



Differentiation of metal-rich meteoritic parent bodies: I. Measurements of PGEs, Re, Mo, W, and Au in meteoritic Fe-Ni metal

M. I. PETAEV^{1,2*} and S. B. JACOBSEN¹

¹Department of Earth and Planetary Sciences, Harvard University, 20 Oxford Street, Cambridge, Massachusetts 02138, USA

²Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02139, USA

*Corresponding author. E-mail: mpetaev@cfa.harvard.edu

(Received 18 July 2003; revision accepted 26 July 2004)

Abstract—We describe an analytical technique for measurements of Fe, Ni, Co, Mo, Ru, Rh, W, Re, Os, Ir, Pt, and Au in bulk samples of iron meteorites. The technique involves EPMA (Fe, Ni, Co) and LA-ICP-MS analyses of individual phases of iron meteorites, followed by calculation of bulk compositions based on the abundances of these phases. We report, for the first time, a consistent set of concentrations of Mo, Ru, Rh, Pd, W, Re, Os, Ir, Pt, and Au in the iron meteorites Arispe, Bennett County, Grant, Cape of Good Hope, Cape York, Carbo, Chinga, Coahuila, Duchesne, Gibeon, Henbury, Mundrabilla, Negrillos, Odessa, Sikhote-Alin, and Toluca and the Divnoe primitive achondrite. The comparison of our LA-ICP-MS data for a number of iron meteorites with high-precision isotope dilution and INAA data demonstrates the good precision and accuracy of our technique.

The narrow ranges of variations of Mo and Pd concentrations within individual groups of iron meteorites suggest that these elements can provide important insights into the evolution of parent bodies of iron meteorites. Under certain assumptions, the Mo concentrations can be used to estimate mass fractions of the metal-sulfide cores in the parent bodies of iron meteorites. It appears that a range of Pd variations within a group of iron meteorites can serve as a useful indicator of S content in the core of its parent body.

INTRODUCTION

There is now increasing evidence that the achondritic parent planets may have formed and differentiated within 2–4 Ma of the origin of the solar system (e.g., Lugmair and Shukolyukov 1998; Srinivasan et al. 1999, 2000; Yin et al. 2002). Since then, many of these parent planets have been disrupted, often leaving behind only fragments of their cores in the form of iron meteorites. Based on some relatively young Re-Os bulk isochron crystallization ages, iron meteorites have been considered to be the products of prolonged crystallization of asteroidal cores (e.g., Smoliar et al. 1996). However, the presence of the decay products of short-lived extinct nuclides such as ¹⁰⁷Pd (half-life of 6.5 Ma; Chen and Wasserburg 1996a; Chen et al. 2002) in some of them, and the deficit in ¹⁸²W in all groups of iron meteorites compared to the bulk chondrites (due to the decay of ¹⁸²Hf with a half-life of 9 Ma; Horan et al. 1998; Yin and Jacobsen 2003), imply that their chemical compositions were established just a few Ma after the birth of the solar system. Therefore, chemical and isotopic studies of iron meteorites can potentially provide new information on the early solar

system in addition to what has been learned from primitive chondritic meteorites.

Because the old metal-silicate segregation ages derived from the extinct nuclide systems (Hf-W) and some of the young crystallization ages derived from the long-lived Re-Pt-Os system are relatively well-established (Smoliar et al. 1996; Chen and Wasserburg 1996a; Shen et al. 1996; Chen et al. 2002; Yin and Jacobsen 2003; Walker et al. 1997; Cook et al. 2004), the difference between them likely is due to the more complex nature of the metal-silicate fractionation and core crystallization in parent planets of iron meteorites compared to the one-step, closed-system model assumed in calculations of Re-Os, Hf-W, and Pd-Ag crystallization ages. These discordant ages potentially provide valuable insight into the open system developments and timescales of formation of mantles and cores in the parent planets of iron meteorites. To make use of this information, we have initiated a study aiming to model the trace element behavior during the early stages of planetary evolution together with the isotopic evolution of both long-lived (Re-Pt-Os) and extinct (Pd-Ag and Hf-W) isotope systems. Ideally, we expect to establish reliable time scales of the metal-silicate fractionation (in the Hf-W system,

both elements are refractory, but Hf is lithophile and W is siderophile) and the core crystallization (in the Re-Pt-Os system, all elements are refractory siderophiles) in the parent planets of iron meteorites as well as the timing of volatile element depletion (in the Pd-Ag system, both elements are siderophile, but Pd is refractory and Ag is volatile in the solar nebula). For the purpose of such a study, we need high quality elemental and isotopic data on Mo, Re, Os, Pt, Pd, Ag, W, and other siderophile elements.

The concentrations of Ni, Ga, Ge, Ir, and a few other trace elements, along with the structure of iron meteorites, are typically used to assign them to one of the chemical groups (e.g., Lovering et al. 1952; Wasson 1967; Scott 1972; Wasson et al. 1998; Wasson and Kallemeyn 2002). The improvements in analytical techniques, mainly INAA, and the systematic study of a large number of iron meteorites resulted in the development of an extensive database on their chemical compositions (e.g., Wasson et al. 1998; Wasson and Richardson 2001; Wasson and Kallemeyn 2002), which has been used in deciphering the origins of iron meteorites. Other sources of high-quality data for trace elements are isotopic studies of iron meteorites (Smoliar et al. 1996; Chen and Wasserburg 1996a; Shen et al. 1996; Chen et al. 2002; Cook et al. 2004). The quality of the analytical data on Mo, Re, Os, Pt, Pd, Ag, W, and other siderophile elements varies depending on the time and technique used to acquire the data. Data on some of these (Os, Re, Pd, Ag) are already available for a large number of iron meteorites, but for others (Mo, Ru, Rh, Pt, W), they are either of low quality or even missing for many samples of interest. Recently, it has been shown (Hirata and Nesbitt 1997; McDonough et al. 1999; Campbell and Humayun 1999a, b) that laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) can be successfully used to measure a wide range of concentrations of trace siderophile elements in Fe-Ni meteoritic metals. To create a consistent database for our project, we started analyzing a series of iron meteorites for PGEs, Mo, Re, W, and other trace elements using our LA-ICP-MS system (Petaev and Jacobsen 2003a, b).

Previous Work

Several research groups have already used the LA-ICP-MS techniques to measure concentrations of trace elements in iron meteorites. Because the main goal of these studies was to measure partitioning of trace elements between different phases of iron meteorites, essentially no data other than the distribution coefficients of siderophile elements between low-Ni (kamacite, bcc α -phase) and high-Ni (taenite, fcc γ -phase; or plessite, $\alpha + \gamma$) phases have been reported so far.

Hirata and Nesbitt (1997) were the first to use a high sensitivity UV laser ablation system (266 nm Nd:YAG laser coupled to a modified S-option VG Elemental PQ2 ICP-MS instrument) for measurements of concentrations of PGEs (Ru,

Rh, Pd, Os, Ir, Pt) and Re in kamacite, taenite, and plessite of the IAB iron meteorites Canyon Diablo, Landes, and Toluca. The small spot sizes (10–15 μm) employed in the study required an enhancement of elemental sensitivities that was achieved by lowering the vacuum in the mass spectrometer and by adding N_2 gas to the carrier Ar gas. The IVB iron Tlacotepec and the glass standards NIST 610 and P&H-DHL8 were used for instrumental standardization. The matrix effects on the ablation characteristics and signal intensities were studied by measuring the intensities of Re and Os in a number of iron meteorites with varying Ni contents (7–34 wt%) and with the Re and Os concentrations previously measured by isotope dilution. No significant matrix effects were found. The results of the study were presented as abundance ratios of PGEs and Re between kamacite and the Ni-rich phases (taenite for Odessa and plessite for Canyon Diablo). It was concluded that: 1) there is no significant fractionation of Ru and Rh between kamacite and Ni-rich phases; 2) the Ni-rich phases are enriched in Pd and Re and depleted in Ir, Os, and Pt.

McDonough et al. (1999) used a VG Elemental PQ2+ mass spectrometer coupled with a deep UV 193 nm laser ablation system to measure concentrations of Cu, W, PGEs, Au, Re, Ga, and Ge in kamacite, taenite, and cohenite from the iron meteorites Canyon Diablo (IAB), Toluca (IA), Coahuila (IIA), Henbury (IIIA), Cape York (IIIA), and Hoba (IVB). The analytical spot sizes varied from 70 to 150 μm . No N_2 was added to the carrier Ar gas. The standards used in the study included NBS 908b (steel), NIST 610 and 612 (silicates), a sulfide standard doped with PGEs at 70 ppm level, and various standard silicate rocks. To take into account matrix effects, the concentrations of trace elements in unknowns were calculated using major elements (dominant matrix constituents) as internal standards. The concentrations of major elements were measured by an electron microprobe. The results of the study are reported in two plots as the kamacite/taenite and kamacite/cohenite abundance ratios. It was found that cohenite in Canyon Diablo is enriched in W and Re and strongly depleted in all other trace elements relative to kamacite. The kamacite/taenite ratios showed significant variability among the meteorites studied; in general, kamacite is depleted in Cu, W, Pd, Rh, Re, and Au, with the other elements being equally partitioned between the kamacite and taenite or only slightly depleted in the former.

