Fe-liquid segregation in deforming planetesimals: coupling core-forming compositions with transport phenomena

Tracy Rushmer¹, Nick Petford², Munir Humayun³, Andrew J. Campbell⁴

¹Department of Geology, Delehantry Hall, University of Vermont, Burlington, VT 04505, USA

²Center for Earth and Environmental Science Research, Kingston University, Kingston-Upon-Thames, Surrey, KT1 2EE, UK

³National High Magnetic Field Laboratory & Department of Geological Sciences, Florida State University, 1800 E. Paul Dirac Drive, Tallahassee, FL 32310, USA

⁴Dept. of the Geology, University of Maryland, College Park, MD 20742, USA

Abstract

The segregation and macroscopic transport phenomena leading ultimately to the formation of metallic cores in planetary silicate mantles is a fundamental yet poorly understood process. Here we report the results of a series of deformation experiments on a sample of partially molten Kernouve H6 chondrite (T = 900 – 1050°C) aimed at determining the siderophile concentrations and associated partition coefficients in both Fe-S-Ni-O quench and Fe-Ni metal as a function of degree of melting, and to provide insight into the melt segregation mechanism(s). The geochemical results show the S content in the segregated Fe-rich liquid metal decreases with increasing degree of melting. As the S content of the liquid metal also strongly affects the partitioning of highly siderophile elements between solid and liquid metal, an increase in porosity (Fe liquid melt fraction) from c. 5 to 30% lowers $D_{\text{sm}/\text{lm}}$ for HSE by several orders of magnitude. The relationship between melt fraction and porosity is used to compare the
migration rate of liquid metal driven by buoyancy pressure gradients with a new theoretical model of melt segregation in a deforming porous medium that takes into account the coupling between volume strain (dilatancy) and shear stress. For buoyancy driven porous flow, highest transport velocities occur at highest porosities, implying the fastest flow velocities will carry Fe-rich liquid metal with low sulfur contents, preferentially enriched in incompatible HSEs. Predicted characteristic timescales of liquid metal transport due to buoyancy effects (diapirism and porous flow) for a c. 100 km-sized planetesimal are contrasted with shear-induced segregation velocities set up in response to external perturbations via impacts, an important process during the final stages of planetary accretion. A novel feature of our analysis is that liquid metal segregated previously into a planetary core by buoyancy instabilities (e.g. porous flow or a raining mechanism), might be drawn locally back into the silicate lower mantle by pressure gradients linked to surface impacts providing a physical mechanism for return flow of siderophile elements across the CMB.

Key words: core formation, siderophile elements, planetesimals, dilatancy, strain rate

1. Introduction

Although liquid iron-rich metal segregating from a molten silicate mantle (magma ocean) is a widely cited mechanism for segregating core forming material on large planets [1-4], the short times (< 30 Ma) required for terrestrial core formation based on W-Hf isotope systematics have reopened the debate on the role of magma oceans and large impacts in core formation [5-8]. The decay of short-lived isotopes (e.g. $^{182}$Hf to $^{182}$W) suggests that most of the bodies for which we have samples formed their cores rapidly, possibly within 3 million years of solar system formation [4]. In addition, studies on extinct radionuclide systems in meteorites suggest estimates of 2 to 10 my after condensation within the solar nebula for planetesimal (<100 km) differentiation and that same short interval for core formation from iron meteorite data [9]. These studies provide supporting evidence that the terrestrial planets and larger asteroids (e.g. Vesta) formed by rapid accretion of planetesimals
that had already undergone early differentiation and contained proto-planetary cores. Therefore, reconciling estimates of primary bulk silicate mantle with candidate planetary bulk compositions (e.g. chondrite) requires not only an understanding of the geochemical consequences of core formation but also the physical mechanisms responsible [4, 10-13].

Previous physical segregation experiments performed under static conditions at elevated pressures and temperatures have shown that reduced metallic liquids (Fe-Ni-S eutectic liquids) are unable to percolate through a solid silicate matrix due to high dihedral angles [14,15]. Although this result is now under revision [12,13,16], it is acknowledged that the complete extraction of Fe-alloy liquids cannot be by simple percolation alone and requires either an environment where permeability is created or high degrees of silicate partial melt are present [13]. Dynamic experiments under non-hydrostatic conditions show that deformation is capable of providing high permeability pathways for metallic liquid segregation in solid silicate matrices [17, 18]. The strong implication of these studies is that shearing stresses may have played a much more important role in core formation than previously recognized [13,19], especially during the latter stages of accretion where impact rates are high [1].

Dynamic segregation of Fe-rich liquid metal during partial melting will also impart a distinct geochemical signature on the composition of residual metal and determine siderophile partitioning behavior [18]. These chemical signatures should vary according to initial parent body composition, segregation mechanisms and the degree to which early S-rich, and possibly O-rich, core-forming liquids were extracted.

This contribution is split broadly into two parts. The first deals with new results from rock deformation experiments on a natural sample (Kernouve H6 chondrite) aimed at gaining insight into the interplay between deformation and geochemistry, in particular the role of sulfur in governing siderophile element behavior during active Fe-rich metal liquid segregation. We highlight the significance of the observed rock textures, drawing attention to a dilatant regime preserved as melt-filled veins in the rock matrix prior to brittle fracture. The second part is concerned with the coupling that must exist between the physical transport mechanism of core forming liquid metal and its compositional characteristics. Using
results from a shear-dilatancy deformation model, we show that strain rate driven metallic liquid segregation can in principle be an extremely rapid process compared with other mechanisms such as creeping flow based on percolation (porosity) thresholds and static material properties, and present a tentative model for physical interaction of core melt and overlying mantle during an externally imposed shearing regime. We then consider the geochemical consequences for upper mantle abundances of the platinum group elements, and show that core melt admixture into the mantle provides a suitable explanation of the “excess siderophile element paradox” for the most highly siderophile elements.

