Partitioning of Si and O between liquid iron and silicate melt: A two-phase ab-initio molecular dynamics study

Yigang Zhang[1] and Guangjun Guo[2]

[1] The magma ocean process in the early history of the Earth has a great influence on the light element identities and contents of the core which subsequently affect the energy of the geodynamo provided by the compositional convection and the inner core growth through their effect on the phase diagram of iron alloy. In the present work, a two-phase ab-initio molecular dynamics method is established to study the solubility of silicon and oxygen in liquid iron in equilibrium with silicate melt. The ab-initio results are found to be in close agreement with experimental data. At the base of a deep magma ocean (39 GPa and 3116 K), liquid iron contains 2.7 wt% silicon and 0.5 wt% oxygen at the current bulk Earth composition. The oxygen content is low compared with its current estimate in the core, indicating a deeper magma ocean may need to be invoked. **Citation:** Zhang, Y., and G. Guo (2009), Partitioning of Si and O between liquid iron and silicate melt: A two-phase ab-initio molecular dynamics study, *Geophys. Res. Lett.*, *36*, L18305, doi:10.1029/2009GL039751.

1. Introduction

[2] The Earth's early accretion events and processes, in particular, the giant impact and the magma ocean process have a great influence on the evolution and the current state of the Earth [*Stevenson*, 2008]. For example, light elements of the core, with their identities and contents largely determined by the magma ocean process, may help sustain the geodynamo through compositional convection [*Braginsky*, 1963], and influence inner core growth through melting point depression [*Jeanloz*, 1990].

[3] To understand the magma ocean process and its effect on the mantle and the core composition, many element partitioning experiments have been performed to derive the temperature, the pressure, and the oxygen fugacity at which the magma ocean process occurs [e.g., *Li and Agee*, 1996; *O'Neill et al.*, 1998; *Walter et al.*, 2000; *Righter*, 2003; *Wade and Wood*, 2005; *Corgne et al.*, 2008; *Wood et al.*, 2008, and references therein]. The inferred temperatures and pressures range from 2000 to 4200 K and 25 to 40 GPa, reflecting both experimental difficulties and complexity of the magma ocean process [*Rubie et al.*, 2007; *Wood*, 2008].

[4] Ab-initio methods have been applied to study element partitioning between the inner and the outer core by calculating chemical potentials of candidate elements in solid and liquid iron [*Alfè et al.*, 2000, 2002]. The two-phase method, which makes two phases in direct contact in a molecular dynamics (MD) simulation cell, is employed in ab-initio studies of the melting temperatures of iron and MgO [*Alfè*, 2005, 2009] and the solubility of argon in liquid iron [*Ostanin et al.*, 2006].

[5] In the present study, we extend the ab-initio two-phase method so that compositions of the two segregated phases can be calculated. Starting from a random distribution of elements (O, Mg, Fe, and Si) in the simulation cell, with the MD progressing, the system segregates into two phases, one is liquid iron and the other is silicate melt. Compositions of the two phases are calculated by using concepts and methods in computational geometry and compared with experimental data. The method is then applied to infer the amounts of Si and O that could be added by the deep magma ocean process to the Earth's core.

2. Method

[6] Calculations are performed by using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) developed at the Institut für Materialphysik of the Universität Wien [*Kresse and Hafner*, 1993, 1994; *Kresse and Furthmüller*, 1996a, 1996b]. The projector augmented wave potentials [*Blöchl*, 1994; *Kresse and Joubert*, 1999] are employed together with the generalized gradient approximation of the exchange-correlation potential (PBE [*Perdew et al.*, 1996]). The Plane-wave basis set cutoff is 400 eV. The accuracy for electronic self-consistent iteration is 10^{-4} eV. The Brillouin zone sampling is performed only at the Gamma point. The Fermi-Dirac smearing is used to consider the temperature effect.

[7] MD simulations are performed in the NVT ensemble with a time step of 1 fs. Internal energy drift slope is 0.7 K/ps in the largest case, which is much smaller than fluctuations of the internal energy. Systems are generally composed of 256 atoms, with one run comprising 400 atoms to study the effect of system size (i.e., number of atoms). 1000 steps are used for scaling, ~20000 steps for the two phases (liquid iron and silicate melt) to segregate, and another ~35000 steps for accumulation of atom positions for composition calculations. With our current computational facilities, each run takes about 3 months to finish.