Campbell and Humayun (1999a, b) used a 266 nm CETAC LSX-200 laser ablation system interfaced to a Finnigan MAT Element ICP mass spectrometer to measure concentrations of PGEs, Re, and Au in 17 iron meteorites on a spatial scale of $<20 \mu\text{m}$. No N_2 was added to the carrier Ar gas. The Hoba ataxite (IVB) was used to standardize the LA-ICP-MS analyses. The concentrations of PGEs in Hoba and the IIA hexahedrite Filomena were measured by isotope dilution ICP-MS before the LA-ICP-MS work. The isotope dilution data for Hoba and Filomena were reported as

enrichment factors (relative to CI) in a scatter plot; the LA-ICP-MS analyses of these meteorites are listed in a table. The authors reported data for nine iron meteorites (IIAB: Coahuila, Filomena, Mount Joy and Negrillos; IIIAB: Cape York, Charcas, Costilla Peak, Grant, and Henbury) in a Ru/Pt ratio versus Pt concentration scatter plot. A LA-ICP-MS line scan measured across a plessite field in the Grant IIIAB iron shows clear M-shaped profiles of Pd, Ru, and, to a lesser degree, Rh, which is typical of Ni distributions in plessite fields. The concentrations of PGEs, Re, and Au in the low- and high-Ni phases of eight iron meteorites (IAB: Canyon Diablo, Odessa, Toluca; IIIAB: Cape York, Charcas, Costilla Peak, Grant, and Henbury) and two pallasites (Glorietta Mountain and Imilac) were measured to calculate average taenite-kamacite distribution coefficients ($D_{t/k}$) of these elements between the kamacite and a high-Ni phase, presumably plessite. The average distribution coefficients (Table 2 of Campbell and Humayun [1999a]) show preferential partitioning of all elements in a high-Ni phase, with the $D_{t/k}$ values ranging from 1.31 (Os) to 4.13 (Pd).

SAMPLES

Our choice of meteorites for this study is largely based on two criteria: 1) the availability of Re-Os, W, and/or Pd-Ag isotopic data on the samples of interest (or planned measurements of W isotopes by our research group); and 2) the coverage of rather large ranges of PGE concentrations exhibited by a certain meteorite group. The following meteorites were analyzed in this initial study: Arispe (IC), Bennett County (IIA), Grant (IIIB), Cape of Good Hope (IVB), Cape York (IIIA), Carbo (IID), Chinga (IVB An), Coahuila (IIA), Duchesne (IVA), Gibeon (IVA), Henbury (IIIA), Mundrabilla (IIICD An), Negrillos (IIA), Odessa (IA), Sikhote-Alin (IIB), and Toluca (IA) irons and the Divnoe primitive achondrite. The latter is chosen because of its origin as the residue of partial melting of a primitive parent body (Petaev et al. 1994), its old Sm-Nd age of 4.62 ± 0.07 Ga, and its ^{142}Nd excess ($\epsilon_{142} = +6.7 \pm 0.9$), which is the largest measured so far in any meteorite (Bogdanovski and Jagoutz 1996).

ANALYTICAL TECHNIQUES

Before the LA-ICP-MS experiments, polished sections of all meteorites were analyzed for Fe, Ni, Co, Cr, S, and P by EMPA using the JEOL SuperProbe 733 electron microprobe operated at a 15 KeV accelerating voltage and a 20 nA beam current. The standards were pure metals, apatite (P), and Fe-Ni alloys of known compositions. All Co analyses were corrected for the interference of Fe K_{β} on the Co K_{α} lines using an empirically derived equation; the typical corrections were ~ 0.1 wt%. Both focused (FBA, ~ 1 μm spots) and defocused (DBA, ~ 50 μm spots) beam analyses were performed on the kamacite, taenite, and plessite of

octahedrites. From 30 to 50 analyses were used to calculate average compositions of the phases. Large, chemically zoned plessite fields were probed along equally spaced traverses (5–20 μm steps) using the FBA. These data were later used to calculate average compositions of the areas analyzed by the LA-ICP-MS. The hexahedrites and ataxites were analyzed by the DBA; the typical deviations from the reported concentrations of Ni were within the range of 0.1–0.3 wt%. The abundances of taenite bands in the studied sections were calculated from the BSE images using dPict32 software.

One of our laser ablation systems (NewWave-Merchantek UP266) interfaced to a VG-PQ2+ ICP-MS was used to measure concentrations of Ni, PGEs, Re, Mo, W, and Au in the kamacite and plessite of the iron meteorites studied. The desktop laser ablation system is based on a 266 nm Nd:YAG laser capable of operating in continuous and pulse modes with a pulse duration of 3–5 nsec and maximum output energy of ~ 3.3 mJ. The repetition rate can be varied from 1 to 20 Hz. The built-in aperture wheel allows the beam diameter to be set incrementally within the 5–160 μm range. The LA system offers five different ablation patterns: 1) raster, 2) grid of spots, 3) line, 4) line of spots, and 5) single spot. The video system controlled by the operating software allows imaging either in reflected or in transmitted light on the sub-micron scale.

Before making the LA-ICP-MS measurements, all octahedrites were lightly etched with 0.5% nital to reveal kamacite bars, taenite bands, and plessite fields. In the LA-ICP-MS analyses we measured the following isotopes: ^{61}Ni , ^{95}Mo , ^{101}Ru , ^{102}Ru , ^{103}Rh , ^{105}Pd , ^{106}Pd , ^{108}Pd , ^{182}W , ^{184}W , ^{185}Re , ^{187}Re , ^{189}Os , ^{192}Os , ^{193}Ir , ^{195}Pt , and ^{197}Au . Ni was used as an internal standard. Before carrying out the analytical work reported below, we explored the response of our LA-ICP-MS system to different ablation and analytical conditions using the Coahuila hexahedrite as a test sample. Following Hirata and Nesbitt (1997), we added N_2 gas to the Ar carrier gas to increase count rates of Mo, Ru, Rh, Pd, W, Re, Os, Ir, and Pt by a factor of 1.9–2.5. Setting the repetition rate to 20 Hz and the pulse energy output to 65% resulted in higher count rates and more stable signals at spot sizes larger than 60 μm . At smaller spot sizes, better results were obtained at the repetition rate of 10 Hz and 100% energy output. The results of our experiments on Coahuila with 5 repetitions at each spot size show that, at spot sizes larger than 30 μm , the standard deviations (1σ) for all elements are within 8%; an increase in spot sizes results in somewhat lower standard deviations. Even at the 20 μm spots, the concentrations of all elements but Mo and Pd can be measured with a standard deviation of $<20\%$. Further increase in analytical precision was achieved by increasing dwell times for the elements with lower count rates; the dwell times used in the analyses reported below are 10.24 msec for Ni, 20.48 msec for Ru, Rh, Re, Os, Ir, and Pt, 40.96 msec for Mo, W, and Au, and 81.92 msec for Pd. We found that the precision of analyses of individual spots (>40 μm) and line scans was essentially identical.

The results reported below were obtained at a laser repetition rate of 20 Hz and energy output of 65% (10–11 J/cm²); the flow rates of the Ar carrier, auxiliary, cool, and N₂ gases were 0.6–0.8, ~1.0, ~13.5, and 0.08 L/min, respectively. The analyses of all iron meteorites were performed on 160- μ m spots to enhance the count rates of the less abundant elements and to achieve better averaging of heterogeneous plessite fields. Divnoe metal grains were analyzed with both 100 and 160 μ m spots; no significant differences between these analyses were found. All spectra were acquired using a time-resolved analysis procedure; typically 30 time slices (10–11 for the background and the rest for the signal) were collected over the total acquisition time of 60 sec. To correct for the drift of the signal and the element/Ni ratios, a monitor standard (Coahuila) was analyzed before and after each sample, including the reference standards. At least three consecutive experiments were performed on each phase in all meteorites and standards. Following Campbell and Humayun (1999a, b), we used the iron meteorites Filomena (IIA) and Hoba (IVB) as the reference standards. When possible, we used the concentrations of trace elements in the standards determined by the isochron isotope dilution because this analytical technique has much better precision and typically uses larger samples than INAA. The compositions of the Filomena and Hoba standards used in this study are listed in Table 1 along with the sources of the data. All the data in Table 1 are from literature sources except for the Pt concentration in Hoba (31.84 $\pm$ 0.69 ppm), which was measured in this study by LA-ICP-MS using Filomena and Coahuila as the standards. The Pt concentration in Coahuila was independently measured by the isotope dilution (Cook et al. 2004).

The raw intensities of elements were first corrected for the procedural blanks and then for interferences. First, the intensities of ¹⁰²Ru, ¹⁰⁶Pd, ¹⁰⁸Pd, ¹⁸⁴W, ¹⁸⁷Re, and ¹⁹²Os were corrected for the direct interferences from ¹⁰²Pd, ¹⁰⁶Cd, ¹⁰⁸Cd, ¹⁸⁴Os, ¹⁸⁷Os, and ¹⁹²Pt, respectively. In the dry plasma used for laser ablation, oxide production is low, and therefore, metal-oxide interferences are, in general, negligible, but Ni-, Cu-, and Zn-argide interferences on the LPGEs can be considerable. All the Ru, Rh, and Pd data were corrected for argide interferences using the method described by Sylvester

(2001). In some runs, there was evidence for small argide interferences on some of the isotopes of these elements, but in others, no significant interferences were found. In general, the elemental abundances reported here for Ru, Pd, W, Re, and Os were chosen from the isotope of each element showing the best calibration curve for a given analytical run (usually ¹⁰²Ru, ¹⁰⁶Pd, ¹⁸²W, ¹⁸⁵Re, ¹⁸⁹Os). Instrumental drift was corrected first by using Ni as an internal drift monitor (all isotope ratios were referenced to ⁶¹Ni) and then standardized by using the Ni concentration obtained for the same spots from EMPA. The element/Ni isotope ratios were further corrected for the drift by using an external drift monitor, the Coahuila meteorite. The elemental concentrations were calculated based on the measured element/Ni intensity ratios in samples compared to the same element/Ni ratios in the standards (Hoba, Coahuila and Filomena). The results reported below in Tables 2 and 3 are based on this data reduction procedure.

The measured chemical compositions of Ni-poor and Ni-rich phases can be used to calculate the bulk chemical compositions of iron meteorites if the proportions of these phases are known. These can be either directly measured in representative polished sections or calculated from the known bulk Ni concentrations using the mass-balance of Ni: $X_{\text{kam}} = (\text{Ni}_{\text{ple}} - \text{Ni}_{\text{bulk}})/(\text{Ni}_{\text{ple}} - \text{Ni}_{\text{kam}})$ and $X_{\text{ple}} = 1 - X_{\text{kam}}$. The bulk compositions of all octahedritic meteorites, except for Toluca and Duchesne, were calculated from the measured concentrations of trace elements in kamacite and plessite, the abundances of which were estimated from the bulk concentrations of Ni measured either by wet chemistry or INAA (Table 2).