2. Experimental Methodology and Analytical Procedure

Deformation experiments were performed in a Griggs solid media rock deformation apparatus at confining pressures of 1.0 – 1.3 GPa with deformation at strain rates of $10^{-5}$ s$^{-1}$ and $10^{-6}$ s$^{-1}$ over a temperature interval of 900 - 1050°C. The starting material used in the study is a natural H6 chondrite (Kernouve), composed of olivine, orthopyroxene, plagioclase, clinopyroxene, chromite and chlorapatite with metal and sulfide phases constituting 20-25 volume%. While not explicitly controlled, $fO_2$ is estimated to be close to QFM in the solid-media deformation apparatus. The experimental study was designed to produce a framework for exploring different physical mechanisms of core formation and a fundamental aspect is the use of a natural starting material that allows us to determine the interplay between deformation and geochemistry. The amount of stress (load) supported by the sample was monitored at all times during the experiments although yield strength was too weak to be measured accurately by the solid-media apparatus (< 50 MPa). Temperature gradients were observed from the lower “hot spot” to the top of the sample. This temperature difference is determined by different liquid metal distribution, deformation textures and strain accommodation in the upper regions of the sample, and silicate melt (if temperature was high enough) in the middle and lower portion of the sample. Strain is focused in the hotter portions of the sample because it is more easily accommodated in the hotter region, however in regions
where significant silicate melt was present, strain is accommodated but not recorded (deformation textures cannot develop as they do in solid material). The temperature of the charges is given from the thermocouple positioned in the center of the sample, which records the temperature located above the hot spot. Strain or strain rates of individual samples are presented (see below) and they refer to bulk strain and/or strain rate based on the change of original sample length to sample length after the experiment. Additional details of the experimental approach are described in [18].

The results of several key experiments (samples KM 10, 11, 12, 17 and 24) are presented here as representative of the textures that develop during deformation of the ordinary chondrite as a function of partial melting in the silicate matrix, the metallic and sulfide phases. We have determined the compositions of both quench metal liquid and residual metal phases at different degrees of partial melting (samples KM 10, 11, 12, 17). Trace element compositions at selected points in the experimental run products were analyzed by laser ablation ICP-MS microanalysis at the University of Chicago and shown in Table 1. Table 1 also shows the calculated partition coefficients (\(D_{\text{SM/LS}}\)) between solid metal (SM) and liquid metal (LM). The locations to be analyzed were selected from a BSE image of the polished run products. Laser ablation ICP-MS analyses were performed using a CETAC LSX-200 laser ablation peripheral coupled to a magnetic sector ICP mass spectrometer, the Finnigan Element\textsuperscript{TM}, using techniques similar to those described by Campbell et al., 2002 [20] and Campbell and Humayun (2004) [21]. Measurements were made by laser ablating spots 25 to 50 µm in diameter and ~15 µm deep. During the analyses, the mass spectrometer was swept repeatedly over the mass range of interest, and counts were accumulated at selected masses. The isotopes monitored during analysis included most or all of the following: \(^{34}\text{S}\), \(^{57}\text{Fe}\), \(^{59}\text{Co}\), \(^{60}\text{Ni}\), \(^{63}\text{Cu}\), \(^{69}\text{Ga}\), \(^{74}\text{Ge}\), \(^{75}\text{As}\), \(^{182}\text{W}\), \(^{185}\text{Re}\), \(^{192}\text{Os}\), \(^{193}\text{Ir}\), \(^{195}\text{Pt}\), and \(^{197}\text{Au}\). Background subtractions were performed using the average of three blank measurements that were run either immediately before or after each set of analyses. Instrumental sensitivity factors for each isotope relative to \(^{57}\text{Fe}\) were determined by measuring the signal intensity from known standards [20], and the corrected intensities were normalized to 100%. When multiple measurements were made, the reported uncertainties are the standard error of the mean of replicate
analyses of each phase; when replicate measurements were not made, the reported uncertainties are calculated from counting statistics, plus an instrumental error of 8% based on replicate analyses of the standards.

We also determined the S and when possible, O content, of the quench liquid residual metal phases at sites measured by LA-ICPMS and these are shown in Table 2. Major element analyses of the quench liquid and metal phase in each sample were collected using a JEOL JXA 8900L electron microprobe with an acceleration voltage of 20 kV, 30nA beam current and employing the ZAF correction method. Analyses used a rastered beam over 50 micron-square area for the quench liquid metal. For O, we required a small beam size of 1-3 microns to reduce the chance of overestimating O by the presence of irregularities of the polished surface. Counting times were 20 seconds for most elements and 40 seconds for S. Natural and synthetic minerals were used as standards. Fe, Ni, P, Co and Cr were also analyzed and are included in Table 2.

3. Results

3.1 Deformation experiments: Textural descriptions

Textural and chemical analyses confirm the mobility of Fe-Ni-S-bearing liquids under conditions where the silicate matrix remained subsolidus or contained < 5% silicate liquid. At greater silicate melt fractions, metal-sulfide liquid geometry takes the form of immiscible, spherical shaped beads within the silicate melt. These gradually become coarser with increasing silicate melt fraction [18, 22]. Figure 1a-e shows the results of deformation experiments on the Kernouve H6 ordinary chondrite that show some key features of a granular matrix undergoing shear. Quench Fe-Ni-S liquids occupy dilatant zones in regions where the olivine-pyroxene dominated silicate matrix has not undergone extensive melting or hydrofracture. Such textures are important in that they provide experimental evidence for the theoretical model that follows, and confirm the presence of a dilatant deformational regime in the material prior to brittle failure.
3.1.1 Liquid metal/solid silicate

Experiments KM-10, KM-12 and KM-24 all show deformation textures associated with liquid metal migration in a solid silicate matrix under applied stress. KM-10 (1.0 GPa, $10^{-5}$ s$^{-1}$) and KM-12 (1.0 GPa, $10^{-6}$ s$^{-1}$) were both deformed at nominally 925°C (temperature measured at the middle of the sample see above) and neither contains silicate melt in the charge. KM-10 was deformed to 40% strain, and KM-12 was strained 10%. KM-24 was deformed at 940°C at $10^{-5}$s$^{-1}$ at 1.3 GPa to 27% strain with no silicate melt present. Deformation is distributed most pervasively throughout this sample.

KM-12 represents the lowest degree of partial melting with < 5 vol% quench metallic liquid present. The sample was strained 10% and shows evidence of migration of liquid metal even in zones of low strain. Fe-Ni metal has been remobilized in the high strain zones, where there is also abundant evidence of veining (Figure 1a).

KM-10 represents low to moderate degree of partial melting (10 vol%), showing quenched metal liquid located in high stress shear domains, and evidence of remobilized Fe-Ni metal. There is further evidence for cataclasis in the hottest portion of the charge (Figure 1b). Microveins seen in orthopyroxene are associated with small beads of FeS that appear to trace the migration of Fe-rich liquid metal within the deformation zones.

