

Carbon driven Chemical Interactions between Alumina and Iron: A possible reaction pathway in Earth's interior

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Seismological and geochemical observations have revealed a complex structure for the earth's core-mantle boundary (CMB) region, with lateral and chemical heterogeneities¹⁻³. The presence of higher than expected concentrations of siderophile elements (Ni, Co, Pt etc) in the earth's mantle, iron enrichment of the lower mantle relative to the upper mantle, and a possible carbon flux from the core suggest the possibility of continual long-term exchange of materials between the core and the mantle⁴⁻⁸. The chemical interactions of molten iron with complex mantle oxides, and diffusion have been postulated as key mechanisms⁹⁻¹⁰. A number of studies have been carried out on the reduction reactions taking into account the extreme conditions of high-temperature and high-pressure in earth's interior¹¹⁻¹³. These studies have, however, neglected to consider the influence of carbon on these reactions. The earth's metallic core is rich in carbon (~ 5 wt% C), and there is a growing evidence for the presence of carbon in the earth's mantle as well¹⁴. Carbon can affect redox conditions through chemical interactions with oxygen, and is a critical element in determining the oxidation state of siderophile elements¹⁵. Here we present a study of the interactions between liquid iron and alumina-carbon substrates at 1,823K in argon atmosphere, and report on the formation of a Fe-Al_{0.25-0.5} alloy at ambient pressure. Iron induced reduction of alumina in the absence of carbon, has been previously reported to occur only at pressures above 60 GPa and temperatures of 2,200K¹⁶. Our results demonstrate that carbon enriched iron is capable of reducing alumina in regions of much lower pressures. These chemical reactions could provide an important mechanism for the reduction reactions occurring in earth's interior, and be responsible for far higher levels of heterogeneities than currently believed.

According to various models for the major-element composition of the bulk silicate earth (primitive mantle), alumina is the fourth abundant refractory oxide component with concentrations ranging between 3.3 to 4.7%¹⁷. It has been postulated that the core-mantle boundary region may be enriched in Al₂O₃ and CaO. Chemical interactions between liquid iron and Al₂O₃ constitute a significant component of possible exchange reactions between the core and the lower mantle. While no chemical reaction is known to occur between iron and Al₂O₃ at ambient pressure, iron was found to reduce alumina at high pressures. Pressure was assumed to reverse the direction of this redox reaction through a modification of the chemical nature of iron, making it more electropositive than aluminum at high pressures¹⁶. Using FactSage™ thermochemical data base¹⁸, we carried out phase equilibria calculations for the Al₂O₃-Fe-C ternary system, aiming to investigate the influence of carbon on the kinetics/direction of this redox reaction at ambient pressures. Computations indicated the presence of small amounts of liquid aluminum co-existing with liquid Fe, Al₂O₃ and C at 1,823K pointing towards a possible local reduction of alumina. Small amounts of Al are known to significantly affect the concentration of ferric ion (Fe³⁺) in (Mg,Fe)(Si,Al)O₃ perovskite¹⁹. Consequently, the high temperature chemistry of Al₂O₃-Fe-C system, and the influence of carbon on the exchange reactions between liquid iron on one side and refractory oxides from another side is very important for understanding the transfer of elements in the interior regions of earth. We, therefore, decided to conduct an in-depth experimental investigation on Al₂O₃ and liquid Fe in the presence of carbon using a sessile-drop method along with x-ray micro-diffraction and back-scattered electron microscopic analysis.

