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# THE ROLE OF REDOX EQUILIBRIA DURING CARBON TRANSFER IN THE MANTLE AND THE STABILITY OF CARBIDES IN THE MANTLE

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The mobility of carbon in subducted crust and the mantle is strongly dependent on oxidation state. While both $CH_4$- or $CO_2$-rich fluids and carbonatite melts are perfectly mobile, elemental carbon in form of graphite or diamond and also carbides are not.

### Redox freezing of MORB derived carbonatite melts

In this study we investigate the evolution of carbonatite melts (generated from subducting MORB) when transferred to a reducing mantle, in particular the redox processes between oxidized carbonates and the reduced ambient deep mantle, thought to be saturated in an Fe,Ni metal phase at > 250 km depth. We located the carbon/carbonate redox equilibrium in terms of $f_{O2}$ and the solidus temperature of carbonated peridotite at P and T relevant for the deep mantle. At 10-23 GPa, solidi temperatures (1535-1675 $^o$C) are in the range of a mantle geotherm implying that small degree carbonatite melting is generally possible through thermal relaxation of subducted lithosphere (Fig.1).
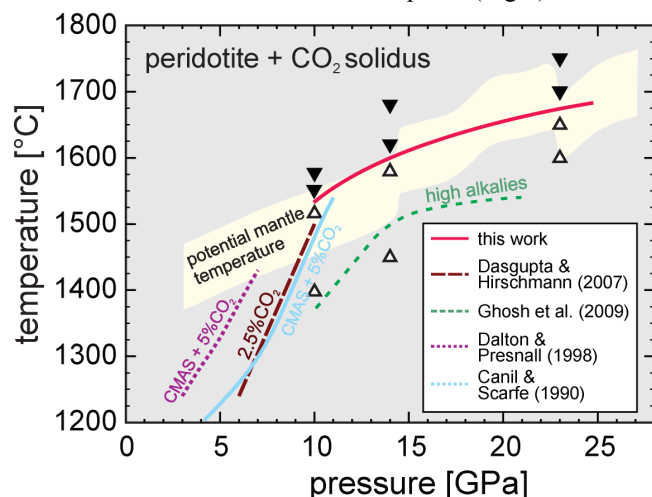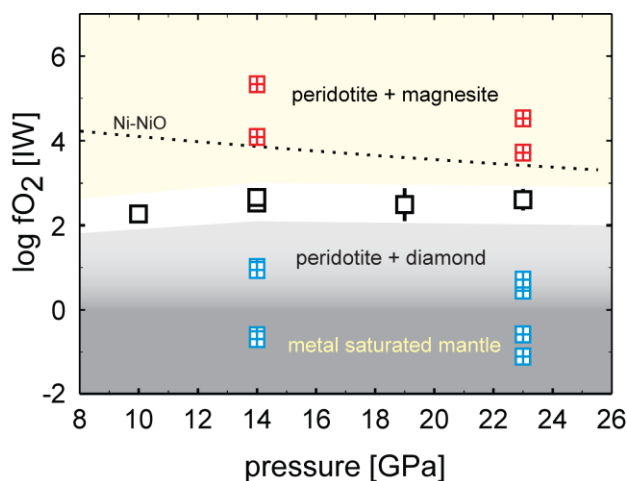


*Fig.2. Position of the magnesite - diamond redox equilibrium with respect to IW. The open symbols have carbonate+diamond coexisting, in these experiments, $f_{O2}$ was determined through the use of Ir-Fe solid solution as redox sensor.*

$f_{O2}$ controlled experiments indicate that the carbon/carbonate equilibrium is situated $\geq2$ log units above IW at 10-23 GPa, i.e. $\geq2$ log units higher than likely $f_{O2}$ conditions of ambient mantle (Fig. 2). The deeper mantle is thought to be metal saturated because of $Fe^{2+}$-disproportionation reactions that yield $Fe^{3+}$-bearing majoritic garnet and perovskite (Frost et al. 2004, Rohrbach et al. 2007) and Fe-metal. Carbonatite melts infiltrating the deeper mantle would thus, sooner or later react with the metal of the ambient deep mantle (Fig.2). Equilibration with the mantle will lead to the reduction of carbon from the carbonatites, a process best described as redox freezing, as reduction of $CO_2$ to diamond will cause the complete immobilization of the carbonatite melts. On a local scale, carbonatite melts will consume the Fe,Ni-metal present in the deeper mantle to leave a mantle domain that contains all