KM-24 also characterizes a low to moderate partial melting partial melting regime, with Fe-Ni and Fe-Ni-S quench occupying dilatant zones formed sub-parallel to the maximum compression direction (Figure 1c). We regard this as a critical observation. In all experiments where silicate melt is absent, metallic liquid is observed in dilatant shear zones, along grain boundaries or in zones of hydrofracture. A key factor in the analysis that follows is that to a first approximation, the silicate matrix comprising a planetesimal is granular, with a stiffness that will evolve under shear according to a deviatoric evolution rule [23]. For this study we thus focus on the initial shearing event, and associated pore pressure driving forces, which is one mechanism of liquid metal segregation.
3.1.2 Liquid metal/silicate melt

Experiments KM-11 and KM-17 contain silicate melt, and the observed textures are consistent with previous experiments where quench liquid metal in contact with silicate melt forms spherical beads [18, 24]. There is no evidence of cataclasis in the charges. Although shortening during deformation produced a minimum of 10% strain, deformation was accommodated in regions dominated by silicate melt. Metal quench blebs range in size from several microns to large, 500 micron beads. Compositional data were collected on beads ranging in size from 50 to 100 microns.

KM-17, deformed at 940°C, 1.2 GPa and at 10^{-6}s^{-1} contains a moderate (5-10 vol%) fraction of silicate melt, and 15-20 vol% quench metallic liquid. Metal-sulfide quench liquid is most common and forms beads in the silicate glass. There is textural evidence that silicate melt has accumulated at the sides of the capsule, which also evidence local dilational sites developed during deformation. The quenched liquid Fe-Ni-S +/- FeNi spherical beads have not migrated and appear trapped in the silicate melt-crystal mush (Figure 1d).

KM-11 was deformed at 990°C, 1.0 GPa and at 10^{-5}s^{-1} and strained by 15%. The sample contains 15-18% silicate melt, but with local pockets of up to 40% by volume. Regions of the charge that contain high fractions of silicate liquid (>40 vol%) are depleted in metal as observed in preliminary experiments (KM-3, [18]). Sulfide quench texturally edges the metal grains, and many of the silicate phases contain metal droplets. Silicates have recrystallized in these zones, but without extensive cataclasis. No veining textures were observed in the silicate melt-bearing regions (Figure 1e).

3.1.3 Silicate matrix - liquid metal reactions

Many of the experimental charges show microveining where modification of the silicate phase compositions is observed. These reaction veins are Fe-rich, and occur predominantly in matrix orthopyroxene. When analyzed, they contain fayalitic olivine [22, 24] that is the product of a reaction between migrating Fe-Ni-S-O melts and host orthopyroxene. The reaction zones sometimes occur along grain boundaries, but are
found mostly within individual grains (evidence of early cracking in the pyroxenes) according to the reaction,

\[ \text{MgSiO}_3 + \text{FeO} = (\text{MgFe})\text{SiO}_4 \] (1)

FeS blebs are also present in the reaction zones as likely remains of migrating liquid. We have also found sites where Fe-S-O rich quench liquids coexist with FeS. Although the breakdown of chromite might provide the FeO, chrome values are not enriched in Fe-olivine.

4. **Geochemistry: melt fraction, sulfur and highly siderophile elements (HSE)**

Compositions of the liquid metal fraction from the experiments were found to change markedly with respect to S content, as a function of degree of melting [25, 26]. As a result, the partitioning of the highly siderophile elements between residual solid FeNi metal and liquid Fe-Ni-S varies. Figure 2 is a plot showing measured HSE concentrations in four samples (KM 10, 11, 12 and 17) in both solid metal residue and Fe-Ni-S quench metal. The siderophile data are ordered according to their compatibility in the solid metal-liquid metal system with the most compatible (Os, Re and Ir) on the left [25]. The most striking difference between the compositions of quench and residue metal domains are the elevated S contents in the quench metal (dashed lines), and the strong relative enrichment in Ir and to a lesser extent Ge in the metal residue (solid lines). Previous KM-17 data are given in [27] show good reproducibility here.

The important modifying effect of sulfur on the $D_{\text{SM/LM}}$ values for two samples, KM-12 and KM-11 (Figure 3), that bracket the experimental range in partial melting and measured S contents have been presented here and in Figure 3 and Table 1. KM-12 has the highest measured sulfur quench compositions (32-36 wt% S) and represents the lowest degree Fe-S-Ni partial melt at c. 5% melt fraction (porosity). KM-11 represents the lowest sulfur quench composition (7-10 wt% S) and has undergone high degrees of partial melting at c. 30 % melt fraction.
Clear differences exist in the data from high to low S content (Table 1, Figure 3). Cu partitions into the S-bearing liquid under all conditions and $D_{\text{SM/LM}}$ range from 0.30 at high S contents to 0.55 at low S contents. Arsenic and Au switch from compatible to incompatible behavior as S content decreases in the liquid. Ir, Ge and Ga show large changes in D as a function of S, ranging from $>100$ to approximately 1.0 from high to low S contents, but remain compatible. W and Os also remain compatible. Both [25, 26] and this study shows the influence of S on siderophile partitioning. In this study we find with the high S content, low volume quench liquid, $D_{\text{SM/LM}}$ values can be $>200$ for some highly siderophile measured (e.g. Ir) elements and $D_{\text{SM/LM}}$ values closer to 1 for the lowest S, high volume metallic quench liquid (Table 1, Figure 3). Figure 4 summarizes the relationship between melt sulfur content in the quench metallic liquid, and the melt fraction (porosity), with highest S contents confined to the smallest melt fractions. This antithetic behavior provides an important link between the chemistry of the migrating metallic liquid and the matrix transport properties, and is discussed in more detail below.

5. Discussion

5.1 Coupling chemistry of core-forming liquids with segregation rates and regimes

In an important recent study, a set of static experiments on olivine – sulfide mixtures performed at high pressures and temperatures (3 GPa, 1,200°C and 1,300°C) used electrical conductivity to determine whether or not metallic liquid was interconnected in the olivine matrix [12,13]. The experimental results showed that connectivity (by proxy, electrical conductivity) occurred at ~5 vol%. An important implication of this result is that planetesimals with radii greater than about 30 km, the minimum size necessary to retain heat from short-lived radioactive nuclei, may already have formed proto-cores before accreting to form larger terrestrial bodies. Building on this, we apply a modeling approach that makes predictions on segregation rates of metallic liquid during porous flow and strain-induced migration and couples the results with metallic liquid geochemistry and highly siderophile element
partitioning behavior. We begin with estimates of the rate of Darcy flow (steady seepage) as a function of porosity, and then use the experimentally determined compositions of the liquid metal fraction to link major element and siderophile chemistry to flow rates.