[8] Composition of the liquid iron phase (i.e., the number of atoms enclosed in the Fe-cluster) is obtained by first constructing a polyhedron for the Fe-cluster and then judging if an atom is enclosed in the polyhedron. Concepts and methods in computational geometry [*O'Rourke*, 1998;

---

[1] State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China.
[2] Key Laboratory of the Study of Earth's Deep Interior, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China.
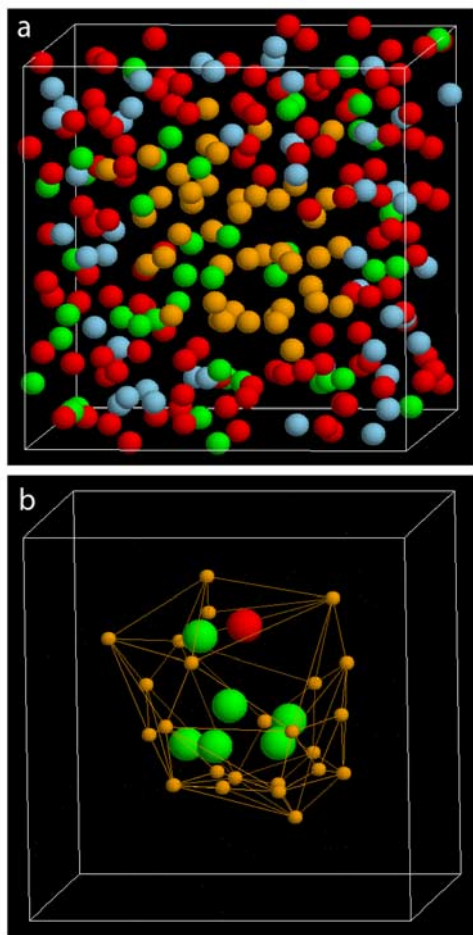
Figure 1. (a) Atom configuration after the phase segregation. The O atoms are in red color, Mg in sky blue, Fe in orange, and Si in green. (b) The alpha shape constructed from the configuration, showing only the Fe atoms on the surface of the alpha shape and the Si and O atoms enclosed in the polyhedron.

de Berg et al., 2000] are used. Basically, three steps are needed.

[9] In the first step, the center of mass of the Fe-cluster is calculated and moved to the center of the simulation cell. All atoms are moved accordingly. The procedure is repeated until the center of mass of the Fe-cluster coincides with the center of the simulation cell. This is the preparatory step and considers mainly the periodic boundary conditions of the simulation cell.

[10] In the second step, an alpha shape is constructed for the Fe-cluster by using the program *hull* [*Clarkson*, 1992; *Clarkson et al.*, 1993], which employs the randomized incremental algorithm. The alpha shape is derived from the Delaunay triangulation and describes different levels of details of the shape formed by the Fe-cluster at different alpha values. Two parameters are important for the calculation. One is the multiplication factor of atom coordinates. The reason for its use is that calculations are performed in the integer format. A large multiplication factor gives more accurate results; the other is the value of alpha, which is a measure of the size of the sphere used to select Delaunay

triangulations and has a strong influence on the calculated compositions, especially when it is small. At large alpha values, the alpha shape converges gradually to the convex hull and the calculated compositions become also stable. After several tests, a very large alpha value of 10^{10} at the multiplication factor of 1000 is used.

[11] In the third step, whether an atom is in the polyhedron constructed in the second step is determined by using the program *inhedron* [*O'Rourke*, 1998], which employs the random ray crossing algorithm, meaning that if an atom is inside a polyhedron, the ray connecting the atom and a point outside the polyhedron will have odd number of crossings with the polyhedron faces. Degeneracies are considered by generating new rays for a given atom.

[12] Once composition of the liquid iron is known, composition of the silicate melt can be directly derived as the bulk composition of the whole system is known.

