

### Congruent melting of Ca-carbonate in static experiment at 3500 K and 10–22 GPa

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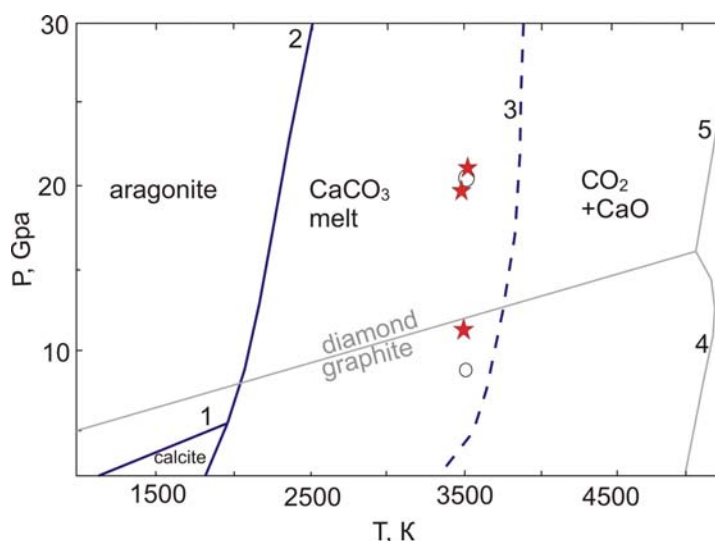
*Key words:* Super deep diamonds, transition zone, lower mantle, parental media, carbonate melts, phase diagram of  $\text{CaCO}_3$ .

**Citation:** Spivak A. V., L. S. Dubrovinsky, Yu. A. Litvin (2011), Congruent melting of Ca-carbonate in static experiment at 3500 K and 10–22 GPa, *Vestn. Otd. nauk Zemle*, 3, NZ6090, doi:10.2205/2011NZ000220.

Carbonate melts have a crucial role for diamond forming carbonatite medium: (1) they are effective solvents of silicates, aluminum silicates, oxides; (2) carbonate melts are the basis of completely miscible carbonate-silicate and carbonate-silicate-oxide melts. Solid carbon (diamond and metastable graphite) is very soluble in the atomic form in these melts at the  $PT$  conditions of diamond stability [Spivak *et al.*, 2008]. Currently, information about the phase state of carbonates is contradictory for the conditions of the transition zone and lower mantle.

The melt of  $\text{CaCO}_3$  undergoes decomposition by the reaction of  $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$  in the shock-wave experiments at 3200–3500 K and 80 GPa [Ivanov *AB*, Deutsch *A.*, 2002]. However, the direct evidence of decomposition reaction of carbonate melt at the maximum degree of compression or under the influence of high residual temperature after short-term relief to the normal pressure could not be obtained in the shock-wave experiment. Nevertheless, the available experimental data and the calculated equations of state of  $\text{CaCO}_3$  and its decomposition products  $\text{CaO}$  and  $\text{CO}_2$  summarized in a phase diagram of  $\text{CaCO}_3$  (fig. 1). Congruent melting curve of  $\text{CaCO}_3$  was studied in a static experiment up to 7 GPa, and extrapolated on the basis of the equation of state [Irving *A.J.*, Wyllie *P.J.*, 1973].

In the interval 10–30 GPa the congruent melting field  $\text{CaCO}_3$  is limited by the melting curve of  $\text{CaCO}_3$  at 2100–2500 K and the proposed curve of decomposition of  $\text{CaCO}_3$  melt to  $\text{CaO}$  and  $\text{CO}_2$  at high temperatures 3500 - 3800 K (fig. 1).

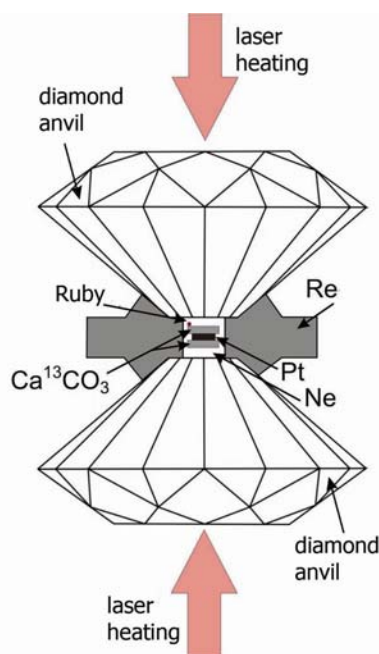


**Fig. 1.** Phase diagram of the Ca-carbonate [Ivanov *AB*, Deutsch *A.*, 2002] (thick lines), combined with the phase diagram of carbon [Bundy *FP et al.*, 1996] (thin lines). Legend: 1 – boundary of polymorphic transformation of calcite-aragonite, 2 – congruent melting curve of calcite and aragonite, 3 – decomposition curve of Ca-carbonate melt to  $\text{CaO}$  and  $\text{CO}_2$ , 4 – the melting curve of graphite, 5 – the melting curve of diamond. Stars - the experimental points of the authors, circles - experimental points by [Bayarjargal *L. et al.*, 2010]