5.2 Porous flow model

The movement of Fe alloy relative to the solid matrix at low to moderate melt fraction (e.g. Figure 1) implies a chemical effect that can be investigated using the permeability relationship described in [13]. Figure 5 shows a plot of melt (Darcian) flow in velocity (m/s) against porosity (n), using the 1D porosity-permeability relationship proposed [13]. The transport properties of the porous matrix depend strongly on the permeability constant \( k \) [28]. The results from sectioned run experiments given in [13] show melt confined to isolated pockets and argue for a 1D tube porosity-permeability relationship of the order \( 10^{-11} \) m\(^2\). An Fe-S liquid viscosity \( (\eta) \) of \( 10^2 \) Pa s seems appropriate, based on recent experimental work by [29]. Two curves are shown that reflect different accelerations due to gravity, one for a planetesimal 1/100 the present day earth diameter, and for comparison a value close to the present day terrestrial gravity field. As expected, highest flow rates occur when the porosity is greatest, with velocities in excess of \( 10^{-6} \) m/s for \( n > 10\% \) (g = 0.1 m/s\(^2\)). Superimposed onto the porosity (melt fraction) axis is the range in measured S content in the quench metal, (Figure 4), along with an estimate of the present day sulfur value of the outer terrestrial core [30,31]. Plotting the data in this way allows some tentative statements to be made regarding the effect of melt fraction on flow rate and hence composition. For example, high flow rates correspond with low metallic liquid S contents, implying that if the matrix transport properties remain constant, then porous flow in this regime will deliver core-forming melts that are relatively low in sulfur. Conversely, low degrees of partial melting (low porosities \( n \) of <10\%) will be more enriched in S, but move at a slower rate. Taking as a reference length scale a 100 km diameter body as modeled previously by [13], the timescales of liquid transport from the surface are c. \( 3 \times 10^3 \) years for an S content of 30 wt\% \( (n = 0.05) \),
and ~ 100 years for an S content of 5 wt.% \((n = 0.30)\). In passing we note that the present day sulfur content of the Earth’s outer core is most recently estimated to be 0.5-1.5% [31]. Assuming an order of magnitude uncertainty in this estimate, a migrating Fe-metal alloy with a present day outer core sulfur composition would be transported through a 100 km deep mantle by uninterrupted porous flow in less than \(10^3\) years.

By combining the S content-porosity relationship with the highly siderophile element (HSE) partitioning data, it is possible to make some further statements regarding HSE geochemical behavior during metallic liquid segregation. At relatively slow flow rates \((0.05 < n < 0.1)\), the associated liquids will have lower Fe metal content and high sulfur contents with high \(D_{\text{SM/LM}}\) values (\(D_{\text{SM/LM}}\) values are > 200 for measured Ir and Ge, Figure 4, Table 1). Although an increase in S will act to lower the metallic liquid viscosity, this compositional effect is small (order of a few percent) compared with changes in temperature [32]. As the porosity increases, so does the flow rate and for melt fractions in excess of 30% (e.g. S wt% < 10), \(D_{\text{SM/LM}}\) values are of the order of unity (Figure 4, Table 1) This effect is significant to the extent that depending upon the local liquid metal flow rate, some HSEs may switch between compatible and incompatible behavior. Indeed, this effect may be as important as changing redox conditions in locally determining the siderophile content of core forming liquids.

A geochemical record of the sulfur content of the percolating liquid maybe preserved during core segregation. For example, at high sulfur contents, a substantial fraction of residual solid metal remains in the mantle and will control HSE abundances there [33]. By using partition coefficients from the parametrization of Chabot and Jones [34] we have calculated the residual metal HSE abundances in equilibrium with liquids of variable sulfur content. We have taken H chondrite HSE abundances as representative, and calculated the metallic liquid composition by assigning all FeS, and the amount of Fe (and all Ni) present as metal, to the melt [35, 36]. The sulfur content of such a liquid is about 8.5%, and the residual metal in equilibrium with such a liquid is shown in Figure 6. We have then considered the effect of variable sulfur and show the residual metal composition for 0-14% S in the
liquid (Figure 6a). The recovery of such a siderophile element pattern in an achondrite would be strong evidence of the presence of residual metal in that planetesimal’s mantle [see also 37].

5.3 Shear-enhanced melt segregation

As shown by the Kernouve deformation experiments (Figure 1a-e), under pure shear the rock matrix passes through a (pre-failure) regime characterized by dilatant behavior. It has long been known that granular materials undergoing pure shear [38] will produce a volume change between granular domains that results in regions of low (excess) pressure in openings between domains that draws in surrounding fluid (metallic liquid in this case, see Figure 1c). The magnitude of the excess pore pressure, defined as the difference between the fluid pressure minus the hydrostatic pressure, will help drive melt segregation.

Recently, a model of melt segregation during matrix shear based on Biot's general theory of consolidation [39], modified to take into account the coupling between volume strain and shear stress has been developed that is relevant to the problem of melt extraction outlined above [23, 40, 41]. The dilatant effect produced in the deformation experiments can be captured mathematically as a function of applied shear stress rate according to:

\[
\dot{\gamma} \frac{\partial^2 p}{\partial y^2} = \frac{1}{\alpha_1} \left( p - Rc(t) \right)
\]

where \( p \) is the excess pore pressure (Pa), \( \dot{\gamma} \) is the shear rate, \( R \) is a non dimensional constant of 1 and \( \alpha_1 \) is the stiffness of the matrix (Pa). The permeability is assumed to be constant (\( k = k_0 \)), and depends on the granular length scale \( d \), melt viscosity \( h \) and melt fraction (porosity). Equation (2) can be solved analytically to yield explicit expressions for the excess pore fluid pressure (Figure 7) and, most importantly, the
local fluid (Fe-rich liquid metal) flow rate \( (\partial p / \partial y )k \). It is important to note that as the model is phrased in terms of shear strain rates, then the fluid flow velocity is largely independent of intensive melt properties. Order of magnitude estimates of the flow rate resulting from shearing are calculated for strain rates \( (\dot{\varepsilon}) \) in the interval \( 10^{-10} \text{ s}^{-1} \) to \( 10^{-5} \text{ s}^{-1} \), chosen to overlap with the experimental range, but also extended to faster rates of \( > 10^{-3} \text{ s}^{-1} \), typical of high velocity impact loading [42]. A summary of the buoyancy driven and shear-induced segregation regimes is shown in Figure 8, where the range in predicted flow velocities is plotted as a function of strain rate. It is apparent that maximum average velocity range estimates based on creeping flow of c. \( 10^{-5} \text{ ms}^{-1} \) correspond to deformation-enhanced melt flow velocities at strain rates below c. \( 10^{-8} \text{ s}^{-1} \) only. By comparison, predicted flow rates in the range of laboratory deformation experiments are much faster, of the order \( 10^{-3} \) to \( 10^{-2} \text{ ms}^{-1} \).

