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Highly Siderophile and Strongly Chalcophile Elements

in High-Temperature Geochemistry and Cosmochemistry

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Front-cover: Proton-induced X-ray emission maps of experimental charges of Fe–Ni–Cu–S. The experimental liquid, quenched at 1000 °C, precipitated an intergrowth of quenched dendritic monosulfide solution [(FeNi)S] and intermediate solid solution [(FeCu)S] grains. Scale 2.5 × 1.8 mm. Image courtesy of Sarah-Jane Barnes, Université du Québec à Chicoutimi, Québec, Canada.

Back-cover: The analytical consideration for the analysis of highly siderophile and strongly chalcophile elements in high-temperature geochemistry and cosmochemistry. Figure courtesy of Thomas Meisel, Montanuniversität, Leoben, Austria.

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in High-Temperature Geochemistry and Cosmochemistry

81 *Reviews in Mineralogy and Geochemistry*

81

FROM THE SERIES EDITOR

It has been a pleasure working with the two volume editors and authors on this 81st volume of *Reviews in Mineralogy and Geochemistry*. Several chapters have associated supplemental materials that can be found at the MSA website. Any future errata will also be posted there.

lan P. Swainson, Series Editor Vienna, Austria November 2015

PREFACE

INTRODUCTION TO HIGHLY SIDEROPHILE AND STRONGLY CHALCOPHILE ELEMENTS IN HIGH TEMPERATURE GEOCHEMISTRY AND COSMOCHEMISTRY

In high-temperature geochemistry and cosmochemistry, highly siderophile and strongly chalophile elements can be defined as strongly preferring metal or sulfide, respectively, relative to silicate or oxide phases. The highly siderophile elements (HSE) comprise Re, Os, Ir, Ru, Pt, Rh, Pd, and Au and are defined by their extreme partitioning (>10⁴) into the metallic phase, but will also strongly partition into sulfide phases, in the absence of metal. The HSE are highly refractory, as indicated by their high melting and condensation temperatures and were therefore concentrated in early accreted nebular materials. Within the HSE are the platinum-group elements (PGE), which include the six elements lying in the *d*-block of the periodic table (groups 8, 9, and 10, periods 5 and 6), i.e., Os, Ir, Ru, Pt, Rh and Pd. These six elements tend to exist in the metallic state, or bond with chalcogens (S, Se, Te) or pnictogens (P, As, Sb, Bi). Rhenium and Au do not necessarily behave as coherently as the PGE, due to their differing electronegativity and oxidation states. For these reasons, a clear definition between the discussion of the PGE and the HSE (PGE, Re and Au) exists in the literature, especially in economic geology, industrial, or bio-medical studies.

The strongly chalcophile elements can be considered to include S, Se, and Te. These three elements are distinguished from other chalcophile elements, such as Cd or Pb, because, like the HSE, they are all in very low abundances in the bulk silicate Earth (Fig. 1). By contrast with the



Figure 1. Elements plotted as a function of atomic number versus their abundance in the bulk silicate Earth normalized to the CI-chondrite composition. Highly siderophile elements (HSE), which tend to exist in the metallic state, and strongly chalcophile elements are shown as dark and light gray symbols, respectively. Omitted naturally occurring elements with atomic numbers of <92 are H, O, and the noble gases (He, Ne, Ar, Kr, Xe). Data are from McDonough and Sun (1995).

HSE, S, Se, and Te all have far lower melting and condensation temperatures, classifying them as highly volatile elements (Table 1). Moreover, these elements are not equally distributed within chondrite meteorite groups (Fig. 2). Since their initial distribution in the Solar nebula, planetary formation and differentiation process have led to large fractionations of the HSE and strongly chalcophile elements, producing a range of absolute and relative inter-element fractionations.

The chemical properties of the HSE, that set them apart from any other elements in the periodic table (Table 2), have made them geochemical tracers par excellence. As tracers of key processes, the HSE have found application in virtually all areas of the physical Earth sciences.



Figure 2. Average Te, Se, S and Os abundances in carbonaceous (CI, C2, CM2, CV3) and ordinary (H, L, LL) chondrite groups. For scaling purposes, S contents are divided by 1000. Data are from compilations in Wang and Becker (2013) and Day et al. (2016).

		Table 1. General	l behí	avior and	discover	y of the highl.	y siderophile	e and stron	gly chalcophile elements	s.
Element		Behavior	z	Melting Point (K)	50% T _c (K)	CI-chondrite abundance	BSE abundance	Discovery date	Discoverers (location)	Meaning of the name
Sulphur	s	High Volatile Chalcophile	16	388	664	54100	250	Prehistory	Unknown	Latin Sulphur, meaning 'burning stone'
Selenium	Se	High Volatile Chalcophile	34	494	697	19.7	0.075	1817	JJ Berzelius (Sweden)	Greek Selene,meaning Moon
Ruthenium	Ru	Refractory Siderophile	4	2606	1551	0.692	0.005	1844	KK Klaus (Russia)	Latin Ruthenia, meaning Russia
Rhodium	Rh	Refractory Siderophile	45	2236	1392	0.141	0.0009	1803	WH Wollaston (England)	Greek Rhodon, meaning Rose
Palladium	Pd	Transitional Siderophile	46	1828	1324	0.588	0.0039	1803	WH Wollaston (England)	After the asteroid Pallas, Greek Pallas, Goddess of Wisdom
Tellurium	Te	High Volatile Chalcophile	52	723	602	2.33	0.012	1783	FJM von Reichstein (Romania)	Latin Tellus, meaning Earth
Rhenium	Re	Refractory Siderophile	75	3458	1821	0.037	0.00028	1925	W Noddack, I Tacke, O Berg (Germany)	Latin Rhenus, meaning Rhine
Osmium	Os	Refractory Siderophile	92	3306	1812	0.486	0.0034	1803	S Tennant (England)	Greek Osme, meaning odour
Iridium	Ir	Refractory Siderophile	LL	2719	1603	0.47	0.0032	1803	S Tennant (England)	Greek goddess Iris, meaning rainbow
Platinum	Pt	Refractory Siderophile	78	2041	1408	1.004	0.0071	1735	Known to native Americans - A de Ulloa (South America)	Spanish Platina, meaning silver
Gold	Au	Mod Volatile Siderophile	79	1337	1060	0.146	0.001	>6000 y bp	Unknown	Anglo-Saxon word Gold, latin word Aurum (Au)

v

These elements have been used to inform on the nucleosynthetic sources and formation of the Solar System, planetary differentiation, late accretion addition of elements to planets, core-formation and possible core-mantle interaction, crust-mantle partitioning, volcanic processes and outgassing, formation of magmatic, hydrothermal and epithermal ore deposits, ocean circulation, climate-related events, weathering, and biogeochemical cycling. More recently, studies of strongly chalcophile elements are finding a similar range of applications. Their utility lies in the fact that these elements will behave as siderophile or strongly chalcophile elements under reducing conditions, but will also behave as lithophile or atmophile elements under oxidizing conditions, as experienced at the present day Earth's surface.

A key aspect of the HSE is that three long-lived, geologically useful decay systems exist with the HSE as parent (¹⁰⁷Pd-¹⁰⁷Ag), or parent-daughter isotopes (¹⁸⁷Re-¹⁸⁷Os and ¹⁹⁰Pt-¹⁸⁶Os). This volume is dedicated to some of the processes that can be investigated at high-temperatures in planets using the HSE and strongly chalcophile elements.

Element	Electro- negativity*	Oxidation states	Density (g/cm ³)	Isotopes	Mass	Atomic Abundance
S	2.58	6,4,2,-2	2.067	32	31.9721	94.99
				33	32.9714	0.75
				34	33.9679	4.25
				36	35.9671	0.01
Se	2.55	6,4,-2	4.809	74	73.9225	0.89
				76	75.9192	9.37
				77	76.9199	7.63
				78	77.9173	23.77
				80	79.9165	49.61
				82	81.9167	8.73
Ru	2.2	8,6,4,3,2,0,-2	12.1	96	95.9076	5.54
				98	97.9053	1.87
				99	98.9059	12.76
				100	99.9042	16.60
				101	100.9056	17.06
				102	101.9043	31.55
				104	103.9054	18.62
Rh	2.28	5,4,3,2,1,0	12.4	103	102.9055	100
Pd	2.2	4,2,0	12	102	101.9056	1.02
				104	103.9040	11.14
				105	104.9051	22.33
				106	105.9035	27.33
				108	107.9039	26.46
				110	109.9052	11.72

Table 2. Chemical properties, isotopes, atomic abundances and geologically important isotope decay schemes of HSE and strongly chalcophile elements (Continued on next page).

Element	Electro- negativity*	Oxidation states	Density (g/cm ³)	Isotopes	Mass	Atomic Abundance	Comments
Te	2.1	6,4,-2	6.232	120	119.9040	0.09	
				122	121.9031	2.55	
				123	122.9043	0.89	
				124	123.9028	4.74	
				125	124.9044	7.07	
				126	125.9033	18.84	
				128	127.9045	31.74	
				130	129.9062	34.08	
Re	1.9	7,6,4,2,1	20.8	185	184.9530	37.4	
				187	186.9557	62.6	$4.16 \times 10^{+10} \text{ yr}^{-1}$
Os	2.2	8,6,4,3,2,0,-2	22.58	184	183.9525	0.02	
				186	185.9538	1.59	Partial decay product ¹⁹⁰ Pt
				187	186.9557	1.96	Partial decay product ¹⁸⁷ Re
				188	187.9558	13.24	
				189	188.9581	16.15	
				190	189.9584	26.26	
				192	191.9615	40.78	
Ir	2.2	6,4,3,2,1,0,-1	22.42	191	190.9606	37.3	
				193	192.9629	62.7	
Pt	2.2	4,2	21.46	190	189.9599	0.014	$4.5 \times 10^{+11} \text{ yr}^{-1}$
				192	191.9610	0.782	
				194	193.9627	32.967	
				195	194.9648	33.832	
				196	195.9649	25.242	
				198	197.9679	7.163	
Au	2.4	5,4,3,2,1,-1	19.282	197	196.9665	100	

Table 2 (**Cont'd**). Chemical properties, isotopes, atomic abundances and geologically important isotope decay schemes of HSE and strongly chalcophile elements.

* Pauling Units, where $E(AB) = [E(AA) \cdot E(BB)]^{1/2} + 96.48(X_A - X_B)^2$. E(AB) is expressed in kJmol⁻¹ (1 eV=96.48 kJmol⁻¹) and $X_A - X_B$ represents the difference in "electronegativity" between the two elements, whose individual electronegativities are given the symbols X_A and X_B . Comments denote geologically and cosmochemically relevant decay schemes. Data source: *http://ww.rsc.org/periodic-table*.

While this volume is not dedicated to the practical applications of the HSE and strongly chalcophile elements, it would be remiss not to briefly discuss the importance of these elements in society. All of these elements have found important societal use (Table 3), from the application of Au as a valued commodity in early societies, through to the present-day; the importance of S and Se in biological processes; the discovery and implementation of Pt, Pd, and subsequently other PGE to catalytic oxidation (Davy 1817), and the importance of the anti-cancer drug cisplatin (*cis*-[Pt(NH₃)₂Cl₂]) to anti-tumour treatments (e.g., Rosenberg et al. 1969). The use of the PGE, most especially Pt, Pd and Rh, in the automotive industry to generate harmless gases has caused some potential collateral effects; the possible environmental impact

Element	Major, current societal uses	World yearly production (in kg)	Estimated cost pure metal (USD/kg)
S	Production of H ₂ SO ₄ (Sulfuric Acid) for fertilizers, polyamides; fungicide; fumigant; vulcanization of natural rubber; gunpowder; bleaching; essential in many biological processes	>69,000,000,000	500
Se	Additive to glass; pigment for ceramics, paints, plastics; photovoltaic and photoconductive; dandruff shampoos; essential in many biological processes	2,000,000	610
Ru	Chip resistors and electrical contacts; electrochemical cells for Cl production; catalysts for production of ammonia and acetic acid; hardener for Pt and Pd alloys; jewelry	12,000	14,000
Rh	Catalytic convertors; catalyst for nitric acid, acetic acid and hydrogenation reactions; headlight reflectors; thermocouple elements; optical mirrors; optic fibre coatings	18,600	130,000
Pd	Catalytic convertors; jewelry; dental fillings and crowns; ceramic capacitors; gas hydrogenation/dehydrogenation reactions	250,000	58,330
Te	Used in alloys of copper or stainless steel, to improve machinability; additive in lead, making it more resistant to acid, improving strength and hardness; semiconductor applications	115,000	240
Re	Additive to W- and Mo-based alloys for filaments; electrical contact material; additive to nickel alloys for single-crystal turbine blades; hydrogenation of fine chemicals	50,000	16,000
Os	Used to produce very hard alloys for fountain pen tips, instrument pivots, needles and electrical contacts; catalyst in chemical processes	500	77,000
Ir	Most corrosion-resistant material. Special alloys; forms alloy with Os, used for pen tips and compass bearings; used in making the standard metre bar (90% Pt-10% Ir); contacts in spark plugs	10,000	42,000
Pt	Catalytic convertors; jewelry; catalyst for nitric acid, benzene, silicon production; electronic industry; chemotherapy; optical fibres; LCDs; turbine blades; spark plugs; pacemakers; dental fillings	200,000	130,000
Au	Bullion; jewelry; alloys; dentistry; electronic components; gold nanoparticles used as industrial catalysts (vinyl acetate, used to make PVA for glue/paint/resin, is made using a gold catalyst)	2,770,000	55,400

and human health-risks from available PGE in the environment (see Rauch and Morrison 2008, for a review). An entire volume can (and should!) equally be written on the utility of the HSE and strongly chalcophile elements during low-temperature geochemistry.

BASIC CONCEPTS AND TERMINOLOGY

Of the eight HSE, only Rh and Au are monoisotopic. Important data on Au and/or Rh abundances can be generated using non-isotope dilution methodologies, but the over-whelming majority of abundance data discussed in this volume for the HSE are for Re, Os, Ir, Ru, Pt, and Pd, which can be measured using isotope-dilution methodologies. Abundances of the strongly chalcophile elements, S, Se, and Te, can also be measured by isotope dilution. Isotope dilution studies to obtain abundances tend to use isotopically enriched tracers (typically ³⁴S, ⁷⁷Se, ⁹⁹Ru, ¹⁰⁵Pd, ¹²⁵Te, ¹⁸⁵Re, ¹⁹⁰Os, ¹⁹¹Ir, ¹⁹⁴Pt), followed by inductively coupled plasma mass spectrometry measurement. Isotopic studies of Os are described below and methods for determination of isotopic variations in other HSE and strongly chalcophile elements have been developed, but are not explicitly discussed here. The reader is referred to Meisel and Horan (2016, this volume), and associated references for details of these isotopic methodologies.

In addition to their strongly siderophile tendencies, HSE exhibit contrasting behaviors during melting, with the platinum-PGE (PPGE; Pt, Pd: melting temperature <2000 °C; Barnes et al. 1985), Re and Au typically being more incompatible during melting and crystallization, relative to the iridium–PGE (IPGE; Os, Ir, Ru: melting temperature >2000 °C; Barnes et al. 1985). For this reason, studies of the cosmochemical behavior of the HSE will often list the HSE in order of melting temperature of the pure metal, whereas studies using the HSE to investigate mantle melting processes will order the HSE according to relative incompatibility during melting. For mantle peridotites, there is general agreement that bulk peridotite-melt partition coefficients follow the sequence (e.g., Fischer-Gödde et al. 2011; Wang and Becker 2013; König et al. 2014):

$$Os \ge Ru \ge Ir > Rh \ge Pt > Pd > Au \ge Te > Se > S \ge Re$$

The ability of relative and absolute HSE abundances to record recent processes acting on rocks are complemented by the existence of the long-lived ¹⁹⁰Pt–¹⁸⁶Os (¹⁹⁰Pt \rightarrow ¹⁸⁶Os + α + Q; λ = 1.48×10⁻¹² a⁻¹; Walker et al. 1997) and ¹⁸⁷Re–¹⁸⁷Os (¹⁸⁷Re - ¹⁸⁷Os + β^- + \overline{v} ; λ =1.6668× 10⁻¹¹ a⁻¹; Selby et al. 2007) chronometers. Both long-lived radiogenically produced isotopes are minor constituents (¹⁸⁶Os=1.6%; ¹⁸⁷Os = 1.5%; Shirey and Walker, 1998) of osmium. In the case of the ¹⁸⁷Re–¹⁸⁷Os system, where ¹⁸⁷Re is a major isotope (62.6%) of rhenium, and has a half-life of 41.6 Ga, the range of natural materials spans several orders of magnitude and ¹⁸⁷Os/¹⁸⁸Os can reasonably range from a Solar System initial ratio of ~ 0.095 to nearly pure ¹⁸⁷Os derived from samples essentially devoid of Os and with high concentrations of Re (e.g., molybdenite; Luck and Allègre 1982). This characteristic means that the percent-level difference of ¹⁸⁷Os/¹⁸⁸Os between natural samples allows routine analysis of low Os abundance samples to percent precision or better, with the most widelyused method of analysis being negative thermal ionisation mass spectrometry (N-TIMS; Creaser et al. 1991; Völkening et al. 1991).

The generally accepted 'chondritic composition' for ¹⁸⁷Os/¹⁸⁸Os is 0.127 (Shirey and Walker 1998), although there are clear differences between carbonaceous chondrites (¹⁸⁷Os/¹⁸⁸Os = ~0.1262), relative to ordinary (¹⁸⁷Os/¹⁸⁸Os = ~0.1284), or enstatite chondrites (¹⁸⁷Os/¹⁸⁸Os = ~0.1280; Day et al. 2016, this volume). Chondritic evolution is established from the most primitive initial ¹⁸⁷Os/¹⁸⁸Os defined from early Solar System iron meteorites (initial ¹⁸⁷Os/¹⁸⁸Os = 0.09531) to the average chondritic composition for the present day. For these parameters, the average ¹⁸⁷Re/¹⁸⁸Os of chondrites is 0.40186. To calculate the ¹⁸⁷Os/¹⁸⁸Os of

chondrites at any time in the past-or future-the following equation can be used:

187
Os/ 188 Os_{time} = 187 Os/ 188 Os_{initial} + 187 Re/ 188 Os_{chondrite} ($e^{\lambda(456800000)} - e^{\lambda t}$)

where λ is equal to 1.6668×10^{-11} a⁻¹ (Selby et al. 2007). For ease of reference, studies will often report the percentage difference between the Os isotope composition of a samples and the average 'chondritic' composition for a specified time, γ_{Os} . Samples with positive γ_{Os} are often described as 'enriched', because it implies long-term elevated ¹⁸⁷Re/¹⁸⁸Os with respect to chondrites. Samples with negative γ_{Os} are often described as 'depleted', due to the opposite implication of long-term low ¹⁸⁷Re/¹⁸⁸Os, in the following way:

$$\gamma_{\rm Os} = \left(\left({}^{187}\text{Os}/{}^{188}\text{Os}_{\text{sample}(t)} / {}^{187}\text{Os}/{}^{188}\text{Os}_{\text{chondrite}(t)} \right) - 1 \right) \times 100$$

Model ages (MA) and relative rhenium depletion ages (RD) ages can all be calculated using the Re–Os isotope system (Fig. 3). Model ages (T_{MA}) represent the timing of separation from chondritic evolution and can be estimated for low Re/Os mantle materials, as well as high Re/ Os melts or crustal materials. The assumption with this method is that the Re/Os measured in the sample is an accurate reflection of its long-term history and has not been affected by later processes:

$$T_{\rm MA} = 1/\lambda \times \ln \left(\left(\frac{^{187}\,{\rm Os}/^{188}{\rm Os}_{\rm chondrite} - ^{187}\,{\rm Os}/^{188}{\rm Os}_{\rm sample}}{^{187}\,{\rm Re}/^{188}{\rm Os}_{\rm chondrite} - ^{187}\,{\rm Re}/^{188}{\rm Os}_{\rm sample}} \right) + 1 \right)$$

By contrast, time of relative Re depletion ages (T_{RD}) , which apply to low Re/Os mantle peridotites, does not rely on the Re/Os measured in the sample, which can be affected by recent Re addition. Instead this method uses sample compositions at the time of eruption and assumes that all of the Re in the sample was removed during melt-depletion. In reality, this method provides a minimum age for samples that have experienced melt-depletion:

$$T_{\rm RD} = 1/\lambda \times \ln\left\{ \left(\frac{\left[{}^{187} \text{Os}/{}^{188} \text{Os}_{\rm chondrite} - {}^{187} \text{Os}/{}^{188} \text{Os}_{\rm sample} \right]}{{}^{187} \text{Re}/{}^{188} \text{Os}_{\rm chondrite}} \right) + 1 \right\}$$

Due to potential disturbance from terrestrial weathering, or from cosmic-ray exposure affecting Re isotopic composition, studies of meteorites and planetary rocks have used Re*, which is the concentration of Re calculated assuming chondritic ¹⁸⁷Os/¹⁸⁸Os at the assumed time of sample crystallization (Day et al. 2010). This notation can be calculated as:

$$\operatorname{Re}^{*} = \frac{\left\{ \left(\left[\operatorname{Os} \right]_{\operatorname{sample}} / At \ \operatorname{wt}_{\operatorname{sample}} \right) \times \left({}^{187} \operatorname{Os} / {}^{188} \operatorname{Os}_{\operatorname{sample}} - {}^{187} \operatorname{Os} / {}^{188} \operatorname{Os}_{\operatorname{chondrite}(t)} \right) \right\}}{0.00336(\ln[\operatorname{Age} \times \lambda] - 1)}$$

By contrast with the ¹⁸⁷Re–¹⁸⁷Os decay system, ¹⁹⁰Pt is a minor isotope of Pt (0.01292%) and has a longer half-life (~450 Ga), so ¹⁸⁶Os/¹⁸⁸Os variations in the mantle are small and of the order of ~0.00015%, with an 'average' mantle value of 0.119837 ± 5 (2 σ). The typically minor variations of ¹⁸⁶Os/¹⁸⁸Os in volcanic settings require external analytical precision of better than 30 ppm. To obtain sufficient analytical precision, large quantities of Os are needed (typically 50–75 ng of Os) to generate sufficient signals on ¹⁸⁶Os given the ionization efficiency of Os by N-TIMS (~2–6%; Creaser et al. 1991). Inevitably, the analytical challenge of measuring ¹⁸⁶Os/¹⁸⁸Os means that there is far less data currently available than there is for ¹⁸⁷Os/¹⁸⁸Os.

The now-extinct ¹⁰⁷Pd was also the parent for ¹⁰⁷Ag in the early Solar System. This extinct radionuclide system had a half-life of 6.5 Ma (¹⁰⁷Pd – ¹⁰⁷Ag + β^- + $\overline{\nu}$; $\lambda = 1.06638 \times 10^{-7}$ a⁻¹; Parrington et al. 1996). The ¹⁰⁷Pd–¹⁰⁷Ag parent–daughter isotopic decay system is a candidate for use in both constraining the timing of early planetary fractionation events, for potentially



Figure 3. Solar System chronology versus ¹⁸⁷Os/¹⁸⁸Os. Shown in (a) is the chondritic evolution curve, curves corresponding to γ_{Os} values of +10 and +20, and the slopes of ¹⁸⁷Re/¹⁸⁸Os of 0.4 (~chondritic), 0.04 (sub-chondritic) and 200 (supra-chondritic). Examples of calculation of model ages and relative Re depletion ages are shown in (b). Example *a* shows an example of mantle-derived basaltic lava that evolved with high ¹⁸⁷Re/¹⁸⁸Os, which, when corrected, indicates a model-age of ~2.9 Ga. Example *b* shows a peridotite that experienced melt depletion. Based solely on the ¹⁸⁷Os/¹⁸⁸Os of the sample, a minimum T_{RD} age of ~3.6 Ga is obtained. If the Re/Os of the sample is considered to be representative and not affected by later addition of Re, then the T_{MA} can be calculated, giving a substantially older age of ~4 Ga. Example *c*, shows the case of a depleted peridotite xenolith that experienced infiltration of Re from the host melt, corrected for Re-ingrowth up to the eruption age (~0.25 Ga). In this scenario, the T_{RD} age of the xenolith prior to entrainment in the melt prevents a T_{MA} from being calculated.

determining whether Earth's core material is incorporated into mantle plumes, and for investigating the timing of volatile-element depletion in planets. The relatively short half-life renders the system sensitive to fractionation events occurring within the first 40 million years of Solar System history (i.e., Kelly and Wasserburg 1978). Because Pd is more siderophile than Ag, planetary differentiation should result in an enrichment of Pd relative to Ag in planetary cores. If this happened during the lifetime of ¹⁰⁷Pd, a correspondingly high ¹⁰⁷Ag core signature would develop. If Earth's differentiation occurred within 40 million years (approximately five half-lives) of the beginning of the Solar System, an isotopic excess of ¹⁰⁷Ag should exist within the core. Equally, because Ag is a moderately volatile element, whereas Pd is more refractory than Ag, large ranges in Pd/Ag have been observed in volatile-depleted iron meteorites (up to 100,000), compared with a Solar Pd/Ag of ~3, leading to ¹⁰⁷Ag/¹⁰⁹Ag ratios >9, compared with the solar value of 1.079 (Chen and Wasserburg 1996). For the Pd–Ag isotope system, the initial ¹⁰⁷Pd/¹⁰⁸Pd has been determined as $5.9 \pm 2.2 \times 10^{-5}$ (Schönbächler et al. 2008), with ¹⁰⁷Ag/¹⁰⁹Ag typically reported in parts per ten thousand notation relative to the NIST SRM978a silver standard (¹⁰⁷Ag/¹⁰⁹Ag=1.07976):

$$\varepsilon^{107} Ag = \left(\left[{}^{107} Ag / {}^{109} Ag_{sample} / {}^{107} Ag / {}^{109} Ag_{NIST SRM978a} \right] - 1 \right) \times 10,000$$

FUNDAMENTAL PROCESSES AND OUTLINE OF THE VOLUME

In this volume, a number of key areas are reviewed in the use of the HSE and strongly chalcophile elements to investigate fundamental processes in high-temperature geochemistry and cosmochemistry. It is divided into five parts. The first part of the volume concerns measurements and experiments. Chapter 1, by Brenan et al. (2016), provides an comprehensive overview of experimental constraints applied to understanding HSE partitioning under a range of conditions, including: liquid metal–solid metal; metal–silicate; silicate–melt; monosulfide solid solution (MSS)–sulfide melt; sulfide melt–silicate melt; silicate melt–aqueous fluid–vapor. Chapter 2, by Meisel and Horan (2016) provides a summary of analytical methods, issues specifically associated with measurement of the HSE, and a review of important reference materials.

The second part of the volume concerns the cosmochemical importance of the HSE and strongly chalcophile elements. In their assessment of nucleosynthetic isotopic variations of siderophile and chalcophile elements in Solar System materials, Yokoyama and Walker (2016, Chapter 3) discuss some of the fundamentals of stellar nucleosynthesis, the evidence for nucleosynthetic anomalies in pre-Solar grains, bulk meteorites and individual components of chondrites, ultimately providing a synthesis on the different information afforded by nucleosynthetic anomalies of Ru, Mo, Os, and other siderophile and chalcophile elements. Chapter 4 concerns the HSE in terrestrial bodies, including the Earth, Moon, Mars and asteroidal bodies for which we have materials as meteorites. Day et al. (2016) provide a summary of HSE abundance and ¹⁸⁷Os/¹⁸⁸Os variations in the range of materials available and a synthesis of initial Solar System composition, evidence for late accretion, and estimates of current planetary mantle composition.

The third part of the volume concerns our understanding of the Earth's mantle from direct study of mantle materials. In Chapter 5, Aulbach et al. (2016) discuss the importance and challenges associated with understanding HSE in the cratonic mantle, providing new HSE alloy solubility modelling for melt extraction at pressures, temperatures, f_{0_2} and f_{s_2} pertaining to conditions of cratonic mantle lithosphere formation. Luguet and Reisberg (2016) provide similar constraints on non-cratonic mantle in Chapter 6, emphasizing the importance of combined geochemical and petrological approaches to fully understand the histories of mantle peridotites. The information derived from studies of Alpine peridotites, obducted ophiolites and oceanic abyssal peridotites are reviewed in Chapter 7 by Becker and Dale (2016).

The fourth part of the volume focusses on important minerals present in the mantle and crust. Chapter 8 provides a broad overview of mantle chalcophiles. In this chapter, Lorand et al. (2016) emphasise that chalcophile and siderophile elements are important tracers that can be strongly affected by host minerals as a function of sulfur-saturation, redox conditions, pressure, temperature, fugacity of sulfur, and silicate melt compositions. Along a similar theme in Chapter 9, O'Driscoll and Gonzalez-Jimenez (2016) provide an overview of platinum-group minerals (PGM), pointing out that, where present PGM dominate the HSE budget of silicate rocks. Finally in this section, Harvey et al. (2016) examine the importance of Re–Os–Pb isotope dating methods of sulfides for improving our understanding of mantle processes (Chapter 10).

The fifth and final part of the volume considers the important of the HSE for studying volcanic and magmatic processes. In Chapter 11, Gannoun et al. (2016) provide a synthesis of the most abundant forms of volcanism currently operating on Earth, including mid-ocean ridge basalts, volcanism unassociated with plate boundaries, and subduction zone magmatism. The volume is completed in Chapter 12 by Barnes and Ripley (2016), by an appraisal of the obvious importance of magmatic HSE ore formation in Earth's crust.

