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Thermodynamic Data for Geochemical Modeling of Carbonate Reactions Associated with CO_2 Sequestration – Literature Review

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September 2010

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Summary

Permanent storage of anthropogenic CO_2 in deep geologic formations is being considered as a means to reduce the concentration of atmospheric CO_2 and thus its contribution to global climate change. To assure safe and effective geologic sequestration, numerous studies have been completed regarding the extent to which CO_2 migrates within geologic formations, and what physical and geochemical changes occur in these formations when CO_2 is injected. Sophisticated, computerized reservoir simulations are used as part of field site and laboratory CO_2 sequestration studies. These simulations use coupled multiphase flow-reactive chemical transport models and/or standalone (i.e., no coupled fluid transport) geochemical models to calculate gas solubility, aqueous complexation, reduction/oxidation (redox), and/or mineral solubility reactions related to CO_2 injection and sequestration.

Thermodynamic data are critical inputs to modeling geochemical processes. The adequacy of thermodynamic data for carbonate compounds has been identified as an important data requirement for the successful application of these geochemical reaction models to CO_2 sequestration. Therefore, a review was completed of thermodynamic data for CO_2 gas and carbonate aqueous species and minerals present in published data compilations and databases used in geochemical reaction models. Published studies that describe mineralogical analyses from CO_2 sequestration field and natural analogue sites and laboratory studies were also reviewed to identify specific carbonate minerals that are important to CO_2 sequestration reactions and therefore require thermodynamic data.

The results of the literature review (Section 5.0) indicate that an extensive thermodynamic database exists for CO_2 and CH_4 gases, carbonate aqueous species, and carbonate minerals. Values of $\Delta_f G_{298}°$ and/or log $K_{r,298}°$ are available for essentially all of these compounds. However, log $K_{r,T}°$ or heat capacity values at temperatures above 298 K exist for less than approximately one-third of these compounds. Because the temperatures of host formations that will be used for CO_2 injection and sequestration will be at temperatures in the range of 50ºC to 100ºC or greater, the lack of high-temperature thermodynamic values for key carbonate compounds, especially minerals, will impact the accuracy of some modeling calculations.

In comparison to the available thermodynamic data for carbonate minerals, only a small number of carbonate minerals have been described in published studies as actually being present in the host rock formations at CO_2 injection test sites or natural analogue sites, reaction products of CO_2 injection/intrusion into a host formation, or as mineral reactants or products of laboratory CO_2 fluid-rock and -mineral experiments. Except for a few carbonate solid-solution minerals (ferroan and magnesian carbonates and ferroan dolomite), thermodynamic data are available for the pure carbonate minerals identified in these natural analogue site and fluid-rock and -mineral laboratory studies. This suggests that the thermodynamic data for the pure common carbonate minerals is at least adequate for geochemical reaction modeling of CO_2 applications. However, more thorough mineralogical characterization in the future might show greater diversity of carbonate mineralogy in host formations used for CO_2 sequestration.

Carbonate mineral solid solutions are common and have been extensively studied. It was not possible from our literature review to assess the importance of solid solutions relative to adequately modeling CO_2

sequestration processes and mineral trapping reactions. Given how common carbonate solid solutions are in nature, one would have to assume inclusion of carbonate solid solutions would be paramount to accurately modeling CO_2 sequestration systems.

Two general approaches are used in geochemical reaction models to calculate activity coefficients of aqueous species. The first type consists of the Debye-Hückel equation and its variant, the Davies equation and its extended B-dot equation form. However, these equations are typically limited in accuracy to modeling relatively dilute solutions with ionic strengths less than that of seawater. The second approach involves the use of virial equations, which are sometimes called specific interaction equations or Pitzer equations. Pitzer equations can be applied accurately to systems to high-ionic strengths such as brines and highly saline groundwaters. Application of geochemical models that include the Pitzer equations is important to accurately model in CO_2 sequestration in saline formations. However, because redox reactions, especially for the Fe(II)/Fe(III) system, and Al system have not been fully parameterized for the Pitzer model, use of the Pitzer method currently will not adequately address Fe- or Al-containing geochemical reactions associated with certain CO_2 sequestration geochemical systems.

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Acronyms and Abbreviations

a	amorphous solid
am	amorphous solid
aq	aqueous
cr	crystalline solid compound
g	gas
LLNL	Lawrence Livermore National Laboratory
PNL	Pacific Northwest Laboratory
PNNL	Pacific Northwest National Laboratory
redox	reduction/oxidation
REE	rare earth element
s	solid compound
$scCO_2$	supercritical CO_2
ss	solid solution

Units of Measure

Å	angstrom, a unit of length equal to 10^{-10} meter or 10^{-4} micrometer
ºC	temperature in degrees Celsius [T(ºC) = T(K) – 273.15)]
cal	thermochemical calorie; 1 cal = 4.1840 J
C_p°	heat capacity at constant pressure in J/(mol·K)
°F	temperature in degrees Fahrenheit {T(°F) = [T(°C) x 9/5] + 32
$\Delta_f G_{298}^\circ$	standard molar Gibbs free energy of formation at 298.15 K and 1 bar
$\Delta_f G_T^\circ$	standard molar Gibbs free energy of formation at temperature T in degrees Kelvin and 1 bar
$\Delta_f H_{298}^\circ$	standard molar enthalpy of formation at 298.15 K and 1 bar
$\Delta_f H_T^\circ$	standard molar enthalpy of formation at temperature T in degrees Kelvin and 1 bar
J	joule; 1 J = 0.239006 cal
K	temperature in degrees (listed without degree symbol) Kelvin [T(K) = T(ºC) + 273.15]
ln	natural logarithm, base e = 2.71828...
log	common logarithm, base 10
$\log K_{r,298}^\circ$	common logarithm of the equilibrium constant of reaction at 298.15 K and 1 bar
$\log K_{r,T}^\circ$	common logarithm of the equilibrium constant of reaction at temperature T in degrees Kelvin and 1 bar
R	gas constant, 8.31451 J/(mol·K)
S_{298}°	standard molar entropy at 298.15 K and 1 bar
S_T°	standard molar entropy at temperature T in degrees Kelvin and 1 bar
V_{298}°	volume of 1 mol of a substance at 298.15 K and 1 bar in cm^3

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1.0 Introduction

Permanent sequestration[1] and storage of CO_2 in deep geologic formations is being considered as a means to reduce the concentration of atmospheric CO_2 and thus its contribution to global climate change. Types of geologic formations that have been studied for CO_2 sequestration include depleted oil and gas fields, deep saline reservoirs, uneconomic coal beds, and basalt formations. The study of CO_2 injection and sequestration in depleted oil and gas reservoirs and deep saline formations has received particular attention because of their widespread extent and large storage capacity, typically good permeability for large-scale CO_2 injection, and extensive industry experience with enhanced oil and gas recovery in these formations (Bachu and Adams 2003). This review focused on issues related to the computer modeling of geochemical reactions associated with CO_2 sequestration in deep saline and basalt formations. Benson and Cole (2008) and Oeklers et al. (2008) present overviews of the CO_2 sequestration in sedimentary formations and by basalt carbonation, respectively.

