonian Institution's National Museum of Natural History, the American Museum of Natural History, the Max-Planck-Institute für Chemie-Mainz, the National History Museum, London, the Center for Meteorite Studies of Arizona State University, the Meteorite Working Group of the U.S. Antarctic Meteorite Collection, and the University of California, Los Angeles, Collection of Meteorites. Chondrites were carefully selected so that no fusion crusts were included in the analyses. In most instances, it was possible to obtain fresh-appearing samples. Several samples, however, were rusted, most notably Forest City. Chondrite chunks were disaggregated and finely ground with an agate mortar and pestle. In instances where metal chunks were visible in the disaggregated meteorite, the metal was removed during grinding but was included in the digestion. The lodranite metal was cut from a 1-cm-sized wafer of metal with a low-speed saw and was cleaned by abrasion with corundum, as has been previously reported for irons (Smoliar et al., 1996).

Some chondrites contain HSE alloys (e.g., Blum et al., 1989) that can potentially be very difficult to dissolve. Traditional digestion techniques utilizing hydrochloric and hydrofluoric acids may not access a substantial fraction of the HSE contained in these phases (e.g., Anders et al., 1975). Consequently, two different sample digestion techniques, Carius tube (CT) digestion and sodium hydroxide-peroxide fusion, were employed for this study. The efficacy of both techniques to dissolve HSE and HSE alloys has been previously demonstrated (e.g., Wichers et al., 1944; Anders et al., 1988).

Most digestions were accomplished by means of the CT technique (Carius, 1865) as modified for the Re-Os system (Shirey and Walker, 1995). Sample powders, along with ^{185}Re and ^{190}Os spikes, were frozen into tubes along with ~6 g (1 g for Allende components) of either normal or reverse *aqua regia*. The tubes were subsequently sealed and heated in steel jackets for a minimum of 12 to 24 h at 220°C. The CT digestion method is effective at dissolving metal, but it is not a total dissolution method for silicate-bearing rocks. Although all silicates appear to react with the *aqua regia*, some solids remain or reprecipitate after heating (e.g., Shirey and Walker, 1995). Becker et al. (2001) demonstrated that the acid digestion process accesses 93 to 100% of the Re and Os contained within refractory CAI separated from Allende. Indeed, four of six acid digestion residues they analyzed (by fusion) indicated >95% recovery of the Os from the inclusions. The phases not completely accessed by the acid digestion were evidently acid-resistant Os-rich alloys. All but one of the residues had Os isotopic compositions within $\pm 2\%$ of the composition determined by acid digestion. Of greatest importance here is the observation that the calculated $^{187}\text{Os}/^{188}\text{Os}$ of the bulk CAI, determined by mathematically combining the Os released by acid digestion to the Os present in the residue, were all within $\pm 0.3\%$ of the $^{187}\text{Os}/^{188}\text{Os}$ determined by acid digestion. Thus, there was minimal or no bias in the $^{187}\text{Os}/^{188}\text{Os}$ ratio determined by acid digestion relative to the bulk CAI.

HSE alloys contained within CAIs are probably the most difficult phases to dissolve in bulk chondrites, so the results of Becker et al. (2001) are probably a worst-case scenario for accessibility of Re and Os from chondrite phases. Therefore, even for chondrites with the highest proportion of CAIs, where the refractory phases may contain 50% of the HSE in the bulk chondrite, CT digestions likely access $\geq 98\%$ of the Re and Os present in the bulk meteorite, and the isotopic compositions of bulk chondrites dissolved by CT should be indistinguishable from those obtained by total digestion methods.

As a means of comparing the acid digestion technique with a total dissolution technique, some samples were digested by the alkaline fusion technique, most recently described by Morgan et al. (1995). This technique has proven successful in the analysis of iron meteorites (e.g., Horan et al., 1992; Morgan et al., 1995) and is effective in the dissolution of both acid-insoluble alloys, such as Os-Ir alloys, and silicates (e.g., Walker et al., 1997). Although the iron meteorite isochrons that were generated via alkaline fusion (Horan et al., 1992; Morgan et al., 1995) were not as precise as those subsequently generated by CT digestion (Smoliar et al., 1996), the difference in precision

most likely reflects improvements in the predigestion treatment of the irons, such as polishing all iron surfaces with corundum, rather than reflecting the superiority of the CT technique.

Spike calibrations were described in Morgan et al. (1995) and Smoliar et al. (1996). It is noted that the Os spike used in this study was calibrated with ammonium hexachloroosmate salt. The stoichiometry of this salt is accurate to no better than $\pm 3\%$, so our spike is calibrated to an accuracy of only approximately $\pm 3\%$, as discussed in Morgan et al. (1995). The spikes used here were either the same as those used by Smoliar et al. (1996), Horan et al. (1998), and Becker et al. (2001), or were calibrated by use of the same standards as were used for those studies. Consequently, the isotopic systematics of the chondrites reported here are internally consistent with those of the irons reported by Smoliar et al. (1996) and Horan et al. (1998), as well as the CAI results reported by Becker et al. (2001). The ^{187}Re decay constant of $1.666 \times 10^{-11} \text{ yr}^{-1}$ reported by Smoliar et al. (1996) is based on the isotopic systematics of group IIIAB irons as assessed by using our spikes, and similarly is appropriate here, despite the possibility that the absolute value of the decay constant is slightly inaccurate.

Two different Os separation techniques were used over the course of this study. For the alkaline fusion digestion and some CT digestions, Os was separated by double distillation (as OsO_4) followed by reduction in an alcohol-HCl mixture (e.g., Shirey and Walker, 1995). Final purification was achieved with an anion-exchange microcolumn. Most CT digestions employed carbon tetrachloride to separate the Os (Cohen and Waters, 1996) followed by microdistillation purification (Roy-Barman, 1993). A more detailed description of the techniques used in our laboratory is provided in Walker et al. (2002). Rhenium was recovered from all residual solutions by anion-exchange column with a final clean-up using a second anion-exchange column (Morgan and Walker, 1989). For the fusion technique, total analytical blanks averaged $\sim 40 \pm 5 \text{ pg}$ for Re and $3 \pm 1 \text{ pg}$ for Os. The isotopic composition of the Re blank was the same as terrestrial Re. The $^{187}\text{Os}/^{188}\text{Os}$ of the Os blank was 0.18 ± 0.01 . For the acid digestion technique, total analytical blanks averaged $\sim 8 \pm 5 \text{ pg}$ for Re and $3 \pm 2 \text{ pg}$ for Os. Again, the isotopic composition of the Re blank was natural and the $^{187}\text{Os}/^{188}\text{Os}$ of the Os blank was 0.18 ± 0.01 . All data were blank corrected and uncertainties in the blank are reflected in specified uncertainties for isotopic and concentration data. Blank corrections were negligible ($\leq 0.1\%$) for Os and Re analyses of bulk chondrites.

For analysis of chondrite components, we mechanically and magnetically separated two matrix fractions (Ma1, Ma2), a single chondrule (Ch1), a collection of chondrule fragments (Ch2), a fraction of coarse sulfide grains (Sc, 100 to 200 μm), and a fraction of finer-grained sulfide (Sf, $< 100 \mu\text{m}$) from Allende sample USNM 3529. It should be noted that these sulfide fractions were misidentified previously as coarse and fine metal (Becker et al., 1999). Ma1 and Ma2 contain 20 to 30 vol% and ~ 40 vol% chondrule fragments, respectively and no CAIs. Ch1 and Ch2 had ~ 20 vol% and 5 to 10 vol% matrix attached, respectively. Sc and Sf contained 5 to 10 vol% matrix. For analysis of these components, the analytical procedures used were similar to whole-rock CT digestions, although smaller quantities of reagents were used, and Re was separated by following a solvent extraction procedure outlined in Becker et al. (2001). Blank corrections were negligible for Os (0.8 to 1.5 pg), but the Re blank of $7 \pm 5 \text{ pg}$ required a significant correction in one sample (9.2% for Ch1). For the other samples, the Re blank correction was $\leq 0.5\%$.

Isotope ratio measurements were carried out at the Isotope Geochemistry Laboratory at the University of Maryland. All Os isotope analyses, as well as some Re isotope analyses, were made with a Sector 54 multicollector mass spectrometer used in a static mode. Corrections for fractionation, spike contributions, and oxide interferences were conducted online. Some Re measurements were made with an NBS-design 68° sector, 12" radius of curvature, single-collector instrument.

Both Re and Os were vaporized from single filaments made from Pt ribbon (0.001" T \times 0.020" W). Rhenium was loaded in a nitrate form with $\text{Ba}(\text{NO}_3)_2$ as electron emitter (Creaser et al., 1991). For some samples, Os was loaded as a bromide then reduced to the metallic form by baking in a vacuum at $\sim 800^\circ\text{C}$ ~ 15 min. After reduction of Os, $\text{Ba}(\text{NO}_3)_2$ was added to the filament as an electron emitter. For most samples, Os was loaded as a bromide, then was covered with a thin coating of Ba-hydroxide. Unlike Re, Os was run with an oxygen bleed

to raise ionization yield (oxygen pressure was normally maintained at the level of 2×10^{-7} mbar).