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Highly Siderophile and Strongly Chalcophile Elements in High-Temperature Geochemistry and Cosmochemistry

81 Reviews in Mineralogy and Geochemistry 81

TABLE OF CONTENTS

Iames M. Brenan Neil R. Bennett, Zoltan Zajacz

1 Experimental Results on Fractionation of the Highly Siderophile Elements (HSE) at Variable Pressures and Temperatures during Planetary and Magmatic Differentiation

	,
INTRODUCTION AND SCOPE	1
SOLID METAL-LIQUID METAL PARTITIONING	2
EXPERIMENTAL APPROACH TO	
SOLID METAL–LIQUID METAL PARTITIONING (D ^{SM/LM})	3
HSE SOLUBILITY EXPERIMENTS:	
IMPLICATIONS FOR METAL-SILICATE PARTITIONING	13
CALCULATING THE METAL–SILICATE MELT	
PARTITION COEFFICIENT FROM SOLUBILITY DATA	14
Controls on the metal-silicate partition coefficient	15
Metal inclusions in experiments and the analysis of contaminated phases	16
Possible mechanisms of metal inclusion formation	17
Experimental methods to measure HSE solubility and metal-silicate partitioning	21
Summary of experimental data	22
Application of results to core formation	33
SILICATE AND OXIDE CONTROL ON HSE FRACTIONATION	35
Experimental approach	35
Spinel-melt partitioning of HSEs	36
Silicate mineral-melt partitioning of HSEs	38
Origin of the variation in partitioning	40
Local PGM saturation during chromite growth	43
MAGMATIC SULFIDE AND ASSOCIATED PHASES	44
Experimental approach	45
MSS-sulfide melt partitioning	48
MSS–ISS–sulfide melt partitioning	51

Sulfide melt-silicate melt and MSS-silicate melt partitioning	51
Role of the chalcogens (Se, Te, As, Bi, Sb)	61
SILICATE MELT-AQUEOUS LIQUID-VAPOR PARTITIONING	63
Theoretical considerations	64
Experimental methods	65
The volatile/melt partitioning of Au	68
The volatile/melt partitioning of PPGE	71
The volatile/melt partitioning of IPGE and Re	72
CONCLUDING REMARKS	73
ACKNOWLEDGMENTS	73
REFERENCES	74

2

Analytical Methods for the Highly Siderophile Elements

Thomas Meisel, Mary F. Horan

INTRODUCTION	
DATA QUALITY CONSIDERATIONS FOR THE HSE	
Sample heterogeneity and reproducibility	
MEASUREMENT PROCEDURES	
Chemical separation of HSE	
REFERENCE MATERIALS FOR HSE ANALYSIS	
APPENDIX	
REFERENCES	

3

Nucleosynthetic Isotope Variations of Siderophile and Chalcophile Elements in the Solar System

Tetsuya Yokoyama, Richard J. Walker

INTRODUCTION	107
ORIGIN OF ELEMENTS: STELLAR NUCLEOSYNTHESIS	109
Production of elements from He to Fe via hydrogen to silicon burning	109
PRESOLAR GRAINS	117
Types of presolar grains and their origin	119
ISOTOPE ANOMALIES OF SIDEROPHILE AND CHALCOPHILE ELEMENTS	
IN BULK METEORITES	126
Isotope anomalies of siderophile elements in bulk meteorites	128
Isotope anomalies of chalcophile elements in bulk meteorites	138
INTERNAL ISOTOPE ANOMALIES PRESENT IN CHONDRITES	140
CAIs	140
Acid leachates and residues	142
Isotopic constraints on the s-process nucleosynthetic component.	148
ORIGIN OF PLANETARY SCALE	
ISOTOPE ANOMALIES IN METEORITES	150
CONCLUDING REMARKS	152
ACKNOWLEDGMENTS	152
REFERENCES	153

4

Highly Siderophile Elements in Earth, Mars, the Moon, and Asteroids

James M.D. Day, Alan D. Brandon, Richard J. Walker

INTRODUCTION	161
MOTIVATION FOR STUDY AND BEHAVIOR OF THE	
HSE IN PLANETARY MATERIALS	163
METHODS APPLIED TO INVESTIGATING SIDEROPHILE	
ELEMENTS IN PLANETARY MATERIALS	164
HSE ABUNDANCES	164
The rhenium-osmium, platinum-osmium and palladium-silver isotope systems	166
Standardization in planetary studies	168
Metal-sulfide-silicate modeling in chondritic systems	168
Partial melt modeling of planetary mantles	172
"Pristinity" of crustal and mantle samples	174
Estimation of planetary mantle composition	175
What do chondritic or nearly/broadly chondritic actually mean?	179
PLANETARY MATERIALS	181
Early Solar System materials	181
Fragments of planetary cores and/or metal-rich melt pools	187
Primitive achondrite meteorites	191
Meteorites from differentiated asteroids	195
Mars	198
The Moon	201
Terrestrial mantle composition	209
Secondary alteration effects	210
PLANETARY FORMATION PROCESSES	212
Initial conditions and homogeneity of starting materials	212
Partial melting and partitioning of the HSE	214
Core crystallization	216
'Late-accretion'	216
Alternative hypotheses for the abundances of the HSE in planetary mantles	218
Magmatic processes	220
Later impacts into planetary crusts	221
COMPARATIVE PLANETOLOGY AND IMPLICATIONS	
FOR TERRESTRIAL FORMATION	222
FUTURE DIRECTIONS	226
ACKNOWLEDGEMENTS	227
REFERENCES	227

5

Distribution and Processing of Highly Siderophile Elements in Cratonic Mantle Lithosphere

Sonja Aulbach, James E. Mungall, D. Graham Pearson

INTRODUCTION	
THE CRATONIC MANTLE SAMPLE: PECULIARITIES, OPPORTUNITIES	
AND PITFALLS	

DATABASE	
MINERALOGY AND HSE HOSTS	
IN CRATONIC MANTLE PERIDOTITES	
ANALYTICAL TECHNIQUES FOR CRATONIC MANTLE PERIDOTITES	
Whole rocks and mineral separates	
Single-grain techniques	252
UTILIZATION OF THE RE-OS ISOTOPE SYSTEM	
IN CRATONIC MANTLE STUDIES	253
EFFECT OF MELT DEPLETION DURING CRATONIC LITHOSPHERE	
STABILIZATION ON SULFUR AND HSE SYSTEMATICS	255
Sulfur and the persistence of sulfides	255
Alloy saturation	256
Chalcogens	
HSE PROCESSING DURING MANTLE METASOMATISM	
Modification during intraplate mantle metasomatism	
Modification during craton margin processes—subduction	
MODELLING OF PRIMARY VS. SECONDARY HSE SIGNATURES	
IN CRATONIC MANTLE	
HSE Concentrations of the Archean convecting mantle (ACM)	
Modelling Rationale	
Effects of partial melt extraction on HSE based on modelling	
Post-core formation, sluggish downward mixing of a late veneer	
SUMMARY	
ACKNOWLEDGMENTS	
REFERENCES	



Highly Siderophile Element and ¹⁸⁷Os Signatures in Non-cratonic Basalt-hosted Peridotite Xenoliths: Unravelling the Origin and Evolution of the Post-Archean Lithospheric Mantle

Ambre Luguet, Laurie Reisberg

INTRODUCTION	305
CONSTRAINING THE HSE AND ¹⁸⁷ Os/ ¹⁸⁸ Os ISOTOPIC COMPOSITION	
OF THE PRIMITIVE BULK SILICATE EARTH	306
PETROLOGY AND LOCATION OF	
NON-CRATONIC PERIDOTITE XENOLITHS	308
A BRIEF REVIEW OF HSE AND Os ISOTOPE ANALYTICAL METHODS AND	
HSE NORMALIZATION VALUES	309
HOST MINERALS OF HIGHLY SIDEROPHILE ELEMENTS IN NON-CRATONIC	
PERIDOTITE XENOLITHS	311
Nature of the host minerals	311
Petrography of the base metal sulfides	312
Origin of the base metal sulfides and platinum group minerals	315
HIGHLY SIDEROPHILE ELEMENTS AND ¹⁸⁷ Os/ ¹⁸⁸ Os RESULTS FROM	
NON-CRATONIC PERIDOTITE XENOLITHS	316
Summary of results from whole-rock studies	317

Summary of results from base metal sulfides and other mineral phases	321
Reconciling ¹⁸⁷ Os/ ¹⁸⁸ Os results from whole-rock and base metal sulfide analyses .	326
THE LIFE OF A XENOLITH, AS RECORDED IN HSE- AND OS-ISOTOPE	
SYSTEMATICS	327
The HSE and ¹⁸⁷ Os composition of the Primitive Upper Mantle	328
Whole-rock observations on samples representing melting residues	330
Mineralogical control of HSE fractionation during partial melting	332
Ancient melt-extraction events recorded by ¹⁸⁷ Os/ ¹⁸⁸ Os systematics	335
Post-melting petrological history	336
Syn- to post-eruptive processes	350
CHRONOLOGICAL INTERPRETATION OF OS-ISOTOPIC DATA AND TECTONIC	
IMPLICATIONS	351
Obtaining age information from Os isotopes of whole rocks	351
Obtaining age information from Os isotopes of base metal sulfides	354
Tectonic interpretation of Os model ages	355
CONCLUSIONS	356
ACKNOWLEDGEMENTS	358
REFERENCES	358

7 Re–Pt–Os Isotopic and Highly Siderophile Element Behavior in Oceanic and Continental Mantle Tectonites

Harry Becker, Christopher W. Dale

INTRODUCTION	.369
BREVIA OF CONCEPTS, TERMINOLOGY, AND ANALYTICAL CAVEATS	.370
Re–Pt–Os parameters	.370
Normalization of concentration data	.370
Precision and accuracy of concentration data and analytical issues	.371
HIGHLY SIDEROPHILE ELEMENTS IN MANTLE TECTONITES FROM	
DIFFERENT GEODYNAMIC SETTINGS	.371
Summary of mantle tectonites and their geodynamic settings	.371
HSE IN ABYSSAL PERIDOTITES FROM SPREADING OCEANIC LITHOSPHERE.	.374
HSE in mantle tectonites from continental extensional domains and	
continent-ocean transitions	.380
HSE in ophiolites that formed at fast spreading ridges with little or no influence	
from subduction processes	.386
High-temperature orogenic peridotites from convergent plate margin settings	.388
Highly siderophile elements in peridotites and melt-reacted lithologies of	
ophiolites influenced by convergent plate margin magmatism	.392
Highly siderophile elements in the mantle sections of ophiolites of uncertain	
origin	.398
DISCUSSION	. 399
Influence of low-temperature alteration processes on the HSE in bulk rocks	200
and minerals	. 399
menula testerites	402
Summery Months malting and months magnetinterestion different sides	.402
of the same coin	116
Or the same colling of the mentle	.410
Os isotopic neterogeneity in the manue	.+10

The role of recycled oceanic lithosphere in producing HSE and Os isotope	
signatures in magmas	423
The relationship between abyssal peridotites and MORB: an osmium isotope	
perspective	426
Interpretation of Re–Os model ages	427
ACKNOWLEDGMENTS	429
REFERENCES	430

8

Chalcophile and Siderophile Elements in Mantle Rocks: Trace Elements Controlled By Trace Minerals

Jean-Pierre Lorand, Ambre Luguet

INTRODUCTION	441
BACKGROUND	442
Sulfides in the upper mantle and mantle rocks	443
Abundance and phase control on chalcophile and siderophile elements in the	
fertile upper mantle	446
Partial melting of the mantle: a BMS-removing and PGM producing	
petrogenetic process.	458
Chalcophile/siderophile element systematics in pyroxenites	466
Low-pressure BMS dissolution in regional-scale open system melting of the	
sub-continental lithospheric mantle	469
BMS precipitation associated with magma percolation/metasomatism	472
Platinum-group minerals and magmatic percolation of the lithospheric mantle	475
CONCLUDING REMARKS	480
ACKNOWLEDGMENTS	481
REFERENCES	481

9

Petrogenesis of the Platinum-Group Minerals

Brian O'Driscoll, José María González-Jiménez

INTRODUCTION	
PHASE RELATIONS AND ORIGIN OF THE PGM	
Chemical properties of the PGM	
Extraterrestrial occurrences of the PGM	
Origin of the terrestrial PGM: Mantle melting, metasomatism, and metal tran	sfer495
PGM IN LAYERED MAFIC-ULTRAMAFIC INTRUSIONS	498
Chromitite-hosted layered intrusion PGM	498
Non-chromitite-hosted PGM in layered intrusions	507
PGM IN OPHIOLITES	516
PGM in ophiolite peridotites	516
PGM in ophiolite chromitites	518
PGM in sulfide-rich ophiolite lithologies	530
PGM IN PERIDOTITES OF THE	
SUBCONTINENTAL LITHOSPHERIC MANTLE	531
Subcontinental lithospheric mantle peridotite massifs	531
SCLM peridotite xenoliths	532

PGM IN CONCENTRICALLY ZONED	
URALIAN-ALASKAN-ALDAN-TYPE COMPLEXES	
PGM in dunite, pyroxenite and gabbro	
Chromitite-hosted PGM in CUAAC	
PGM and sulfide mineralization in CUAAC	539
PGM IN NI-SULFIDE DEPOSITS	
Komatiite-associations	
Magmatic Ni-(±Cu-±PGE)-sulfide deposits in non-komatiitic rocks	
EXAMPLES OF UNCONVENTIONAL PGM OCCURRENCES	
Kimberlite- and Cu-porphyry-hosted PGM	
OUTLOOK AND FUTURE WORK	
Assessing the mineralogical and textural complexity of PGM assemblages	
Constraints on quantifying the distribution and grain size of PGM	
Advancing our understanding of the link between PGM assemblage and	
PGE geochemistry	553
ACKNOWLEDGEMENTS	
REFERENCES	
APPENDIX	
PGM in placers associated with ophiolite complexes	
PGM mineralization in CUAAC placer deposits	
REFERENCES	
4.0	

10

Mantle Sulfides and their Role in Re–Os and Pb Isotope Geochronology

Jason Harvey, Jessica M. Warren, Steven B. Shirey

INTRODUCTION	579
BACKGROUND	581
ANALYTICAL METHODS AND PRACTICAL ASPECTS	
OF SAMPLE PREPARATION	585
BASE-METAL SULFIDE OCCURRENCE, MAJOR ELEMENT GEOCHEMISTRY	
AND PETROLOGY	589
Peridotite-hosted sulfides	592
Pyroxenite-hosted sulfides	603
Diamond-hosted sulfides	606
Re-Os-Pb MASS BALANCE IN ULTRAMAFIC SAMPLES	610
Osmium mass balance	610
Rhenium mass balance.	613
Lead mass balance	614
GEOCHRONOLOGICAL METHODS, MODEL AGES,	
AND POTENTIAL PITFALLS.	615
Sulfide Re–Os isochrons, T_{MA} , T_{RD} , and γOs	615
Potential pitfalls with sulfide geochronology.	620
THE UTILITY OF Re-Os AND Pb ISOTOPE GEOCHRONOLOGY	626
Dating the formation of diamonds	626
Diamond formation through time	628
The age of the continental lithospheric mantle and the assembly of its domains	628
The relationship between the age of the SCLM and the overlying crust	630

The inherent heterogeneity within the oceanic mantle	
CONCLUDING REMARKS AND FUTURE DIRECTIONS	635
ACKNOWLEDGMENTS	
REFERENCES	635

11 Highly Siderophile Element and Os Isotope Systematics of Volcanic Rocks at Divergent and Convergent Plate Boundaries and in Intraplate Settings

Abdelmouhcine Gannoun, Kevin W. Burton, James M.D. Day, Jason Harvey, Pierre Schiano, Ian Parkinson

INTRODUCTION	
HIGHLY SIDEROPHILE ELEMENT DISTRIBUTION AND BEHAVIOR	
IN THE UPPER MANTLE	654
Core formation and the late accretion of impactor material	654
Highly siderophile elements in mantle minerals	655
Highly siderophile element behavior accompanying fractional crystallization	
THE ¹⁸⁷ Re– ¹⁸⁷ Os ISOTOPE SYSTEM AND THE FORMATION OF	
MID-OCEAN RIDGE BASALT (MORB)	
Introduction	661
Analytical techniques	662
Rhenium-Osmium elemental variations in MORB glass	663
The ¹⁸⁷ Os/ ¹⁸⁸ Os isotope variations in MORB glass	
Analytical issues associated with MORB	668
SULFIDES IN MID-OCEAN RIDGE BASALTS	677
Petrology and chemistry	677
¹⁸⁷ Re– ¹⁸⁷ Os behavior in MORB sulfide	680
The ¹⁸⁷ Os/ ¹⁸⁸ Os composition of the MORB mantle source	682
LOWER OCEANIC CRUST	
Assimilation of gabbroic lower crust	686
HSE ABUNDANCES AND Re–Os ISOTOPE SYSTEMATICS	
OF INTRAPLATE VOLCANISM	686
Mantle melting processes	687
Osmium isotopes as tracers of hotspot sources	688
Crustal and lithospheric mantle assimilation/contamination	691
The origin of Continental Flood Basalts (CFB) and	
Large Igneous Provinces (LIP)	693
Continental intraplate alkaline volcanism	696
Processes affecting the HSE compositions of sub-aerial volcanism	699
HIGHLY SIDEROPHILE ELEMENT SYSTEMATICS OF ARCS	700
HSE and ¹⁸⁷ Os/ ¹⁸⁸ Os in arc lavas	700
HSE and ¹⁸⁷ Os/ ¹⁸⁸ Os in arc xenoliths	704
Radiogenic Os from slab components or from crustal contamination	705
Mechanical mixing processes	706
CONCLUSIONS AND PERSPECTIVES	707
ACKNOWLEDGMENTS	708
REFERENCES	

12 Highly Siderophile and Strongly Chalcophile Elements in Magmatic Ore Deposits

Sarah-Jane Barnes, Edward M. Ripley

INTRODUCTION	725
CLASSIFICATION OF THE DEPOSITS	731
Reef or stratiform deposits	731
Contact deposits	731
Ni-sulfide deposits	732
MINERALS HOSTING THE PLATINUM-GROUP ELEMENTS	734
Base metal sulfides	734
Platinum-group minerals	737
Chromite	738
Mass Balance	738
GEOCHEMISTRY	739
Introduction	739
Normalization to mantle or chondrite?	740
Recalculation to 100% Sulfides or whole rock	740
Other chalcophile elements	742
INTERPRETATION	743
Composition of the silicate melt	743
Saturation of the magma in a sulfide liquid	746
Upgrading of the Sulfides	747
Crystallization of a sulfide liquid	752
Late magmatic fluids	754
Subsolidus events	755
UTILIZATION OF THE Re–Os ISOTOPE SYSTEM IN STUDIES OF MAGMATIC	
Ni–Cu–PGE ORE GENESIS	756
Background	756
The " <i>R</i> -factor" and its application to Re–Os isotopes	759
Examples of the application of the Re-Os isotope system	
to magmatic ore deposits	759
CONCLUSIONS	765
ACKNOWLEDGMENTS	766
REFERENCES	766

Experimental Results on Fractionation of the Highly Siderophile Elements (HSE) at Variable Pressures and Temperatures during Planetary and Magmatic Differentiation

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INTRODUCTION AND SCOPE

The platinum-group elements (PGEs; Os, Ir, Ru, Rh, Pt, Pd), along with rhenium and gold, are grouped together as the highly siderophile elements (HSEs), defined by their extreme partitioning into the metallic, relative to the oxide phase (>10⁴). The HSEs are highly refractory, as gauged by their high melting and condensation temperatures, and were therefore relatively concentrated in the feedstock for the terrestrial planets, as defined by the composition of chondritic meteorites (e.g., Anders and Ebihara 1982; Horan et al. 2003; Fischer-Gödde et al. 2010). However, the planetary formation and differentiation process has since acted on this chemical group to produce a rich variety of absolute and relative inter-element fractionations. For example, analysis of iron meteorites suggests a significant decoupling of the HSE in the cores of planetesimals, and likely Earth's core, with Os, Ir, Ru (IPGE-group) and Re concentrated in the metal phase, and Pt, Rh, Pd (PPGE-group) plus Au usually concentrated in the residual liquid (Goldstein et al. 2009). In terms of the silicate Earth, analysis of mantle rocks reveals very low levels of the HSE, but relative abundances similar to chondrites (see review by Day et al.

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2016, this volume), in part reflecting HSE segregation into core-forming iron (Ringwood 1966; Ganapathy et al. 1970). This is in contrast to mantle-derived melts, whose HSE abundances are highly fractionated, with relative depletions in the IPGE-group compared to PPGE-group, as well as Re and Au (Barnes et al. 1985). Resulting Re/Os and Pt/Os fractionation also influence the long-term evolution of the ¹⁸⁷Re to ¹⁸⁷Os and ¹⁹⁰Pt to ¹⁸⁶Os decay systems, and, hence, the development of distinctive Os-isotope reservoirs (Walker et al. 1997; Shirey and Walker 1998; Day 2013). The emplacement of mantle-derived magmas into Earth's crust results in a further decoupling of the HSE suite. Crystallization of mafic and ultramafic magmas appears to leave the IPGE in magmatic cumulates, while concentrating the PPGEs, Re and Au in the more differentiated products (e.g., Brugmann et al. 1987; Puchtel and Humayan 2001, 2005). The onset of sulfide liquid saturation in these systems can produce a wholesale reduction of HSE concentrations in the silicate melt, reflecting the highly chalcophile nature of this element suite. Magmatic sulfide liquids may differentiate internally, with further concentration of the IPGEs and Re into accumulations of the early formed monosulfide solid solution (MSS), and subsequent enrichment in the liquid residue in the PPGEs and Au (Barnes and Ripley 2016, this volume). As the silicate magma differentiates further, an orthomagmatic fluid may develop, possibly disturbing the primary distribution of the HSE within the pile of accumulated solids (e.g., Boudreau et al. 1986; Boudreau and Meurer 1999). More evolved magmas emplaced at a high level in the crust, or even erupted, may have some of their remaining HSE collected into a low-density vapor phase, which may be deposited in a hydrothermal stockwork (Richards 2011), or dispersed into the atmosphere during volcanic eruptions (e.g., Naughton et al. 1976; Zoller et al. 1983; Toutain and Meyer 1989; Crocket 2000; Yudovskay et al. 2008). Hence, the HSE are not only fractionated during planetary differentiation, but during this process, these elements may exhibit four out of the five geochemical classifications originally proposed by Goldschmidt (1958; Table VI, page 25); concentration in the core, and magmatic sulfides (siderophile and chalcophile), partitioning into silicates/oxides (lithophile), and expulsion in volcanic emanations (atmophile). In order to make full use of this unique suite of elements to understand the planetary differentiation process, information on their partitioning amongst solid/liquid iron metal, sulfide, silicate, oxide phases, and vapour/fluid, as well as the stability of HSE-bearing accessory phases is required. The advent of procedures to detect very low concentrations of the HSE in these various phases has greatly expanded our empirical understanding of this behavior (Meisel and Horan 2016, this volume), but significant uncertainties still remain. Laboratory experiments offer a complimentary approach to the empirical studies, providing constraints on the nature of HSE fractionation involving specific phases, and variation with intensive parameters. This chapter provides a review of that work, with an emphasis on results pertaining to processes occurring mostly at the magmatic stage. For each of the experimental systems considered, we have provided some information on how the experiments are done, the methods of analysis and attempt to place the results in a theoretical framework.

SOLID METAL-LIQUID METAL PARTITIONING

Studies of the iron meteorites have shown large variations in both the relative and absolute abundances of the HSE (e.g., McCoy et al. 2011; see review by Day et al. 2016, this volume). In part, this variation may derive from differences in the bulk HSE composition of the meteorite parent bodies, but significant differences exist within groups derived from a single parent body, reflecting the role of internal differentiation processes (e.g., Scott 1972; Scott and Wasson 1976; Goldstein et al. 2009). So-called non-magmatic iron meteorites (Types IAB and IIICD) are thought to derive by impact melting of planetesimals, with the variation in HSE concentrations due to mixing of different melt fractions (e.g., Choi et al. 1995). In contrast, HSE variation in the magmatic iron group is consistent with crystal–liquid fractionation during solidification of the parent body core; as mentioned, segregating metal concentrating the IPGE

and Re, with enrichments in the PPGE+Au in residual melt (e.g., Scott 1972; Pernicka and Wasson 1987; Walker et al. 2008; Goldstein et al. 2009). Studies of the magmatic iron group have also emphasized the possible role of non-metal components, such as S, C, Si, and P, in affecting the solid metal-liquid metal partitioning, as accessory phases containing those elements are ubiquitous (Goldstein et al. 2009). This is also consistent with the need for a light-element component in the cores of the terrestrial planets, in order to explain their density deficit, and to satisfy cosmochemical constraints (Dreibus and Wanke 1985; McSween 1994; McDonough 2003). Laboratory experiments of solid metal-liquid metal partitioning have provided the means to verify the core crystallization model for the magmatic irons, and also inform about the effects of non-metal components (Willis and Goldstein 1982; Chabot and Drake 1999; Goldstein et al. 2009) as well as the influence of the crystalline metal (Van Orman et al. 2008; Stewart et al. 2009; Rai et al. 2013) on HSE distribution during solidification. Also, a major focus of study in recent years has been the relative fractionation of Re/Os and Pt/Os arising from inner core solidification, which bears on the development of deep planetary reservoirs with distinct ¹⁸⁷Os/¹⁸⁸Os and ¹⁸⁶Os/¹⁸⁸Os isotopic compositions (e.g., Walker et al. 1995, 1997; Brandon et al. 1998). The following sections outline the parameterizations used to describe variation in the solid-metal/liquid metal partition coefficient, D^{SM/LM}, as a function of either liquid metal composition or solid metal structure. Several considerations for experiments at both ambient and high pressure are first described.

EXPERIMENTAL APPROACH TO SOLID METAL-LIQUID METAL PARTITIONING (D^{SM/LM})

Past studies have focused on the separate roles of the liquid and solid phases on controlling the absolute and relative magnitudes of $D^{\text{SM/LM}}$. The structure of solid Fe is expected to undergo changes due to both pressure and the incorporation of light elements. The consequences of increasing pressure are manifold, including control on the stable atomic arrangement (e.g., the FCC to HCP transition at high *T*; Komabayashi et al. 2009), unit cell volume, and effect on the solubility of light elements in the Fe-metal structure (e.g., Zhang and Fei 2008). Although temperature is likely to play a second-order role, most experimental data have been acquired at conditions significantly cooler than those expected to accompany core crystallization in larger planetary bodies. This makes *T* worthy of investigation in future work. Outlined here are several different experimental approaches that have been used to determine $D^{\text{SM/LM}}$ over a range of P-T-X conditions.

Most of the early experimental studies of HSE partitioning in solid metal-liquid metal systems were conducted at 0.1 MPa and temperatures corresponding to the Fe(+Ni) - X liquidus, with X being C, S, O, Si, and P, with more recent work focusing on the effect of pressure. The primary concerns for experiments in the Fe-rich systems of interest here are the attainment of equilibrium and the potential for reaction between the container material and the charge. The compositional space that can be accessed is governed by phase relations in the chosen system and must also be considered in the experimental design. For experiments done at ambient pressure, there is the additional consideration of volatile element loss from the sample. With these in mind, the experimental protocol adopted for experiments to determine siderophile element partitioning at ambient pressure in the Fe±S,P,C systems has remained essentially unchanged since the pioneering experiments of Drake et al. (1978). The light element components are typically introduced to starting materials as Fe-sulfide, elemental phosphorus and graphite powder, for S, P, and C, respectively, which are mixed and ground with metallic Fe, Ni, and typically one HSE dopant at the wt% level (e.g., Jones and Drake 1983; Malvin et al. 1986; Chabot et al. 2006), although multiple HSE can be added at ppm levels. As shown by Fleet et al. (1999), constant partitioning is obtained over the ppm to wt% concentration range. The most commonly



Figure 1. (a) Experimental arrangement used to perform equilibrium partitioning experiments in solid metal–liquid metal systems at 0.1 MPa. (b) Back scattered electron images of the run-product texture from an experiment at 0.1 MPa and 1350 °C. When quenched, the liquid portion of the sample unmixes to produce sulfur-rich (darker) and sulfur-poor (brighter) domains in the sample.

employed crucible material is vitreous alumina, as it is unreactive with the alloy phase and stable to the required temperatures (e.g., Drake et al. 1978; Jones and Drake 1983). Owing to the volatile nature of the light element additives, most past experiments at low pressure have been done in evacuated and sealed silica glass ampoules (Fig. 1a), although some early results (free of S and P) were obtained with open crucibles in contact with an Ar–H₂ atmosphere (Willis and Goldstein 1982; Jones and Drake 1983).

In order to aid sample homogenization and reduce the time required for equilibrium, some studies have employed a superliquidus step lasting for several hours, then cooling to the intended equilibration temperature of the experiment (Drake et al. 1978; Chabot et al. 2006, 2007). Typical experiment durations are between 12 and 200 h (e.g., Chabot et al. 2006, 2007), although runs as short as 5 h appear to be sufficient for equilibrium in the Fe–Ni–S–P system at 0.1 MPa and 1250 °C (Malvin et al. 1986). Experiments are terminated by immersing the sample in cold water. Although the rate of heat loss is high, quenching an iron-rich liquid containing S, P or C by this method still results in precipitation of a heterogeneous intergrowth of Fe-rich metal with a light element-rich component (Fig. 1b). In order to obtain an average composition of the quenched melt phase, run product analysis by electron microprobe, or more recently by LA-ICPMS, employs a defocused or rastered beam.