To assure safe and effective geologic sequestration, there have been numerous studies of the extent to which supercritical CO_2 ($scCO_2$) migrates within geologic formations and what physical and geochemical changes occur in these formations when CO_2 is injected. Rochelle et al. (2004) review the geochemical reactions that may occur during CO_2 injection in geologic formations and the effect of these reactions on CO_2 sequestration. Sequestration of CO_2 within geologic media can occur by one or more of the following main processes:

- structural trapping
- hydrodynamic trapping
- solubility and ionic trapping
- mineral trapping.

When CO_2 is initially injected into the permeable host (or reservoir) geologic formation, a “bubble” of CO_2 is formed that is more buoyant than the saline formation water. This CO_2 will then rise through the porous rock until it becomes trapped by an impermeable layer of the caprock or aquitard. This process is known as structural or stratigraphic trapping. Hydrodynamic or residual trapping of CO_2 occurs when CO_2 becomes trapped as a gas or supercritical fluid in the pore spaces of the reservoir formation and does not move. Because CO_2 gas is soluble in dilute and saline waters, injected CO_2 will also be trapped when it dissolves in the formation water to form carbonic acid (solubility trapping) and other dissolved carbonate species (ionic trapping). The formation water containing the dissolved CO_2 will also react with minerals in the reservoir formation, resulting in dissolution of these primary phases and potentially precipitating carbonate mineral phases in the pore spaces. Because many carbonate minerals [e.g., calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$], siderite ($FeCO_3$)] remain stable for geologically significant timeframes, mineral trapping is considered as having the greatest potential for long-term, stable geologic CO_2 sequestration (Bachu et al. 1994).

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[1] Bachu and Adams (2003) define geologic CO_2 sequestration and storage “...as the removal of CO_2 directly from anthropogenic sources (capture) and its disposal in geologic media, either permanently (sequestration) or for significant time periods (storage).” Sequestration in this report refers to both CO_2 sequestration and storage unless a distinction must be made from a technical basis.

In addition to these CO_2 trapping processes, there are also other geochemical interactions between the $scCO_2$ fluid, the CO_2/formation water mixture, and the minerals in the reservoir and caprock formations that impact safe and effective CO_2 sequestration. These include the dissolution of primary minerals by these fluids and subsequent precipitation of new secondary minerals, including carbonates, in the pore spaces in the reservoir formation at the contact between the reservoir formation and caprock, and in any fractures in the caprock that already exist or are newly formed because of these geochemical processes (Bentham and Kirby 2005). Additional geochemical reactions may also occur at the interface between the $scCO_2$ fluid and CO_2/formation water two-phase system, and minerals in the reservoir formation and in the caprock formation. Kaszuba et al. (2003) observed in laboratory studies the desiccation of the saline formation water when water migrates from the aqueous phase and partitions into the $scCO_2$ phase. Kaszuba et al. (2003) proposed that the geochemical reactions at these interfaces may differ from the reactions that occur in the bulk geologic media and therefore impact our conceptualization and technical evaluation of geological CO_2 sequestration at different sites. For example, they noted that brine desiccation could potentially create a localized environment of higher ionic strength at the interface between the $scCO_2$ and pore water in the reservoir formation (Kaszuba et al. 2003).

Superimposed on the abiotic geochemical interactions described above are the potential roles that subsurface microorganisms might have through biomineralization reactions affecting the effectiveness of CO_2 injection, stability of primary minerals in the reservoir and caprock, and precipitation of secondary carbonate minerals. Only nine studies of the effects of microbiological processes on geologic CO_2 sequestration could be identified in the journal literature. Mitchell et al. (2009) studied biofilms as a means of reducing the permeability of porous geological matrices to reduce $scCO_2$ leakage and thus enhance the geologic sequestration of CO_2. Dupraz et al. (2009a, 2009b) report the results of laboratory studies of CO_2 biomineralization processes in saline solutions at conditions associated with deep saline aquifers. To interpret their experimental results, Dupraz et al. (2009b) used the geochemical code CHESS, which was adapted to account for the enzymatically catalyzed ureolysis reaction, the kinetics of gas/solution exchanges ,and the rate of $CaCO_3$ precipitation. Power et al. (2007, 2009) characterized the weathering regime of the hydromagnesite [$Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$] playas and associated ultramafic bedrock of Atlin, British Columbia, as a natural model for CO_2 sequestration from the perspective of biogeochemical processes that accelerate mineral carbonation. The results of other studies of the effects of biomineral-fluid reactions on geologic CO_2 sequestration were reported in the recent abstracts by Dupraz et al. (2007, 2008), Martinez et al. (2007), and Mitchell et al. (2008). Given the extensive body of information that currently exists in the literature on the effects of microorganisms on mineral dissolution and precipitation under a variety of subsurface environments (see collection of review papers in Banfield and Nealson [1997]), biomineralization reactions will likely be important to certain geochemical processes associated with geological CO_2 sequestration and will thus be a focus of future research.

Geochemical interactions between injected $scCO_2$ and CO_2/formation water and cement present in wellbores is another set of geochemical processes that has received recent attention relative to their importance to geological CO_2 sequestration. Cement is used for the construction and completion of CO_2 injection and monitoring wells and for abandonment (i.e., closure) of existing wells. Abandoned wells may act as preferential pathways for the leakage of CO_2 through the degraded cement used to plug the wells or through openings between the cement casing and the host formation. Cements will degrade when contacted by acids, and this degradation may occur more rapidly under some conditions when contacted by $scCO_2$. This leakage is enhanced by CO_2 buoyancy because free-phase CO_2 is less dense than the waters in the geologic formations. Carey et al. (2007) have analyzed actual core samples of cement taken from an oil well that had been exposed to CO_2 injection for several decades. During the past 4 years, results have been reported from several laboratory studies of the mineralogical changes that occur when cement is reacted with CO_2-rich aqueous fluids and $scCO_2$ (Bachu and Bennion 2009; Barlet-Gouédard et al. 2007, 2009; Brunet et al. 2009; Centeno et al. 2005, 2007, 2009; Jacquemet et al. 2005, 2008; Kunieda et al. 2008; Kutchko et al. 2007, 2008, 2009; Regnault et al. 2009; Rimmelé et al. 2008; Scherer et al. 2005; Wigand et al. 2009). Some of these studies have included testing of the cement durability and degradation from exposure to CO_2-H_2S mixtures (Centeno et al. 2005, 2007, 2009; Jacquemet et al. 2005, 2008). Development of computer models specific to simulating and evaluating the reactivity of cement and its constituent mineral phases to CO_2-brine fluid mixtures has started (Carey and Lichtner 2007; Corvisier et al. 2009, 2010; Huet et al. 2006). Well construction and abandonment procedures have changed significantly over the last 100 years and cement quality has also varied significantly over this time frame. For example, new CO_2-resistant cement has been introduced and is being tested with respect application of CO_2 sequestration (Barlet-Gouédard et al. 2007, 2009). The consequences to geological storage of CO_2 from leakage from abandoned wells are discussed by Celia and Bachu (2003), Watson and Bachu (2007), and others. The implications of such leakage from the perspective of CO_2 sequestration are beginning to be modeled by researchers, such as Nordbotten et al. (2005).