Platinum filaments for Os were used without pretreatment. Some improvement of the Re filament blank was made by fusion of Pt ribbon in $\text{K}_2\text{S}_2\text{O}_7$, and in most cases fused Pt ribbon was used for Re analyses. In all cases during this work the filament contribution to blank was below 100 fg for Os and at the level of 0.3 to 0.6 pg for Re.

Long-term external reproducibility of $^{185}\text{Re}/^{187}\text{Re}$ and $^{187}\text{Os}/^{188}\text{Os}$ via repeated analysis of 1 ng of a Re standard and 15 ng of an Os standard, run at signal levels comparable to samples, were $\pm 0.11\%$ and $\pm 0.03\%$, respectively. Total external uncertainties (2σ) in Re, Os, $^{187}\text{Os}/^{188}\text{Os}$, and $^{187}\text{Re}/^{188}\text{Os}$ are estimated to be ± 0.14 , 0.05, 0.03, and 0.17%, respectively. Uncertainties for some Allende components are higher because of blank corrections or use of electron multiplier instead of Faraday cups (Table 1).

The ^{190}Pt - ^{186}Os isotope system is also of potential utility in the study of geochemical and cosmochemical systems (e.g., Walker et al., 1997). For this study, all Os that was analyzed for $^{187}\text{Os}/^{188}\text{Os}$ by Faraday cup was also analyzed for $^{186}\text{Os}/^{188}\text{Os}$. The measured ratios ranged from 0.11983 to 0.11985. All individual $^{186}\text{Os}/^{188}\text{Os}$ ratios were within analytical uncertainties of the higher precision chondritic ratio of 0.119834 reported by Walker et al. (1997).

4. RESULTS

Concentration and isotopic data are provided in Table 1. Concentrations of Re and Os for bulk samples of chondrites are generally comparable to those reported by previous studies that used neutron activation analysis or isotope dilution analysis (Fig. 1). As will be discussed below, however, the new results significantly differ from some previous studies with respect to the constancy and magnitude of Re/Os ratios.

Replicate concentration data for separate aliquants of the same meteorite typically vary by as much as several tens of percent. Such concentration heterogeneities are not unexpected in chondrites. The heterogeneities reflect the variable proportions of refractory inclusions (in carbonaceous chondrites) and metal present in different aliquants of a chondrite. Refractory inclusions and metal are typically characterized by very high abundances of the HSE. Indeed, one aliquant of the CO3 carbonaceous chondrite Lancé yielded concentrations of Re and Os (and Pt, Ru, and Ir) that are approximately one order of magnitude higher than a second aliquant (Table 1). The relative abundances of the HSE in the enriched sample, especially with respect to a large negative Pd anomaly, are similar to those of some types of CAIs (Palme and Wlotzka, 1976; Horan et al., in press). Consequently, it is likely that the HSE budget of the enriched aliquant was dominated by a CAI.

Rhenium concentrations in the bulk chondrites (excluding the enriched Lancé sample and HaH 237, the metal-rich Ben-cubbin-like meteorite) range from 23.57 ppb, for the EL6 Blithfield, to 118.9 ppb, for the H3 Dhajala. Osmium concentrations in the same two meteorites define the range for Os as between 276.7 and 1394 ppb. Thus, concentrations vary by approximately a factor of 4. The concentration ranges of Re and Os for ordinary, carbonaceous, and enstatite chondrites overlap (Fig. 1), so there is no discrimination among the major chondrite groups via concentration data. The new data, in combination with previously reported data (Morgan and Lovering, 1967; Ebihara et al., 1982; Jochum, 1996), suggest that CI carbonaceous chondrites and some L and LL ordinary chondrites have average Re and Os concentrations $\sim 25\%$ lower than other carbonaceous, enstatite, and ordinary chondrite groups. In addition, carbonaceous chondrites do not range to as

Table 1. Re-Os isotopic and composition data for chondrites.^a

Meteorite	Shock	Specimen	Weight (g)	Re (ppb)	Os (ppb)	¹⁸⁷ Os/ ¹⁸⁸ Os	¹⁸⁷ Re/ ¹⁸⁸ Os	Δ ^b
<i>Carbonaceous</i>								
Orgueil (CI1)	—	MPI-318/5	0.122	38.310	458.51	0.12644	0.40248	−5.4
Replicate	—	"	0.082	38.032	459.25	0.12638	0.39898	−3.3
Ivuna (CI1)	—	USNM 2478	0.101	37.083	449.97	0.12646	0.39704	−1.0
Replicate	—	"	0.092	35.018	428.76	0.12654	0.39349	2.7
A1 Rais ^c (CR2)	S1	USNM 1794	0.119	42.300	546.08	0.12543	0.37310	7.7
Replicate		"	0.086	46.140	600.82	0.12535	0.36993	9.3
Replicate		"	0.122	50.516	637.16	0.12541	0.38188	0.5
EET 92042 (CR2)	—	EET 92042,34	0.067	58.074	699.85	0.12718	0.39985	4.0
Renazzo (CR2)	S1-3	USNM 6172	0.070	52.116	632.90	0.12652	0.39672	−0.1
Murchison (CM2)	S1-2	USNM 5453	0.262	49.540	606.73	0.12644	0.39334	1.8
Replicate		MPI-319/19	0.049	45.975	579.99	0.12526	0.38184	−1.0
Murray ^c (CM2)	S1	ASU-635.2	0.158	54.130	672.42	0.12559	0.38777	−2.4
Replicate		"	0.099	53.425	661.74	0.12534	0.38891	−5.8
Mighei (CM2)	S1	USNM 1081	0.106	44.766	569.29	0.12513	0.37879	0.1
Replicate ^c		"	0.154	49.050	593.20	0.12610	0.39350	−1.8
Lancé (CO3)	S1	USNM 6643	0.117	59.322	764.49	0.12731	0.37389	25.8
Replicate		"	0.102	683.43	8843.4	0.12582	0.37227	12.2
Ornans (CO3)	S1	MPI-459/1	0.256	55.160	674.67	0.12658	0.39389	2.8
Replicate		"	0.134	56.362	689.04	0.12679	0.39410	4.7
Replicate		"	0.062	71.409	885.88	0.12633	0.38835	4.6
Allende ^c (CV3-ox)	S1	USNM 3529	0.219	63.230	773.92	0.12620	0.39355	−0.8
Replicate ^c		"	0.238	62.580	770.06	0.12643	0.39149	3.1
Replicate		"	0.117	60.078	748.73	0.12615	0.38657	4.2
Replicate		"	0.110	61.798	767.18	0.12614	0.38807	2.9
Vigarano (CV3-red)	—	MPI-102/18	0.108	62.800	686.04	0.12606	0.44100	−39.6
Replicate		"	0.126	63.063	745.58	0.12654	0.40751	−8.4
Replicate		USNM 477	0.095	60.271	690.27	0.12625	0.42066	−21.7
Karoonda (CK4)	S2	USNM 2275	0.104	44.226	686.93	0.11980	0.30991	1.2
HaH 237 (Bencub)	S3	MPI	0.093	201.27	2452.0	0.12687	0.39540	4.4
					Avg.	0.12596	0.38946	
					SD (1σ)	0.00131	0.02099	
<i>Allende Components</i>								
Ch1 chondrule		USNM 3529	0.0019	35.8	486	0.1305(4)	0.355(26)	72.6
Ch2 chondrule fragments		"	0.0189	72.90	718.9	0.12725(5)	0.4886(18)	−65.3
Ma2 matrix + chondrules		"	0.0438	53.63	676.5	0.12549(5)	0.3818(8)	0.7
Ma1 matrix		"	0.0239	47.72	675.9	0.12096(5)	0.3398(15)	−10.8
Sc sulfide coarse		"	0.0600	67.20	802.0	0.12731(5)	0.4037(8)	2.3
Sf sulfide fine		"	0.0423	84.41	971.3	0.12801(5)	0.4187(8)	−2.5
<i>Enstatite</i>								
Kota-Kota ^c (EH3)	S3	NHM 1905,355	0.164	56.990	637.33	0.12850	0.43069	−7.1
Replicate		"	0.100	53.902	592.97	0.12845	0.43806	−13.4
Replicate		"	0.107	52.784	614.02	0.12849	0.41423	5.8
Indarch ^c (EH4)	S3	USNM 3482	0.168	49.420	573.26	0.12809	0.41537	0.9
Replicate		"	0.115	53.899	625.50	0.12811	0.41524	1.2
Adhi Kot ^c (EH4)	S3	USNM 2358	0.168	56.960	648.19	0.12833	0.42346	−3.1
Replicate		"	0.092	45.289	500.96	0.12838	0.43566	−12.2
Abee (EH4)	S3	USNM 2096	0.108	49.200	582.53	0.12757	0.40693	2.3
Saint-Sauveur (EH5)	S3	USNM 5285	0.079	57.434	666.38	0.12762	0.41530	−3.8
St. Mark's (EH5)	S3	USNM 3027	0.098	54.476	604.91	0.12825	0.43394	−12.1
Khairpur ^c (EL6)	S2	NHM51366	0.252	72.730	823.23	0.12857	0.42572	−2.5
Jajh deh Kot Lalu ^c (EL6)	S2	USNM 1260	0.149	46.770	543.46	0.12813	0.41468	1.8
Replicate		"	0.093	60.081	693.09	0.12783	0.41771	−3.6
Daniel's Kuil ^c (EL6)	S2	NHM1985 M143	0.171	88.050	998.88	0.12853	0.42477	−2.1
Replicate		"	0.126	73.261	827.91	0.12835	0.42643	−5.2
Atlanta ^c (EL6)	S2	AMNH 3923	0.145	81.080	843.46	0.12901	0.46322	−27.7
Yilmia ^c (EL6)	S2	NHM 1972,132	0.156	78.810	940.53	0.12723	0.40370	1.5
Replicate		"	0.101	61.786	710.90	0.12724	0.41878	−10.3
Hvittis* (EL6)	S2	USNM 2827	0.091	44.690	538.42	0.12848	0.39992	17.0
Pillistfer (EL6)	S2	USNM 523	0.296	71.330	831.25	0.12800	0.41345	1.5
Replicate ^c		"	0.155	52.410	607.50	0.12817	0.41561	1.5
Replicate		"	0.099	62.439	725.51	0.12832	0.41473	3.7
Blithfield (EL6)	S2	USNM 534	0.107	23.575	276.75	0.12784	0.41044	2.3
					Avg.	0.12815	0.42078	
					SD (1σ)	0.00044	0.01348	

