

## Highly siderophile elements in chondrites

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### Abstract

The abundances of the highly siderophile elements (HSE), Re, Os, Ir, Ru, Pt and Pd, were determined by isotope dilution mass spectrometry for bulk samples of 13 carbonaceous chondrites, 13 ordinary chondrites and 9 enstatite chondrites. These data are coupled with corresponding <sup>187</sup>Re–<sup>187</sup>Os isotopic data reported by Walker et al. [Geochim. Cosmochim. Acta, 2002] in order to constrain the nature and timing of chemical fractionation relating to these elements in the early solar system. The suite of chondrites examined displays considerable variations in absolute abundances of the HSE, and in the ratios of certain HSE. Absolute abundances of the HSE vary by nearly a factor of 80 among the chondrite groups, although most vary within a factor of only 2. Variations in concentration largely reflect heterogeneities in the sample aliquants. Different aliquants of the same chondrite may contain variable proportions of metal and/or refractory inclusions that are HSE-rich, and sulfides that are HSE-poor. The relatively low concentrations of the HSE in CI1 chondrites likely reflect dilution by the presence of volatile components.

Carbonaceous chondrites have Re/Os ratios that are, on average, approximately 8% lower than ratios for ordinary and enstatite chondrites. This is also reflected in <sup>187</sup>Os/<sup>188</sup>Os ratios that are approximately 3% lower for carbonaceous chondrites than for ordinary and enstatite chondrites. Given the similarly refractory natures of Re and Os, this fractionation may have occurred within a narrow range of high temperatures, during condensation of these elements from the solar nebula. Superimposed on this major fractionation are more modest movements of Re or Os that occurred within the last 0–2 Ga, as indicated by minor open-system behavior of the Re–Os isotope systematics of some chondrites.

The relative abundances of other HSE can also be used to discriminate among the major classes of chondrites. For example, in comparison to the enstatite chondrites, carbonaceous and ordinary chondrites have distinctly lower ratios of Pd to the more refractory HSE (Re, Os, Ir, Ru and Pt). Differences are particularly well resolved for the EH chondrites that have Pd/Ir ratios that average more than 40% higher than for carbonaceous and ordinary chondrite classes. This fractionation probably occurred at lower temperatures, and may be associated with fractionation processes that also affected the major refractory lithophile elements. Combined, <sup>187</sup>Os/<sup>188</sup>Os ratios and HSE ratios reflect unique early solar system processing of HSE for each major chondrite class.

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## 1. Introduction

Advances in mass spectrometry, coupled with isotope dilution, now permit high precision measurement of the concentrations of Re, Os, Ir, Ru, Pt and Pd in chondrites. We report new data for 35 bulk samples of carbonaceous, ordinary and enstatite chondrites. These elements were analyzed by isotope dilution and by negative thermal ionization mass spectrometry (N-TIMS: Re and Os) and multi-collector, inductively coupled plasma mass spectrometry (MC-ICP-MS: Ir, Ru, Pt and Pd). The abundances of these elements in chondrites, coupled with their  $^{187}\text{Re}$ – $^{187}\text{Os}$  isotopic systematics, may help constrain the nature and timing of chemical fractionation relating to these elements in the early solar system. These elements have been termed highly siderophile elements (HSE) because of their extremely high affinity for Fe-metal relative to silicate. Rhenium and Os also are especially refractory, among the highest-temperature condensates from the early solar nebula. Indeed, all of the measured HSE, except Pd, condense at temperatures higher than the most abundant of the major early nebular condensates including forsterite, enstatite and Fe–Ni metal, and so may record some of the highest-temperature, and therefore probably earliest, processes in the nebula (Larimer, 1988; Wasson, 1985). Palladium condenses at a somewhat lower temperature, just below the condensation temperatures of the magnesian silicates and Fe–Ni metal. Among the many opportunities for fractionation of the HSE to occur are the periods during condensation from the nebular gas and chondrule formation; during alteration at lower temperatures, both prior to and after incorporation into a parent body; and during partial or complete melting caused by shock.

## 2. Samples

The chondrites examined by this study consist of bulk samples of 13 carbonaceous chondrites, 13 ordinary chondrites and 9 enstatite chondrites. To a large extent, we have attempted to avoid analysis of weathered and shocked chondrites, because such materials might be expected to display non-primitive, late-stage fractionations of the HSE. In order to assess the effects of shock on the abundances of the HSE,

however, we also analyzed four well-studied, shock-altered ordinary chondrites: Zag (H3–6), Rose City (H5), Farmington (L5) and Chico (L6). The latter is a relatively fresh find; the other three are falls.

## 3. Analytical techniques

Samples were ground to powder using an agate mortar and pestle. Approximately 100 mg of powder, a mixed  $^{187}\text{Re}$ – $^{190}\text{Os}$  spike and a mixed HSE spike consisting of  $^{104}\text{Ru}$ ,  $^{110}\text{Pd}$ ,  $^{191}\text{Ir}$  and  $^{198}\text{Pt}$  were digested at 493 K (220°) for at least 1 day in 2 ml of HCl and 4 ml of  $\text{HNO}_3$  in sealed quartz glass tubes (Carius, 1865). Osmium was separated from the other HSE by solvent extraction into  $\text{CCl}_4$  and back-extraction into HBr (Cohen and Waters, 1996). Osmium fractions were further purified by micro-distillation into HBr from a  $\text{H}_2\text{SO}_4$ –dichromate solution (Roy-Barman, 1993). The *aqua regia* fraction, containing the other HSE, was dried gently, re-dried with HF, and re-dissolved in 1 M HCl. Anion exchange resin (AG1  $\times$  8, 100–200 mesh) was used to separate the Re fraction (in 4M  $\text{HNO}_3$ ), a Pt–Ir–Ru fraction (in 13 M  $\text{HNO}_3$ ) having minimal Pd, and a Pd fraction (in 9 M HCl). Each of these fractions was dried gently. The Pt–Ir–Ru and Pd fractions were redissolved in 5% nitric acid for analysis by ICP-MS.

Rhenium and Os were measured by negative thermal ionization (N-TIMS) on the *Sector 54* mass spectrometer at the University of Maryland. Further details of the Re–Os procedure are given in Walker et al. (2002) and references therein. Platinum, Ir, Ru and Pd abundances were measured on the *Plasma-54* MC-ICP-MS at the Department of Terrestrial Magnetism, Carnegie Institution of Washington, using faraday cups in a static multicollection mode. This instrument is configured with nine faraday cups, and utilizes a Cetac MCN-1000 desolvation nebulizer. This sample introduction system provided good sensitivity and minimized the formation of possible interferences from oxides and hydrides.

Platinum and Ir fractions were analyzed simultaneously. Mass fractionation for both Pt and Ir was corrected using an exponential law and the  $^{194}\text{Pt}/^{195}\text{Pt}$  ratio (0.9744, Taylor and De Bieve, 1996) measured in standards that were run alternately with samples. The intensity of  $^{199}\text{Hg}$  was monitored, and was

always less than 0.1% of the total mass 198 measured. From the same Pt–Ir fraction, Ru also was analyzed. Ruthenium was corrected for mass fractionation using an exponential law and  $^{100}\text{Ru}/^{101}\text{Ru}=0.73843$  (Huang and Masuda, 1997). Interference from  $^{104}\text{Pd}$  on  $^{104}\text{Ru}$  was corrected online by measurement of  $^{105}\text{Pd}$ , and the correction was usually less than 10%. Fractionation was corrected off-line by comparison with standards run on the same day. The Pd fraction was analyzed separately, and corrected online for occasional Cd interference above the detection limit by monitoring  $^{111}\text{Cd}/^{105}\text{Pd}$ . Palladium analyses were corrected offline for fractionation using an exponential law and  $^{108}\text{Pd}/^{105}\text{Pd}=1.1890$  (Carlson and Hauri, 2001) by comparison with standards run the same day. Standard solutions of Ir, Ru, Pt and Pd were prepared in our laboratories from high-purity metal. Long-term external reproducibility of the isotopic compositions of the standard solutions as measured by ICP-MS is  $\pm 0.1\%$  or better.

