A diffusion mechanism for core–mantle interaction

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Understanding the geochemical behaviour of the siderophile elements — those tending to form alloys with iron in natural environments — is important in the search for a deep-mantle chemical 'fingerprint' in upper mantle rocks, and also in the evaluation of models of large-scale differentiation of the Earth and terrestrial planets. These elements are highly concentrated in the core relative to the silicate mantle, but their concentrations in upper mantle rocks are higher than predicted by most core-formation models[1,2]. It has been suggested that mixing of outer-core material back into the mantle following core formation may be responsible for the siderophile element ratios observed in upper mantle rocks[3]. Such re-mixing has been attributed to an unspecified metal–silicate interaction in the reactive D″ layer just above the core–mantle boundary[4]. The siderophile elements are excellent candidates as indicators of an outer-core contribution to the mantle, but the nature and existence of possible core–mantle interactions is controversial[5]. In light of the recent findings that grain-boundary diffusion of oxygen through a dry intergranular medium may be effective over geologically significant length scales[6] and that grain boundaries can be primary storage sites for incompatible lithophile elements[7], the question arises as to whether siderophile elements might exhibit similar (or greater) grain-boundary mobility. Here we report experimental results from a study of grain-boundary diffusion of siderophile elements through polycrystalline MgO that were obtained by quantifying the extent of alloy formation between initially pure metals separated by ~1 mm of polycrystalline MgO. Grain-boundary diffusion resulted in significant alloying of sink and source particles, enabling calculation of grain-boundary fluxes. Our computed diffusivities were high enough to allow transport of a number of siderophile elements over geologically significant length scales (tens of kilometres) over the age of the Earth. This finding establishes grain-boundary diffusion as a potential fast pathway for chemical communication between the core and mantle.

The distribution of the chemical elements in the Earth has traditionally been characterized according to their partitioning behaviour towards minerals, melts and fluid phases. In general, grain boundaries have not been considered significant storage sites for most elements, though this view is changing following the recent demonstration that localization at grain boundaries is potentially important for at least some elements[8]. The capacity of grain boundaries to transport a given element (as opposed to simply store it) is a function of both the partitioning of that element into the grain boundary and its grain-boundary diffusivity. These combine to determine the potential grain-boundary flux. Grain-boundary diffusivities of cations and oxygen in oxides and silicates are typically several orders of magnitude higher than lattice values[9,10]. To our knowledge, no data are available for grain-boundary diffusion of electrically neutral, highly incompatible metal atoms in oxides, as conventional studies of grain-boundary diffusion rely upon the compatibility of the diffusant in the crystal lattice to detect grain-boundary transport[11]. The highly and moderately siderophile

elements (HSE and MSE) are not only very incompatible in the lattices of mantle phases, but also likely to have very low lattice diffusivities—an extreme case of 'type C' grain-boundary diffusion in the terminology of Harrison[12]. These elements may nevertheless be present and mobile in the grain boundaries of mantle phases, which would lead to a previously unrecognized reservoir and pathway for storage and transport. Grain-boundary concentrations are expected to be very low, so direct detection is beyond any means currently available. In this study we chose to explore the grain-boundary mobility of siderophile elements in polycrystalline MgO (periclase). A simple, dense oxide that is stable over a wide range of pressure–temperature conditions, this mineral is a suitable analogue for deep-mantle materials that can be studied in adequately sized samples at conditions accessible to solid–media devices.

All elements selected for this study are mobile in grain boundaries of polycrystalline MgO. Grain-boundary transport caused 0.07–95% alloying with Pt, depending on the source element and the run duration. Overall, Os and Re consistently displayed the smallest grain-boundary fluxes, while Au, W and Rh displayed the largest. The amount of alloying with Pt differed not only between different elements but also from particle to particle within the same experiment by up to a factor of 5. Not all of the Pt sink particles contained the same concentration of the source element. The distribution of alloying source atoms was also not homogenous in the Pt foils used in place of particles in some experiments. This implies that not all grain boundaries are equally 'conductive' pathways.