(continued)

Table 1. (Continued)

Meteorite	Shock	Specimen	Weight (g)	Re (ppb)	Os (ppb)	$^{187}\text{Os}/^{188}\text{Os}$	$^{187}\text{Re}/^{188}\text{Os}$	Δ^b
<i>Ordinary</i>								
Sharps (H3.4)	S3	USNM 640	0.235	74.520	876.10	0.12721	0.40990	-3.6
Replicate ^c		"	0.100	82.850	1072.23	0.12352	0.37212	-10.7
Ceniceros (H3.7)	—	MPI 709/1	0.097	36.362	491.50	0.12922	0.35655	58.6
Replicate		"	0.115	43.915	546.95	0.12964	0.38695	38.8
Dhajala^c (H3.8)	S1	USNM 5832	0.310	73.910	816.90	0.12853	0.43610	-11.1
Replicate		"	0.058	118.87	1394.4	0.12786	0.41080	2.2
Replicate		"	0.112	82.973	920.53	0.12968	0.43444	1.8
Bremervörde ^c (H3.9)	S2	ASU 3365	0.248	51.830	583.51	0.12889	0.42808	-1.1
Replicate		"	0.095	60.821	668.59	0.12938	0.43845	-4.4
Replicate		"	0.115	65.758	743.55	0.12890	0.42621	0.4
Zag (H3-6)	S3	UCLA	0.137	77.840	920.44	0.12725	0.40744	-1.3
Forest Vale ^c (H4)	S2	AMNH 4055	0.308	78.790	794.42	0.12972	0.47800	-32.2
Replicate ^c		"	0.336	80.670	824.33	0.12926	0.47164	-31.8
Ochansk (H4)	S3	MPI 169/2	0.134	73.773	819.51	0.12968	0.43385	2.2
Avanhandava^c (H4)	S2	USNM 5719	0.245	78.750	842.70	0.13045	0.45050	-3.2
Anlong^c (H5)	S2	UCLA 1116	0.267	96.960	1048.0	0.13033	0.44580	-0.7
Changde^c (H5)	S2	UCLA 1118	0.202	44.660	498.20	0.12853	0.43210	-7.9
Allegan^c (H5)	S1	USNM 215	0.234	79.330	888.50	0.12961	0.43030	4.3
Replicate ^c		"	0.320	76.720	860.20	0.12877	0.42980	-3.7
Forest City^c (H5)	S2	USNM 6649	0.250	78.640	862.80	0.12841	0.43930	-14.8
Replicate ^c		"	0.251	69.600	802.30	0.12649	0.41800	-17.2
Replicate		"	0.115	77.216	860.35	0.12954	0.43257	1.8
Rose City (H5)	S6	UCLA	0.152	89.389	975.06	0.12970	0.44182	-3.9
Guareña^c (H6)	S1	USNM 1469	0.273	84.170	982.50	0.12817	0.41290	3.6
Xingyang^c (H6)	S2	UCLA 1135	0.227	86.210	976.70	0.13021	0.42550	14.1
Farmington (L5)	S5	UCLA	0.112	41.438	497.34	0.12727	0.40143	3.7
Chico (L6)	S6	"	0.120	56.990	696.32	0.12441	0.39417	-19.1
Replicate		"	0.119	54.437	638.59	0.12439	0.41055	-32.3
Semarkona (LL3.0)	S2	USNM 1805	0.093	27.877	334.21	0.12776	0.40193	8.2
Replicate		"	0.120	26.253	288.65	0.12897	0.43830	-8.4
Chainpur^c (LL3.4)	S1	AMNH 4020	0.370	35.760	417.90	0.12793	0.41220	1.8
Replicate		"	0.107	30.479	351.23	0.12821	0.41817	-0.2
Replicate		"	0.098	33.643	392.14	0.12769	0.41340	-1.6
Replicate		"	0.205	33.755	<u>410.76</u>	<u>0.12752</u>	<u>0.39597</u>	10.5
					Avg	0.12833	0.42162	
					SD (1 σ)	0.00166	0.02479	
<i>Lodranite</i>								
GRA 95209 metal	—	GRA 95209,10	0.065	424.57	4995.3	0.12793	0.40956	3.9

^a Uncertainties (2 σ) in Re and Os concentrations, and $^{187}\text{Re}/^{188}\text{Os}$ and $^{188}\text{Os}/^{188}\text{Os}$ are: ± 0.14 , 0.05 , 0.17 , and 0.03% , respectively, except where uncertainties in last digits are enclosed in parentheses. Boldface indicates digestion by alkaline fusion. Shock stages use the scheme of Stöffler et al. (1991). Abbreviations: SD = standard deviation; Bencub = Bencubbin-like meteorite; ox = oxidized; red = reduced; MPI = Max Planck Institute (Mainz); USNM = U.S. National Museum of Natural History; AMNH = American Museum of Natural History; UCLA = University of California, Los Angeles, Meteorite Collection; ASU = Arizona State University; NHM = Natural History Museum, London.

^b $\Delta = 10^4 (^{187}\text{Os}/^{188}\text{Os}_{\text{Chondrite}} - (0.09524 + 0.07887 \times ^{187}\text{Re}/^{188}\text{Os}_{\text{Chondrite}}))$.

^c Previously reported in Meisel et al (1996).

high concentrations as enstatite and ordinary chondrites (Fig. 1). Metal from lodranite GRA 95209 has Re and Os concentrations of 423.6 and 4995 ppb, respectively. Such high concentrations are typical for low-Ni iron meteorites (Smoliar et al., 1996).

Corresponding data for alkaline fusion and CT digestion can be compared for several meteorites. In a given meteorite, variations in concentrations obtained by the different chemical processing methods are within the range of concentrations obtained for different aliquants processed by the same method. In some instances, the CT digestion results provide higher concentrations. In one instance, the fusion yielded a higher concentration (Table 1). There is no suggestion that the acid digestion technique fails to liberate a significant portion of the Re or Os from any chondrite.

In contrast to concentrations, $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$

ratios vary less than a total of ± 27 and $\pm 4.4\%$ respectively, within the suite of bulk chondrites examined. Indeed, most of this range results from inclusion of the CK4 carbonaceous chondrite Karoonda, with its exceptionally low Re/Os and $^{187}\text{Os}/^{188}\text{Os}$. Thus, unlike with the variably fractionated magmatic iron groups, there is insufficient range in the Re/Os ratio of this suite of chondrites to obtain meaningful isochron ages for the different chondrite groups.