Total analytical blanks were measured for each set of chemistry by isotope dilution. Measured blanks were  $8 \pm 5$  pg Re,  $3 \pm 2$  pg Os,  $22 \pm 10$  pg Ir,  $120 \pm 80$  pg Pt,  $35 \pm 5$  pg Ru, and  $250 \pm 150$  pg Pd, except for one set of samples that had a Pd blank of  $1.6 \pm 0.4$  ng. Blank corrections were much less than 0.5% for all of the HSE elements, except those samples analyzed in the set having a high Pd blank. These samples required blank corrections of as much as 5%. Isotopic ratios were measured to a precision of  $\pm 0.1\%$  or better, which is close to the theoretical limit of precision based on the repeated analysis of standard solutions. For the samples from the set with the high Pd blank, however, the precision of their Pd abundance determinations is approximately  $\pm 1\%$ , dominated by the uncertainty in their blank corrections.

#### 4. Results

Blank-corrected abundances of HSE are provided in Table 1. Some of these data were reported previously in abstract form (Horan and Walker, 2000). We note that the Ru abundances in Horan and Walker (2000) have been corrected for a mathematical error in the data reduction. Rhenium and Os abundances and  $^{187}\text{Os}/^{188}\text{Os}$ , given in Walker et al. (2002), are repeated here so that those abundances may be linked

to abundances for the other HSE that were determined on the same sample aliquant.

Walker et al. (2002) reported more limited variations in Re/Os ratios in this suite of chondrites than was found in some previous studies. Most of the scatter reported in earlier studies was interpreted to have been caused by analytical difficulties, or large uncertainties in the analyses, rather than chemical variations among the chondrites. The new data suggest that the actual variations in Re/Os ratios within each of the chondrite classes are minor. If the  $^{187}\text{Os}/^{188}\text{Os}$  ratio is used to infer the time-averaged Re/Os ratio, then the variation in Re/Os with the suite of chondrites is even smaller. Use of the Os isotopic data provides the best estimate for the Re/Os ratio in CI chondrites, which is 0.0826, about 7% higher than the ratio of 0.0768 given in Anders and Grevesse (1989).

A similar comparison of Ir, Ru, Pt and Pd abundances with previously published results is more difficult for several reasons. First, because the Re–Os isotope system is long-lived, the accuracy of the measured Re/Os ratio of a sample can be checked by comparison with its  $^{187}\text{Os}/^{188}\text{Os}$ , assuming that any open-system behavior occurred relatively recently (Walker et al., 2002). Such a check is not possible for the ratios of the other HSE. Second, the abundances of the HSE in individual aliquants of samples can vary considerably because of the uneven distribution of phases and inclusions with high abundances of the HSE, such as metal and calcium–aluminum inclusions (CAIs). Duplicate analyses of some of the chondrites we analyzed yielded results that varied by less than a few percent, but duplicates of other chondrites show a much larger range. It is clear that HSE ratios within the same meteorite aliquant, and within a given class, group, or type, generally are more reproducible than absolute abundances (e.g., Morgan et al., 1985; McDonald et al., 2001; Walker et al., 2002). This issue of sample inhomogeneity is discussed in more detail later. Third, there are relatively few multi-element data in the literature on the same sample aliquants of a given chondrite that can be used to assess the accuracy our data. Previously published data for Orgueil and Allende, the most frequently analyzed chondrites, are compiled in Table 2. Our abundance data are generally consistent with previously published compositional data,

Table 1  
Concentrations of the highly siderophile elements, in ppb, and Os isotopic ratios

Meteorite	Group/shock	ID <sup>a</sup>	Weight (g)	Re	Os	Ir	Ru	Pt	Pd	Pd/Ir	<sup>187</sup> Os/ <sup>188</sup> Os
<i>Carbonaceous</i>											
Orgueil	C1I/–	MPI-318/5	0.082	38.03	459.2	455.6	651.5	858.3	562.9	1.236	0.12644
Replicate			0.089	41.04	456.9	432.3	647.6	874.3	573.5	1.327	n.d.
Ivuna	C1I/–	USNM 2478	0.092	35.17	428.8	406.0	608.7	829.4	528.5	1.302	0.12654
Replicate			0.101	37.08	450.0	428.2	636.3	860.0	n.d.	n.d.	0.12646
Al Rais	CR2/S1	USNM 1794	0.086	46.14	600.8	570.0	881.2	1096	576.2	1.011	0.12535
Replicate			0.122	50.52	637.2	568.1	828.7	1092	637.9	1.123	0.12541
EET 92042	CR2/–	EET92042,34	0.067	58.07	699.8	714.2	1001	1294	713.3	0.999	0.12718
Replicate			0.106	48.60	589.4	549.6	841.3	1115	750.8	1.366	n.d.
Renazzo	CR2/S1–3	USNM6172	0.077	61.70	719.5	670.2	1009	1329	890.7	1.329	n.d.
Replicate			0.070	52.12	632.9	595.1	937.8	1217	577.8	0.971	0.12652
Murchison	CM2/S1–2	MPI-319/19	0.049	45.97	580.0	557.7	740.8	1043	618.9	1.110	0.12526
Murray	CM2/S1	ASU-635.2	0.099	53.43	661.7	613.1	851.0	1067	578.0	0.943	0.12534
Mighei	CM2/S1	USNM 1081	0.106	44.77	569.3	544.2	791.4	1041	576.8	1.060	0.12513
Lancé	CO3/S1	USNM 6643	0.102	683.4	8843	8364	10510	3926	771.6	0.092	0.12582
Replicate			0.117	59.32	764.5	698.3	1017	1323	762.3	1.092	0.12731
Ormans	CO3/S1	MPI-459/1	0.062	71.41	885.9	849.4	979.3	1213	666.6	0.786	0.12633
Allende	CV3-ox/S1	USNM 3529	0.117	60.08	748.7	704.4	n.d.	1336	661.9	0.940	0.12615
Replicate			0.110	61.80	767.2	716.3	n.d.	1345	681.8	0.952	0.12614
Replicate			0.202	n.d.	n.d.	716.7	1016	1364	678.3	0.946	n.d.
Vigarano	CV3-red/–	MPI-102/18	0.126	63.06	745.6	716.1	1097	1415	652.5	0.912	0.12654
Karoonda	CK4/S2	USNM 2275	0.104	44.23	686.9	599.6	912.8	1183	649.5	1.083	0.11980
<i>Ordinary</i>											
Sharps	H3.4/S3	USNM 640	0.100	82.85	1072	980.6	1256	1702	871.6	0.889	0.12352
Ceniceros	H3.7/–	MPI 709/1	0.097	36.36	491.5	464.9	726.0	908.9	590.9	1.271	0.12922
Replicate			0.115	43.91	546.9	505.8	778.8	1021	659.1	1.303	0.12964
Dhajala	H3.8/S1	USNM 5832	0.112	82.97	920.5	825.1	1243	1728	943.5	1.144	0.12968
Bremervörde	H3.9/S2	ASU 3365	0.115	65.76	743.6	660.4	1007	1361	784.4	1.188	0.12890
Zag	H3–6/S3–5	UCLA	0.137	77.84	920.4	809.6	1160	1617	816.5	1.009	0.12725
Forest Vale	H4/S2	AMNH 4055	0.107	79.81	809.8	730.6	1105	1504	812.6	1.112	n.d.
Ochansk	H4/S3	MPI 169/2	0.134	73.77	819.5	735.3	1141	1568	853.9	1.161	0.12968
Forest City	H5/S2	USNM 6649	0.115	77.34	860.4	762.0	1188	1611	912.7	1.198	0.12954
Rose City	H5/S6	UCLA	0.126	n.d.	n.d.	111.7	169.0	234.9	121.6	1.089	n.d.
Replicate			0.152	89.39	975.1	843.3	1364	1842	1009	1.197	0.12970
Farmington	L5/S5	UCLA	0.112	41.44	497.3	441.8	606.9	867.1	486.1	1.100	0.12727
Chico	L6/S6	UCLA	0.120	56.99	696.3	627.8	970.1	1295	624.8	0.995	0.12441
Replicate			0.119	54.44	638.6	594.2	919.5	1212	599.1	1.008	0.12439
Semarkona	LL3.0/S2	USNM 1805	0.120	26.25	288.6	260.6	400.6	513.5	390.8	1.500	0.12897
Replicate			0.093	28.03	334.2	309.2	484.6	635.3	442.7	1.432	0.12776
Chainpur	LL3.4/S1	AMNH 4020	0.107	30.48	351.2	316.7	537.4	672.3	346.0	1.093	0.12821
<i>Enstatite</i>											
Kota-Kota	EH3/S3	NHM 1905,355	0.100	53.90	593.0	545.6	850.7	1116	923.2	1.692	0.12845
Replicate			0.107	52.78	614.0	563.4	845.8	1146	871.3	1.547	0.12849
Indarch	EH4/S3	USNM 3482	0.115	53.90	625.5	566.9	855.9	1162	891.0	1.572	0.12811
Adhi Kot	EH4/S3	USNM 2358	0.092	45.29	501.0	468.7	734.1	962.7	835.2	1.782	0.12838
St. Sauveur	EH5/S3	USNM5285	0.079	57.43	666.4	610.5	907.4	1246	919.1	1.506	0.12762
St. Mark's	EH5/S3	USNM3027	0.098	54.48	604.9	555.7	838.9	1126	887.1	1.597	0.12825
Daniel's Kuil	EL6/S2	NHM1985 M143	0.127	73.26	827.9	748.8	1168	1528	920.8	1.230	0.12835
Yilmia	EL6/S2	NHM1972,132	0.101	61.79	710.9	642.9	929.0	1262	887.7	1.381	0.12724
Replicate			0.121	76.01	861.3	781.8	1090	1544	957.1	1.224	n.d.