Results are shown in Fig. 1. The grain-boundary fluxes vary over approximately three orders of magnitude among the elements studied. There is good reproducibility among experiments, as results are generally within the same order of magnitude. The elements in
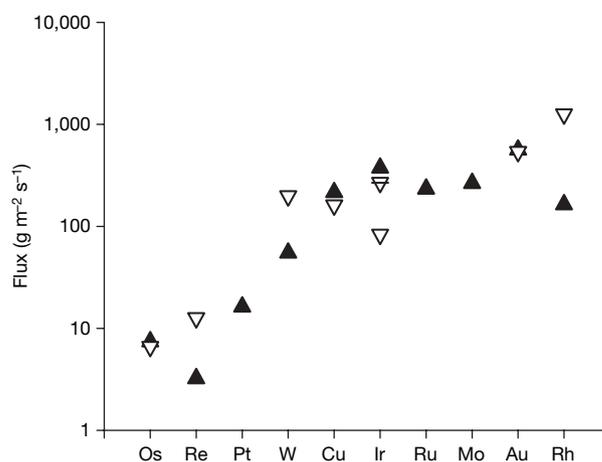
Figure 1 | Results of single-sink experiments. All the experiments shown were run at 1,600 °C and 2.5 GPa for 10 h, with a sink layer located ~1 mm from the source layer. Filled triangles represent initial series of experiments; open triangles represent experiments repeated in duplicate or triplicate.

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Fig. 1 are listed in order of increasing flux; at this time there does not appear to be a clear correlation between an element's grain-boundary diffusivity and any single atomic property, such as mass, volatility or siderophility.

For selected siderophile elements, additional experiments were performed with modified experimental conditions such that the sink layer was moved farther away from the source, the experiments were run for a longer time or both conditions were modified. The results of this series of experiments are shown in Fig. 2. The flux values for these modified runs have been normalized (to $x = 1$ mm and $t = 10$ h, where x is the distance between the source and sink, and t is the run duration) in order to better compare the results. There is again very good agreement among samples, and this series produced results that make sense in the context of well-understood diffusion principles[13]. A run duration of 50 h resulted in a lower time-averaged flux than one of 10 h. Increasing the distance between the source and sink horizons from 1 mm to 5 mm resulted in a markedly decreased average flux. The time-integrated flux should be proportional to time for steady-state transport. Steady-state conditions are assumed to hold here for the purpose of obtaining diffusivity estimates, but this is not strictly realistic because of the dynamic nature of the system, which exhibits coarsening of MgO grains and compositional changes in both the source and sink particles. These results are also consistent with the data in Fig. 1.

Back-scattered electron imaging of the polycrystalline MgO revealed a distinct increase in average grain size with increasing run duration. This is due to normal grain coarsening, but its occurrence in these experiments is potentially significant because it reduces the total grain-boundary area (or volume) of the MgO. The bulk flux of siderophile diffusant atoms through the MgO must undergo a gradual diminution with time as some grain-boundary pathways are modified and others eliminated completely. It is possible that coarsening effects are responsible for some of the scatter in Fig. 2. With the exception of Pt, the (normalized) time integrated fluxes of source atoms were smaller in the longer runs, due in part to grain growth causing decreased total grain-boundary volume.