Certain experimental systems offer unique challenges. Phase relations in the Fe–Si system show that for compositions more Fe-rich than the eutectic that exists between Fe and Fe₂Si, the solid and liquid alloy phases contain similar quantities of Si (Kubaschewski 1982). Isolating the effect of liquid composition on partitioning is therefore not straightforward. To circumvent this problem, Chabot et al. (2010) conducted experiments in the Fe–S–Si system and monitored trace element distribution between immiscible melt pairs; one rich in the S and the other in Si. By comparison to the well-established effects of S on partitioning, the role of Si could be evaluated independently. The effect of oxygen on $D^{SM/LM}$ has also been difficult to evaluate, as the solubility of oxygen in molten Fe is diminishingly small at low pressure. However, work by Naldrett (1969), and later by Fonseca et al. (2008), has shown that the

oxygen content of molten Fe–S can reach several wt%. Taking advantage of this effect, Chabot et al. (2015) measured partitioning in the Fe–S–O system, and again, by comparison to partitioning systematics in the Fe–S system, were able to evaluate the role of O.

Experiments done at elevated pressures have utilized both piston-cylinder and multi-anvil apparatus. Crushable MgO is often employed as a sample container, as it is unreactive with Fe-rich alloys over a broad spectrum of conditions, and promotes a homogenous pressure distribution (e.g., Jones and Walker 1991; Walker 2000; Lazar et al. 2004; Van Orman et al. 2008). In order to prevent leakage of the liquid alloy phase during the experiment, the crushable MgO is annealed at $\sim 600-800$ °C for $\sim 8-12$ hrs at the target pressure (e.g., Jones and Walker 1991; Walker 2000). Hard-fired alumina crucibles have also been employed successfully to investigate partitioning in the Fe-S and Fe-C systems (Chabot et al. 2008, 2011; Rai et al. 2013), as well as graphite to study HSE partitioning in the Fe–S–O system (Fleet et al. 1991). At the low temperatures and high-sulfur content of the experiments done by Fleet et al. (1991), the solubility of carbon in the sulfur-rich liquid phase is negligible. However, partial closure of the Fe-C and Fe-S liquids miscibility gap with increasing pressure (Corgne et al. 2008), may result in significant levels of carbon in the resulting liquid, and therefore difficulty in isolating the separate effects of C and S. Graphite-saturated experiments in the Fe-S-C system may also become saturated in cementite (Fe_3C), rather than Fe, as the solid phase coexisting with sulfur-rich liquids (Dasgupta et al. 2009; Buono et al. 2013).

Refractory Os–Ir±Fe alloy grains, in some cases rimmed by Pt, were observed by Fleet et al. (1991) in experiments conducted in the Fe–S-O system at 1100–1200°C and 4.5–11 GPa. Some experiments done at ambient pressure and temperatures of 1000-1200 °C in the Fe-Ni-S system also display evidence for heterogeneous Os concentrations in the solid metal phase (Fleet et al. 1999). A similar problem with Ir homogeneity was noted by Jones and Drake (1983). These grains result from the use of HSE-rich starting materials that are resistant to dissolution at the chosen experimental temperatures and durations. A factor which might have exacerbated the equilibration problem in the Fleet et al. experiments was the loading of several of the PGEs into each experiment, producing significant domains of Fe-poor, IPGE-rich alloy in which diffusion of all the PGEs is intrinsically slow (Watson and Watson 2003). To prevent the formation of refractory HSE grains in experiments done at 10 GPa and 1400-1500 °C, Walker (2000) used a novel experimental arrangement to prevent alloying between the HSEs and Fe early in the experiment. This was achieved by taking advantage of the large thermal gradient intrinsic to the multianvil assembly, and positioning powdered Pt, Os, and Re metal in what would become the hot zone of the capsule, causing complete dissolution and precipitation with newly formed Fe-Ni crystals at the cold end. Experiments that exploit a thermal gradient have also been used to determine solid metal-liquid metal partitioning in the Fe-Si system (Morard et al. 2014). As the melting loop in the Fe–Si system is only a few tens of degrees, Morard et al. (2014) imposed a vertical temperature gradient across samples so as to increase the relative proportions of metal and liquid for a given bulk composition.

Effect of liquid metal composition on $D^{\text{SM/LM}}$. The effect on $D^{\text{SM/LM}}$ resulting from changes to the liquid metal composition has been parameterized by Jones and Malvin (1990) in terms of a non-metal interaction model. Jones and Malvin (1990) consider partitioning of an element (*i*) between solid (SM) and liquid (LM) metal. At equilibrium, the chemical potential of *i* is equal in both phases:

$$\mu_i^{\rm SM} = \mu_i^{\rm LM} \tag{1}$$

Expressing these chemical potentials in terms of the standard state chemical potential and the activity of element *i* in each phase (a_i) yields:

$$\mu_i^{\rm SM^{\rm o}} + RT \ln a_i^{\rm SM} = \mu_i^{\rm LM^{\rm o}} + RT \ln a_i^{\rm LM}$$
(2)

Recalling $a_i = \gamma_i X_i$ (where γ_i and X_i are the activity coefficient and mole fraction of *i* respectively), the activity terms may be replaced to provide an expanded form of Equation (2):

$$\mu_i^{\text{SM}^{\circ}} + RT \Big[\ln \gamma_i^{\text{SM}} + \ln X_i^{\text{SM}} \Big] = \mu_i^{\text{Liq}^{\circ}} + RT \Big[\ln \gamma_i^{\text{LM}} + \ln X_i^{\text{LM}} \Big]$$
(3)

Equation (3) may be rearranged to yield:

$$\ln \left[\frac{X_i^{SM}}{X_i^{LM}} \right] = \frac{\mu_i^{LM^\circ} - \mu_i^{SM^\circ}}{RT} - \ln \left[\frac{\gamma_i^{SM}}{\gamma_i^{LM}} \right]$$
(4)

Substituting the molar partition coefficient $(D_i^{*SM/LM})$ into the left hand side of Equation (4) and the Gibbs free energy of reaction (ΔG_r^o) for $\mu_i^{LM^o} - \mu_i^{SM^o}$ yields:

$$\ln D_i^{*SM/LM} = \frac{-\Delta G_r^{O}}{RT} - \ln \left[\frac{\gamma_i^{SM}}{\gamma_i^{LM}} \right]$$
(5)

From Equation (5) we see that for a system at constant pressure, the molar partition coefficient will depend upon temperature and changes to the activity coefficient of element *i* in both the solid- and liquid-metal phase. Jones and Malvin (1990) argue that both *T* and changes to γ_i^{SM} have a negligible effect on D_i^{SSMLM} relative to changes in γ_i^{LM} .

The effect of *T* can be assessed by considering an ideal system, in which the ratio $\gamma_i^{\text{SM}} / \gamma_i^{\text{LM}}$ is unity, and variation in $D_i^{\text{SM/LM}}$ depends only on the free energy term. ΔG_r^{O} in Equation (5) corresponds to the melting reaction for pure solid and liquid phases of element *i*, and can be written in terms of the heat of fusion (ΔH_m) for the element of interest. Remembering that $-\Delta G_r^{\text{O}} = -(\Delta H_r^{\text{O}} - T\Delta S_r^{\text{O}})$ and replacing the subscript *r* with *m*, to denote the melting reaction, Equation (5) becomes:

$$\ln D_i^{*\rm SMLM} = -\frac{\Delta H_m}{RT} + \frac{\Delta S_m}{R} \tag{6}$$

At the melting temperature of i, $-\Delta G_r^o = 0$ and so $\Delta S_m = \Delta H_m / T_m$. Substituting this identity into Equation (6) yields the following expression:

$$\ln D_i^{*\text{SM/LM}} = \frac{\Delta H_m}{R} \left[\frac{1}{T_m} - \frac{1}{T} \right]$$
(7)

Equation (7) can be used to assess the variation in $D_i^{\text{*SM/LM}}$ arising from changes in temperature. Table 1 lists the melting temperatures and enthalpies of fusion for the highly siderophile elements. Selecting osmium, which has the largest enthalpy of fusion, we calculate that $D_i^{\text{*SM/LM}}$ will only vary by a factor of ~2.5 if *T* changes by 1000°C. The weak dependence of $D_i^{\text{*SM/LM}}$ on temperature suggested by this analysis is borne out by the similar correlation coefficients (R^2) obtained from simple regression of $D_i^{\text{*SM/LM}}$ vs. liquid-metal composition and multiple linear regression vs. both liquid-metal composition and 1/*T* (Jones and Malvin 1990).

For systems at relatively low *P*, in which the solubility of light elements in solid Fe–Ni alloy is small, Jones and Malvin (1990) argue that changes in γ_i^{SM} are negligible relative to changes in γ_i^{LM} . They support this assertion by noting that values of $D_i^{*SM/LM}$ in the light-element free system are typically close to unity, the solid Fe–Ni system is itself relatively ideal, and that their 0.1 MPa experimental data can be adequately modeled considering only the γ_i^{LM} term. Chabot and Jones (2003) later used a modified version of the Jones and Malvin (1990) parameterization to successfully model a much larger database of 0.1 MPa partitioning data, providing further support for an approach that considers only changes in γ_i^{LM} .

Element	$T_{\rm m}\left({f K} ight)$	$H_{\rm m}$ (kJ/mol)
Re	3458	34.08
Os	3306	57.85
Ir	2739	41.12
Ru	2606	38.59
Pt	2041	22.175
Rh	2236	26.59
Pd	1828	16.74
Au	1337	12.55

Table 1. Heats of fusion of the highly siderophile elements.

From data summarized in Haynes (2014).

Accepting that changes in T and γ_i^{SM} do not strongly drive changes to the solid metal– liquid metal partition coefficient, we can return to the relationship given in Equation (5) and simplify it to yield

$$\ln D_i^{\text{SM/LM}} = -\ln \left[\frac{1}{\gamma_i^{\text{LM}}}\right] + \text{constant} = \ln \gamma_i^{\text{LM}} + \text{constant}$$
(8)

For geo- and cosmochemical purposes, the more useful independent variable is liquid-metal composition rather than γ_i^{LM} . These are linked, however, through interaction parameters which describe the excess free energy of mixing. For a liquid-iron alloy containing solutes *i* through *N* in dilute concentration, the activity coefficient of *i* is often described using only the first-order interaction parameters (ϵ):

$$\ln \gamma_i^{\rm LM} = \ln \gamma_i^0 + \sum_{j=2}^N \varepsilon_j^j X_j \tag{9}$$

where γ_i^0 is the activity coefficient of *i* at infinite dilution in liquid iron and X_j is the mole fraction of the subscript component in solution. It should be noted that by ignoring interaction parameters greater than first order, Equation (9) is not thermodynamically rigorous and should only be applied to alloys in which the solutes are dilute (Ma 2001 and references therein). Despite this, the following model adequately describes the experimentally determined partitioning of several HSEs in systems containing up to ~ 30 wt% sulfur (Jones and Malvin 1990). Although Ni is also typically present in moderate concentrations, it's relatively weak interactions with Fe, S, P, and C permit the simplification embodied by Equation (9) while still allowing most experimental data to be modeled successfully (Jones and Malvin 1990).

As an example, if we consider the case of iridium partitioning in an Fe–Ni–S alloy, the activity coefficient of Ir, as given by Equation (9) is:

$$\ln \gamma_{\rm Ir}^{\rm LM} = \ln \gamma_{\rm Ir}^0 + \varepsilon_{\rm Ir}^{\rm Ni} X_{\rm Ni} + \varepsilon_{\rm Ir}^{\rm S} X_{\rm S} + \varepsilon_{\rm Ir}^{\rm Ir} X_{\rm Ir}$$
(10)

From Equations (8) and (10) it is apparent that the solid metal–liquid metal partition coefficient of Ir can be expressed in terms of the component mole fractions weighted by their corresponding interaction parameters. Jones and Malvin (1990) propose a further simplification, whereby the alloy is described as comprising only metal and non-metal domains, which either accept or reject the HSEs respectively. In this framework, changes to the activity coefficient as a function of liquid composition can be described by a single modified interaction parameter, termed the β factor. For Ir in the Fe–Ni–S system:

$$\ln \gamma_{\rm Ir}^{\rm LM} = \beta_{\rm Ir} \ln \left(1 - \alpha n X_{\rm S} \right) \tag{11}$$

where α is a constant specific to the compositional system being investigated and *n* is a stoichiometric coefficient related to the speciation of the non-metal component in the alloy. Equation (11) retains the linear dependence of the activity coefficient on composition inherent in Equation (10) and is subject to the same limitations discussed above. Substituting Equation (11) into (8), yields $D_{\rm ir}^{\rm *SM/LM}$ as a function of the non-metal content of the alloy and the β factor:

$$\ln D_{\rm Ir}^{\rm *SM/LM} = \beta_{\rm Ir} \ln (1 - \alpha n X_{\rm S}) + C \tag{12}$$

where *C* is a constant. As the sulfur (or other light-element) content of the alloy tends towards zero, $\ln D_{lr}^{*SM/LM}$ will tend towards *C*, such that in the limiting case of $X_s = 0$, *C* will equal the partition coefficient in the light-element-free system $(\ln D_i^0)$. Figure 2 provides an example of partitioning data for Au and Re in the Fe–Ni–S system plotted in the form of Equation (12), illustrating the overall linearity of the data. For partitioning of an element *i* in a system containing light elements *j* through *N*, the general form of Equation (12), therefore, becomes:

$$\ln D_i^{*\text{SM/LM}} = \ln D_i^0 + \beta_i \ln \left(1 - \sum_j^N \alpha_j n_j X_j \right)$$
(13)

The value of β_i in Equation (13) for a system containing multiple light elements is related to the β factors in each of the individual light-element-bearing systems. Jones and Malvin (1990) express this relationship as a weighted average of the effects in the end-member systems:

$$\beta_i^{j...N} = \beta_i^j \left(\frac{nX_j}{\sum_j^N nX_j} \right) + \beta_i^k \left(\frac{nX_k}{\sum_j^N nX_j} \right) \dots + \beta_i^N \left(\frac{nX_N}{\sum_j^N nX_j} \right)$$
(14)

For example, the β factor for element *i* in the Fe–Ni–S–P system, where $n_{\rm S}$ and $n_{\rm P}$ are 2 and 4, respectively, is described as:



Figure 2. The variation in $\ln D^{\text{SM/LM}}$ as a function of liquid metal composition, as described by the parameter $\ln(1-2\alpha X_s)$, for Au (a) and Re (b). Despite differences in *P* and *T* between the experiments, each element is adequately described by a single linear fit. The partition coefficient for Re, however, is significantly more sensitive to liquid composition, owing to the larger value for β_{Re} .

$$\beta_i^{\rm SP} = \beta_i^{\rm S} \left(\frac{2X_{\rm S}}{2X_{\rm S} + 4X_{\rm P}} \right) + \beta_i^{\rm P} \left(\frac{4X_{\rm P}}{2X_{\rm S} + 4X_{\rm P}} \right)$$
(15)

Chabot and Jones (2003) develop further the parameterization outlined here, such that only a single beta factor need be determined in systems containing multiple light elements.

In order to implement predictive models of partitioning in light-element-bearing systems, the key parameters to determine from experiments are therefore $D^{\text{SM/LM}}$ and the β factors. Table 2 provides a summary of these values determined for the HSE at 0.1 MPa as defined using the Jones–Malvin formalism. Values of $D^{SM/LM}$ and β show a ~5-fold difference in magnitude amongst the HSE, with the strongest melt composition effects implied for Re-Os-Ir, and the least for Pd and Au. These differences serve to further decouple the HSE during core solidification as the light-element component builds up in the residual melt. Significantly, although values of β for Re, Os, and Pt are similar, there are resolvable differences in the values of $D^{\text{SM/LM}}$, in the order Os>Re>Pt. This result was noted based on empirical estimates from magmatic iron meteorites (Walker et al. 1995), and used to develop the hypothesis that mafic magmas with anomalous enrichments in ¹⁸⁷Os/¹⁸⁸Os and ¹⁸⁶Os/¹⁸⁸Os contain an outer core component (Walker et al. 1995, 1997; Brandon et al. 1998). Subsequently, experiments have been done to document the effect of pressure on the relative partitioning of these elements (3-22 GPa; Walker 2000; Van Orman et al. 2008; Hayashi et al. 2009). Some of these studies suggest that D^{SM/LM} becomes smaller, and more similar, likely due to an increased size misfit in Fe metal (Van Orman et al. 2008), as described below.

The role of the solid phase on $D^{\text{SM/LM}}$. As described in the previous section, much of the available solid metal–liquid metal partitioning data can be adequately described using a parameterization which takes into account metal-solvent interactions in the liquid (e.g., Jones and Malvin 1990; Chabot and Jones 2003). This approach however, provides no theoretical explanation for the role of the crystalline Fe–Ni solid phase, as manifested by ~5-fold difference in values of $D^{\text{SM/LM}}$ between the HSE (Table 2). Several recent studies have sought to provide this theoretical framework through application of a modified form of the lattice strain model (Van Orman et al. 2008; Stewart et al. 2009; Chabot et al. 2011; Rai et al. 2013). This model, as commonly applied to silicate systems, quantifies the parabolic relationship between log $D^{\text{Crystal/Melt}}$ and ionic radius (Blundy and Wood 1994). This functional form arises because the variation in partition coefficients for a suite of isovalent cations originates purely in the elastic strain incurred

Element	$\ln D_0^{-1}$	β (Soret) ²	Error	n^1	β (Partitioning) ¹	Error	<i>n</i> ³
Ru	0.12	1.72	0.31	4	2.10	0.15	15
Rh		1.31	0.27	4	1.94	0.08	3
Pd		0.52	0.13	4	0.54	0.15	6
Re	0.47	2.34	0.40	4	2.72	0.05	37
Os	0.63	2.36	0.40	4	2.79	0.07	49
Ir		2.17	0.38	4	2.83	0.13	36
Pt	-0.18	1.80	0.33	4	2.45	0.09	34
Au	-1.24	0.71	0.19	4	1.06	0.07	23

Table 2. Summary of parameters to predict solid metal-liquid metal partitioning.

Notes:

¹Values derived from regression of the ambient pressure data summarized by Chabot and Jones (2003) and the high-pressure results of Jones and Walker (1991), Walker (2000), Lazar et al. (2004), Van Orman et al. (2008), and Hayashi et al. (2009).

²Beta determined by the Soret experiments of Brenan and Bennett (2014).

3Number of experiments.

by the size mismatch between the substituent cation and the optimal radius for that site. An analogous approach has been taken for application to metallic systems, with $D_i^{SM/LM}$ cast as:

$$\ln D_{i}^{\text{SM/LM}} = \ln D_{0}^{\text{SM/LM}} + \left[-4\pi N_{\text{A}} E_{\text{M}} \left[\frac{1}{2} r_{0(\text{M})} \left(r_{i} - r_{0(\text{M})} \right)^{2} + \frac{1}{3} \left(r_{i} - r_{0(\text{M})} \right)^{3} \right] \right] / \text{R}T$$
(16)

where $D_0^{\text{SM/LM}}$ is the partition coefficient for an element with the 'ideal' neutral atomic radius for site M ($r_{0(M)}$), N_A is Avogadro's constant, E_M is the apparent Young's modulus for site M and r_i is the radius of a neutral atom of element *i*. Some previous studies have used the neutral atomic radii of Clementi et al. (1967) for values of r_i and fit the experimental data to Equation (16) by varying D_0 , r_0 and E_M (Stewart et al. 2009; Chabot et al. 2011; Rai et al. 2013). Application of this model by Stewart et al. (2009) to previous results for HSE partitioning in the Fe–S and Fe–C systems, at 0.1 MPa to 22 GPa (Chabot and Jones 2003; Chabot et al. 2006; Van Orman et al. 2008), suggests incorporation of these elements in the lattice does not occur through simple replacement of Fe. The large value of r_0 (1.83 Å) for the parabola defined by the 3rd row transition elements, Au through W, is significantly greater than the atomic radius of Fe (1.56 Å) and may instead suggest the accommodation of these elements in defects resulting from the presence of light elements in the Fe lattice (Stewart et al. 2009). However, Van Orman et al. (2008) showed that the partitioning of Re, Os, and Pt was consistent with their relative increase in *metallic* radius compared to that of Fe in the FCC structure. Chabot et al. (2011) considered a larger suite of data in this context, and found that the systematic partitioning trends using atomic radii as the ordinate broke down for the 1^{st-} and 2nd-row transition elements when plotted as a function of the metallic radius. The reason for these differences are unclear, but certainly bear on our interpretation of which sites the HSE partition in the solid-metal phase, and the fundamental controls on inter-element fractionation.

As a final point to this section, we note that the ~5-fold variation in β is similar to the differences in D^{SM/LM} for the HSE, with the latter related to the elastic strain generated by size mismatch from the optimal site size in FCC iron. Values of β provide a measure of the affinity of a particular HSE for Fe-rich domains within the liquid structure, with larger values of β signifying enhanced sulfur avoidance (Jones and Malvin 1990). Thus, it seems reasonable that the extent to which a particular HSE will concentrate in more Fe-rich, non-metal-poor melts should be related to the size of the metal atom, provided Fe-solid and Fe-rich melt have similar structures. The structural similarity between liquid and solid metal is implied by the small ΔV for the solid-to-liquid metal transfer of components, as indicated by the relatively small effect of pressure on D^{SM/LM} as documented in previous work (e.g., Van Orman et al. 2008; Chabot et al. 2011). As shown by Brenan and Bennett (2010), values of D^{SM/LM} show a somewhat stronger dependence on metal, or atomic radius than β , but there is a sympathetic variation between the two, suggesting similar origins of the HSE "selectivity" for Fe-rich domains. As proposed by Van Orman et al. (2008), with increasing pressure the difference in absolute and relative values of $D^{\text{SM/LM}}$ for Pt, Re, and Os (and likely the other HSE) decrease due to the increased size mismatch between the substituent metal and Fe, and between individual HSE. If so, then we expect that not only will pressure decrease the absolute and relative values of $D^{\text{SM/LM}}$ (as per Van Orman et al. 2008), but, by analogy, pressure may also reduce the differences between individual values of β . The effects of increased pressure are not straightforward, however, as exemplified by the results of high-pressure experiments for Pt, Re, and Os done in the Fe-Ni-S system (vs. the Fe-S system studied by Van Orman et al.), which instead show a slight increase in $D^{\text{SM/LM}}$ with increasing P (Hayashi et al. 2009).

Soret Diffusion Experiments. The effect of liquid composition on solid metal–liquid metal partitioning can also be determined from experiments that impose a thermal gradient on non-ideal Fe-alloy solutions (e.g., Fe–S; Brenan and Bennett 2010). These experiments produce run-

products with major-element compositional gradients that reflect the opposing mass fluxes of Soret and chemical diffusion. Soret diffusion arises when the system contains components that possess a different partial molar enthalpy when undergoing activated transport in the medium. A component with higher enthalpy in transport will migrate from hot to cold; transporting heat to the cold portion of the system and acting to ameliorate the imposed temperature imbalance. The opposite sense of migration is expected for components with a lower enthalpy in transit, thus also redistributing heat so as to reduce the thermal gradient. Details of the Soret process and its application to complex geologic systems are treated in detail by Lesher and Walker (1986, 1991). Chemical diffusion can limit the magnitude of segregation by Soret diffusion, due to the chemical potential gradients that arise from compositional differences along the sample length. In ideal systems, chemical diffusion may be quite effective in limiting compositional gradients due to the large change in chemical potential with composition. In strongly non-ideal systems however, which contain P-T-X regions where $d\mu_i/dX \approx 0$, and hence the driving force for chemical diffusion is negligible, experiments may exhibit large gradients in major-element composition. The magnitude of the compositional gradient is described by the Soret coefficient (σ) , which for a binary system is given as (Lesher and Walker 1986):

$$\sigma = \frac{X_{\text{Hot}} - X_{\text{Cold}}}{\overline{X} \left(1 - \overline{X}\right) \Delta T}$$
(17)

where X_{Hot} and X_{Cold} are the component mole fractions measured at the hot and cold ends of the sample respectively and \overline{X} is the average component mole fraction in the sample. Trace elements in the system are distributed to maintain a constant activity along the sample and concentration gradients therefore depend upon changes to the activity coefficient with major element composition (Jones and Walker 1990). The following derivation relates the compositional gradient for a trace element (*i*), measured in a Soret diffusion experiment, to β . Values of β obtained from these experiments may then be used to predict partitioning through the use of Equation (13) (Brenan and Bennett 2010).

Assuming a hypothetical solid Fe phase in equilibrium with the melt at all points along a Soret diffusion experiment, the solid metal-liquid partition coefficient for i can be defined at two points along the sample (T1 and T2) as:

$$\ln D_{i,T1}^{\rm SM/LM} = \ln D_i^0 + \ln \gamma_{i,T1}^{\rm LM}$$
(18)

$$\ln D_{i,T2}^{\rm SM/LM} = \ln D_i^0 + \ln \gamma_{i,T2}^{\rm LM}$$
(19)

Subtracting Equation (19) from Equation (18) and taking the exponent yields:

$$\frac{\gamma_{i,T1}^{LM}}{\gamma_{i,T2}^{LM}} = \frac{D_{i,T1}^{SM/LM}}{D_{i,T2}^{SM/LM}}$$
(20)

Substituting $X_i^{\text{SM}} / X_i^{\text{LM}}$ for $D_i^{\text{SM/LM}}$:

$$\frac{\gamma_{i,\text{T1}}^{\text{LM}}}{\gamma_{i,\text{T2}}^{\text{LM}}} = \frac{\left(X_{i,\text{T1}}^{\text{SM}} \mid X_{i,\text{T1}}^{\text{LM}}\right)}{\left(X_{i,\text{T2}}^{\text{SM}} \mid X_{i,\text{T2}}^{\text{LM}}\right)}$$
(21)

For adjacent positions along the sample, it can be shown that $X_{i,T1}^{SM} / X_{i,T2}^{SM} \approx 1$, simplifying Equation (21) to give:

$$\frac{\gamma_{i,T1}^{LM}}{\gamma_{i,T2}^{LM}} = \frac{X_{i,T1}^{LM}}{X_{i,T2}^{LM}}$$
(22)

Taking the natural log of Equation (22) and substituting Equation (11) for the activity coefficients relates β for trace element *i* to a given mole fraction of light element (*X*_l):

$$\ln X_{i,T1}^{LM} - \ln X_{i,T2}^{LM} = -\beta_i \Big[\ln \big(1 - n\alpha X_{i,T1} \big) - \ln \big(1 - n\alpha X_{i,T2} \big) \Big]$$
(23)

Or more simply:

$$\Delta \ln X_i^{\rm LM} = -\beta_i \Delta \left\lceil \ln \left(1 - n\alpha X_i \right) \right\rceil \tag{24}$$

Values of β are therefore extracted from plots of $\ln X_i^{\text{LM}}$ vs. $\ln(1 - n\alpha X_i)$ and are assumed to be temperature independent. Evidence for the lack of a strong *T* dependence for β is provided by previous equilibrium experiments (Jones and Malvin 1990; Chabot and Jones 2003) and the linearity of data plotted in the manner described above (Brenan and Bennett 2010). An example of the major and trace element data produced by Soret experiments is provided in Figure 3.

Soret diffusion experiments are subject to the same design considerations as those described previously for ambient pressure and high pressure studies. The primary advantage of this approach is that a small number of experiments can provide information comparable to a large suite of isothermal solid–liquid partitioning experiments. A further application of this method is to determine the effects of light-elements that have a low solubility in Fe-rich melt. Phase relations in the Fe–O system for example, preclude large volume experiments to directly measure solid metal–liquid metal partition coefficients for liquids that span a broad range of O-contents (i.e., ≤ 2.2 wt% O at 15 GPa, Langlade et al. 2008). Soret experiments, however, can be performed at super-liquidus temperatures where light-element components more readily dissolve in the melt. This can provide access to compositional space that may be relevant to high-pressure planetary differentiation processes. A disadvantage of this approach, however, is the lack of information for the solid phase, which also exerts a strong control on inter-element fractionation, as noted above.



Figure 3. The results of Soret experiments performed by Brenan and Bennett (2010) in the Fe–Ni–S system. Panel (a) displays the change in sulfur content as a function of *T* along the sample length, that arises due to the Soret effect. Panel (b) displays the corresponding gradients in Re concentration, that result from trace element redistribution to maintain isoactivity along the sample length. Values of β_{Re} are determined from the slope defined by linear regression of ln X_{Re} vs. $\ln(1-2\alpha X_s)$ for each experiment.
HSE SOLUBILITY EXPERIMENTS: IMPLICATIONS FOR METAL–SILICATE PARTITIONING

Accretion of the Earth from planetesimals of chondritic composition (McDonough and Sun 1995; Wood et al. 2006), with concurrent differentiation into a metal core and silicate mantle, is generally thought to have occurred over the first ~ 30 Ma of Earth's history (e.g., Kleine et al. 2002; Yu and Jacobsen 2011). During accretion, heat generated by the decay of short-lived isotopes and the collision of large impactors is likely to have raised global temperatures sufficiently to cause widespread melting and the formation of a magma ocean, through which more dense Fe-Ni liquid could descend (e.g., Ringwood 1966; Karato and Murthy 1997; Wood et al. 2006; Rubie et al. 2007). In this scenario, the siderophile elements would be transported to the growing core, leaving a depleted silicate mantle with element ratios that depend upon the differing affinities for the metal phase (e.g., Chou 1978; Newsom and Palme 1984; Wänke et al. 1984). Past work has ascribed the behavior of the moderately siderophile elements (MSEs; Mo, W, Cr, V, Mn, etc) to a combination of metal extraction and accretion of compositionally distinct components (Wänke and Dreibus 1988; Schmitt et al. 1989; O'Neill 1991). More recently it has been shown that, if metal-silicate partitioning is appropriately parameterized, a match to mantle MSE abundances can be achieved at appropriately high pressure and temperature (e.g., Wade and Wood 2005; Righter 2011; Siebert et al. 2011; Wade et al. 2012). In contrast, metal-silicate partitioning of the HSE has provided a somewhat conflicting view on the accretion model. The majority of past work on HSE partitioning has been at 0.1 MPa and relatively low temperature (~1300-1400 °C) and showed that at the relatively reduced f_{O_2} attending core formation¹ (i.e., 1.5 log units more reduced than the iron-wustite buffer; IW-1.5) metal-silicate partitioning of all the HSEs is likely to exceed $10^5 - 10^8$ (e.g., Borisov and Palme 1995, 1996; Ertel et al. 1999, 2001). Such results predict the quantitative removal of the HSEs from the silicate mantle, which is inconsistent with their estimated abundances in the primitive mantle (Becker et al. 2006). This apparent lack of mantle HSE depletion is a long-standing issue in geochemistry, and has come to be known as the "excess siderophile element problem". Importantly, moderate to large differences in the relative mantle abundances of the HSEs are also predicted by the low- temperature partitioning data (compare Borisov and Palme 1996 to Ertel et al. 1999), in conflict with observed chondritic relative abundances (Becker et al. 2006) and a mantle Os-isotope time evolution requiring Pt/Os and Re/Os ratios to match those of chondritic meteorites (Meisel et al. 2001; Brandon et al. 2006). These combined observations support a model for late accretion of a small amount of dominantly chondritic material which postdated core formation; the so-called later veneer (e.g., Kimura et al. 1974). The veracity of this model came into question, however, following the proposal of Murthy (1991) that there should be a convergence of metal-silicate partitioning values at the very high temperatures likely during core formation (i.e., >2700 °C), resulting in a mantle HSE composition set by metal-silicate equilibrium. Although the strategy to estimate high temperature partitioning was shown to be flawed (e.g., Capobianco et al. 1993) more recent results have indeed shown that temperature is a key variable to be considered, as is the importance of measurements at reduced conditions, at which some HSE may exhibit unanticipated and unusual redox behavior, as described in the subsequent sections.