Table 1 (continued)

Meteorite	Group/shock	ID <sup>a</sup>	Weight (g)	Re	Os	Ir	Ru	Pt	Pd	Pd/Ir	<sup>187</sup> Os/ <sup>188</sup> Os
<i>Enstatite</i>											
Bliethfield	EL6/S2	USNM 534	0.107	23.57	276.7	253.5	366.7	502.8	360.0	1.420	0.12784
Pillistfer	EL6/S2	USNM523	0.099	62.44	725.5	672.5	1021	1447	907.6	1.350	0.12832

<sup>a</sup> MPI—Max Planck Institute (Mainz); USNM—U.S. National Museum of Natural History; AMNH—American Museum of Natural History; UCLA—UCLA Collection of Meteorites, University of California, Los Angeles; ASU—Arizona State University; NHM—Natural History Museum, London; MWG—Meteorite Working Group. n.d. = not determined.

although the large ranges in previously reported abundances severely limits the utility of such comparisons. Data for Pt, which is difficult to analyze by neutron activation, are particularly rare. Finally, an a priori assumption that all HSE ratios should be identical within a given chondrite group or type is not necessarily always correct for all groups and types. This is true, in part, because of ambiguities in the classification of some chondrites, but also could result from compositional heterogeneities within a given parent body.

The new data are normalized to the concentrations we obtained for Orgueil, a CI1 chondrite (Figs. 1–3). The HSE abundances are not further normalized to any major elements. All of the chondrite groups,

except the LL group of ordinary chondrites, are enriched in absolute abundances of the HSE, relative to CI1 chondrites. These relatively low abundances of HSE in the CI1 chondrites, in part, result from dilution of all their components by up to 30% volatiles, including high concentrations of H<sub>2</sub>O, C and S. In comparison, the CR2 chondrites have higher but relatively unfractionated HSE abundances, except for Pd concentrations in some samples that are similar to concentrations in CI1 chondrites. The CM2, CO3 and CV3 chondrites also have higher concentrations than CI1, with the CM2 group concentrations intermediate between the CO3–CV3 groups and CI1. Of these, the CO3 chondrite Ornans is enriched in Re, Os and Ir, with decreasing concentrations of Ru, Pt and

Table 2  
A comparison of our data with data from the literature

Meteorite	Re	Os	Ir	Ru	Pt	Pd	Source	
Orgueil	38.03	459.3	455.6	649.6	859.2	574.5	this paper	
	41.04	456.9	432.3	647.6	874.3	573.5	this paper	
	37.1	483	474	714	973	556	Anders and Grevesse (1989) <sup>a</sup>	
	39.5	490	456	719	947	590	Kallemeyn and Wasson (1981)	
		480	420	750			Jochum (1996)	
	38.2	532	466	462	633	920	Crockett et al. (1967)	
							555	Loss et al. (1984)
							535	Ebihara et al. (1982)
							534	Takahashi et al. (1978)
	35.3	488	450	450	633	930	570	Yi and Masuda (1996)
Allende	60.08	748.7	704.4		1338	670.1	this paper	
	61.8	767.2	716.3		1347	690.4	this paper	
			716.7	1016	1366	683.0	this paper	
	60.2	759	730	843	1290			Jochum (1996)
		868	806			841		Morgan et al. (1985)
	64.2	812	773				830	Kallemeyn and Wasson (1981)
							701	Loss et al. (1984)
619							Ebihara et al. (1982)	
68.4	926	931				856	Carlson and Hauri (2001)	
							Takahashi et al. (1978)	

Abundances are given in ppb.

<sup>a</sup> Average of previously published data.

