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Solubility of NaCl in CO_2 at high pressure and temperature: First experimental measurements

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Abstract

NaCl solubility in gaseous carbon dioxide has been measured in the pressure range from 30 to 70 MPa at 623 and 673 K. Our originally-designed high pressure apparatus allows in situ sampling of a portion of the fluid phase for chemical analysis. The results indicate that the solubility of NaCl increases with both temperature and pressure, and is about 4–5 orders of magnitude higher than saturated NaCl pressure values at the same temperature conditions (6.02×10^{-12} at 623 K and 1.51×10^{-10} at 673 K). It is also 1–2 orders of magnitude greater than predictions according to the Equation of State of the ternary H_2O–CO_2–NaCl system by Duan, Moeller and Weare [Duan, Z., Moller, N., and Weare, J. H. (1995) Equation of state for the NaCl–H_2O–CO_2 system: prediction of phase equilibria and volumetric properties. *Geochim. Cosmochim. Acta* **59**, 2869] and has the opposite pressure dependence. The activity values of NaCl in the vapor phase, calculated from the experiments (with pure molten NaCl as a standard state in the vapor), have been fitted to the Darken Quadratic Formalism: $RT \ln a_{\mathrm{NaCl,v}} = RT \ln x_{\mathrm{NaCl,v}} - 2W^G_{\mathrm{NaCl\text{–}CO_2}} \cdot x_{\mathrm{NaCl,v}} + B^G_{\mathrm{NaCl\text{–}CO_2}}$, where, $x_{\mathrm{NaCl,v}}$ is mole the fraction of NaCl in the vapor phase, $W^G_{\mathrm{NaCl\text{–}CO_2}} = (1936.3 - 43.669 \cdot P) \times 10^6$, $B^G_{\mathrm{NaCl\text{–}CO_2}} = 83,754 - 420.1 \cdot P$, where P is the pressure in MPa and T the absolute temperature. Caution should be exerted while extrapolating this empirical equation far beyond the experimental P–T-compositional range.

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1. INTRODUCTION

Fluid-driven processes have operated in the Earth's interior to shape the lithosphere. Degassing has led to concentration of the volatile, hyper fusible and radioactive elements in the outer parts of the Earth, resulting in a more stably stratified planet. Recycling of these constituents by subduction is now considered to be a major process in the development of the continents. Large-scale crust-modifying processes, such as regional metamorphism, classically considered as closed-system processes, except for the escape of H_2O and CO_2, are now thought to be profoundly metasomatic in character, recording the passage of large quantities of fluids of exotic origin (e.g., Korzhinskii, 1959; Aranovich et al., 1987; Perchuk and Gerya, 1993; Newton et al., 1998). A particularly important finding of these studies is a major involvement of alkalis in the high-grade metamorphic processes. Recent synthetic fluid inclusion experiments (Shmulovich and Graham, 1999), interpretation of phase relations in high-temperature calc-silicates (Skippen and Trommsdorf, 1986; Heinrich et al., 2004) and direct observations on high-grade inter-granular salt present in metamorphic environments (Trommsdorff et al., 1985; Markl and Bucher, 1998)—all point to a crucial role played by the complex H_2O–CO_2–strong electrolyte fluids in the development of metamorphic assemblages. As a first approximation, these fluids may be modeled by the system H_2O–CO_2–NaCl. Despite its evident importance for predicting metamorphic and magmatic phase relations, thermodynamics of this system remain somewhat obscure,

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particularly at high pressure (*P*), temperature (*T*) and salt concentration. This is partly due to the extremely scarce experimental information on the behavior of the boundary binary system NaCl–CO_2 at high *P*–*T* conditions. The only experiments on this system at high temperature are those by Grjotheim et al. (1962) on the CO_2 solubility in molten NaCl at ambient pressure and by Chou (1988) on the depression of melting temperature of halite in presence of CO_2 at 2 kbar. As might be intuitively expected, the solubility at 1 atmosphere is very low (on the order of 5×10^{-6} mol CO_2/mol NaCl; Grjotheim et al. (1962)). Authors of all existing equations of state (EOS) for the ternary system (e.g., Bowers and Helgeson, 1983; Duan et al., 1995) have been, therefore, forced to extract quantitative description of the mixing properties for the NaCl–CO_2 binary from experiments on the ternary system, which is known to be a rather unreliable procedure.