Because of the low concentrations of the siderophile elements in the grain boundaries (below detection with an electron microprobe) and the very narrow (~ 1 nm) width of individual grain boundaries[13,14], direct measurement of the atoms of interest in the grain boundaries was not possible. Ideally, knowledge of the concentration gradient along the grain boundaries from source to sink is necessary for calculation of diffusivity. In order to translate the calculated relative fluxes of the elements into an estimate of diffusivity, a series of experiments was run using multiple evenly spaced Pt foil sink
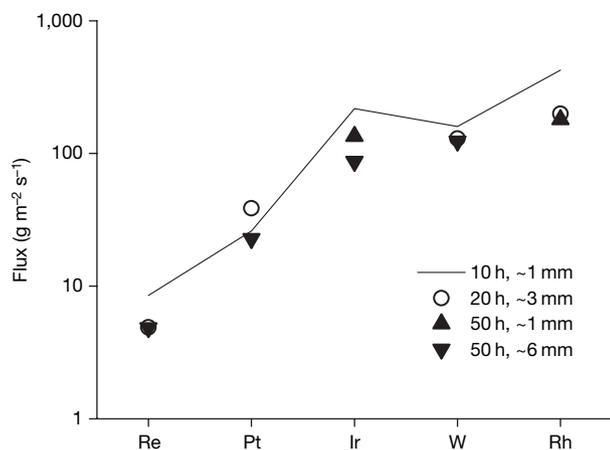
layers in the MgO. Results of these multi-sink experiments are shown as the solid line in Fig. 3. These experiments also differ in that they each had two elements in the source layer, effectively setting up a diffusion 'race'. Figure 3 shows the fluxes from the source layer to the first sink layer only, and these results are generally consistent with the results of the single-sink experiments. The presence of a competing element does not seem to have a significant effect on the mobility compared to that element diffusing alone. The concentrations at each sink horizon were determined and plotted as a function of distance from the source layer, then fitted with a simple error function solution to estimate diffusivity: $C_{(x,t)} = C_0[1 - \mathrm{erf}(x/\sqrt{4Dt})]$, where C_0 is the initial concentration of the source element (~ 1 for the pure starting metal), x is the distance from the source layer, D is the diffusivity and t is the experiment duration. Given local equilibrium between the metal particles and the grain boundaries, the varying concentrations in the metal particles as a function of distance from the source provide a relative measure of concentration variation in a grain boundary that connects a source particle to a sink. The resulting diffusivities range from 10^{-12} m^2 s^{-1} to 10^{-7} m^2 s^{-1} (Supplementary Fig. 3). These diffusivities represent minimum values due to the fact that some of the diffusing source particles are 'trapped' upon reaching the initial Pt sink layer, and source concentrations in the more distant sinks are lower than they would be in the absence of this chemical (and physical) boundary.

To put these diffusivity values in perspective, the characteristic diffusion distance ($x^2 = Dt$) over the Earth's history for these elements is on the order of 1–100 km (Fig. 4). Grain-boundary diffusion of siderophile elements is thus fast enough to allow significant core–mantle communication, especially if material diffused into the lowermost mantle from the outer core is swept into the mantle convective cycle.

When considering the implications of this experimental work to the environment at the core–mantle boundary (CMB), there are a few parameters to take into consideration. First, these experiments were done at temperatures and pressures significantly lower than the conditions at the CMB. Increasing temperature and pressure generally have opposing effects on diffusion; that is, diffusivity increases with temperature and decreases with pressure. Preliminary work[15] has shown that tungsten mobility increases dramatically between 1,450 and 1,600 °C. Second, although MgO (as magnesiowüstite) is widely believed to be present in the lower mantle[16], the predominant phase is Mg-perovskite. It seems unlikely that the grain-boundary mobility of HSE and MSE observed in MgO would be hampered by the presence of Mg-perovskite, but it is premature to assume that perovskite grain boundaries would also serve as high-diffusivity pathways for these
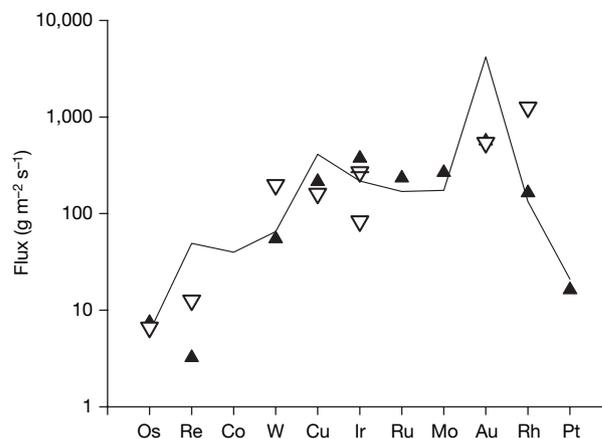

Figure 2 | Time-averaged flux values. Flux values for selected elements were derived from the time series. The solid line represents the 'standard' set-up with the shortest run duration. The open circles, triangles and inverted triangles represent experiments with modified run conditions, as shown in the key.