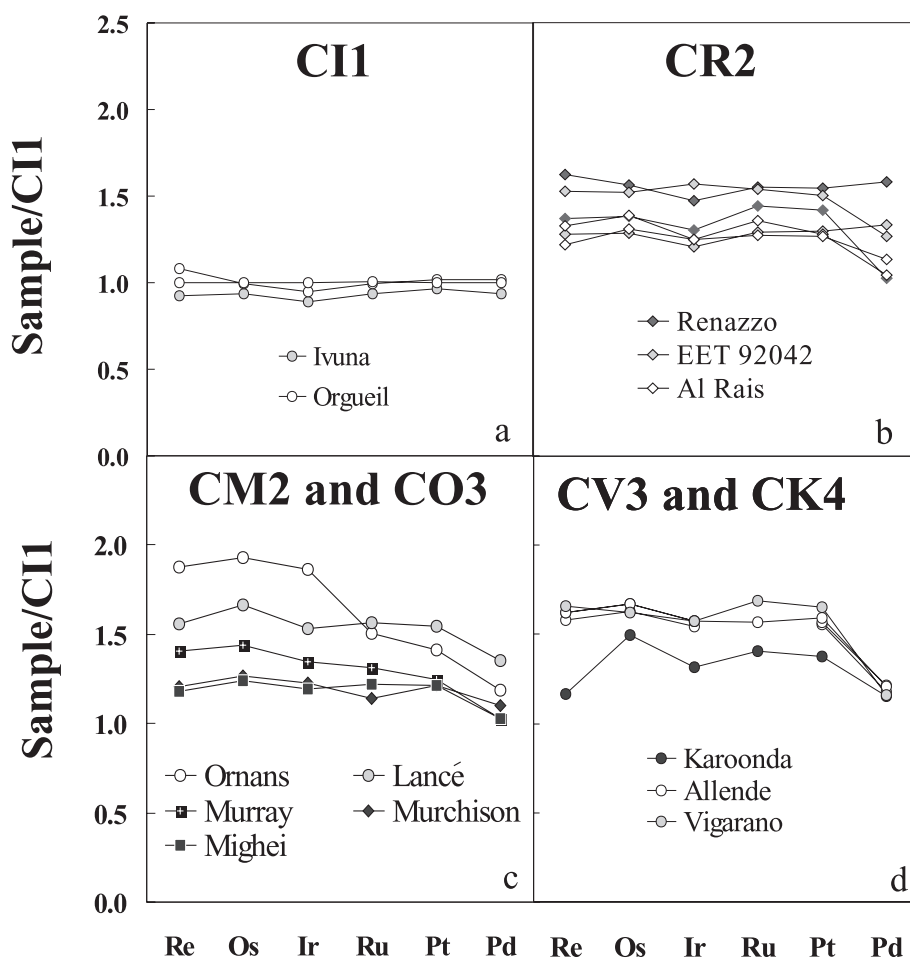


Fig. 1. Abundances of the HSE in carbonaceous chondrites, normalized to Orgueil abundances reported in this study. The elements are arranged in order of decreasing 50% condensation temperatures (Wasson, 1985). (a) Data for CI1 (Orgueil and Ivuna); (b) data for CR2 (EET 92042, Renazzo, Al Rais, a CR2-anomalous chondrites); (c) data for CM2 (Murchison, Murray, and Mighei) and CO3 (Lancé and Ornans) chondrites; (d) data for CV3 (Allende and Vigarano) and CK4 (Karoonda) chondrites.

Pd. Both CV3 chondrites analyzed, Allende and Vigarano display significant depletions in Pd relative to the other HSE. The CK chondrite, Karoonda, is unusually enriched in Os and depleted in Re compared to the other HSE. The Re–Os isotopic systematics of this meteorite indicate that this large fractionation was caused by an early solar system process (Walker et al., 2002). Karoonda, like the CV3 chondrites is also characterized by a depletion in Pd relative to the other HSE (except Re).

The relative abundances of the HSE in ordinary chondrites are highly variable. Several of the H chondrites have significantly fractionated HSE abundances,

with enriched Re and Os relative to Pd (Fig. 2b,c). Equilibrated H chondrites, Forest Vale (H4), Ochansk (H4) and Forest City (H5), have similar HSE abundances and elemental ratios. The H3 chondrites, Sharps and Dhajala, have similar abundances and ratios to the equilibrated H chondrites. Results for Bremervörde (classed as an H/L3.9 chondrite) are consistent with results reported by previous studies (Kallemeyn et al., 1989; Morgan et al., 1985), and show lower abundances of HSE and more CI1-like ratios, compared to most other H3 chondrites. This supports the possibility that it may be better grouped with the L chondrites (e.g., Kallemeyn et al., 1989).



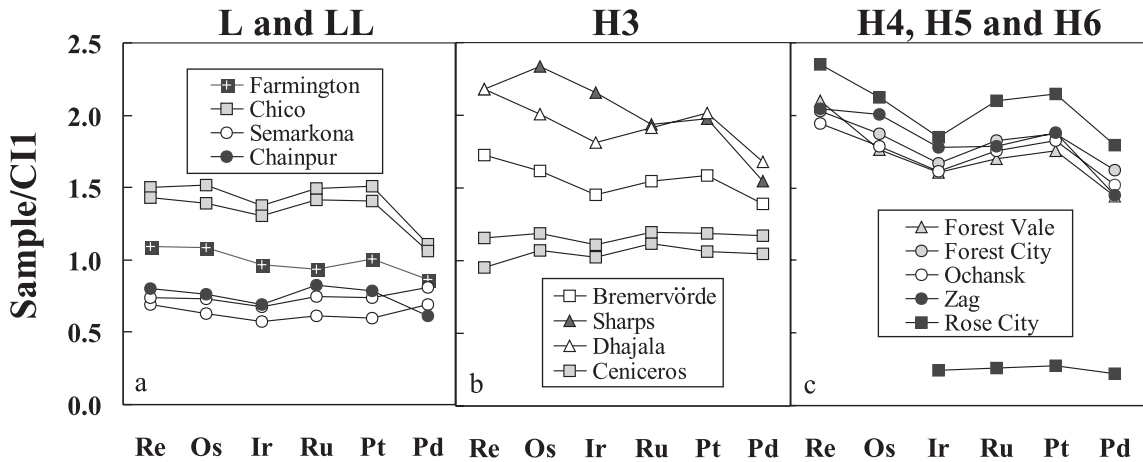


Fig. 2. HSE abundance data for ordinary chondrites, normalized to abundances in Orgueil. (a) Data for L (Farmington and Chico) and LL (Semarkona and Chainpur) chondrites; (b) data for unequilibrated (H3) chondrites; (c) data for equilibrated (H4, H5 and H6) chondrites.

Cenicerros, classed as an H3 chondrite, also has relatively low and unfractionated abundances of HSE compared to other H chondrites. Zag (H3–6), which contains some shocked clasts, has HSE contents similar to those of equilibrated H chondrites. Duplicate analyses of Rose City (H5), a highly shocked chondrite, yielded very different abundances, but similar HSE ratios. Data for both Zag and Rose City are discussed in more detail below. The L chondrites have

HSE abundances that overlap the lower end of the range of H3 chondrites, while LL chondrites have lower abundances of HSE compared to the CI chondrites (Fig. 2a). These data confirm previously published work (Morgan et al., 1985; Kallemeyn et al., 1989; Kong and Ebihara, 1997; McDonald et al., 2001) that shows decreasing average HSE contents with decreasing metal content (H>L>LL) in the ordinary chondrites.