Obviously, the approaches outlined above ignore troilite (which is depleted in siderophile elements) as well as the accessory amounts of schreibersite and cohenite. Another potential source of uncertainties lies in the chemical heterogeneity of plessite fields, which typically show M-shaped zoning in Ni, Co, and trace elements (Campbell and Humayun 1999a, b). Because the high-Ni and PGE-rich taenite bands of a plessite field constitute a volumetrically small portion of a meteorite (~0.9–3 vol% in the meteorite sections studied), we analyzed the central portions of plessite fields as representative samples of plessite. Comparison of

Table 1. Concentrations of Ni (wt%) and trace elements (ppm) in Hoba and Filomena.

Meteorite	Ni ^a	Mo ^b	Ru ^c	Rh ^c	Pd ^d	W ^e	Re ^f	Os ^f	Ir ^a	Pt ^g	Au ^h
Filomena	5.63	7.20	15.20	2.86	1.91	2.52	0.202	1.039	3.6	25.34	0.610
Hoba	16.56	24.50	28.61	4.86	6.94	3.20	2.81	40.17	27	31.84	0.084

^aWasson et al. 1998 (Filomena); Schaudy et al. 1972 (Hoba).

^bSmales et al. 1967.

^cCampbell et al. 2002.

^dChen and Wasserburg 1996a, b; Pd concentration in Filomena is assumed to be equal to that in Tocopilla.

^eRasmussen et al. 1984 (Hoba); Wasson et al. 1998 (Filomena).

^fSmoliar et al. 1996 (Hoba); Cook et al. 2004 (Filomena).

^gCook et al. 2004 (Filomena); this study (Hoba).

^hRasmussen et al. 1984 (Hoba); Wasson et al. 1998 (Filomena).

Table 2. Concentrations of Ni (wt%) and trace elements (ppm).

Meteorite	Ni ^a	Mo	Ru	Rh	Pd	W	Re	Os	Ir	Pt	Au
Arispe, bulk	6.54	6.67 ± 0.30 ^b	15.23 ± 0.83	3.008 ± 0.059	2.844 ± 0.083	2.34 ± 0.20	0.922 ± 0.045	8.16 ± 0.41	11.06 ± 0.60	22.85 ± 1.07	0.771 ± 0.020
Bennett County, bulk	5.28	6.515 ± 0.093	26.93 ± 0.20	3.53 ± 0.15	1.695 ± 0.057	3.463 ± 0.082	4.792 ± 0.097	58.81 ± 0.92	43.87 ± 1.32	38.89 ± 0.76	0.419 ± 0.019
Cape of Good Hope, bulk	16.50	22.35 ± 0.72	31.30 ± 0.80	5.08 ± 0.22	6.48 ± 0.41	2.96 ± 0.16	3.51 ± 0.12	51.3 ± 2.5	31.7 ± 1.5	31.8 ± 1.0	0.055 ± 0.012
Cape York, bulk	7.58	5.96 ± 0.29	7.47 ± 0.24	2.064 ± 0.069	3.38 ± 0.13	0.875 ± 0.037	0.264 ± 0.022	2.469 ± 0.064	3.13 ± 0.13	11.85 ± 0.32	0.848 ± 0.036
Kamacite	6.76	5.80 ± 0.27	6.97 ± 0.25	1.986 ± 0.067	3.05 ± 0.14	0.899 ± 0.036	0.262 ± 0.022	2.474 ± 0.056	3.13 ± 0.12	11.82 ± 0.20	0.823 ± 0.040
Plessite	15.04	7.5 ± 1.6	15.05 ± 0.82	2.78 ± 0.34	6.36 ± 0.30	0.66 ± 0.19	0.283 ± 0.075	2.43 ± 0.40	3.13 ± 0.80	12.67 ± 2.68	1.079 ± 0.055
Carbo, bulk	10.02	7.39 ± 0.28	15.17 ± 0.74	2.89 ± 0.26	3.42 ± 0.43	2.79 ± 0.14	1.376 ± 0.058	17.25 ± 0.60	14.73 ± 0.71	21.96 ± 0.76	0.621 ± 0.032
Kamacite	7.23	6.57 ± 0.32	12.42 ± 0.68	2.39 ± 0.34	2.30 ± 0.52	2.81 ± 0.17	1.314 ± 0.071	16.63 ± 0.70	14.13 ± 0.91	21.21 ± 0.99	0.520 ± 0.037
Plessite	17.52	9.60 ± 0.59	22.6 ± 2.0	4.23 ± 0.31	6.43 ± 0.70	2.73 ± 0.25	1.54 ± 0.10	18.9 ± 1.2	16.35 ± 0.93	23.96 ± 0.96	0.892 ± 0.062
Chinga, bulk	16.20	7.42 ± 0.41	7.86 ± 0.19	2.464 ± 0.083	7.89 ± 0.34	0.569 ± 0.014	1.028 ± 0.040	8.34 ± 0.47	4.13 ± 0.22	9.56 ± 0.32	0.524 ± 0.054
Coahuila, bulk	5.49	6.66 ± 0.16	19.86 ± 0.89	2.98 ± 0.12	1.693 ± 0.076	2.869 ± 0.076	1.203 ± 0.057	9.48 ± 0.27	14.63 ± 0.38	30.26 ± 0.99	0.489 ± 0.033
Divnoe, bulk	7.33	8.11 ± 0.14	14.9 ± 2.2	3.516 ± 0.089	3.475 ± 0.035	1.92 ± 0.19	0.88 ± 0.21	13.4 ± 2.5	12.5 ± 2.6	22.8 ± 3.8	1.725 ± 0.040
Kamacite	6.46	7.11 ± 0.23	10.44 ± 0.55	2.940 ± 0.012	3.024 ± 0.006	1.65 ± 0.34	0.581 ± 0.052	8.41 ± 0.59	8.05 ± 0.64	12.55 ± 0.29	1.473 ± 0.076
Plessite	8.25	9.16 ± 0.14	19.6 ± 4.6	4.13 ± 0.18	3.952 ± 0.071	2.21 ± 0.17	1.21 ± 0.44	18.8 ± 5.2	17.1 ± 5.3	33.7 ± 7.9	1.991 ± 0.009
Duchesne, bulk ^c	9.32	7.37 ± 0.35	2.119 ± 0.086	0.891 ± 0.033	6.58 ± 0.12	0.283 ± 0.023	0.031 ± 0.005	0.261 ± 0.038	0.418 ± 0.013	3.33 ± 0.11	2.338 ± 0.058
Kamacite	7.04	6.44 ± 0.23	1.692 ± 0.079	0.735 ± 0.053	4.83 ± 0.20	0.303 ± 0.004	0.030 ± 0.008	0.237 ± 0.013	0.411 ± 0.004	3.073 ± 0.088	2.015 ± 0.070
Plessite	9.15	7.37 ± 0.35	2.119 ± 0.086	0.891 ± 0.033	6.58 ± 0.12	0.283 ± 0.023	0.031 ± 0.005	0.261 ± 0.038	0.418 ± 0.013	3.33 ± 0.11	2.338 ± 0.058
Gibeon, bulk	7.68	6.26 ± 0.30	4.0 ± 1.3	1.201 ± 0.069	3.75 ± 0.12	0.636 ± 0.053	0.327 ± 0.027	3.094 ± 0.087	2.710 ± 0.061	6.91 ± 0.10	1.04 ± 0.16
Kamacite	7.24	6.00 ± 0.31	3.7 ± 1.3	1.128 ± 0.071	3.51 ± 0.13	0.610 ± 0.055	0.310 ± 0.028	2.918 ± 0.088	2.575 ± 0.058	6.509 ± 0.083	0.99 ± 0.17
Plessite	16.51	11.5 ± 1.3	10.7 ± 2.6	2.67 ± 0.23	8.60 ± 0.22	1.14 ± 0.20	0.669 ± 0.069	6.62 ± 0.52	5.42 ± 0.52	14.9 ± 1.4	2.03 ± 0.21
Grant, bulk	9.24	6.71 ± 0.39	1.85 ± 0.11	1.317 ± 0.062	4.78 ± 0.11	0.193 ± 0.019	<0.01	0.042 ± 0.010	<0.01	2.84 ± 0.15	1.910 ± 0.031
Kamacite	6.73	5.881 ± 0.015	1.521 ± 0.030	1.122 ± 0.074	3.55 ± 0.10	0.220 ± 0.012	<0.01	0.038 ± 0.005	<0.01	2.61 ± 0.15	1.618 ± 0.033
Plessite	11.82	7.57 ± 0.79	2.20 ± 0.22	1.518 ± 0.099	6.04 ± 0.21	0.166 ± 0.038	<0.01	0.046 ± 0.020	<0.01	3.06 ± 0.25	2.210 ± 0.053
Henbury, bulk	7.47	6.28 ± 0.10	14.04 ± 0.42	2.249 ± 0.020	2.353 ± 0.055	1.200 ± 0.039	1.455 ± 0.085	15.96 ± 0.20	13.78 ± 0.18	18.31 ± 0.26	0.422 ± 0.015
Kamacite	6.60	5.798 ± 0.086	12.78 ± 0.44	2.040 ± 0.015	2.072 ± 0.026	1.122 ± 0.016	1.324 ± 0.087	14.55 ± 0.10	12.574 ± 0.026	16.881 ± 0.079	0.385 ± 0.004
Plessite	16.59	11.36 ± 0.73	27.2 ± 1.4	4.43 ± 0.17	5.29 ± 0.57	2.02 ± 0.41	2.83 ± 0.34	30.7 ± 2.1	26.5 ± 2.1	33.3 ± 2.9	0.81 ± 0.17
Mundrabilla, bulk	7.72	4.99 ± 0.28	3.399 ± 0.054	1.220 ± 0.063	4.12 ± 0.13	0.481 ± 0.032	0.096 ± 0.003	0.886 ± 0.029	1.114 ± 0.033	4.54 ± 0.31	1.909 ± 0.078
Kamacite	6.61	4.42 ± 0.29	3.069 ± 0.058	1.072 ± 0.067	3.60 ± 0.13	0.416 ± 0.030	0.086 ± 0.003	0.804 ± 0.028	0.998 ± 0.031	4.12 ± 0.32	1.654 ± 0.077
Plessite	21.45	12.1 ± 1.2	7.477 ± 0.078	3.05 ± 0.17	10.58 ± 0.65	1.28 ± 0.20	0.214 ± 0.008	1.90 ± 0.19	2.55 ± 0.22	9.79 ± 0.86	5.05 ± 0.41
Negrillos, bulk	5.41	6.79 ± 0.44	27.0 ± 1.7	3.49 ± 0.21	1.83 ± 0.13	3.72 ± 0.22	5.09 ± 0.21	66.8 ± 3.5	47.2 ± 2.3	39.3 ± 1.5	0.417 ± 0.021
Odessa, bulk	7.2	2.71 ± 0.28	5.14 ± 0.12	1.664 ± 0.036	4.09 ± 0.17	0.594 ± 0.040	0.264 ± 0.023	2.46 ± 0.19	2.72 ± 0.22	7.33 ± 0.31	1.78 ± 0.10
Kamacite	6.59	2.64 ± 0.31	4.80 ± 0.11	1.615 ± 0.038	3.72 ± 0.18	0.592 ± 0.040	0.257 ± 0.024	2.44 ± 0.20	2.70 ± 0.23	7.33 ± 0.28	1.67 ± 0.11
Plessite	13.18	3.37 ± 0.49	8.50 ± 0.71	2.14 ± 0.12	7.67 ± 0.29	0.62 ± 0.17	0.335 ± 0.060	2.75 ± 0.68	2.84 ± 0.76	7.4 ± 1.9	2.89 ± 0.14
Sikhote-Alin, kamacite	5.87	7.30 ± 0.43	4.27 ± 0.20	2.24 ± 0.28	2.84 ± 0.50	0.747 ± 0.062	0.003 ± 0.002	0.019 ± 0.014	<0.05	5.42 ± 0.34	0.958 ± 0.056
Toluca, kamacite	7.08	5.72 ± 0.36	4.070 ± 0.078	1.55 ± 0.14	4.11 ± 0.44	0.614 ± 0.056	0.187 ± 0.031	2.48 ± 0.24	2.375 ± 0.048	5.47 ± 0.27	1.432 ± 0.057