Figure 3 | Comparison of single and multi-sink experiments. The solid line represents multi-sink runs with three sink horizons of Pt foil located ~1.5, 3 and 4.5 mm from the source layer. Elements were run in pairs: Os-Rh, Re-Ru, Co-Au, W-Ir and Cu-Mo. Solid and open triangles represent initial and replicate experiments, respectively.
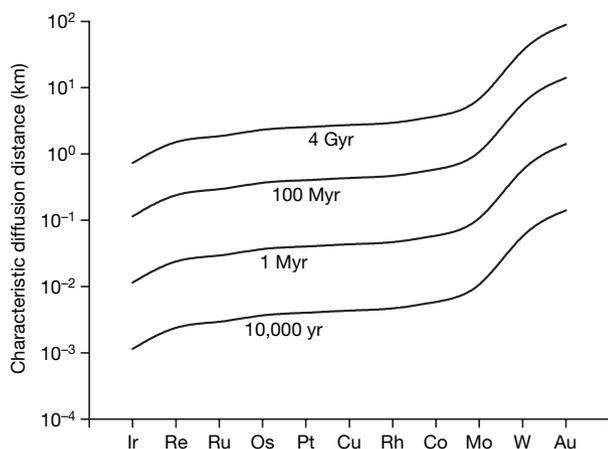
Figure 4 | Characteristic diffusion distance. This value was determined using the relation $x = \sqrt{Dt}$ based on calculated grain-boundary diffusivity for MSE and HSE over various time periods: 10,000 yr, 1 Myr, 100 Myr and 4 Gyr.

elements. The contiguity (extent of grain-to-grain contact) of magnesiowüstite, in addition to the possible existence of discontinuous zones or layers in the lower mantle phases, may also influence the potential for long-distance transport. Finally, diffusion between two pure metals is not representative of CMB conditions, but represents a simple experimental design from which data can be obtained over laboratory timescales and within analytical constraints.

Here we have shown that a large number of siderophile elements are mobile in the grain boundaries of polycrystalline MgO. The diffusivities of these elements are high enough to suggest that grain-boundary diffusion could occur on a geologically significant length scale. Grain-boundary diffusion (combined with convective overturn of the mantle) is thus a plausible mechanism for chemical interaction at and above the core-mantle boundary. Understanding the grain-boundary segregation and diffusion behaviour of these elements would provide a new tool for interpreting the abundance patterns and isotope systematics of siderophile elements in mantle rocks and thus understanding the geochemical processes in the Earth's mantle.

METHODS SUMMARY

The general experimental strategy was to establish a one-dimensional gradient in the chemical potential of each metal of interest (Os, Ir, Ru, Rh, Pt, Re, Au, W, Mo, Co or Cu) across a volume of polycrystalline MgO having an equilibrium microstructure. Our technique involved pre-fabrication of MgO wafers (~3 mm diameter × 1 mm thick), the opposing faces of which were smeared with metal powders—a 'source' of the diffusant of interest on one side and a suitable 'sink' metal (Pt powder or foil) on the other. During the actual diffusion anneals, the faces created source and sink horizons of metal particles separated by ~1 mm of polycrystalline MgO, typically ~50 µm in grain size. The wafers were placed in a standard 12.7 mm diameter piston-cylinder assembly and held at 1,600 °C and 2.5 GPa for 10 to 50 h. Viewed in terms of a single planar grain boundary, the 'source-sink' experimental strategy works as follows: diffusant atoms (for example, Au) are partitioned into the grain boundary at the source and diffuse

along the boundary until they encounter the sink phase (Pt) into which they dissolve. The time-integrated grain-boundary flux (J_{gb}) can be evaluated by measuring the total number of diffusant atoms (n) accumulated in the sink in a given time:

$$n = A_{int} \int_{t=0}^{t} J_{gb} \, dt \qquad (1)$$

where A_{int} is the effective cross-sectional area of the grain boundary that is intersected by the sink phase. The implementation of this idea for a volume of MgO having numerous grain boundaries of diverse orientation is discussed in the Methods section. The run products were analysed with an electron microprobe by measuring the concentration of the source element in the Pt (essentially determining n in equation (1)). The alloying (or 'communication') of the two initially pure metals separated by polycrystalline MgO is taken as proof of the existence of grain-boundary diffusion pathways in the MgO.

Full Methods and any associated references are available in the online version of the paper at www.nature.com/nature.