Despite this, by far the quickest way to transport liquid Fe-metal through a planetary interior is the raining mechanism proposed by Stevenson [1], where the host material is a low viscosity fluid (magma ocean). However, and as noted previously by [1], diapiric transport of liquid metal through a viscous (solid or semi-solid silicate mantle) is effectively inhibited for country rock viscosities \( > 10^{18} \text{ Pa s} \). In addition, the presence of silicate melt can trap percolating liquid metal because of the high surface energy between liquid metal and silicate melt [13]. Thus, as the embryonic planet cools, migration of metallic liquid through a deforming partially molten silicate framework could become the dominant core-forming liquid metal transport mechanism. During the early raining stage, migrating metal is likely to be in chemical equilibration with surrounding mantle material [43]. However, during the latter stages of accretion and core formation, we envisage a situation where remaining metallic liquids with a range of S contents are transported rapidly implying core forming liquids with different S contents can migrate quickly and concurrently to planetary interiors depending upon the transport properties and available melt fraction. Because the coupled variation between sulfur content and melt fraction will strongly influence the partitioning behavior of siderophile elements during differentiation, in principle the geochemistry may be used to determine the prevailing segregation regime. However, we do not yet know how sensitive the metallic liquid composition is to pore
pressure changes during these different deformation events. Although we observe equilibrium partitioning at the experimental deformation strain rates, very rapid segregation by porous flow during the latter stages of accretion may not allow for full equilibrium between percolating liquid metal and silicate matrix.

5.5 Return flow of liquid core metal back into a differentiating mantle?

The mechanical model of melt segregation outlined above opens up a novel way of locally transporting a more dense fluid upwards into an overlying layer of lower density [41], provided a critical strain rate threshold is reached. This threshold for rock with a shear modulus of the order 300 GPa is $c. 10^{-10} \text{s}^{-1}$. Suppose that towards the end of planetesimal accretion, a reservoir of liquid core metal resides in its center. If the body, now assumed mostly solid, is subject to external deformation by a high velocity impact capable of bringing about an abrupt change in angular momentum of the mantle [e.g. 44], the imposed shear stress at the core-mantle boundary may be sufficient to promote dilatancy, allowing core melt to be drawn back up into the overlying mantle in a way similar to that proposed recently for the D” region [45]. Shearing stresses are, of course, potentially important at any stage in the development of planetary bodies. However, our deformation model of return flow requires a mostly solid (> 50%) planetary interior at time of impact, implying that the effect will work best during the later stages of accretion, where conditions are cool enough for a significant portion of the planetary mantle to have crystallized. This is the situation envisaged in Figure 8.

Recently Drake and Righter [46] estimated the mass of material required to produce the mantle siderophile element abundances characteristic of the ‘late veneer’ ($10^{-3}$ x CI carbonaceous chondrite) at c. $10^{22}$ kg. Taking an Earth-sized planet as an example, and assuming a modest deformation induced strain rate of c. $10^{-3} \text{s}^{-1}$ at the core-mantle boundary (note according to [41] the surface strain rate would lie in the range $10^{-5}$-$10^{0} \text{s}^{-1}$ for an impactor of c. $10^{15}$ kg), the order of magnitude mass flux of core material across the CMB due to dilatancy is c. $10^{19}$ kg s$^{-1}$. It is thus possible in principle for a single impact to deliver a mass of core material equivalent to that of the
late veneer into the overlying mantle on the order of 300 seconds. Note that unlike the late veneer model, our proposed mechanism is not contingent upon impactor composition, so that the precise value of impactor mass is not directly relevant (it could for example be a comet). Instead the governing variable is the strain rate gradient, which for an Earth-sized planet should be of order 100 m$^{-1}$. Perhaps a more likely scenario involves a rapid succession of smaller impacts, whose time integrated strain rate would provide a pseudo-constant loading rate. In this case, the cumulative effect could produce the same result (return flow of core material to the mantle) over a longer time period.

Significantly, the impact model outlined above can be tested geochemically. The Earth’s mantle has a siderophile element pattern where the abundances of the platinum group elements (PGEs: Os, Ir, Ru, Pt and Pd), Re and Au are more depleted than that of any other siderophile element. Nonetheless, these elements occur in chondritic relative proportions [46]. The abundances of the PGEs, Re and Au are usually explained in terms of a late chondritic “veneer” accreting after core formation had removed nearly all the HSEs from the mantle [47]. For the Earth’s mantle, this explanation is no longer extended to other siderophile elements (moderately siderophile elements), such as Co, Ni, Mo, W, etc., the mantle abundances of which are now thought to have resulted from high P-T equilibration at the base of a magma ocean [46,48]. Thus, the elemental abundances most sensitive to return flow of outer core material are the PGEs, Au and Re. In Figure 6b, we show the abundances of the PGEs with minimum errors of 30% as indicated by [31], along with a recent estimate of the PGE composition of the Earth’s bulk core [48]. The bulk core composition is calculated assuming a CI relative pattern of each of the PGEs. A liquid outer core composition after segregation of about 5% solid Fe to form the inner core is also shown in Figure 6b. Palladium is modestly enriched, while Os and Ir are depleted in the outer core. We have then calculated the PGE pattern of mantle that has had either 1% or 0.1% outer core admixture, using both undifferentiated (i.e. bulk) core and differentiated outer core, and assuming that the PGE abundances in the silicate mantle were negligible prior to the admixture. Given that the outer core has an approximately chondritic PGE pattern, return flow of about 0.1-0.2% liquid outer core provides a
satisfactory explanation of the upper mantle PGE pattern without the need for invoking a late chondritic veneer. Such a return flow may have occurred during the entire early accretionary history of the Earth (4.56-4.45?), and satisfies the constraint imposed on mixing timescales of Re and Os by Bennett [49] that mantle Re/Os ratios were homogenized by 3.8 Ga.

Clearly, there is much in these arguments that is speculative, not least the assumptions made regarding stress propagation during impact in relation to core formation processes. Nonetheless, applied to the Earth it raises the intriguing possibility that at least some of the ‘late veneer’ component may result from return flow of siderophile elements across the CMB, triggered by external impacts with subsequent mixing and dispersal in the overlying mantle (Figure 9).

