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A thermodynamic model for phase equilibria in the H_2O-CO_2-NaCl system

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The H_2O-CO_2-NaCl system is key in understanding the processes at work in many geological contexts, including mantle wedge metasomatism, seawater composition, the global carbon cycle and CO_2 underground sequestration. Despite numerous thermodynamic models allowing calculation of CO_2 solubility and various fluid properties as a function of pressure, temperature, and aqueous phase composition, there is still a need for an accurate thermodynamic model valid over a large range of conditions. We present a semi-empirical thermodynamic model with uncertainties that encompasses the full range of compositions in H_2O-CO_2-NaCl mixtures in the range of 10-380°Cand 1-3500 bars. We use a simple formalism derived from metamorphic petrology (Holland and Powell, 2003; Evans and Powell, 2006) to describe activity-composition relations, which we parametrise using a combination of solubility experiments, density and conductivity measurements. With this formalism, activities are described by interaction parameters varying with intensive properties such as pressure and temperature but not with concentration or ionic strength.

The parameters describing interactions between H_2O and CO_2 are evaluated independently of the thermodynamic properties of the end-members and vary strongly non-linearly with pressure and temperature. The activity of water is shown to remain higher than 0.88 in CO_2-saturated solutions across the entire pressure-temperature range.

In the H_2O-NaCl system, the thermodynamic model reproduces solubility experiments of halite up to 650°Cand 10 kbar, and accounts for ion pairing of aqueous sodium and chloride ions with the use of associated and dissociated aqueous sodium chloride end-members whose relative proportions vary with salinity.

In the H_2O-CO_2-NaCl system, an activity-composition model reproduces the salting-out effect with interactions parameters between aqueous CO_2 and the aqueous species created by halite dissolution. The proposed thermodynamic properties are compatible with the THERMOCALC database (Holland and Powell, 2011) and the equations used to retrieve the activity model in H_2O-CO_2 can be readily applied to other binary systems, including minerals.

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