Sophisticated, computerized reservoir simulations of geologic CO_2 sequestration are now conducted routinely as part of field site and laboratory CO_2 sequestration studies. Schnaar and Digiulio (2009) review the use of computer modeling techniques in project design, site characterization, assessments of leakage, and site monitoring activities associated with geologic sequestration of CO_2. These modeling techniques typically use coupled multiphase flow-reactive chemical transport models and/or standalone (i.e., no coupled fluid transport) geochemical models[1] to calculate gas solubility, aqueous complexation, reduction/oxidation (redox), and/or mineral solubility reactions related to CO_2 injection and sequestration. For a review of geochemical reaction models, the reader is referred to Bethke (2008), Loeppert et al. (1995), Carmichael and Eugster (1987), and the references or papers therein.

Of particular note is the recent book by Marini (2007) entitled *Geological Sequestration of Carbon Dioxide: Thermodynamics, Kinetics, and Reaction Path Modeling*, and the review journal article by Gaus et al. (2008) entitled "Geochemical and Solute Transport Modelling for CO_2 Storage, What to Expect From It?" in the *International Journal of Greenhouse Gas Control*. Marini (2007) reviews in detail the issues associated with the thermodynamic, kinetic, and reaction path modeling of geologic sequestration. Marini includes detailed discussions of the thermodynamic properties of CO_2 and the CO_2-H_2O system; the interactions of CO_2 in aqueous solution; the thermodynamic stability of solid product phases; volume changes that accompany carbonation reactions; and the kinetics of dissolution and precipitation reactions of carbonate, silicate, oxide, and hydroxide minerals relevant to CO_2 sequestration. Marini (2007) also takes the reader through some modeling exercises to show the reader how to apply reaction path modeling to geological CO_2 sequestration, and then describes the results of several CO_2 sequestration modeling studies published in the literature.

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[1] When referring to the capability of calculating these geochemical reactions with a computer model, we will refer to these two groups of models collectively in the remainder of this paper as geochemical reaction models.

Gaus et al. (2008) presents a detailed review with an extensive supporting reference list of the application of coupled multiphase flow-reactive chemical transport and geochemical modeling to CO_2 sequestration. They identify the following four application areas (taken essentially verbatim from Gaus et al. [2008]):

- Long-term integrity modeling to assess the ultimate fate of injected CO_2 and impact on physical properties
- Injectivity modeling to evaluate if the direct environment of the well is not changing in terms of physical and chemical properties in such a way that the injection rates are affected
- Well integrity modeling to assess the geochemical effects on CO_2 on the well completion itself, whether the well is an injection well built for CO_2 storage project, or an abandoned well in case of storage in a depleted oil or gas reservoir or in a deep saline aquifer penetrated by exploration or production wells
- Modeling of laboratory or small-scale field experiments for the calibration of geochemical and solute transport models, identification of case specific chemical or physical parameters, and validation testing of newly developed codes.

Gaus et al. (2008) reviews the data requirements and gaps and presents examples of specific progress over the last 10 years with respect to using reactive chemical transport and geochemical modeling in these four application areas. In all four application areas, Gaus et al. (2008) identifies the lack of thermodynamic and kinetic data, especially for precipitating minerals, as a chronic problem in each of these four modeling application areas. Gaus et al. (2008) also identifies several new emerging application areas for reactive chemical transport and geochemical modeling with respect to CO_2 sequestration. These include understanding the relationship between fluid flow, geochemistry, and geomechanics; co-injection of other gases with CO_2; and geochemical behavior at the pore scale and how dissolution/precipitations reactions impact porosity and permeability (Gaus et al. 2008).

2.0 Objective of Study

Geochemical reaction models require thermodynamic data to calculate the geochemical reactions associated with CO_2 sequestration. This is an important data requirement for the successful application of geochemical reaction modeling to CO_2 sequestration (Gaus et al. 2008; Marini 2007). The objective of our study was to review the availability of thermodynamic data for CO_2 gas and carbonate aqueous species and minerals present in published data compilations and database files used in geochemical reaction models. Our evaluation also discusses issues pertinent to modeling geochemical reactions involving carbonate mineral solid solutions and carbonate solution equilibria in high-ionic strength saline (brine) solutions relevant to CO_2 sequestration in deep saline formations.

Thermodynamic data may not exist for some minerals that are important to reactions that are known to occur from field site and laboratory studies of CO_2 sequestration. Therefore, a review of published papers that describe mineralogical analyses from field sites and laboratory studies was also completed. This component of our review was needed to identify other important carbon-containing solids that are not included in existing databases but for which thermodynamic values need to be determined and added to databases.

Our evaluation was limited to pure carbonate compounds and carbonate compounds containing common alkali and alkaline-earth elements and the transition elements Fe and Mn. Carbonate compounds containing other transition, rare earth, and radionuclide elements are not included in this assessment because they are not expected to be relevant to the carbonate reactions associated with CO_2 sequestration.

These subject areas are obviously are not the only data needs that impact a researcher's ability to accurately model geochemical reactions for CO_2 sequestration. We would be remiss in not acknowledging that simulations of geological CO_2 sequestration to the relevant time scales are very difficult. Many of the geochemical processes described above, especially those involving dissolution and precipitation of minerals in the reservoir and caprock formations, will take long time periods to reach equilibrium. Therefore, reaction rates for these processes must be included when trying to accurately model these interactions for data from CO_2 field injection and natural analogue sites and laboratory studies of CO_2 fluid-rock interactions. There is no question that such information is sparse or not well known. Researchers—such as Bateman et al. (2005), Gaus et al. (2008), Marini (2007), Xu et al. (2004), and others—have identified this as an important data need for accurately geochemical modeling of CO_2 sequestration. However, we estimate that a review of thermodynamic data availability for carbonate species provides a baseline for other future reviews of related subject areas, such as reaction rates for precipitation and dissolution of carbonate mineral and minerals present in reservoir and caprock formations.