3. Results and Discussion

[13] Figure 1a shows a typical atom configuration with segregated liquid iron and silicate melt phases. The liquid iron phase is located at the center of the simulation cell. Figure 1b displays the alpha shape constructed from the configuration and the Si and O atoms found to be enclosed in the polyhedron.

[14] System size is restricted severely in ab-initio MD compared with classical MD. Its effect on element partitioning is studied using runs M4 and M6 (Table 1), which are made at the same temperature, pressure, and composition, but with different numbers of atoms (256 and 400, respectively). Their Si and O compositions in both the liquid iron and the silicate melt phases are very similar, indicating a negligible system size effect. As a result, all the subsequent simulations are performed using 256 atoms.

[15] To validate our ab-initio method, results obtained in the present study are compared with experimental data for all the four elements O, Mg, Fe, and Si. For silicon, Figure 2 shows clearly that the solubility of Si in liquid Fe is in close agreement with experimental results; for oxygen, its solubility in liquid iron is 0.26 wt% at the relatively oxidized condition (run M7) and 0.06 wt% at the reduced condition (run M8). *Corgne et al.* [2008] give an oxygen solubility of ~0.2 wt% for both their oxidized and reduced experimental series. The values of $\log(X_{SiO2(silicate)}/X_{Si(metal)})$, which is a reflection of the oxygen fugacity, are about 2.8 and 0.5, respectively, for the two series of runs of *Corgne et al.* [2008], while they are 1.8 and 0.9 for M7 and M8. Thus the oxygen fugacity implied in M7 and M8 are in between those of the two series of the experiments of *Corgne et al.* [2008]. Together with the similarity of the temperature and pressure conditions of the ab-initio and the experimental works, the ab-initio calculations thus predict correctly the solubility of oxygen in liquid iron; for magnesium, its solubility in liquid iron often is not listed in previous publications and presumably negligible. In our calculations, the solubility of Mg in liquid iron is found to be smaller than 0.009 wt%. Thus the Mg solubility is also correctly predicted; for iron, the amount of Fe that should dissolve in silicate melt at the compositional conditions of runs M7 and M8 can be estimated by first setting up a relation between $\log(X_{SiO2(silicate)}/X_{Si(metal)})$ and $\log(wt\%_{Fe(silicate)})$ using the

Table 1. Compositions of Liquid Iron and Silicate Melt[a]

Runs	M4	M6	M7	M8	M9
T (K)	3000±30	3000±13	2273±78	2273±66	3116±26
P (GPa)	37.6±1.5	37.0±1.2	3.6±1.1	3.1±1.1	38.8±1.6
CL[b] (Å)	13.09	15.1896	14.11	14.21	13.06
			Starting Bulk Compositions (Number of Atoms)		
O	121	189	130	125	123
Mg	47	73	51	51	51
Fe	45	71	36	37	44
Si	43	67	38	43	38
			Compositions of Liquid Iron (wt%)[c]		
O	0.41±0.42	0.71±0.52	0.26±0.42	0.06±0.22	0.48±0.61
Si	5.46±1.28	5.23±1.10	0.35±0.63	3.20±1.06	2.69±1.29
			Compositions of Silicate Melt (wt%)[d]		
O	46.62±0.27	46.57±0.34	47.43±0.19	45.66±0.11	46.63±0.37
Si	25.72±0.64	25.84±0.80	24.24±0.45	26.03±0.25	23.82±0.84
			Partitioning Coefficients[e]		
O	0.0087±0.0091	0.0152±0.0113	0.0056±0.0089	0.0014±0.0048	0.0102±0.0131
Si	0.2123±0.0549	0.2026±0.0489	0.0144±0.0263	0.1231±0.0417	0.1129±0.0582

[a]Numbers after ± are standard deviations calculated from the fluctuations of MD simulations, except those of the partition coefficient, which are calculated from error transfer.
[b]Cell length.
[c]The Mg content is zero, and the Fe content is 100%-O wt%-Si wt%.
[d]The Fe content is zero, and the Mg content is 100%-O wt%-Si wt%.
[e]The partitioning coefficient is defined as wt% in liquid iron divided by wt% in silicate melt.