Despite the poor reproducibility of Re/Os ratios for some chondrites, it is evident there is a significant offset in the ratios for carbonaceous chondrites compared with enstatite and ordinary chondrites. The average $^{187}\text{Re}/^{188}\text{Os}$ for carbonaceous chondrites is 0.389 ± 0.021 (1 σ standard deviation; this value becomes 0.392 ± 0.015 if Karoonda is excluded), compared with 0.422 ± 0.025 and 0.421 ± 0.013 for ordinary and enstatite chondrites, respectively (averages include replicate

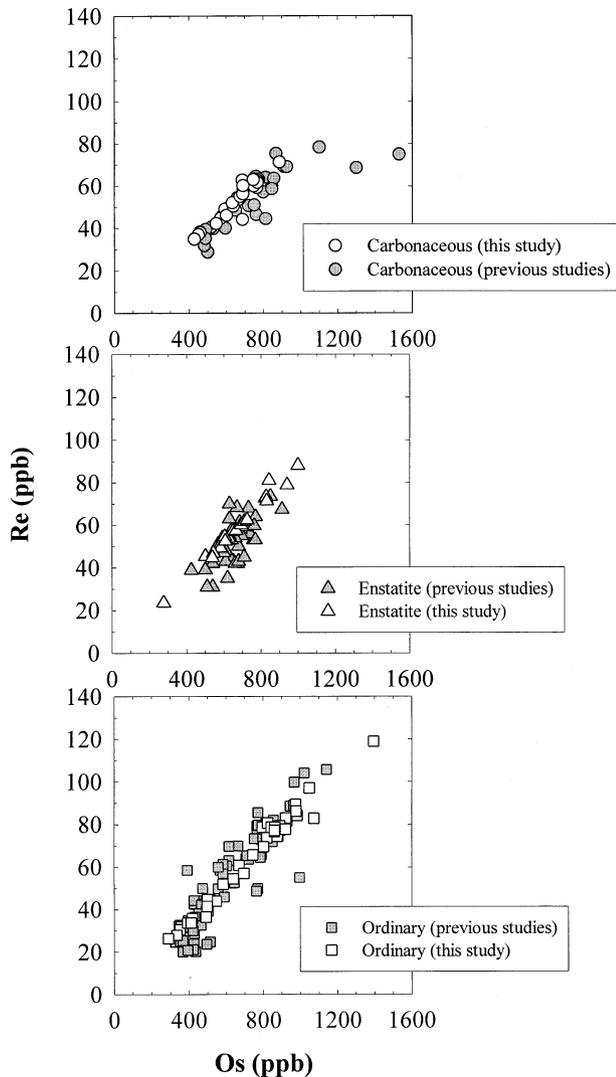


Fig. 1. Plots of Re vs. Os (ppb) for carbonaceous chondrites, enstatite chondrites and ordinary chondrites. Open symbols are data from this study; gray symbols are data from previous studies. Analytical uncertainties are smaller than symbol size. Note the significant overlap in abundances between the three major chondrite groups. Ordinary chondrites generally range to the highest concentrations, presumably because of the presence, in some aliquants, of greater proportions of metal that contains high Re and Os concentrations. One aliquant of the carbonaceous chondrite Lancé plots above the scale of this diagram. Data reported in previous studies are from the following: Ebihara et al. (1982), Jochum (1996), Morgan and Lovering (1967), Hertogen et al. (1983), Anders and Grevesse (1989), Wolf et al. (1980), Morgan et al. (1985), Takahashi et al. (1978a,b), Kallemeyn and Wasson (1986), Ebihara and Ozaki (1995), Rambaldi et al. (1979), and Chen et al. (1998).

analyses). These ratios, recast into elemental Re/Os ratios, are as follows: 0.0814 ± 0.0031 , 0.0876 ± 0.0052 , and 0.0874 ± 0.0027 , respectively.

The difference in the Re/Os ratios between these groups is a long-term effect, not the result of recent open-system behavior, as indicated by corresponding differences in $^{187}\text{Os}/^{188}\text{Os}$ (Fig. 2). By using all available data, ordinary chondrites define a narrow range of present day $^{187}\text{Os}/^{188}\text{Os}$ of 0.1283 ± 0.0017 (1σ standard deviation). Enstatite chondrites define a very

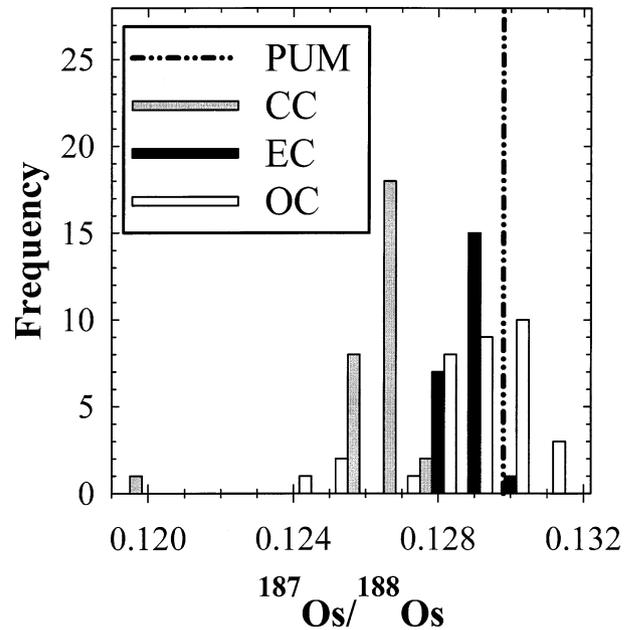


Fig. 2. Modal histogram of $^{187}\text{Os}/^{188}\text{Os}$ data for carbonaceous, enstatite, and ordinary chondrites. Data are taken from Table 1. Modes are plotted for data with values between the ratio defined for each tick mark and the next higher tick mark. The data for each of the three chondrite groups are plotted for each interval from zero (CC to left of tick mark, EC centered on tick mark, OC to right of tick mark). The modes include data for replicate analyses of the same meteorites. Also shown is the minimum estimated $^{187}\text{Os}/^{188}\text{Os}$ for Earth's PUM reported by Meisel et al. (2001). Note the limited overlap between carbonaceous chondrites and enstatite + ordinary chondrites. Note too the match between ordinary and enstatite chondrites and the PUM estimate.

similar average with an even narrower range and $^{187}\text{Os}/^{188}\text{Os}$ of 0.1281 ± 0.0004 . In contrast, carbonaceous chondrites define a 2 to 3% lower $^{187}\text{Os}/^{188}\text{Os}$ of 0.1260 ± 0.0013 (0.1262 ± 0.0006 if Karoonda is excluded). There is minimal overlap between the ordinary and enstatite chondrites vs. carbonaceous chondrites. One of the few ordinary chondrites that plots in the range of carbonaceous chondrites is Sharps, which contains abundant CM-like clasts and C-rich aggregates. The difference in isotopic compositions between carbonaceous vs. ordinary and enstatite chondrites requires that the time integrated Re/Os of carbonaceous chondrites has been, on average, ~ 7 to 8% lower than that of ordinary and enstatite chondrites, consistent with the differences in the measured $^{187}\text{Re}/^{188}\text{Os}$ ratios.

5. DISCUSSION

5.1. Nonisochronous Behavior

Chondrites are among the most primitive of solar system materials. Assuming derivation from a reservoir with a uniform initial $^{187}\text{Os}/^{188}\text{Os}$ ratio, it would be expected that bulk chondrites should plot very close to the Re-Os isochron defined by the IIIAB irons, which are assumed to have crystallized within ~ 10 to 20 Ma of the inception of the solar system (Smoliar et al., 1996). Only 34% of the bulk chondrites (including duplicates) plot within $\pm 2.5 \Delta$ units of the IIIAB isochron (Fig. 3), where Δ is per mil combined deviation in $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ of a datum from the reference IIIAB iron meteorite

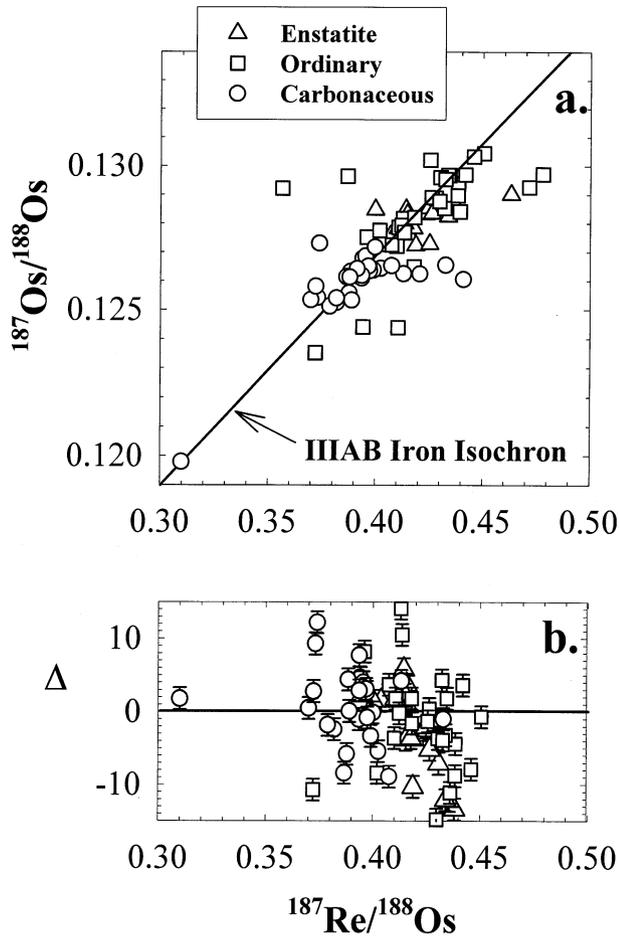


Fig. 3. (a) $^{187}\text{Re}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ for all bulk chondrites analyzed by this study. Analytical uncertainties are the same size or smaller than the symbols. Shown for reference is the 4.558-Ga group IIIAB iron meteorite isochron reported by Smoliar et al. (1996). Although many chondrites plot close to the reference isochron, a significant fraction of the chondrite suite plot either to the right or left of the isochron. (b) $^{187}\text{Re}/^{188}\text{Os}$ vs. Δ for all bulk chondrites analyzed by this study. Δ is the per mil deviation of a sample from the IIIAB iron isochron of Smoliar et al. (1996) (see Table 1 and text for details). Analytical uncertainties are shown as error bars. Note that some samples plot above and below the Δ scale of this figure. Reasons for the lack of isochronous behavior for many of the bulk chondrites are discussed in the text.

isochron (Table 1). This level of scatter about the isochron is significantly greater than for irons, as has been noted in previous studies of chondrites (Meisel et al., 1996; Chen et al., 1998). For comparison, all lower-Ni IIAB and IIIAB irons analyzed by Smoliar et al. (1996) plotted within $\pm 2 \Delta$ units of their respective isochrons (that article defined the deviation as ϵ , although the calculation is identical).