3.0 Thermodynamic Properties Needed for Geochemical Reaction Modeling

Geochemical models require thermodynamic data to calculate the aqueous speciation, redox, mineral and gas solubility reactions associated with laboratory, field-scale, and site-specific studies of geological sequestration. The thermodynamic principles and equations that are the foundation for calculating these geochemical equilibria are discussed in detail by others such as Appelo and Postma (2005), Langmuir (1997), Marini (2007), and Nordstrom and Munoz (1985) and therefore will not be discussed in detail here. However, to provide a basis to discuss what thermodynamic parameters are included in various published compilations of thermodynamic data or computer model thermodynamic databases, a few thermodynamic relationships are presented here. The authors recognize that the following treatment of thermodynamic equations is elementary and that numerous important nuances exist between the acquisition, evaluation, and tabulation of thermodynamic data for gases, liquids, aqueous species, or solids. Some of these nuances will be addressed later in this report. However, a rigorous discussion of all these issues, such as reference and standard states used for thermodynamic data compiled in difference sources, is beyond the scope of this report. For this background information, the reader should review the introductory sections of thermodynamic data compilations such as those by Wagman et al. (1982) and Robie and Hemingway (1972, 1995), as well as references such as Langmuir (1997) and Nordstrom and Munoz (1985).

Fundamental to modeling such geochemical equilibria is the need for thermodynamic values for Gibbs free energy of formation ($\Delta_f G_T°$) or for the common logarithm (base 10) of the equilibrium constant of reaction ($\log K_{r,T}°$), for each gaseous, aqueous, liquid, and solid species of interest. Equation (3.1) provides a general reaction (or equilibrium):

$$aA + bB = cC + dD \tag{3.1}$$

where the lower-case letters refer to the number of moles of reactants A and B and products C and D, the $\log K_{r,T}°$ is defined in Equation (3.2):

$$\log K_{r,T}^{o} = - \frac{\Delta_r G_T^{o}}{2.303\ R\ T} \tag{3.2}$$

where $\Delta_r G_T°$ is the change in Gibbs free energy for the specified reaction at temperature T, R is the gas constant [8.31451 J/(mol·K)], and T is temperature in degrees Kelvin.[1] As most published compilations of thermodynamic data and computer model thermodynamic databases list thermodynamic values at reference conditions of T = 298.15 K (25.0 °C) and P = 1 bar (10^5 pascals or 0.98 atm), Equation (3.2) becomes Equation (3.3):

$$\log K_{r,298}^{o} = - \frac{\Delta_r G_{298}^{o}}{5709.07} \tag{3.3}$$

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[1] Thermodynamic values are by convention referenced to the Kelvin temperature scale.

where $\Delta_r G_{298}°$ is in J/mol. For reaction in Equation (3.1), $\Delta_r G_{298}°$ in Equation (3.3) equates to that in Equation (3.4):

$$\Delta_r G_{298}^{o} = c\Delta_f G_{298,C}^{o} + d\Delta_f G_{298,D}^{o} - a\Delta_f G_{298,A}^{o} - b\Delta_f G_{298,B}^{o} \tag{3.4}$$

where $\Delta_f G_{298}°$ is the standard molar Gibbs free energy of formation at 298.15 K for the indicated reactant or product (as shown by capital letter in subscript).

For any substance *i* at 298.15 K and 1 bar, $\Delta_f G_{298}°$ is defined in Equation (3.5):

$$\Delta_f G_{298}^{o} = \Delta_f H_{298}^{o} + T\ \Delta_f S_{298}^{o} \tag{3.5}$$

where $\Delta_f H_{298}°$ is the standard molar enthalpy of formation and $\Delta_f S_{298}°$ is entropy of formation of substance *i*. The entropy of formation is the difference of $S_{298}°$ for substance *i* and the sum of the $S_{298}°$ values for its constituent elements in their standard reference states at the specified T and P conditions.

Values of $\Delta_f G_T°$ and $\log K_{r,T}°$ can be calculated at temperatures other than 298.15 K if data exist for parameters such as $\Delta_f H_T°$ and $S_T°$ as a function of temperature from 298.15 K to T of interest. At temperatures other than 298.15 K, Equation (3.6) is defined as follows:

$$\Delta_f G_T^{o} = \Delta_f H_T^{o} + T\ \Delta_f S_T^{o} \tag{3.6}$$

The enthalpy of formation at temperature T ($\Delta_f H_T°$) can be derived from $\Delta_f H_{298}°$ and $\Delta(H_T° – H_{298}°)$, which is the difference in relative enthalpy for substance *i* and its constituent elements between temperature T and 298.15 as shown in Equation (3.7):

$$\Delta_f H_T^{o} = \Delta_f H_{298}^{o} + \Delta(H_T^{o} - H_{298}^{o}) \tag{3.7}$$

The relative enthalpy for substance *i* at temperature T in turn is related to its molar heat capacity ($C_p°$) measured as a function of temperature from 298.15 K to T as shown in Equation (3.8):

$$H_T^{o} - H_{298}^{o} = \int_{298}^{T} C_P^{o} dT \tag{3.8}$$

Similarly, the entropy for substance *i* at temperature T is related to its molar heat capacity ($C_p°$) from 298.15 K to T as shown in Equation (3.9):

$$S_T^{o} = S_0^{o} + \int_0^T \frac{C_P^{o}}{T} dT = (S_0^{o} + \int_0^{298} \frac{C_P^{o}}{T} dT) + \int_{298}^{T} \frac{C_P^{o}}{T} dT = S_{298}^{o} + \int_{298}^{T} \frac{C_P^{o}}{T} dT \tag{3.9}$$

where $S_0°$ and $S_{298}°$ are the entropies of substance *i* at absolute zero (T = 0.0 K) and 298.15 K, respectively.