High purity (99.8%) fused alumina was mixed thoroughly with synthetic graphite (0-40 wt%) with 5% phenolic resin as a binder. Refractory substrates were prepared by compacting the mixture in a steel die using a hydraulic press and pressing to a pressure up to 10MPa. The compacted cylindrical substrates (25 mm diameter, 3-4 mm thick) were baked at 423 K for 48 hrs for enhancing their structural integrity; the evaporation of binder volatiles created a micro-porous substrate thereby providing possible channels for the penetration of small amounts of molten iron into the refractory substrate. Sessile drop investigations on the $\text{Al}_2\text{O}_3\text{-C}$ /liquid iron system were carried out at 1,823 K in a laboratory scale, horizontal tube resistance furnace²⁰. Initially, the sample was held on a specimen holder, which could be pushed to the centre of the hot zone in the furnace with the help of a stainless steel rod. The weight of the metallic iron used was 1.0 gm. The furnace tube was purged with pure argon throughout the duration of the experiment with a flow rate of 1.0 l/min. The assembly was held in the cold zone of the furnace until the desired temperature was attained and was then inserted into the hot zone. This eliminated any reaction that could occur at lower temperatures and possibly influence the phenomena to be studied at the temperature of interest. The melting of the metal droplet marked the beginning of the reaction time; the $\text{Al}_2\text{O}_3\text{-C/Fe}$ drop assembly was quenched after fixed periods of reaction time (30 min., 60 min.) by withdrawing the tray into the cold zone of the furnace. A high resolution charge-coupled device (CCD) camera fitted with an IRIS lens was used to capture the live in-situ phenomena in the furnace. The output from the CCD camera was channelled to a digital video recorder (DVD) and a television monitor to record the entire experimental process as a function of time. For microscopic investigations, the reacted assembly was set in an epoxy resin mould; the set assembly was then sectioned carefully to expose a cross-

sectional view of the $\text{Al}_2\text{O}_3\text{-C}$ substrate/metal assembly and was again reset in a mould. Due to very poor wetting between the refractory substrate and liquid iron, the reacted metal droplet was loosely attached to the substrate and could be easily removed. The exposed interfacial region was reset in an epoxy mould to prevent substrate degradation due to the hygroscopic nature of alumina, was characterised using x-ray micro-diffraction analysis.

X-ray micro-diffraction data was obtained using Philips X'pert Materials Research Diffractometer using Cu K_α radiation (50 KV, 40 mA). We used a mono-capillary (0.5 mm) attachment in the incident beam for selected area diffraction studies, 0.04° Soller slits in the diffracted beam, and high resolution ($55\mu\text{m} \times 55\mu\text{m}$) PIXcel solid state x-ray detector. As Fe-Al intermetallic was expected to form in the sub-surface region in very small quantities, it was important to apriori identify local regions of high concentration. Using (220) Fe_3Al peak position (44.187° , 100%), diffraction mapping of the substrate surface was carried out to locate regions of high intensity for this peak. X-ray diffraction results are presented in Fig. 1 for three $\text{Al}_2\text{O}_3\text{-C}$ substrates (0%C, 10%C and 20%C) which had been in contact with liquid iron for 30 minutes. For the substrate containing 0%C, the diffraction pattern showed only corundum peaks (R-3c; $a = 4.7588\text{\AA}$, $c = 12.992\text{\AA}$). However for alumina substrates containing carbon (10% and 20%), several additional peaks belonging to cubic aluminium-iron alloys (Fe_3Al : Fm3m, $a = 5.7934\text{\AA}$; FeAl: Pm3m, $a = 2.8954\text{\AA}$) were observed. The locations of several of these peaks were quite distinct from the corundum peaks resulting in an unambiguous characterization of the new phase. This phase was observed for carbon concentrations up to 60%. Diffraction mapping was also carried out for pure iron and

pure aluminium peaks; we could not locate any regions of local high concentration and/or diffraction peaks for these metals in the substrate.

Back-scattered scanning electron microscopic results on Al_2O_3 -10%C substrate are shown in Fig. 2 along with EDS results on selected regions. While several small droplets of $\text{Fe-Al}_{0.25-0.5}$ (bright regions) were found close to the refractory substrate-liquid iron interface, much higher concentrations of the alloy were seen precipitated deeper in the substrate. These deposits formed a quenched fluid-like network that appeared to co-exist with alumina, a result consistent with good wettability between molten Fe_3Al (melting point: 1,803 K) and alumina²¹. Although we could clearly locate several regions containing simultaneously high concentrations of Fe and Al, we did not find any local regions containing pure Fe which was consistent with x-ray diffraction results. Due to poor wetting between molten iron and Al_2O_3 -C (up to 40%) and a tendency between alumina and iron to be mutually exclusive from their immediate neighbourhood, very small amounts of molten iron were expected to penetrate the refractory substrate²²⁻²³. Molten iron, that managed to diffuse into the refractory substrate, participated in reduction reactions with Al_2O_3 and C to produce $\text{Fe-Al}_{0.25-0.5}$ intermetallics. A key feature of these EDS profiles was the low levels of carbon and oxygen observed in the regions of high Fe/Al concentrations. A high magnification SEM image for the Al_2O_3 -20%C substrate shows clear evidence for the simultaneous co-existence of Al_2O_3 , C and Fe-Al alloy (see Fig.S1 Supplementary Information).