The Re-Os isotopic behaviors of bulk chondrites fall into four broad categories, as defined for samples that have been analyzed multiple times: (1) chondrites, such as Allende (CV3), that plot very close to the iron meteorite reference isochron and display reproducibility in $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ similar to that of irons; (2) chondrites for which $^{187}\text{Os}/^{188}\text{Os}$ is generally reproducible, but $^{187}\text{Re}/^{188}\text{Os}$ is highly variable, such as Vigarano (CV3); (3) chondrites, such as Forest Vale (H4), that

plot well off the reference isochron, but are reproducibly offset from the reference isochron; and (4) chondrites that have variable $^{187}\text{Os}/^{188}\text{Os}$ and that either plot reproducibly close to the iron reference isochron, such as Pillistfer (EL6), or plot at variable distances from the isochron, such as Sharps (H3).

The possible causes of nonisochronous behavior for chondrites and chondritic components have been discussed previously (e.g., Chen et al., 1998; Becker et al., 2001). The main possibilities considered have been (1) early solar system heterogeneities and processes, (2) analytical issues, and (3) late-stage open-system behavior.

Early solar system heterogeneities and processes can be dismissed for bulk chondrites. Large nebular heterogeneities in $^{187}\text{Os}/^{188}\text{Os}$ would almost certainly be accompanied by deviations in the relative abundances of other Os isotopes. Despite examination of several bulk chondrites and CAIs for these effects, none has been discovered (e.g., Walker et al., 1997; Becker et al., 2001). Deviations from the reference isochron that appear today but that were created within the first 50 Ma of the solar system would require large perturbations in Re/Os from chondritic for several tens of millions of years, followed by an event that returned the Re/Os of the rock back to a level such that the $^{187}\text{Os}/^{188}\text{Os}$ of the sample today remains in the range of other chondrites. Such fractionation processes are unknown, and the two-stage requirement is highly improbable.

Analytical issues have been raised in previous studies that dealt with bulk chondrites and chondrite components (Chen et al., 1998; Becker et al., 2001). Concerns have largely been focused on chemical blanks and the possibility of incomplete digestion of sample. These issues are not major concerns for most samples analyzed here. For the case of the bulk chondrites, blank corrections are minor, and the nonisochronous behavior of samples cannot be attributed to inadequate blank corrections. As discussed above, the proportion of Re or Os not accessed by CT digestion is minor and should have no impact on Re-Os isotopic systematics. It should also be noted that there is no correlation between the digestion technique used and deviation from the reference isochron. Thus, the total digestion achieved by alkaline fusion seems no more likely to produce isochronous results than the CT (e.g., Dhajala).

We conclude that relatively late-stage open-system behavior of the Re-Os system is the best explanation for most deviations of bulk chondrites from the iron meteorite reference isochron. This is consistent with the observation that reproducibility within analytical uncertainties of Re/Os ratios for separate aliquants of the meteorites examined is the exception rather than the rule. The variability in Re/Os ratios cannot solely be the result of primary concentration heterogeneities in the materials, because Os isotopic ratios are, in many instances, very reproducible ($\pm 0.2\%$ or better), suggesting that the present day “whole-rock” Os isotopic compositions of chondrites may reflect the time integrated compositions of the pristine Re/Os ratio of each meteorite.

Redistribution of Re or Os could have occurred during an impact on the parent body via recrystallization and/or vapor-transport of certain phases, by aqueous alteration on the parent body, or as a consequence of terrestrial alteration, such as rusting of metal (e.g., Smoliar et al., 1996). The open-system behavior documented here for various samples probably reflects processes ranging from very recent terrestrial alteration to

metamorphism on the parent body as much as 1 to 3 billion years ago. Most of the open-system behavior, however, is probably at the younger end of this scale. For example, bulk chondrites with highly reproducible $^{187}\text{Os}/^{188}\text{Os}$ but highly variable $^{187}\text{Re}/^{188}\text{Os}$, such as Vigarano, essentially require quite recent open-system behavior, possibly terrestrial alteration. In addition, the magnitude of the Re/Os ratio heterogeneity present for Vigarano implies redistribution of Re and/or Os on a scale that is sufficiently large that homogenization cannot be achieved in a finely ground powder. This likely implies movements of >1 to 10 mm for some samples.

Another example to consider is Forest Vale. Duplicate analyses of Forest Vale exhibit large negative deviations from the iron meteorite reference isochron, but unlike Vigarano, the deviations are quite reproducible. The fact that the replicate aliquants had much higher Re/Os ratios than the average ordinary chondrites, but typical $^{187}\text{Os}/^{188}\text{Os}$, also suggests a relatively recent addition of Re or loss of Os. The excellent reproducibility of Re/Os in comparison to Vigarano, however, suggests a much more pervasive, uniform process, such as the rusting of metal.

No bulk chondrite samples for which there are more than two analyses plot on secondary isochrons with plausible ages, nor do the two Allende chondrules (Ch1 and Ch2; Table 1). Nonetheless, it is possible that other nonisochronous samples may reflect processes that occurred on their parent bodies well before the present. Becker et al. (2001) established that redistribution of Re or Os occurred within an Allende CAI ~ 1.6 Ga ago. Determining whether larger pieces of bulk chondrites were affected by similar redistribution of Re or Os will require more intensive analysis of individual meteorites. Finally, it is important to keep the magnitude of the open-system behavior in perspective. Even if the movement of Re or Os was very recent, the isotope systematics require a gain or loss of the elements of no more than 2 to 3% for even the most nonisochronous samples. Also, whereas the processes involved have clearly affected Re/Os by as much as several percent, in most instances, there is no evidence for a significant disruption of the $^{187}\text{Os}/^{188}\text{Os}$ of individual samples.

5.2. Re/Os Variations in Bulk Chondrites

If it is assumed that open-system behavior in Re/Os occurred very recently for most of the samples that do not plot on the iron meteorite isochron, then the long-term $^{187}\text{Re}/^{188}\text{Os}$ of individual aliquants of unaltered chondrites may be calculated by assuming that each chondrite evolved from a $^{187}\text{Os}/^{188}\text{Os}$ of 0.09524 ± 11 at 4.558 Ga (consistent with the precise age and initial ratio determined for group IIIAB irons; Smoliar et al., 1996), and evolved with closed-system Re/Os until the present. The average calculated $^{187}\text{Re}/^{188}\text{Os}$ ratios and 1σ standard deviations for carbonaceous (excluding Karoonda), ordinary and enstatite chondrites are 0.3915 ± 0.0074 , 0.419 ± 0.021 and 0.4166 ± 0.0055 , respectively. These ratios recast into elemental Re/Os ratios are: 0.0813 ± 0.0015 , 0.0869 ± 0.0043 and 0.0865 ± 0.0011 , respectively. Calculated Re/Os ratios (elemental ratios are subsequently cited so that the new data can be compared with published concentration data) for the three major chondrite divisions generally show less variation within group than for the measured values (Fig. 4). We con-

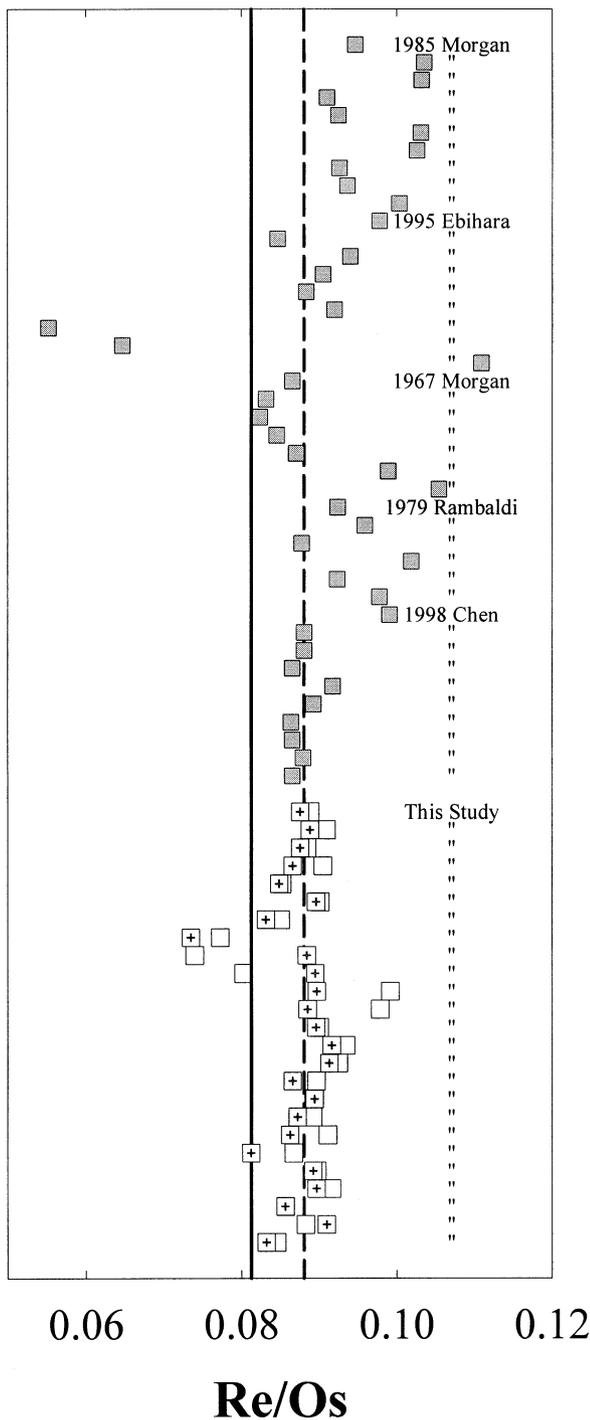
clude that the calculated Re/Os ratios provide the best estimate of the long-term elemental ratios for chondrites.

