



The stability of Fe–Ni carbides in the Earth's mantle: Evidence for a low Fe–Ni–C melt fraction in the deep mantle



Arno Rohrbach^{a,b,*}, Sujoy Ghosh^b, Max W. Schmidt^b, Clazina H. Wijbrans^a,
Stephan Klemme^a

^a Institut für Mineralogie, Westfälische Wilhelms-Universität Münster, Germany

^b Institut für Geochemie und Petrologie, ETH, Zürich, Switzerland

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ABSTRACT

The Earth's mantle contains significant amounts of carbon and is at depths greater than ~250–300 km potentially so reducing that the Fe–C redox couple determines the nature of the reduced phase(s), which may be diamond, metal and carbides. Carbides will be Fe-rich but their stability also depends on the presence of Ni. We thus have experimentally investigated the Fe–Ni–C subsolidus ternary at 10 GPa, and secondly determined eutectic melting temperatures in this system. At subsolidus, the Fe-rich side of the ternary has two of the phases: diamond, Fe₇C₃ (to a molar $X_{Ni} = Ni/(Fe + Ni) = 0.11$), Fe₃C (to $X_{Ni} = 0.24$) and metal stable, depending on bulk C-contents. At higher Ni-contents, (Fe,Ni)₃C coexists with diamond and metal while at $X_{Ni} \geq 0.53$, carbides are absent and diamond coexists with metal. Because Ni is more noble than Fe, it partitions strongly into the reduced phases such that at low metal fractions the metal phase reaches $X_{Ni} > 0.5$ (at a bulk Ni-content of 1800 ppm for the mantle). Thermodynamic calculations at subsolidus conditions suggest that the mantle contains 50–700 ppm Fe, Ni metal at ~300 km depth. Adopting bulk C contents of 50 to 500 ppm in the mantle would result in the phase association (Fe,Ni)₃C + metal + diamond (at 10 GPa).

An unexpected finding of this study is that eutectic temperatures in the Fe–Ni–C system are very low, 1210 °C at the Fe–C side, decreasing to 1125 °C at an X_{Ni} of 0.5 in the reduced phase. Hence we postulate that most of the deep reducing mantle will contain a small Fe–Ni–C melt fraction. These melts should be ubiquitous in the mantle, only those mantle regions where C-contents are less than what can be dissolved in the solid metal (50 ppm at 400 km depth) would not contain such a melt phase. However, the presence of a metal–carbon melt phase is probably of little long term consequence to mantle geochemistry as this melt is expected to remain in isolated pockets.

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1. Introduction

In the Earth's mantle, oxygen fugacity (f_{O_2}), buffered by ferric–ferrous iron equilibria, can be expected to decrease with increasing depth. Three lines of evidence are in support of this hypothesis:

(1) The oxygen fugacities of natural garnet peridotites as measured by oxy-thermobarometry show a trend towards more reducing conditions with increasing depth (Creighton et al., 2009; Frost and McCammon, 2008; McCammon and Kopylova, 2004; Stagno et al., 2013; Woodland and Koch, 2003; Yaxley et al., 2012). This behavior mainly reflects that redox equilibria involving the ferric iron bearing garnets skiaquite and andradite have molar volume changes that favor the stability of these garnets with increasing pressure (Gudmundsson and Wood, 1995; Stagno et al., 2013).

The recent calculation of Stagno et al. (2013) based on andradite suggests that the deepest peridotites are ~1 log unit more oxidized when compared to calculations based on the calibration using skiaquite (Gudmundsson and Wood, 1995). Depending on which oxy-thermobarometer is employed; extrapolating the f_{O_2} trend of natural samples, results in redox conditions that are sufficiently reducing to stabilize an iron–nickel rich metal phase at ~8–12 GPa and deeper. This is in agreement with the absence of metal saturation in peridotites to the maximum pressure of 6 GPa where such samples are available.