¹ In this chapter two different, but related, f_{O_2} references are used. The first, fayalite–magnetite–quartz (FMQ) denotes relatively oxidized conditions, and is near the f_{O_2} of most terrestrial magmas. Iron–wustite (IW) is the other reference point, corresponding to highly reduced conditions, with the conversion that IW is approximately 3.5 log units more reduced than FMQ, i.e., IW ~ FMQ–3.5.

CALCULATING THE METAL–SILICATE MELT PARTITION COEFFICIENT FROM SOLUBILITY DATA

Experiments that equilibrate silicate melt with an Fe-rich metal liquid usually result in vanishingly low HSE concentrations in the quenched silicate melt, owing to high values for metal/silicate partition coefficients, $D_i^{\text{Met/Sil}}$. For example, a sample doped with 200 ppm of element *i* and comprising equal fractions of metal and silicate melt will result in $C_i^{\text{Sil}} < 0.004$ ppm for values of $D_i^{\text{Met/Sil}} > 10^5$. Hence, in order to generate run-products with measurable HSE levels in the quenched silicate phase, solubility experiments are performed. In this case, pure HSE metal, or an HSE-rich alloy, is equilibrated with silicate melt at the desired $P-T-f_{O_2}$ conditions and values of $D_i^{\text{Met/Sil}}$ are calculated using the formulation of Borisov et al. (1994), described as follows. The dissolution reaction for a metal in silicate melt is:

$$M_{(Met)} + \frac{n}{4}O_{2(g)} = M^{n+}O_{n/2(Sil)}$$
(25)

where *n* is the oxidation state of the dissolved metal cation. Two equilibrium constants can be defined for this reaction, one for an experiment at saturation in an HSE phase (K_{Sat}) and the other pertaining to a natural system with dilute HSE concentrations (K_{Dil}):

$$\log K_{\text{Sat}} = \log \left[a_{\text{MO}_{n/2}}^{\text{Sat}} \right] - \frac{n}{4} \log f_{O_2}$$
(26)

$$\log K_{\text{Dil}} = \log \left[a_{\text{MO}_{u/2}} \right] - \log \left[a_{\text{M}} \right] - \frac{n}{4} \log f_{\text{O}_2}$$

$$\tag{27}$$

where aM and aMO_{n/2} are the activity of the metal and metal oxide and components. Substituting $a_i = X_i \gamma_i$ into Equations (26) and (27), where X_i and γ_i are the mole fraction and activity coefficient respectively, yields:

$$\log K_{\text{Sat}} = \log \left[X_{\text{MO}_{n/2}}^{\text{Sat}} \right] + \log \left[\gamma_{\text{MO}_{n/2}}^{\text{Sat}} \right] - \frac{n}{4} \log f_{\text{O}_2}$$
(28)

$$\log K_{\text{Dil}} = \log \left[X_{\text{MO}_{n/2}} \right] + \log \left[\gamma_{\text{MO}_{n/2}} \right] - \log \left[X_{\text{M}} \right] - \log \left[\gamma_{\text{M}} \right] - \frac{n}{4} \log f_{O_2}$$
(29)

At fixed P and T, subtracting Equation (28) from (29) and rearranging gives:

$$\log\left[\frac{X_{\text{MO}_{n/2}}}{X_{\text{M}}}\right] = \log\left[X_{\text{MO}_{n/2}}^{\text{Sat}}\right] + \log\left[\gamma_{\text{M}}\right] - \log\left[\frac{\gamma_{\text{MO}_{n/2}}}{\gamma_{\text{MO}_{n/2}}^{\text{Sat}}}\right]$$
(30)

The molar partition coefficient ($D^{*Met/Sil} = X^{Met}/X^{Sil}$) may then be substituted into the left-hand side of Equation (30), yielding:

$$\log\left[\frac{1}{D^{*Met/Sil}}\right] = \log\left[X_{MO_{n/2}}^{Sat}\right] + \log\left[\gamma_{M}\right] - \log\left[\frac{\gamma_{MO_{n/2}}}{\gamma_{MO_{n/2}}^{Sat}}\right]$$
(31)

The very low solubility of HSEs in silicate melt, even when saturated in a pure metal phase, results in negligible changes to $\gamma_{MO_{n/2}}$ over the possible range for $X_{MO_{n/2}}$ and the ratio $\gamma_{MO_{n/2}} / \gamma_{MO_{n/2}}^{Sat}$ may therefore be treated as unity. After taking the exponent, Equation (31) then becomes:

$$\frac{1}{D^{*Met/Sil}} = X_{MO_{n/2}}^{Sat} \gamma_M$$
(32)

Typically. it is the concentration by weight rather than mole fraction of a trace element that is reported and conversion of Equation (32) to the weight-based, rather than molar, partition coefficient is accomplished using the following conversion factors (A and B):

$$X_{\rm M} = A \times C_{\rm M \, (Met)} \tag{33}$$

$$X_{\rm MO_{n/2}} = B \times C_{\rm M \, (Sil)} \tag{34}$$

where $C_{\rm M}$ is the concentration of trace element M in the indicated phase. Rearranging, and substituting Equations (33) and (34) into Equation (32) yields:

$$D^{\text{Met/Sil}} = \left(\frac{B}{A}\right) D^{*\text{Met/Sil}} = \left(\frac{B}{A}\right) \left(\frac{1}{B \times C_{\text{M}(\text{Sil})}^{\text{Sat}} \times \gamma_{\text{M}}}\right)$$
(35)

which simplifies to:

$$D^{\text{Met/Sil}} = \frac{1}{A \times C_{M}^{\text{Sat}} (\text{Sil}) \times \gamma_{M}}$$
(36)

where C_{M}^{Sat} is the concentration of M measured in the silicate melt at the solubility limit and γ_{M} is the activity of M at infinite dilution in Fe metal. Values of A tend toward a constant value as the concentration of M in Fe-alloy decreases.

Controls on the metal-silicate partition coefficient

Temperature, pressure, oxygen fugacity and melt composition may all play a role in determining the value of $D^{\text{Met/Sil}}$. The equilibrium constant for Reaction (26), describing the dissolution of a trace metal into silicate melt may be equated with the Gibbs free energy of reaction (ΔG_r°) as follows:

$$\frac{\Delta G_r^\circ}{-\mathbf{R}T} = \ln K = \ln \left[a_{\mathrm{MO}_{n/2}} \right] - \ln \left[a_{\mathrm{M}} \right] - \frac{n}{4} \ln f_{\mathrm{O}_2}$$
(37)

Replacing the activity terms $(a_i = X_i \gamma_i)$ and rearranging yields:

$$\ln\left(\frac{X_{\rm M}}{X_{{\rm MO}_{n/2}}}\right) = \frac{\Delta G_r^{\circ}}{-{\rm R}T} - \frac{n}{4} \ln f_{{\rm O}_2} + \ln\left(\frac{\gamma_{{\rm MO}_{n/2}}}{\gamma_{\rm M}}\right)$$
(38)

Expanding the free energy term $(\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ + P\Delta V_r^\circ)$ and substituting the molar partition coefficient into the left hand side of Equation (38) reveals the variables that might be expected to affect HSE partitioning:

$$\ln D^{*\text{Met/Sil}} = \frac{\Delta H_r^\circ}{RT} - \frac{\Delta S_r^\circ}{R} + \frac{P\Delta V_r^\circ}{RT} - \frac{n}{4} \ln f_{O_2} + \ln\left(\frac{\gamma_{\text{MO}_{n/2}}}{\gamma_{\text{M}}}\right)$$
(39)

where ΔH_r° , ΔS_r° and ΔV_r° are the enthalpy, entropy, and volume change of reaction respectively. Assuming these three parameters do not themselves depend strongly on *P* or *T*, Equation (39) can be simplified to yield the following relationship:

$$\ln D^{*Met/Sil} = \frac{a}{T} + \frac{bP}{T} - \frac{n}{4} \ln f_{O_2} + \ln \left(\frac{\gamma_{MO_{n/2}}}{\gamma_M}\right) + c$$
(40)

where *a*, *b*, and *c* are constants determined by regression of the experimental data. The partition coefficient is therefore expected to depend on temperature, pressure, oxygen fugacity

and the composition of both the silicate and metallic melt. Equation (40) provides the basis for the various approaches employed in past work to parameterize the results of either metal solubility measurements or direct determinations of metal–silicate partitioning. A summary of such work is provided in Table A1 in the appendix.

Whereas the dependence of solubility and partitioning on f_{O_2} is reasonably well established under oxidizing conditions (i.e., >FMQ), experiments done at reducing conditions often display strongly disparate results. The origin of this variation is thought to arise from the presence of dispersed metal inclusions in silicate run-products². This effect has introduced some uncertainty in the accuracy of past measurements, of both metal solubility and mineral-silicate melt partitioning (see *Silicate and Oxide Control on HSE Fractionation*). Hence, before reviewing the partitioning results for the various HSEs, it is instructive to briefly describe the inclusion problem, and efforts to overcome it in experiments.

Metal inclusions in experiments and the analysis of contaminated phases

The presence of a dispersed metallic phase contaminant in quenched silicate melts from solubility experiments has been recognized since the earliest efforts to determine values of D^{Met/Sil} for the HSE (Kimura et al. 1974). An array of different particle sizes have been implied, ranging from $\sim 0.05 \,\mu\text{m}$ to $\sim 5 \,\mu\text{m}$, also with varied spatial distributions (compare Ertel et al. 1999; Cottrell and Walker 2006; Fortenfant et al. 2006; Mann et al. 2012). Owing to their small size and dispersed nature, it has been difficult to fully document the characteristics of these inclusions, even by high resolution electron microscopy. Hence, the most commonlyused indication of their presence has been poorly reproducible solubility measurements and heterogeneous time-resolved LA-ICPMS spectra (e.g., Ertel et al. 2001, 2006). Any study of solubility and partitioning where metal inclusions are suspected must therefore assess their presence as either an exsolved, but once dissolved, component of the silicate melt, or instead a discrete metal phase at the conditions of the experiment (hereafter referred to as 'quench' and 'stable' inclusions respectively). If the metal particles have the latter origin, then their contribution to the analyses of silicate run-products whose intrinsic HSE concentration is very low will increase the apparent solubility. This issue embodies much of the ambiguity over the true solubility and partitioning of HSEs at reducing conditions.

Early efforts to determine HSE solubility used bulk analytical techniques (e.g., neutron activation analysis, scintillation spectrometry), which required extra care to ensure a minimum level of metal contamination, including reversal experiments, measurements on different aliquot sizes, thorough cleaning of the exterior portion of glass shards, etc. For the cases of Pd (Borisov et al. 1994) and Au (Borisov and Palme 1996), solubility determined by these methods produced reproducible results, and systematics with f_{0} , consistent with thermodynamic expectations. Other metals, such as Ir, Os, and Re, produced more scattered results, which is now suspected to be a result of metal contamination (Ertel et al. 2001; Fonseca et al. 2011). The arrival of LA-ICPMS as a readily available tool for trace element analysis (e.g., Jackson et al. 1992) provided an alternative, in situ, approach to solubility measurements. The time-resolved spectra produced during sample ablation revealed metal inclusions manifested as high count-rate 'peaks' separated by low count-rate 'troughs', the latter thought to more closely represent the intrinsic signal from metal dissolved in the silicate (Fig. 4). Under this pretext, several studies have filtered their analytical results by calculating concentrations from only the "trough" portion of the spectra, (e.g., Ertel et al. 2001, 2006; Laurenz et al. 2013), yielding reasonably systematic relations between solubility and f_{0} , at conditions at least as reducing as the FMQ buffer. How closely the low count-rate portions of spectra represent truly inclusion-free silicate however, will depend upon the nature of both the sample (inclusion size, spatial distribution) and the analytical

² Note that there is a similar problem encountered in sulfide-bearing silicate systems, further described in the Section *Sulfide–melt/silicate melt and MSS–silicate melt partitioning*.



Figure 4. Time-resolved LA-ICPMS spectra for Pt in the silicate portion of inclusion-contaminated experiments by Bennett et al. (2014) (a) and Ertel et al. 2006 (b). In panel (a), counts per second Pt are normalized to the signal for Ca, an abundant lithophile element that is unaffected by the presence of metal inclusions. This procedure isolates heterogeneity arising due to the ablation of metal inclusions from instrumental signal variability. The small grey area in panel (b) shows the region used for data-reduction by Ertel et al. (2006) to determine 'filtered' Pt concentrations (see Metal Inclusions in Experiments and the Analysis of Contaminated Phases for details).

conditions (spot-size, wash-out time of the ablation cell). Most importantly, solubilities determined using this method still rest upon assigning all of the heterogeneity to inclusions having a stable origin, which does not account for the possibly of some exsolved metal. The difficulty associated with analysis of inclusion-contaminated silicate run-products has driven attempts to suppress the formation of the metal particles (Borisov and Palme 1995; Ertel et al. 1999, 2001; Borisov and Walker 2000; Ertel et al. 2001; Brenan and McDonough 2009; Bennett and Brenan 2013; Bennett et al. 2014; Médard et al. 2015). Due to the success of these efforts, the database of inclusion-free solubility measurements is now sufficient to assess the oxidation state of most HSEs dissolved in silicate melt at reducing conditions, and derive accurate values of metal–silicate partitioning. The experimental and analytical approaches used to generate this database are outlined in the section *Experimental methods to measure HSE solubility and metal/silicate partitioning*.

Prior to describing the methods to measure partitioning, and their results, a brief review is provided of some of the proposed mechanisms for inclusion formation.

Possible mechanisms of metal inclusion formation

A diverse range of mechanisms have been proposed for the formation of dispersed metal inclusions in glasses synthesized at high temperature and low f_{O_2} . In the following discussion two categories of metal inclusions are considered: 1) 'quench' inclusions that form by exsolution from the silicate melt during the cooling step that accompanies the termination of an experiment and 2) 'stable' inclusions that are present as a discrete metal phase at the *P* and *T* of the experiment.

Quench metal inclusions. HSE solubility experiments are terminated by rapid cooling of the sample, so if the solubility of the HSE is prograde, then this step may cause oversaturation in HSE metal. In some instances, the silicate melt does not quench to a glass, so HSE metal may also form by local saturation due to a build-up in concentration in the residual melt by the crystallization of phases that exclude the HSE. The increase in solubility with temperature documented for nearly all of the HSE (See: Summary of experimental data) suggests that if quench rates are sufficiently slow, then HSE metal grains will begin to nucleate and grow. Cottrell and Walker (2006) outline several expectations for inclusions formed in this manner: an increase in diameter with decreased cooling rate, spatial variability in the distribution of inclusions due to differences in cooling rate across the sample, and a compositional difference between inclusions and the bulk HSE \pm Fe source metal. Cottrell and Walker (2006) document all of these features in experiments to measure Pt solubility done at 2.2–2.3 GPa and 1940–2500 °C, providing a strong argument that the inclusions observed in their silicate run-products were formed by exsolution when the sample was quenched. These authors also measured comparable Pt concentrations in portions of the sample both with and without visible contamination by metal inclusions; consistent with a spatial variability in the quench rate within the sample.

In the metal–silicate partitioning study of Mann et al. (2012), the silicate melt phase did not quench to a glass, but instead to a fine intergrowth of quench crystals. This is a common result for melt compositions which are poor in network-forming cations, as in this case. Metal particles were found to be concentrated along the boundaries of skeletal olivine crystals that formed during quenching. These particles were interpreted to form by HSE buildup during quench crystallization, and included as part of the original high P-T melt composition, on the basis of uniform element concentrations measured across the sample and smooth correlations between $D^{\text{Met/Sil}}$ and f_{O_2} . It is noteworthy that even if metal-inclusions in the Mann et al. (2012) study did not form exclusively upon quench, and values of $D^{\text{Met/Sil}}$ were thus underestimated, Re, Ir and Ru are still found to be too siderophile to account for their PUM abundance.

Although there is good evidence for the formation of a metal phase during quench in both these previous studies, it remains possible that experiments also contain stable inclusions. However, at the very high experimental temperatures, and associated high solubilities, the relative contribution of stable inclusions to the measured concentrations is likely to be small.

Stable metal inclusions. Unlike inclusions that form when the sample is quenched, stable metal inclusions are expected to display a relatively uniform spatial distribution and possess the same composition as that measured for the bulk metal source. Although cooling rate should not have any effect on the nominal size of stable inclusions, it is foreseeable that they may act as sites for heterogeneous nucleation of metal precipitated by over-saturation of the melt during quench. The small size of stable inclusions can render them undetectable by scanning electron microscopy, preventing their distribution and composition from being accurately determined and their origin confirmed. Conclusive evidence that metal inclusions can form as a stable phase in experiments has now been provided by Yokoyama et al. (2009) and Médard et al. (2015). Yokoyama et al. (2009) measured metal-silicate partitioning of Os using a natural meteorite starting material. The Os isotopic compositions of inclusion-contaminated run-product glasses define a mixing array between the meteorite starting material, and inclusion-free glass. This implies that inclusions in these experiments possess the same isotopic composition as the meteorite starting material. The measured array in Os concentration and isotope composition therefore reflects different glass to inclusion ratios in the individual aliquots. By contrast, inclusions formed upon quench should resemble the isotopic composition of the silicate melt and not define mixing lines that extend to the meteoritic starting material. Médard et al. (2015) performed solubility experiments in a centrifuge piston-cylinder, and found that the Pt content of melts subject to high acceleration was lowest in the top-most portion of the sample, suggesting partial segregation of stable metal particles to the base of the sample. Combined, these results confirm the assertions of earlier studies that suggest a stable origin for inclusions on the basis of sample heterogeneity (Borisov and Palme 1997; Ertel et al. 1999, 2006).

Perhaps the most obvious means to introduce metal particles into silicate melt is by erosion of the metal source. This mechanism was advocated by Yokoyama et al. (2009) based on the similarity in the isotopic composition of the metal contaminant with the metal phase added to experiments. In contrast, Ginther (1971) proposed that contamination of glass by platinum inclusions occurred *via* oxidation of the Pt container, caused by the dissociation and evaporation of alkali or alkali-earth oxide complexes in the melt. This mechanism was based on the observation that inclusions were restricted to surface layers of the unstirred melt and independent of the f_{O_2} of the atmosphere within which the experiment was performed. Borisov and Palme (1997) noted that this mechanism would be most effective under reducing conditions, where alkali metal evaporation is enhanced, and may potentially explain the formation of Pt and Ir inclusions in their low f_{O_2} experiments. Although this may be a viable process in open-system experiments performed using gas-mixing at ambient pressure, it cannot explain the formation of metal inclusions in experiments done at high confining pressure and is unlikely to afflict experiments performed in vacuum-sealed silica tubes.

Metallic Pt inclusions have been well documented during the synthesis of large volumes (>0.5 L) of phosphate laser glass. Campbell et al. (1989) summarized previous studies of laser glass synthesized in Pt containers and concluded that thermal gradients were responsible for the formation of metal inclusions. The experimental design used in these studies involved induction heating of the sample in a Pt crucible. Once the sample was molten, more feedstock was added to increase the level in the crucible. Campbell et al. (1989) identify relatively large thermal gradients will force precipitation of metal inclusions. Most petrologic experiments done at 0.1 MPa however, are performed using small sample sizes (<2 mL), in the absence of significant thermal gradients, suggesting that this mechanism does not account for the formation of inclusions in most of the studies discussed as part of the present work.

The formation of metal particles in experiments containing certain alloy-forming impurities is a mechanism proposed by Borisov and Palme (1997) that may potentially apply to both ambient- and high-pressure studies. In this scenario, dissolved oxide components in the melt react with the HSE source material to produce oxygen and an HSE alloy as the product. For example the reaction proposed by Borisov and Palme (1997) for Pd is:

$$Pd_{(Met)} + xSiO_{2(Sil)} = PdSi_{x(Met)} + xO_{2(g)}$$

$$(41)$$

Decreasing f_{O_2} therefore favours the formation of stable alloy grains. Borisov and Palme (1997) suggest that the presence of impurities that react more readily with HSEs than Si, such as As, Sb, Bi, Ge, Sn, and Pb, may increase the likelihood of alloy formation. In open-system gas mixing experiments, the volatile nature of potential alloying elements should lead to progressive loss at high *T*, resulting in metal inclusions free of these impurities by the end of an experiment (Borisov and Palme 1997). Borisov and Walker (2000) made use of these concepts and removed volatile contaminants from starting materials by fusion at controlled f_{O_2} conditions. This resulted in inclusion-free run-product glasses produced at a f_{O_2} lower than past work. Although it may have been the removal of contaminants from reagents that prevented inclusions from forming, pre-reduction of the sample may also have played a role (see below).

Fortenfant et al. (2006) found that erosion of the sample crucible or stirring spindle was an unlikely source of the Os inclusions in their experiments, after identifying components in an inclusion that were not present in the labware used to perform the experiment. On this basis, the authors instead suggested that inclusions originate as a result of exsolution from silicate melt, driven by changes in sample f_{O_2} . Bennett et al. (2014) developed this idea and proposed a mechanism for stable metal inclusion formation based on the time-evolution of f_{O_2} during the initial stages of an experiment. Most metal solubility experiments use starting materials that are fully or partially oxidized (i.e., Fe present as Fe²⁺, Fe³⁺ and sample capsules loaded



Figure 5. Schematic for the formation of metal inclusions as described by Bennett et al. (2014). The process can be subdivided into three steps, 1) initial, high sample f_{O_2} and rapid HSE in-diffusion; 2) reduction in sample f_{O_2} causes oversaturation in HSE and precipitation of metal inclusions; 3) equilibrium f_{O_2} conditions, small size of inclusions prevents gravitationally-driven segregation. Low solubility also hinders inclusion growth by Ostwald ripening (Médard et al. 2015). [Used by permission of Elsevier Limited, from Bennett, Brenan and Koga (2014) *Geochimica et Cosmochimica Acta*, Vol 133, Fig. 2, p. 427.]

in air), but then subject to a reducing atmosphere or encapsulated in a reducing material (e.g., graphite). Once the sample is heated, reaction between the sample and the reductant occurs, and the initially high f_{O_2} , imposed by the starting materials, begins to fall. For the case of a graphite-encapsulated experiment initially undersaturated in a fluid phase, the redox reaction is:

$$C_{(s)} + \frac{3}{2}O_{2(g)} = CO_{3}^{2-}(sil)$$
 (42)

This reaction will proceed until an equilibrium CO_3^{2-} concentration is obtained.³ With reference to Equation (25), the dissolution of HSEs in silicate melt requires oxidation of the metal phase, hence reduction of oxidized starting materials by Reaction (42) causes an accompanying decrease in metal solubility. If the kinetics of HSE dissolution are suitably rapid, the silicate melt may be endowed with elevated metal concentrations initially, but as f_{O_2} drops, saturation occurs and HSE grains may precipitate. This process is portrayed schematically in Figure 5. Médard et al. (2015) note that in all past experiments in which stable metal inclusions are observed, the equilibrium f_{O_2} of the experiment is lower than that of the starting materials, consistent with the operation of the proposed reduction mechanism. Borisov and Walker (2000)

³ The carbonate anion is chosen in this case to represent the dissolved carbon species as it has previously been identified as an oxidized carbon species present in silicate melts (e.g., Mysen et al. 2011).

also reported that experiments in which starting glasses were synthesized at the same conditions as the subsequent solubility determination were less susceptible to contamination by Os metal inclusions—procedures that would have suppressed an initially oversaturated state.

Experimental methods to measure HSE solubility and metal-silicate partitioning

A simple method for measuring HSE solubility is by suspending a silicate melt bead within a wire loop, or encapsulated in foil, made of the pure metal, then equilibrating the sample in a gas-mixing furnace at high temperature. Samples are rapidly quenched, then analysed for the HSE by either bulk (e.g., Borisov et al. 1994; Borisov and Palme 1995, 1997) or *in situ* methods (Laurenz et al. 2013). Variations on this approach involve the use of alloys, whose composition either allow higher equilibration temperatures without melting (e.g., Pd-Au; Borisov and Palme 1996) or involve a combination of metals, one of which is wire-forming (e.g., Ni) with those that are not (e.g., Os; Borisov and Palme 1998; Borisov and Walker 2000). Borisov and Walker (2000) modified this technique to suppress the formation of stable Os metal nuggets by using Ni-Os alloy in the wire loop, and pre-saturating the silicate melt in Ni prior to the solubility experiment. This pre-saturation step was considered to suppress chemical erosion of the Ni-Os loop, and subsequent entrainment of metal particles in the melt. Note that for experiments employing alloy source material, HSE concentrations measured in the silicate melt must be corrected to solubilities corresponding to equilibrium with the pure $C_{\rm M}^{\rm Meas}$ HSE phase ∽Sat

$$C_{M (Sil)} = \frac{1}{a_{M (Met)}}$$

The mechanically assisted equilibration (MAE) method allows for the approach to metalsilicate melt equilibrium to be monitored over the course of an experiment, while the sample is subject to continuous stirring (Dingwell et al. 1994). In this technique, a relatively large mass of silicate melt is contained in a metal crucible within the hot zone of a gas-mixing furnace. The melt is subject to forced convection by a rotating metal spindle suspended axially, with material sampled from the crucible sequentially so as to obtain a solubility vs. time history. The purpose of the rotating spindle is to promote metal–silicate equilibration involving advective as well as diffusive exchange with the metal source. An extensive review of this technique as applied to HSE solubility measurements is given by Ertel et al. (2008). Despite this advance, however, it has been difficult to obtain reproducible solubility measurements at f_0 , more reducing than FMQ.

Brenan and McDonough (2009) and later Bennett and Brenan (2013) were able to suppress the formation of stable Ir, Os, and Re inclusions in high-pressure (2 GPa) experiments by adding these metals encapsulated in a pre-melted gold bead. This approach yields a unique experimental geometry that changes the relationship between f_{O_2} evolution and HSE indiffusion during the early stages of an experiment. Molten Au strongly wets Re, Os, and Ir at high *T* to form a rind that physically separates the bulk HSE source in the experiments from the silicate melt (Fig. 6). This rind slows the diffusive transfer of the encapsulated metal into the silicate melt, thus allowing the melt to undergo reduction prior to the onset of metal dissolution. This technique has proved successful in suppressing metal inclusion formation under conditions as reducing as IW – 1.2 (Brenan and McDonough 2009). One tenet of the Au rind method is that the HSE of interest must be sparingly soluble in molten Au, so as to limit the HSE flux to the silicate melt. It is therefore unsuitable for investigating elements such as Pt and Pd, which display complete miscibility with Au at high temperature.

Bennett et al. (2014) performed experiments to measure Pt solubility in molten silicate by adding elemental Si to starting materials, which serves to strongly suppress any initial oxidation of the melt, and thereby inhibit the formation of inclusions by initial oversaturation. The veracity of this approach was tested in experiments done both with and without added Si, with the time-resolved analysis of run-products as a guide to inclusion abundance. Control experiments, which



Figure 6. Example of a run-product from a piston-cylinder experiment to measure the solubility of Au and Os in molten silicate at 2000°C and 2 GPa. (a) Reflected light image of the run-product showing the quenched silicate melt (now glass) surrounded by the graphite capsule. At the bottom of the glass portion is a bead of gold, quenched from the liquid state, encapsulating grains of osmium metal, which were solid during the experiment ($T_{melting}$ for Os=3027°C). (b) Close-up of outlined area in (a) showing the efficient wetting of the osmium grains by the gold melt. (c) Schematic showing the distance, *x*, through which the HSE of interest must diffuse before HSE begins to dissolve into the melt.

had no silicon added, display significant heterogeneity of the time-resolved spectra for Pt, in contrast to the uniform (and relatively low intensity) signal for Pt in experiments done with 0.75–2 wt% added Si. Although this technique was successful in producing uncontaminated samples as reduced as IW – 1.6 at temperatures \geq 1900°C, inclusions were identified in experiments at 1800°C and ~IW, suggesting this method may be less effective at lower temperatures.