^aThe concentrations of Ni in kamacite and plessite were measured by EMPA. The Ni contents in the bulk samples are from Wasson (1969, 1970), Wasson and Goldstein (1968), Schaudy et al. (1972), Scott et al. (1973), and Scott (1977, 1978a, b).

^bAll uncertainties of directly measured concentrations are 2σ standard deviations of the mean calculated for three replicate analyses except for six replicates of Negrillos, Toluca, and Cape of Good Hope. The uncertainties of the calculated bulk compositions are 2σ weighted standard deviations of both kamacite and plessite: $\sigma_{\text{bulk}} = (\sigma_{\text{kam}}^2 \times X_{\text{kam}}^2 + \sigma_{\text{ple}}^2 \times X_{\text{ple}}^2)^{1/2}$.

^cAssumed to be equal to that of plessite; see discussion in the text.

Table 3. Concentrations of trace elements (ppm) in Coahuila.

Date	Mo	Ru	Rh	Pd	W	Re	Os	Ir	Pt	Au
13-Dec-02	6.35	19.92	3.03	1.63	2.82	1.26	9.46	14.37	30.58	0.539
16-Dec-02	6.68	18.88	2.92	1.62	2.99	1.17	9.08	14.35	30.50	0.514
17-Dec-02	6.82	20.54	3.18	1.83	2.86	1.27	9.92	15.33	31.81	0.444
26-Dec-02	6.70	21.06	2.89	1.70	2.90	1.20	9.50	14.76	29.49	0.477
27-Dec-02	6.76	18.91	2.86	1.69	2.77	1.12	9.45	14.35	28.93	0.470
Average	6.66	19.86	2.98	1.693	2.869	1.203	9.48	14.63	30.26	0.489
2 σ	0.16	0.87	0.12	0.076	0.076	0.057	0.27	0.38	0.99	0.033
%Dev	2	4	4	4	3	5	3	3	3	7
Literature ^a	5.90	25.40	2.99	1.77	3.55	1.23	10.14	16	32.17	0.52

^aMo: Smales et al. 1967; Ru, Ir, Au: Pernicka and Wasson 1987; Rh: Ryan et al. 1990; Pd: Chen and Wasserburg 1996b; W: Scott 1978b; Re, Os, Pt: Cook et al. 2004.

our data with the precise ID data for a number of elements and meteorites (see the Reproducibility and Accuracy of the LA-ICP-MS Data section) shows that the large spot sizes used in this study seem to result in good average compositions of chemically and structurally heterogeneous plessite fields.

RESULTS AND DISCUSSION

The concentrations of PGEs, Re, W, Mo, and Au measured in the plessite and/or kamacite of all the meteorites studied are listed in Table 2 along with the bulk concentrations calculated from these data. The corresponding uncertainties are 2 σ standard deviations of the mean. The much smaller uncertainties of kamacite analyses reflect its homogeneous composition; because of this, the differences between the replicate analyses are mainly caused by counting statistics, with the time-dependent effect making only a minor contribution (Table 3). The larger uncertainties of plessite analyses include both the counting statistics and the compositional variations across zoned plessite fields.

No plessite fields large enough for the LA-ICP-MS measurements were found in Toluca and Sikhote-Alin. The bulk concentration of Ni in Sikhote-Alin of 5.87 wt% (Wasson 1969) is very close to that in kamacite, so neglecting the high-Ni phase introduces only a minor error. Therefore, comparing our LA-ICP-MS data with those obtained by different analytical techniques, we assume that the bulk concentrations of PGEs, Re, Mo, W, and Au in Sikhote-Alin are identical to those in its kamacite. On the contrary, Toluca is known to contain about 20% of plessite in addition to kamacite (Buchwald 1975), which is consistent with the bulk Ni content (8.07 wt%; Wasson 1970) being much higher than in kamacite (7.08 wt%). Therefore, to facilitate the comparison of our LA-ICP-MS data with the isotope dilution and INAA data, the bulk concentrations of Pd, Re, Os, Pt, Ir, and Au in Toluca were calculated based on the concentrations of these elements measured in kamacite, the average values of the plessite/kamacite distribution coefficients calculated by us in the Odessa IAB iron, and the modes of Toluca kamacite and plessite (Buchwald 1975). Although both kamacite and plessite were analyzed in

Duchesne, the average Ni concentrations measured by us in kamacite (7.04 wt%) and plessite (9.15 wt%) are lower than the bulk Ni content of 9.32 wt% (Schaudy et al. 1972). Because the kamacite and plessite are equally abundant in Duchesne (Buchwald 1975), a few percent of a high-Ni phase is necessary to account for the observed Ni deficit. An obvious candidate for such a high-Ni phase are the taenite bands, which are quite abundant in Duchesne (~2.8 vol% in the section studied) but too thin to be analyzed by our LA-ICP-MS technique. In the discussion below, we assume that the measured average composition of plessite fields represents the average composition of the meteorite. This assumption is based on the fact that the cores of plessite fields may retain chemical compositions of primary homogeneous taenite crystals that have later exsolved into fine-grained intergrowths of α - and γ -phases of plessite during slow subsolidus cooling. This assumption will be tested by the comparison of our LA-ICP-MS data with those obtained by other techniques.

Although a number of iron meteorites were analyzed in previous LA-ICP-MS studies (Hirata and Nesbitt 1997; McDonough et al. 1999; Campbell and Humayun 1999a, b), Table 2 lists, for the first time, relatively large body of LA-ICP-MS data on bulk PGE concentrations of iron meteorites, which provides a good basis for the quantitative comparison of the LA-ICP-MS technique with other well-established methods of trace element analysis such as INAA and isotope dilution. In the discussion below, we first test our results against well-characterized meteorites for reproducibility and accuracy. Then, we briefly discuss the trace element patterns in the studied meteorites and their implications for the origin of iron meteorites.

Reproducibility and Accuracy of the LA-ICP-MS Data

The Coahuila hexahedrite provides a good test for the internal reproducibility of our analytical technique because it has been analyzed as a drift monitor standard in every run. The accuracy of our data can be tested by comparing our concentrations of Pd, Re, Os, Pt, Ir, and Au with either the isotope dilution data or the INAA data.

Table 3 lists concentrations of PGEs, Re, Mo, W, and Au in Coahuila obtained over a two-week time span. The reproducibility of the analyses is better than 5% for all elements except Au (7%), which has a relatively low concentration. Our LA-ICP-MS data agree with corresponding literature data (Chen and Wasserburg 1996b; Cook et al. 2004; Pernicka and Wasson 1987; Ryan et al. 1990; Scott 1978b; Smales et al. 1967) within 12%, except for W, which is 19% lower than the old INAA value of Scott (1978b).

Fig. 1 compares our LA-ICP-MS and literature data for Pd, Re, Os, Pt (isotope dilution), Ir, and Au (INAA) in bulk samples of sixteen meteorites.

Our concentrations of Pd in 11 meteorites (Fig. 1a) agree with the ID data (Chen and Wasserburg 1996a, b; Mermelengas et al. 1979) within 9%, except for 15% and 24%

deviations for Carbo and Odessa, respectively, which have much larger uncertainties compared to other meteorites studied by Mermelengas et al. (1979).