experimental data of *Corgne et al.* [2008] and *Rose-Weston et al.* [2009] and then using the values of $\log(X_{SiO2(silicate)}/X_{Si(metal)})$ of M7 and M8 to derive wt%$_{Fe(silicate)}$. At the compositional conditions of M7 and M8, the silicate melt should contain 1.5~2.4 and 0.5~0.8 wt% Fe, respectively. In our ab-initio calculations, no Fe is found in silicate melt. Thus, although it is quite successful for elements O, Si, and Mg, the current method cannot be used to study the partitioning of Fe between liquid iron and silicate melt. The reason for the failure is not clear at present, but may be the still limited system size or the exchange-correlation potential model used.

[16] To derive the Si and O compositions of liquid Fe in equilibrium with silicate melt at the base of a deep magma ocean, a simulation is made at the temperature and the pressure close to those inferred by *Wood et al.* [2008] (~44 GPa and ~3230 K) and at the composition of the bulk Earth [*McDonough*, 2003]. At 3116 K and 39 GPa, the O and Si contents of liquid Fe are 0.5 and 2.7 wt%, respectively (run M9 in Table 1). To understand the meaning of these two values, current estimates of light element content of Earth's core need to be discussed in the first place.

[17] *Badro et al.* [2007], using both density and sound velocity, constrain that Earth's inner core contains 2.3 wt% Si. By using the ab-initio partition coefficient of D_{Si}(liquid iron/solid iron) = 1.26 [*Alfè et al.*, 2002] the outer core then contains 2.9 wt% Si [*Badro et al.*, 2007]. This gives a whole core (inner + outer) Si content of 2.9 wt% by using the mass ratio of the inner and the outer core [*Stacey*, 1992].

[18] *Badro et al.* [2007] use the experiment of *Takafuji et al.* [2005] and the ab-initio partition coefficient of *Alfè et al.* [2002] to constrain further the O content of the outer core. The constraint is not as strong as that for Si since the O content may not be determined by the equilibrium between liquid iron and perovskite at 97 GPa and that the error in the estimated O content of the inner core may have a large influence on the inferred O content of the outer core due

to the large value of the O partition coefficient (D_O(liquid iron/solid iron) of *Alfè et al.* [2002] is 43 if weight percent is used as the unit of concentration). The O content of the outer core may be better constrained using the methodology of *Alfè et al.* [2002] because O has the largest effect on the density jump between the inner and the outer core compared with Si and S. *Alfè et al.* [2002] give 2.6 wt% oxygen in the outer core. The O content of the whole core is thus 2.4 wt% by using again the inner and the outer core mass ratio and the O partition coefficient.

[19] The values given above for the Si and O contents of the outer core (2.9 wt% Si and 2.6 wt% O) are in close
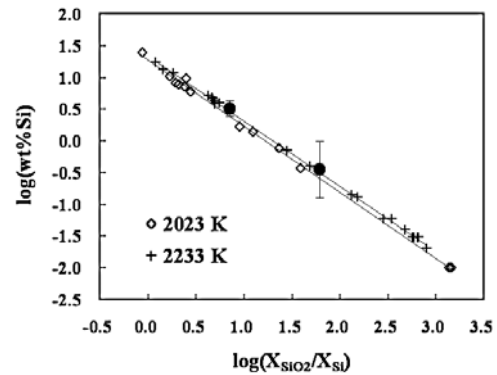
Figure 2. Comparison of experimental and ab initio results for the solubility of Si in liquid iron (wt%Si). X_{SiO2} is the mole fraction of SiO_2 in silicate melt and X_{Si} that of Si in liquid Fe. The solid circles represent the ab-initio data M7 and M8 in Table 1. The experimental data at 2023 K (2.5 GPa) are from *Kilburn and Wood* [1997], *Wade and Wood* [2001], and *Wood et al.* [2008], and those at 2233 K (1~3 GPa) from *Rose-Weston et al.* [2009]. The two straight lines are linear least square fits of the experimental data at the two temperatures. The error bars for the two ab-initio data points are calculated from the standard deviations of MD steps.

agreement with the density deficit given by *Anderson and Isaak* [2002]. According to the work, 1% density deficit can be considered by either 1.69 wt% Si or 0.73 wt% O at the iron melting temperature of 6350 K at the inner and the outer core boundary [*Alfè*, 2009]. Similar value for Si is also given by *Chen et al.* [2007]. Thus the amounts of O and Si inferred above would create a density deficit of 2.9/1.69+2.6/0.73=5.5% in the outer core, quite similar to the value of *Anderson and Isaak* [2002] based on equation of state calculations.