The small size of stable inclusions and the low solubility of the HSE in general would seem to preclude the segregation of metal grains from silicate melt without the assistance of stirring; an effect not easily achieved in high pressure experiments. Subjecting the molten sample to high acceleration however, increases the settling velocity of dense particles from the silicate melt. With this in mind, Médard et al. (2015) used a piston-cylinder mounted in a centrifuge to perform Pt solubility experiments at accelerations of up to ~1500 g₀. Run products from synthetic Fe-free melts achieved partial cleansing by this method. Experiments done with a natural FeO-bearing melt yielded similar solubility for static and high-g₀ experiments, which was attributed to the role of dissolved FeO as an oxygen donor to facilitate.

In addition to experiments which have measured the solubility of pure metals, or binary metal alloys, then calculating partition coefficients from Equation (36), other work has focused on more direct determinations using Fe-rich alloy compositions. As gold is the most soluble of the HSE in molten silicate, it is possible to measure Fe metal–silicate melt partitioning for relatively dilute Fe–Au alloys (i.e., <4 wt% Au), for which results have been reported by Brenan and McDonough (2009) and Danielson et al. (2005). A comparison of partitioning calculated from the solubility of pure Au with this more direct method has yielded very good agreement (see *Effect of oxygen fugacity*). Other experiments have also involved Fe-bearing multicomponent alloys, but with the HSE more concentrated (Mann et al. 2012). In that case, the challenge is access to an accurate solution model for extrapolating apparent partition coefficients to infinite dilution.

Summary of experimental data

The existing database of HSE solubility and partitioning data contains significant complexity, arising from the issues surrounding metal inclusions discussed above. To simplify the following overview of HSE behavior as a function of *P*, *T*, *X*, and f_{O_2} , only those data which are demonstrably free from contamination or have been shown to agree well with the data

from such experiments (e.g., data from filtered LA-ICP-MS spectra) are presented. Unless otherwise stated, the oxidation states quoted below have been determined by linear regression of solubility vs. f_{0} , plots using the following relationship:

$$\log C_{\rm M (sil)}^{\rm Sat} = \frac{n}{4} \log f_{\rm O_2} + \rm Constant$$
(43)

Effect of oxygen fugacity–Rhenium: Several studies have determined the solubility of Re as a function of f_{O_2} and data now exists at 0.1 MPa to 18 GPa and 1400–2500°C (Fig. 7). At 0.1 MPa and above ~IW + 1, Re is thought to be dissolved as a mixture of 4+ and 6+ species, with 6+ being dominant across most of the f_{O_2} range (Ertel et al. 2001). This result is consistent with crystal–melt partitioning experiments that also indicate 4+ and 6+ species for Re above ~IW (Mallmann and



Figure 7. Solubility vs. f_{0_2} relative to the iron–wustite buffer for all the HSEs, after correction to unit activity of HSE metal. Also indicated are slopes for the likely oxidation states of these elements in the melt. Data are from the following sources and are ambient pressure results unless otherwise noted: (**Au**) Borisov and Palme (1996) 1300–1480°C; Brenan and McDonough (2009) 2 GPa, 2000°C; Bennett and Brenan (2013) 2 GPa, 2000°C; (**Pd**) Borisov et al. (1994) 1350–1415°C; Laurenz et al. (2010) 1300°C; Mann et al. (2012) 6–18 GPa, 2150–2200°C; (**Pt**) Borisov and Palme (1997) 1400°C; Ertel et al. (1999) 1300°C; Cottrell and Walker (2006) 2.2–2.3 GPa, 2000°C; Mann et al. (2012) 6 GPa, 2150°C; Bennett et al. (2014) 2 GPa 2000°C; Médard et al. (2015) 1.2 GPa, 1900°C; (**Ir**) Borisov and Palme (1995) 1300–1480°C; Brenan and McDonough (2009) 2 GPa, 2000°C; Mann et al. (2011) 1500°C (**Rh**) Ertel et al. (1999) 1300°C; Fortenfant et al. (2003) 1300°C; Mann et al. (2012) 6–18 GPa, 2150–2200°C; (**Ru**) Borisov and Walker (2000), 1400°C; Fortenfant et al. (2006) 1350°C; Brenan and McDonough (2009) 2 GPan 2000°C; (**Ru**) Borisov and McDonough (2009) 1300°C; (**Ru**) Borisov and Nachtweyh (1998) 1400°C; Laurenz et al. (2013) 1300°C; Mann et al. (2013) 1300°C; (**Ru**) Borisov and Nachtweyh (1998) 1400°C; Eurenz et al. (2001) 1400°C; Bennett and Brenan (2013) 2 GPa, 2000°C; (**Ru**) Reprisov and McDonough (2009) 2 GPan 2000°C; (**Ru**) Borisov and Nachtweyh (1998) 1400°C; Eurenz et al. (2013) 1300°C; Mann et al. (2012) 6 GPa, 2150°C; (**Re**) Righter and Drake (1997) 1150–1350°C; Ertel et al. (2001) 1400°C; Bennett and Brenan (2013) 2 GPa, 2000°C.

Neill 2007; see also *Silicate and Oxide Control on HSE Fractionation*). The lowest f_{O_2} timeseries experiment of (Ertel et al. 2001), however, does suggest a minor contribution from a more reduced species. In isolation, high *P*–*T* data acquired between IW+2.5 and IW-1.5 suggest Re is dissolved in silicate melt as a 2+ species (Mann et al. 2012; Bennett and Brenan 2013). Correction of the data at 1400°C from Ertel et al. (2001) to 2000°C for comparison with the data of Bennett and Brenan (2013), however, reveals moderately good agreement between these datasets above ~IW+1 but evidence for a more reduced species in the higher *T* dataset at lower f_{O_2} (Bennett and Brenan 2013). At present, there is insufficient data to thoroughly assess at what f_{O_2} Re²⁺ becomes the dominant dissolved species, or to what extent this transition may depend upon *P* or *T*.

Osmium: Experiments at 0.1 MPa and 1350–1400 °C using Fe-free melts suggest Os is dissolved primarily as a 3+ species between ~IW+1 and IW+4, although the presence of Os⁴⁺ cannot be excluded on the basis of these data (Borisov and Walker 2000; Fortenfant et al. 2006). Data from 0.1 MPa experiments performed at more reducing conditions display evidence for contamination by metal inclusions, preventing straightforward measurement of Os concentrations. Filtering of time-resolved LA-ICP-MS signals was found to be impossible due to the very low concentration of Os dissolved in the melt and the high Os background associated with available sulphide standards (Fortenfant et al. 2006). Brenan and McDonough (2009) however, were able to measure Os solubilities by LA-ICPMS in uncontaminated Fe-bearing experiments performed at 2 GPa 2000 °C and as reduced as IW –1.6. These authors suggest solution as mixed 1+ and 2+ species based on the slope of 0.38 defined by their data. Although neither of these oxidation states is suggested by the 0.1 MPa data, it is worth noting that a mixture of 1+ and 3+ species also yields an adequate fit to the high *T* data. Importantly, the high *T*, low f_{O_2} experiments suggest there must be some contribution from a species more reduced that Os²⁺ (expected slope of 0.5).

Iridium: O'Neill et al. (1995) determined the solubility of Ir in CaO-MgO-Al₂O₃-SiO₂ (CMAS) melt at 1400°C between IW-1.5 and IW+10. At conditions more oxidizing than \sim IW+4, the change in Ir solubility is consistent with solution as a 2+ species (slope of ~0.5). At more reducing conditions however, O'Neill et al. (1995) observed no change in solubility with f_{0} and ascribe this to either contamination by metal inclusions or solution as either Ir⁰ or Ir-carbonyl species. More recent solubility measurements at 1500°C on a similar composition over a comparable f_{O_2} interval, reported by Fonseca et al. (2011), yielded results consistent with Ir^{3+} (slope of 0.75). A possible reason for the discrepancy between the two studies is that the metal contamination suggested in the experiments of O'Neill et al. (1995) are largely avoided in the work of Fonseca et al. (2011), as that study employed LA-ICPMS for sample analysis. Borisov and Palme (1995) determined the solubility of Ir-poor alloys ($Ir_{10}Pt_{90}$) over a similar range of f_{0} , and melt composition at 1300 °C and 1480 °C. Their data are consistent with solution as a 1+ species between ~IW-1 and IW+8 and mixed 2+ and 3+ species at more oxidizing conditions (slope of 0.68). Results from 2 GPa experiments at 2000 °C also suggest Ir dissolves predominantly as a 1+ species between IW + 0.5 and IW + 2.7 in basaltic melt. Mann et al. (2012) determined Ir partitioning at high P-T conditions (3.5-18 GPa, 2150-2500°C) and their data suggest Ir^{2+} as the dissolved species between ~IW-1.5 and IW+0.5, although the authors acknowledge that this trend is not well defined. Spinel-melt partition coefficients measured at \sim IW + 1 to + 6 are also consistent with Ir²⁺ in the crystal lattice (Brenan et al. 2012). It is therefore likely that Ir²⁺ persists as a subordinate species at these more reducing conditions.

Ruthenium: Borisov and Nachtweyh (1998) investigated Ru solubility at 0.1 MPa and 1400 °C in anorthite-diopside melts between ~IW+6 and IW+10. Their results define a slope of 0.73, corresponding to a 3+ oxidation state (Fig. 7). These results are consistent with the crystalmelt partitioning of Ru in olivine and spinel, that also suggest Ru³⁺ is present over much of the terrestrial f_{O_2} range (Brenan et al. 2003, 2012). Laurenz et al. (2013) measured Ru solubility in picrite melts at 1300 °C, 0.1 MPa and IW+3.5 to IW+5.5, obtaining results consistent with Ru dissolved as a 4+ species (Fig. 7). These authors suggest the difference in their data is due to the use of Fe-bearing melt compositions, that stabilize more oxidized species through redox exchange reactions analogous to those observed for Pd (Laurenz et al. 2010):

$$\operatorname{RuO}_{3/2(\operatorname{sil})} + \operatorname{FeO}_{3/2(\operatorname{sil})} = \operatorname{RuO}_{2(\operatorname{sil})} + \operatorname{FeO}_{(\operatorname{sil})}$$
(44)

In experiments done using Fe-bearing melt compositions at 6–18 GPa, 2150–2300 °C and IW –1.5 to IW+0.5 measured solubilities suggest Ru²⁺ is the dominant species (Mann et al. 2012). This is consistent with evidence from chromite-melt partitioning experiments, done at lower *P-T* conditions, that Ru²⁺ becomes dominant at conditions more reducing than ~IW+2.5 (Brenan et al. 2012).

Rhodium: Ertel et al. (1999) determined the solubility of Rh in experiments performed at 0.1 MPa and 1300 °C in melts with a composition close to the anorthite-diopside eutectic (Fig. 7). Between ~IW+6 and IW+11, their data suggest Rh is dissolved primarily in the 2+ oxidation state, with a minor contribution from either a 3+ or 4+ species. Ertel et al. (1999) consider Rh³⁺ more plausible however, as the 3+ solid oxide is the stable phase at high temperature in air (Nell and O'Neill 1997). At more reducing conditions, measurements of Rh solubility at 0.1 MPa display evidence for contamination by stable metal inclusions. Regression of high *P*–*T* (6–18 GPa, 2150–2300 °C) experiments at IW – 1.5 to IW +0.5 yields a slope of 0.36, suggesting a mixture of Rh²⁺ and a more reduced species (Mann et al. 2012). Experiments to determine the olivine-melt (0.1 MPa, ~1330 °C) and chromite-melt (0.1 MPa–2 GPa, 1400–1900 °C) partitioning of Rh (see *Spinel–melt partitioning of HSEs*) are also consistent with the prevalence of a 2+ species between ~IW+5 and IW+7 (Brenan et al. 2003, 2012).

Platinum: At relatively oxidizing conditions (above \sim IW+5), isothermal suites of experiments at 0.1 MPa define slopes of \sim 0.5 between 1300 and 1560°C, suggesting Pt is dissolved as a 2+ species (Borisov and Palme 1997; Ertel et al. 1999). Spectroscopic determination of Pt oxidation state in CAS glasses synthesized at 1630°C in air indicate the presence of 4+ species at highly oxidized conditions (Farges et al. 1999).

At more reducing conditions (~IW –0.8 to IW + 3.4), in experiments which were demonstrably free of contamination by metal inclusions, Bennett et al. (2014) observed a slight increase in Pt solubility with decreasing f_{O_2} in basaltic glasses at 2 GPa and 2000 °C. They interpret these results as owing to the presence of both neutral Pt and an unidentified Pt cationic complex. The solution of Pt-carbonyl species at low f_{O_2} is discounted however, as no correlation is observed between Pt solubility and the carbon content of the melt (Bennett et al. 2014). A similar increase in solubility with decreasing f_{O_2} was found by Médard et al. (2015) at more reducing conditions (~IW – 2.5 to IW – 0.5) in experiments at 1.2 GPa and 1900 °C. At lower T (1400 °C and 1600 °C) but similar f_{O_2} , however, Médard et al. (2015) measure constant Pt solubility with changing f_{O_2} . They interpret data with approximately constant solubility as suggesting Pt⁰ dissolved in the melt. Results from both Médard et al. (2015) and Bennett et al. (2014), that define a trend of increasing solubility as conditions become more reducing, are more consistent with the presence of either anionic platinum or the formation of complexes such as PtSi_x.

Although solubilities are broadly consistent with past work at similar conditions, Mann et al. (2012) observe a slight *decrease* in Pt solubility with decreasing f_{O_2} between IW+0.5 and IW-1.5 at conditions of 3.5–18 GPa and 2150–2500 °C. Isothermal, isobaric sets of experiments from that study define an average slope of 0.29, consistent with Pt¹⁺ dissolved in the melt. It is unclear why these experiments yield a different result to the studies of Bennett et al. (2014) and Médard et al. (2015), as all were conducted using Fe-bearing melt compositions, and pressure appears to have little effect on Pt solubility (see *Temperature and pressure*). It is also unlikely that the higher temperatures employed in the Mann et al. (2012) study are

responsible, as measurements of Au and Pt solubility both suggest that increased *T* favours the reduced species (Borisov and Palme 1996; Médard et al. 2015). Cottrell and Walker (2006) also investigated Pt partitioning over a similar range of *P*–*T* conditions to Bennett et al. (2014) and Médard et al. (2015), but measured Pt solubilities that are systematically higher. Between IW–0.75 and IW–5.32, these authors observe no systematic dependence of solubility on f_{O_2} . These experiments may represent a continued increase in solubility with decreasing f_{O_2} , as suggested by extrapolation of the trend defined by 2000°C data from Bennett et al. (2014).

In summary, Pt is dissolved in silicate melt predominantly as 2+ species above $\sim IW+5$, with evidence for 4+ species at the most oxidizing conditions. At more reducing conditions the data is consistent with solution as Pt^0 , with either anionic species or non-oxide complexes becoming significant at the lowest oxygen fugacities investigated.

Palladium: Borisov et al. (1994) measured Pd solubility in experiments at 0.1 MPa and 1350 °C over a wide range of $f_{0,}$ (~IW to IW + 10) in anorthite-diopside melts (Fig. 7). These authors used a 3-species model to fit the data, comprising Pd²⁺, Pd¹⁺ and Pd⁰. The data were found to be consistent with Pd¹⁺ and Pd⁰ as the dominant species over the f_{Ω} range investigated, with Pd²⁺ contributing most significantly to the dissolved Pd contents in experiments more oxidized than ~IW+7. Further experiments at 0.1 MPa using anorthite-diopside melts extended the database of Pd solubility measurements to lower f_{0} , (~IW-1) and temperatures of 1300, 1400, and 1480°C (Borisov and Palme 1996). These data are consistent with the oxidation states for Pd indicated by the earlier study of Borisov et al. (1994). Experimentallydetermined olivine-melt partition coefficients at ~IW+7.8 and ~IW+3.0 (0.1 MPa, 1335 °C) also indicate a change from Pd^{2+} to Pd^{1+} as conditions become more reducing, in agreement with the solubility measurements (Brenan et al. 2003; Origin of the variation in partitioning). In experiments employing Fe-bearing melts however, Laurenz et al. (2010) observe lower solubilities below ~IW+3.5 than either Borisov et al. (1994) or Borisov and Palme (1996), and a dependence of solubility on f_{0} , that suggests Pd¹⁺ not Pd⁰ is the predominant dissolved species. Between ~IW+3.5 and +5.5 the data of Laurenz et al. (2010) again suggest Pd is dissolved as a more oxidized species than Borisov et al. 1994 (Pd²⁺ vs. Pd¹⁺), and report higher solubilities for this f_{0} , range accordingly. These authors attribute the higher oxidation state of Pd indicated by their data between \sim IW+3.5 and+5.5 to redox exchange reactions with Fe, analogous to those described above for Ru. However, it is important to note that it can be difficult to assess speciation in Fe-bearing experiments which cover the high f_{O_2} range in which both Fe²⁺ and Fe³⁺ are present, as the melt structural role of Fe³⁺ is different than Fe^{2+} (Farges et al. 2004). Hence, changes in solubility may also derive from changes in the activity coefficient for a single HSE species in response to melt structure, instead of a change in speciation (see Role of silicate melt composition on melt structure effects).

Figure 7 displays the high pressure data of Righter et al. (2008) and Mann et al. (2012) collected at 1.5 GPa and 6–18 GPa respectively, corrected to unit activity of Pd. For data from the Mann et al. (2012) study, activity coefficients for Pd in the metal were taken as the values calculated in their activity model. Correction of the data from Righter et al. (2008) was made using the Margules parameters summarized by Borisov and Palme (2000) for the Pd-Fe system and ignoring the presence of Sb (<7 wt%) in the alloy. Although only a limited number of isothermal high *P* data are available, those of Mann et al. (2012) (2150–2200 °C) appear to be broadly consistent with the speciation model employed by Borisov et al. (1994). The lower *T* data of Righter et al. (2008) (1800 °C) cover an insufficient range in f_{O_2} for speciation to be reliably determined from only these datapoints. However, the solubilities recorded by their experiments are similar to those found by Mann et al. (2012) at similar f_{O_2} but higher *T*. For temperatures >1800 °C, the experiments of Righter et al. (2008) suggest much greater Pd solubilities than measured by Mann et al. (2012). Although the reason for this discrepancy is not entirely clear, it is possible that the

presence of Sb in the alloys used by Righter et al. (2008) affects the partitioning behavior of Pd, and subsequently, the solubilities at Pd saturation we calculate from their data.

Gold: At 0.1 MPa and 1300–1480 °C, experiments performed between ~IW + 10 and IW using anorthite–diopside melt suggest Au is dissolved as 1+ species (average slope of ~ 0.23 ; Borisov and Palme 1996). Results also showed that at f_{O_2} below ~IW, however, the positive relationship between f_{0} , and solubility expected for the solution of metal-oxide species is reversed and solubility instead increases as conditions become more reducing. Borisov and Palme (1996) proposed that dissolution by way of an oxygen-producing reaction, such as the formation of silicide or carbide species, was most likely responsible for the observed increase in solubility at reducing conditions. Au solubility has also been determined in basaltic melts at 2 GPa and 2000 °C (Brenan and McDonough 2009; Bennett and Brenan 2013). These studies reveal a weak negative dependence of solubility on f_{O_2} between ~IW-1.2 and IW+2.6, suggesting Au is dissolved in the melt as Au⁰ with the possibility of an additional contribution from either a silicide or other cationic species. The formation of carbide or carbonyl complexes in the studies of Brenan and McDonough (2009) and Bennett and Brenan (2013) is considered unlikely, as no difference in solubility is observed between experiments performed in graphite vs. metal-alloy capsules. From the regression of partitioning experiments done at 3–23 GPa and 1750-2500 °C, Danielson et al. (2005) found D^{Met/Sil} decreases as conditions become more reducing, consistent with the results of solubility experiments. The fact that Au¹⁺ is not suggested by the high P-T data is also consistent with the experiments of Borisov and Palme (1996), which indicate the transition to reduced species occurs at a higher relative f_0 , at elevated temperatures. Results of gold solubility measurements in hydrous, S- and Cl-bearing compositions at low-P and -T are discussed in Concluding Remarks.

Role of silicate melt composition. Several studies have sought to determine the effect of silicate melt composition on HSE solubility. Borisov and Danyushevsky (2011) conducted a systematic investigation of Pt, Rh, and Pd solubility in air at 0.1 MPa and 1450–1550°C. Experiments performed in the CMAS system, with variable quantities of SiO_2 added to an anorthite-diopside eutectic composition, reveal markedly different behavior for Pd compared with Pt or Rh. Pd solubility increases by \sim 55 ppm with increasing silica content between \sim 50 and 55 wt% SiO₂. The addition of further silica to the system then causes a gradual decrease in solubility by ~75 ppm between ~55 and 70 wt% SiO₂. Pt and Rh, however, display a monotonic decline in solubility as the SiO₂ content increases from ~ 50 to 70 wt% SiO₂. The change in both Pt and Rh solubility over this interval is linear and more pronounced for Rh than Pt. Wheeler et al. (2011) observed a decrease in the concentration of Pd in the silicate portion of their metal-silicate partitioning experiments with increasing bulk Pd contents. They rationalized this result, and its relationship to earlier studies, by positing the existence of a curved silicate saturation surface; which is intersected by tie-lines between co-existing liquids at progressively lower Pd concentrations as the metal alloy becomes more Pd-rich. Analogous behavior, in which a curved silicate saturation surface exists in the Pd–Si–silicate melt system, may explain the variation in Pd concentration observed by Borisov and Danyushevsky (2011) in the CMAS system. Borisov and Danyushevsky (2011) also performed experiments for Pt and Rh in the CA \pm S system, and again observed a decrease in solubility for these elements with increasing silica content. Unlike the CMAS system, however, these experiments define a non-linear relationship between solubility and SiO₂ content. After correcting their solubility data for CMAS melts to 1550°C for comparison with results from the CA \pm S system, Borisov and Danyushevsky (2011) proposed the following relationships for Pt and Rh solubility as a function of melt composition:

$$\log C_{\rm Pt} = -4.59X_{\rm SiO_2} + 2.09X_{\rm SiO_2}^2 + 1.35X_{\rm Al_2O_3} + 2.92 \tag{45}$$

$$\log C_{\rm Rh} = -3.23X_{\rm SiO_2} + 1.65X_{\rm SiO_2}^2 - 1.03X_{\rm Al_2O_2} + 2.91 \tag{46}$$



Figure 8. Solubility as a function of composition for CMAS melts at 0.1 MPa and 1550 °C, as determined by Borisov and Danyushevsky (2011). Black triangles denote melts of anorthite–diopside eutectic+silica compositions, white triangles are for calcium–aluminium–silica melts (molar (CaO+MgO)/Al₂O₃=1.54 and 4.36 respectively).

The family of solubility vs. SiO_2 curves produced by Equations (45) and (46) for different (CaO+MgO)/Al₂O₃ ratios are portrayed in Figure 8, with the accompanying experimental data. These results are qualitatively consistent with those of Dable et al. (2001), also obtained in the CAS system (0.1 MPa, 1227 °C), who observe lower Pt solubility in melts with 70 wt% SiO₂ than those with 40 wt% SiO_2 for experiments done in air. In the experiments of Dable et al. (2001), however, this difference becomes less pronounced at low $f_{0,}$, suggesting the compositional effect may be smaller for reduced Pt species in the melt. A negligible compositional dependence for Pt solubility at low f_{0} is also supported by the agreement between high pressure experiments using basaltic to komatilitic melts (Mann et al. 2012; Bennett et al. 2014; Médard 2015). Nakamura and Sano (1997) conducted Pt solubility experiments at 0.1 MPa and 1600 °C in air, using a variety of binary oxide melt compositions (BaO-Al₂O₃, BaO-SiO₂, CaO-Al₂O₃, CaO-SiO₂, Na₂O-SiO₂). These authors cast their solubility measurements as a function of theoretical optical basicity, a measure of the electron donation capacity of the melt components. Results show a linear increase in the logarithmic Pt concentration with optical basicity, where the slope of this trend is identical for each of the studied oxide pairs. The absolute Pt solubility however, is ~100 times greater for melts containing BaO as the basic oxide component. The results of Nakamura and Sano (1997) indicate a similar relationship between melt composition and solubility to those of Borisov and Palme (1997) and Borisov and Danyushevsky (2011), but also suggest that the identity of the acidic melt component (i.e., Al_2O_3 or SiO_2) is unimportant relative to that of the basic component. Bond valence modeling of Pt in CAS melts suggests Pt is bonded to non-bridging oxygens surrounded by Ca second neighbors (Farges et al. 1999). This is also consistent with the observation that Pt solubility is enhanced in depolymerized melt compositions and tracks positively with CaO content. The study of Farges et al. (1999), however, also identifies Pt⁴⁺ not Pt²⁺ as the dissolved species in melts synthesized at 1630°C in air, contrary to that suggested by the dependence of solubility on f_{O_2} , albeit at lower T. Their model may, therefore, not apply directly to Pt in melts at low f_{0} . Most geologically important melt compositions contain iron, but most 0.1 MPa studies of HSE solubility have been performed using Fe-free melts. More recently, several studies have highlighted the role of Fe in both the solubility and speciation of HSEs in silicate melts (Laurenz et al. 2010, 2013). When compared with the solubilities of Pd



Figure 9. Solubility as a function of the melt structure parameter NBO/T (see the section *Role of silicate melt composition* for definition) for Pt and Rh at 0.1 MPa, 1400 °C. Solid lines represent a polynomial fit to the Fe-bearing experiments of Turchairo (2013). Dashed lines represent the same fit, translated to best match the Fe-free experiments of Borisov and Danyushevsky (2011). Both studies display a similar dependence on melt polymerization, however, solubilities in the Fe-bearing composition are systematically higher.

and Ru measured in Fe-free melts, these authors observed the stabilization of more oxidized dissolved species at a given relative f_{O_1} . They suggest this difference results from redox exchange equilibria with Fe as described, for example, by Equation (44). Whether solubility in Fe-bearing melts is higher or lower than seen for Fe-free melts will therefore depend upon the f_{O} conditions being investigated. Turchiaro (2013) investigated Pt and Rh solubility in basalt-rhyolite mixtures at 0.1 MPa, 1400 °C and ~IW+6.8. The solubility of both elements was seen to decrease with increasing proportions of the rhyolite component. When plotted as a function of non-bridging oxygens over tetrahedrally coordinated cations (NBO/T), a measure of melt polymerization, the variation in solubility measured by Turchiaro (2013) is comparable to that measured by Borisov and Danyushevsky (2011) in CMAS melts. After correction of their data to account for differences in T and $f_{\rm O}$ however, the absolute solubilities measured by Turchiaro (2013) are systematically higher than those of Borisov and Danyushevsky (2011) (Fig. 9). This is consistent with the idea that Fe may enhance HSE solubility through exchange equilibria of the type suggested by Laurenz et al. (2010). It should also be noted however, that the experiments of Turchiaro (2013) used natural starting materials containing several weight percent of alkali elements (Na₂O, K₂O) and TiO_2 that may also modify HSE solubility (Borisov et al. 2004, 2006).

Borisov et al. (2006) investigated the effect of sodium content on the solubility of Pd by adding various quantities of Na_2O to melts with an An–Di eutectic composition. In experiments done at 0.1 MPa, 1300°C and in either air or a CO₂ atmosphere, Pd solubility was seen to decrease by 20–30% with increasing sodium content, up to ~4 wt% Na_2O . Further addition of Na_2O however, elicits no change in Pd solubility up to ~11 wt% Na_2O , the most sodium rich composition investigated. The inverse behavior is observed for the addition of titanium oxide to CMAS melts, where little or no increase in Pd solubility is observed up to ~4 wt% TiO₂, after which the log Pd solubility increases in a linear fashion up to ~25 wt% TiO₂ (Borisov et al. 2004). A similar increase in solubility with TiO₂ content is observed for Ni and Fe (Borisov et al. 2004). Furthermore, the dependencies of both Ni and Co solubility on melt SiO₂ content are similar to that observed for Pd, but not Pt or Rh (Borisov and Danyushevsky 2011). These features suggest a similar structural environment might be shared by Pd, Ni, Fe, and Co, which is distinct from certain other HSEs such as Pt and Rh.

Sulfur may also affect HSE solubility by providing an additional ligand for the formation of dissolved species. In experiments saturated in an HSE metal phase, but undersaturated with respect to an immiscible sulphide phase, solubility may be enhanced through reactions with the form (Laurenz et al. 2013):

$$MO_{x/2 (met)} + \frac{x}{2} S^{2^{-}}{}_{(g)} = MS_{x/2 (sil)} + \frac{x}{2} O^{2^{-}}{}_{(g)}$$
(47)

Experiments for Ru at 1300 °C, 0.1 MPa and $\log f_{S_2}$ of -2.3 display an order of magnitude increase in solubility compared with sulfur-free experiments at otherwise identical conditions (Laurenz et al. 2013). It is possible that the addition of other complexing anions (e.g., Cl, P) may also enhance HSE solubility through reactions analogous to Reaction (47); however, Blaine et al. (2011) observed no increase in Pt solubility in Cl-bearing experiments.