Compilations of results from previous studies (e.g., Morgan and Lovering, 1967; Morgan, 1985) suggested systematic differences in Re/Os among the various major divisions of chondrite groups (i.e., carbonaceous, enstatite, ordinary). Aside from the large difference between carbonaceous vs. ordinary and enstatite, the new results indicate that there are no major systematic variations among chondrite groups within each major division (e.g., L vs. LL). Despite the apparent lack of large-scale variations in Re/Os between the major chondrite groups of each division, there are two smaller-scale differences that should be noted. First, CM and CR chondrites have slightly lower average Re/Os than CI, CO and CV chondrites (Fig. 4a). Second, there is a negative correlation between Re/Os and petrologic grade for H chondrites with a petrologic grade of 4 or higher (Fig. 5a). For H chondrites of lower petrologic grade there is significant scatter in Re/Os. The correlation at the higher grades may be an oxidation effect. Rubin (1990) showed that in each OC group (H, L and LL) there is a tendency for the higher petrologic types to be more oxidized. The oxidation is indicated by higher olivine Fa contents and higher kamacite Co contents. The experiments by Palme et al. (1998) show that, in general, Re is lost more readily than Os as a result of oxidation, even at fairly low oxygen fugacities. Hence, during parent-body metamorphism, the oxidation state increased in the OC, olivine acquired more FeO, kamacite acquired more Co and Re formed volatile oxides and was lost from the whole rock to a greater extent than Os, leading to decreasing Re/Os ratios in going from type 4 to type 6. The number of data is too limited to assess whether such a correlation exists for L and LL chondrites.

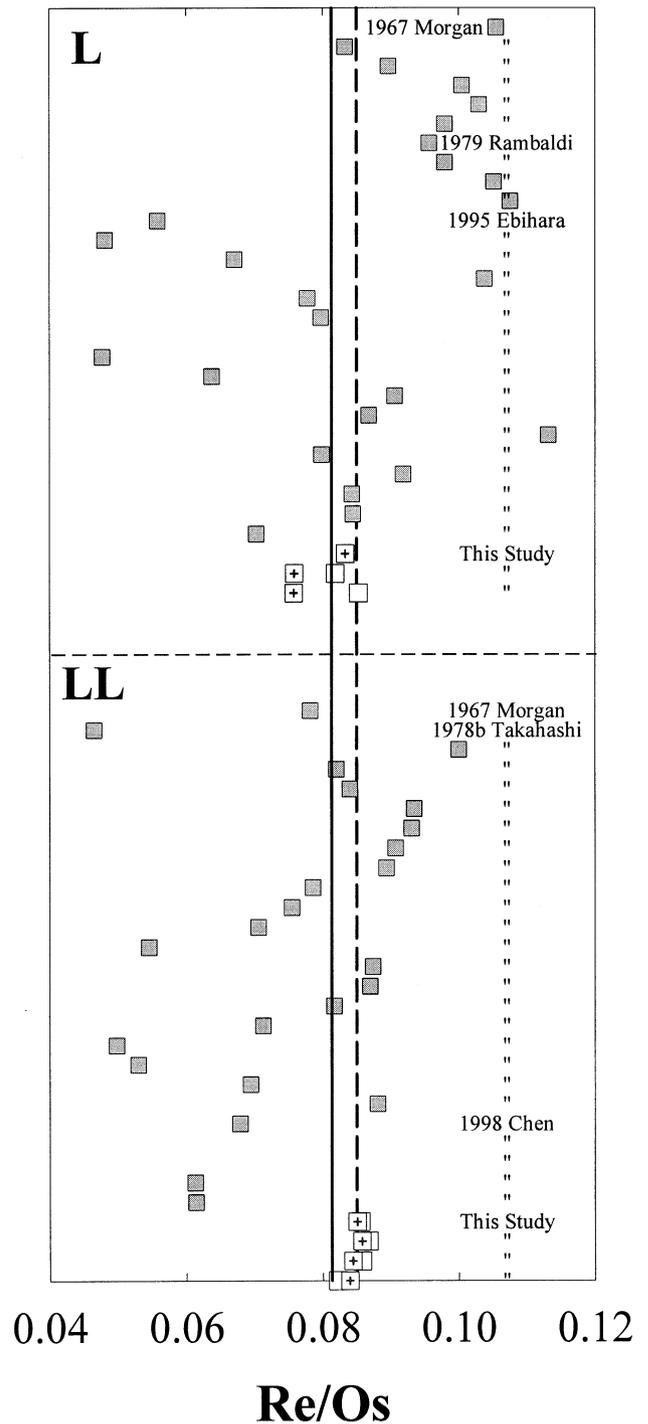
An important aspect of the new data is that they generally do not confirm earlier reports with respect to two issues. First, the limited variations in Re/Os ratios in our suite suggest that the large scatter reported by some previous studies (e.g., Kallemeyn et al., 1986; Ebihara and Ozaki, 1995) is not real. The reported scatter was most likely caused by analytical problems or large uncertainties in the analyses, rather than chemical variations among the chondrites. The new results suggest that actual variations in Re/Os are very minor.

Second, it is apparent from Figure 4 that some of the previously published Re/Os ratios were biased to higher or lower average ratios than are reported here. We emphasize the robust nature of the present data, given isotopic compositional data that buttress the measured Re/Os. Again the most likely cause of the previous biases is analytical problems. Of greatest concern here is the widely cited CI average values of Anders and Grevesse (1989). That study reported Re and Os concentrations for CI meteorites averaging 37.1 and 483 ppb, respectively, resulting in a Re/Os of 0.0769. In comparison, our averages for 2 CI chondrites (each in duplicate) give 37.0 ppb and 449 ppb, respectively, yielding a Re/Os of 0.0826. The 7% difference between the two ratios is within the ± 5 to 10% uncertainties cited by Anders and Grevesse, but we note that use of the earlier compilation value would result in major calculation errors for the evolution of Os isotopes in the solar system and planetary mantles. Consequently, we recommend that the ratios obtained from earlier compilations for Re and Os should not be used.

H Chondrites



L & LL Chondrites



In shocked chondrites, variations in Re/Os might reflect the shock stage or the age at which the shock event occurred. For the ordinary chondrites, no correlation between shock stage and Re/Os is discernible (Fig. 5b). There may, however, be some effects related to the age of shock. Relatively recent open-system behavior during shock metamorphism is suggested for two aliquants of Chico, which have variable $^{187}\text{Re}/^{188}\text{Os}$ ratios within the range of other ordinary chondrites, but have nearly identical

$^{187}\text{Os}/^{188}\text{Os}$ ratios that are even lower than the carbonaceous chondrite average. The interpretation of late-stage open-system behavior is supported by the $^{40}\text{Ar}-^{39}\text{Ar}$ age of 0.5 to 0.6 Ga for Chico.