(2) Theoretical analysis of the mantle f_{O_2} evolution with increasing depth (Ballhaus, 1995; Ballhaus and Frost, 1994) predicts that an isochemical mantle composition becomes reduced by ~0.6 log units/GPa in f_{O_2} as a result of molar volume changes of redox equilibria and changing mantle mineralogy (see also O'Neill et al., 1993a, 1993b). The result of this analysis is that rocks of upper mantle composition and Fe³⁺ content become metal saturated at pressures around 9 GPa (Ballhaus, 1995; Ballhaus and Frost, 1994).

* Corresponding author at: Corrensstr. 24, 48149 Münster, Germany. Tel.: +49 251 83 36138; fax: +49 251 83 38197.

E-mail address: arno.rohrbach@uni-muenster.de (A. Rohrbach).

(3) Experimental studies show that some of the major phases in the deep mantle, namely aluminous Si–Mg perovskite and majoritic garnet are sinks for ferric iron, which force ferrous iron to disproportionate into a ferric component in majorite or perovskite and Fe-metal ($3\text{FeO} = \text{Fe}_2\text{O}_3 + \text{Fe}^0$; Frost et al., 2004; McCammon, 1997; Rohrbach et al., 2007, 2011). With increasing pressure and enhanced disproportionation, the metal phase changes its composition from Ni-rich ($\sim\text{Fe}_{40}\text{Ni}_{60}$) when crossing the Ni precipitation curve (Frost and McCammon, 2008; O'Neill and Wall, 1987) towards more Fe-rich compositions at the base of the transition zone ($\sim\text{Fe}_{65}\text{Ni}_{35}$; Rohrbach and Schmidt, 2011) and the lower mantle ($\text{Fe}_{90}\text{Ni}_{10}$; Frost et al., 2004).

Oxygen fugacity conditions determine the speciation of redox sensitive elements like carbon and thus determine the cycling and mobility of these elements in the Earth's mantle. Recent studies calibrating redox equilibria between elemental carbon (graphite or diamond) and solid or liquid carbonate with respect to f_{O_2} (Rohrbach and Schmidt, 2011; Stagno et al., 2011, 2013; Stagno and Frost, 2010) conclude that carbon in its oxidized form, i.e. carbonate or carbonate melt is unstable with respect to the f_{O_2} regime of the ambient mantle at depths greater than ~ 150 km. Consequently, carbon will be present in its reduced and immobile form, either as graphite or diamond (Stagno and Frost, 2010). If theoretical predictions and experimental evidence are correct and a metal phase is present below 250–300 km depth, carbon in the mantle is expected to reside in metal and/or carbide phases. Previous studies proposed that at the lower end of mantle C-concentrations (~ 20 – 120 ppm C for MORB source mantle; Marty, 2012) all C might be dissolved in the metal, whereas in regions with higher C contents (300–800 ppm for OIB source mantle; Marty, 2012) carbon might be stored in carbides (Fe_3C and/or Fe_7C_3 ; Dasgupta and Hirschmann, 2010; Frost and McCammon, 2008). Carbides are also expected to form in mantle regions affected by redox freezing, i.e. where a carbonate influx into the mantle in the context of deep subduction will become reduced and immobilized through redox reactions with the surrounding metal bearing mantle (Rohrbach and Schmidt, 2011).

Natural carbides, cohenite (Fe_3C) and chalybite (Fe_2C), are rarely found along with native iron as inclusions in diamond and garnet (Jacob et al., 2004; Kaminsky and Wirth, 2011; Stachel et al., 1998). To our knowledge, Fe_7C_3 was never observed in natural samples which may be the result of decomposition of Fe_7C_3 to $\text{Fe}_3\text{C} + \text{C}$ during decompression (Kaminsky and Wirth, 2011). A distinct characteristic of natural metal and iron carbide inclusions is that they have a remarkably low Ni content (up to 3 wt%) which indicates that they were not in equilibrium with mantle peridotite but originate from more evolved, eclogitic or pyroxenitic lithologies (Jacob et al., 2004).