[20] From above discussions, the O and Si contents of Earth's core are probably 2.4 and 2.9 wt%, respectively. Addition of a small amount of sulphur is feasible but will probably replace mainly the Si content as the two elements behave similarly in terms of their partitioning and their contribution to the density jump between the inner and the outer core [*Alfè et al.*, 2002]. When the two values (2.4 wt% O and 2.9 wt% Si) for the estimates of light-element content of the core are compared with the solubility of O ands Si in liquid iron at the base of a deep magma ocean (0.5 wt% O and 2.7 wt% Si), it's clear that O added by the deep magma ocean process is insufficient.

[21] Experimental works show that when liquid Fe coexists with perovskite and post-perovskite, its O content can increase from ~1 wt% at 40 GPa to ~5 wt% at 100 GPa; the Si content increases from ~1 wt% to ~3 wt%, correspondingly [*Takafuji et al.*, 2005; *Sakai et al.*, 2006]. Similarly, significant amount of O is found in liquid iron in equilibrium with another major lower mantle mineral ferropericlase [*Rubie et al.*, 2004; *Ozawa et al.*, 2008]. These higher values of light-element solubility hint at the possibility that significant amount of O and Si could dissolve into liquid iron simultaneously if temperature and pressure are high enough. This means that a deeper magma ocean may be required, which is quite possible, considering the recent calculation of *Stixrude et al.* [2009]. The specific temperature and pressure at which we can arrive at the current estimate of the light element content of Earth's core are still unclear at present due to the lack of data and require further experimental and theoretical investigations.

4. Conclusions

[22] A two-phase ab-initio molecular dynamics simulation method is established to investigate the partitioning of Si and O between liquid iron and silicate melt in the system O-Mg-Fe-Si. The results from the ab-initio calculations are found to be in close agreement with experimental data.

[23] Calculations indicate 2.7 wt% silicon and 0.5 wt% oxygen could be added to the core through the magma ocean process if liquid iron is in equilibrium with silicate melt at the base of a deep magma ocean (39 GPa and 3116 K) and at the current bulk Earth composition. The oxygen content is lower than the current estimate of the core, implying a deeper magma ocean may need to be invoked.

References

Alfè, D. (2005), Melting curve of MgO from first-principles simulations, *Phys. Rev. Lett.*, *94*, 235701, doi:10.1103/PhysRevLett.94.235701.

Alfè, D. (2009), Temperature of the inner-core boundary of the Earth: Melting of iron at high pressure from first-principles coexistence simulations, *Phys. Rev. B*, *79*, 060101, doi:10.1103/PhysRevB.79.060101.

Alfè, D., M. J. Gillan, and G. D. Price (2000), Constraints on the composition of the Earth's core from ab-initio calculations, *Nature*, *405*, 172–175, doi:10.1038/35012056.

Alfè, D., M. J. Gillan, and G. D. Price (2002), Composition and temperature of the Earth's core constrained by combining ab initio calculations and seismic data, *Earth Planet. Sci. Lett.*, *195*, 91–98, doi:10.1016/S0012-821X(01)00568-4.

Anderson, O. L., and D. G. Isaak (2002), Another look at the core density deficit of Earth's outer core, *Phys. Earth Planet. Inter.*, *131*, 19–27, doi:10.1016/S0031-9201(02)00017-1.

Badro, J., G. Fiquet, F. Guyot, E. Gregoryanz, F. Occelli, D. Antonangeli, and M. d'Astuto (2007), Effect of light elements on the sound velocities in solid iron: Implications for the composition of Earth's core, *Earth Planet. Sci. Lett.*, *254*, 233–238, doi:10.1016/j.epsl.2006.11.025.