In this paper we present first experimental measurements of the NaCl solubility in gaseous CO_2, obtained at 623 and 673 K in the pressure range of 35–70 MPa, employing an originally designed apparatus that permits in situ sampling of the fluid phase. We then compare the results with the predictions of the most recent EOS (Duan et al., 1995) and provide a provisional set of parameters to be used in thermodynamic modeling of the ternary system.

2. EXPERIMENTAL METHODS

2.1. Apparatus

The in-house built apparatus for measuring solubility of various solids in liquid and gaseous water and non-aqueous solvents at *T*–*P* parameters up to 773 K and 100 MPa is shown schematically in Fig. 1. The apparatus consists of a Ti-based alloy pressure vessel with a standard nut seal. Inside the vessel is placed a capsule, made of the same alloy, with a carefully pre-measured inner volume (19.2 cm^3). The capsule has an independent "hot" valve that operates at the experiment *P*–*T* conditions and allows sampling of the fluid phase during the run. Pressure during the runs is measured with a high-precision gauge connected to the vessel through a Ti capillary tube welded into the notch seal of the vessel. The gauge was calibrated against a standard piston gauge (Russian National Bureau of Standards). A small container with purified CO_2 (source of the fluid in experiments) is connected to the capillary through a micro-valve. Temperature during the runs is measured and controlled with a number of sheathed S-type thermocouples. Temperature gradient along the vessel is less than 0.1°/cm. *T*–*P* parameters during the runs are measured, controlled and monitored automatically using a specially-designed interface connected to a PC. Uncertainties in pressure and temperature measurements (including fluctuations during the runs) are ±10 kPa and 2 K, respectively.

2.2. Run procedure

All parts of the apparatus are carefully dried in an oven at 423 K just before assembling a run. About 100 mg of ultra-high purity NaCl, annealed at 573 K for several hours just before loading, is placed on the bottom of the Ti pressure vessel and sealed with the nut. The inner Ti capsule is closed with the valve. Then a certain amount of CO_2 is let into the vessel by slightly heating the CO_2 container while keeping the micro-valve open. To eliminate any presence of water, the CO_2 loaded into the vessel is passed through a warm (353 K) zeolite sieve. Then the micro-valve is closed, and the container is separated and carefully weighed on an analytical semi-micro balance (10^{-5} g) to measure the total amount of CO_2 in the run (40–50 g CO_2 was typically loaded). After that the vessel is heated to the required temperature, and the valve of the inner Ti capsule is slowly opened. A slight drop in pressure occurs on the inner capsule opening due to a small increase in the total volume of the system. After 24–30 h (to let the system equilibrate) the inner capsule is closed and the vessel is quenched in running water to room temperature (quenching time from 673 to 298 K is about 4 min). On quenching, the salt dissolved in CO_2 during the run precipitates on the walls of both the inner Ti capsule and the vessel. After quenching, the inner capsule is taken out and its internal salt content is carefully washed out with a well-known quantity of doubly distilled de-ionized H_2O into a glass vial.