Temperature and Pressure. It has been recognized for some time that the solubility of many siderophile elements in silicate melt increases with temperature (e.g., Murthy 1991; Capobianco et al. 1993; Walker et al. 1993; Hillgren et al. 1994). Recent studies have expanded the database for HSEs significantly and confirmed the presence of a *T* dependence for elements which previously had little or inconclusive data (e.g., Righter et al. 2008; Brenan and McDonough 2009; Mann et al. 2012; Bennett and Brenan 2013; Bennett et al. 2014; Médard et al. 2015). Measurements of HSE solubility are most often used to estimate metal–silicate partition coefficients, which can be calculated from Equation (36). This calculation however, depends not only on the HSE concentration in the melt at the solubility limit, but also on the activity coefficient for that HSE at infinite dilution in a liquid Fe solvent, γ_M . Values of γ_M may themselves vary with temperature and pressure, meaning an observed dependence of HSE solubility on these variables may not directly translate to similar behavior during metal–silicate partitioning. Where suitable thermodynamic data is available, γ_M may be calculated at the appropriate *P*–*T* conditions with a binary asymmetric mixing model (Thompson 1967):

$$RT\ln\gamma_{\rm M} = X_{\rm Fe}^2 \Big[W_{\rm M} + 2X_{\rm M} \Big(W_{\rm Fe} - W_{\rm M} \Big) \Big]$$
(48)

where $W_{\rm M}$ and $W_{\rm Fe}$ are Margules interaction parameters for the HSE of interest (M) and Fe respectively, that are calculated at the required *P* and *T* from individual components relating to the excess enthalpy (W_H) , entropy (W_S) and volume (W_V) of mixing:

$$W = W_H - TW_S + (P - P^\circ)W_V \tag{49}$$

where P° is the reference pressure at which W_H , W_S , and W_V were determined; typically 0.1 MPa (1 bar). The *T* dependence of *W* for most Fe–HSE binaries is relatively small, and Equation (49) provides a suitable value for *W*. For systems such as Fe–Pd and Fe–Pt, however, which have a greater dependence on temperature, it may be required to extrapolate values of *W* from the reference *T* at which the interaction parameters were acquired (T°), to the conditions of the experiment (Mann et al. 2012). This can be accomplished using the following relationship (Japan Society for the Promotion of Science 1988):

$$W = \left(W_H - T^{\circ}W_S + \left(P - P^{\circ}\right)W_V\right)\frac{T^{\circ}}{T}$$
(50)

A summary of the available thermodynamic data for Fe–HSE and HSE–HSE systems, and more detailed discussion of modeling the activity-composition relationships in multi-component HSE–Fe alloys can be found in Mann et al. (2012).

With these considerations in mind, Figure 10 displays the variation in $D^{\text{Met/Sil}}$ for the HSEs as a function of inverse temperature. All data show a decrease in $D^{\text{Met/Sil}}$ with increasing *T*, in



Figure 10. Metal–silicate partition coefficients for the HSE as a function of inverse temperature. The solid lines in each figure represent fits to the following data: (**Au**) 2 GPa, IW+1.7 to +2.0 Brenan and McDonough (2009), Bennett and Brenan (2013); (**Pd**) 0.1 MPa, IW-0.7 to +1.0 (excepting a single, anomalously low datapoint) Borisov et al. (1994), Borisov and Palme (1996); (**Pt**) 2 GPa, IW to IW+0.2 Bennett et al. (2014); (**Ir**) 2 GPa, IW+1.8 to +2.1 Brenan and McDonough (2009); (**Rh**) 0.1 MPa, ~IW+0.2 Usenate et al. (2014); (**Ir**) 2 GPa, IW+1.8 to +2.1 Brenan and McDonough (2009); (**Rh**) 0.1 MPa, ~IW+6 to IW+8 Fortenfant et al. (2003); (**Os**) 2 GPa, IW+1.7 to +2.3 Brenan and McDonough (2009); (**Ru**) 0.1 MPa, IW+7.4 to +7.8; (**Re**) 2 GPa, IW+1.7 to +2.0 Bennett and Brenan (2013). Dashed line in the panel for Pd represents the low P fit adjusted to best match the data of Righter et al. (2008). For Rh, the dashed line represents the same fit as the solid line, adjusted to match the low- f_{O_2} experiment of Ertel et al. (1999). The dashed triangles for Ru are high- f_{O_2} measurements re-calculated to correspond to IW as described in the text. The dashed line in this panel is the fit to the 0.1 MPa data adjusted to match the high-pressure data, suggesting a negligible role for pressure. For Re and Ir, only data from experiments more oxidizing than IW are plotted for the Mann et al. (2012) study, for straightforward comparison with the other high-*P* data.

the order $Pt > Os \approx Ir > Pd > Ru \approx Au > Rh > Re$. The solid lines in each panel of Figure 10 represent fits to an isobaric dataset acquired at the conditions noted in the caption. For most elements the dependence of $D^{Met/Sil}$ on *T* appears independent of *P* and f_{O_2} . At low *T* however (<1400 °C), some data for Pt fall systematically below the trend defined by data at higher *T* and pressures ranging from 0.1 MPa to 18 GPa. For the data of Ertel et al. (1999) and Fortenfant et al. (2003), this is due to the higher f_{O_2} of their experiments. It should also be noted that the weaker dependence of $D^{Met/Sil}$ on *T* indicated by the data of Fortenfant et al. (2003) is from

experiments performed at the same absolute f_{O_2} but different relative f_{O_2} , unlike data used to define the solid line in Figure 10 which represent experiments at a similar relative f_{O_2} .

For Pt, Re, Ru, Au, and to a lesser extent Pd, results from experiments done at 0.1 MPa to 18 GPa are generally well reproduced by a single linear regression, indicating only a weak or negligible effect of pressure on the partition coefficient. There are, however, several noteworthy exceptions. For Au, data collected at ≥ 21 GPa fall below the trend defined by results at 0.1 MPa to 13 GPa, suggesting pressure may cause a decrease in $D^{\text{Met/Sil}}$ at these conditions. Data for Pd also suggest little effect of *P* on $D^{\text{Met/Sil}}$ between 0.1 MPa and 3.5 GPa. Results from Mann et al. (2012) done at >6 GPa however, fall systematically below the trend defined by 0.1 MPa data. Experiments from the study of Righter et al. (2008) done at 1.5 GPa to 15 GPa also suggest lower values of $D^{\text{Met/Sil}}$ for Pd than expected from the 0.1 MPa trend (Fig. 10), although this may be due to the presence of Sb±Re±S±P±C in the alloy phase used in those experiments.

The effect of *P* on $D^{\text{Met/Sil}}$ for Os is difficult to assess due to the use of Os–Ni alloys as the HSE source in experiments at 0.1 MPa. Activity–composition relationships in this binary system are unknown and the measured concentrations of Os in the silicate portion of experiments performed by Borisov and Walker (2000) and Fortenfant et al. (2006) have been corrected to those expected for the pure metal by assuming ideality in the Os–Ni alloy. This leads to rather high corrected Os solubilities, accompanied by low values for $D^{\text{Met/Sil}}$. The presence of a miscibility gap in the Ni–Os system (Okamoto 2009), however, indicates the assumption of ideality for these alloys is an oversimplification and calculated values of $D^{\text{Met/Sil}}$ should therefore be considered minimumvalues. The experiments of Yokoyama et al. (2009), done at 1–2 GPa yield values of $D^{\text{Met/Sil}}$ that lie between those of Brenan and McDonough (2009) done at 2 GPa, and the ambient pressure studies, but provide little extra constraint on the pressure effect.

There are no data for Ru partitioning at 0.1 MPa and conditions more reducing than ~IW+5.5, preventing direct comparison to the available high-*P* results of Mann et al. (2012) obtained at more reducing conditions (~IW –1 to IW+0.5). Correction of the solubilities obtained from 0.1 MPa experiments at oxidizing conditions to the average relative f_{O_2} of high-*P* experiments, however, reveals good agreement between data at different pressures (0.1 MPa to 18 GPa). Correction of the 0.1 MPa data was done assuming either a 3+ (Borisov and Nachtweyh 1998) or 4+ (Laurenz et al. 2013) oxidation state for Ru dissolved in the melt, as found in the respective studies.

Metal-silicate partition coefficients for Au, Ir, Pd, and Rh, suggest a reduction in values with increasing P, for at least part of the investigated pressure range. For the case of Au, the effect of P is difficult to isolate, as the partitioning experiments of Danielson et al. (2005) that suggest a reduction in $D^{\text{Met/Sil}}$ at high \hat{P} are also sulfur-bearing. Values of $D^{\text{Met/Sil}}$ for Au are expected to decrease with increasing S contents of the metal phase (e.g., Jones and Malvin 1990) and S itself becomes more siderophile with increasing P (Boujibar et al. 2014). Runproduct compositions are not quoted by Danielson et al. (2005), making it difficult to quantify if the low values of D^{Met/Sil} recorded by experiments at 21 and 23 GPa are the direct result of P or the coupled effects of P and composition. Values of $D^{\text{Met/Sil}}$ for Rh at high P appear to lie along the trend defined by 0.1 MPa experiments (Fig. 10), however, there is a significant difference (> 4 log units) in relative f_0 , between these data. Plotting the same trend through an experiment done at 0.1 MPa, 1300°C and more reducing conditions (dashed line in Fig. 10), reveals the discrepancy between high and low pressure experiments. Fig. 11 displays D^{Met/Sil} for Rh as a function of pressure for the experiments of Mann et al. (2012) (\sim IW – 1.5 to IW + 1.5, 2150-2500 °C) and the 0.1 MPa experiments shown in Figure 10, corrected to 2180 °C and IW using the T dependence of Fortenfant et al. (2003) and assuming Rh^{2+} in the melt. Figure 11 portrays the negative dependence of $D^{Met/Sil}$ on P, which likely changes magnitude somewhere between 6 and 18 GPa (Mann et al. 2012). A similar comparison of D^{Met/Sil} vs. P can be made for Ir, after correction of data at similar f_{O_2} (~IW+0.5 to IW+0.7) to the same T, using the trend found by Brenan and McDonough (2009). Although there is a dependence of $D^{Met/Sil}$ on P for



Figure 11. Metal-silicate partitioning for Ir, Pd and Rh as a function of pressure. All three elements display a significant decrease in $D^{Met/Sil}$ with increasing *P*. For Ir, all data are at ~IW+0.5 and the data of Mann et al. 2012 and Borisov and Palme (1995) have been corrected to 2000 °C using the *T*-dependence found by Brenan and McDonough (2009). For Pd, we have plotted experiments done at conditions more reducing than ~IW-0.2 from Borisov and Palme (1996) and the high *P* data of Mann et al. (2012) (~IW-1 to IW+0.6). Both datasets were corrected to 2000 °C using the dependence shown in Figure 10. Data for Rh are from Ertel et al. (1999), Fortenfant et al. (2003) and Mann et al. (2012). Data from the 0.1 MPa studies was corrected to IW assuming Rh²⁺ in the melt. All data were corrected to 2000 °C using the *T*-dependence found by Fortenfant et al. (2003).

Ir, its magnitude rests heavily on the datapoint at 6 GPa, which defines a minimum in the data. Further experiments are therefore required to better quantify the effects of *P* on $D^{Met/Sil}$ for Ir. Figure 11 shows $D^{Met/Sil}$ vs. *P* for Pd, from experiments done at conditions more reducing than $\sim IW - 0.2$. As observed for Rh and Ir, the magnitude of the *P* dependence changes above 6 GPa, although the difference is weaker for Pd than indicated for either Rh or Ir (Mann et al. 2012).

In summary, all of the HSEs display a decrease in $D^{\text{Met/Sil}}$ with increasing *T*. Compilation of the literature data also suggests that $D^{\text{Met/Sil}}$ for several elements decreases significantly with increasing *P* and the magnitude of this change may vary across the investigated *P* range (Mann et al. 2012).

Application of results to core formation

In order to apply the results of solubility and partitioning experiments to models of terrestrial accretion and core formation, values are parameterized according to Equation (40). To demonstrate this approach, we have chosen to parameterize $D^{\text{Met/Sil}}$ for Pt, Re, and Os as these elements comprise the long-lived Re–Os and Pt–Os isotope systems. The data summarized in earlier sections suggest that for reducing conditions, *T* and f_{O_2} are the important controls on $D^{\text{Met/Sil}}$. Equation 40 may thus be simplified to yield:

$$\log D_i^{\text{Met/Sil}} = \frac{a}{T} + \frac{n}{4} \Delta I W + c \tag{51}$$

Values for the coefficients *a*, *n*, and *c* and their sources are listed in Table 3. For equilibration between metal and silicate reservoirs at a chosen set of conditions, the concentration of trace element *i* in the silicate phase (C_i^{Sil}) can then be calculated using the following relationship:

$$C_i^{\text{Sil}} = \frac{C_i^{\text{TOT}}}{\left(f + \left(1 - f\right)D_i^{\text{Met/Sil}}\right)}$$
(52)

where C_i^{TOT} is the concentration of *i* in the bulk system (typically chondritic concentrations when considering core formation) and *f* is the fraction of silicate melt being equilibrated. Figures 12a and b display the change in C_i^{Sil} for a primitive upper mantle composition (PUM) following metal–silicate equilibrium over a range of *T* and f_{O_2} conditions. It can be seen from these figures that the PUM concentrations of Re and Os are not reproduced by metal–silicate equilibrium over a wide range of T– f_{O_2} space. Conversely, PUM concentrations of platinum can be accounted for if metal–silicate equilibrium occurs at high *T* and low f_{O_2} (e.g., ~ 3250 °C at IW – 2). Figures 12c and d display the change in Re/Os and Pt/Os ratio over the same *T* and f_{O_2} interval as shown in 12a and b. Approximately chondritic Pt/Os, as required to account for the Os isotopic composition of PUM, is not reproduced under any conditions. The PUM Re/Os ratio is only reproduced at relatively low *T* (<1830 °C) for redox conditions appropriate to core formation (<IW – 2). Values of $D^{\text{Met/Sil}}$ at these temperatures however, result in absolute PUM concentrations for all three elements that are many orders of magnitude lower than observed. It is observations such as these that have led to the conclusion that metal–silicate equilibrium is insufficient to account for the HSE budget of PUM.



Figure 12. The results of single-stage core-formation models for Re, Pt, and Os using parameterization for $D^{\text{Met/Sil}}$ as described in the section *Application of Results to Core Formation*. Black lines indicate the calculated PUM composition following metal–silicate equilibrium at a range of *T* and f_{O_2} conditions. Grey bars indicate the range of estimated PUM values (Becker et al. 2006).

	а	с	- <i>n</i>
Pt	20,900	-2.78	-1.2
Os	15,800	1.96	1.52
Re (<iw+2)< th=""><th>5,000</th><th>4.87</th><th>2</th></iw+2)<>	5,000	4.87	2
Re (>IW+2)	5,000	7.04	6

Table 3. Summary of coefficients to predict metal-silicate partitioning (Eqn. 51)

Values from Bennett (2013).

SILICATE AND OXIDE CONTROL ON HSE FRACTIONATION

Studies of sulfide-undersaturated mafic and ultramafic igneous systems reveal that Re, Au, and PPGE-group elements (Pt, Pd, Rh) are incompatible in early-crystallizing phases, principally olivine and chromite (e.g., Brugmann et al. 1987; Barnes and Picard 1993; Walker, et al. 1999; Puchtel and Humayun 2001; Pitcher et al. 2009; see also summary in Day 2013), whereas Re may be compatible in titanomagnetite in more evolved magmas (Righter et al. 2001; Gleißner et al. 2012). This is in contrast to the IPGE-group elements (Os, Ir, Ru), which typically show decreasing levels with measures of magmatic differentiation, such as whole-rock MgO, Ni, and Cr abundances (e.g., Brugmann et al. 1987; Puchtel and Humayun 2001; Pitcher et al. 2009), suggesting removal by olivine and/or chromite. Compatibility of Os, Ir, and Ru in olivine and chromite has also been implied by the preferential concentration of these elements in mineral separates relative to estimates of the coexisting melt (Puchtel and Humayun 2001; Puchtel et al. 2004). There arises some ambiguity, however, as to whether olivine and chromite are indeed the host phases for these elements, as it is now widely recognized that both minerals may contain microinclusions of platinum-group minerals (PGMs), such as Os-Ir-Pt-bearing alloy and laurite-erlichmanite (RuS2-OsS2; (Legendre and Augé 1986; Talkington and Lipin 1986; Merkle 1992; Cabri et al. 1996; Garuti et al. 1999; Gervilla and Kojonen 2002; Zaccarini et al. 2002). Despite this, in situ LA-ICP-MS studies have shown homogeneous Ru, Ir, Os, and Rh concentrations in some chromites from komatiite, komatiitic basalt and oxidized arc basalt (Locmelis et al. 2011, 2013; Pagé et al. 2012; Park et al. 2012), suggesting that the IPGEs and Rh may substitute into the spinel structure under certain circumstances.

Given the evidence from natural systems, laboratory partitioning studies for the HSE have therefore focused on olivine and spinel, although limited results have also been obtained for other minerals. As summarized below, results suggest that olivine and spinel-structured minerals may selectively concentrate the IPGEs, Rh, and in some cases Re, while excluding Au, Pt, and Pd. Experimental studies also reveal the important role of oxygen fugacity to control the magnitude of partitioning, as this variable affects both the speciation of the HSE, and, for the case of spinel, the availability of favorable partitioning sites.

Experimental approach

As described in HSE Solubility Experiments: Implications for Metal–Silicate Partitioning, a fundamental difficulty of experiments to measure the mineral/melt partitioning of the HSEs, is the very low solubility of some of these elements (ppb levels for Os, Ir, Pt, Rh, and Ru) in molten or solid oxide at the relatively reduced conditions relevant to terrestrial magmas (i.e., FMQ \pm 1). To impose the maximum concentration allowable, experiments are usually done at saturation in the metal of interest. At such low oxygen fugacities, however, even trace amounts of undissolved metal (so-called micronuggets, as described in Metal Inclusions in Experiments and the Analysis of Contaminated Phases) incorporated into a phase analysis can completely obscure the intrinsic HSE concentration. To overcome this problem, most past partitioning studies have adopted two common approaches. First, experiments are done at relatively high f_{O_1} , corresponding to conditions at which all the HSE are significantly soluble (ppm levels and above) in the phases of interest. Oxygen fugacity is also an important parameter to control, as the oxidation state of the HSEs may change with f_{0} . Second, the HSE content of coexisting phases is determined using a microanalytical method with good spatial resolution, including electron microprobe, secondary ion mass spectrometry (SIMS) and LA-ICPMS. Although the latter technique is the most destructive of the three, it offers the combined benefit of good sensitivity (ppm to ppb detection limits), and significant sampling depth (10s of µm vs. sub-µm for SIMS) such that phase homogeneity, and the presence of HSE metal contamination, can be readily assessed. Application of the LA-ICPMS technique is optimized using a relatively large diameter laser spot, producing more ablated material, resulting in lower limits of detection. Hence, it becomes a challenge to the experimentalist to grow crystals of sufficient size to take full advantage of this technique (Fig. 13). This aspect can be optimized by employing an experiment timetemperature history which minimizes the nucleation density, usually by slow cooling over a small temperature interval from the pre-determined liquidus (Brenan et al. 2003, 2005). Methods to achieve metal saturation include the wire loop technique, in which the melt+crystals are held by surface tension in a loop of the HSE wire of interest (Ir, Pt, Rh, Pd, Au; Brenan et al. 2012), or contained in a metal capsule (Righter et al. 2008); Ru and Os are not readily available as wires or tubing, and hence are added as powders. Other experiments have contained samples in crucibles made from natural or synthetic minerals (e.g., olivine and spinel; Brenan et al. 2003, 2005; Capobianco and Drake 1990; Fig. 13), with the metal added separately as wire or powder. The most convenient way to control and vary oxygen fugacity in partitioning experiments done at low pressure and high temperature is to suspend samples in a sealed furnace with a controlled flow of gas (air, CO₂–CO, O₂, etc; Capobianco and Drake 1990; Brenan et al. 2003, 2005). As an added twist, however, Re and Os are quite volatile at high oxygen fugacity, with Os forming the toxic OsO₄ gaseous species. Partitioning experiments involving these elements have been done at low pressure using gas-mixing, but at relative reduced conditions (Brenan et al. 2003), or with samples encapsulated with an oxygen buffer in vacuum-sealed silica glass ampoules (Righter et al. 2004), or done at high confining pressure (Righter and Hauri 1998; Righter et al. 2004; Mallman and O'Neill 2007) using internal buffers. A summary of the studies to measure silicateand oxide-silicate melt partitioning of the HSEs is provided in Table A2 in the Appendix.

Spinel-melt partitioning of HSEs

Capobianco and Drake (1990) and Capobianco et al. (1994) measured spinel- and magnetite-silicate melt partition coefficients for Rh, Ru, and Pd at 0.1 MPa, 1250-1450 °C and relatively high oxygen fugacities (i.e., FMQ+1 to FMQ+7), with their work revealing large partition coefficients for Ru (~20 to >4000) and Rh (~80-300), and uniformly low values for Pd (i.e., <1). These results have been confirmed for Cr-bearing spinel at similar conditions in the more recent work of Righter et al. (2004), who also report a $D^{\text{mineral/melt}}$ for Ir of 5 to >10,000, and that Au and Re are incompatible (D^{mineral/melt} of 0.08 and 0.0012-0.21, respectively). Results obtained by Brenan et al. (2012) for Cr-spinel at 0.1 MPa and 2 GPa, 1400-1900°C and more reduced f_{O_2} (FMQ-2 to FMQ+4) yielded generally lower partition coefficients for the IPGE than previous work, with Ru as the most compatible ($D^{\text{mineral/melt}}$ of ~ 4), followed by Rh and Ir, which are moderately incompatible to compatible $(D^{\text{mineral/melt}} \text{ range of } 0.04 \text{ to } \sim 1)$, with Pt and Pd the most incompatible (D^{mineral/melt} < 0.2). Mallmann and O'Neill (2007) investigated the (Mg-Al) spinel-melt partitioning of Re at 1275-1450°C and pressure of 1.5-3.2 GPa with fo, ranging from FMQ-2.9 to +5.6. Their results show a remarkably systematic decrease in the $D^{\text{mineral/melt}}$ for Re over this f_{0} , interval, ranging from ~0.3 to < 3 × 10⁻⁵. A summary of partition coefficients measured in these studies is provided in Figure 14, with the logical abscissa being experiment f_{Ω} . Although there is significant scatter to the data, an overall consistent result is that Ir, Ru, and Rh are more compatible in spinel then Pt, Pd, Au, and Re. In contrast to the results for Re, partition coefficients for Ir, Ru, and Rh show an overall decrease as conditions become more reducing.



Figure 13. Experimental configuration and run products from experiments to measure mineral-silicate melt partitioning of the HSE. (a) Example of sample configuration for an olivine-silicate melt partitioning experiment done at 0.1 MPa in a gas-mixing furnace. The olivine crucible (fabricated from single crystals of San Carlos olivine) is filled with basalt plus metal powder, then hung using a wire (in this case Pd) from a hook made from high purity fused silica, within the hot zone of a vertical tube furnace. The thermocouple, enclosed in a high purity alumina sheath, is located next to the sample during the experiment. (b) Backscattered electron image of the sectioned olivine crucible from an experiment done using the configuration shown in (a), cooled from 1350 to 1338 °C over 5 days and $\log f_{O_2} = -3.1$. The sample consists of quenched Fe-bearing silicate melt (=glass), olivine phenocrysts (=new olivine) and metal source, which were Ir metal grains encapsulated in molten Au (similar to the configuration employed for the metal/silicate partitioning experiment, see also Figure 6). Circular features correspond to areas ablated for ICP-MS analysis. [Used by permission of Elsevier Limited, from Brenan, McDonough and Ash (2005), Earth and Planetary Science Letters, Vol. 237, Fig. 1a, p. 861.] (c) and (d) Reflected light photomicrographs of the sectioned run product from a chromite-silicate melt partitioning experiment done at 1850 °C, 2 GPa, for 2.8 h. The field of view in (d) corresponds to the rectangle in (c). Chromite, which was added as a finely ground powder, with a grain size less than 40 µm, has dissolved and re-precipitated to form equant crystals. The melt has quenched to a fine intergrowth of silicate and oxide crystals plus glass. Note the preferential wetting of the Ir alloy by Au. [Used by permission of Elsevier Limited, from Brenan, Finnigan, McDonough and Homolova (2012), Chemical Geology, Vol. 302-303, Fig. 2, p. 24.]



Figure 14. Summary of spinel–melt partitioning of the HSE. Dashed curve is for the calculated variation in spinel-melt partitioning of rhenium after the model of Mallmann and O'Neill (2007), using Equation (60) in the text. Values of the end-member partition coefficients for Re⁴⁺ and Re⁶⁺ are fit to the partitioning data, whereas rhenium speciation is determined from the metal solubility measurements of Ertel et al (2001). Data are from the following sources: (**Rh**) Righter et al. (2004), Homolova (2008), Brenan et al. (2012); Capobianco and Drake (1990), Capobianco et al. (1994); (**Pd**) Homolova (2008), Brenan et al. (2012); (**Re**) Mallman and O'Neill (2007); (**Ru**) Homolova (2008), Brenan et al. (2014), Homolova (2008), Brenan et al. (2004), Homolova (2008), Brenan et al. (2012); (**Re**) Homolova (2008), Brenan et al. (2012).

Silicate mineral-melt partitioning of HSEs

Aside from spinel, most of the previous mineral-silicate melt partitioning measurements for the HSE have been measured for olivine, with a generally similar sense of fractionation: Ir, Ru, and Rh moderately compatible, and Pt, Pd, Au, and Re incompatible. Results are summarized as a function of f_{O_2} in Figure 15. Olivine melt partition coefficients measured at 0.1 MPa and 1330–1343 °C for Ru and Ir increase from values of ~0.5 at FMQ >+4 to ~2 at lower f_{O_2} . Values for Rh partitioning are ~2 over the entire f_{O_2} range considered thus far (FMQ+2 to+7; Brenan et al. 2003, 2005; unpublished data). Partition coefficients for Au and



Figure 15. Summary of olivine–melt partitioning of the HSE. Dashed curves are for the calculated variation in olivine–melt partitioning of Re and Pd, after the model of Mallmann and O'Neill (2007), using Equation (60) in the text. Values of the end-member partition coefficients for Re⁴⁺ and Re⁶⁺ and rhenium speciation are determined as per the caption to Figure 14. The palladium partitioning model assumes speciation determined from the metal solubility measurements of Borisov et al. (1994), with end-member partition coefficients for Pd¹⁺ and Pd²⁺ fit to the data. Data are from the following sources: (**Ru**) Brenan et al. (2003), black inverted triangles; (**Pd**) Brenan et al. (2003), and unpublished, black circles; Righter et al. (2004), gray circles; (**Re**) Mallman and O'Neill (2007), black diamonds; **B**renan et al. (2003), gray diamonds; **Righter** et al. (2004), open diamonds; (**Rh, Pt**) Brenan et al. (2003); (**Ir**) Brenan et al. (2005).

Pt measured at similar conditions are uniformly low (0.12 or less), with no apparent change with f_{O_2} (Righter et al. 2004; Brenan et al. 2005). Values for Pd measured by Brenan et al. (2003; unpublished data) decrease systematically with f_{O_2} : from 0.05 at FMQ+7 to ~0.006 at FMQ-0.5. The single value of ~0.1 reported by Righter et al. (2004) under oxidizing conditions is somewhat higher, but broadly consistent with this trend. In contrast to Pd, olivine-melt partition coefficients for Re measured by Mallmann and O'Neill (2007) increase with decreasing f_{O_2} , from 1.5×10⁻⁵ at ~FMQ+6 to ~0.5 at FMQ-3, showing a similar trend

to the results for spinel. Values for Re partitioning measured by Righter et al. (2004) are systematically larger than those measured by Mallmann and O'Neill (2007) at similar relative f_{O_2} , possibly reflecting some metal contamination in the run-product olivines. Re partition coefficients measured by Brenan et al. (2003) are significantly *lower* than the Mallmann and O'Neill (2007) determinations, which the latter authors attribute to a low abundance of charge balancing hydrogen-related point defects, present in their high pressure experiments, but absent in the 0.1 MPa, dry experiments of Brenan et al. (2003). Watson et al. (1987) did a reconnaissance study on clinopyroxene at 1275 °C and 0.1 MPa, obtaining $D^{\text{mineral/melt}}$ of ~0.04 for Re, and ~0.08 for Os, but f_{O_2} was not controlled.

Results of other silicate mineral–melt partitioning experiments are summarized in Table A2. Aside from the extensive data for Re, of note is the $D^{\text{mineral/melt}}$ for Pt of 1.5 determined for clinopyroxene by Righter et al. (2004). This value is somewhat unexpected, however, given that Pt²⁺ is the likely species at the f_{O_2} of those experiments (Ertel et al. 1999), with an ionic radius of 0.8 in VI-fold coordination (Shannon 1976), and therefore an expected partition coefficient of ~0.1 based on the Blundy–Wood partitioning model (see next section). Results for Re partitioning include the measurements of Mallmann and O'Neill (2007) for clinopyroxene, orthopyroxene, and garnet (in addition to olivine and spinel mentioned above) determined over a significant range in f_{O_2} (FMQ: 2.9 to+5.6) at 1.5 to 3.2 GPa. Re was found to be highly incompatible in these phases at the most oxidized conditions, but values increase with decreasing f_{O_2} . Values of $D^{\text{mineral/melt}}$ for Re involving clinopyroxene and garnet approach or exceed unity at ~FMQ-2, whereas Re is incompatible in orthopyroxene at all conditions studied. Righter et al. (2004) and Righter and Hauri (1998) also found Re to be incompatible in clinopyroxene and orthopyroxene at similar f_{O_2} , and Righter and Hauri (1998) measured $D_{\text{Re}} > 1$ for garnet at FMQ-2.9 to -4.8.