*Fig.1 Mantle adiabate in comparison to carbonatite solidi, after Rohrbach and Schmidt (2011).*

iron as $Fe^{2+}$ and $Fe^{3+}$ in silicates ($Fe^{3+}$ in particular in garnet and perovskite) and all carbon as diamond. The process is self-buffering: as long as carbonatite percolates through a given mantle domain, Fe-metal will be oxidized and exactly the redox-capacity equivalent of carbon precipitated (on a 9:1 Fe:C mass ratio). Once the metal is exhausted, the carbonatite melt may proceed through this mantle volume without further redox reaction, as all metal is already oxidized. Such mantle domains will have all Fe-metal oxidized to $Fe^{2+}$, all $Fe^{3+}$ originally present in perovskite and majorite preserved, and a $C^0$ content that has the exact redox capacity to reduce all $Fe^{3+}$ to $Fe^{2+}$ thus completely oxidizing to $CO_2$ upon reaction. The redox-freezing process would lead to mantle domains which have diamonds growing through a redox process in a mantle of > 250 km depth. These domains are part of the convecting mantle, and should be stable at any deeper mantle condition. However, once entrained in upwelling mantle, the decomposition of $Fe^{3+}$-bearing perovskite and majoritic garnet will cause the diamond to oxidize to $CO_2$. Adiabatic upwelling provides temperatures very similar to the carbonate melting curve in the mantle (in the alkali-free system, for K- and Na-bearing systems melting temperatures are significantly lower, Brey et al. 2011, Ghosh et al. 2009). Thus, the inverse process, carbonatitic redox melting, consuming $Fe^{3+}$ and diamond in favor of $CO_2$ and $Fe^{2+}$ would occur when such heterogeneities are entrained in upwellings. We thus propose that deep mantle melts would originate as carbonatites from $Fe^{3+}$+diamond containing domains upon breakdown of perovskite and of the majoritic garnet component.

**Stability of (Fe,Ni)-carbides: are there carbide-melts in the mantle ?**

When carbonatites react with Fe-metal, graphite or diamond are not supposed to form as long as excess Fe-metal is present, as a carbide, either $Fe_3C$ or $Fe_7C_3$ would be stable. We expect that in an intermittent stage, first Fe,Ni-carbides result from infiltration of carbonatites into a metal bearing mantle. Such carbides would remain stable along the boundaries of carbonatite infiltration zones, where the mass of pervasively infiltrating carbonatites from the oxidized subducting crust is insufficient to oxidize all metal. We have thus undertaken experiments in the Fe-Ni-C ternary, to define the stability of the various carbides in this system. The first series of experiments indicates that melting temperatures in this system are significantly lower than previously thought (1420 $^o$C at 10 GPa, Lord et al. 2009): at 10 GPa, melting is observed down to 1150 $^o$C, i.e. to at least 200 $^o$C below the average mantle geotherm. These results still need to be confirmed by additional experiments. The

subsolidus ternary was determined at 1050 $^o$C, 10 GPa: Diamond coexists with Ni-Fe metal to an $X_{Fe}$ (molar, =Fe/(Fe+Ni) of ~0.52, and no carbide is stable at the Ni-rich side of the ternary (Fig.3). $(Fe,Ni)_3C$ is only stable in the range of $X_{Fe}$ = 1.00 to ~0.76, opening a 3-phase field Fe-Ni-metal – $(Fe,Ni)_3C$ cementite – diamond. The phase $(Fe,Ni)_7C_3$ is only stable to max. Ni-content of $X_{Fe}$ of ~0.88. Nevertheless, for terrestrial Fe-Ni ratios, both $(Fe,Ni)_7C_3$ and $(Fe,Ni)_3C$ would be stable.