2.3. Analytical procedure

The amount of sodium dissolved in CO_2 during the runs and precipitated on quenching in the inner capsule (ranging from 0.5 to 15 μg, see Table 1) was determined by the atomic emission spectroscopy with inductively coupled plasma (ICP-AES), with argon as the plasma source. Standard solutions for calibration were prepared with ultra-high purity Titrisol® (Merck). The linear part of the calibration curve was used in the analysis. Sensitivity of the method corresponds to 0.5 ppb Na. Several potentially important sources of errors had to be considered with relation to the analysis of the very low NaCl solubility of the present study. First, the NaCl content in the H_2O used to collect the dissolved NaCl was found to be near detection limit of the instrument. No salt was detected in the source CO_2. As was suggested by one of the reviewers of this paper, contamination of the inner capsule might have occurred due to the mechanical transport of the NaCl charge from the bottom of the vessel on the inner capsule opening. To check for this possibility we made a dummy run at the highest *P*–*T* conditions of the present study (60 MPa, 673 K), in which the inner capsule was opened for only a very short time to let the pressure of the system equilibrate, and then quenched. The analysis revealed no salt in the inner capsule, thus indicating that mechanical transport of NaCl did not take place. Water content of the source CO_2 appears to be the most important consideration of the solubility measurements. As was noted above, a highly pure CO_2 was used in experiments. Gas chromatographic analysis of the CO_2 showed no presence of H_2O. Overall uncertainties in the measured NaCl content are estimated as 10–12 relative %, with the greater value corresponding to the lowest NaCl concentrations.

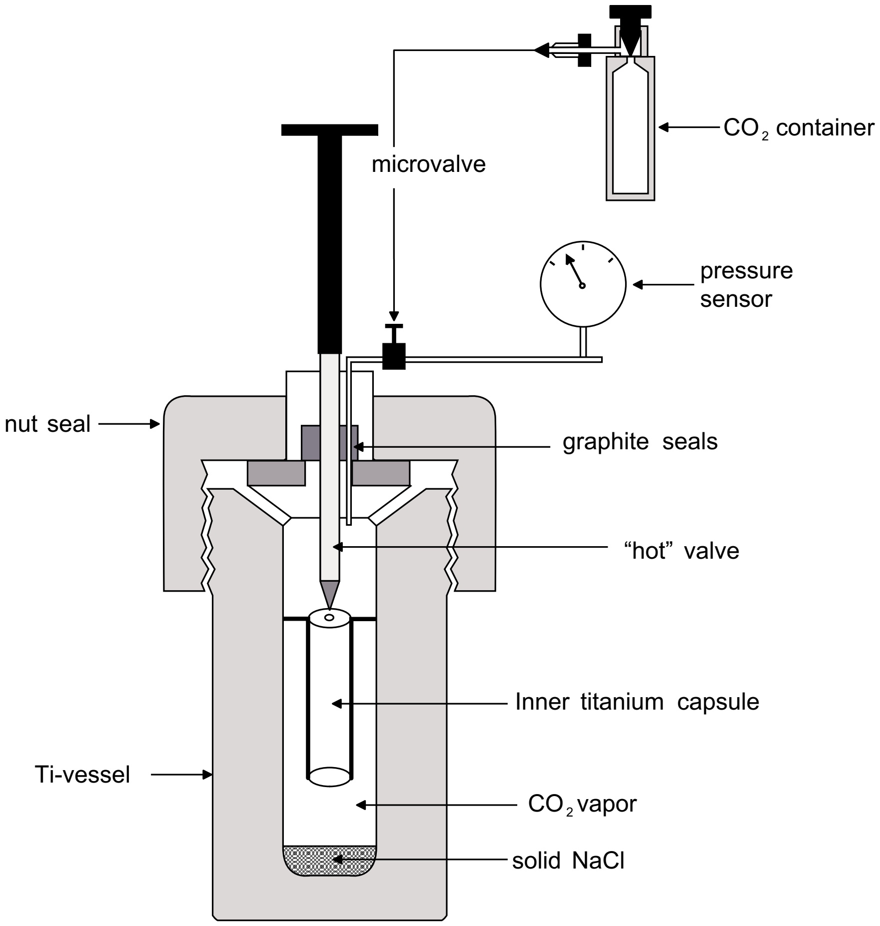

Fig. 1. Sketch of the apparatus for in situ solubility measurements.

