

1.2.-1 Carbonates under high Pressure and Temperatures: CarboPaT

Thursday, 12/Sep/2019: 12:45pm–1:45pm

Session Chair: Melanie Jutta Sieber

Location: Hall C

The missing source of hydrocarbon emissions to the atmosphere

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Nowadays, the exponential growth of hydrocarbon emissions to the atmosphere is a rising problem of society, politics and science. The focus on the role of CO₂ emissions left in shade the problem of hydrocarbons, which have their own strong impact on the Earth. Emissions of hydrocarbons, mainly methane and its closest homologues (ethane, propane and butanes) lead to a complex series of chemical, physical or physicochemical transformations leading to various problems and natural disasters. If with the role of CO₂ emissions and its sources we have a more or less clear understanding, the sources of hydrocarbons still remain questionable due to the attribution mainly to human activity. However, complex studies of Etiope and his group showed that there is a geological source of hydrocarbons in the atmosphere, which, in the case of methane, was recently appraised, while in the case of ethane, propane and butanes are always neglected. In this study, we modelled the synthesis of hydrocarbons from carbonates with the help of high-pressure techniques under the thermobaric conditions of Earth's mantle and proposed the source of various hydrocarbon mixtures which could be generated in the deep Earth's interior and then transported to the surface through the deep faults and cracks.

Elasticity and structure evolution of carbonates at upper mantle conditions

Lea Pennacchioni

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In this PhD work the attention will be focused on the carbon reservoirs in the Earth's mantle.

A lot is known about the carbon cycle on the surface of the Earth but little is known about the Carbon in the Earth's deep interior. In particular, the aim of my PhD is the study of the elastic properties of the most abundant carbon-bearing minerals, the carbonates.

The focus of my PhD work is on the systematic characterization of the elastic properties of carbonates as a function of their structure and chemical composition, which is essential in order to be able to identify their presence and distribution in the lithosphere and upper mantle. In particular the study will be performed on the main carbonates such as calcite, aragonite, magnesite, dolomite, siderite and ankerite.

The structure and composition of the samples will be studied by means of Electron Micro Probe Analysis (EMPA) and single crystal diffraction.

Experimental studies by means of Brillouin spectroscopy and ab-initio methods will be used to measure the elastic tensor of the carbonates of interest. The experiments will be performed at both ambient conditions, high pressures up to 18 GPa and high pressure, high temperature conditions (up to 10 GPa and 800 K).

Reaction and elemental redistribution processes between magnesite and mantle phases at transition zone to lower mantle conditions.

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Carbonate inclusions in natural diamonds from lower mantle evidence the existence of carbonates in the mantle (e.g. Brenker et al. 2007). Additionally, these carbonate bearing inclusions show high REE enrichment and thus, raise the question on the role of carbonates as a possible trace-element carrier in the Earth's Mantle. Stability of carbonates in presence of mantle silicates at deep mantle conditions remains unclear. Similarly, the distribution processes of trace-elements between carbonates and silicates mantle minerals at

these depths are not well understood. Experimental studies support that pure magnesite (MgCO_3) in absence of other minerals, is stable at P,T-conditions corresponding to the lowermost mantle conditions (>110GPa). Reaction between magnesite and silica may form bridgmanite+ CO_2 . By increasing P-T, CO_2 breaks down to diamond and oxygen under geotherm condition in diamond anvil cell experiments and could indicate that magnesite is related to diamond formation in lower mantle. To better constrain the magnesite's stability in the deep Earth, reactions have to be studied in a chemical system that is closer to the natural one.

Therefore, in-situ experiments will be performed with laser-heated diamond anvil cell to investigate the reaction between magnesite and silicate mantle composition. Two silicate glasses will be investigated, enstatite-ferrosilite and hablobasalt composition, respectively, at conditions relevant to the upper lower mantle (20–30GPa and 800-2000°C). Later, same reactions will be investigated with Sr/La/Eu-doped materials to show the trace-element distribution between silicate phases and magnesite.

