

The stability of iron–nickel carbides in the Earth's mantle

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A substantial amount of carbonate entrained in partially altered lithosphere likely survives shallow devolatilisation during subduction [1] and will thus be carried by the downgoing plate deep into Earth's mantle. Such carbonates are liberated as carbonatitic liquids whenever the subducting plate is heated to ambient mantle temperatures [2], e.g. when the lithosphere deflects into the transition zone above the 660 km discontinuity. When such carbonatites infiltrate the mantle they have to face an environment where oxygen fugacity is potentially lower than defined by the iron–wustite equilibrium, i.e. where (Fe,Ni)-metal is likely to be an accessory phase (at depths greater than ~250 km) [3–5]. When carbonatites become reduced by such (Fe,Ni)-metal, graphite or diamond would not form as long as excess metal is present, but instead (Fe,Ni)-carbides should be stable. Such carbides may form along the boundaries of carbonatite infiltration zones, where the mass of pervasively infiltrating carbonatites is insufficient to oxidize all metal. We thus performed experiments in the Fe–Ni–C ternary, to define the stability of the various carbides in this system. The subsolidus ternary was determined at 1050 °C, 10 GPa. Diamond coexists with (Fe,Ni)-metal to an X_{Fe} (molar, =Fe/(Fe+Ni)) of ~0.48, and no carbide is stable on the Ni-rich side of the ternary. (Fe,Ni)₃C is only stable in the range of X_{Fe} = 1.00 to ~0.75, opening a 3-phase field (Fe,Ni)-metal – (Fe,Ni)₃C – diamond. The phase (Fe,Ni)₇C₃ is stable up to X_{Fe} ~0.89 and defines together with (Fe,Ni)₃C (X_{Fe} ~0.82) and diamond a second 3-phase field. A second series of experiments indicates that Fe–Ni–C melting temperatures appear to be lower than expected; at 10 GPa, melting is observed down to 1150 °C, which is at least 200 °C lower than both an average mantle geotherm and the previously determined eutectic temperature in the Fe–C binary [6]. If confirmed by further experiments, such low eutectic temperatures would imply that any adiabatic mantle containing metallic iron and iron carbide, i.e. any mantle at depths >300 km with an average mantle C-content, must contain a small (0.1–1 wt%) fraction of (Fe,Ni)-C melt. The infiltration of carbonatite melts should then also lead – in an intermittent stage – to such (Fe,Ni)-carbide melts.

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Bio-inspired Fe₃S₄ catalyst for CO₂ reduction: DFT study

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Introduction

Carbon dioxide capture and utilisation is gaining attention, driven not only by environmental factors but by the possibility to use it as chemical feedstock. The main challenge in CO₂ reduction is increasing the energy efficiency of the process, which is hindered primarily by its high reduction over-potentials. However, this process takes place under mild conditions in chemoautotrophic bacteria catalysed by FeS cubane clusters [1]. Similar structures are found in the iron thiospinel mineral (Fe₃S₄) which is present in deep sea vents and marine anoxic sediments. We present a theoretical (DFT+U) [2] investigation using Fe₃S₄ as a catalyst to transform CO₂.

Results and Conclusions

In agreement with previous benchmarks, we find that the CO₂ adsorption/activation process is the determinant step. This step consists of an electron transfer from the metallic atom in the surface to the empty antibonding orbital on the molecule leading to CO₂^{•-}. The presence of other transition metals, such as Ni, can enhance the electronic rearrangement making the CO₂ activation energetically possible. A thermodynamically more favorable process is the H₂ dissociative adsorption either on pure or doped greigite. Thus, H₂ becomes a source of (H⁺+e⁻) which can be added to the co-adsorbed CO₂^{•-} molecule by a common Langmuir-Hinshelwood mechanism. We also find a downhill pathway for that addition leading to products of interest, such as formic acid (Fig. 1).

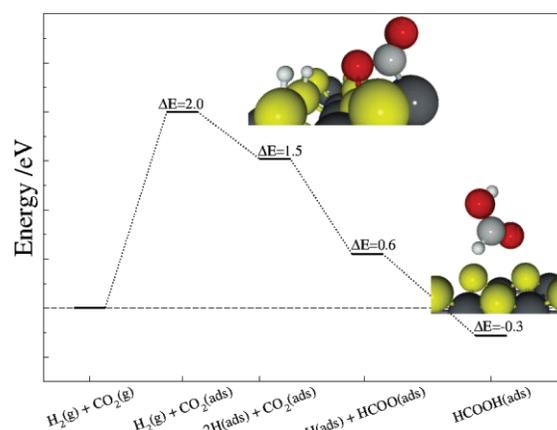


Figure 1: Potential energy diagram for CO₂ transformation to formic acid catalysed by pure greigite.

[1] Huber, C.; Wachtershauser, G. (1997) *Science*, **276**, 245-247.
[2] Devey, A. J.; Grau-Crespo, R.; de Leeuw, N. H. (2009) *Phys. Rev. B*, **79**, 195126-195133.