Taken at face value, our melting temperatures for the Fe-$Fe_3C$ eutectic imply that any adiabatic mantle that contains metallic iron and iron carbide, i.e. any mantle with an average C-content at > 300 km depth would contain a small (0.1-1 wt%) fraction of Fe-C melt. The infiltration of carbonatite melts should then also lead – in an intermittent stage – to Fe-carbide melts. At present we are undertaking further experiments to precisely locate the eutectic and peritectic in this system as a function of $X_{Fe}$..
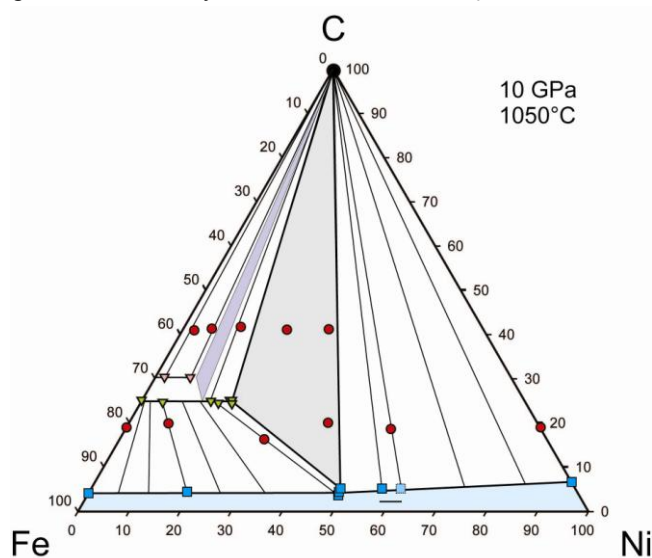


*Fig.3 Fe-Ni-C ternary at 1050 $^o$C, 10 GPa. The grey field indicates the approximate location of the C-$(Fe,Ni)_7C_3$-$(Fe,Ni)_3C$ 3-phase field. Carbides with compositions more Fe-poor than ~24 mol% are not stable.*

**Natural Moissanite: a low temperature phase resulting from infiltration of relatively reducing fluids or carbonatites**

A second facet of our study concerns the formation of moissanite, a not uncommon mineral in peridotites (see Lyakhovich, 1980; Xu et al. 2008, Trumbull et al. 2009). Moissanite also occurs in association with diamonds (Moore and Gurney, 1989, Gorshkov et al. 1997). Hitherto the origin of moissanite remains nebulous: while there is

agreement that formation conditions must be fairly reducing, wild speculations about lower mantle or core-mantle boundary origins have been persistent. A recent study (Xu et al. 2008) also attributed moissanite formation to a deep subduction environment.

We have thus studied the conditions of SiC equilibration with harzburgite assemblages at 2 and 10 GPa. Because of the very sluggish reaction kinetics of SiC, we were forced to equilibrate the material at 1500-1700 °C. The successful experiments resulted in olivine, opx, an FeSi-alloy (with ~18 wt% Si) and moissanite with all phases grown sufficiently large to measure phase compositions. Initial attempts to monitor oxygen fugacity with Iridium failed as a ternary Fe-Si-Ir solid solution formed, which thermodynamic properties are largely unknown and thus not suitable to calculate oxygen fugacity.

The most important experimental result is that olivine and orthopyroxene in equilibrium with SiC have typical $X_{Mg}$-values of 0.995-0.998, with the lower values in this range at 10 GPa and the higher ones at 2 GPa. These experimentally determined values agree reasonably well with thermodynamic calculations (Fig.4). These calculations were made on a harzburgitic mantle composition and essentially show that the XMg of silicates remains relatively invariant with oxygen fugacity at conditions above metal stability, but XMg decreases rapidly at lower oxygen fugacity until silicates are essentially Fe-free near the C-SiC equilibrium. These calculations actually lack Fe-carbides as phase, also there is no Fe-Si solid solution nd thus have to be taken as preliminary.