Brenker, et al (2007). Carbonates from the lower part of transition zone or even the lower mantle. *EPSL*, 260(1-2),1-9.

High pressure, high temperature phase stabilities of iron-poor dolomite and a new structure of dolomite V

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During the subduction of oceanic crust significant amounts of carbon bearing sediments may be transported into the Earth's mantle [1]. Dolomite, $\text{CaMg}(\text{CO}_3)_2$, is thought to constitute up to 50 % of the world's surface carbonate reservoirs [2] and diamond inclusions show evidence for the presence of dolomite in the mantle [3]. Further, experimental studies have provided indication for the existence of high pressure high temperature polymorphs of dolomite [4,5].

Here, we have studied the phase stability of dolomite at high pressures and temperatures, employing a combination of Raman-spectroscopy and synchrotron single-crystal X-ray diffraction using laser-heated diamond anvil cells. We observed the formation of a new dolomite polymorph at 50 GPa and after annealing at 2300 K, which persisted upon pressure release to 12 GPa. A preliminary data analysis indicated that this compound has the structure of a polymorph recently predicted by DFT based calculations [6]. Since this new structure is stable at pressure and temperature conditions found along the Earth's geotherm, we conclude that significant amounts of the phase may be present in the mantle.

Financial support by the DFG (FOR2125/CarboPaT, BA4020 and WI1232) is gratefully acknowledged.

[1] Litasov and Ohtani, *Phys. Earth Planet. Interiors* 177, 46 (2009).

[2] Zenger et al., *SEPM Spec. Publ.* 28, (1980).

[3] Brenker et al., *Earth Planet. Sci. Lett.* 260, 1 (2007).

[4] Mao et al., *Geophys. Res. Lett.* 38 (2011).

[5] Merlini et al., *Am. Min. Lett.* 102, 1763 (2017).

[6] Solomatova and Asimow, *Am. Min.* 102, 210 (2017).

1.2.-2 Carbonates under high Pressure and Temperatures: CarboPaT

Thursday, 12/Sep/2019: 2:15pm–3:15pm

Session Chair: Melanie Jutta Sieber

Location: Hall C

Experimental modeling of the CaCO₃–peridotite–Fe system and its role in the formation of Ca-rich inclusions in diamonds

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Carbonates and carbonatite melts are often found as syngenetic inclusions in diamonds [1]. In the same time, mantle redox conditions are too reduced to favor stability of the oxidized forms of carbon. Below ~250 km mantle rocks may contain metallic Fe or Fe-Ni alloy [2]. Under such conditions, carbonates and carbonatite melts will react with Fe to form diamonds [3].

In the present work, we studied CaCO₃-olivine-Fe and CaCO₃-peridotite-Fe systems, which allow to model phase relations in the carbonate-silicate system in the presence of Fe. Experiments were conducted at 6-8 GPa and 1100-1300°C using multi-anvil apparatus. Samples were analyzed by EDS and Raman-spectroscopy. Formation of merwinite (Mw), monticellite (Mtc), ferropericlase (Fp), graphite (Gr), carbide (Fe₇C₃) and silicate-bearing carbonate-oxide melt (CL) was observed. Crystallization of Fe₇C₃ and Gr occurs due to the carbonate–Fe redox reaction.

The present data show that at the upper mantle conditions formation of Mw and Mtc requires specific Ca-rich and Mg- and Si-depleted environments, and can indicate the CaCO₃ metasomatic activity in the ultramafic assemblages. A discovery of merwinite inclusions coexisting with Ca-carbonate and olivine in natural diamonds from Juina, Brazil [1] confirms our experimental evidence.

This work was supported by the Russian Foundation of Basic Research projects no 18-35-00104

[1] Zedgenizov, D.A., et al., 2014. Am. Min., 99: 547-550.

[2] Frost, D.J., McCammon, C.A., 2008. Ann. Rev. of Earth and Planetary Sciences 36, 389-420.