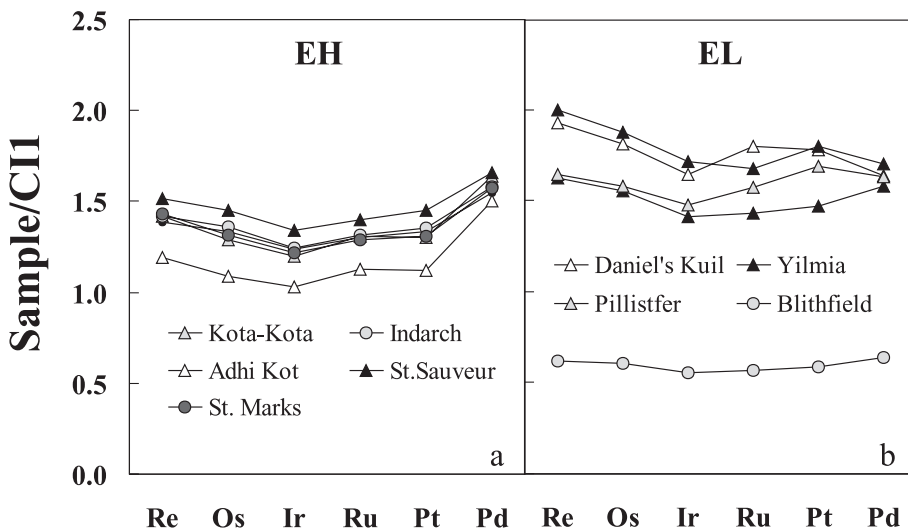


Fig. 3. HSE abundance data for enstatite chondrites, normalized to abundances in Orgueil. (a) Data for EH chondrites, (b) data for EL chondrites.

Enstatite chondrites have distinctive relative abundances of the HSE (Fig. 3a,b). Both EL and especially EH chondrites (Fig. 3a,b) are more enriched in Pd, compared to the more refractory HSE, than are ordinary chondrites or the CO and CV groups, as has been observed in previous studies (e.g., Hertogen et al., 1983). The more metal-rich (EH) samples have lower absolute abundances of HSE than the more metal-poor (EL) samples; the Ni-normalized abundances of the more refractory HSE (Re, Os, Ir, Ru and Pt) in the EH chondrites, however, are the lowest of all of the chondrite groups (Wasson and Kallemeyn, 1988). These systematics are opposite to those of ordinary chondrites in which HSE abundances are positively correlated with Fe abundances and metal content. The HSE abundances of the EH and EL chondrites are more similar to each other, however, if they are normalized to their silicon abundances (Wasson and Kallemeyn, 1988). Blithfield, a brecciated EL6 chondrite, has approximately one-third lower abundances of the HSE compared to the other EL chondrites we analyzed. Its HSE ratios, however, all are within about  $\pm 10\%$  of the average of EL chondrites. Blithfield is made up of centimeter-size troilite-rich clasts in a Fe, Ni-rich matrix, and is an impact-melt breccia that may have reached higher temperatures than other enstatite chondrites (Rubin, 1984). It appears that we preferentially sampled a sulfide-rich clast, which would be expected to have lower abundances of HSE than metal.

The contrasting distributions of Pd and Os abundances in carbonaceous and ordinary chondrites, compared to enstatite chondrites, is shown in Fig. 4. In ordinary chondrites, Pd is positively correlated with Os contents, with a slope of  $0.85 \pm 0.17$  ( $2\sigma$ ) and an intercept indistinguishable from zero. Carbonaceous chondrites have a slope and an intercept indistinguishable from ordinary chondrites. Differences among the carbonaceous chondrite groups are not distinguished well on this figure. Osmium and Pd abundances are also positively correlated in enstatite chondrites (with the exception of Blithfield), but they have a shallower slope ( $0.32 \pm 0.19$ ) and an intercept of  $680 \pm 130$  ppb Pd. Because its HSE content has been diluted by an apparently low-HSE component, Blithfield lies on the correlation line that intersects near the origin, as defined by

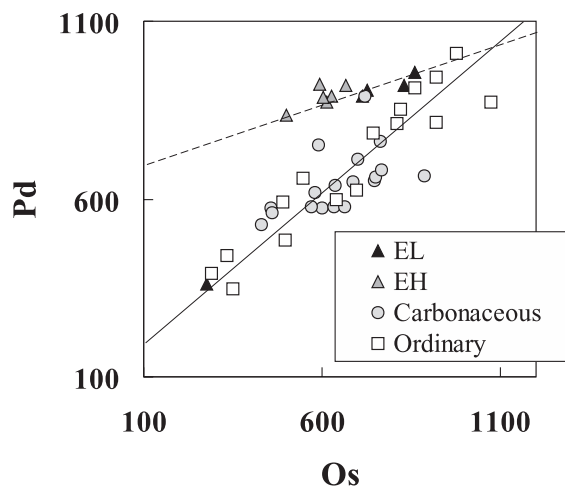


Fig. 4. Pd vs. Os abundances, in ppb. A linear regression of data for ordinary chondrites is shown as a solid line; the dashed line shows a linear regression of data for enstatite chondrites. Carbonaceous chondrites and Blithfield, an enstatite chondrite, plot near the regression line for ordinary chondrites.

ordinary and carbonaceous chondrites. Plots of Pd abundances vs. Re, Ir, Ru and Pt show similar systematics.

The combination of more refractory and less refractory HSE ratios can discriminate each of the three major chondrite classes. Both present-day Re/Os ratios and Os isotopic data support a difference in long-term Re/Os ratios (as shown in their modern  $^{187}\text{Os}/^{188}\text{Os}$ ) between the carbonaceous chondrite class relative to ordinary and enstatite chondrite classes (Walker et al., 2002). In Fig. 5,  $^{187}\text{Os}/^{188}\text{Os}$  is used as a proxy for Re/Os ratio, because the measured Os isotopic ratio is little disturbed by recent changes in the Re/Os ratio, and it shows the difference between the major chondrite classes more effectively. Ordinary chondrites have  $^{187}\text{Os}/^{188}\text{Os} = 0.1283 \pm 0.0017$  ( $1\sigma$  standard deviation); enstatite chondrites have  $^{187}\text{Os}/^{188}\text{Os} = 0.1281 \pm 0.0004$ ; and carbonaceous chondrites have  $^{187}\text{Os}/^{188}\text{Os} = 0.1262 \pm 0.0006$  (excluding the CK chondrite, Karoonda). These differences reflect a 7–8% lower Re/Os ratio in carbonaceous chondrites, compared to enstatite and ordinary chondrite classes. Carbonaceous chondrites and ordinary chondrites have distinctly lower Pd/Ir ratios than the enstatite chondrites and are clearly resolvable from the EH chondrites. Our new data show that enstatite



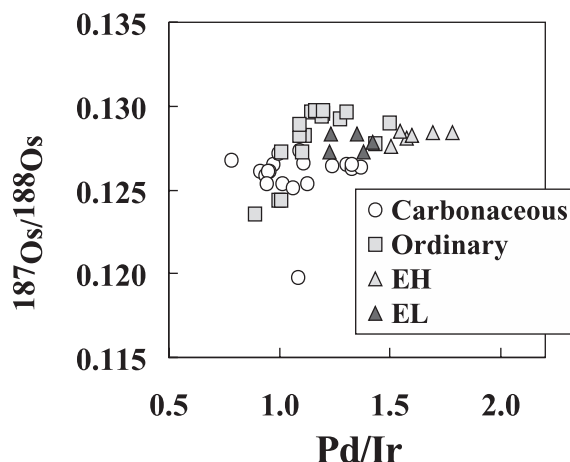


Fig. 5.  $^{187}\text{Os}/^{188}\text{Os}$  vs. Pd/Ir for carbonaceous, ordinary and enstatite chondrites. Each of the major classes of chondrites can be discriminated, although there is minor overlap. The present-day, measured  $^{187}\text{Os}/^{188}\text{Os}$  reflects the long-term average Re/Os ratio in the sample.

chondrites have Pd/Ir ratios of  $1.48 \pm 0.18$  ( $1\sigma$ ), and that EH and EL chondrites also have resolvable Pd/Ir:  $1.62 \pm 0.10$  and  $1.32 \pm 0.09$ , respectively. Pd/Ir in carbonaceous chondrites average  $1.08 \pm 0.17$ , and ordinary chondrites have average Pd/Ir ratios of  $1.15 \pm 0.15$ .

