



# Uncertainties of geochemical codes and thermodynamic databases for predicting the impact of carbon dioxide on geologic formations



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## ABSTRACT

Numerical codes are applied to calculate chemical reactions following geologic carbon sequestration in deep formations and CO<sub>2</sub> leakage in shallow formations. However, using different thermodynamic databases generates variations in the simulation results, which are referred to as the model uncertainty. The PHREEQC and The Geochemist's Workbench codes were used to simulate anorthite dissolution for storage, retention, transfer, and near-surface formation waters in the respective geological units. For each of the formation waters, a simple one-dimensional scenario was simulated using eight different thermodynamic databases. Groundwaters in shallow aquifers commonly exhibit low ionic strengths (<0.5 mol/kgw) and low temperatures, whereas storage formation waters are characterized by high ionic strength (>1.0 mol/kgw) and high temperatures. In storage formations, mineral trapping is the most efficient process for long-term CO<sub>2</sub> storage. However, with respect to the geological formations and the time needed for anorthite dissolution, the model uncertainties associated with using different combinations of numerical codes and thermodynamic databases were largest (~90%) for the storage formation waters at 58 °C and  $I = 6.5$  mol/l. Conversely, in near-surface formation waters, the model uncertainty was less than 1%. Due to CO<sub>2</sub> dissolution, the calculated pH of the formation waters decreased to a range between pH 4.0 and 5.5. In this pH range, the dissolution mechanism of anorthite switches from the slow neutral mechanism to the faster acid mechanism, causing dissolution time length variations. The calculated pH variation further increased with rising ionic strength. A detailed examination of the reasons revealed the activity coefficient calculation method of the main aquatic species to have the largest impact on the simulated model results. The calculation method of the CO<sub>2</sub> activity coefficient had the second largest impact. Via calibration with the experimental data, a specific thermodynamic database can be chosen to represent these experimental results. However, the calibration of thermodynamic databases is not possible for all potential reactions in more complex geological systems at large ranges of temperature, ionic strength and pressure conditions. The uncertainties associated with using thermodynamic databases quantified in this study for CO<sub>2</sub> storage systems will therefore persist independently from previously conducted calibrations of thermodynamic databases with experimental or field data. In view of these model uncertainties, the modeller is encouraged to include a routine in the simulations for quantification of the model uncertainty depending on the specific scenario or to assess the simulation results as a range of values that represent a soft outcome.

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## 1. Introduction

Geologic carbon storage in deep saline aquifers has been proposed as a strategy to reduce CO<sub>2</sub> emissions from power plants and industrial processes. Quantifying the chemical implications of CO<sub>2</sub> injected into saline aquifers (referred to as storage formations) is

crucial for estimating the storage capacity of geologic formations and for assessing safety issues for geological storage sites. The knowledge of the chemical reactions of CO<sub>2</sub> in highly mineralized formation waters (ionic strengths of >1.0 mol/kgw) and with minerals is important for identifying prevalent mechanisms responsible for long-term and safe carbon storage.

For example, mineral dissolution can provide cations and can be followed by precipitation of secondary mineral phases, such as carbonates or silicates, thereby improving mineral trapping for

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permanent and long-term carbon storage (Bachu et al., 2007; Gunter et al., 1993; Matter and Kelemen, 2009; Metz et al., 2005). Due to incomplete dissolution, a proportion of the injected CO<sub>2</sub> may remain as a supercritical phase. In case of a possible CO<sub>2</sub> leakage gaseous CO<sub>2</sub> may migrate into overlying formations through permeable reactivated or newly emerging faults in the caprock due to increasing formation pressure (Kampman et al., 2014), through stratigraphic gaps, or along the well bore casings of poorly abandoned injection wells (Ide et al., 2006). These overlying formations (referred to as retention formations) can hold back gaseous CO<sub>2</sub> by dissolution in the formation water (Dethlefsen et al., 2013; Großmann et al., 2011). If a supercritical or gaseous phase remains, depending on pressure and temperature, it can potentially migrate further upward via transfer formations into near-surface formations (shallow aquifers), where protected potable water resources may become acidified (Peter et al., 2012; Trautz et al., 2013). CO<sub>2</sub> intrusion results in a decrease in pH, whereby the potable water quality of near-surface aquifers can be endangered by the release of trace and heavy metals (Zheng et al., 2009a, 2009b; Lu et al., 2010). The hazard for protected water resources is one of the major risks of carbon capture and storage (CCS) technology.

Numerical codes were applied to predict CO<sub>2</sub> impact on deep geologic formations in order to quantify CO<sub>2</sub> storage mechanisms and to assess the mineral and solution trapping potential (i.e., Audigane et al., 2006; Gaus et al., 2005; Gherardi et al., 2007; Zheng et al., 2009a; Carroll et al., 2009) and the impact of CO<sub>2</sub> on near-surface formations in case of leakage (i.e., Wilkin and Digiulio, 2010; Humez et al., 2011; Zheng et al., 2009a, 2009b, 2012; Cahill and Jakobsen, 2013; Cahill and Jakobsen, 2015). To simulate a possible CO<sub>2</sub> leakage The Geochemist's Workbench using the *thermo.dat* database (Wilkin and Digiulio, 2010), TOUGHREACT in combination with various modified EQ3/6 databases (Humez et al., 2011; Zheng et al., 2009a,b; 2012; Trautz et al., 2013) and PHREEQC (Cahill and Jakobsen, 2013) combined with a modified *wateq4f.dat* database (Cahill and Jakobsen, 2015) have been applied. These studies all show negative shifts in pH and exhibit an increase in major and minor ions (i.e., Ca, Mg, Mn, Ni, Sr, Ba, Na and K, depending on formation mineralogy; Cahill and Jakobsen, 2013) following a CO<sub>2</sub> intrusion. Wang and Jaffe (2004) showed lead mobilization and Zheng et al. (2012) showed lead and arsenic mobilization associated with CO<sub>2</sub> leakage; however, mobilization of chemical components is not the aim of our study.