The LA-ICP-MS and isotope dilution data (Cook et al. 2004; Smoliar et al. 1996; Hirata and Masuda 1992) on Re and Os in Bennett County, Cape York, Coahuila, Duchesne, Gibeon, Grant, Henbury, Negrillos, Odessa, Sikhote-Alin, and Toluca are compared in Figs. 1b and 1c. At Re concentrations higher than ~300 ppb, our LA-ICP-MS data agree with the isotope dilution data (Cook et al. 2004; Smoliar et al. 1996) within 3% (Fig. 1b); at lower Os concentrations, the discrepancy between the LA-ICP-MS and ID data varies from 10 to 25%, except for 60% in Sikhote-Alin with very low Os concentration of 7.5 ppb (Hirata and Masuda 1992). Our Os data (Fig. 1c) agree with the ID data within 12%

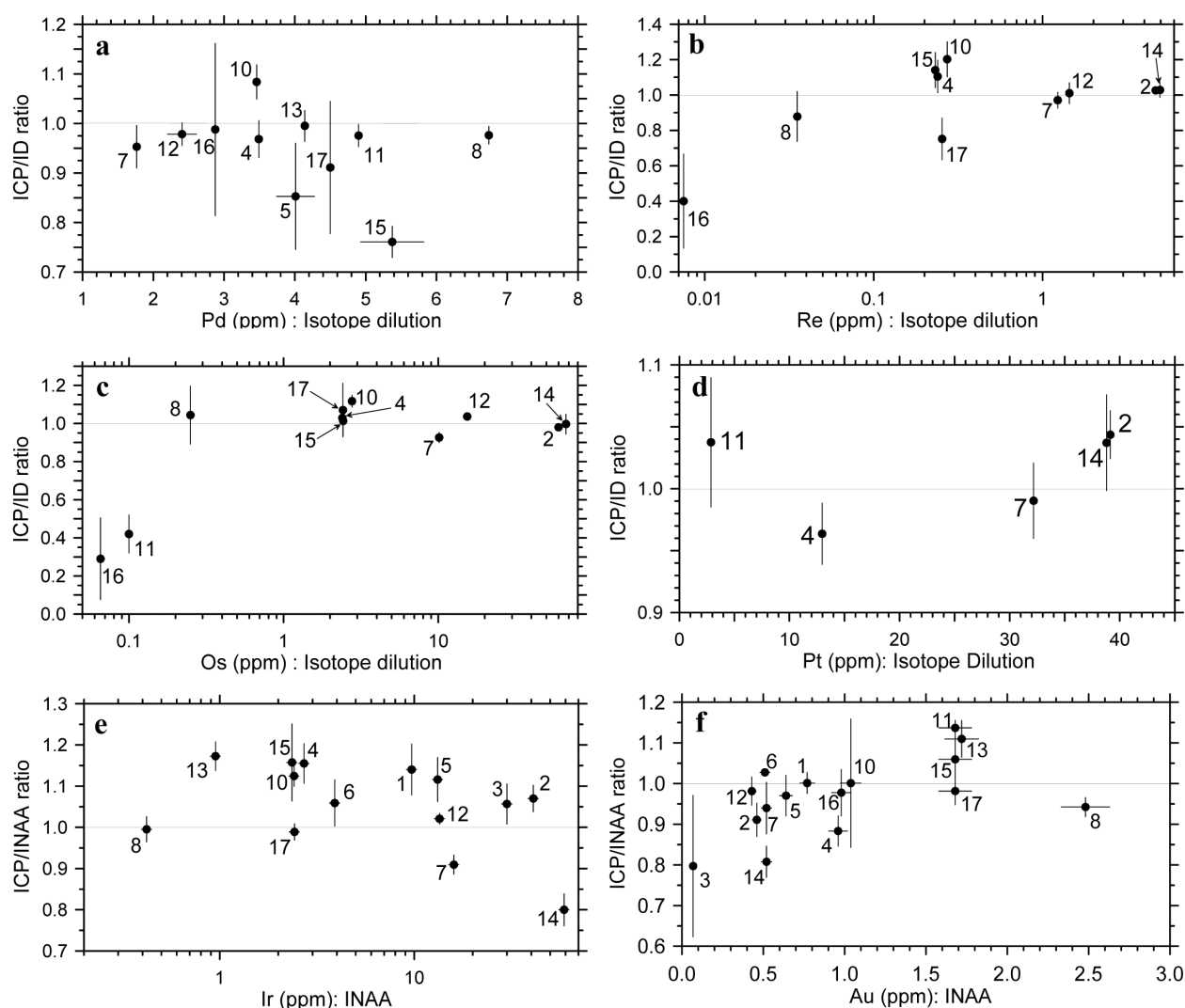


Fig. 1. Comparison of our LA-ICP-MS data for Pd (a), Re (b), Os (c), Pt (d), Ir (e), and Au (f) with literature isotope dilution and INAA data. All uncertainties are 2σ . The numbers on the plots designate the following meteorites: Arispe (1), Bennett County (2), Cape of Good Hope (3), Cape York (4), Carbo (5), Chinga (6), Coahuila (7), Duchesne (8), Gibeon (10), Grant (11), Henbury (12), Mundrabilla (13), Negrillos (14), Odessa (15), Sikhote-Alin (16), and Toluca (17). See text for the sources of literature data and discussion.

except for Grant (58%) and Sikhote-Alin (71%), which have Os concentrations less than 100 ppb.

The Pt concentrations measured by us in Bennett County, Coahuila, Cape York, Grant, and Negrillos are compared with those measured by isotope dilution (Walker et al. 1997; Cook et al. 2004) in Fig. 1d. The two data sets agree within 9%.

Our LA-ICP-MS data on Ir and Au are compared with the INAA data (Scott 1977; 1978a, b; Pernicka and Wasson 1987; Scott et al. 1973; Wasson 1969; Schaudy et al. 1972; Wasson et al. 1998; Wasson and Wang 1986; Wasson and Quyang 1990) in Figs. 1e and 1f. Although the INAA technique is not as precise as the isotope dilution, it has been used to analyze essentially every iron meteorite with the precision of 3–5 rel% for both Ir and Au (e.g., Wasson and Kallemeyn 2002). The data plot along 1:1 lines in both diagrams (Figs. 1e and 1f), but the scatter is somewhat larger than that exhibited by Pd, Re, Os, and Pt (Figs. 1a–1d), with the largest deviations being ~20 rel% for Ir in Negrillos (Fig. 1e) and Au in Cape of Good Hope (Fig. 1f). 50% of the LA-ICP-MS analyses of Ir agree with the INAA data within 10%; for ~79% of analyses the deviations are less than 15%. In the case of Au, ~69% of the LA-ICP-MS data agree with the INAA analyses within 10%, and ~88% of data deviate by less than 15%.

The good match between the LA-ICP-MS, isotope dilution, and INAA data not only for homogeneous hexahedrites and ataxites but for heterogeneous octahedrites indicates that our LA-ICP-MS system can be successfully used for accurate and reproducible analyses of iron meteorites. It also supports the validity of our approach to calculating bulk compositions of Fe, Ni metal of iron meteorites from chemical compositions of kamacite and plessite.

The comparison of our plessite data for Duchesne with those measured by the isotope dilution and INAA techniques on the bulk samples shows that our assumption on the proximity of the average plessite composition to the bulk composition of the meteorite seems to be correct. The concentrations of the elements with high values of the plessite/kamacite distribution coefficients, such as Pd and Au, agree with the isotope dilution and INAA data within 2 and 6 rel%, respectively. The elements with no preferential partitioning between kamacite and plessite, such as Os (4 rel%) and Ir (0.5 rel%), also show excellent agreement with the ID and INAA data; the somewhat larger deviation in Re (12 rel%) from the isotope dilution data is probably due to the low concentration (31 ppb; Table 2) and relatively high analytical error (16 rel%) of Re in Duchesne.

Trace Element Patterns

The CI-normalized concentrations of PGEs, Re, Mo, W, and Au in the bulk samples of the meteorites studied by us are plotted in the six panels of Fig. 2. All data are divided into five groups—IAB-IIICD, IIAB, IIIAB, IVA, and IVB—which are believed to represent petrogenetic associations

formed on individual parent bodies. The sixth group includes metal of the Divnoe primitive achondrite and the Arispe IC iron meteorite, which have remarkably similar HSE patterns. Because the residual nature of the Divnoe primitive achondrite is well-established (Petaev et al. 1994), the nearly identical HSE patterns of Arispe and Divnoe metal suggest that Arispe may be a residue of partial melting too, although these two meteorites are not genetically related.

The HSE patterns of Figs. 2a–2e, with a few exceptions, have similar shapes characteristic of igneous fractionation, which is well-established at least in the IIAB and IIIAB iron meteorites. Essentially all the patterns have two regions, either concave or convex, separated by Pd, which shows a very limited range of variations. Mo, which is on the far left of the smaller region that includes LPGEs (Ru, Rh, Pd), is another element that shows an even narrower range of variations. The range of variations of Au, which borders the larger region of HPGEs, Re, and W, is somewhat wider than that of Pd. The LPGEs and HPGEs display similar behavior during fractional crystallization (e.g., Figs. 2a and 2b), which is generally consistent with experimentally determined solid/liquid distribution coefficients, $D_{s/l}$, (e.g., Liu and Fleet 2001). The early differentiates are enriched in Re, Rh, and HPGEs relative to Mo, Pd, and, to a lesser degree, Au, with the HPGEs being enriched to a higher degree than the LPGEs. The late differentiates show a complementary behavior, with the HPGEs being depleted to a much higher degree than the LPGEs.