6. Summary

We have investigated experimentally the relationship between melt fraction, liquid metal composition and physical deformation textures in the Kernouve ordinary chondrite that provides insight into the liquid metal segregation mechanism and associated liquid metallic composition. Deformation textures show that dilatancy is a common pre-failure phenomenon in the silicate matrix. Siderophile element concentrations and associated partition coefficients in both Fe-S-Ni-O quench and Fe-Ni metal as a function of degree of melting show that the S content in the segregated Fe-metal liquid decreases with increasing degree of melting, while the siderophile elements become more incompatible the higher the S content in the Fe liquid. We argue that the style of fluid dynamical instability responsible for driving core-metal transport during planetesimal accretion changes with time, from early diapirism to late stage porous media flow with localized shear induced dilatancy. If true, these temporal changes in transport phenomena should be reflected in the major element and siderophile composition of the Fe-liquid phase being delivered to the growing core. These chemical signatures are expected to vary according to initial parent body composition, segregation mechanisms and the degree to which early S-rich, and
possibly O-rich, core-forming liquids are extracted. The relationship between melt fraction and porosity is used to compare the migration rate of liquid metal driven by buoyancy pressure gradients with a new theoretical model of melt segregation in a deforming porous medium that takes into account the coupling between volume strain (dilatancy) and shear stress. Predicted characteristic timescales of Fe-liquid metal transport due to buoyancy effects (diapirism and porous flow) for a 100 km-sized planetesimal are $< 10^4$ years given constant matrix transport properties. During the latter (impact) stage of accretion that is likely to favor shear-enhanced melt flow, it is feasible that existing core material may be transported locally upwards back into the silicate proto-mantle, providing a way of imparting a late-stage siderophile imprint that is analogous to the late veneer. Our geochemical modeling for the Earth has shown that the approximately chondritic relative abundances of PGEs in the upper mantle can be explained by about 0.1-0.2% admixture of bulk core liquid, without the need to invoke a late chondritic veneer.

Acknowledgements

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material transfer across the core-mantle boundary aided by the post-perovskite phase


Figure Captions

Fig. 1. Textural development in the deformation experiments as a function of increasing temperature. Quenched Fe-S-Ni liquid and Fe-Ni metal are most reflective phases; silicates (olivine, clinopyroxene and plagioclase) the least reflective. Images are oriented so applied stress ($s_1$) is applied vertically from the top, except for c. a) Backscatter image of KM-12. This experiment represents the lowest degree of partial melting. Veins are of quench Fe-Ni-S and S measurements range between 32-35%. Sites noted are from LA-ICPMS analyses; b) Backscatter image of KM-10 which represents low to moderate degrees of partial melting. Quench metallic liquid showing migration of liquid Fe-Ni-S quench linking unmelted Fe-Ni residua. The S content of quench liquids range between 26 and 29 wt% S. c) Backscatter image of experiment KM-24. The metallic liquid, quenched to metal phase FeNi and sulfide FeS at the end of the experiment, occupies a dilatant zone that has formed sub-parallel to the maximum compression direction (compression direction is parallel to sample edge shown in image). This texture contrasts with that of extensive veining and migration of S-rich metallic liquids observed in experiments where the silicate matrix has ultimately undergone fracturing. Note shear bearing quench Fe-Ni-S liquid occurs in a region where the olivine-pyroxene dominated silicate matrix has not fractured; d) KM-17 two-phase quench (FeNi and FeS) texture in silicate melt (more reflective silicate) and olivine. LA-ICPMS sites are visible in the Fe-Ni-S quench and FeNi residua. S content ranges between 12 and 18 wt% in the quench Fe-Ni-S liquid. e) KM-11 has undergone the highest degree of partial melting and shows both quench (FeS and FeNi) bleb texture in silicate melt (the more reflective silicate as in KM-17) and olivine. LA-ICPMS sites are marked and visible in the Fe-Ni-S quench and FeNi residua. S content ranges between 7 and 10 wt% in the quench Fe-Ni-S liquid.

Fig. 2 Siderophile abundances in deformation experiments normalized to Fe and H chondrite compositions using the values of [35]. Solid metal (solid lines) and associated quench Fe-S-Ni (dashed lines) are shown for most elements given in Table 1. In order of increasing degree of partial melting, filled and open diamonds are for KM-
11, filled and open circles are for KM-10, open triangle and cross are for KM-17 and filled and open squares are for KM-11.

Fig. 3 Plot of the D values (vertical axis) of siderophile elements measured in the KM experiments. Symbols for the experiments are the following: black diamonds are KM-12 and represent the lowest degree of partial melting (highest S content in liquid metal), grey circles are KM-10 and open triangles are KM-17 and represent moderate degrees of partial melting, black squares are KM-11 and represent the highest degree of partial melting and lowest S content in the liquid metal. The ordering of the elements is based on the value of the beta parameter in Chabot & Jones (2003) [25]. The elements are ordered from left to right according to decreasing beta value. The S content of the liquid metal decreases as a function of increasing melt fraction (n) and modifies siderophile element partitioning. These observations have also been made by [25, 26].

Fig. 4. Diagram showing the relationship between sulfur content (S wt%) and porosity (liquid metal fraction, n). Highest S contents (>30 wt.%) correlate with lowest porosities. The composition of solid metal residue and Fe-Ni-S metallic liquids changes during partial melting and segregation and the coupled variation between sulfur content in the metallic liquid at different melt fractions determines the partitioning behavior of siderophile elements during differentiation [Figure 3, 25, 26].

Fig. 5. Plot of porosity (melt fraction) versus melt velocity based on the porosity (n) permeability (k) relationship in [13]. The buoyancy-driven average flow rate is calculated for metallic liquid of viscosity $10^{-2}$ Pa s through a porous matrix, using $Dr = \text{density difference between metallic liquid and solid is } 3500 \text{ kg m}^{-3}$ and $g = 0.1 \text{ m/s}^2$, corresponding to a planetesimal of 0.01 earth diameters. For comparison, the flow rate for an earth-sized planet ($g = 10 \text{ m/s}^2$) is also shown. An increase in S content in the liquid metal of c. 5-30% corresponds with an order of magnitude decrease in average flow velocity (given fixed matrix transport and fluid properties).
Fig. 6a. Plot of the concentrations in solid residual metal normalized to CI chondrites for metals residual from an H chondrite liquid metal using the Chabot-Jones model for siderophile element partitioning [34]. Shown above are the siderophile element patterns for residual metals formed by partial melt removal from an H6 chondrite, as a function of S content from S=0-14 wt % in 2% increments (thin dark lines). The siderophile element patterns for average H chondrite (dotted line), and for the inferred liquid metal (thick dark line) are also shown. Elements are grouped into the highly siderophile (Os-Au), and the moderately siderophiles (Ni-Ge). As expected, the abundances of Os, Re and Ir in residual metal increase with increasing S content of the liquid. We have found no natural data against which to compare the model for an H chondrite composition. Note the low abundances of incompatible Pd, Au and As in the metal.