Alumina can not be reduced by pure liquid iron at ambient pressures. It is possible that the reduction reactions are being driven by the carbon present in the substrate. Carbon has a high solubility in liquid iron at 1,823 K; molten iron can therefore easily dissolve carbon from the Al_2O_3 -C refractory during its penetration in

the substrate²³⁻²⁴. With solute carbon having a very high activity for reduction, it is quite likely that alumina gets reduced by the solute carbon producing aluminium, which in-turn reacts locally with molten iron to produce Fe-Al alloy. With higher levels of metal penetration expected with increasing carbon in the refractory substrate²⁴, copious amounts of Fe-Al observed in the Al₂O₃-40%C substrate, further support this mechanism (see Fig.S2 Supplementary Information). Experiments were also carried out on alumina-20% natural graphite substrates to investigate the influence of ash impurities. Silica and alumina were both reduced by the carbon enriched molten iron as no oxygen peak was observed in EDS results (see Fig.S3 Supplementary Information). The presence of other oxides did not prevent this reaction from occurring. This result is of great significance for carbon based reduction reactions due to simultaneous presence several oxides and their complexes in the CMB region.

We conclude that alumina can undergo reduction in Al₂O₃-Fe-C ternary system at ambient pressures. Our results reveal that carbon induced reduction reactions can provide an alternative reaction pathway in earth's interior, supplementing other modes of reactions. Extreme conditions of pressure/temperature, and high concentrations of carbon are simultaneously present in the earth's outer core and in the core-mantle boundary region; each of these is individually capable of the driving the reduction of alumina by liquid iron. For making a realistic comparison with geochemical data, it is important to determine the combined influence of carbon and high pressure/temperature conditions on the reduction reactions between complex mantle oxides and liquid iron.

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Figure Legends

Figure 1 X-ray diffraction profiles collected from the Al_2O_3 -C substrates after contact with molten iron at 1,823 K for 30 minutes (C, corundum; G, Graphite; Fe_3Al , iron-aluminium alloy; (hkl) indices given in parenthesis). As most of the peak positions for Fe-Al and Fe_3Al tended to overlap, the stoichiometry of Fe-Al alloy could not be determined from XRD patterns. (hkl) indices for Fe_3Al have been given in this figure.

Figure 2 Back scattered SEM image and EDS data for a region deep in the reacted Al_2O_3 -10%C substrate. Liquid iron droplet was in contact with the substrate near the top right corner. While region 'A' represents concentrated Fe-Al alloy, region 'B' shows a fluid network of Fe-Al on top of Al_2O_3 .