1. O'Neill, H. St C. The origin of the moon and the early history of the Earth—a chemical model. Part 2: the Earth. *Geochim. Cosmochim. Acta* **55,** 1159–1172 (1991).
2. Jones, J. H. & Drake, M. J. Geochemical constraints on core formation in the Earth. *Nature* **322,** 221–228 (1986).
3. Walker, R. J. & Walker, D. Does the core leak? *Eos* **86,** 237–244 (2005).
4. Brandon, A. D., Walker, R. J., Morgan, J. W., Norman, M. D. & Pritchard, H. M. Coupled [186]Os and [187]Os evidence for core-mantle interaction. *Science* **280,** 1570–1573 (1998).
5. Brandon, A. D. & Walker, R. J. The debate over core-mantle interaction. *Earth Planet. Sci. Lett.* **232,** 211–225 (2005).
6. Van Orman, J. A., Fei, Y., Hauri, E. H. & Wang, J. Diffusion in MgO at high pressures: Constraints on deformation mechanisms and chemical transport at the core-mantle boundary. *Geophys. Res. Lett.* **30,** 1056–1059 (2003).
7. Hiraga, T., Anderson, I. M. & Kohlstedt, D. L. Chemistry of grain boundaries in mantle rocks. *Am. Mineral.* **88,** 1015–1019 (2003).
8. Hiraga, T., Anderson, I. M. & Kohlstedt, D. L. Grain boundaries as reservoirs of incompatible elements in the Earth's mantle. *Nature* **427,** 699–703 (2004).
9. Farver, J. R. & Yund, R. A. Measurement of oxygen grain boundary diffusion in natural, fine-grained, quartz aggregates. *Geochim. Cosmochim. Acta* **97,** 1597–1607 (1991).
10. Kingery, W. D. *Introduction to Ceramics* 2nd edn 250–257 (Wiley, New York, 1976).
11. Fisher, J. C. Calculation of diffusion penetration curves for surface and grain-boundary diffusion. *J. Appl. Phys.* **22,** 74–77 (1951).
12. Harrison, L. G. Influence of dislocations on diffusion kinetics in solids with particular reference to the alkali halides. *Trans. Faraday Soc.* **57,** 1191–1199 (1961).
13. Ricoult, D. L. & Kohlstedt, D. L. Structural width of low-angle grain boundaries in olivine. *Phys. Chem. Mineral.* **9,** 133–138 (1983).
14. Sutton, A. P. & Balluffi, R. W. *Interfaces in Crystalline Materials* 305–310 (Oxford Univ. Press, New York, 1995).
15. Watson, E. B. Mobility of siderophile elements in grain boundaries of periclase and periclase/olivine aggregates. *Eos* **83** (Spring Meet. Suppl.), abstr. V52B-05 (2002).
16. Ringwood, A. E. Phase transformations and their bearing on the constitution and dynamics of the mantle. *Geochim. Cosmochim. Acta* **55,** 2083–2110 (1991).

METHODS

Traditional methods of characterizing grain-boundary diffusion depend on the compatibility of the element of interest in the crystal lattice. However, in cases where the diffusant can be presumed to exist primarily in the grain boundaries, as with the HSEs, its mobility may be undetected by most bulk analysis methods. Therefore the characterization of grain-boundary transport of siderophile elements in oxides requires a different experimental strategy, using 'source' and 'sink' layers of metal to detect movement through grain boundaries.

In the most basic type of experiment, cylindrical MgO wafers, approximately 1 mm in length, were presynthesized to obtain an equilibrium microstructure. Powdered metal particles were smeared on each side of the wafer; the upper horizon with the diffusant or 'source' (Os, Ir, Ru, Rh, Pt, Re, Au, W, Mo, Co, Cu) and the lower horizon with the 'sink' element, Pt (in some experiments thin Pt foil was used instead of metal powder) (Supplementary Fig. 1). As the source elements are highly incompatible in the lattice, alloying of the source element with the initially pure Pt 'sink' particles implies a grain-boundary diffusion pathway. The wafers were placed in a graphite furnace in a standard 12.7 mm piston-cylinder assembly in which the furnace was separated from the NaCl pressure medium by a thermally insulating silica glass sleeve (Supplementary Fig. 1). Experiments were run at 1,600 °C and 2.5 GPa for 10–50 h. There was also a series of experiments containing multiple sink layers involving three Pt foil horizons located ~1.5, 3 and 4.5 mm from the source layer; as well as a 'time series' for selected elements in which either the run duration (up to 50 h) or diffusion distance (up to 6 mm) was modified.

