Slutskiy A.B.[1,2] and Bagdassarov N. S.[1]

Pressure dependence of phase transformations in calcite from electrical impedance measurements

[1]Institute fur Meteorologie und Geophysik, Johann Wolfgang Goethe Universitдt-Frankfurt, FeldbergstraЯe 47, 60323 Frankfurt am Main, Germany

[2]Vernadskiy Institute of Geochemistry and Analytical Chemistry (GEOKHI), Russian Academy of Sciences, Kosygin str. 17, 117975 GSP-1, Moscow Russian Federation

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In this study we have used a conventional piston-cylinder apparatus to perform the electrical conductivity measurements at pressures up to 25 kbar and temperatures up to 1200°C.

The pressure calibration of the apparatus has been done at high temperature by determination of melting curves of NaCl and CsCl . Melting points of these substances as a function of pressure up to 25 kbar has been determined *in-situ* by electrical conductivity measurements. The performed pressure calibration is believed to be within an accuracy of ± 30 MPa. The temperature gradient in the cell has been estimated on dummy samples of pressed Al_2O_3 powder by the use of three thermocouples. The estimation for a radial temperature gradient is 1°/mm, for a vertical temperature gradient is 2°/mm in the temperature range up to 900°C.

Electrical impedance measurements have been done with Solartron 1260 Phase-Gain-Analyser interfaced with a PC. In high pressure experiments we applied 1 V sine signal in frequency range 0.01 Hz to 100 kHz. A cell for electrical impedance measurements represents a coaxial cylindrical capacitor (Slutskiy, 1969) with a geometric factor 5-7 cm filled with a sample under test. The exact geometric factor of a cell has been evaluated independently from calibration measurements on NaCl solutions (0.01M - 3 M) at 22°C and pressure 0.1 MPa. The difference between a calculated geometric factor of a cylindrical capacitor and a measured geometric factor was about 25%. The main advantage of using a coaxial cylinder geometry before a parallel plate geometry is a negligible change of the geometric factor under loading the sample. During impedance measurements the press was separated from the ground of Solartron 1260. One wire of Pt-thermocouple and the mass of the high pressure autoclave were used to connect the measuring device and the cell electrodes. At high pressure and temperature the measurements of the electrical impedance were conducted without an automatic temperature control in order to reduce electrical noise of the heater. The oil pressure in loading hydraulic rams was maintained within 0.05 MPa.

At constant pressure for each temperature the AC-conductivity of calcite was estimated from a frequency scan of the electrical impedance *Z*. The bulk conductivity was determined from Argand plots by a fitting of data of the dependence *Im(Z)* from *Re(Z)* to the frequency dependence (Bagdassarov et al,2001). The temperature of transformation was assessed from Arrhenius plots (Z'_1 as function of *1/T,°K*) as kink point (T_c) of the activation energy (Fig.1 and Fig.2). The low temperature kink point (Fig.1) may corresponds to previously discussed in the literature (Mirwald,1976) phase transformation Calcite I ⇔ Calcite IV. It should be noted that the position of this kink point and the change of activation energy is kinetically depended on the thermal history of the sample: cooling rate from higher temperatures and/or annealing time at low temperatures. More likely the increase of activation energy may corresponds to a kinetic phenomena of retaining $R\bar{3}c$ symmetry at temperatures above 850°C. The kink point at higher temperatures is the result of rotational ordered -disorder (Calcite V) phase transformation $R\bar{3}c \Leftrightarrow R\bar{3}m$ (Redfern et al.,1989). For this transformation the bending point on the Arrhenius plot is reversible and kinetics is instantaneous.