In contrast to Chico, Rose City, with a similar, young shock age, plots close to the reference isochron, as does Farmington. Both have $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios similar to other ordinary chondrites. Zag, with a pre-4.25-Ga shock history,

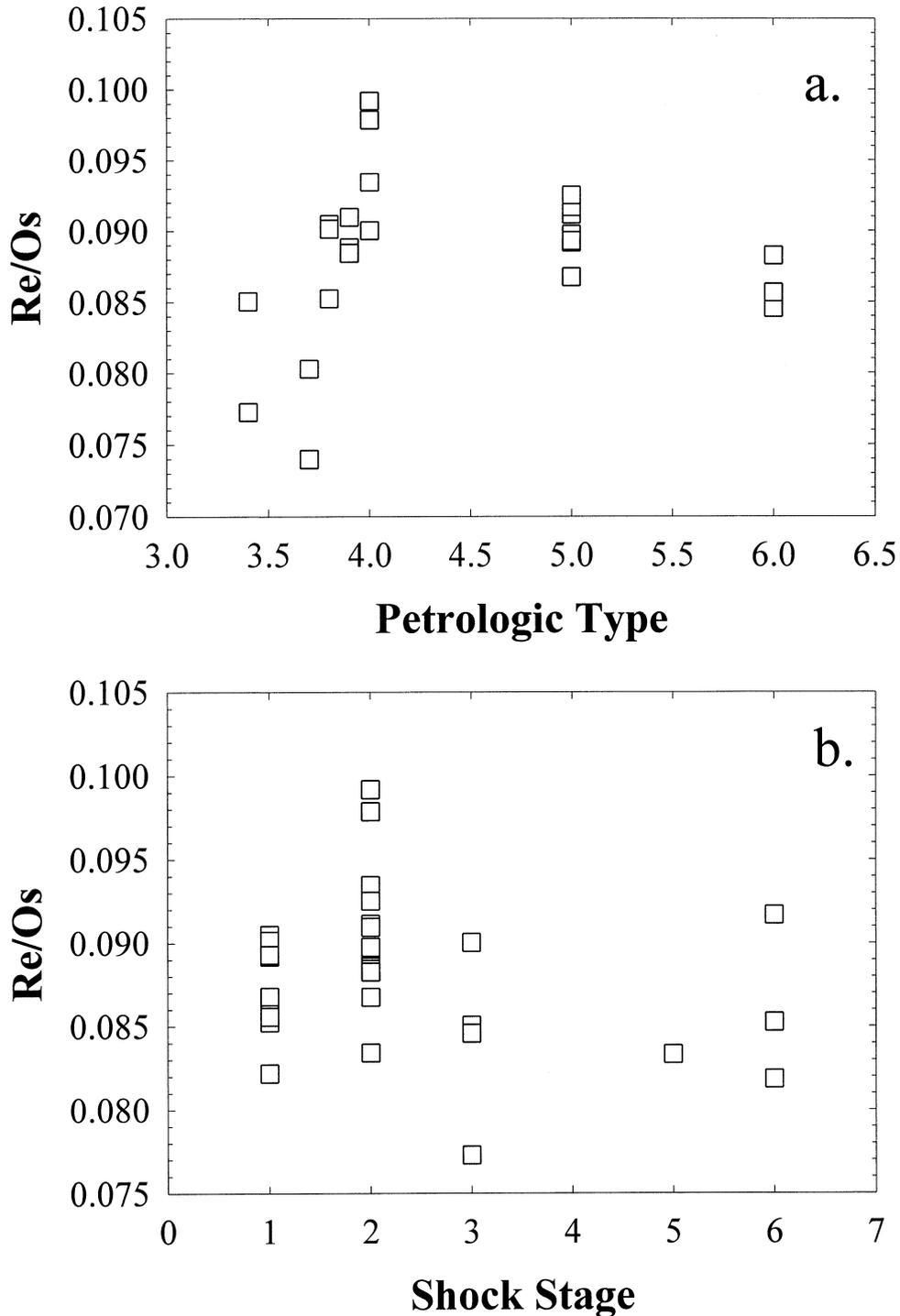


Fig. 5. (a) Re/Os ratio of H chondrites vs. petrologic type. Note the negative correlation between Re/Os and petrologic grade for chondrites with petrologic grades of 4 and above. The Re/Os of H chondrites below a petrologic grade of 4 is highly variable and ranges to lower ratios. (b) Re/Os ratio of ordinary chondrites vs. shock stage. There is no detectible correlation between these two parameters.

plots within uncertainty of the reference isochron. Evidently, extensive variation in the Re/Os ratio of bulk chondrite samples occurs only in some chondrites as a result of postaggregation shock heating, partial melting, and remobilization of Re and/or Os, as has been noted previously for the LL6 ordinary chondrite St. Séverin (Chen et al., 1998).

5.3. Systematics of Allende Components

Becker et al. (2001) reported that the measured $^{187}\text{Os}/^{188}\text{Os}$ of bulk Allende CAIs and CAI fragments (except Group II CAIs) form a distribution similar to bulk Allende and other carbonaceous chondrites, with the mean for the CAIs overlap-

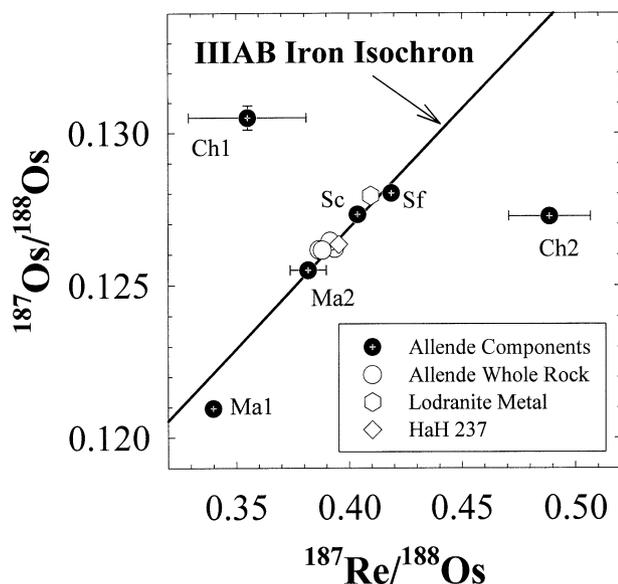


Fig. 6. $^{187}\text{Re}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ for Allende components and bulk samples. Analytical uncertainties, if not shown by error bar, are the same size or smaller than the symbols. Shown for reference is the 4.558-Ga group IIIAB iron meteorite isochron reported by Smoliar et al. (1996). Ch1 and 2 are chondrules, Sc and Sf are coarse- and fine-grained sulfide fractions, and Ma1 and Ma2 are matrix samples. Also shown for comparison is the metal from lodranite GRA 95209 and the metal-rich Bencubbin-like meteorite HaH 237.

ping with the CI chondrite mean. Other components separated from Allende display significant variability in Re/Os and $^{187}\text{Os}/^{188}\text{Os}$ (Fig. 6), although the level of variations are not as great as were reported for components from the LL6 ordinary chondrite St. Séverin (Chen et al., 1998). The sulfide fractions Sc (sulfide-coarse) and Sf (sulfide-fine) plot very close to the iron reference isochron and have $^{187}\text{Os}/^{188}\text{Os}$ ratios that are only 1 to 2% higher than bulk Allende (0.1262), and are much less fractionated with respect to Re/Os than metal fractions reported for ordinary chondrites (Chen et al., 1998). The high Re/Os of metal from these ordinary chondrites may reflect the higher metamorphic grade and localized melting and metal-sulfide partitioning (Chen et al., 1998). That Sc and Sf plot so close to the iron isochron suggests similar histories for the two sulfide size fractions and closed-system behavior since formation. Chondrule Ch1 lies significantly to the left of the iron isochron and has a $^{187}\text{Os}/^{188}\text{Os}$ more than 3% higher than bulk Allende. Chondrule fragments Ch2 have $^{187}\text{Os}/^{188}\text{Os}$ only ~1% higher than bulk Allende, but plot to the right of the iron isochron. The nonisochronous behavior of these components cannot be explained as a consequence of uncertainty in Re blanks, given the relatively high sample/blank for these materials, and instead presumably reflect relatively recent open-system behavior.

In contrast to chondrules, matrix sample Ma1 has Re/Os and $^{187}\text{Os}/^{188}\text{Os}$ ratios that are much lower than bulk Allende, and plots significantly to the right of the iron meteorite isochron. Matrix-chondrule mix Ma2 is only ~1% less radiogenic than bulk Allende, and plots on the iron isochron. The Os isotopic composition of this sample is probably higher than Ma1 because of the higher fraction of chondrule fragments in Ma2 compared with Ma1. It is important to note that although

Allende components display open-system Re-Os behavior that is evident on the millimeter-level scale of some CAIs (Becker et al., 2001), chondrules, and matrix, neither the larger-scale bulk meteorite nor the sulfide grains show evidence of open-system behavior. On the basis of these limited results, it is suggested that for Allende, recent redistribution of Re or Os has affected components in the order chondrules > matrix > sulfide + bulk.

It has been reported that the carrier of HSE in ordinary chondrite matrix is very fine grained metal (Rambaldi and Wasson, 1981). Very oxidized carbonaceous chondrites contain very little metal (e.g., McSween, 1977). Thus, HSE may be concentrated in sulfides and possibly even some oxides, which are oxidation products of primary FeNi metal. The concentrations of Re and Os are slightly higher in the sulfides than in the bulk meteorites, but these elements are evidently not highly concentrated in the sulfide. The low Re/Os of the matrix may reflect preferential leaching of Re during alteration under oxidizing conditions on the parent body. Leaching would not have affected the much coarser sulfide components Sc and Sf that show a higher Re/Os than the Allende bulk rock. The fractionation between low-Re/Os matrix and high-Re/Os sulfides plausibly could reflect small-scale Re-Os redistribution by grain boundary diffusion processes. It is also possible that the Re/Os matrix-sulfide dichotomy observed in Allende represents a primary feature of the metal precursors that reflect processes in the solar nebula. It should be noted that the metal-rich (>80%) Bencubbin-like carbonaceous chondrite HaH 237 shows a Re/Os that, like the sulfide fractions in Allende, is on the high side of the distribution of Re/Os in carbonaceous chondrites. The abundances and pattern of the HSE in HaH 237 have been interpreted to reflect condensation in the solar nebula (Zipfel et al., 1998).