The high temperature experiments and the calculations demonstrate that moissanite cannot be in equilibrium with typical mantle olivine, even if the oxygen fugacity of such mantle would be slightly below iron-wustite. To our knowledge, extremely magnesian olivines (or opx) have not been described in the context of moissanite formation, although admittedly, most publications on moissanite do not describe the silicate parageneses. In several cases, the coexisting silicates are unknown, as moissanite is recovered (with diamond) from mineral segregates.

Fe-diffusion in olivine is rather fast and diffusion distances are in the order of 10-50 m for 10 Ma at typical mantle temperatures (diffusion coefficients from Morioka, 1981). We thus suggest, that natural moissanite does not form through a high temperature process where olivine and pyroxenes would have to equilibrate at oxygen fugacities 4-7 log units below metal saturation.

Instead, SiC could form from relatively low temperature fluids or carbonatite melts. If such melts or fluids have bulk compositions only a little less oxidized (i.e. more hydrogen rich) than the $CO_2$-$H_2O$ join (Fig.5), then their crystallization or reaction with the anhydrous mantle during cooling could drive the residual fluids to extremely oxygen poor compositions, in the extreme case to the SiC-C equilibrium. Cooling of such melts or fluids would precipitate minerals that contain, with respect to the fluid, the oxidized species ($CO_2$ in carbonates, $H_2O$ e.g. in serpentine) and thus, the bulk fluid composition would be invariably moving towards the C-$H_2$-side of the C-$O_2$-$H_2$ triangle. In most cases, carbon bearing fluids would move
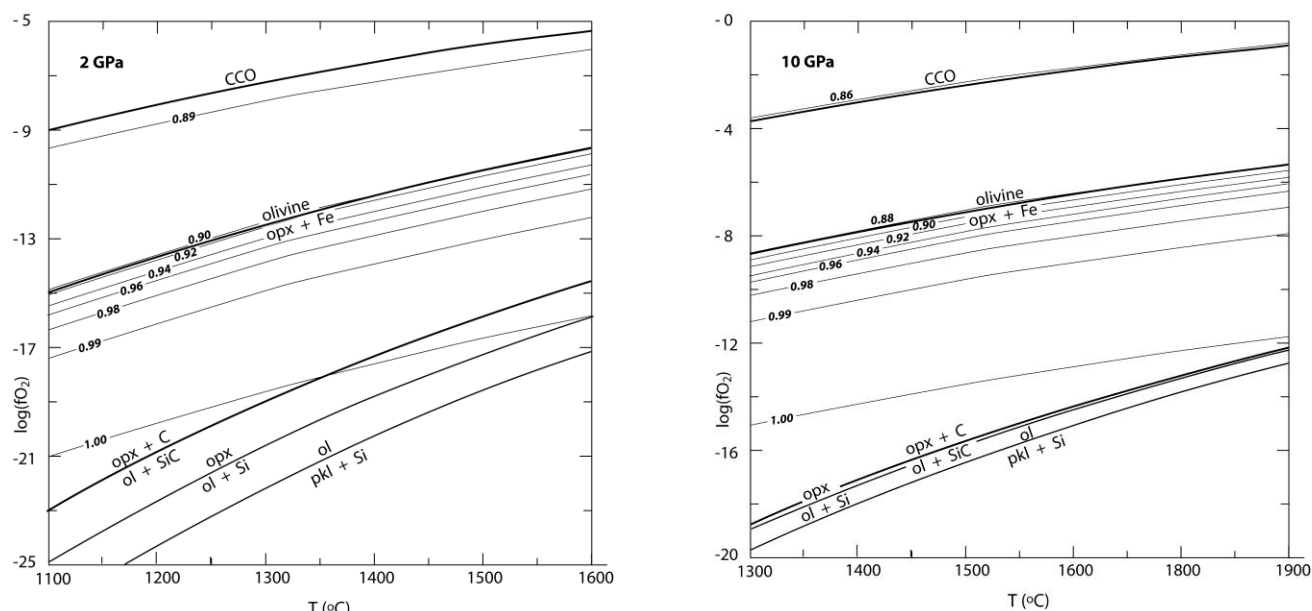