3. RESULTS AND DISCUSSION

The measured values of the NaCl solubility in CO_2 in each individual run are given in Table 1. As it was impossible to load exactly the same amount of CO_2 in every run, the resulting pressure varied slightly for each "isobaric" series (see Table 1). The average values of the NaCl solubility for the P–T range of this study are given in Table 2. As one might expect, they are rather low, but, nevertheless 4–5 orders of magnitude higher than saturated NaCl pressure under the same temperature, calculated with the reference data of Gurvitch et al. (1978) (6.02×10^{-12} at 623 K and 1.51×10^{-10} at 673 K). They are also 1–2 orders of magnitude higher than those calculated with the binary CO_2–NaCl parameters of the EOS for the ternary H_2O–CO_2–NaCl system derived by Duan et al. (1995) (Fig. 2). It should be noted that according to our measurements the solubility increases with both temperature and pressure, while the EOS predictions indicate negative correlation of the solubility with pressure (see Fig. 2). The pressure-induced increase of the solubility found in this work suggests a certain bonding of the NaCl and CO_2 molecules in the gas, which may be related to the existence of the dipole moment in NaCl and the quadrupole moment in CO_2.

Equilibrium conditions for the NaCl solubility in CO_2 are expressed as:

$$\mu^0_{\mathrm{NaCl,s}} + RT \ln a_{\mathrm{NaCl,s}} = \mu^0_{\mathrm{NaCl,v}} + RT \ln a_{\mathrm{NaCl,v}}, \qquad (1)$$

where $\mu^0_{\mathrm{NaCl,s}}$, $\mu^0_{\mathrm{NaCl,v}}$ are standard state chemical potentials of NaCl in solid (s) and vapor (v) phases, respectively, and $a_{\mathrm{NaCl,s}}$ $a_{\mathrm{NaCl,v}}$ are corresponding activity values. Solid NaCl is a pure substance, and its activity is equal to 1. Following the approach used for the H_2O–NaCl binary (Chou et al., 1992; Aranovich and Newton, 1996) and H_2O–CO_2–NaCl ternary (Heinrich et al., 2004) systems, (metastable) molten NaCl has been chosen as a standard state of NaCl in the vapor phase. Standard state chemical potentials of both solid and molten NaCl were calculated according to the equations given by Holland and Powell (1998) and the difference

$$\mu^0_{\mathrm{NaCl,s}} - \mu^0_{\mathrm{NaCl,v}} = RT \ \ln a_{\mathrm{NaCl,v}} \qquad (2)$$

is tabulated in Table 2 for the experimental P–T conditions. Because of the very dilute range of concentrations in our experiments, we employed the Darken Quadratic Formalism (DQF) (Darken, 1967; Aranovich, 1991) for the analytical representation of the NaCl activity–composition relationships in gaseous CO_2.

Table 1
Results of experiments on the NaCl solubility in gaseous CO_2

T (K)	P (Mpa)	m_{CO_2}(tot), g	m_{Na^+} (in), μg	m_{CO_2} (in), g
623	33	27.8	0.46	5.64
	33.3	27.9	0.47	5.67
	54	39	3.80	7.92
	54.6	41.5	3.60	8.43
	54.2	41	3.90	8.33
	53.6	40.8	3.70	8.29
	56	44.5	4.48	9.04
	55.6	44.1	4.50	8.96
	55	44.2	4.25	8.98
	56.4	44.5	4.45	9.04
	56.7	44.8	4.65	9.10
	65.2	47	6.80	9.55
	65	46.6	6.72	9.47
	64.9	47.2	6.83	9.59
	65	46.8	6.88	9.51
673	27.5	20.3	1.22	4.12
	27	20	1.08	4.06
	45	30.9	4.24	6.28
	45.5	31.2	4.08	6.34
	45.1	30	4.48	6.10
	62.5	44.1	12.17	8.96
	62.8	44.6	13.75	9.06
	62.1	44	11.00	8.94
	67.4	44.7	13.80	9.08
	67.2	44	14.50	8.94

Note. m_{CO_2}(tot), total amount of CO_2 loaded in the vessel; m_{Na^+}(in), sodium content of the inner capsule; m_{CO_2}(in), the amount of CO_2 in the inner capsule.