## 5. Discussion

### 5.1. Issues affecting reproducibility

In order to assess the reproducibility of both the chemical processing method and of the HSE distributions in individual chondrites, a relatively large number of duplicate analyses were conducted. These replicates were analyses of separate dissolutions of powdered chondrite performed at different times over a 2-year period. Replicate analyses are compared in Table 3, in which are given the percent range in the abundance determinations and in selected HSE ratios for each chondrite analyzed in replicate. The reproducibility of the chondrites fall into a few broad categories: (1) chondrites, such as Allende, Kota Kota, Orgueil and Chico, for which both concentrations and HSE ratios are reproducible within a few percent; (2) chondrites, such as Yilmia, Rose City, Cenceros and Semarkona, for which HSE ratios are more reproducible than absolute abundances, and (3) chondrites, such as Lancé and the CR2 chondrites, for which some abundances or ratios differ considerably.

Reproducibility of HSE abundances and HSE ratios for chondrites in the first category is  $\pm$  a few percent or better. This may represent the maximum contribution to uncertainty that is caused by analyt-

Table 3  
Ranges, in percent, of abundances and ratios in our replicate analyses of chondrites

	Re	Os	Ir	Ru	Pt	Pd	Pd/Ir	Ru/Ir	Re/Os	Os/Ir	Pt/Pd	Ir/Pt
<i>Carbonaceous</i>												
Orgueil	7.3	0.5	5.4	0.6	1.8	1.8	6.9	4.5	7.8	4.6	<0.1	7.3
Ivuna	5.2	14.2	5.2	4.3	3.6	–	–	0.9	10.6	9.6	–	1.7
Allende	2.8	2.4	1.7	–	1.4	2.4	1.3	–	0.4	0.8	2.2	0.4
Al Rais	8.3	5.7	0.3	6.3	0.4	9.7	10.0	6.0	2.8	6.0	11.1	0.0
Renazzo	15.5	11.8	11.2	7.1	8.4	35.1	26.9	4.7	4.3	0.6	29.2	3.0
EET 92042	16.3	15.8	23.0	15.9	13.9	5.0	26.9	8.4	0.6	8.6	18.2	11.9
Lancé	91.3	91.4	91.7	90.3	66.3	1.2	91.5	13.7	0.4	3.5	65.9	75.2
<i>Ordinary</i>												
Semarkona	6.3	13.6	15.7	17.3	19.2	11.7	4.5	1.9	7.8	2.4	9.2	4.1
Cenceros	17.2	10.1	8.1	6.8	11.0	10.3	2.5	1.4	7.9	2.2	0.7	3.2
Chico	4.7	9.0	5.7	5.5	6.9	4.3	1.3	0.1	4.0	3.2	2.5	1.1
Rose City	–	–	86.8	87.6	87.2	88.0	9.0	6.4	–	–	5.8	3.9
<i>Enstatite</i>												
Yilmia	18.7	17.2	17.8	14.7	18.2	7.2	12.8	3.7	1.8	0.7	11.9	0.6
Kota-Kota	2.1	3.4	3.2	0.6	2.6	6.0	9.4	3.9	5.7	0.3	8.1	0.5

ical-related issues. Such issues include the degree of completeness of the spike-sample equilibration and sample dissolution, and uncertainties in blank corrections. These issues are discussed more fully in Walker et al. (2002) and Becker et al. (2001), specifically for the case of Re and Os.

The second category of replicate analyses includes those whose HSE profiles (Figs. 1–3) are sub-parallel; that is, the individual HSE abundances may vary between replicate analyses by over several percent, but the variation in HSE ratios is much less. These variations most likely result from inhomogeneity in the distribution of HSE in the meteorite. The abundances of HSE in magnetic fractions of ordinary, CR, EL and EH chondrites typically are enriched, relative to the bulk meteorite, by factors of 3–5 (Rambaldi et al., 1978, 1979; Kong and Ebihara, 1997; Kong et al., 1997, 1999). The data for metal fractions also show that HSE fractionations outside of analytical uncertainties are generally small (Rambaldi et al., 1978, 1979; Kong and Ebihara, 1997; Kong et al., 1997, 1999). During sample preparation, the metal is not easily ground to the same extent as the silicates, and is typically heterogeneously distributed in our powder aliquants. Variations in the amount of metal in the sample aliquants, therefore, would be expected to result in different measured abundances, with subparallel HSE element profiles. Ceniceros, for example, has large metal grains in its matrix and is susceptible to this kind of sample inhomogeneity.

Rose City (Fig. 3c) provides an extreme example of subparallel HSE profiles in replicate analyses. Our two analyses differ in abundances of Ir, Ru, Pt and Pd by factors 7.6 to 8.3, but all of the HSE ratios differ by less than  $\pm 10\%$ . (There are no replicate analyses of Re and Os.) This suggests that the two aliquants contained differing amounts of HSE-rich material, but that little fractionation occurred among these HSE. Note that these enrichment factors are slightly larger than typical enrichment between magnetic and bulk components in ordinary chondrites (Rambaldi et al., 1978, 1979; Kong and Ebihara, 1997; Kong et al., 1997, 1999). Rose City is an impact melt breccia (shock stage S6) containing relict chondritic (H5) clasts surrounded by re-crystallized, shock-melted matrix (Rubin, 1995, and references cited therein). The large difference in HSE abundances supports the observation of Yocubal et al. (1997) that siderophile

elements were strongly fractionated between silicate and the metal segregated from it. Rubin (1995) noted compositionally distinct 0.5-mm-sized regions within metal segregations that exhibit relative enrichment and depletion of Ir and Os. He attributed the differences in concentrations to vaporization of the refractory siderophile elements during shock and variable amounts of condensation of these elements onto molten metal. Our data suggest that Ru, Pt and Pd were partitioned in a manner similar to the more refractory Ir and Os. This, in turn, suggests that, if compositionally distinct regions of metal were sampled, then any fractionation of siderophile elements must have occurred below the condensation temperature of Pd. If the condensation temperature of Pd is similar to that of Fe–Ni metal (e.g., Wasson, 1985), then the HSE may have condensed along with the metal, not just onto its surface.

Two analyses of different aliquants of Lancé exemplify the third category of replicate analyses that have very different abundances and abundance profiles (Fig. 6a). One sample of Lancé has an abundance profile similar to CI chondrites, and similar to other published analyses of that meteorite (Kallemeyn and Wasson, 1981). The other aliquant is enriched in Re=Os=Ir>Ru>Pt. The Pd contents of both aliquants, however, were essentially identical. CO3 chondrites, such as Lancé, contain relatively abundant refractory inclusions, some of which have small, opaque, metal-rich blebs (e.g., fremdlinge) (McSween, 1977; Fegley and Palme, 1985). We are unaware of any published analyses of opaque, refractory inclusions from Lancé; however, fremdlinge within refractory inclusions from other carbonaceous chondrites show extreme enrichments in the refractory HSE (Fegley and Palme, 1985; Palme and Wlotzka, 1976). Three examples are shown in Fig 6b; note the similarity between the abundance profiles for the inclusions from Leoville and Ornans with the abundance profile from the more HSE-enriched aliquant of Lancé. Even a very small amount of a similar opaque inclusion in one of our aliquants of Lancé could have drastically affected its HSE contents. For example, mass balance calculations suggest that the aliquant of Lancé having higher HSE abundances could have preferentially sampled less than 0.1% (approximately 0.1 mg, in our case) of an opaque inclusion having similar HSE contents to the opaque inclusion from Leoville (Fegley and Palme, 1985).