Origin of the variation in partitioning

As described previously for solid metal-liquid metal partitioning (see The role of the solid phase on D^{SM/LM}), Equation (16) relates the mineral-melt partition coefficient to the degree of size misfit between the substituent cation, and the optimal value for the crystallographic site (Blundy and Wood 1994). This model accounts well for HSE partitioning into olivine and spinel, (Mallman and O'Neill 2007; Brenan et al. 2003, 2005), with the additional importance of crystallographic site occupancy, and its variation with composition, to fully account for the spinel partitioning data (Brenan et al. 2012). A further complication to the partitioning of the HSE is that the valence state for some changes over the f_0 at which partitioning has been investigated, thus influencing cation size misfit, and possible substitution mechanisms as well. A change in valence state with f_{O_1} has been demonstrated by Mallmann and O'Neill (2007) to control Re partitioning into pyroxene, olivine and spinel, and suggested by Brenan et al. (2003, 2005) for Ru, Ir, and Pd substitution into olivine. In the latter case, the increase in D for Ru and Ir was interpreted to result in a shift from Ir^{3+} and Ru^{3+} in the melt to divalent species, as the ionic radius of Ru²⁺ and Ir²⁺ is estimated to be close to Mg²⁺, hence nearly optimal for substitution into the olivine structure, as predicted by the model of Blundy and Wood (2001). Estimates of valence state from Ir and Ru solubility experiments are somewhat conflicting, however, as it is possible to fit both 2⁺ and 3⁺ species to some data (Ru, Borisov and Nachtweyh 1998; Ir, Brenan et al. 2005), whereas other results suggest higher valence states (Ru⁴⁺, Laurenz et al. 2013; Ir³⁺, Fonseca et al. 2011). Partitioning experiments over a broader range of f_0 would be useful to better understand this behavior.

Changes in element partitioning involving a shift in valence state can be understood by considering the case for Re partitioning, in which there is very good agreement between partitioning systematics and valence state changes implied by the solubility data. Following the approach of Mallman and O'Neill (2007), the solution of Re metal into silicate melt can be described by the reaction:

$$\text{Re}_{\text{metal}} + x/4 \text{ O}_2 = \text{Re}^{x+}\text{O}_{x/2}$$
 (53)

which has a solubility product of the form:

$$Q^{x+} = [\text{Re}^{x+}O_{x/2}] / f_{O_x}^{x/4}$$
(54)

As demonstrated by Ertel et al. (2001), the variation in the solubility of Re with f_{O_2} in the basalt-analogue they investigated can be modeled by contributions from both Re⁴⁺ and Re⁶⁺ species. Hence, the total solubility of Re in the melt at a given f_{O_2} can be expressed as:

$$[\Sigma \text{ReO}_{x/2}] = [\text{Re}^{4+}\text{O}_2] + [\text{Re}^{6+}\text{O}_3]$$
(55)

with square brackets denoting the melt phase. Substituting the individual solubility products yields:

$$[\Sigma \operatorname{ReO}_{x/2}] = Q^{4+} + Q^{6+} f_{O_2}^{3/2}$$
(56)

Values of Q^{x+} are calculated by fitting the experimental solubility data. An equation equivalent to Equation (55) can be written for the crystalline phase, yielding the following relation for the partition coefficient including all melt species:

$$D_{\rm Re} = (\{{\rm Re}^{4+}{\rm O}_2\} + \{{\rm Re}^{6+}{\rm O}_3\})/([{\rm Re}^{4+}{\rm O}_2] + [{\rm Re}^{6+}{\rm O}_3])$$
(57)

in which curly brackets denote the crystalline phase. Partition coefficients for the individual melt species can be written as:

$$D_{\text{Re}}^{x+} = \{\text{Re}^{x+}\text{O}_{x/2}\} / [\text{Re}^{x+}\text{O}_{x/2}]$$
(58)

Equation (58) can be used to eliminate the crystalline phase terms from Equation (57), yielding the relation:

$$D_{\text{Re}} = ([\text{Re}^{4+}\text{O}_2]D^{4+}) + ([\text{Re}^{6+}\text{O}_3]D^{6+}) / ([\text{Re}^{4+}\text{O}_2] + [\text{Re}^{6+}\text{O}_3])$$
(59)

and expressing $[\text{Re}^{x+}O_{x/2}]$ in terms of the solubility product yields:

$$D_{\rm Re} = (Q^{4+} f_{\rm O_2} D^{4+}) + (Q^{6+} f_{\rm O_2}^{3/2} D^{6+}) / ((Q^{4+} f_{\rm O_2}) + (Q^{6+} f_{\rm O_2}^{3/2}))$$
(60)

Hence, a full description of the partitioning in systems involving multiple valence states can be obtained with knowledge of the partition coefficients for the pure valence state, as well as the solubility product for the metal dissolution reactions. Mallman and O'Neill (2007) applied this analysis to their Re partitioning data, using values of Q^{x+} obtained from the Re solubility experiments of Ertel et al. (2001), and estimates for D^{x+} that provided a best fit to their data. Results of fitting the Re partitioning data for olivine and spinel to Equation (60) are shown in Figures 14 and 15, with similar behavior for the other minerals studied. Re⁶⁺ is highly incompatible in olivine and spinel, owing to charge and size mismatch, with Re4+ much less so, behaving similar to Ti4+ (Mallmann and O'Neill 2007), accounting for the significant variation in partitioning with f_0 . Following a similar approach, the olivine-melt partitioning for Pd (Brenan et al. 2003; unpublished data) can also be well fit to a form of Equation (60), but assuming Pd²⁺ and Pd¹⁺ (Fig. 15), consistent with the metal solubility data of Borisov et al. (1994) and Laurenz et al. (2010). By this analysis, the partition coefficients are expected to change markedly for the f_{O_2} interval within which both species are abundant, then level off to constant values at more reduced, or oxidized conditions, in which a single species dominates. Given the evidence for changes in valence state of the HSEs described in Solid Metal-Liquid Metal Partitioning, it seems clear that characterizing partition coefficients over a range of f_{0_1} is essential to capture the behavior likely for natural magmas.

In addition to the role of ionic radius and charge, changes in the crystallographic site occupancy as a function of composition is an additional factor that may influence the HSE

incorporation into spinels. The structural formula for spinel can be written as

 $(A_{1-x}B_x)[A_xB_{2-x}]O_4$

in which A and B are di- and trivalent cations (so-called 2,3 spinel) or di- and tetravalent cations (so-called 2,4 spinel) in IV-fold (curved brackets) or VI-fold (square brackets) coordination, and *x* is the inversion parameter. The inversion parameter ranges from 0, corresponding to fully "normal" spinel, to 1, or fully "inverted" spinel, in which half of the octahedral sites are occupied by divalent cations. Hence, the availability of sites for di- and trivalent cations stabilized by VI-fold coordination will vary according to the degree of inversion. As demonstrated by Brenan et al. (2012), this effect may become evident when considering the partitioning involving spinels in which the chromite component is replaced by magnetite with increasing f_{O_2} , which is an important exchange in spinels from mafic and ultramafic magmas. Chromite (FeCr₂O₄) is a normal spinel, with all Cr in VI-fold coordination owing to the very high octahedral site preference energy (OSPE) of Cr³⁺ (d^3 valence electron configuration; McClure 1957; Dunitz and Orgel 1957). In contrast, magnetite (Fe₃O₄) is an inverse spinel at room temperature, but can show a decrease in the amount of divalent octahedral substitution at high temperature (e.g., Wißmann et al. 1998). A general formula for magnetite—chromite solid solutions takes the form:

$$(Fe^{2+}_{1-x}Fe^{3+}_{x})[Fe^{2+}_{x}Fe^{3+}_{2-2z-x}Cr_{2z}]O_4$$

where $z=Cr^{3+}/(Fe^{3+}+Cr^{3+})$. Site occupancies across the chromite–magnetite join, calculated after the method of Kurepin (2005), are displayed in Figure 16. For end-member chromite, the octahedral site is completely filled by trivalent cations (Cr^{3+}), thereby restricting the uptake of divalent cations which prefer VI-fold coordination. As the magnetite component increases, however, there is a rise in the divalent cation occupancy of the octahedral site. In terms of HSE partitioning, Rh and Ir are likely to be dissolved as divalent species in oxide solutions at the f_{O_2} of terrestrial magmas (Borisov and Palme 1995; O'Neill et al. 1995; Ertel et al. 1999; Brenan et al. 2005), with a d^7 valence electron configuration and in the low spin state (e.g., Zhang et al. 2010). There is, however, evidence for Ir³⁺ in the CMAS system at 1500°C (Fonseca et



Figure 16. Variation in the tetrahedral and octahedral site occupancies for di- and trivalent cations across the magnetite-chromite join. Curves are labeled according to the identity of the cation and the site occupied, e.g., $Fe^{3+}(oct)$ refers to the fraction of trivalent iron in VI-fold coordination. Note that the curve for $Fe^{2+}(oct)$ also corresponds to the amount of Fe^{3+} in tetrahedral coordination. All of the Cr^{3+} is assumed to be in VI-fold coordination. Values of the inversion parameter, *x* (see text) are calculated at 1300 °C after the method of Kurepin (2005). The species Ru^{3+} , Rh^{2+} , and Ir^{2+} are likely to have strong affinity for octahedral coordination, so their substitution into spinel will be controlled by the proportion of di- and trivalent octahedral sites. Consequently, end-member chromite can accomodate Ru^{3+} , but only with increased magnetite component are divalent octahedral sites available for Rh^{2+} and Ir^{2+} . [Used by permission of Elsevier Limited, from Brenan, Finnigan, McDonough and Homolova (2012), *Chemical Geology*, Vol. 302–303, Fig. 1, p. 24.]

al. 2011). Based on trends in cation size with charge in VI-fold coordination, Rh²⁺ and Ir²⁺ are estimated to have ionic radii of \sim 72 and 74 pm (1 pm = 10⁻¹² m), respectively, similar to Fe²⁺ and Mg²⁺ (78 and 72 pm, respectively; Shannon 1976). Both HSE cations are therefore expected to have a high affinity for octahedral sites in the chromite structure, and owing to their divalent charge, incorporation of Rh and Ir into chromite is predicted to be sensitive to the degree of inversion, as influenced principally by the magnetite component. As described above, results of metal solubility measurements suggest that Ru is dissolved as a 3⁺ or 4⁺ cation in oxide solutions at moderate to high f_0 (Borisov and Nachtweyh 1998; Laurenz et al. 2013). Results of mineral-melt partitioning experiments seem to be most consistent with a 3⁺ oxidation state, which has a d^5 electron configuration, in low spin state (Geschwind and Remeika 1962), suggesting a strong affinity for octahedral coordination. Based on trends in cation size with charge in VI-fold coordination, Ru³⁺ is estimated to have an ionic radius of ~68 pm, similar to Fe³⁺ and Cr³⁺ (64.5 and 61.5 pm, respectively; Shannon 1976). These considerations are consistent with the overall compatibility of the IPGEs in chromium-rich spinels, and with larger partition coefficients as the magnetite component increases, owing to a higher abundance of divalent octahedral sites (Righter et al. 2004; Brenan et al. 2012). Brenan et al. (2012) developed a model for partitioning of di- and trivalent cations into chromiumspinel taking into account the variation in site occupancy with magnetite component, which provides reasonable agreement to the existing experimental data, as well as empirical estimates from natural samples (i.e., Puchtel and Humayun 2001; Locmelis et al. 2011; Pagé et al. 2012).

In terms of the HSEs that are highly incompatible in olivine and spinel (Au, Pd, and Pt) either ionic radius or steric effects account for this behavior. At the conditions of the partitioning experiments, Au and Pd solubility systematics indicate the predominance of Au¹⁺ and Pd¹⁺ (Borisov et al. 1994; Borisov and Palme 1996), which in VI-fold coordination have ionic radii of 150 pm and 100 pm, respectively (estimated from Shannon 1976). These are considerably larger than either Mg²⁺ (72 pm) or Fe²⁺ (78 pm), so the low D values are consistent with a large mismatch in ionic radius compared to the dominant substituent cations in these phases. Metal solubility experiments have shown that Pt²⁺ is the likely oxidation state at the f_0 of past partitioning experiments (Ertel et al. 1999), although Pt⁴⁺ has been inferred spectroscopically, but only under highly oxidizing conditions (Farges et al. 1999). Pt²⁺ has a d^8 electronic configuration, and an ionic radius of 80 pm in VI-fold coordination (Shannon 1976), similar to Mg²⁺ and Fe²⁺, predicting a strong preference for octahedral sites in the olivine and spinel structures. The relatively low values for $D_{\rm Pt}$ would therefore seem anomalous. Documented occurrences of VI-fold complexes containing Pt2+ are rare, however, with the square planar coordination being most common, stabilized by the enhanced bond strength overwhelming the pairing energy required for this configuration (Cotton and Wilkinson 1988). Although square planar sites are unavailable in chromite and olivine, it may be that Pt²⁺ forms such complexes in the coexisting silicate melt, accounting for the low value for $D_{\rm Pt}$.

Local PGM saturation during chromite growth

Both empirical observations and recent experiments suggest that the HSE may not always be fractionated by forming a homogeneous solution in a mineral or melt phase. For example, the occurrence of PGM inclusions in chromite is well-documented, with the most common association involving minerals of the laurite–erlichmanite series (RuS_2-OsS_2), as well as Pt–Fe and Os–Ir–Ru-bearing alloy (Legendre and Augé 1986; Talkington and Lipin 1986; Garuti et al. 1999; Merkle 1992; Cabri et al. 1996; Gervilla and Kojonen 2002; Zaccarini et al. 2002). Phase equilibrium experiments confirm these PGMs are stable at chromian spinel liquidus temperatures over some range of f_{S_2} , provided the system is undersaturated with sulfide liquid, indicating that such inclusions can be interpreted as a primary magmatic texture (Brenan and Andrews 2001; Andrews and Brenan 2002; Bockrath et al. 2004). The origin of these inclusions has been somewhat enigmatic, but may in part account for the association between chromite and enrichment of certain HSE. In the course of experiments designed to measure chromite-silicate melt partitioning of the HSE, which involved re-equilibration or growth of chromite in molten silicate, Finnigan et al. (2008) documented the occurrence of PGMs (including metal alloys and laurite) at the crystal-liquid interface. The mechanism of formation proposed by these authors involves the development of a redox gradient, owing to local reduction within the mineral-melt interfacial region, occurring as a consequence of the selective uptake of trivalent Cr and Fe from the melt, relative to the divalent species. Recalling that at conditions more oxidizing than the IW buffer, the solubility of the HSE increases with f_0 , hence local reduction provides a driving force for precipitation of the PGMs in magmas that are not too far from metal saturation. Finnigan et al. (2008) modeled the processes of growth, as well as crystal-melt re-equilibration by Cr-Al exchange, to show that sufficient reduction occurs such that metal solubilities will decrease by several percent in the silicate melt at the melt-crystal interface. Once a sufficient degree of oversaturation occurs, the PGMs nucleate and continue to grow until either the redox gradient dissipates, or they become entrapped within the adjacent chromite crystal. Inclusion of such PGMs, then subsequent accumulation of chromite, constitutes a mechanism to fractionate the HSEs via mechanical means, rather than as a dissolved component in a major crystallizing phase. González-Jimenez et al. (2009) argue that the occurrence of zoned laurite-erlichmanite grains entrapped in chromite from different ophiolite localities arise from the redox gradients induced by chromite growth, providing support for the Finnigan et al. (2008) model.

MAGMATIC SULFIDE AND ASSOCIATED PHASES

During melting or solidification, sulfur-bearing silicate magmas can reach saturation in a sulfide phase, typically rich in Fe, with lesser amounts of Ni and Cu. Phase equilibrium experiments on typical magmatic sulfide compositions predict an immiscible sulfide liquid to form crystalline Fe-rich monosulfide solid solution (MSS; $[Fe,Ni]_{1,r}S$), which at 0.1 MPa occurs at T_{max} of 1190°C, corresponding to Fe_{0.917}S (Jensen 1942). The exact liquidus will depend on pressure, Ni and Cu content and $f_{\rm S}/f_{\rm O_3}$ (Naldrett 1969; Fleet and Pan 1994; Ebel and Naldrett 1996; Bockrath et al. 2004). With cooling, MSS is followed at T of ≤ 900 °C by a Cu-rich Intermediate Solid Solution ([Cu,Fe]_{1-x}S; ISS; Dutrizac 1976), and magnetite, with the MSS-ISS assemblage undergoing subsolidus crystallization to mostly pyrrhotite ($Fe_{1-x}S$), pentlandite (($Fe_{Ni})_{9}S_{8}$) and chalcopyrite ($CuFeS_{2}$). In the crustal environment, there is evidence for efficient magmatic sulfide differentiation associated with relatively large igneous bodies, as documented in the world-class Ni-Cu-PGE deposits of the Sudbury (Canada) and Norilsk-Talnakh (Russia) Districts, for example, with separation of ores rich in Fe and Ni, interpreted as MSS cumulates, from those which are Cu-rich, representing mixtures of evolved sulfide liquid and cumulate ISS (e.g., Naldrett et al. 1992, 1996; Li and Naldrett 1992; Zientek et al. 1994; Ballhaus et al. 2001; see also Barnes and Ripley 2016, this volume). This process has resulted in a significant separation of the HSE, with the IPGE and Re concentrated in the MSS cumulates, and the PPGE and Au following the evolved liquid. Past studies of sulfide in upper mantle peridotites and diamonds have also identified both trapped sulfide liquid and residual MSS, albeit on a much smaller scale (Szabó and Bodnar 1995; Guo et al. 1999; Alard et al. 2000; Lorand and Alard 2001; Luguet et al. 2001, 2004). In that context, a distinction is made between so-called Type 1 and Type 2 sulfides, using criteria and nomenclature from Luguet et al. (2001). Type 1 sulfides are characterized by high Ni relative to Cu abundances, and primitive upper mantle (PUM)normalized depletions in Rh and Pd relative to Ir (as well as Ru and Os), and interpreted to be residual MSS. Type 2 sulfides have variable Ni/Cu, and similar PUM-normalized abundances of Ir (Ru, Os), Rh, and Pd, considered to be consistent with trapped immiscible sulfide liquid. Although sulfur has long been implicated as an important ligand in the

concentration of the HSE in magmatic sulfide systems, field evidence suggests that As, and the other chalcogens Se, Te, and Bi could be important in some cases. For example, Gervilla et al. (1996, 1998), Hanley (2007) and Godel et al. (2012) have reported a close textural relationship between relatively PGE-(Au)-depleted base-metal sulfide and coexisting PGE-(Au)-rich arsenide phases (NiAs, nickeline; Ni₁₁As₈, maucherite; NiAsS, gersdorffite) in the magmatic sulfide segregations within the Ronda and Beni Besoura peridotite bodies, the Kylmakoski (Finland) Ni-Cu deposit and komatiite-hosted base-metal sulfide mineralization (Dundonald Beach South, Ontario; Rosie Ni Prospect, Western Australia), implying the presence of an immiscible arsenide melt at the magmatic stage. Recent work on samples from Creighton Mine, Sudbury (Dare et al. 2010) have shown that the base-metal sulfides are not the dominant hosts for some PGE, and that Ir, Rh, Pt occur as chalcogenrich discrete platinum-group minerals (PGMs; i.e., irarsite-hollingsworthite, IrAsS-RhAsS; sperrylite, PtAs₂), possibly crystallizing before or with MSS. Chalcogen-bearing phases are also associated with late-stage low sulfur precious metal haloes around massive sulfide bodies, as has been documented at various locations around Sudbury, Ontario (Farrow and Watkinson 1997). There is also evidence for remobilized chalcogen-rich melts associated with high grade metamorphism of base-metal deposits (Frost et al. 2002; Tomkins et al. 2007). Thus the chalgogens may affect the distribution of HSE within a magmatic sulfide system in several ways, including early sequestration as immiscible semi-metal-rich liquids or discrete PGMs at the magmatic stage, ligands to maintain the PGEs in solution during ore solidification, and agents of remobilization during subsequent metamorphism.

In this section, we focus primarily on the results of experiments to measure the partitioning between base-metal sulfide phases (MSS, sulfide melt) and silicate melt, but also include the limited (but likely to grow) body of results available for the chalcogens. Past experimental studies to measure partitioning amongst MSS–sulfide melt–arsenide melt–silicate melt are listed in Tables A3 and A4 in the Appendix.

Experimental approach

As is the case for solid metal–liquid metal partitioning experiments, loss of volatile sulfur, and some of the HSEs, is a concern, so experiments to measure sulfide–silicate partitioning are done using gas-tight containers, or under a S-bearing vapour phase. At 0.1 MPa, this involves either encapsulation in vacuum-sealed silica ampoules, or the use of sulfur-bearing gas mixtures (i.e., SO₂–CO₂–CO), whereas at high pressure, experiments are done in containers made from high purity graphite or natural mineral capsules (i.e., olivine), which prevents chemical interaction between the sample and the outer noble metal capsule which is typically used to ensure a gas-tight seal. In order to assist in the efficient separation of sulfide and silicate liquids during the experiment, Brenan (2008) and Mungall and Brenan (2014) subject samples to high acceleration at high temperature using a specially-designed centrifuge furnace (Roeder and Dixon 1977).

Partitioning experiments done at 0.1 MPa with evacuated silica ampoules have employed several methods for either buffering, or monitoring of f_{O_2} and f_{S_2} . For example, Mungall et al. (2005) used synthetic solid buffers to fix both f_{O_2} and f_{S_2} in their MSS–sulfide melt partitioning experiments ($D^{\text{MSS/SulLiq}}$) done at 950–1050°C, using the combined equilibria:

$$3Fe_2SiO_4 + O_2 = 2Fe_3O_4 + 3SiO_2 (FMQ)$$
 (61)

and:

$$Pt + 1/2S_2 = PtS \tag{62}$$

This was accomplished by loading the buffer powders, along with the sample, in silica cups placed within an outer silica ampoule, with the experiment physically separated below the buffers, but in communication via the gas phase. Liu and Brenan (2015) employed a similar approach in their MSS–ISS–sulfide melt partitioning experiments done at 860–926 °C (Fig. 17), but without the Pt/PtS mixture, as it was found to readily absorb the chalcogens, As, Se, and Te for which partition coefficients were also measured, in addition to the HSE. Instead the f_{S_2} was adjusted by the metal/sulfur ratio in the sample, and monitored using the FeS content of pyrrhotite added to the FMQ assemblage, using the calibration of Toulmin and Barton (1964). A similar approach was employed by Fleet and coworkers (Stone et al. 1990; Fleet et al. 1996, 1999) in their experiments to measure sulfide melt/silicate melt partitioning ($D^{SulLiq/SilLiq}$) of PGEs and Au, with f_{O_2} buffered at relatively reducing conditions using materials representing the following equilibria:

$$2Fe + SiO_2 + O_2 = Fe_2SiO_4 (IQF)$$
(63)

$$FeO + O_2 = Fe_3O_4 (MW)$$
(64)

$$Fe + \frac{1}{2}O_2 = FeO(IW)$$
 (65)

or C-O gas equilibrium involving graphite, used either as a sample holder or added as a solid rod, also known as the CCO buffer, defined by the reactions:

$$C_{\text{graphite}} + \frac{1}{2}O_2 = CO \tag{66}$$

$$CO + \frac{1}{2}O_2 = CO_2$$
 (67)

Brenan (2008) and Mungall and Brenan (2014) achieved somewhat more oxidizing conditions in their sulfide melt-silicate melt partitioning in experiments done at 0.1 MPa and 1200 °C, in which samples were encapsulated in crucibles made from natural olivine or chromite (see Figure 2 of Mungall and Brenan 2014). Sulfur fugacity was fixed using either Pt–PtS, Ru–RuS₂ or Ir₂S₃–IrS₂ buffers, the latter two involving the sulfidation reactions:

$$Ru + S_2 = RuS_2 \tag{68}$$

and

$$Ir_2S_3 + \frac{1}{2}S_2 = 2IrS_2 \tag{69}$$

Once sulfur fugacity is fixed, Brenan (2008) calculated f_{O_2} from the heterogeneous equilibrium:

$$FeO_{silicate melt} + \frac{1}{2}S_2 = FeS_{sulfide melt} + \frac{1}{2}O_2$$
(70)

whereas Mungall and Brenan (2014) used the Cr content of the silicate melt, held in a chromite crucible, to estimate f_{O_2} , as the solubility of chromite varies in response to changes in the speciation of chromium (Cr²⁺ and Cr³⁺; Berry and O'Neill 2004), hence f_{O_2} , as demonstrated by Roeder and Reynolds (1991).

Partitioning experiments done at high pressure have employed graphite caspules (in some cases in a sealed Pt outer capsule; Peach et al. 1994; Sattari et al. 2002), which fix f_{O_2} near the CCO buffer, or techniques in which the external f_{H_2} is controlled, allowing a range of f_{O_2} to be investigated. One method of external f_{H_2} control employs a double capsule configuration, in which the sample + H₂O is loaded into a hydrogen permeable noble metal inner capsule, then sealed, and placed into an outer capsule containing an assemblage of H₂O plus solid metal + oxides (i.e., Ni–NiO) or mineral mixtures (i.e., assemblages for Reactions (61), (63), and (64); Li and Audétat 2012). The external buffer fixes both f_{H_2} and f_{O_2} , which is transmitted to the inner sample by H₂ diffusion through the noble metal capsule. For experiments done with pressurized gas vessels, the f_{H_2} can be buffered using water as the pressure medium, and the intrinsic f_{O_2} of the vessel (Jugo et al. 1999; Simon et al. 2008), or by adding known amounts of H₂ gas to the Ar pressure medium



Figure 17 (a) Configuration for experiments to measure MSS–sulfide melt partitioning of PGEs and the chalcogens employed by Liu and Brenan (2015) in which f_{O_2} is controlled by the FMQ buffer (Eqn. 61 in the text), and f_{S_2} is monitored using the composition of pyrrhoitte added with the FMQ mixture (method of Toulmin and Barton 1964). (b) Backscattered electron image showing homogeneous MSS crystals coexisting with quenched sulfide liquid from experiment done at 915 °C at 0.1 MPa for three days. Dark globular structures are bubbles. [Used by permission of Elsevier Limited, from Liu and Brenan (2015), *Geochimica et Cosmochimica Acta*, Vol. 159, Fig. 1, p. 140 and Fig. 5a, p. 149.]

(Bezmen et al. 1994; Botcharnikov et al. 2011, 2013). The f_{S_2} in the experiments in which f_{H_2} is buffered is estimated using the FeS content of an added pyrrhotite sensor.

Control of f_{S_2} and f_{O_2} in these experiments is important for several reasons. First, the oxidation state of the HSE can change with f_{O_2} , as has been previously described, as well as with f_{S_2} , as documented by Fonseca et al. (2007, 2009, 2011, 2012). Also, the degree of metal deficiency (metal/sulfur) in MSS varies with f_{S_2} , with metal-deficient MSS dissolving more of the HSE (Ballhaus and Ulmer 1995). The stability of sulfide liquid in molten silicate depends on the FeO content of the silicate, as well as the f_{O_2}/f_{S_2} ratio (e.g., O'Neill and Mavrogenes 2002) through the heterogeneous equilibrium described by Equation (70), so sulfide may be absent if inappropriate f_{O_2} or f_{S_2} are imposed on the system. As the partitioning of the HSEs between sulfide and silicate melt can be expressed as an exchange reaction similar to 70 (see below), then the magnitude of partition coefficients will in turn depend on the relative f_{O_2}/f_{S_2} ratio. Some of the past experiments to measure partitioning amongst MSS-sulfide melt–silicate melt were done unbuffered, however, with the metal/sulfur of the MSS and sulfide melt varying with the bulk composition of the sample. It then becomes important, therefore, to relate the metal/sulfur to the f_{O_2}/f_{S_2} in order to accurately apply the data to modeling natural systems. For experiments in which f_{O_2} and f_{S_2} can be measured or estimated, extrapolation of results to natural systems is less uncertain.

As for the case of previous solubility and partitioning experiments, analysis of run products requires careful avoidance of inclusions (metal or sulfide) which contain a significantly higher HSE concentration than the phase of interest. This problem is not so acute in experiments involving sulfide mineral-sulfide melt equilibrium, although high spatial resolution is still important to obtain single phase analyses. The majority of past experiments to measure MSS–ISS–sulfide melt partitioning were doped at the 10–100 ppm level, which is close to the natural concentration range, then analyzed by either secondary ion mass spectrometry (SIMS; Fleet et al. 1993) or LA-ICPMS (Ballhaus et al. 2001; Mungall et al. 2005; Li and Audétat 2012; Liu and Brenan 2015). As sulfides dissolve relatively high concentrations of most HSE, some MSS-sulfide melt partitioning experiments were doped up to wt% levels, with run-products measured by electron microprobe (Li et al. 1996; Brenan 2002), with the results of Li et al. (1996) reproduced using the more sensitive proton microprobe method (Barnes et al. 2001). In that case, it must be shown that Henry's Law is valid over the concentration range investigated; this is demonstrated for Os at the ~2–5000 ppm levels and for Rh and Pd

at the ~10–20,000 ppm levels, by comparison of concentrations in MSS of similar metal/ sulfur ratio in the studies of Fleet et al. (1993), Li et al. (1996) and Brenan (2002). Earlier experiments to measure $D^{\text{SulLiq/SilLiq}}$ for the PGEs and Au were doped at the ~100–1000 ppm level, and analyzed by bulk methods (neutron activation; see summary in Table A3), whereas more recent determinations have been done at the >1000 ppm doping level, with analyses by LA-ICPMS. As discussed below, extreme partitioning of the PGEs into the sulfide melt, as revealed by the *in situ* LA-ICPMS measurements, renders bulk measurements of quenched silicate highly susceptible to overestimation, (hence, underestimation of sulfide melt/silicate melt *D*-values) even if only miniscule amounts of sulfide contamination are present.