Table 2
Average values of NaCl mole fraction in gaseous CO_2 and corresponding values of NaCl activity in the vapor phase

T (K)	P (MPa)	$X_{NaCl} \times 10^7$	$-RT\ln a_{NaCl,v}$[a] (J/mol)
623	33	1.569	10,789
	54	8.655	10,868
	56	9.520	10,875
	65	13.631	10,908
673	27.5	5.680	9724
	44	14.172	9790
	62.5	25.965	9863
	67	30.292	9881

[a] Calculated from the dataset by Holland and Powell (1998) (see Eq. (2) in the text).

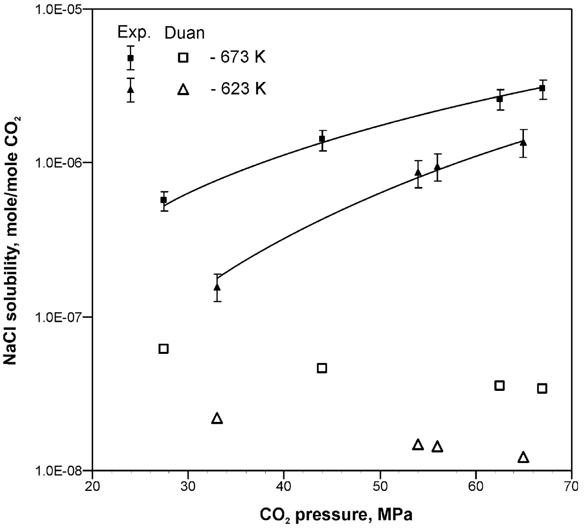

Fig. 2. Experimental values (filled symbols with uncertainty bars) of NaCl solubility in gaseous CO_2 as a function of CO_2 pressure. Solid curves, fit to the experimental points according to the DQF model (Eq. (3) in the text). Open symbols, calculations according to Duan et al. (1995).

For the present experiments DQF corresponds to:

$$RT\ln a_{NaCl,v} = RT\ln x_{NaCl,v} + W^G_{NaCl\text{–}CO_2} \cdot x_{NaCl,v} \cdot (x_{NaCl,v} - 2) + B^G_{NaCl\text{–}CO_2}, \qquad (3)$$

where $x_{NaCl,v}$ is mole fraction of NaCl in the vapor phase, and $W^G_{NaCl\text{–}CO_2}$, $B^G_{NaCl\text{–}CO_2}$ are constants. Noting that, for the very low $x_{NaCl,v}$ of the present experiments $(x_{NaCl,v} - 2) \approx -2$, Eq. (3) can be rearranged to:

$$RT\ln a_{NaCl,v} = RT\ln x_{NaCl,v} - 2W^G_{NaCl\text{–}CO_2} \cdot x_{NaCl,v} + B^G_{NaCl\text{–}CO_2} \qquad (3')$$

Parameters in (3) and (3') can be further expanded in P and T according to Gibbs–Helmholtz relation (Darken, 1967):

$$W^G = W^H - TW^S + PW^V, \quad B^G = B^H - TB^S + PB^V. \qquad (4)$$

Numerical values of the parameters associated with Eqs. (3) and (4) were found by least-squares fitting the experimental data (Table 2). It was found by trial and error that only four parameters are sufficient to adequately represent the experiments with the DQF model:

$$W^G_{NaCl\text{–}CO_2} = (1936.3 - 43.669 \cdot P) \times 10^6$$

$$B^G_{NaCl\text{–}CO_2} = 83754 - 420.1 \cdot P$$

The DQF model very well reproduces the experimentally observed NaCl solubility values (see curves in Fig. 2). However, it should not be used for extrapolation far beyond the experimental P–T-composition range. The applicability of the DQF model implies that the experimental data may help better constrain mixing properties of the H_2O–CO_2–NaCl ternary system employing a model similar to that suggested in (Aranovich et al., 2000). The above parameters should be considered as only provisional because a much more rigorous treatment is needed to obtain a quantitative description satisfying the experimental data in the ternary system, which were collected within the considerably larger pressure–temperature–composition range than the present study (see Duan et al., 1995; Shmulovich and Graham, 1999, and references therein).

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