Although the oxygen fugacity during the run was not measured or quantified, it can be constrained to a reducing environment. The graphite furnace shows the presence of reduced carbon. The inherent stability (absence of oxidation) of the W-Re thermocouple and the stability of the metal phase in experiments run with oxide-forming siderophiles (Mo-MoO_2) are also indications of reducing conditions.

The run products were analysed with a Cameca SX-100 electron microprobe by measuring the concentration of the source element in the sink particles/foils. The source particles were also analysed for the presence of sink materials. Analyses were performed with a 1 or 10 μm beam (for analyses of particles and foils, respectively) at 15 kV accelerating potential and sample currents of 100 nA. K_α X-rays were collected through LiF crystals for Co and Cu; L_α X-rays were collected through PET (pentaerythritol) crystals for Rh, Ru and Mo and through a LiF crystal for Pt; and M_α X-rays were collected through PET crystals for Au, Ir, Os, Re and W. Acquisition times were 60 s for all elements except Pt, for which it was 10 s. These analytical procedures resulted in detection limits on the order of ~10 p.p.m. for Mo and Os; ~300 p.p.m. for Co, Cu, Ir, Re, Rh and Ru; and ~1,000 p.p.m. for Au, Pt and W. In the experiments with Pt powder in the sink horizon, owing to beam limitations only particles larger than a few micrometres in diameter were analysed. In experiments with foils, analyses were done along the length of the foil in approximately ~40 μm steps. To ensure that neither the furnace nor the silica glass sleeves were breached by NaCl, energy

dispersive X-ray spectrometer analyses for NaCl were performed on both the polycrystalline MgO medium and the graphite and silica sleeves. Back-scattered electron images were also taken of the sectioned samples.

The raw microprobe data were used in conjunction with SigmaScan image software to determine the grain-boundary volume in the sample and ultimately the flux of source atoms through the MgO (Supplementary Fig. 2). This was done by first calibrating the scale of the back-scattered electron image, then using the software to determine the area of the Pt particles or foils. The two-dimensional image was assigned a depth of 10 μm, which seems a reasonable estimate given the general shape of the Pt particles. This volume was then converted to a mass of Pt via its density. The number of atoms and then the mass of the source element in each particle (or foil) can then be determined. The average concentration (for runs with Pt particles) is essentially the summation of the total mass of source element divided by the summation of the total mass of sink element.

The time-integrated grain-boundary flux (Jgb) can be evaluated by measuring the total number of diffusant atoms (n) accumulated in the sink in a given time via equation (1) in the main text.

In order to determine the grain-boundary volume, the total length of the grain boundaries was carefully measured, again with the software, and assigned a width of 1 nm. The distance between the source and sink horizons was measured and then multiplied by a factor of 1.7 to represent the tortuosity of the pathway. These three parameters—mass transport, grain-boundary volume and diffusion distance—plus the duration of the experiment were then used to calculate the flux of the source element through the grain boundaries. This amounts to a practical implementation of equation (1) for a complex, polycrystalline sample.

The flux alone has value as a qualitative indicator of the effectiveness of grain-boundary diffusant transport, but additional information or assumptions are needed to calculate diffusivity. Assuming the system quickly establishes a (near) steady-state condition, the relationship between diffusivity and flux in the grain boundary is given approximately by

$$D_{gb} = -J_{gb}\left[\frac{dc}{dx}\right] \qquad (2)$$

where dc/dx is the concentration gradient of the diffusant in the grain boundary. Complications arise in this simplistic approach, of course, because neither the absolute concentrations in the grain boundary nor dc/dx is expected to be directly measurable (or strictly constant), but in the total absence of data even approximate diffusivities have value. A semi-infinite model for diffusion

$$C_{(x,t)} = C_0[1 - \mathrm{erf}(x/\sqrt{4Dt})] \qquad (3)$$

was used to calculate D from the 'concentration profile' from multi-sink experiments. This approach is appropriate—even for fast diffusing elements like Au and W, the mass transfer via diffusion is very small compared to the mass of the source layer. However, this is by no means a rigorous mathematical treatment, because no such treatment is available for these and similar experiments. It was implemented to approximate diffusivity within an order of magnitude.