Implications to the Origin of Iron Meteorites

The narrow ranges of Mo and Pd variations within individual groups of igneous iron meteorites have important implications for deciphering the origin of these meteorites. Both elements are rather refractory; because of the highly siderophile behavior, they are both expected to be completely segregated into the metal-sulfide melts during metal-silicate fractionation of their parent bodies. This makes them suitable for estimating mass fractions of the cores in their parent bodies. In principle, a variation of concentrations of any refractory and highly siderophile element in a suite of iron meteorites from the same parent body can be used to estimate the mass fraction of the core in the parent body. A good estimate of the initial concentration of an element in the core melt is needed. This is, of course, easiest for elements that show a very limited range of variations, and there are only three such elements: Ni, Mo, and Pd. For this purpose, we prefer Mo to Pd because of its highly refractory behavior and smaller range of variations ($D_{s/l}$ value close to 1) in all groups of iron meteorites (Fig. 2). The $D_{s/l}$ value of Ni is also close to 1, but its complex non-ideal behavior, as shown by the Fe-Ni-S phase diagram (Hsieh et al. 1987), makes it a less desirable choice (that is, if we have concentration data of equal quality for both elements). Assuming that the parent

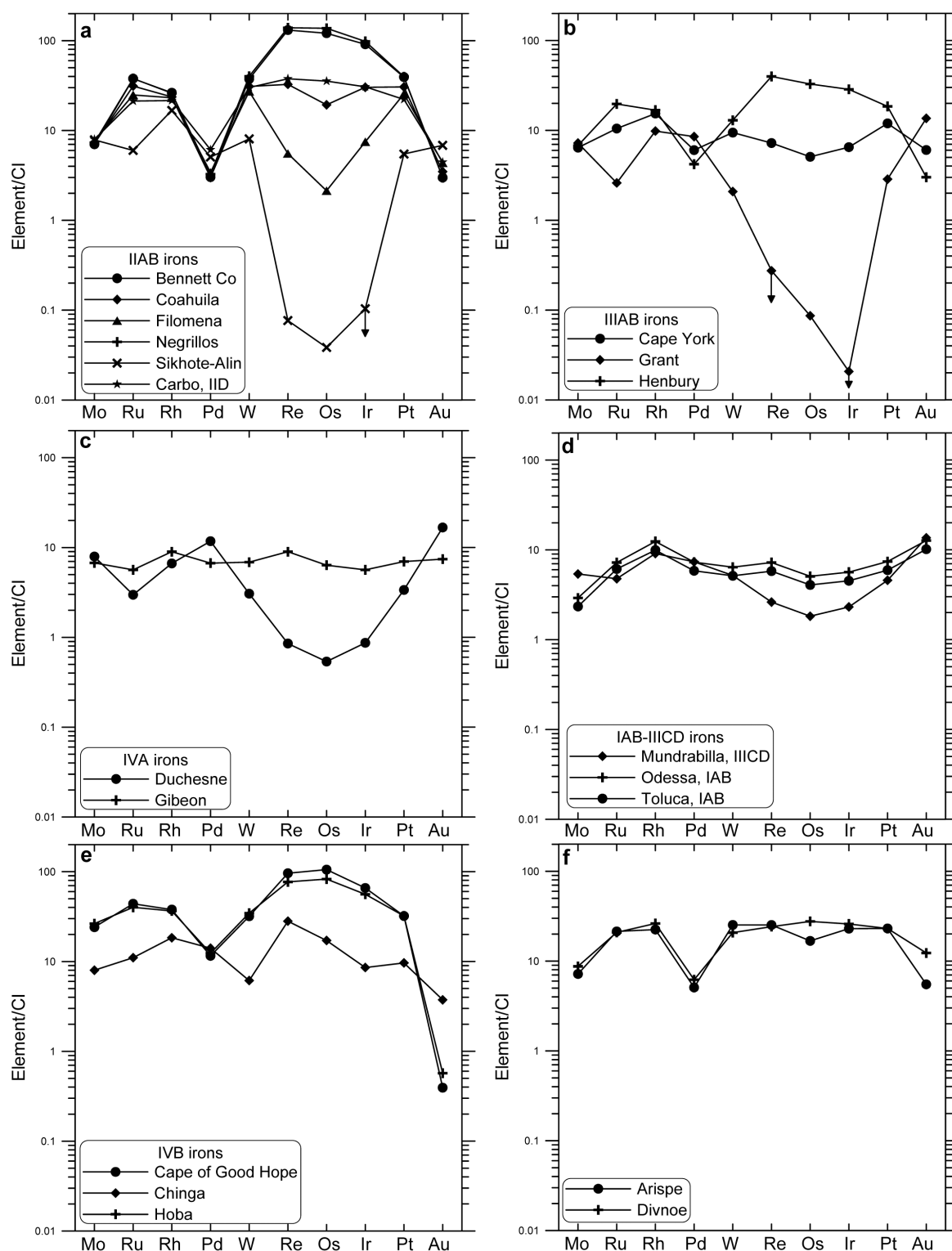


Fig. 2. Trace element patterns of the iron meteorites studied. The symbols with arrows indicate lower limits: a) group II irons: Bennett County (IIAB), Coahuila (IIAB), Filomena (IIAB), Negrillos (IIAB), Sikhote-Alin (IIAB), and Carbo (IID); b) group IIIAB irons: Cape York, Grant, and Henbury. A somewhat strange, asymmetric appearance of the HPGE pattern of Grant is due to the large uncertainties for Re, Os, and Ir in this meteorite; c) group IVA irons: Duchesne and Gibeon; d) group IAB-IIICD irons: Mundrabilla (Anom), Odessa, and Toluca; e) group IVB irons: Cape of Good Hope, Chinga (Anom), and Hoba; f) partial melting residues: Arispe (an IC iron) and metal of Divnoe (a primitive achondrite). The trace element patterns of Mundrabilla (IIICD) and Chinga (IVB) clearly show the anomalous nature of these meteorites.

bodies of iron meteorites initially contained the cosmic inventory of refractory siderophiles, the enrichment factor of Mo relative to the CI chondrites is simply reciprocal to the mass fraction of the metal-sulfide core on a meteorite parent body. Using the Mo enrichment factors from Figs. 2a–2e, one can estimate the mass fractions of the cores of parent bodies for different groups of iron meteorites: ~14% (IIA, IIB, and IVA), ~16% for IIIAB, and ~4% for IVB. In contrast, the low Mo enrichment factors in the IAB irons Odessa and Toluca, 2.34 and 2.92, respectively, point either to a much larger fraction of Fe–Ni melt in their parental chondritic igneous source (not an asteroidal core) or, more likely, to an inefficient Mo extraction to the Fe–Ni melt during localized (impact?; Wasson and Kallemeyn 2002) melting on their parent body.

The narrow ranges of Pd variations in the IIAB and IIIAB iron meteorites are somewhat surprising given its relatively low $D_{s/l}$ value (~0.2) in S-poor systems (Liu and Fleet 2001). However, in S-rich systems, the $D_{s/l}$ value of Pd may increase up to ~1 or even higher, depending upon the S concentration in the melt. The $D_{s/l}$ values of other elements will also increase, so it may be possible to achieve a large

range of fractionation of other PGEs. To test this possibility, we carried out a series of runs to model fractional crystallization in systems with different S contents using our FeNiSPIs code (see Appendix). While this code has many options, the results discussed below are only for the case of perfect fractional crystallization, with D values varying as a function of the S content in the melt (and, therefore, as a function of the degree of crystallization). Sulfur is treated as a perfectly incompatible element, so its concentration in the melt increases as crystallization proceeds.

The bulk composition of each system contained ~6.9–7.6 wt% Ni and PGEs, Re, W, Mo, and Au concentrations of $10 \times$ CI. The S content varied from ~2 wt% (Wasson 1999) to 17 wt% (Chabot and Drake 2000), and the Fe and Ni contents were calculated from the mass-balance considerations keeping the enrichment factors of Ni and trace elements constant ($10 \times$ CI). The experimental $D_{s/l}$ values for PGEs, Re, W, Mo, and Au are from Liu et al. (1999) and Liu and Fleet (2001). The PGEs patterns calculated for the systems with 2.13, 5.99, 8.24, and 12.00 wt% S are shown in Figs. 3a–3d. The comparison of modeling results with the HSE

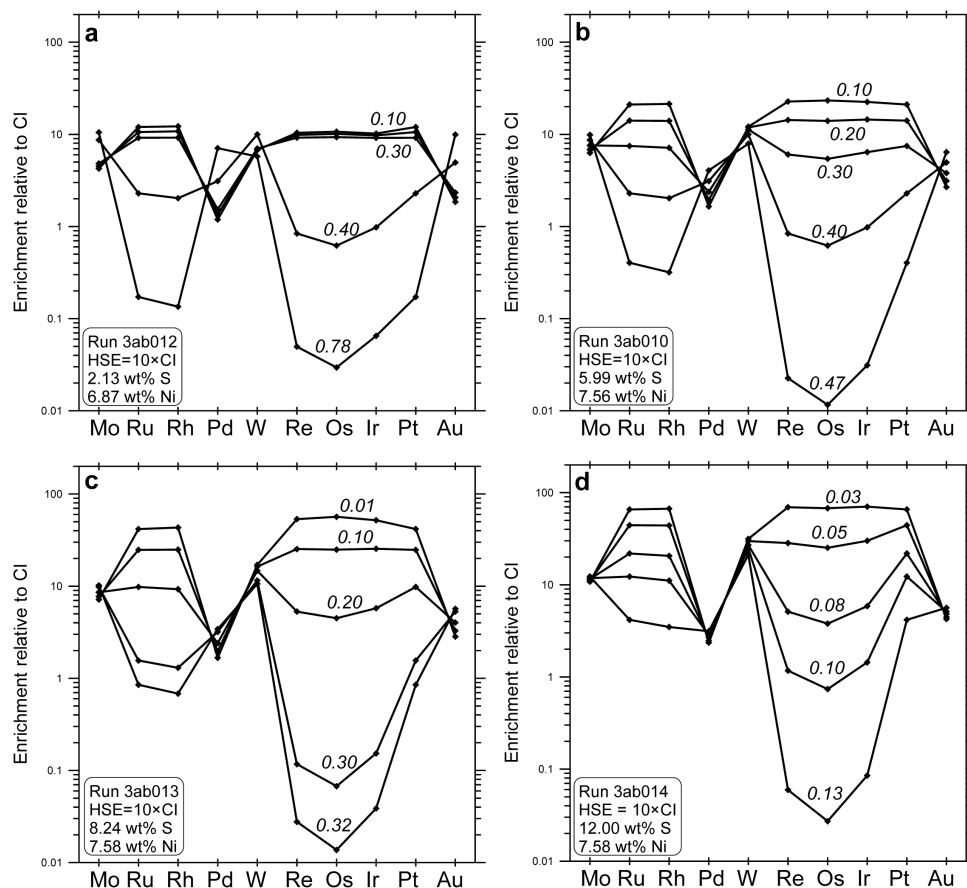


Fig. 3. Calculated HSE patterns of metals fractionally crystallized in Fe–Ni–S systems. The numbers on the curves are the degrees of crystallization. The concentrations of the major elements in the initial melts are listed in the legends, with the sums of Fe, Ni, and S being 100 wt%. In all systems, the enrichment factors for Ni and trace elements are $10 \times$ chondritic. As S content in the initial melt increases (from [a] to [d]), the range of Pd variations decreases, making Pd a potential indicator of S content in the igneous source regions of iron meteorites.

patterns of IIAB (Fig. 2a) and IIIAB (Fig. 2b) irons clearly shows that the observed large ranges of Os fractionation accompanied by the narrow ranges of Mo and Pd fractionation can only be achieved in the igneous systems with relatively high S contents of ~6–10 wt%. Although the details of the calculated and measured HSE patterns do not match very well (pointing to a more complicated history of core crystallization on real meteorite parent bodies and/or to problems with D values; for more detailed discussion, see Chabot et al. [2003]), the general narrowing of the range of Pd fractionation, as the S content in the system increases, suggests that the variations in the Pd concentrations of iron meteorites can be potentially used for estimating S contents in the cores of iron meteorite parent bodies, which are still poorly constrained (e.g., Wasson 1999).