Blöchl, P. E. (1994), Projector augmented-wave method, *Phys. Rev. B*, *50*, 17,953–17,979, doi:10.1103/PhysRevB.50.17953.

Braginsky, S. I. (1963), Structure of the F layer and reasons for convection in the core, *Dokl. Akad. Nauk SSSR*, English Transl., *149*, 1311–1314.

Chen, B., L. L. Gao, K. I. Funakoshi, and J. Li (2007), Thermal expansion of iron-rich alloys and implications for the Earth's core, *Proc. Natl. Sci. Acad. U. S. A.*, *104*, 9162–9167, doi:10.1073/pnas.0610474104.

Clarkson, K. L. (1992), Safe and effective determinant evaluation, in *Proceedings of 31st IEEE Symposium on Foundations of Computer Science*, pp. 387–395, Inst. of Electr. and Electron. Eng., New York.

Clarkson, K. L., K. Mehlhorn, and R. Seidel (1993), Four results on randomized incremental constructions, *Lect. Notes Comput. Sci.*, *577*, 461–474.

Corgne, A., S. Keshav, B. J. Wood, W. F. McDonough, and Y. Fei (2008), Metal-silicate partitioning and constraints on core composition and oxygen fugacity during earth accretion, *Geochim. Cosmochim. Acta*, *72*, 574–589, doi:10.1016/j.gca.2007.10.006.

de Berg, M., M. van Kreveld, M. Overmars, and O. Schwarzkopf (2000), *Computational Geometry: Algorithms and Applications*, 2nd ed., 379 pp., Springer, Berlin.

Jeanloz, R. (1990), The nature of the Earth's core, *Annu. Rev. Earth Planet. Sci.*, *18*, 357–386, doi:10.1146/annurev.ea.18.050190.002041.

Kilburn, M. R., and B. J. Wood (1997), Metal-silicate partitioning and the incompatibility of S and Si during core formation, *Earth Planet. Sci. Lett.*, *152*, 139–148, doi:10.1016/S0012-821X(97)00125-8.

Kresse, G., and J. Furthmüller (1996a), Efficiency of ab initio total-energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.*, *6*, 15–50, doi:10.1016/0927-0256(96)00008-0.

Kresse, G., and J. Furthmüller (1996b), Efficient iterative schemes for ab-initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B*, *54*, 11,169–11,186, doi:10.1103/PhysRevB.54.11169.

Kresse, G., and J. Hafner (1993), Ab initio molecular dynamics for liquid metals, *Phys. Rev. B*, *47*, 558–561, doi:10.1103/PhysRevB.47.558.

Kresse, G., and J. Hafner (1994), Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium, *Phys. Rev. B*, *49*, 14,251–14,269, doi:10.1103/PhysRevB.49.14251.

Kresse, G., and D. Joubert (1999), From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B*, *59*, 1758–1775, doi:10.1103/PhysRevB.59.1758.

Li, J., and C. B. Agee (1996), Geochemistry of mantle-core formation at high pressure, *Nature*, *381*, 686–689, doi:10.1038/381686a0.

McDonough, W. F. (2003), Compositional model for the Earth's core, in *The Mantle and Core*, *Treatise Geochem.*, vol. 2, edited by R. W. Carlson, Elsevier-Pergamon, Oxford, U. K.

O'Neill, H. S. C., D. Canil, and D. Rubie (1998), Oxide-metal equilibria at 2500 C and 25 GPa: Implications for core formation and the light element component in the Earth's core, *J. Geophys. Res.*, *103*, 12,239–12,260, doi:10.1029/97JB02601.

O'Rourke, J. (1998), *Computational Geometry in C*, 2nd ed., 376 pp., Cambridge Univ. Press, Cambridge, U. K.

Ostanin, S., D. Alfè, D. Dobson, L. Vocadlo, J. P. Brodholt, and G. D. Price (2006), Ab initio study of the phase separation of argon in molten iron at high pressures, *Geophys. Res. Lett.*, *33*, L06303, doi:10.1029/2005GL024276.