In the absence of any structural transitions (e.g., change from trigonal to monoclinic) or phase changes (e.g., melting), $C_p°$ is typically a well-behaved function for most substances especially at temperatures above 298.15 K. When high temperature $C_P°$ values are reported in the literature, the values are commonly fitted by an empirical equation as a function of temperature (e.g., Robie and Hemingway 1995). These equations can be used to interpolate $C_P°$ values at any temperature between the minimum and maximum temperatures used for fitting or to easily do the $C_P°$ integrations necessary to derive values for $\Delta(H_T° - H_{298}°)$ and $S_T°$ as defined by Equations (3.8) and (3.9), respectively. Two functions commonly used to represent $C_P°$ as a function of temperature include what is now referred to as the Maier–Kelly equation (Maier and Kelly 1932):

$$C_P{}^{o} = a + bT + \frac{c}{T^2} \tag{3.10}$$

and an extended form of Equation (3.10)

$$C_P{}^{o} = a + bT + \frac{c}{T^2} + \frac{d}{T^{0.5}} + eT^2 \tag{3.11}$$

which was suggested by Hass and Fisher (1976). Typically, Equation (3.11) provides a superior fit to highly precise $C_P°$ measurements. However, extrapolations using the extended Equation (3.11) beyond the temperature limits used for fitting are not valid physically, whereas the Maier–Kelly equation can usually be extrapolated with fair predictability for a short temperature range (Krupka et al. 1985). The reader should refer to Nordstrom and Munoz (1985) for a discussion of technical issues related to the fitting of $C_P°$ data sets with empirical equations.

A variety of techniques can be used to measure or estimate the thermodynamic properties of gases, liquids, aqueous species, and solids relevant to geochemical systems. Nordstrom and Munoz (1985) present a good review of these methods. Possible measurement techniques include calorimetric measurements, phase-equilibria studies, volume measurements, solubility measurements, conductivity measurements, and electromotive force measurements. Because spectrophotometric and spectroscopic techniques provide information about the structures of gases, aqueous species, liquids, and solids, data from these methods can also be used to help derive or estimate thermodynamic values.

4.0 Carbonate Mineralogy

This section presents a brief review of mineralogy of the most common carbonate species. It also provides some perspective for later sections that discuss the extent of thermodynamic data available for carbonate minerals. For more detailed reviews of the geochemistry, mineralogy, crystal chemistry, and phase relations of carbonate minerals, readers are referred to such sources as Morse and Mackenzie (1990), Railsback (1999), and the review papers in Reeder (1983b).

Carbonate minerals are one of the most common groups of non-silicate minerals. They are found in several rock types including sedimentary rocks such as limestones, dolomites, evaporites; metamorphosed carbonate sediments such as marbles; and ultrabasic igneous rocks such as carbonatites and serpentinites. Carbonate minerals are also common in soils and sediments. In sandstones and other detrital rocks, carbonate minerals are present as cements between mineral grains, coatings on grains, and/or fillings in the interstitial spaces between grains. The crystal chemistry and phase relations of carbonate sedimentary rocks and secondary carbonate mineralization in detrital rocks are pertinent to understanding the impact of CO_2 injection and sequestration to the carbonate geochemistry of the aquifer host rock.

Although most geoscientists know of one or two dozen carbonate minerals, there are at least 277 carbonate-containing minerals (Railsback 1999). Although calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] make up more than 90% of the natural rock-forming carbonate minerals, Railsback (1999) advises researchers not to limit their thinking and analyses of mineral systems to the familiar divalent cation carbonate minerals. In addition to the natural geological systems that have historically been studied by geoscientists, geoscience research today also includes a diverse range of studies in support of contaminant remediation technologies that are based on mineral systems and of cleanup or siting of surface and subsurface geological systems that have been or will be impacted by anthropogenic activities. Railsback (1999) suggests that more thorough mineralogical characterization by x-ray diffraction, electron microscopy, and various spectroscopy techniques may possibly show greater mineralogical diversity than traditional assumptions would suggest for such environmental systems.

To help show the diversity of carbonate-containing minerals discussed by Railsback (1999), we have included in the appendix listings of mineral names and formula for the following:

- Pure carbonate minerals in which only HCO_3^-, CO_3^{2-}, OH^-, or O^{2-} account for all the negative charge
- Carbonate-containing minerals that contain chloride, sulfate, or fluoride
- Carbonate-containing minerals that contain phosphate or silicate
- Carbonate-containing minerals that contain two or more other anions.

These tables were prepared from the extensive listing of carbonate-containing minerals compiled by LB Railsback (Department of Geology, University of Georgia, Athens, Georgia) with help of JA Mandarino (Royal Ontario Museum, Toronto, Ontario, Canada). Railsback's tables are provided online at http://www.gly.uga.edu/railsback/CO3mins_intro.html, and as an appendix to his 1999 paper on "Patterns in the Compositions, Properties, and Geochemistry of Carbonate Minerals" in *Carbonates and*

Evaporites (Railsback 1999). Railsback notes that many of the carbonate-containing minerals listed in his tables would not be classified as carbonate minerals but derive at least part of their negative charge from CO_3^{2-} or HCO_3^-.

To limit the number of minerals listed in the tables in our appendix, the authors of this report did not include any carbonate-containing minerals tabulated by Railsback (1999), which include As, B, Ba, Bi, Cd, Ce, Co, Cr, Cu, F, Ge, Hg, La, Li, NH_4, Nb, Nd, Ni, Pb, REE, Sr, Ta U, Y, Zn, and/or Zr. This was done because there is an assumed lack of importance of such carbonate-species to CO_2 sequestration. However, it should be noted that carbonate-containing minerals containing transition metals and non-carbonate anions may exert important geochemical controls on the solution concentrations and environmental mobility of these metals and non-carbonate anions even though the particular carbonate-containing mineral makes up a small weight percentage of the total mineralogy of the aquifer system.

Carbonate minerals can be grouped as 1) anhydrous normal carbonates, 2) hydrated normal carbonates, 3) acid carbonates (bicarbonates), and 4) compound carbonates containing hydroxide, halide, or other anions in addition to the carbonate. Carbonate minerals are defined as mineral[1] species that contain the carbonate ion (CO_3^{2-}) as the fundamental anionic unit. The CO_3 group occurs as a rigid structure consisting of one central C atom surrounded by three O atoms in a trigonal planar arrangement. Most of the common carbonates belong to the anhydrous normal carbonate group. Carbonate minerals of the other three groups are less common to very rare, and are typically associated with relatively low temperature geological environments.

Calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$], and aragonite ($CaCO_3$) are probably the most commonly known of all the carbonate minerals. Calcite and dolomite are the most abundant and constitute more than 90% of the natural rock-forming carbonate minerals (Reeder 1983a). Calcite and aragonite are two of five $CaCO_3$ minerals known to naturally exist. There are three crystalline anhydrous $CaCO_3$ polymorphs[2] – calcite, aragonite, and vaterite, and amorphous anhydrous $CaCO_3$ is also known. The $CaCO_3$ polymorphs and their crystallization and transformation mechanisms are discussed in Carlson (1983), Cölfen (2003), Jiménez-López et al. (2001), Kitamura (2001), Nissenbaum et al. (2008), Ogino et al. (1987, 1990), Perdikouri et al. (2008), and the references therein. Crystals of calcite, aragonite, and vaterite are typically rhombohedral, acicular (needle-like), and polycrystalline spherical, respectively, in morphology. Thermodynamically, calcite is considered the most stable $CaCO_3$ polymorph at ambient conditions. Aragonite is a high pressure, low temperature $CaCO_3$ polymorph, which can also form at ambient pressure and temperature conditions by biomineralization processes. Vaterite is the rarest and most soluble of the three $CaCO_3$ polymorphs. Although vaterite can form under laboratory conditions that produce rapid $CaCO_3$ supersaturation, vaterite is considered metastable with respect to calcite and aragonite and to the geochemical conditions of sedimentary systems (Morse and Mackenzie [1990] and references therein). Morse et al. (2008) have reported the precipitation of vaterite crystals on substrates of Iceland spar calcite in high-ionic strength NaCl solutions. The vaterite subsequently recrystallized to

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[1] A mineral is defined as a solid that must have a crystalline structure, must be homogeneous substance with a defined chemical composition, and must have formed as a result of naturally occurring geological processes. Although traditional definitions excluded organically derived solids, modern mineral classifications include an organic class. Naturally occurring solid substances that do not meet this definition are typically referred to as mineraloids. Examples include obsidian, opal, jet, and pearls.

[2] Polymorphism is a characteristic of a chemical substance with a defined composition to crystallize in more than one crystal form.

euhedral calcite crystals. Anhydrous amorphous $CaCO_3$ is a transient phase, which also occurs as a product of biomineralization. Two hydrous $CaCO_3$ minerals also exist; these include ikaite ($CaCO_3 \cdot 6H_2O$) and monohydrocalcite ($CaCO_3 \cdot H_2O$). Their formation is favored by low temperatures and high hydrostatic pressures (Morse and Mackenzie 1990).

Besides calcite, dolomite, and aragonite, other commonly known, but less abundant, carbonates include the alkaline earth- and transition metal-containing minerals such as the following:

- ankerite [$CaFe(CO_3)_2$]
- artinite [$Mg_2CO_3(OH)_2 \cdot 3H_2O$]
- azurite [$Cu_3(CO_3)_2(OH)_2$]
- cerussite ($PbCO_3$)
- huntite [$Mg_3Ca(CO_3)_4$]
- hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$]
- magnesite ($MgCO_3$)
- malachite [$Cu_2CO_3(OH)_2$]
- nahcolite ($NaHCO_3$)
- natrite (Na_2CO_3)
- natron ($Na_2CO_3 \cdot 10H_2O$)
- nesquehonite ($MgCO_3 \cdot 3H_2O$)
- otavite ($CdCO_3$)
- rhodochrosite ($MnCO_3$)
- siderite ($FeCO_3$)
- smithsonite ($ZnCO_3$)
- soda (natron) ($Na_2CO_3 \cdot 10H_2O$)
- strontianite ($SrCO_3$)
- thermonatrite ($Na_2CO_3 \cdot H_2O$)
- trona ($Na_3HCO_3CO_3 \cdot 2H_2O$)
- witherite ($BaCO_3$)

The anhydrous normal carbonates can be divided into two groups depending on the ionic radii of the cation. In one of these two groups, the carbonates crystallize with rhombohedral (trigonal) symmetry (calcite type) in which the cations are in six-fold coordination with the O atoms. Reeder (1983a) and Goldsmith (1983) discuss in detail with extensive supporting references the crystal chemistry and phase relations, respectively, of rhombohedral carbonates. Calcite and dolomite are examples of carbonates that form in this group. In the second group, the carbonates have orthorhombic symmetry (aragonite type) where the cations are in nine-fold coordination with O atoms. Speer (1983) reviews in detail with extensive supporting references the crystal chemistry and phase relations of orthorhombic carbonates. The six-fold and nine-fold coordination sites in these two carbonate structure groups can accommodate relatively small (e.g., Fe^{2+}, Mg^{2+}, Mn^{2+}, and Zn^{2+}) and large cations (e.g., Ba^{2+}, Pb^{2+}, and Sr^{2+}), respectively, with Ca^{2+} fortuitously on the limit of cation sizes for the two groups. This relationship between carbonate structure symmetry and cation sizes is shown by the values listed in Table 4.1.

In the calcite structure group, the divalent atoms are located at the points of a face-centered rhombohedron, and the CO_3^{2-} groups are positioned midway between the Ca atoms along rows parallel to the rhombohedral cleavage edges. Magnesite, rhodochrosite, siderite, and smithsonite are isostructural[1] with calcite. In the dolomite structure, there is a regular ordered substitution of alternate Ca atoms along the *c* axis in the calcite rhombohedral structure by another divalent metal such as Fe^{2+}, Mg^{2+}, or Mn^{2+}. Examples of carbonates with this structure type include dolomite and ankerite. The highly ordered structure of dolomite is believed to inhibit its precipitation from aqueous solutions at low temperatures.

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[1] Isostructural is a characteristic of two or more chemical substances with similar crystal structures but do not exhibit polymorphism (i.e., not having the same composition).

Dolomite formation continues to be debated and discussed in further detail in most journal articles and textbooks that address the geochemistry of sedimentary carbonates.

Table 4.1. Anhydrous Normal Carbonate Minerals Listed as a Function of Cation Radius (in Å) Versus Carbonate Structure Symmetry

Mineral Name	**Formula**	**Cation Radius[(a)] (Å)**	**Structure Symmetry**
Magnesite	$MgCO_3$	0.72	Rhombohedral
Smithsonite	$ZnCO_3$	0.74	Rhombohedral
Siderite	$FeCO_3$	0.78	Rhombohedral
Rhodochrosite	$MnCO_3$	0.83	Rhombohedral
Otavite	$CdCO_3$	0.95	Rhombohedral
Calcite	$CaCO_3$	1.00	Rhombohedral
Aragonite	$CaCO_3$	1.00	Orthorhombic
Strontianite	$SrCO_3$	1.18	Orthorhombic
Cerussite	$PbCO_3$	1.19	Orthorhombic
Witherite	$BaCO_3$	1.35	Orthorhombic
(a) Values for cation radii are from Shannon (1976).			

In the aragonite structure, the Ca atoms lie approximately in the positions of hexagonal close packing that gives aragonite a pseudo-hexagonal character. The CO_3 groups form planar trigonal groups parallel to [001], and each CO_3 lies between six Ca atoms. Cerussite, strontianite, and witherite are isostructural with aragonite.