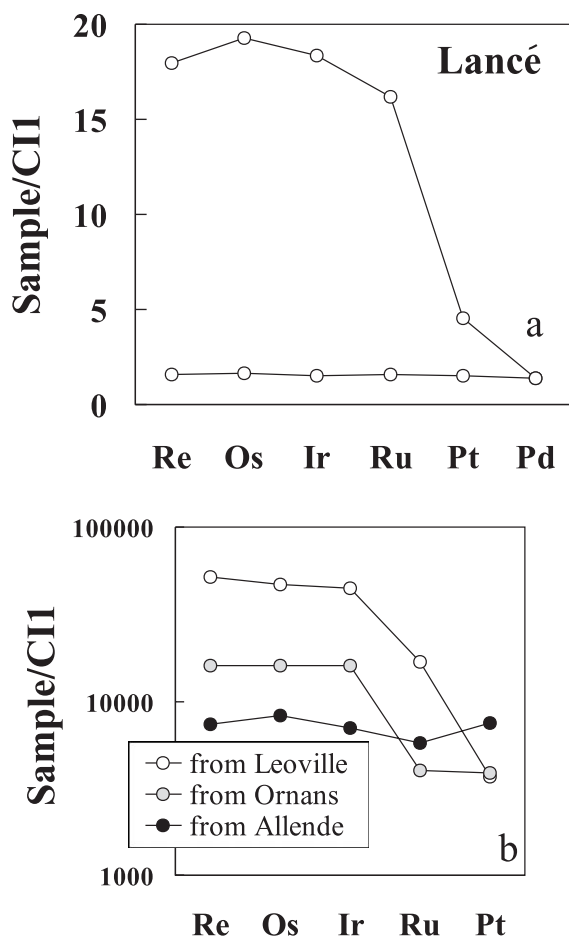


Fig. 6. (a) Two analyses of different aliquants of Lancé. One aliquant has HSE contents similar to other CO chondrites and is also shown in Fig 1b. The other is highly enriched in Re, Os, Ir, Ru and Pt, but has Pd abundances similar to the other aliquant. (b) Abundances of HSE in fremdlinge in CAIs in the meteorites shown (Fegley and Palme, 1985; Palme and Wlotzka, 1976). Note the similarity between the abundance profiles for the inclusions from Leoville and Ormans with the abundance profile from the more HSE-enriched aliquant of Lancé. No Pd was detected in the fremdlinge from Allende (Palme and Wlotzka, 1976).

Elements with lower condensation temperatures, including Au, Ge, Ga and Pd, were not detected in a fremdlinge from Allende (Palme and Wlotzka, 1976), consistent with the reproducible abundances of Pd obtained on our aliquants of Lancé.

Duplicate analyses of the CR2 chondrites (Renazzo, EET 92042 and Al Rais, an anomalous CR2) exhibit another style of variability in the HSE patterns

of duplicates. All have unfractionated abundances of Re, Os, Ir, Ru and Pt, relative to CI1. In contrast, Pd abundances in duplicate analyses of each vary from unfractionated to significantly depleted. It has been shown previously that siderophile elements with lower condensation temperatures than Pd are always depleted in bulk samples of CR2 chondrites, relative to CI1 (Kallemeyn et al., 1994; Kong et al., 1999). Analyses of the magnetic fractions from several CR chondrites indicate variable depletion in Pd in the metal, relative to the more refractory HSE (Kong and Palme, 1999). Connolly et al. (2001) and Humayun et al. (2002) found that individual metal grains on chondrule surfaces in CR2s have different compositions than those found in chondrule interiors. Individual metal grains from CR2 chondrites show constant and chondritic ratios of Os, Ir, and Pt (Connolly et al., 2001), but variable ratios of Pd/Fe (Humayun et al., 2002). Much of the metal on chondrule rims is depleted in Os, Ir and Pt, while the same grains are enriched in Pd and in the more volatile elements Au and P, relative to metal from chondrule interiors (Connolly et al., 2001; Humayun et al., 2002). These observations suggest that the varying depletions in Pd measured in bulk CR2 chondrites may reflect a sampling difference between fractions rich in metal from chondrule rims and from chondrule interiors.

### 5.2. Fractionation of HSE in carbonaceous chondrites

Carbonaceous chondrites are characterized by 7–8% lower Re/Os than ordinary and enstatite chondrites. This is a long-term effect as indicated by correspondingly lower radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  (Walker et al., 2002). Variability in the Re/Os ratio of bulk chondrites is minor within each major division of chondrites (carbonaceous, enstatite and ordinary chondrites). Why the carbonaceous chondrites should have lower Re/Os than enstatite and ordinary chondrites is clear. Sylvester et al. (1990, 1993) measured subchondritic Re/Os ratios in some fremdlinge from CV3 chondrites, and used thermodynamic modeling to suggest that the fractionation resulted from an early, high-temperature fractionation in the solar nebula. This interpretation is somewhat controversial because of uncertainties in the accuracy of condensation temperatures (the difference

between condensation temperatures of Re and Os may be only a few K), and uncertainties in the non-ideal, solid solution properties of high-temperature metal alloys (Fegley and Palme, 1985; H. Palme, personal communication, 2002). However, if such a high-temperature fractionation of Re and Os occurred, then isolation and incorporation of resulting refractory element alloys into the precursor materials of some chondrite groups may be responsible for the lower Re/Os ratios present in the carbonaceous chondrite groups, compared to the enstatite and ordinary chondrites. It is also possible that the lower Re/Os in carbonaceous chondrites could result from oxidation and heating loss of Re at lower temperatures in the precursor materials of carbonaceous chondrite components (Walker et al., 2002).

Among the groups of carbonaceous chondrites, ratios of the most refractory HSE show little variation, e.g., average Re/Os, Re/Ir and Re/Ru ratios for each of the carbonaceous chondrite groups are not distinguishable. Average Pd/Ir ratios for the carbonaceous chondrite groups, however, decrease in the order CI>CM  $\approx$  CO>CV. Previous work has shown that carbonaceous chondrite groups, other than CII, are enriched in the most refractory HSE (Re, Os, Ir) (Takahashi et al., 1978; Jochum, 1996). Our work supports this observation, and extends the trend with Ru and Pt data. These systematics could represent progressive enrichment of the bulk carbonaceous chondrites in a component similar to that measured in the HSE-rich aliquant of Lancé, i.e., a component rich in the more refractory siderophile elements and poor in Pd. Wasson and Kallemeyn (1988) additionally noted that, in the carbonaceous chondrite groups, the refractory lithophile elements are progressively enriched in roughly the same order (CV>CO  $\approx$  CM>CI) as the refractory siderophile elements, and suggested that the siderophile and lithophile excesses were contained in the same nebular component.