Meanwhile, accurate understanding of physical and chemical behavior of  $\text{CaCO}_3$  and other carbonates is of fundamental significance for a number of important problems of mineralogy and geochemistry of the transition zone and lower mantle. Especially, genesis of super deep diamonds, as well as the origin and evolution of carbonate-containing melts (carbonatites, kimberlites, etc.) are among the problems

The goal of this work is experimental study of the phase state of  $\text{CaCO}_3$  at static pressure of 11–22 GPa (generated in the apparatus with diamond anvils) and temperatures up to 3500 K, obtained by laser heating of a strongly compressed sample (for details see [Eremets M., 1996]). The  $PT$ -parameters of the experiment is consistent with the physical conditions of formation of super deep diamonds, which overlap with the possible field of congruent melting of Ca-carbonate (fig. 1). An important feature of this work is the use of isotope individual carbonate  $\text{Ca}^{13}\text{CO}_3$  that excludes the possibility of distortion of results of  $^{12}\text{C}$  of the anvils (natural diamond) is unexpectedly involved into products of the experiments.

Starting materials were chemical reagents of  $\text{Ca}^{13}\text{CO}_3$  (prepared on the basis of the isotope  $^{13}\text{C}$ ). The experimental sample consists of two layers of powder  $\text{Ca}^{13}\text{CO}_3$ , and a thin layer of platinum powder between them. The sample is placed into the hole of 150  $\mu\text{m}$  diameter (filled by an inert gas neon) in a metallic gasquet of rhenium. The gasquet is clamped between the diamond anvils with a working surface 350  $\mu\text{m}$  (fig. 2). Nd: YLF infrared laser (wavelength 1064 nm) was used for heating. The duration of heat was about 5 minutes.



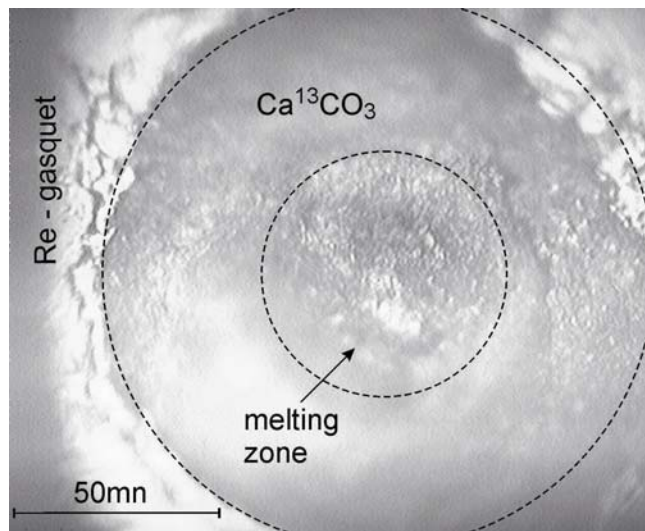
**Fig. 2.** The diamond anvil cell

The pressure in the sample is determined by the shift of the ruby luminescence. A ruby grain of  $\sim 5 \mu\text{m}$

size is placed inside the sample. During lowering the heating temperature to the room value, the sample has remained under strong compression inside Re gasquet. Products of experiments were studied using micro-Raman spectroscopy. The system LabRam with He-Nd-laser (exciting wavelength 632 nm) was used for register Raman spectra. Spectra from different parts of the sample collected at the gradual decompression, as well as after quenching, when the sample is completely extracted from the working holes in rhenium gasquet.

Experimental samples are marked (fig. 3) with the visible zone of calcium carbonate melting (about 50 microns) in experiments at 20–22 GPa and 3500 K (fig. 1). The sample in the experiment at 11 GPa and 3500 K are not visually different from them, but their Raman spectra include a peak of graphite. The samples were not heated along the perimeter, and these areas were used for comparative estimation. Raman spectra of samples under pressure were collected before and after heating. Also, the spectra of  $\text{Ca}^{12}\text{CO}_3$  and  $\text{C}^{13}\text{CO}_3$ ,

graphite on the basis of the isotopes  $^{12}\text{C}$  and  $^{13}\text{C}$  were obtained for the comparison.