In contrast to Ca-containing carbonates that are mostly anhydrous, there are several hydrous Mg carbonates. Hydrated carbonates have different crystal structures than anhydrous carbonates and many have monoclinic crystal symmetries. In modern sediments, some hydrous Mg carbonates are more common that anhydrous magnesite and dolomite. This is estimated to be due to the high energy of hydration of the Mg ion relative to the Ca ion (Morse and Mackenzie 1990).

Solid solutions of different carbonate minerals are common. A solid solution is defined as a compositional variation of a crystalline substance due to substitution or omission of various atomic constituents within a crystal structure, within limits determined by the degree of deformation allowed by the crystal structure. The extent of solid solution depends upon the charges and relative sizes of the constituent ions, the coexistence and composition of other minerals or liquid, and the temperature and pressure conditions of formation. For the purpose of this report, the term “coprecipitation” refers to the process of the substitutional or interstitial incorporation of trace concentrations of metals (or anions) during the formation of minerals. However, the term “solid solution” is typically used to refer to more extensive compositional variations, such as a few 10s to a 100 mol%. When the concentration of a coprecipitate reaches considerable level (e.g., greater than 1%), its presence in the structure can significantly affect the chemical properties, such as solubility, of that mineral. Morse and Mackenszie (1990) present the general concepts of coprecipitation reactions and solid solutions of carbonate minerals.

Examples of carbonate solid solutions include the random substitution of Mg for Ca in the calcite structure, and Sr for Ca in aragonite structure. Calcite containing a range of Mg in solid solution is usually termed Mg (or magnesian) calcites. Mackenzie et al. (1983) presents a detailed review of Mg calcites. In some instances, biogenic calcites may contain up to 30 mol% Mg. Magnesian calcites are usually described as either low Mg-calcites with less than 5 mol% Mg, or high Mg-calcites with 5–30 mol% Mg (Appelo and Postma 2005).

Dolomite also exhibits solid solution. The Ca-to-Mg ratio may vary and substitution of Fe and Mn is common in dolomites. However, note that dolomite is structurally different than 50 mol% high Mg-calcite. In dolomite, the Mg atoms are substituted in a regular order with alternate Ca atoms along the *c* axis, whereas the Ca and Mg atoms in a Mg calcite are distributed more or less randomly. Therefore, dolomite should be treated thermodynamically as a pure phase, while a solid solution model applies for the thermodynamic properties of Mg calcites (Appelo and Postma 2005). Dolomite and ankerite end members also form part of a solid solution series that extends from $CaMg(CO_3)_2$ to 70 mol% $CaFe(CO_3)_2$. The boundary between dolomite and ankerite is arbitrarily set at 20 mol% $CaFe(CO_3)_2$.

Carbonate mineral solid solutions and their effect on CO_2 sequestration reactions are discussed further in a later section of this report.

5.0 Literature Review

As a starting point for this assessment, published literature was reviewed to identify studies pertaining to computer modeling simulations, field injection sites, natural analogue sites, and laboratory fluid-rock and -mineral studies of the carbonate reactions associated with the subsurface injection and sequestration of CO_2 and acid gases (co-injection of H_2S or SO_2 with CO_2). Our review was extensive and provides a reasonable cross section of the types of geochemical reaction modeling, site, and laboratory studies of CO_2 sequestration that have been completed or are ongoing by the research and development community. The literature material included our review is based on literature published primarily through the end of September 2009.

This review was completed by a combination of using online computerized search tools and literature databases and then identifying additional relevant publications by examining the reference lists in publications found through the online searches. However, our review was not intended to be completely comprehensive and capture every published study related to the geochemistry of CO_2 sequestration. As typically is the case for such reviews, we likely missed some relevant published studies, such as those published in proceedings from technical meetings or as company technical reports. These types of publications are not indexed for online search tools, referenced in journal publications, and/or not readily available to the public.

Those studies identified via the literature review that pertain to computer modeling simulation, field injection site, natural analogues, and laboratory fluid-rock and -mineral studies of the carbonate reactions are listed in Tables 5.1, 5.2, 5.3, and 5.4, respectively. The studies in Table 5.1 describe the results of essentially modeling simulation studies only, and typically do not present any new site geochemical characterization data from field injection and natural analogue sites or from laboratory fluid-rock or -mineral studies. Many of the studies listed in Tables 5.2, 5.3, and 5.4 also include the application of geochemical reaction models and are so noted. In these studies, geochemical reaction models were used to interpret characterization data from site or laboratory studies and/or complete sensitivity analyses to evaluate how the geochemistry at a site or in the fluid-rock materials in an autoclave might respond to changes in geochemical parameters such as temperature, CO_2 pressure, fluid chemistry, and/or mineralogy. Some of the cited studies in Tables 5.1 through 5.4 are only available at the time this report was published (September 2010) as extended abstracts. These abstracts were published in *Geochimica et Cosmochimica Acta*, and were for presentations given at recent Goldschmidt Conference meetings, which is one of the premier annual conferences in geochemistry. These abstracts were included in our review, because they are published (and accessible) in a prestigious journal and represent studies of ongoing or recently completed studies in the geochemistry of CO_2 sequestration.

Note that Table 5.4 includes two studies related to the carbonate geochemistry of CO_2 sequestration as affected by biotic reactions involving microorganisms. Although only two studies were identified (both published as abstracts from Goldschmidt Conferences), both biotic and abiotic processes studies should be considered with respect to thermodynamic data needs associated with modeling geochemical reactions associated with CO_2 sequestration.

Table 5.1. Computer Modeling Simulation Studies of the Carbonate Reactions Associated with CO_2 Sequestration