### 5.3. Fractionation of HSE in ordinary chondrites

The ordinary chondrite groups have average HSE contents that decrease in the order H>L>LL. The more refractory HSE (Re, Os, Ir, Ru and Pt) were fractionated relative to Pd in a similar way to the carbonaceous chondrite groups, as shown in Fig. 4. In

contrast, their Re/Os (and  $^{187}\text{Os}/^{188}\text{Os}$ ) ratios are distinct from and higher than the carbonaceous chondrite groups (Fig. 5). The inclusion of highly shocked ordinary chondrites in this dataset permits an evaluation of the effects of shock on the HSE abundance distributions. The apparent effects of shock on the HSE are variable. In the case of Rose City, as discussed earlier, there was unusually large fractionation between HSE-rich and HSE-poor material, larger than that observed in more weakly shocked chondrites. Nevertheless, fractionation between Pd and the more refractory HSE was minor.

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 region of the parent asteroid from which Zag was derived appears to have experienced a series of superposed shock, heating and alteration events prior to 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). The present-day Re–Os isotopic systematics apparently were little affected by shock heating (Walker et al., 2002), probably because the shock was so ancient. Abundance patterns of the highly siderophile elements are similar to those in other equilibrated, but more weakly shocked H chondrites (Ochansk, Forest Vale and Forest City). Zag, however, has slight depletions in Re and Ru relative to the other equilibrated H chondrites that we analyzed (Fig. 3c). Palme et al. (1998) found these elements to be more susceptible to oxidation—and therefore possibly more mobile—than the other HSE. Such oxidation might have occurred during hydrothermal activity or may have been induced by shock.

Chico (L6) consists of  $\sim 60$  vol.% impact melt and  $\sim 40$  vol.% shocked chondritic host material (Bogard et al., 1995). Chico appears to have formed in a relatively recent impact event on its parent body, approximately  $\sim 0.5$ – $0.6$  Ga before present (Nakamura et al., 1990; Fujiwara and Nakamura, 1992; Garrison and Bogard, 1992). Norman and Mittlefehldt (2002) reported Ir/Au ratios that are similar in the host chondrite and melt rock, although varying by about a

factor of 6 among different aliquants of the melt rock. Our sample of Chico consists mostly of silicate glass. Chico has HSE abundance patterns that are intermediate between H and LL chondrites, as expected for an L chondrite. The Re–Os isotopic systematics for Chico were disturbed relatively recently, and may indicate a partial loss (oxidation?) of Re during impact or during terrestrial weathering (Walker et al., 2002). Shock appears to have had little effect on the distribution of the other HSE.

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 1–5 mm rounded to elongated metal nodules and thin metal veins several millimeters in length. In contrast to Chico, the Re–Os isotopic systematics of Farmington have remained undisturbed since early in the history of the solar system. This could indicate that the partial melting and deformation displayed in Farmington occurred early in its history, although this interpretation is problematic because of its young Ar age of 500 Ma (Bogard and Hirsch, 1980). It is more likely that, during the late-stage shock event, Re and Os were simply not fractionated beyond the scale of our sample (ca. 0.5 g) (Walker et al., 2002). Abundances of the other HSE are also relatively unfractionated, like those of Chico.

#### 5.4. Fractionation of HSE in enstatite chondrites

EH chondrites have distinctively high relative Pd abundances, and generally unfractionated abundances of the more refractory HSE (Re, Os, Ir, Ru and Pt) (Fig. 4). Refractory HSE are depleted relative to Ni, suggesting depletion in HSE elements relative to Fe-metal, yet the silicon-normalized abundances of the refractory HSE are similar to CI, despite their extreme depletions in refractory silicates (e.g., Wasson and Kallemeyn, 1988). The EH chondrites also show enrichment in Au>Pd, and in As and Ga (Baedecker and Wasson, 1975; Hertogen et al., 1983; Kallemeyn and Wasson, 1986). These are moderately volatile elements with condensation temperatures of 918K (Ga), 1157K (As), and 1225K (Au) (Wasson, 1985), all of which apparently behaved as siderophile ele-

ments under the reducing conditions of the location at which enstatite chondrites formed (e.g., Baedecker and Wasson 1975; Hertogen et al., 1983).

Taken together, these observations clearly indicate that the EH chondrites experienced some process capable of fractionating the more refractory HSE (Re, Os, Ir, Ru and Pt) from the moderately volatile siderophile elements (Pd, Au, As and Ga). Our data suggest the depletions in the refractory HSE occurred between the condensation temperatures of Pt (1411 K at  $10^{-4}$  atm or 100 Pa) and Pd (1334 K) (Wasson, 1985). It is within this temperature range that much of the major nebular condensates including forsterite, enstatite and Fe-metal likely formed: (e.g., Larimer, 1988). Ehman et al. (1970) and Baedecker and Wasson (1975) suggested a model in which some portion of the refractory siderophile elements were removed from the enstatite chondrite formation region (probably as refractory metal alloys) at the same time as the refractory silicate component was removed. The moderately volatile siderophile elements then condensed onto (or into) Fe-metal. If the Pd–Os correlation line (Fig. 4) is interpreted as a mixing line, then it supports the presence of two HSE-bearing components. While it is not possible to quantify the Pd and Os contents of the endmembers, it appears that one had Pd/Os similar to or less than that of carbonaceous and ordinary chondrites, and may represent an early-formed refractory alloy. The other endmember had moderate Pd and low Os abundances, and may represent late-formed metal. Complete fractionation between Os-bearing components and Pd-bearing components would have created a correlation with a negative slope. Because the slope of the correlation is shallow and positive, it suggests that fractionation between Os and Pd was incomplete. This is consistent with the observation that depletions in the refractory silicate component in the EH chondrites was substantial, albeit also incomplete.

The composition of the EL chondrites is similar to, but less extreme, than the EH chondrites (e.g., Wasson and Kallemeyn, 1988). In EL chondrites, the less refractory HSE, including Pd, Au, As and Ga are all enriched to approximately the same extent as the more refractory elements Re, Os, Ir, and Pt; when normalized to their Ni contents, all are more similar to CI concentrations. Mg-silicate depletion was less severe than the EH chondrites. The fact that



the EL chondrites lie on the same Pd–Os correlation line in Fig. 4 as the EH chondrites, suggests that HSE fractionation processes in the EL chondrites were similar to those in the EH chondrites, but apparently affected the EL chondrites to a much lesser extent.

## 6. Conclusions

New, high precision abundance data for the HSE in chondrites, coupled with Re–Os isotopic data for the same meteorites, indicate that each of the three major chondrite classes can be discriminated based on their HSE characteristics. Re–Os isotopic data show evidence for a difference in long-term Re/Os (as shown in their modern  $^{187}\text{Os}/^{188}\text{Os}$ ) between carbonaceous chondrites relative to ordinary and enstatite chondrites. The Re/Os fractionation between these major classes of chondrites most likely occurred at high temperatures in the solar nebula during condensation of these elements, prior to the condensation of the major silicate and metal phases. Palladium enrichments in the enstatite chondrites, particularly the EH chondrites, indicate a lower temperature fractionation between moderately volatile siderophile elements and the more refractory siderophile elements (Re, Os, Ir, Ru and Pt). This fractionation may have been concurrent with removal of a refractory silicate component from the formation region of the enstatite chondrites. Shock can create domains of high- and low concentrations of HSE, but appears to cause, at most, minor fractionations among the HSE, with Re and Ru being most susceptible to oxidation and loss. Minor fractionation of Re and Os during late-stage shock events may partially reset the Re–Os isotopic systematics.

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