The codes can calculate long-term reactions at large spatial dimensions, which can only be reproduced with significant effort by laboratory or field experiments. Representation of time scales appropriate for CO<sub>2</sub> storage (>1000 years) in experiments is not possible and an upscaling of experimental results is not feasible. The time scales of experiments for CO<sub>2</sub> leakage applied in recent studies were 300 days for laboratory experiments (Little and Jackson, 2010), 150 days and 182 days for field site injection experiments including monitoring periods (Trautz et al., 2013; Cahill and Jakobsen, 2013), and 72 days of injection followed by 252 days of monitoring (Cahill and Jakobsen, 2015). Experiments conducted under CO<sub>2</sub> storage conditions reached maximal time-spans of ~600 days (Tarkowski et al., 2015) and ~1200 days (Fischer et al., 2013). Investigation of longer time scales is associated with great effort and cost.

To predict the impacts of CO<sub>2</sub> on geologic formations for longer time scales and larger spatial dimensions compared to the limited experimental conditions, numerical codes must be applied. However, until today, it has not been known which thermodynamic database produces the most reliable results for CO<sub>2</sub> storage and leakage scenarios (Dethlefsen et al., 2012; Haase et al., 2013). The databases can only be calibrated by experiments for simple reaction systems. Therefore, by selecting a thermodynamic database, a

degree of model uncertainty is involved in the calculated results and is reflected by the range of the results simulated using the available thermodynamic databases (Haase et al., 2013, 2014). Several thermodynamic databases have been applied for reactive transport models simulating CO<sub>2</sub> injection in storage formations until now: the database *phreeqc.dat* or *lnl.dat* from PHREEQC (Cantucci et al., 2009; Gaus et al., 2005; Gundogan et al., 2011; Hellevang et al., 2013), the EQ3/6 databases adapted to TOUGHREACT (Pruess et al., 2003; Xu et al., 2003; Xu et al., 2005, 2014; Xiao et al., 2009), and the *thermo.dat* database from The Geochemist's Workbench (Moore et al., 2005; Berger et al., 2009; Johnson, 2004). However, the current databases are not valid for the formation waters with high ionic strengths that occur in potential CO<sub>2</sub> storage formations. The equations calculating activity coefficients provide reliable results only at ionic strengths of up to approximately 1 molal (i.e., the Davies, Debye–Hückel, or WATEQ–Debye–Hückel equations), which are typical for groundwater in studies investigating CO<sub>2</sub> leakage (0.001–0.15 mol/kgw; i.e., Zheng et al., 2009a, 2009b; Wilkin and Digiulio, 2010; Cahill and Jakobsen, 2015). At ionic strengths higher than 1 molal, only the WATEQ–Debye–Hückel equation can provide accurate activity coefficients in NaCl-dominated solutions (Parkhurst and Appelo, 1999; Truesdell and Jones, 1974). Bethke and Yeakel (2012) and Helgeson (1969) document valid results up to ionic strengths of 3 molal for the WATEQ–Debye–Hückel equation. At higher ionic strengths, the Pitzer model can calculate accurate activity coefficients (Pitzer and Mayorga, 1974; Pitzer, 1973). However, the interaction coefficients for the Pitzer databases are usually limited to 25 °C and to geochemical systems without Si and Al mineral phases. This situation does not allow for the consideration of silicates as essential for the simulation of reactions occurring during CO<sub>2</sub> storage in sedimentary formations.

Additionally to model uncertainties caused by thermodynamic data, model parameterizations—i.e., mineral reactions or concentrations, kinetic rate constants, surface areas and activation energies—cause variations in the simulation results of numerical codes. For example, the selection of the kinetic parameters can influence mineral dissolution rates (Balashov et al., 2013; Black et al., 2015; Haase et al., 2014). To determine the calcite dissolution rates, a large number of experiments have been conducted, i.e., by Berner and Morse (1974), Compton and Daly (1987), Plummer et al. (1978), Reddy et al. (1981), and Svensson and Dreybrodt (1992). Within these experiments, the rate constants for calcite dissolution differ by one order of magnitude (Arvidson et al., 2003), mostly due to differences in the experimental design (Hellmann, 1994). Anorthite dissolution has been examined intensively by Busenberg and Clemency (1976); Chou and Wollast (1985); Knauss and Wolery (1986); Holdren and Speyer (1987); Casey et al. (1991); Amrhein and Suarez (1992); Hellmann (1994, 1995); Oelkers and Schott (1995); and Berg and Banwart (2000). Comparing different experimental studies, the rate constant of anorthite dissolution varies by four orders of magnitude (Palandri and Kharaka, 2004). However, the impact of the model parameterization on the predictions of numerical codes has not yet been quantified.

CO<sub>2</sub> dissolution in formation waters causes the pH to drop to values of approximately 5.0 in siliciclastic formations with naturally occurring CO<sub>2</sub> systems and induces mineral reactions (Gilfillan et al., 2009). Anorthite dissolution can lead to increased Ca<sup>2+</sup> concentrations in the formation waters, followed by precipitation of kaolinite and calcite immobilizing the injected CO<sub>2</sub> (Bachu et al., 1994; Marini, 2006; Cardoso and Andres, 2014; Varre et al., 2015). This key process is especially important for CO<sub>2</sub> storage and is referred to as mineral trapping because it facilitates long-term storage of CO<sub>2</sub>. Mineral trapping provides a large storage capacity in certain geochemical settings (Matter and Kelemen, 2009).

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