CONCLUDING REMARKS

The major conclusion of this paper is that we have developed a LA-ICP-MS technique for precise and accurate determination of highly siderophile elements such as Mo, Ru, Rh, W, Re, Os, Ir, Pt, and Au in meteoritic Fe, Ni-metals on the ppm and ppb levels. The technique has been used to analyze a suite of meteorites that covers rather wide ranges of concentrations of these elements. This is the first report of a set of the Mo, Ru, Rh, W, Re, Os, Ir, Pt, and Au data measured by an LA-ICP-MS technique that allows comparing it with other analytical techniques frequently applied to iron meteorites. The good match between the LA-ICP-MS, the isotope dilution, and the INAA data, not only for homogeneous hexahedrites and ataxites but for heterogeneous octahedrites, clearly shows that our LA-ICP-MS system can be used successfully for analyses of iron meteorites. It also proves the validity of our approach to calculating bulk compositions of Fe, Ni metal of iron meteorites from the chemical compositions of kamacite and plessite.

A consistent set of Mo and Pd concentrations obtained in this study and the narrow ranges of their variations within individual groups of iron meteorites suggest that these elements can provide important insights into the evolution of parent bodies of iron meteorites. Under certain assumptions, the Mo concentrations can be used to estimate mass fractions of the metal-sulfide cores in the parent bodies of iron meteorites. It appears that a range of Pd variations within a group of iron meteorites can serve as a useful indicator of S content in the core of its parent body.

Acknowledgments—We thank Carl Francis of the Harvard Museum of Natural History for the specimens of Coahuila and Filomena. M. I. Petaev is indebted to Elizabeth Gier for training and help in carrying out LA-ICP-MS analyses. Reviews by Takafumi Hirata, Munir Humayun, and John Wasson and the editorial handling by Hiroko Nagahara helped to improve the clarity of the paper and are greatly appreciated.

This study was supported by the NASA grants NAG5–10484, NAG5–13164, NAG5–11925 to Stein B. Jacobsen and NAG5–13226 to Michail I. Petaev.

Editorial Handling—Dr. Hiroko Nagahara

REFERENCES

- Bogdanovski O. and Jagoutz E. 1996. Sm-Nd system in Divnoe meteorite (abstract). 27th Lunar and Planetary Science Conference. pp. 129–130.
- Buchwald V. F. 1975. *Handbook of iron meteorites*. Los Angeles: University of California Press. 1426 p.
- Campbell A. J. and Humayun M. 1999a. Microanalysis of platinum group elements in iron meteorites using laser ablation ICP-MS (abstract #1974). 30th Lunar and Planetary Science Conference. CD-ROM.
- Campbell A. J. and Humayun M. 1999b. Trace element microanalysis in iron meteorites by laser ablation ICPMS. *Analytical Chemistry* 71:939–946.
- Campbell A. J., Humayun M., and Weisberg M. K. 2002. Siderophile element constraints on the formation of metal in the metal-rich chondrites Bencubbin, Weatherford, and Gujba. *Geochimica et Cosmochimica Acta* 66:647–660.
- Chabot N. L. and Drake M. J. 1999. Crystallization of magmatic iron meteorites: The role of mixing in the molten core. *Meteoritics & Planetary Science* 34:235–246.
- Chabot N. L. and Drake M. J. 2000. Crystallization of magmatic iron meteorites: The effect of phosphorus and liquid immiscibility. *Meteoritics & Planetary Science* 35:807–816.
- Chabot N. L., Campbell A. J., Jones J. H., Humayun M., and Agee C. B. 2003. An experimental test of Henry's Law in solid metal-liquid metal systems with implications for iron meteorites. *Meteoritics & Planetary Science* 38:181–196.
- Chen J. H. and Wasserburg J. G. 1996a. Live ^{107}Pd in the early solar system and implications for planetary evolution. In *Earth processes: Reading the isotopic code*, edited by Basu A. and Hart S. Geophysical Monograph 95. Washington D. C.: American Geophysical Union. pp. 1–20.
- Chen J. H. and Wasserburg J. G. 1996b. Live ^{107}Pd in some group II and III irons and the time scales of Fe-Ni segregations in the early solar system (abstract). 27th Lunar and Planetary Science Conference. pp. 209–210.
- Chen J. H., Papanastassiou D. A., and Wasserburg J. G. 2002. Re-Os and Pd-Ag systematics in group IIIAB irons and in pallasites. *Geochimica et Cosmochimica Acta* 66:3793–3810.
- Cook D. L., Walker R. J., Horan M. F., Wasson J. T., and Morgan J. W. 2004. Pt-Re-Os systematics of group IIAB and IIIAB iron meteorites. *Geochimica et Cosmochimica Acta* 68:1413–1431.
- Haack H. and Scott E. R. D. 1992. Asteroid core crystallization by inward dendritic growth. *Journal of Geophysical Research* 97: 14727–14734.
- Haack H. and Scott E. R. D. 1993. Chemical fractionations in group IIIAB iron meteorites: Origin by dendritic crystallization of an asteroidal core. *Geochimica et Cosmochimica Acta* 57:3457–3472.
- Hirata T. and Nesbitt R. W. 1997. Distribution of platinum group elements and rhenium between metallic phases of iron meteorites. *Earth and Planetary Science Letters* 147:11–24.
- Hirata T. and Masuda A. 1992. Rhenium and osmium systematics of iron and stony iron meteorites. *Meteoritics* 27:568–575.
- Horan M. F., Smoliar M. I., and Walker R. J. 1998. ^{182}W and ^{187}Re - ^{187}Os systematics of iron meteorites: Chronology for melting,