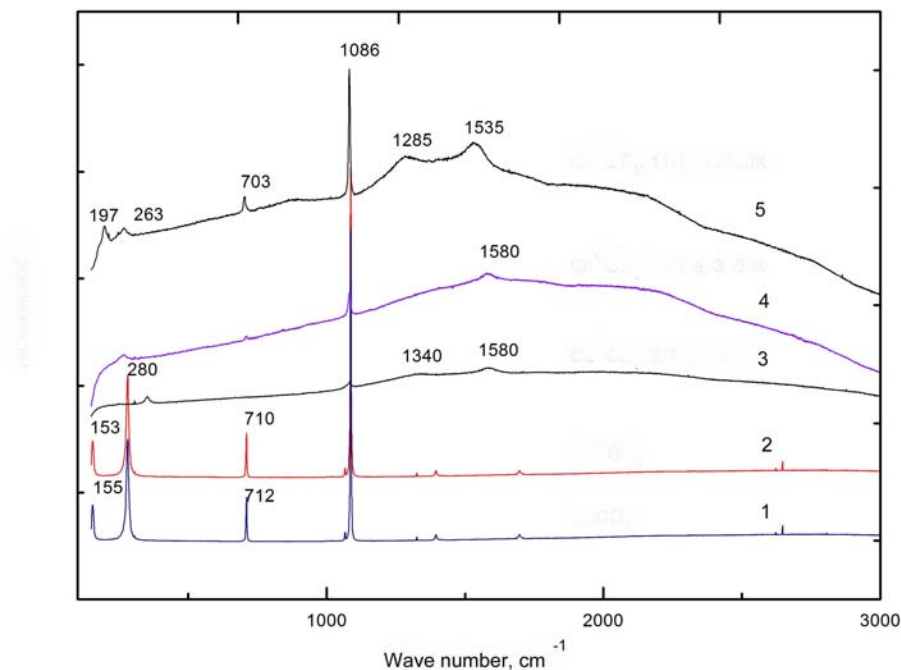
**Fig. 3.** Image of  $\text{Ca}^{13}\text{CO}_3$  sample after melting and quenching under pressure

Representative Raman spectra of various matters are shown in fig. 4. Under normal conditions, Raman spectra  $\text{Ca}^{12}\text{CO}_3$  have characteristic bands at 155, 280, 712 and  $1086\text{ cm}^{-1}$  [Rutt H.N., Nicola J.H., 1974]. The spectra of  $\text{Ca}^{13}\text{CO}_3$  contain the main band at 153, 278, 710,  $1086\text{ cm}^{-1}$ , and the spectra of graphite on the basis of the isotope  $^{13}\text{C}$  – the band at 1278 and  $1535\text{ cm}^{-1}$ . Calcite on the basis of the isotope  $^{13}\text{C}$  transforms into aragonite in experiments at high pressures and temperatures, as evidenced the spectra which have the characteristic bands of aragonite 703 and  $197\text{ cm}^{-1}$  (according to their displacement due to the presence of the isotope  $^{13}\text{C}$ ). The most intense band at  $1086\text{ cm}^{-1}$  is characteristic for the two polymorphic modifications of calcium carbonate and can not be used as a distinctive feature of them.