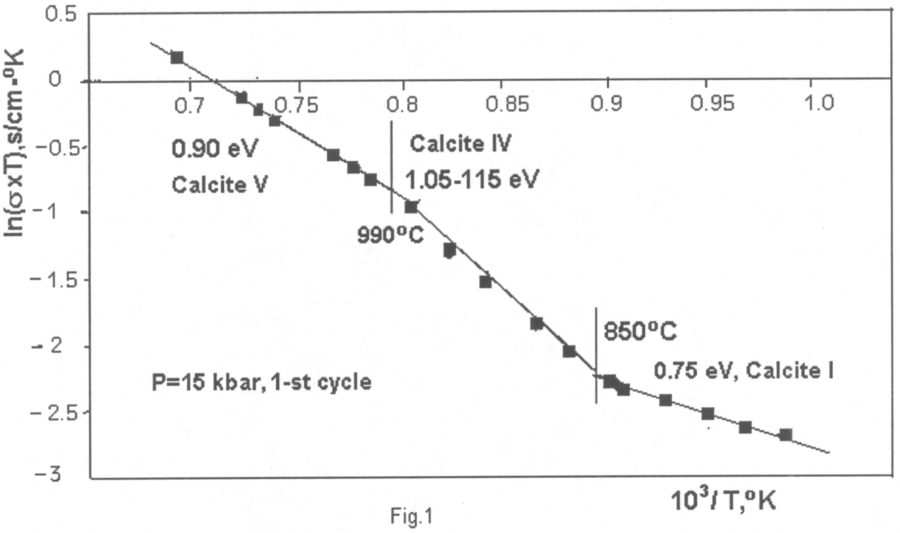

Fig.1

Fig.1. Determination of t_c temperature for the calcite transformations. these data are obtained on synthetic calcite samples as well as on natural crystals.

The phase transformation Calcite ⇔ Aragonite is of a reconstructive type, which means that the characteristic time of this phase transformation is determined by a self diffusion coefficients of Ca and O. Depending on temperature the characteristic time (τ) of the phase transformation may vary in a wide range (Hacker et al., 1992). Few experiments aiming to determine a characteristic time (τ) of the phase transformation Calcite ⇔ Aragonite were performed in this study, Fig.2. Calcite sample was cooled down and kept in the stability field of Aragonite during a long time until the electrical bulk resistance reaches a steady state value corresponding to the accomplished phase transformation. The followed heating of aragonite was stopped at temperature corresponding to the kink point of this transformation and a relative change of the electrical resistance was monitored as a function of time. The data were fitted to the equation $R(\tau) = R_o \cdot [1- \exp(- t / \tau)]$, where $R(\tau)$ and R_o stands for an excess of the electrical resistance of Aragonite in comparison with Calcite in time τ and in a steady state. According to the diffractograms data variations of electrical resistance with time correlate with the degree of the phase transformation $\xi(\tau)$. The degree of aragonite to calcite transformation has been fitted to the analogous expression:

$\xi(\tau) \sim [1 - \exp(- t / \tau)]$, where τ is a characteristic time of the phase transformation at a temperature t.