- differentiation, and crystallization in asteroids. *Geochimica et Cosmochimica Acta* 62:545–554.
- Hsieh K. C., Vlach K. C., and Chang Y. A. 1987. The Fe-Ni-S system. I. A thermodynamic analysis of the phase equilibria and calculation of the phase diagram from 1173–1623 K. *High Temperature Science* 23:17–38.
- Jones J. H. and Drake M. J. 1983. Experimental investigation of trace element fractionation in iron meteorites, II: The influence of sulfur. *Geochimica et Cosmochimica Acta* 47:1199–1209.
- Jones J. H. and Malvin D. J. 1990. A nonmetal interaction model for the segregation of trace metals during solidification of Fe-Ni-S, Fe-Ni-P, and Fe-Ni-S-P alloys. *Metallurgical Transactions* 21B: 697–706.
- Kracher A. and Wasson J. T. 1982. The role of S in the evolution of the parent cores of the iron meteorites. *Geochimica et Cosmochimica Acta* 4:2419–2426.
- Liu M. and Fleet M. E. 2001. Partitioning of siderophile elements (W, Mo, As, Ag, Ge, Ga, and Sn) and Si in the Fe-S system and their fractionation in iron meteorites. *Geochimica et Cosmochimica Acta* 65:671–682.
- Liu M., Fleet M. E., and Crockett J. H. 1999. Partitioning of trace amounts of highly siderophile elements in the Fe-Ni-S system and their fractionation in nature. *Geochimica et Cosmochimica Acta* 63:2611–2622.
- Lovering J. F., Nichiporuk W., Chodos A., and Brown H. 1957. The distribution of gallium, germanium, cobalt, chromium, and copper in iron and stony-iron meteorites in relation to nickel content and structure. *Geochimica et Cosmochimica Acta* 11: 263–278.
- Lugmair G. W. and Shukolyukov A. 1998. Early solar system timescales according to ^{53}Mn - ^{53}Cr systematics. *Geochimica et Cosmochimica Acta* 62:2863–2886.
- McDonough W. F., Horn I., Lange D., and Rudnick R. L. 1999. Distribution of platinum group elements between phases in iron meteorites (abstract #2062). 30th Lunar and Planetary Science Conference. CD-ROM.
- Mermelengas N., De Laeter J. R., and Rosman K. J. R. 1979. New data on the abundance of palladium in meteorites. *Geochimica et Cosmochimica Acta* 43:747–753.
- Narayan C. and Goldstein J. I. 1982. A dendritic crystallization model to explain Ge-Ni variations in iron meteorite chemical groups. *Geochimica et Cosmochimica Acta* 46:259–268.
- Pernicka E. and Wasson J. T. 1987. Ru, Re, Os, Pt, and Au in iron meteorites. *Geochimica et Cosmochimica Acta* 51:1717–1726.
- Petaev M. I. and Jacobsen S. B. 2003a. Measurement of PGEs, Re, Mo, W, and Au in meteoritic Fe-Ni metal (abstract #1732). 34th Lunar and Planetary Science Conference. CD-ROM.
- Petaev M. I. and Jacobsen S. B. 2003b. Differentiation of metal-rich meteoritic parent bodies (abstract #1747). 34th Lunar and Planetary Science Conference. CD-ROM.
- Petaev M. I., Barsukova L. D., Lipschutz M. E., Wang M. S., Ariskin A. A., Clayton R. N., and Mayeda T. K. 1994. The Divnoe meteorite: Petrology, chemistry, oxygen isotopes and origin. *Meteoritics* 29:182–199.
- Rasmussen K. L., Malvin D. J., Buchvald V. F., and Wasson J. T. 1984. Compositional trends and cooling rates of group IVB iron meteorites. *Geochimica et Cosmochimica Acta* 48:805–811.
- Ryan D. E., Holzbecher J., and Brooks R. R. 1990. Rhodium and osmium in iron meteorites. *Chemical Geology* 85:295–303.
- Schaudy R., Wasson J. T., and Buchwald V. F. 1972. The chemical classification of iron meteorites, a reinvestigation of irons with Ge concentrations lower than 1 ppm. *Icarus* 17:174–192.
- Scott E. R. D. 1972. Chemical fractionation in iron meteorites and its interpretation. *Geochimica et Cosmochimica Acta* 36:1205–1236.
- Scott E. R. D. 1977. Composition, mineralogy, and origin of group IC iron meteorites. *Earth and Planetary Science Letters* 37:273–284.
- Scott E. R. D. 1978a. Iron meteorites with low Ga and Ge concentrations—Composition, structure, and genetic relationships. *Geochimica et Cosmochimica Acta* 42:1243–1251.
- Scott E. R. D. 1978b. Tungsten in iron meteorites. *Earth and Planetary Science Letters* 39:363–370.
- Scott E. R. D., Wasson J. T., and Buchwald V. F. 1973. The chemical classification of iron meteorites: VII. Reinvestigation of irons with Ge concentrations between 25 and 80 ppm. *Geochimica et Cosmochimica Acta* 37:1957–1983.
- Scott E. R. D., Haack H., and McCoy T. J. 1996. Core crystallization and silicate-metal mixing in the parent body of the IVA iron and stony-iron meteorites. *Geochimica et Cosmochimica Acta* 60: 1615–1631.
- Shen J. J., Papanastassiou D. A., and Wasserburg G. J. 1996. Precise Re-Os determinations and systematics of iron meteorites. *Geochimica et Cosmochimica Acta* 60:2887–2900.
- Smales A. A., Mapper D., and Fouche K. F. 1967. The distribution of some trace elements in iron meteorites, as determined by neutron activation. *Geochimica et Cosmochimica Acta* 31:673–720.
- Smoliar M. I., Walker R. J., and Morgan J. W. 1996. Re-Os ages of group IIA, IIIA, IVA, and IVB iron meteorites. *Science* 271: 1099–1102.
- Srinivasan G., Goswami J. N., and Bhandari N. 1999. ^{26}Al in eucrite Piplia Kalan: Possible heat source and formation chronology. *Science* 284:1348–1350.
- Srinivasan G., Papanastassiou D. A., Wasserburg G. J., Bhandari N., and Goswami J. N. 2000. Re-examination of ^{26}Al - ^{26}Mg systematics in the Piplia Kalan eucrite (abstract #1795). 31st Lunar and Planetary Science Conference. CD-ROM.
- Sylvester P. J. 2001. A practical guide to platinum-group element analysis of sulfides by laser-ablation ICPMS. In *Laser-ablation-ICPMS in the earth sciences: Principles and applications*, edited by Sylvester P. J. Ottawa: Mineralogical Association of Canada. pp. 203–211.
- Ulf-Møller F. 1998. Effects of liquid immiscibility on trace element fractionation in magmatic iron meteorites: A case study of group IIIAB. *Meteoritics & Planetary Science* 33:207–220.
- Walker R. J., Morgan J. W., Beary E. S., Smoliar M. I., Czamanske G. K., and Horan M. F. 1997. Applications of the ^{190}Pt - ^{186}Os isotope system to geochemistry and cosmochemistry. *Geochimica et Cosmochimica Acta* 22:4799–4807.
- Wasson J. T. 1967. The chemical classification of iron meteorites—I. A study of iron meteorites with low concentrations of gallium and germanium. *Geochimica et Cosmochimica Acta* 31:161–180.
- Wasson J. T. 1969. The chemical classification of iron meteorites: III. Hexahedrites and other irons with germanium concentrations between 80 and 120 ppm. *Geochimica et Cosmochimica Acta* 33: 859–876.
- Wasson J. T. 1970. The chemical classification of iron meteorites: IV. Irons with Ge concentrations greater than 190 ppm and other meteorites associated with group I. *Icarus* 12:407–423.
- Wasson J. T. 1999. Trapped melt in IIIAB irons; Solid/liquid elemental partitioning during the fractionation of the IIIAB magma. *Geochimica et Cosmochimica Acta* 63:2875–2889.
- Wasson J. T. and Goldstein J. I. 1968. The north Chilean hexahedrites: Variations in composition and structure. *Geochimica et Cosmochimica Acta* 32:329–339.
- Wasson J. T. and Kallemeyn G. W. 2002. The IAB iron-meteorite complex: A group, five subgroups, numerous grouplets, closely related, mainly formed by crystal segregation in rapidly cooling melts. *Geochimica et Cosmochimica Acta* 66:2445–2473.

- Wasson J. T. and Quyang X. 1990. Compositional range of Canyon Diablo meteoroid. *Geochimica et Cosmochimica Acta* 54:3175–3183.
- Wasson J. T. and Richardson J. W. 2001. Fractionation trends among IVA iron meteorites: Contrasts with IIIAB trends. *Geochimica et Cosmochimica Acta* 65:951–970.
- Wasson J. T. and Wang J. 1986. A non-magmatic origin of group IIE iron meteorites. *Geochimica et Cosmochimica Acta* 50:725–732.
- Wasson J. T., Choi B. G., Jerde E. A., and Ulf-Møller F. 1998. Chemical classification of iron meteorites: XII. New members of the magmatic groups. *Geochimica et Cosmochimica Acta* 62: 715–724.
- Yin Q. Z. and Jacobsen S. B. 2003. The initial $^{182}\text{W}/^{183}\text{W}$ and $^{182}\text{Hf}/^{180}\text{Hf}$ of the solar system and a consistent chronology with Pb-Pb ages (abstract #1857). 34th Lunar and Planetary Science Conference. CD-ROM.
- Yin Q. Z., Jacobsen S. B., Yamashita K., Blichert-Toft J., Telouk P., and Albarede F. 2002. A short timescale of terrestrial planet formation determined by Hf-W chronometry. *Nature* 418:949–952.

APPENDIX: FeNiSPIs CODE FOR MODELING CRYSTALLIZATION OF Fe-Ni-S-P MELTS

Ever since Scott (1972) recognized the important role of fractional crystallization in the formation of iron meteorites, a number of models of core crystallization have been developed (e.g. Scott 1972; Kracher and Wasson 1982; Jones and Drake 1983; Haack and Scott 1992; 1993; Scott et al. 1996; Ulf-Møller 1998; Wasson 1999; Chabot and Drake 1999; 2000; Liu and Fleet 2001; Chabot et al. 2003). Besides using different $D_{s/l}$ values, different models explore how the chemical compositions of the magmatic iron meteorites are affected by the presence of sulfur and phosphorus in the melt (Kracher and Wasson 1982; Jones and Drake 1983; Chabot and Drake 2000; Liu and Fleet 2001), by dendritic growth of metal crystals (Narayan and Goldstein 1982; Haack and Scott 1992, 1993), by liquid immiscibility (Ulf-Møller 1998; Chabot and Drake 2000), by entrapment of sulfur-rich melt (Haack and Scott 1993; Wasson 1999), and by the mixing in the molten core (Chabot and Drake 1999).

We (Petaev and Jacobsen 2003b) have developed a new code (FeNiSPIs = Fe, Ni, S, P, Isotopes) for modeling crystallization of Fe-Ni-S-P melts that calculates partitioning of Fe, Ni, S, P, Cr, Co, Ga, Ge, As, Mo, Ru, Rh, Pd, Ag, W, Re, Os, Ir, Pt, and Au between the solid and liquid phases during crystallization of a Fe-Ni-S-P-rich melt as well as radiogenic isotope evolution (Re-Pt-Os, Pd-Ag, etc.) of the melt and solid phases as a function of time and cooling rate. The input parameters of the FeNiSPIs code include the bulk composition of the system, the range of the degree of crystallization, the increment in the degree of crystallization, and the values of distribution coefficients (S, P-dependent), with the S- and P-

dependence parameterized according to the Jones and Malvin (1990) formulation. Additional input parameters include the mode of crystallization expressed as the fraction of crystals isolated from the melt at each iteration (F_{is}), the fraction of the melt trapped by growing crystals (F_{tr}), the age of the solar system, and the initial isotopic ratios and decay constants for the isotopic systems of interest. The addition of F_{is} allows us to explore, if necessary, modes of crystallization intermediate between the full equilibrium ($F_{is} = 0$) and the Rayleigh fractional crystallization ($F_{is} = 1$). The addition of F_{tr} permits us to explore more complicated models of crystallization of asteroidal cores (e.g., Haack and Scott 1993; Wasson 1999) that have been put forward to account for the presence of troilite nodules in some iron meteorites.

When necessary, the values of distribution coefficients can be changed without changing the code. At each step, FeNiSPIs calculates the equilibrium partitioning of all elements, except Fe and S, between the residual liquid and the solid metal. The concentrations of the Fe and S are calculated by mass-balancing the amounts of these elements in the system, assuming that all S resides in the melt. After subtracting the appropriate portion of solid metal from the bulk composition of the core, the process continues until either the maximum crystallization degree specified or the metal-troilite eutectic is reached. Once troilite becomes a liquidus phase, the calculation is terminated because of the lack of appropriate partitioning data for troilite. The code outputs chemical compositions and the abundances of liquid and solid phases for the values of crystallization degrees specified as well as the isotopic ratios for appropriate isotope systems as a function of time tied to crystallization degrees by an assumed cooling rate.