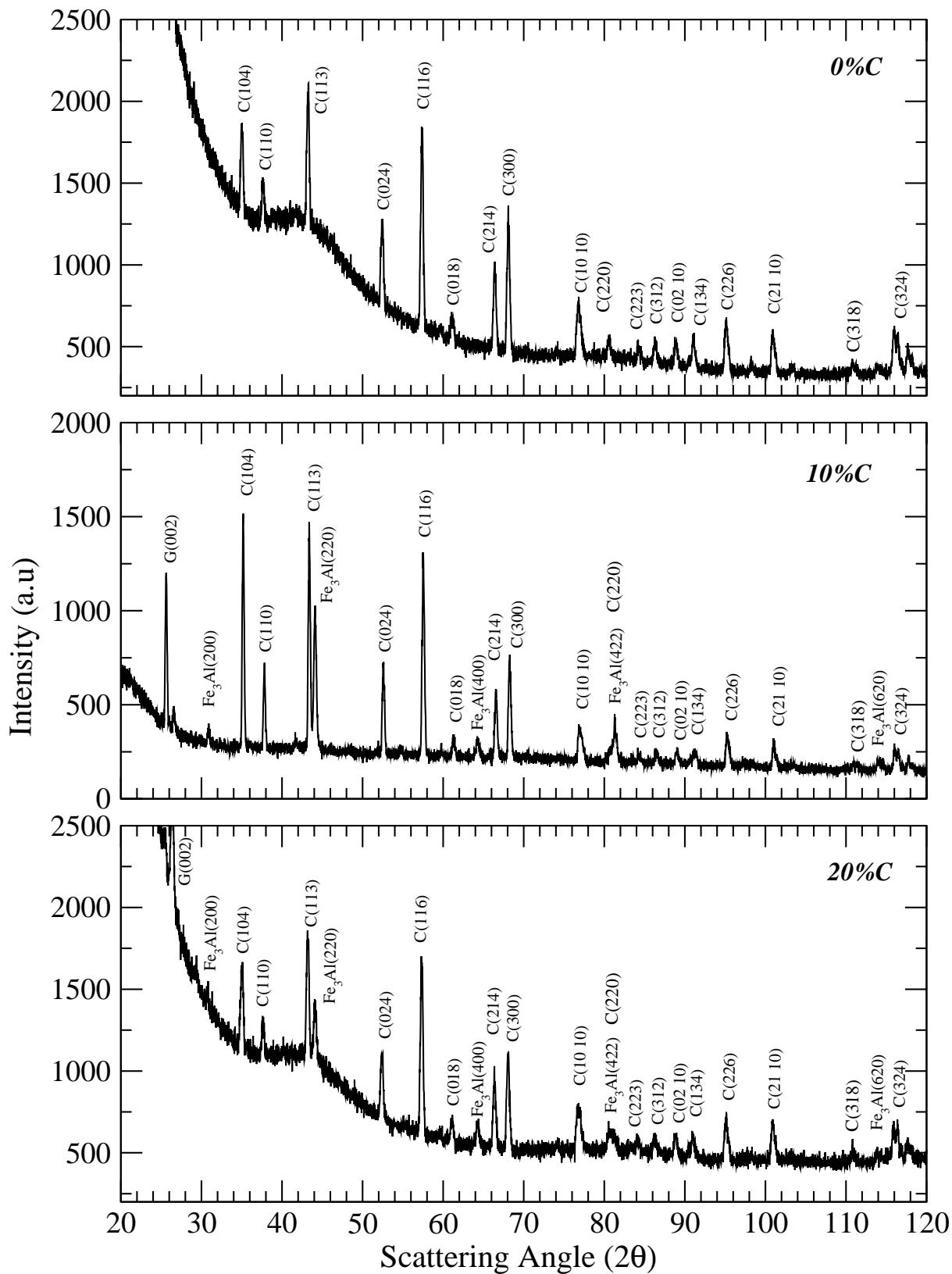


Figure 1

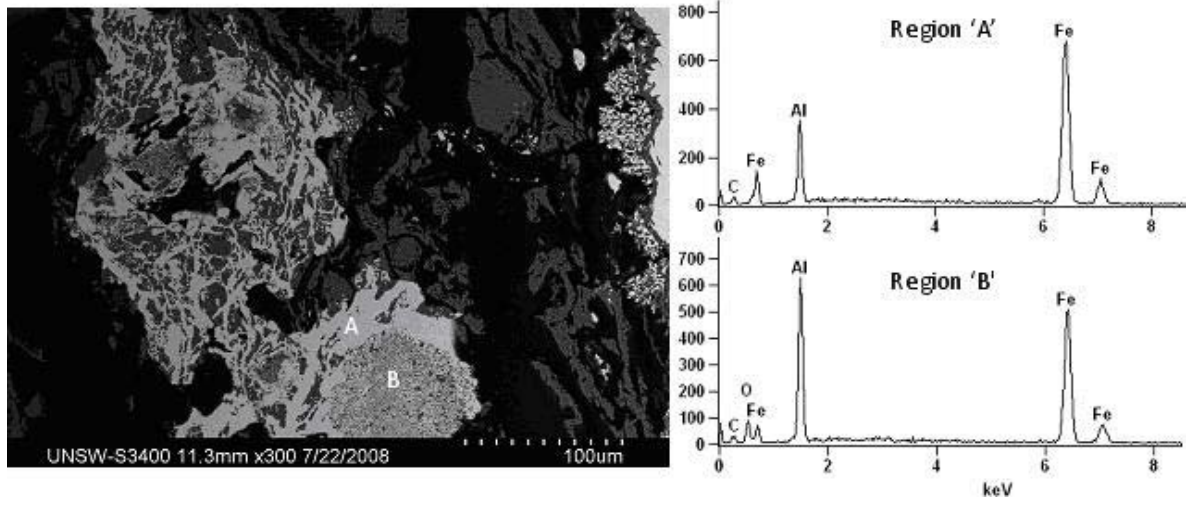


Figure 2