*Fig.4. Calculated $X_{Mg}$-isopleths in olivine as a function of oxygen fugacity. While $X_{Mg}$ in olivine (and opx) is almost invariable with $f_{O2}$ between QFM and IW (here olivine=opx+Fe), $X_{Mg}$ values drop dramatically within the next two log-units, leading to almost Fe-free silicates at SiC saturation.*

along the graphite saturation boundary by co-precipitation of carbonate+graphite. To become more reduced, $H_2O$ has to be removed from the fluid, i.e. in form of hydrous phases. Support for low temperature $H_2$-rich fluids comes from serpentinization processes, where significant fractions of $H_2$ are observed in vent-fluids. In this context, metal-bearing serpentinites are occasionally observed (for hydrogen production during serpentinization, see Sleep et al. 2004). As all peridotite bodies at the surface are principally serpentinized, we propose that magnetite and then serpentine precipitation during low temperature peridotite alteration may result in conditions sufficiently reducing for SiC precipitation. If SiC-precipitation occurs at sufficiently low temperatures, the non-serpentinized high-temperature minerals would not be in equilibrium which such fluids and thus not be affected.

In conclusion, we suggest a relatively low temperature formation of natural moissanite, i.e. at temperatures that are at least sufficiently low to precipitate hydrous phases. In For many moissanite occurrences, the principle mechanism might be late stage serpentinization known to involve $CH_4$-$H_2$-rich fluids. For higher pressure moissanite, associated with diamonds, directly precipitation from $CH_4$–rich fluids that result from carbonatite melt crystallization is proposed. In all cases, local, grain scale equilibrium is likely to lead to extremely $H_2$-enriched reduced fluid compositions and moissanite precipitation.

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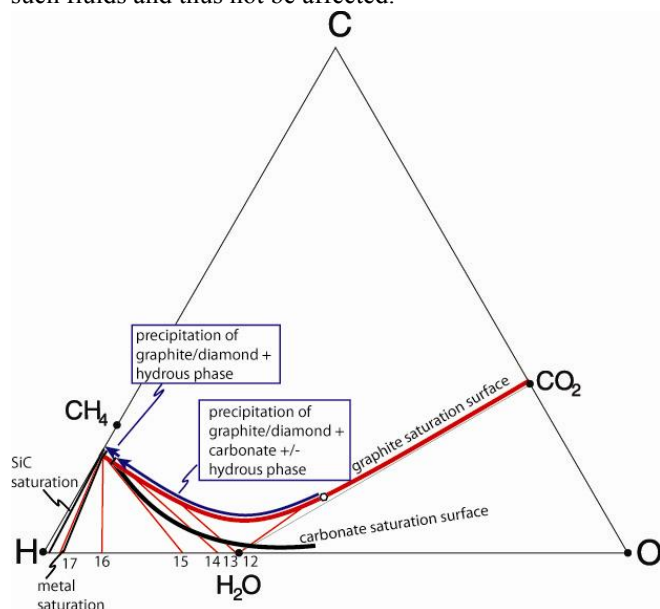*Xu S. et al. (2008), Min.Mag. 72, 899-908.*

*Fig.5 Fluid compositions calculated in a Ca-Mg-Fe-Si-C-H-O-system and the principle of driving a fluid to extremely C-H-rich compositions. The red line is the graphite (or diamond) saturation surface, fluids with compositions above the red line do not exist. The bold black line is the carbonate saturation surface. In this example, metal saturation occurs at a $-log(f_{O2})$ of 17, SiC-saturation at a $-log(f_{O2})$ of 21. The precipitation of carbonates(+graphite) (from a carbonatite melt or a fluid) will drive fluids to O-poor compositions until the carbonate-saturation surface is reached. From this point (typically 1-3 log-units above metal saturation), removal of $H_2O$ through hydrous phases will drive fluids to metal saturation and in the extreme case further to SiC-saturation.*
*In serpentinites without carbon, magnetite precipitation (magnetite would project to the O-corner) would drive the fluid to the metal saturation surface and precipitation of hydrous phases may lead to saturation in SiC.*