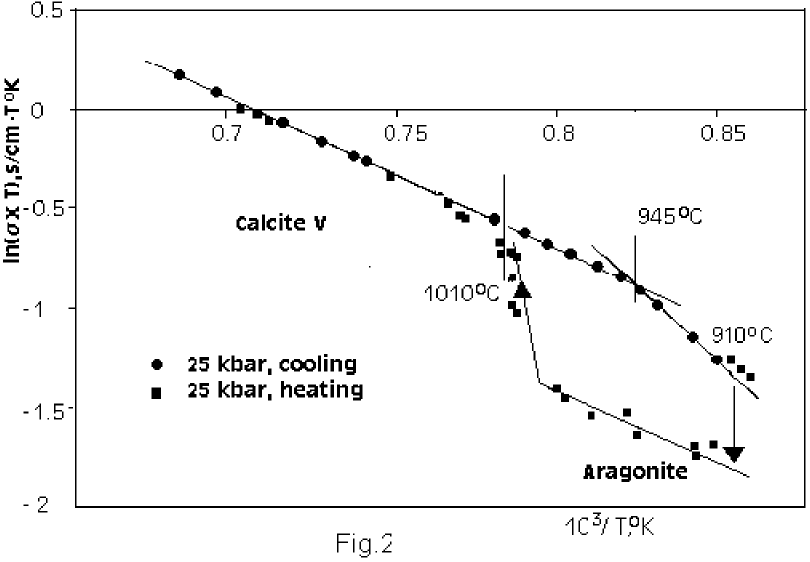

Fig.2

Fig.2 Change of electrical conductivity during phase transformation calcite ⇔ aragonite. Conductivity of Aragonite is lower than Calcite. Arrows indicate on kinetic experiments performed near the calcite-aragonite phase boundary. The abrupt drop of conductivity under cooling corresponds to the transformation of Calcite into Aragonite. Heating and cooling curves demonstrate a large temperature hysteresis of this transformation.

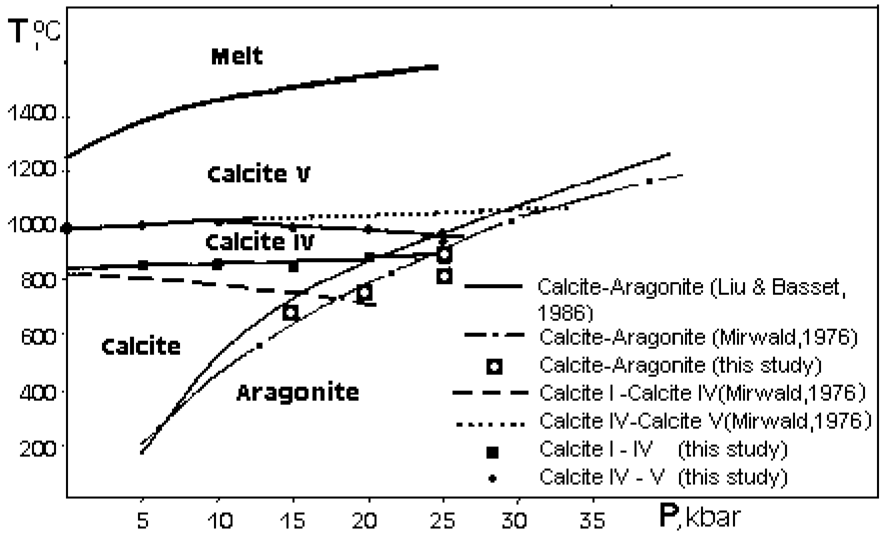

Fig.3

Fig.3 Phase diagram of $CaCO_3$. From this study the Calcite V ($R\bar{3}c$ ⇔ $R\bar{3}m$) boundary is described by the equation $T^oC = -0.18\ P\ (kbar)^2 + 3.21\ P\ (kbar) + 987$. The slope of Calcite I – Calcite IV transformation is positive, $T^oC = 1.4\ P\ (kbar) + 841$.

Conclusions:

1. Electrical impedance measurements may be successfully used to identify phase transitions in Calcite, ordered $R\bar{3}c$ ⇔ orientational disordered $R\bar{3}m$ phases. The data indicate the decrease of Tc at pressures above 10 kbar. This may be caused by a close location of Calcite-Aragonite phase boundary to $R\bar{3}c$ ⇔ $R\bar{3}m$ phase transformation boundary as consequence of a strong coupling between orientational and out-of-plane translational variables of these two phase transformations (Ferrario et al., 1994).
2. The phase transformation Calcite I ⇔ Calcite IV Previously discussed in the literature (Mirwald, 1976;79a and b) is difficult to identify. This kinetical phase boundary depends on the thermal history of the calcite sample and it is likely that Calcite IV is a metastable phase.
3. Kinetics of Calcite ⇔ Aragonite transformation may be estimated from time dependence of electrical bulk resistance. The results show that the kinetics of this transformation depends on temperature according to an Arrhenius dependence, and on δP – δT amplitude of the phase boundary crossover. For example, at 15 kbar and 680°C the characteristic transformation time τ is 8.8 h, at 25 kbar and 910°C $\tau \sim 0.5$ h.

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