Ozawa, H., K. Hirose, M. Mitome, Y. Bando, N. Sata, and Y. Ohishi (2008), Chemical equilibrium between ferropericlase and molten iron to 1345 GPa and implications for iron content at the bottom of the mantle, *Geophys. Res. Lett.*, *35*, L05308, doi:10.1029/2007GL032648.

Perdew, J. P., K. Burke, and M. Ernzerhof (1996), Generalized gradient approximation made simple, *Phys. Rev. Lett.*, *77*, 3865–3868, doi:10.1103/PhysRevLett.77.3865.

Righter, K. (2003), Metal-silicate partitioning of siderophile elements and core formation in the early Earth, *Annu. Rev. Earth Planet. Sci.*, *31*, 135–174, doi:10.1146/annurev.earth.31.100901.145451.

Rose-Weston, L., J. M. Brenan, Y. Fei, R. A. Secco, and D. J. Frost (2009), Effect of pressure, temperature, and oxygen fugacity on the metal-silicate partitioning of Te, Se, and S: Implications for earth differentiation, *Geochim. Cosmochim. Acta*, *73*, 4598–4615, doi:10.1016/j.gca.2009.04.028.

Rubie, D. C., C. K. Gessmann, and D. J. Frost (2004), Partitioning of oxygen during core formation on the Earth and Mars, *Nature*, *429*, 58–61, doi:10.1038/nature02473.

Rubie, D. C., F. Nimmo, and H. J. Melosh (2007), Formation of Earth's core, in *Evolution of the Earth*, *Treatise Geophys.*, vol. 9, edited by D. Stevenson, pp. 51–90, Elsevier, Amsterdam.

Sakai, T., T. Kondo, E. Ohtani, H. Terasaki, N. Endo, T. Kuba, T. Suzuki, and T. Kikegawa (2006), Interaction between iron and post-perovskite at core-mantle boundary and core signature in plume source region, *Geophys. Res. Lett.*, *33*, L15317, doi:10.1029/2006GL026868.

Stacey, F. D. (1992), *Physics of the Earth*, 3rd ed., 513 pp., Brookfield, New York.

Stevenson, D. J. (2008), A planetary perspective on the deep Earth, *Nature*, *451*, 261–265, doi:10.1038/nature06582.

Stixrude, L., N. de Koker, N. Sun, M. Mookherjee, and B. B. Karki (2009), Thermodynamics of silicate liquids in the deep Earth, *Earth Planet. Sci. Lett.*, *278*, 226–232, doi:10.1016/j.epsl.2008.12.006.

Takafuji, N., K. Hirose, M. Mitome, and Y. Bando (2005), Solubilities of O and Si in liquid iron in equilibrium with $(Mg,Fe)SiO_3$ perovskite and the light elements in the core, *Geophys. Res. Lett.*, *32*, L06313, doi:10.1029/2005GL022773.

Wade, J., and B. J. Wood (2001), The Earth's "missing" niobium may be in the core, *Nature*, *409*, 75–78, doi:10.1038/35051064.

Wade, J., and B. J. Wood (2005), Core formation and the oxidation state of the Earth, *Earth Planet. Sci. Lett.*, *236*, 78–95, doi:10.1016/j.epsl.2005.05.017.

Walter, M. J., H. E. Newsom, W. Ertel, and A. Holzheid (2000), Siderophile elements in the Earth and Moon: Metal-silicate partitioning and implications for core formation, in *Origin of the Earth and Moon*, edited by R. M. Canup and K. Righter, pp. 265–289, Univ. of Ariz. Press, Tucson.

Wood, B. J. (2008), Accretion and core formation: Constraints from metal-silicate partitioning, *Philos. Trans. R. Soc., Ser. A*, *366*, 4339–4355, doi:10.1098/rsta.2008.0115.

Wood, B. J., J. Wade, and M. R. Kilburn (2008), Core formation and the oxidation state of the Earth: Additional constraints from Nb, V and Cr partitioning, *Geochim. Cosmochim. Acta*, *72*, 1415–1426, doi:10.1016/j.gca.2007.11.036.

─────────────────

G. Guo, Key Laboratory of the Study of Earth's Deep Interior, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China.

Y. Zhang, State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China. (zhangyg@mail.iggcas.ac.cn)