MSS-sulfide melt partitioning

A summary of MSS–sulfide melt partitioning of the HSEs is provided in Figure 18. With the exception of some data for Re, Os and Au obtained at 1–3 GPa (Brenan 2008; Li and Audétat 2012, 2013), all other past measurements are from experiments done at 0.1 MPa, using evacuated silica ampoules (buffered or not). Values of $D^{\text{MSS/SulLiq}}$ for Ru, Os, Ir, Re, and Rh are >1, with Ru as the most compatible ($D^{\text{MSS/SulLiq}}$ for Ru as high as ~20; Liu and Brenan 2015), and $D_{\text{Os}}^{\text{MSS/SulLiq}} > D_{\text{Re}}^{\text{MSS/SulLiq}}$, giving rise to significant differences in the Os isotopic evolution within magmatic ore bodies (e.g., Lambert et al. 1998). In contrast, values of $D^{\text{MSS/SulLiq}}$ for Pt, Pd, and Au are all <1. Fleet et al. (1993) noted that the partition coefficients between MSS and sulfide liquid change progressively between the three chemical subgroups of PGE, being higher for the iron triad (Ru, Os) and the lower for the nickel triad (Pd, Pt). Subsequent experiments have confirmed this observation, and extended it to the copper triad (Ag, Au), representing the most incompatible transition elements in MSS. In addition to these inter-element fractionations, there are some systematic differences in partitioning behavior amongst past studies, as noted below. These observations can be rationalized in the context of ligand field theory, as well as the effect of MSS and sulfide melt composition.

Monosulfide solid solution has a NiAs-type structure, with triangular Fe clusters surrounded by distorted S octahedra, incorporating vacancies on the Fe sites and Fe³⁺ holes to satisfy the charge imbalance in metal deficient MSS (see review by Wang and Salveson 2005). Ballhaus and Ulmer (1995) showed that Pt and Pd (and by extension, the other PGEs, Re and Au) substitute for Fe in MSS on a one-for-one basis. Insight into the possible mineral structure control on HSE incorporation into MSS can therefore be gained by considering the relative solubilities of the PGEs in MSS compared to a fixed standard state (pure metal or



Figure 18. Summary of MSS/sulfide melt partitioning of the HSEs. [Used by permission of Elsevier Limited, from Liu and Brenan (2015), *Geochimica et Cosmochimica Acta*, Vol. 159, Fig. 7, p. 149.]
pure metal sulfide). Past work has shown that the solubilities of Os. Rh. Pt. and Pd in MSS increase with decreasing metal/sulfur, M/S (Makovicky and Karup-Møller 1993, 2002; Karup-Møller and Makovicky 2002; Majzan et al. 2002; Makovicky et al. 2002), indicating a decrease in metal activity coefficients, and that PGE substitution is enhanced by the presence of Fe vacancies (Ballhaus and Ulmer 1995). With this in mind, values of $D^{MSS/SulLiq}$ for the PGEs and Au are portrayed as a function of the M/S in the MSS in Figure 19. Where there are data for a significant range in MSS composition (Rh, Ir, Pd, Pt), partition coefficients show a weak increase with decreasing M/S—a trend consistent with the metal solubility results. Although the overall variation in partitioning with MSS composition seems consistent with expectations, the sense of HSE fractionation by MSS-melt partitioning is not reflected in the metal solubility data. Specifically, 1) Rh is found to be more soluble than Os, 2) the solubility of Pd is significantly higher than Pt, and 3) Os and Pt have similar solubilities. These differences are inconsistent with the overall incompatibility of Pt and Pd relative to Os and Rh, and the generally similar D^{MSS/SulLiq} for the pairs Pt-Pd and Os-Rh (Fig. 18). As proposed by Liu and Brenan (2015), the inconsistencies in this comparison imply that MSS-melt partitioning of the PGEs must also be controlled by coordination complexes formed in the sulfide melt phase. Whereas Ru, Rh, Ir, and Os and Re are inoctahedral coordination in their known sulfides, both Pd and Pt are in IV-fold coordination (summarized in Raybaud et al. 1997). Notably, at the conditions of past experiments, the likely oxidation state for Pt and Pd in molten sulfide is 2^+ (Fonseca et al. 2009), which has a d^8 electronic configuration, and hence stabilized by square planar coordination (cf., Cotton and Wilkinson, 1988). In the absence of such sites in the NiAs-type structure, it therefore seems reasonable that both Pt and Pd are stabilized in IV-fold coordination by the more "permissive" sulfide-liquid structure. A similar argument may also hold for Au, which, assuming a 1+ oxidation state, is stabilized in low coordination number (II-fold to IV-fold) complexes (Carvajal et al. 2004). Hence, although the PGEs may be soluble in the MSS structure, it seems that their relative preference for the melt or solid phase depends on which coordination environment is most energetically favored.

Both Mungall et al. (2005) and Liu and Brenan (2015) report partition coefficients for the compatible HSE (Ru, Re, Os, Ir, and Rh) that are systematically higher than other studies for a given MSS composition (Fig. 19). Whereas all previous work to measure partitioning of these elements was done unbuffered, and nominally oxygen free, as noted above, both Mungall et al. (2005) and Liu and Brenan (2015) employed techniques to fix f_{0} , at the FMQ buffer, resulting in sulfide melt with oxygen contents at the 1-2 wt% level. Results of previous experiments have documented a sharp decrease in the solubilities of Re, Os, Ir, Ru (and Pt) in molten sulfide at an f_{0} of ~FMQ-2 to -3 (depending on the metal, and the f_{S} ; Fonseca et al. 2007, 2009, 2011; Andrews and Brenan 2002), corresponding to a sharp rise in the oxygen content of the sulfide liquid from nil to $\sim 1-5$ wt%. The solubility decrease over this interval is ~ 10 -fold, and implies a complementary increase in the activity coefficient for these metals in the melt. The effect of an increase in the activity coefficient for a metal in the melt phase would be to increase $D^{MSS/SulLiq}$, which is the sense of the offset noted above. In this context, it is also worth mentioning that the addition of Cu and Ni to an Fe-S melt composition has been shown to change the solubility of Ru, Ir and Os (Fonseca et al. 2007, 2009, 2011; Andrews and Brenan 2002; Brenan 2008) with these additives acting in opposite ways. Whereas Ni increases the solubility of these metals (e.g., 0-23 wt% Ni results in ~2-fold increase in Os solubility), Cu results in a decrease (e.g., 0-26wt% Cu results in a 3-fold drop in Os solubility; Fonseca et al. 2011), implying sympathetic changes in the activity coefficients for these PGEs in the melt phase. Hence, the relatively high copper content (~30 wt%) of the melts produced in the study of Liu and Brenan (2015) compared to previous work (~4 to 13 wt%) would also result in a modest increase in partition coefficients. Although the variation in D with M/S for the compatible PGEs seems consistent with known activity-composition relations in the sulfide melt, the significant differences in partitioning seen for Au, and to a lesser extent Pt and Pd, is less clear. For MSS with a similar range in M/S, values of $D^{MSS/SulLiq}$ for Au are found to vary by ~10-fold, with results from Li and Audétat (2013) and



Figure 19. Summary of MSS/sulfide melt partition coefficients for the HSE plotted as a function of the metal/sulfur (M/S) ratio of the coexisting MSS. With the exception of the studies by Mungall et al. (2005), Liu and Brenan (2015) and Li and Audétat (2012, 2013), all other experiments were done unbuffered, with the sulfide liquid nominally oxygen-free. [Used by permission of Elsevier Limited, from Liu and Brenan (2015), *Geochimica et Cosmochimica Acta*, Vol, 159, Fig. 13, p. 154–155.]

Fleet et al. (1993) recording higher values than past determinations. Unlike past experiments, in which the HSE were added at ppm to low wt% levels, experiments done by Li and Audétat (2013) were at saturation in pure Au, corresponding to 9 to ~15 wt% Au in the sulfide liquid. The effect of such high metal loading on partitioning is unknown, but could very well be outside the concentration limits of Henryian behavior, and are certainly beyond natural abundance levels. Hence, such anomalously high values of $D^{MSS/SulLiq}$ for Au could be reasonably excluded as applicable to modeling natural processes. Fleet et al. (1993) also measured elevated values of $D^{MSS/SulLiq}$ for Au, as well as Pt and Pd. HSE dopant levels were low, so adherence to Henry's Law is likely not an issue, and the composition of MSS and sulfide melt are similar to previous work. The only difference in method was the use of SIMS for sample analysis, with partition coefficients for Au determined using the ratio of sulfur-normalized count rates in the MSS and sulfide melt. As documented by Fleet et al. (1993), this is a robust technique for measuring Au in sulfides. However, it is possible that the rather small spot employed (20–30 µm), and small number of analyses acquired (2) might not have fully captured the true variation in the Au content of the texturally inhomogeneous quenched sulfide melt (see Fig. 17b).

MSS-ISS-sulfide melt partitioning

Experiments to measure the partitioning of the HSE between ISS and MSS have been done by Jugo et al. (1999) at 100 MPa, 850°C (Au) and Liu and Brenan (2015) at 0.1 MPa and 850–875°C (PGEs, Re, Au). Results are summarized in Figure 20, which shows that Ru, Os, Ir, Rh, and Re are more compatible in MSS than in ISS, whereas Pd, Pt, and Au partition preferentially into ISS. Results for Au partitioning are consistent between the two studies. ISS–sulfide melt partition coefficients (*D*^{ISS/SulLiq}) were estimated by Liu and Brenan (2015) by combining their average values for MSS–sulfide melt, and MSS–ISS partitioning (Fig. 20). The calculated partition coefficients indicate that all the HSE should behave similarly to each other when partitioning between ISS and melt, with each weakly preferring melt relative to ISS.

Sulfide melt-silicate melt and MSS-silicate melt partitioning

Experiments to measure the sulfide melt-silicate melt partitioning of the HSEs have been of two types. Most experiments involve equilibration of both sulfide and silicate in the same sample, with the added HSE usually below the solubility limit (i.e., activity of the HSE, $a_{\rm HSE}$, < 1). Another, much smaller subset of experiments are of the "indirect" type, in which the concentration of a particular HSE in either sulfide or silicate melt is measured at (or corrected to) saturation



Figure 20. Measured values of MSS/ISS partitioning (Liu and Brenan 2015; Jugo et al. 1999), and calculated values of ISS–sulfide melt partitioning based on the average MSS–sulfide melt partition coefficients of Liu and Brenan (2015).

 $(a_{\text{HSE}}=1)$, but in separate experiments involving a single sulfide or silicate melt phase (Andrews and Brenan 2002; Fonseca et al. 2007, 2009, 2011). In this approach, partition coefficients are calculated by the ratio of concentrations in the sulfide melt–silicate melt measured in the separate experiments, for which the metal activity is the same. The rationale for this approach is that it allows for the f_{O_2} – f_{S_2} solubility systematics for each phase to be measured independently, and without the complication of sulfide contamination of the silicate phase.

Rhenium. Experiments to measure values of D^{SulLiq/SilLiq} for rhenium have employed both of the aforementioned methods. In terms of the "indirect" approach, Fonseca et al. (2007) measured the solubility of rhenium metal in molten sulfide at 0.1 MPa, 1200-1400 °C and $f_{0.0}$ of ~FMQ-6 to -2 (and variable f_s , using a gas-mixing furnace) which, combined with the solubility measurements of Ertel et al. (2001) for rhenium in diopside-anorthite eutectic melt, yielded estimates of $D^{\text{SulLiq/SilLiq}}$. Fonseca et al. (2007) showed that, up to an f_0 , equivalent to FMQ-2, the solubility of Re in molten sulfide is independent of f_{O_2} , but then exhibits a sharp decrease (data at higher f_0 could not be obtained). At fixed f_0 of FMQ-4.4, Re solubility in molten sulfide shows a progressive increase with $f_{\rm S}$, consistent with a change in speciation from Re⁰ (low $f_{\rm S}$) to Re⁴⁺ (high $f_{\rm S}$). As mentioned previously in the context of the mineral-melt partitioning of Re, Ertel et al. (2001) modeled their silicate melt solubility data in terms of contributions from both Re⁴⁺ and Re^{6+} , with the species equivalence point at ~FMQ-3, so the presence of Re^{4+} is consistent with expectations. Fonseca et al. (2007) developed a partitioning model which takes into account the combined f_{O_2} and f_{S_2} dependences on solubility, and showed that at the $f_{O_2}-f_{S_2}$ conditions of mid-ocean ridge basalt (MORB) genesis (high $f_{S,}$, and reduced; FMQ – 1 to –2), $D^{SulLiq/SilLiq}$ for Re is $\sim 1-100$, thereby exhibiting chalcophile behavior. However, at the conditions of island arc basalt (IAB) genesis (low $f_{\rm S}$; oxidized; FMQ+2), partition coefficients are ~1×10⁻⁴, hence Re would become strongly lithophile. Brenan (2008) measured the partitioning of Re between coexisting sulfide melt and silicate melt at 1200 °C, 0.1 MPa and ~FMQ-2 to FMQ+1, with f_{s} . buffered using Equilibria (62), (68), and (69). Most experiments were done by first equilibrating the two melts at static conditions, then subjecting samples to high acceleration to enhance phase separation. Similar to the results predicted from the work of Fonseca et al. (2007), D^{SulLiq/SilLiq} for Re was found to vary over a wide range, from >20,000 to ~20, depending on the $f_0 - f_s$. conditions imposed on an experiment. Following the approach of Gaetani and Grove (1997), the origin of this variation was modeled by Brenan (2008) according to the exchange of rhenium between molten sulfide and silicate as expressed by the reaction:

$$\operatorname{Re}_{x}\operatorname{O}_{y,\text{silicate}} + z/2 \operatorname{S}_{2} = \operatorname{Re}_{x}\operatorname{S}_{z,\text{sulfide}} + y/2 \operatorname{O}_{2}$$
(71)

The extent to which the partition coefficient is sensitive to f_{O_2} and f_{S_2} depends on the value of the stoichiometric coefficients, *x*, *y* and z^4 . Normalized to one cation, this reaction becomes:

$$\operatorname{ReO}_{y/x, \text{silicate}} + z/2x \operatorname{S}_2 = \operatorname{ReS}_{z/x, \text{sulfide}} + y/2x \operatorname{O}_2$$
(72)

which has an equilibrium constant of the form:

$$K_{5-12} = [\text{ReS}_{z/x,\text{sulfide}}] f_{O_2} y/2x / [\text{ReO}_{y/x,\text{silicate}}] f_{S_2} z/2x$$
(73)

(square brackets denoting activities) and can be rearranged to yield:

$$\log \{ [\text{ReS}_{z/x, \text{sulfide}}] / [\text{ReO}_{y/x, \text{silicate}}] \} = \log f_{\text{S}_2} z/2x - \log f_{\text{O}_2} y/2x + \log K_{5-12}$$
(74)

Assuming that the ratio of activity coefficients in the sulfide and silicate melts is constant

⁴ The reader is also referred to Kiseeva and Wood (2013) who propose an alternate approach, that makes use of an exchange reaction involving the element of interest and Fe in the sulfide or silicate, and does not have an explicit dependence on f_{O_2} or f_{S_2} ; this requires knowledge of the silicate melt FeO content, however, making it difficult to compare results with the model of Fonseca (2007).

over the f_{0_2} - f_{S_2} range of experiments, then this value can be combined with K_{5-12} and the factor to convert moles to wt%, to yield a single constant, KK_{5-14} . Then, by assuming that z = y, Equation (74) becomes:

$$\log D^{\text{SulLiq/SilLiq}} = y/x \left\{ \frac{1}{2} \log f_{S_2} - \frac{1}{2} \log f_{O_2} \right\} + KK_{5-14}$$
(75)

If the above conditions are satisfied, then a plot of log $D^{\text{SulLiq/SilLiq}}$ vs. $\frac{1}{2}\log f_{S_2} - \frac{1}{2}\log f_{O_2}$ should yield a linear relationship, with the slope equal to the anion to cation ratio for the rhenium species. The variation in $D^{\text{SulLiq/SilLiq}}$ modeled in this way yielded two linear, but offset, data trends, defined by the f_{S_2} of the experiments (Fig. 21). Treated separately, the low f_{S_2} data define a slope of ~3, consistent with predominantly Re⁶⁺ in both silicate and sulfide, whereas the high f_{S_2} data are defined by a shallower slope (2.4). A possible reason for the shallower slope in the high f_{S_2} data set is the presence of Re–S species in the silicate melt, which has been shown to occur for Ru (Laurenz et al. 2013), Pt (Mungall and Brenan 2014), Ni (Peach and Mathez 1993; Li et al. 2003), and Cu (Ripley et al. 2002). For example, Re could be dissolving in molten silicate as a mixed Re–O–S species, by the model reaction (assuming Re⁶⁺ as the dissolved species in molten sulfide at the f_{O_1} of experiments):

$$\text{ReO}_q S_{3-q, \text{ silicate}} + q/2 S_2 = \text{ReS}_{3, \text{ sulfide}} + q/2 O_2$$
 (76)

which has an equilibrium constant of the form:

$$K_{5-16} = [\text{ReS}_{3,\text{sulfide}}] f_{O_2}^{q/2} / [\text{ReO}_q S_{3-q,\text{silicate}}] f_{S_2}^{q/2}$$
(77)

and can be cast in a similar fashion as Equation (75) to yield:

$$\log D^{\text{SulLiq/SilLiq}} = q \left\{ \frac{1}{2} \log f_{\text{S}_2} - \frac{1}{2} \log f_{\text{O}_2} \right\} + KK_{5-17}$$
(78)

in which KK_{5-17} is a combination of K_{5-16} and a mole to wt% conversion factor. For the slope of 2.4 exhibited by the high f_{S_2} experiments, the proportion of sulfur-bonded Re is estimated



Figure 21. Sulfide melt–silicate melt partition coefficients for Re as a function of $\frac{1}{2} \log f_{S_2} - \frac{1}{2} \log f_{O_2}$, for experiments involving direct measurements on coexisting sulfide and silicate (Sattari et al. 2002; Brenan 2008), as well as empirical estimates from coexisting phases in oceanic basalts (Roy-Barman et al. 1998; Sun et al. 2003). Curves are calculated from the model of Fonseca et al. (2007) based on the solubility of Re metal in sulfide and silicate melts, corrected to 1200 °C.

as $(3-2.4)/3 \times 100 = 20\%$. Also included in Figure 21 are the partition coefficients estimated empirically from sulfide and glass in oceanic basalts from Loihi and FAMOUS using data from Roy-Barman et al. (1998) and Sun et al. (2003), as well as curves calculated using the model of Fonseca et al. (2007) corrected to 1200 °C. The model curves capture the low f_{S_2} measurements remarkably well, although the slope of the model curve is more shallow, as it assumes Re⁴⁺ as the main sulfide species. Calculated partition coefficients are systematically higher than the high f_{S_2} measurements, however. If the lower values of $D^{SulLiq/SilLiq}$ determined by Brenan (2008) result from sulfur complexing in the silicate melt, then this would not be captured in the Fonseca et al. (2007) model, as it relies on Re solubility measured for molten silicate under sulfur-free conditions. This is one aspect of the "indirect" method that may compromise the accuracy of calculated values for $D^{SulLiq/SilLiq}$, given the evidence for metal-sulfur complexing.

In light of the strong dependence of $D^{\text{SulLiq/SilLiq}}$ for Re on $\frac{1}{2} \log f_{\text{S}_2} - \frac{1}{2} \log f_{\text{O}_2}$, it is worth considering whether large variations in sulfide-silicate partitioning are likely in different mantle environments, as predicted by the model of Fonseca et al. (2007). Although Fonseca et al. (2007) correctly point out that differences in f_{O_2} and f_{S_2} likely exist between MORB and IAB sources, an important aspect not considered is the requirement that, for coexisting sulfide and silicate melts, the value of $\frac{1}{2} \log f_{S_1} - \frac{1}{2} \log f_{O_1}$ will be fixed by the heterogeneous equilibrium between FeO in the silicate melt and FeS in the sulfide melt (described by Reaction 70), and therefore if the [FeO] and [FeS] in the melts does not vary much, neither will D^{SulLiq/SilLiq} (see also Kiseeva and Wood 2013). Although it is not easy to predict the variation in [FeS] in different basalt sources, the range in [FeO] during melting is reasonably well constrained by the iron content of primitive magmas evolving by olivine control (Francis 1985, 1995). In this context, the range in the iron content of primary Phanerozoic magmas is rather limited, and bounded by picritic lavas from Iceland (~8 wt% FeO; Jakobsson et al. 1978) and Hawaii (~11 wt% FeO; Humayun et al. 2004). For a fixed [FeS] of ~0.7, which corresponds to X_{FeS} in a sulfide liquid with 15 wt% Ni, meant to be in equilibrium with mantle olivine with 3000 ppm Ni (Bockrath et al. 2004), this range corresponds to values of $\frac{1}{2} \log f_{S_2} - \frac{1}{2} \log f_{O_2}$ of 3.99 (11 wt% FeO) to 4.13 (8 wt% FeO) or $D^{\text{sulfide/silicate}}$ of ~380 to ~820 (using the high f_{S} , partitioning trend, for example). It is important to note that although $D^{SulLiq/SilLiq}$ is not likely to vary more than ~2-fold for this range of FeO, the bulk partition coefficient for Re could change markedly, due to the effect of f_{0} , on the silicate and oxide-melt partition coefficients (Mallmann and O'Neill 2007), or by differences in modal sulfide content. For example, low Re/Os and Re abundances in lunar basalts suggest that Re becomes more compatible in the residual assemblage at the reduced f_{0} of the lunar mantle (Birck and Allegre 1994; Day et al. 2007). If the lunar basalt source is sulfide saturated, D^{sulfide/silicate} for Re may be somewhat higher than for terrestrial MORB genesis, owing to the much lower f_{S_2} required for sulfide saturation, making the low f_{S_2} partitioning results most applicable. Compounding this effect is the overall increase in bulk solid-melt partition coefficients for Re, as a consequence of the higher compatibility of Re⁴⁺ in the peridotite phase assemblage (Mallmann and O'Neill 2007). For the case of highly oxidized arc environments, sulfide is likely to be destabilized in the mantle source (Mungall 2002), combined with a higher abundance of the more incompatible Re⁶⁺, resulting in very low bulk partition coefficients.

Gold. Values of $D^{\text{SulLiq/SilLiq}}$ and $D^{\text{MSS/SilLiq}}$ for gold are summarized in Figure 22. With reference to the exchange reaction described by Equation (72), past solubility experiments have shown that Au¹⁺ is the likely dissolved species in molten silicate at conditions more oxidizing than FMQ-4 (Borisov and Palme 1996), so partitioning data plotted in the form of Equation (75) should have a slope of one half. Consideration of the full datasets for either MSS—or sulfide liquid–silicate liquid partitioning shows considerable scatter, with no well-defined linear relation in the manner predicted. Selecting just experiments done below Au saturation (for reasons described in MSS–ISS–sulfide melt partitioning), and measured by



Figure 22. Sulfide–silicate partitioning of Au as a function of $\frac{1}{2} \log f_{S_2} - \frac{1}{2} \log f_{O_2}$. Solid symbols: MSS as the stable sulfide; open symbols: sulfide liquid as stable sulfide. Experiments labeled R and A were done with rhyolite and andesite silicate melt compositions, whereas all other experiments were done with basaltic silicate melts. Small font symbols are experiments measured by bulk analytical techniques (Fleet et al. 1990; 1999; Stone et al. 1990; Bezmen et al. 1994; Crocket et al. 1997; Jugo et al. 1999).

LA-ICPMS, presents a somewhat more coherent behavior for sulfide liquid–silicate liquid partitioning, as the data show a weak, albeit scattered correlation with the abscissa parameter, defining a slope of ~0.4 (single low value from Li and Audétat 2012, excluded), and an inferred oxidation state of +0.8. The significant scatter, and generally low values of $D^{\text{SulLiq/SilLiq}}$ obtained by bulk analytical methods likely results from the presence of small amounts of sulfide contamination in the glass separate, which is avoided by the LA-ICP-MS method. However, the much larger values of $D^{\text{SulLiq/SilLiq}}$ reported by Bezmen et al. (1994) suggest more extreme partitioning of Au into sulfide liquid than suggested by any other studies. Bezmen et al. (1994) noted this discrepancy and attributed such large partition coefficients to the presence of hydrogen in the sulfide melt, enhancing the uptake of Au (and PGEs) in some undefined way. This interpretation is in conflict with the results for $D^{\text{SulLiq/SilLiq}}$ measured by Li and Audétat (2012), which were also done under high pressure, hydrous conditions, but overlap with values measured by Mungall and Brenan (2014) done under dry conditions at 0.1 MPa.

Silicate melt composition may also affect HSE partitioning in sulfide-bearing systems, as Zajacz et al. (2013) has documented ~ 10-fold decrease in $D^{\text{MSS/SilLiq}}$ for melt compositions varying from rhyolite to basalt. The enhanced levels of Au (and therefore lower $D^{\text{MSS/SulLiq}}$) in melts with lower silica content reflect a similar decrease in the activity coefficient for the dissolved HSE species as implied by the metal solubility data (see *Role of silicate melt composition*). The much lower values of $D^{\text{MSS/SulLiq}}$ measured for a rhyolite composition by Jugo et al. (1999) could reflect small amounts of trapped sulfide in the glass, as samples were analyzed by bulk methods. This does not seem surprising, since the more viscous rhyolite could trap small emulsified sulfide droplets easily. Simon et al. (2008) also report low values of $D^{\text{MSS/SulLiq}}$ involving a rhyolite composition, but with glasses measured by LA-ICPMS. Reported glass compositions are not homogeneous, however, with Au concentrations varying from <0.2–6 ppm, suggesting either chemical equilibrium was not obtained, or the higher glass values are contaminated by

ablated sulfide. Glasses produced in the study of Zajacz et al. (2013) are reported to contain Au metal contamination, which was minimized by accepting only the lowest portion of the time-resolved signal for quantitation. Accepting the lower glass values reported by Simon et al. (2008) would result in high values of $D^{\text{MSS/SilLiq}}$, in line with the measurements of Zajacz et al. (2013). Hence, the Au-scavenging potential by early MSS crystallization in felsic systems may have been significantly underestimated by Simon et al. (2008).

Perhaps the most notable aspect of the Au partitioning dataset is the systematically smaller values of $\hat{D}^{MSS/SilLiq}$ than $D^{SulLiq/SilLiq}$, which is especially well-defined when considering only those studies in which run-products were measured in situ by LA-ICPMS (e.g., Jugo et al. 1999; Li and Audétat 2012, 2013; Botcharnikov et al. 2011, 2013; Mungall and Brenan 2014) and involving similar melt compositions. The average value of D^{SulLiq/SilLiq} measured from the *in situ* analytical studies on basaltic melts is ~4400. This contrasts with $D^{\text{MSS/SilLiq}}$ of ~170 measured in previous studies on the same composition (Li and Audétat 2012; Botcharnikov et al. 2011, 2013; Zajacz et al. 2013), yielding D^{SulLiq/SilLiq}/D^{MSS/SilLiq} of ~30, similar to the value of ~20 measured by Li and Audétat (2012), in which MSS, sulfide and silicate liquids coexist in the same experiment. Clearly, the identity of the residual sulfide phase will have a significant impact on the efficiency of gold partitioning into the silicate melt during mantle melting, and therefore the crust-tomantle transfer of this element. As shown by Bockrath et al. (2004), residual MSS can coexist with silicate melt, in the absence of sulfide liquid, along the low temperature, hydrous peridotite solidus. One may therefore expect that relatively low temperature mantle-derived melts, such as hydrous, alkalic compositions, produced in the presence of MSS, would contain a higher inventory of gold than dryer, high temperature magmas which leave behind residual sulfide liquid. This behavior was modeled in detail by Botcharnikov et al. (2013) and Li and Audétat (2013), who also emphasized the strong control of f_{0} , on the efficiency of mantle-to-crust transfer of gold, favouring environments in which residual sulfide is either eliminated by oxidation (Mungall 2002) or rapidly dissolved into the silicate melt under oxidizing conditions (Jugo 2009).

Platinum-Group Elements (PGEs). A summary of sulfide-silicate melt partition coefficients for PGEs is shown in Figure 23, which includes the results from both laboratory measurements and values from natural samples. Most past measurements of D^{SulLiq/SilLiq} have used bulk analytical methods to measure the metal content of glass and sulfide. The exceptions to this are the studies of Brenan (2008), and Mungall and Brenan (2014) in which analyses were done by LA-ICPMS. Also included in this comparison are the "indirect" estimates of sulfide-silicate partitioning done by Andrews and Brenan (2002) and Fonseca et al. (2009, 2012), which are based on the solubility of the metal in sulfide and silicate, measured in separate experiments involving only one melt phase. As is clear from the figure, nearly all of the previous measurements involving bulk analysis of the quenched silicate melt yield partition coefficients which are significantly lower than values determined either by in situ analysis of coexisting phases, or by the "indirect" method. Mungall and Brenan (2014) provide evidence to suggest the presence of micro-inclusions of sulfide melt in the silicate glass produced in their experiments, which would likely result in an overestimation of the intrinsic PGE content of the silicate melt, if measured by bulk methods. First, the time-resolved spectrum for the PGEs in run-product glasses was found to be inhomogeneous, with intensity peaks and troughs (similar to Fig. 4), with count-rates on all the PGEs added to a given experiment oscillating in unison. This is in contrast to the uniform signal observed for lithophile elements, like Ca, monitored at the same time. Second, both static and centrifuge partitioning experiments were done on Pt-doped experiments, and it was found that the Pt content of run-product glasses was always lower (by 24-70%) in the sample subject to high acceleration (~500 g). This suggests the high acceleration step had a cleansing effect on the silicate melt, removing some of the sulfide contamination owing to enhanced settling. In light of these observations, Mungall and Brenan (2014) concluded that past work, in which glasses were analysed by bulk methods, provided