Fig. 6b. Plot of the concentrations in liquid metal, complementary to Fig 5a. PGE abundances in the Earth’s upper mantle (solid symbols) are compared with estimated PGE abundances in the Earth’s Bulk Core (upper dashed line), and outer core liquid after removal of 5% solid inner core (upper dotted line). The PGE abundances for model core compositions are from [47]. Admixtures of 1% and 0.1% outer core into the upper mantle, assumed to be initially devoid of PGEs, are shown as dashed (undifferentiated bulk core) or dotted (differentiated outer core) lines. A 30% error bar is shown on the upper mantle PGE abundances, which was a minimum error estimated by [30]. This figure shows that admixture of 0.1-0.2% outer core could account for the siderophile element pattern of the Earth’s upper mantle.

Fig. 7. Plot of calculated maximum excess pore pressure as a function of strain rate for three initial porosities (melt fractions) of 10, 20 and 30% and a fixed melt viscosity of $10^{-2}$ Pa s [29]. Vertical ruled line is the strain rate used in the accompanying deformation experiments of the Kernouve chondrite and implies a conservative estimate of maximum excess pore pressures of 1 bar to 1 MPa, depending upon the initial porosity. The result shows the strong effect of strain rate on excess pore pressure, with
maximum estimated values in excess of 1 GPa for strain rates > c. 10^{-3} s^{-1}. Very high instantaneous pressures (up to 10^{12} GPa) are predicted to accompany friction-induced melting in planetesimal bodies due to hypervelocity impacts [42]. Values in italics indicate the range where the ratio of maximum excess pore pressure approaches the matrix strength.

**Fig. 8.** Calculated Fe metal liquid flow velocities versus strain rate (\dot{\varepsilon}) in a deforming porous media. Estimates of flow based on Darcy’s law for porosities up to 0.3 are shown for comparison (boxed region) and define a maximum velocity of 10^{-5} m s^{-1} corresponding to deformation-enhanced melt flow velocities at strain rates < 10^{-8} s^{-1}. Hypervelocity impacts induce loading rates of c. 10^{-1} – 10^{0}, with predicted melt flow velocities > 1m/s.

**Fig. 9.** Cartoon summarizing the two-stage transport mechanism for upwelling core material during the final stages of planetary accretion. a) Impact stage: a surface impact results in shearing stresses that promotes a dilatant effect in the silicate mantle and CMB region. Outer core liquid metal, enriched in siderophile elements is drawn rapidly upwards across the boundary into lower mantle at a rate proportional to the loading time. b) post impact stage: following stress relaxation, core metal may sink back into core if gravitationally unstable (e.g. drops exceed a critical radius \( r_c \)), or remained trapped in-situ (\( r < r_c \)) due to surface tension effects [14], see also Fig 1d. Over time, successive episodes of surface impact “deep shearing” core liquid upwelling, followed by mixing and dispersal of entrained HSE elements, results in a distinctive HSE mantle signature (late veneer).

**Table 1:** Laser ablation ICPMS data and D values from experimental runs. Temperatures given are measured in the center of the charge (see text). All compositions in ppm unless otherwise indicated.

**Table 2:** Major element data collected by electron microprobe is shown for experiments (KM- 12, 10, 17 and 11). Data are collected by raster beam (50 m) for the
higher quench metal liquid fraction samples. O data collected by focused beam to reduce error (see text).
Figure 1a

Figure 1b
Figure 1c

Figure 1d
Figure 1e
Figure 3
Figure 4

Sulfur content (wt %)

Porosity (n)

Melt flow rate 
($10^{-8} - 10^{-7}$ m/s)

Melt flow rate 
($10^{-6} - 10^{-5}$ m/s)
Figure 5

The graph shows the relationship between Fe-S metal flow velocity (m/s) and porosity (n) for different gravitational accelerations (g). The horizontal axis represents the weight percent of S (wt % S), while the vertical axis depicts the Fe-S metal flow velocity in m/s. Two curves are depicted, each corresponding to a different gravitational acceleration: $g = 10 \text{ m/s}^2$ and $g = 0.1 \text{ m/s}^2$. The Earth core estimate is indicated by a dashed vertical line at a porosity of approximately 0.3. The graph demonstrates an increase in Fe-S metal flow velocity as porosity increases, with a more pronounced effect at higher gravitational accelerations.
Figure 6a
Figure 6b

- Bulk core
- Outer core (94.5%)

Elements: Os, Ir, Ru, Pt, Pd
Figure 9

(a) Core metal flux
(by raining, diapirs / percolation)

(b) Post-impact
Crater and impact melt

Stress relaxation

(a) Core metal sinks back again if droplets $r > r_c$
(b) Core metal trapped by surface tension $r < r_c$

Subsequent mixing and dispersal produces 'late veneer'

Enriched in Fe, HSE
# Laser ablation ICP-MS analyses of experimental runs

Temperatures given as measured in the center of the charge (see text).

All compositions in ppm unless otherwise indicated.

## Table 1

<table>
<thead>
<tr>
<th>KM-12</th>
<th>KM-10</th>
<th>KM-17</th>
<th>KM-11</th>
</tr>
</thead>
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<td>(1.0 GPa, 925°C, 10^-6 s/1)</td>
<td>(1.0 GPa, 925°C, 10^-5 s/1)</td>
<td>(1.0 GPa, 940°C, 10^-6 s/1)</td>
<td>(1.0 GPa, 990°C, 10^-5 s/1)</td>
</tr>
</tbody>
</table>