Graphite on the basis of the isotope  $^{12}\text{C}$  was found in the central parts with a diameter of 50 microns after heating to 3000 K at 20–22 GPa. Raman spectra of the experimental samples contain bands of graphite  $^{12}\text{C}$ , including a broad band with a peak in the range at  $1580\text{--}1585\text{ cm}^{-1}$ , known as “band G”, and a broad band with a peak in the range at  $1340\text{--}1355\text{ cm}^{-1}$  – “band D”. The position and width of the G band are determined by the perfection of graphite structure and the position of the D band is identified with various types of violations of the order in the structure of graphite. Because  $\text{Ca}^{13}\text{CO}_3$  was used as the starting material, the formation of graphite  $^{12}\text{C}$  by carbon  $^{13}\text{C}$  from this carbonate should be entirely avoided entirely. Source of carbon for graphite  $^{12}\text{C}$  could be just the carbon from diamond anvils. It can not exclude that in the experiments described in [Bayarjargal L. et al., 2010], the same occurred. Thus, the effect of the congruent melting of  $\text{Ca}^{13}\text{CO}_3$  is determined in experiments at 3000–3500 K and 20 GPa. However, the Raman spectra of the sample obtained at 11 GPa and 3500 K, contain a broad band G with a maximum in the range at  $1528\text{--}1537\text{ cm}^{-1}$ , “echo” of the band at  $1580\text{ cm}^{-1}$  and D band with a peak in the range at  $1275\text{--}1285\text{ cm}^{-1}$ . In this case we can meet the formation of graphite phase, with a source of carbon from the calcium carbonate on the basis of  $^{13}\text{C}$  isotope. The reality of this process is supported by *RT*-conditions of the experiment, which refers to the corresponding field on the carbon phase diagram (fig. 1). This fact may testify of the reality of  $\text{Ca}^{13}\text{CO}_3$  decomposition process on a two-step mechanism, which was discussed in [Bayarjargal L. et al., 2010]. Characteristic bands of graphite were not observed in Raman spectra of “unheated” parts of the sample.

As a result of the experiments, it is showed that calcium carbonate melts congruently at 20–21 GPa and 3500 K. The experimental data are in agreement with the preliminary phase diagram of  $\text{CaCO}_3$  [Ivanov AB, Deutsch A., 2002], constructed on the basis of shock experiments and thermodynamic calculations. The data confirm the fact of congruent melting of  $\text{CaCO}_3$  (aragonite) at 20–21 GPa and 3500 K. This means that the field of congruent melting of calcium carbonate is quite wide, extending from 2300 to 3500–3800 K at 20–21 GPa. However, the results of experiments at 11 GPa and 3500 K demonstrate the possibility of high-temperature phase boundary of the decomposition of  $\text{CaCO}_3$  to CaO melt and compressed  $\text{CO}_2$  fluid phase.

$\text{CaCO}_3$  is a representative inclusion in diamonds from transition zone and lower mantle. Existence of a broad field of  $\text{CaCO}_3$  congruent melting allows us to consider deep carbonate melts based on  $\text{CaCO}_3$  as a possible parental media for super deep diamonds.



**Fig. 4.** Raman spectra of the experimental samples: 1 –  $\text{CaCO}_3$  under normal conditions, 2 –  $\text{Ca}^{13}\text{CO}_3$  under normal conditions, 3 –  $\text{Ca}^{13}\text{CO}_3$  at 11 GPa and 3500 K (after extraction of the sample), 4 –  $\text{Ca}^{13}\text{CO}_3$  at 20 GPa and 3500 K (after extraction of the sample), 5 –  $\text{Ca}^{13}\text{CO}_3$  at 21 GPa and 3500 K (after extraction of the sample)

Support: MK-913.2011.5, Program RAS №02, 10-05-00654, 11-05-00401, NSh-3654-2011-5.

#### References

- Bayarjargal, L., T. G. Shumilova, A. Friedrich, B. Winkler (2010), Diamond formation from  $\text{CaCO}_3$  at high pressure and temperature, *Eur. J. Miner.*, V. 22, P. 29–34.
- Bundy, F. P., W. A. Bassett, M. S. Weathers, R. J. Hemley, H. K. Mao, A. F. Goncharov (1996), The pressure-temperature phase and transformation diagram for carbon; updated through 1994. *Carbon*, V. 34, № 2, P. 141–153.
- Eremets, M. (1996), *High Pressure Experimental Methods*. New York, Oxford University Press Inc, 390 p.
- Irving, A. J., P. J. Wyllie (1973), Melting relationships in  $\text{CaO-CO}_2$  and  $\text{MgO-CO}_2$  to 33 kbar, *Earth Planet. Sci. Lett.*, V. 20, P. 220–225.
- Ivanov, A. B., A. Deutsch (2002), The phase diagram of  $\text{CaCO}_3$  in relation to shock compression and decomposition. *Phys. Earth Planet. Inter.*, V. 129, P. 131–143.
- Rutt H.N., J.H. Nicola (1974), Raman spectra of carbonates of calcite structure. *J. Phys. C: Solid State Phys.*, 7, 4522–4528.
- Spivak A.V., Yu.A. Litvin, A.V. Shushkanova, V.Yu. Litvin, A.A. Shiryaev (2008), Diamond formation in carbonate-silicate-sulfide-carbon melts: Raman- and IR-spectroscopy. *Eur. J. Mineral.*, 20, 341–347.