5.4. Controls on the Re/Os of Parental Materials

On average, bulk carbonaceous chondrites have a 7 to 8% lower Re/Os ratio compared with enstatite and ordinary chondrites. As noted above, this is most strongly reflected in the 2 to 3% lower average $^{187}\text{Os}/^{188}\text{Os}$. Thus, ordinary and enstatite chondrites were derived from materials with substantially fractionated Re/Os relative to the bulk nebula, as may be recorded by CAIs (e.g., Becker et al., 2001), and relative to carbonaceous chondrites. This fractionation could have been achieved either via high-temperature nebular condensation effects, or as a consequence of subsequent early solar system processes at much lower temperatures.

First, consider high-temperature processes. Model condensation calculations for Re and Os have suggested that Re may become fractionated from Os in high-temperature nebular condensates (Palme and Wlotzka, 1976; Sylvester et al., 1990). Published condensation curves for high temperatures, however, do not allow meaningful specific predictions to be made regarding the order of condensation for Re and Os. This is because the models are based on the unlikely assumption of ideal solid solution. The actual solid solution properties of the complex alloys that are likely involved are currently beyond conjecture because of uncertainties in activity coefficients for these elements at high temperatures (H. Palme, personal communication). Nonetheless, if Re and Os fractionate during

equilibrium condensation, or if Os condenses before or after Re, the variation in Re/Os ratios among the chondrite groups could reflect high-temperature nebular processing. For example, preferential incorporation of Re relative to Os into high-temperature condensates, followed by subsequent sequestration of the condensates could lead to the formation of a sizable reservoir with enriched Re/Os relative to the bulk nebula. This process could also lead to the formation of a residual reservoir with depleted Re/Os ratio relative to the bulk nebula. Indeed, early removal of a high-temperature condensate is one mechanism Sylvester et al. (1990) considered to generate a reservoir with low Re/Os from which to form certain refractory inclusion-bearing components characterized by Re/Os less than CI.

Much lower temperature processes, such as oxidation plus heating of Re and Os-bearing alloys, can modify the Re/Os of phases that are highly enriched in HSE. For example, Palme et al. (1998) experimentally showed that variations in the Re/Os of several percent can occur as a consequence of oxidation and subsequent volatilization of pure metals at oxygen fugacities of QFM and higher. Such volatilization losses would remove Re preferentially to Os and would result in a decrease in Re/Os in the residual solids.

There are limitations in both high-temperature condensation and lower-temperature volatilization models. If the high-temperature condensation characteristics of Re and Os are quite similar, as has been presumed, the condensation models require significant isolation of materials formed within a rather narrow temperature range. Conversely, the lower-temperature alteration models require processes that can produce the nearly uniform Re/Os ratios observed within the chondrite types.

Other models to explain HSE fractionations within chondrite components and among chondrite groups have been reported. For example, Chen et al. (1998) outlined a mechanism for generating chondrules with variably fractionated Re/Os (and other HSE) inside planetesimals. They hypothesized that the relative abundances of HSE are largely controlled by their abundances in metal. The HSE could become fractionated via melting and crystal-liquid fractionation processes on or near the surface of a planetesimal. Mixing of the variably fractionated metals with silicates and dust upon the break-up of the planetesimal could then lead to the construction of chondrules (and ultimately chondrites) with fractionated Re/Os. As with the aqueous alteration model reviewed above, it is difficult to envision this process leading to the generation of chondrite types with relatively uniform Re/Os, but it could account for variations in individual chondrules. Grossman (1988) and Rubin (2000) have discussed shortcomings of models that require the formation of chondrules on planetesimals.

Given the now much tightened constraints on Re/Os of chondrites imposed by Os isotopes, it will be critical to reexamine the fractionations of other HSE in tandem with the Re-Os data to finally constrain the process or processes involved.

5.5. Re-Os Isotopic Systematics of Lodranite Metal

Lodranites are meteorites that have been modeled as residues of partial melting within a relatively small asteroid. All lodranites share common O isotopic compositions, suggestive of formation in a single parent body. Fe-Ni metal, constituting 0.5

to 20 vol% of lodranites, formed at temperatures between 1050 and 1200°C (McCoy et al., 1997). The only lodranite for which there is age information is Gibson. The $^{40}\text{Ar}/^{39}\text{Ar}$ plateau age of this meteorite is 4.49 ± 0.04 Ga (McCoy et al., 1997), presumably the age of system closure for Ar. Lodranites may provide useful information about the timing and magnitude of HSE partitioning during the transformation of a primitive, undifferentiated body to a differentiated body with separate metallic core and silicate mantle.

The high concentrations of Re and Os present in the GRA 95209 metal suggest partitioning of Re and Os into the metal phase consistent with the very high metal-silicate distribution coefficients that have been previously reported (e.g., Borisov and Walker, 2000; Ertel et al., 2001).

Sample GRA 95209 metal plots very close to the iron meteorite isochron (Fig. 6). The Re-Os systematics provide little age constraint on its melting history or metal segregation. This sample has $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios that overlap the composition range of both ordinary and enstatite chondrites. Because there was evidently little or no fractionation of Re from Os during the transition from undifferentiated precursor materials to the metal, there is no deviation from chondritic evolution for this sample. This result suggests that partial melting of chondritic material and accumulation of metal does not, by itself, lead to a significant fractionation of Re from Os, consistent also with the results for the shocked ordinary chondrites Rose City, Farmington and Zag. Subsequent crystal-liquid fractionation would be required to produce the fractionations envisioned by the model of Chen et al. (1998) for fractionating HSE on a planetesimal.

5.6. Implications for Planetary Late Veneers

Generally chondritic ^{187}Re - ^{187}Os and ^{190}Pt - ^{186}Os isotope systematics, and approximately chondritic proportions of the HSE in terrestrial upper mantle rocks suggest the presence of a chondrite-like component in undepleted mantle, which is currently best explained by late accretion of large planetesimals after formation of the Earth's core and the Moon (e.g., Chou, 1978; Morgan, 1986; Morgan et al., 2001). This period of late influx was a major event in Earth history, adding as much as 0.3% to the mass of the Earth and establishing the abundances of the HSE at their present level in, at least, the upper mantle.

The new chondrite results are important for late accretionary models. Meisel et al. (2001) reported a minimum $^{187}\text{Os}/^{188}\text{Os}$ of 0.1296 ± 0.0008 for the Earth's primitive upper mantle (PUM). This estimate was made via analysis of suites of variably melt-depleted mantle xenoliths that were extracted from mantle underlying three continents. These results suggest that the Re/Os ratio, and by inference, the budget of other HSE elements in the Earth's upper mantle, was dominated by late accretion of materials having Re/Os more similar to enstatite or ordinary chondrites, not carbonaceous chondrites (Fig. 2). During the late stages of terrestrial accretion, however, the Earth accreted material from throughout the inner solar system (Canup and Agnor, 2000). Consequently, there is no a priori reason why the HSE characteristics of the late veneer should match any particular group of chondrites. Thus, rather than suggesting the impact by materials from an enstatite chondrite parent body, a more likely scenario is the involvement of

planetesimals whose HSE were processed in a manner similar to those present in enstatite chondrites.

Despite the recent progress characterizing the PUM and chondrites, there are many uncertainties that remain with regard to the nature and timing of the late veneer. Apparent regional variations in terrestrial HSE patterns may be a consequence of a late influx of very large objects of variable composition that were not subsequently well homogenized throughout the upper mantle. The variations, however, could also reflect analytical biases between different laboratories (Morgan et al., 2001), and there have as yet been only limited attempts to deconvolute the HSE characteristics of upper mantle materials from processes that occur within the mantle, such as partial melting and fluid and melt percolation. Solution of these issues will rest with future study.

6. SUMMARY

Carbonaceous chondrites are characterized by 7 to 8% lower Re/Os than ordinary and enstatite chondrites. This is a long-term effect as indicated by correspondingly lower $^{187}\text{Os}/^{188}\text{Os}$ ratio. Variability in the Re/Os ratio of bulk chondrites is minor within each major division of chondrites (carbonaceous, enstatite, and ordinary chondrites), in contrast to the findings of some previous studies.

The Re-Os isotopic compositions of greater than 60% of the bulk chondrites plot beyond analytical uncertainties off the iron meteorite reference isochron, indicating open-system behavior of Re and Os at some time significantly post formation. This open-system behavior occurred within the past 3 Ga and in most cases reflects very recent, perhaps terrestrial alteration. Components separated from Allende indicate relatively major movement of Re and/or Os into or out of chondrules and matrix on the scale of millimeters to centimeters, but no appreciable movement within sulfides.

The division of bulk chondrites into two groups with disparate Re/Os is most likely the result of high-temperature nebular condensation of refractory element-bearing alloys and their subsequent isolation and incorporation into the precursor materials of certain chondrite groups. However, lower-temperature oxidation and heating loss of Re in the precursor materials of carbonaceous chondrite components could also be responsible for the differences.

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