[3] Palyanov, Y.N. et al., 2013. PNAS, 110: 20408-20413.

Probing redox conditions in diamond anvil cell experiments

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Redox conditions (i.e., oxygen fugacity) in Earth's interior affect many petrological processes as well as the stability of mineral phases. Oxygen fugacity is challenging to measure in high-pressure experiments, so development of a metal alloy sensor for large volume apparatus experiments has been a breakthrough. But what if this approach could be transferred to diamond anvil cell (DAC) experiments? Monitoring redox conditions during DAC experiments can, for example, reconcile contradictory results that have been observed in studies of carbonate stability at lower mantle conditions.

We performed DAC experiments using a mixture of synthetic ferropericlase and pure Ir powder, with the main goal to crystallize an Fe-Ir alloy to use as a sensor for oxygen fugacity. Pressure was applied by mechanically tightening DAC screws and temperature was applied using a double-sided laser heating system. At the European Synchrotron Radiation Facility (Grenoble, France) we used X-ray diffraction and Mössbauer spectroscopy to measure the compressibility and iron oxidation state, respectively, at high pressure. After recovering the sample, we used state-of-the-art microanalysis methods to determine the chemical composition. Using these data combined with a thermodynamic model, we made the first calculations of oxygen fugacity in a DAC using a metal alloy sensor. Our results show that redox conditions are quite reducing and close to the iron-wüstite buffer.

Carbon's role in crystal chemistry of the Earth lower mantle minerals

Luliia Koemets

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Global carbon cycle has a great impact on the climate changes, being responsible for example in the past for NeoProterozoic “snowball” Earth and Cretaceous warm period. While quantity of carbon on our planet is still uncertain, there is general consensus that deep Earth is the main reservoir of carbon-bearing compounds. The lower mantle mainly consists of high-pressure phases silicates and oxides, making these compounds important candidates for studies possible reactions with carbon-bearing materials, or hosts for dissolved carbon.

Experimental investigation of possible reactions between carbon-bearing phases and deep mantle silicates and oxides requires accurate knowledge of high-pressure high-temperature behavior of all these phases. A series of recent studies showed that been chemically quite simple, under extreme conditions iron oxides could appear in a wide variety of crystal structures (Bykova et al., 2016, Nat. Com.) and iron carbonate could form previously unknown tetrarbonates (Cerantola et al. 2017, Nat. Com.). We investigate the behavior of geophysically

important materials (with a focus on crystal chemistry of dense silicates) at pressures and temperatures relevant for Earth lower mantle. Our results indicate that interplay between ferrous and ferric iron, oxygen, and carbon define geochemistry of last one.

A portable setup to establish extreme conditions for the study of tetrarbonates

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Iron-bearing carbonates are candidates for carbon storage in the deep Earth, therefore their physical properties and chemistry at high pressure and high temperature are in focus of recent research [1, 2].

We present a setup to establish the conditions in the lower mantle (100 GPa, 3000 K). The required pressure is accomplished by diamond anvil cells [3], in which the sample is heated double-sided by a Nd:YAG-Laser. We use this setup to heat and pressurize FeCO₃ and (Mg,Fe)CO₃ samples at core-mantle boundary conditions. The temperature-quenched samples are characterized at pressure using X-ray diffraction and optical Raman spectroscopy. Via combined X-ray emission and X-ray Raman spectroscopy [4] the electronic structure of the synthesized compounds can be analyzed. We present first results and discuss the capabilities of this setup for in-situ x-ray spectroscopic studies.

[1] V. Cerantola et al., Nature. Communications. 8, 15960 (2017)

[2] M. Merlini et al., American Mineralogist, 100, 2001, (2015)

[3] I. Kantor et al., Review of Scientific Instruments 83, 125102 (2012)

[4] C. Weis et al., Journal of Analytical Atomic Spectroscopy 34, 384 (2019)