Whilst in the Fe–C system, Fe-metal and graphite/diamond are never stable together but form carbides (Lord et al., 2009), this is not the case for the Ni–C system, where carbides are unknown under upper mantle pressures (Turkevich and Kulik, 1995). Hence, the storage of C in the deep reducing mantle must also depend on the Fe/Ni ratio of the reduced phase. To test the various hypotheses experimentally, we have investigated (1) the subsolidus phase relations in the Fe–Ni–C ternary and (2) the influence of increasing Ni-content on melting temperatures in this system.

2. Methods

2.1. Starting composition

Starting materials were prepared by mixing pure powders of Fe and Ni (99.9% purity powder from “Alfa Aesar”) with graphite powder (Table 1). All ingredients were stored in a sensor controlled desiccator to avoid their hydration or oxidation. Some starting

mixes contained mono crystalline diamond powder (1/4–3/4 μm grain size from “Microdiamant”) instead of graphite to investigate if slower reaction kinetics prevent the charges from reaching equilibrium, and to avoid slight compositional heterogeneities that may stem from segregation of graphite flakes during mixing under ethanol/acetone in the agate mortar. The powders were stored in a drying furnace at 110°C until used. In general, starting mixes were prepared shortly prior to experimentation to avoid oxidation. Nevertheless, a small amount of oxygen reacted with Fe and produced minor wüstite in most of our experimental charges.

2.2. Multianvil experiments

Experiments were performed in 1000 and 600 t multianvil devices at the Institute of Geochemistry and Petrology, ETH Zurich and at the Institute for Mineralogy, University of Münster. We used 18/11 and 14/8 assemblies with chromium doped MgO octahedra, stepped LaCrO_3 furnaces and pyrophyllite gaskets. Details of assembly design and pressure calibration of the Zurich multianvil can be found in Grassi and Schmidt (2011). The 14/8 assembly in Münster was calibrated using the phase transitions of Bi-metal (room temperature) as well as the CaGeO_3 garnet–perovskite and coesite–stishovite phase transitions (1100°C).

The starting powder was encapsulated into polycrystalline crushable Al_2O_3 containers, two of which were stacked upside down into the furnace center part. Run temperature was measured with type B or C thermocouples and no pressure correction on the emf was applied. Experiments were brought up to pressure, heated to the desired temperature at a rate of $\sim 50^\circ/\text{min}$ and then kept constant during the entire run using a Eurotherm controller. The combined uncertainty of the temperature measurement, which results from temperature fluctuations during the run ($\pm 5^\circ\text{C}$) and temperature gradients within the assembly, is estimated to be about $\pm 20^\circ\text{C}$. Samples were quenched by turning off the power supply, resulting in reducing the temperature to below 500°C in less than 1 s.

2.3. Analytical methods

The mechanically coherent experimental charges were taken out of both the octahedron and the alumina capsule and were each mounted into epoxy resin blocks. The mounts were polished for SEM and EPMA inspection using $1/4 \mu\text{m}$ diamond powder on a lapidary wheel for the final polish. Water was used as lubricant during polishing. After a polished surface was achieved, samples were cleaned in an ultrasonic bath. Diamond bearing samples could be easily identified during preparation as these charges were extremely hard to polish. Samples were inspected with JEOL JSX 6610 scanning electron microscopes and a JEOL JXA 8900 electron microprobe in Münster. The samples and standards were left uncoated but surrounded with silver bearing conductive varnish to avoid charging during SEM and EPMA analysis. We used 99.9% pure Ni and Fe metal as standards for iron and nickel and synthetic Fe_3C and Fe_7C_3 as standards for carbon measurements. The carbide standards were synthesized in piston cylinder and multianvil devices following the procedure of Dasgupta and Walker (2008). Aliquots of the standard material were investigated with powder X-ray diffraction and EPMA. The resultant diffraction patterns agree well with literature data for the respective phases. The Fe contents of both Fe_3C and Fe_7C_3 were independently checked with the iron standard and vice versa. Aluminum was also analyzed to check whether capsule material contaminated the metal charge (standard was corundum); no contamination could be identified. Uncoated samples were measured at 15 kV and 15 nA, counting times on peak and background were 20 s and 10 s respectively. The counting rate of the carbon $K\alpha$ peak was constant during the

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