### Metal compositions:

<table>
<thead>
<tr>
<th>Element</th>
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<th>KM-10</th>
<th>KM-17</th>
<th>KM-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co (wt%)</td>
<td>1.33 ± 0.11</td>
<td>0.39 ± 0.01</td>
<td>0.82 ± 0.07</td>
<td>1.21 ± 0.10</td>
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<tr>
<td>Ni (wt%)</td>
<td>19.1 ± 1.5</td>
<td>9.1 ± 0.7</td>
<td>9.6 ± 0.8</td>
<td>15.8 ± 1.3</td>
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<tr>
<td>Cu</td>
<td>359 ± 29</td>
<td>84 ± 2</td>
<td>117 ± 10</td>
<td>244 ± 20</td>
</tr>
<tr>
<td>Ga</td>
<td>19 ± 5</td>
<td>21 ± 3</td>
<td>49 ± 4</td>
<td>32 ± 3</td>
</tr>
<tr>
<td>Ge</td>
<td>154 ± 12</td>
<td>78 ± 16</td>
<td>95 ± 8</td>
<td>115 ± 9</td>
</tr>
<tr>
<td>As</td>
<td>58 ± 5</td>
<td>12 ± 1</td>
<td>15 ± 2</td>
<td>9 ± 1</td>
</tr>
<tr>
<td>W</td>
<td>n.a.</td>
<td>n.a.</td>
<td>2.9 ± 0.3</td>
<td>26 ± 2</td>
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<tr>
<td>Re</td>
<td>n.a.</td>
<td>n.a.</td>
<td>1.0 ± 0.1</td>
<td>1.5 ± 0.2</td>
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<tr>
<td>Os</td>
<td>n.a.</td>
<td>n.a.</td>
<td>10.4 ± 0.9</td>
<td>17.9 ± 1.5</td>
</tr>
<tr>
<td>Ir</td>
<td>6.2 ± 0.5</td>
<td>12.6 ± 1.3</td>
<td>11.8 ± 1.0</td>
<td>16.0 ± 1.3</td>
</tr>
<tr>
<td>Au</td>
<td>4.2 ± 0.4</td>
<td>0.9 ± 0.1</td>
<td>n.a.</td>
<td>1.1 ± 0.1</td>
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</tbody>
</table>

### Sulfide/melt compositions:

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<th>KM-17</th>
<th>KM-11</th>
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<tr>
<td>Co (wt%)</td>
<td>0.32 ± 0.03</td>
<td>0.15 ± 0.02</td>
<td>0.52 ± 0.10</td>
<td>0.79 ± 0.13</td>
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<tr>
<td>Ni (wt%)</td>
<td>12.9 ± 1.0</td>
<td>6.2 ± 0.9</td>
<td>10.3 ± 1.2</td>
<td>14.3 ± 0.8</td>
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<tr>
<td>Cu</td>
<td>1208 ± 97</td>
<td>434 ± 36</td>
<td>275 ± 9</td>
<td>441 ± 22</td>
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<tr>
<td>Ga</td>
<td>&lt;0.9</td>
<td>3 ± 1</td>
<td>21 ± 4</td>
<td>20 ± 3</td>
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<tr>
<td>Ge</td>
<td>0.5 ± 0.4</td>
<td>3.0 ± 3</td>
<td>47 ± 8</td>
<td>87 ± 18</td>
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<tr>
<td>As</td>
<td>3.7 ± 0.8</td>
<td>5.4 ± 0.1</td>
<td>31 ± 8</td>
<td>25 ± 4</td>
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<td>W</td>
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<td>n.a.</td>
<td>0.6 ± 0.1</td>
<td>16.4 ± 0.7</td>
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<tr>
<td>Re</td>
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<td>n.a.</td>
<td>0.12 ± 0.03</td>
<td>0.39 ± 0.01</td>
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<tr>
<td>Os</td>
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<td>1.0 ± 0.2</td>
<td>3.5 ± 0.3</td>
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<tr>
<td>Ir</td>
<td>&lt;0.02</td>
<td>0.15 ± 0.15</td>
<td>1.3 ± 0.1</td>
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<td>Au</td>
<td>0.32 ± 0.05</td>
<td>0.53 ± 0.05</td>
<td>n.a.</td>
<td>2.13 ± 0.30</td>
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</table>

### D(metal/melt):

<table>
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<th>KM-17</th>
<th>KM-11</th>
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<tbody>
<tr>
<td>Co</td>
<td>4.2 ± 0.5</td>
<td>2.6 ± 0.4</td>
<td>1.6 ± 0.3</td>
<td>1.5 ± 0.3</td>
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<tr>
<td>Ni</td>
<td>1.5 ± 0.2</td>
<td>1.5 ± 0.2</td>
<td>0.9 ± 0.1</td>
<td>1.1 ± 0.1</td>
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<tr>
<td>Cu</td>
<td>0.30 ± 0.03</td>
<td>0.19 ± 0.02</td>
<td>0.43 ± 0.04</td>
<td>0.55 ± 0.05</td>
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<td>Ga</td>
<td>&gt;20</td>
<td>6.1 ± 2.3</td>
<td>2.3 ± 0.5</td>
<td>1.6 ± 0.3</td>
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<tr>
<td>Ge</td>
<td>291 ± 201</td>
<td>&gt;25</td>
<td>2.0 ± 0.4</td>
<td>1.3 ± 0.3</td>
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<tr>
<td>As</td>
<td>16 ± 4</td>
<td>2.1 ± 0.2</td>
<td>0.5 ± 0.1</td>
<td>0.4 ± 0.1</td>
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<tr>
<td>W</td>
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<tr>
<td>Re</td>
<td>8.4 ± 2.3</td>
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<td>10.7 ± 2.2</td>
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<tr>
<td>Ir</td>
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<td>&gt;84</td>
<td>9.5 ± 1.4</td>
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<td>Au</td>
<td>13 ± 2</td>
<td>1.6 ± 0.3</td>
<td>0.5 ± 0.1</td>
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**Table 2:** Major element analyses (in wt %) by electron microprobe of quench liquids and residual metal from experiments KM – 10, 11, 12 and 17 that represent different degrees of partial melting. The quench analyses were performed at the sites where LA-ICPMS (LA) was performed for siderophile analyses (see Table 1).

<table>
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<tr>
<th>Element</th>
<th>KM-12: Lowest degree</th>
<th>KM-10: Low-mod degree</th>
<th>KM-17: mod-high degree</th>
<th>KM-11: high degree</th>
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<td></td>
<td>Liquid quench</td>
<td>Residual metal</td>
<td>Liquid quench</td>
<td>Residual metal</td>
</tr>
<tr>
<td>Fe</td>
<td>60.10 +/- 3.9</td>
<td>82.02 +/- 2.1</td>
<td>62.17 +/- 1.6</td>
<td>89.53</td>
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<tr>
<td>Ni</td>
<td>6.81 +/- 6.1</td>
<td>17.52 +/- 1.4</td>
<td>5.82 +/- 0.1</td>
<td>7.51</td>
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<tr>
<td>S</td>
<td>33.85 +/- 3.4</td>
<td>0.09 +/- 0.006</td>
<td>28.32 +/- 2.9</td>
<td>3.26</td>
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<tr>
<td>Co</td>
<td>0.32 +/- 0.2</td>
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<td>0.13 +/- 0.03</td>
<td>0.41</td>
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<tr>
<td>Cr</td>
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<td>n.a.</td>
<td>0.05 +/- 0.04</td>
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<td>O</td>
<td>0.26 +/- 0.04</td>
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<td>1.86 +/- 1.03</td>
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