Reference	Sites or Conditions Studied	Computer Code(s) Used for Geochemical Reaction Modeling
Allen et al. (2005)	CO_2 gas and calcite solubility in NaCl fluid; fluid-rock interactions in a natural brine contacting a fictitious sandstone (quartz, K-feldspar, albite, and kaolinite)	Geochemist's Workbench, PHREEQC, and CO_2 solubility models of Enick and Klara (1990) and Duan and Sun (2003)
	Title of Reference: Modeling Carbon Dioxide Sequestration in Saline Aquifers: Significance of Elevated Pressures and Salinities	
André et al. (2007)	Dogger Aquifer (carbonate reservoir), Paris Basin, France	TOUGHREAC; SCALE2000
	Title of Reference: Numerical Modeling of Fluid-Rock Chemical Interactions at the Supercritical CO_2-Liquid Interface during CO_2 Injection into a Carbonate Reservoir, the Dogger Aquifer (Paris Basin, France)	
Audigane et al. (2007)	Utsira formation in Sleipner West natural gas field, North Sea	TOUGHREACT
	Title of Reference: Two-Dimensional Reactive Transport Modeling of CO_2 Injection in a Saline Aquifer at the Sleipner Site, North Sea	
Bachu and Adams (2003)	Viking aquifer; Alberta Basin; Canada	SOLMINDB; SOLMINEQ
	Title of Reference: Sequestration of CO_2 in Geological Media in Response to Climate Change: Capacity of Deep Saline Aquifers to Sequester CO_2 in Solution	
Brosse et al. (2005)	Limestone made of pure calcite	DIAPHORE
	Title of Reference: Modeling Fluid-Rock Interaction Induced by the Percolation of CO_2-Enriched Solutions in Core Samples: The Role of Reactive Surface Area	
Cantucci et al. (2009a) (abstract only)	Saline reservoirs relative to sites in Italy	TOUGHREACT
	Title of Reference: Overview of the Geochemical Modeling on CO_2 Capture and Storage in Italian Feasibility Studies	
Cantucci et al. (2009b)	CO_2 injection enhancing oil recovery project at Weyburn Oil Field in Saskatchewan, Canada	PHREEQC
	Title of Reference: Geochemical Modeling of CO_2 Storage in Deep Reservoirs: The Weyburn Project (Canada) Case Study	
Carey and Lichtner (2007)	Carbonation of oilwell cement; SACROC Unit reservoir (continuous CO_2-flooding operation) (see Carey et al. [2007] in Table 5.2) in the Cisco and Canyon formations with the Wolfcamp shale forming the caprock, in the Permian Basin in West Texas, United States	FLOTRAN
	Title of Reference: Calcium Silicate Hydrate (C-S-H) Solid Solution Model Applied to Cement Degradation Using the Continuum Reactive Transport Model FLOTRAN	

Table 5.1. (contd)

Reference	Sites or Conditions Studied	Computer Code(s) Used for Geochemical Reaction Modeling
Cipolli et al. (2004)	Serpentinite aquifers such as serpentinites of the Gruppo di Voltri, Genova, Italy	EQ3/EQ6
	Title of Reference: Geochemistry of High-pH Waters from Serpentinites of the Gruppo di Voltri (Genova, Italy) and Reaction Path Modeling of CO_2 Sequestration in Serpentinite Aquifers	
Ennis-King and Paterson (2007)	Calcite/anorthite-cemented sandstone and a siliciclastic sandstone	TOUGHREACT
	Title of Reference: Coupling of Geochemical Reactions and Convective Mixing in the Long-Term Geological Storage of Carbon Dioxide	
Flukiger and Bernard (2009)	Dissolution of a limestone that is assumed to be pure calcite	Not named
	Title of Reference: A New Numerical Model for Pore Scale Dissolution of Calcite due to CO_2 Saturated Water Flow in 3D Realistic Geometry: Principles and First Results	
Gaus et al. (2005)	Nordland shale cap rock at Sleipner, North Sea	PHREEQC
	Title of Reference: Reactive Transport Modelling of the Impact of CO_2 Injection on the Clayey Cap Rock at Sleipner (North Sea)	
Gherardi et al. (2007)	Caprock consisting of carbonate-rich shale	TOUGH-REACT
	Title of Reference: Numerical Modeling of Self-Limiting and Self-Enhancing Caprock Alteration Induced by CO_2 Storage in a Depleted Gas Reservoir	
Gunter et al. (2000)	Deep siliciclastic and carbonate aquifers in the Alberta Sedimentary Basin, Canada	PATHARC.94
	Title of Reference: Aquifer Disposal of Acid Gases: Modelling of Water-Rock Reactions for Trapping of Acid Wastes	
Gysi and Stefánsson (2008)	Basaltic glass from Stapafee, southwest Iceland	PHREEQC
	Title of Reference: Numerical Modelling of CO_2-Water-Basalt Interaction	
Hurter et al. (2007) (abstract only)	Northern German Basin	No details
	Title of Reference: Simulations of Dry-Out and Halite Precipitation due to CO_2 Injection	
Izgec et al. (2008b)	Carbonate formations – Midyat formation, southeast Turkey; and St. Maximim, France	STARS, also see Izgec et al. (2008a) in Table 5.4
	Title of Reference: CO_2 Injection into Saline Carbonate Aquifer Formations II: Comparison of Numerical Simulations to Experiments	

Table 5.1. (contd)

Reference	Sites or Conditions Studied	Computer Code(s) Used for Geochemical Reaction Modeling
Johnson et al. (2001)	Shale-capped sandstone aquifer at Sleipner facility, North Sea	NUFT
	Title of Reference: Reactive Transport Modeling of Geologic CO_2 Sequestration in Saline Aquifers: The Influence of Intra-Aquifer Shales and the Relative Effectiveness of Structural, Solubility, and Mineral Trapping During Prograde and Retrograde Sequestration	
Johnson et al. (2004)	Shale-capped sandstone aquifer at Sleipner facility, North Sea	NUFT
	Title of Reference: Reactive Transport Modelling of CO_2 Storage in Saline Aquifers to Elucidate Fundamental Processes, Trapping Mechanisms, and Sequestration Partitioning	
Kervévan et al. (2005)	Carbonated reservoir with brine composition from Smackover site, Arkansas, United States	SCALE2000; PHREEQC
	Title of Reference: Improvement of the Calculation Accuracy of Acid Gas Solubility in Deep Reservoir Brines: Application to the Geological Storage of CO_2	
Knauss et al. (2005)	Frio Formation pilot site, Texas, United States	CRUNCH
	Title of Reference: Evaluation of the Impact of CO_2, Co-contaminant Gas, Aqueous Fluid and Reservoir Rock Interactions on the Geologic Sequestration of CO_2	
Kühn and Clauser (2007) (abstract only)	Sandstone aquifers in Germany	No details of modeling
	Title of Reference: Reactive Transport Simulation of Mineral Trapping of CO_2 in Operated Geothermal Aquifers	
Lagneau et al. (2005)	Carbonate aquifer of the Dogger, Paris Basin in France; sandstone aquifer of the Bunter in the North Sea	Chess
	Title of Reference: Reactive Transport Modelling of CO_2 Sequestration in Saline Aquifers	
Mito and Nakagawa (2009) (abstract only)	Deep saline aquifer at pilot-scale CO_2 injection test at Nagaoka site in Japan	PHREEQC
	Title of Reference: Influence of Formation Water Composition on Mineral Trapping of CO_2	
Ozah et al. (2005)	Deep saline aquifer typical of U.S. Gulf Coast	GEM-GHG
	Title of Reference: Numerical Simulation of the Storage of Pure CO_2 and CO_2-H_2S Gas Mixtures in Deep Saline Aquifers	
Palandri and Kharaka (2005)	Fe^{III}-bearing quartz arenite (synthetic redbed)	CHILLER; GAMSPATH
	Title of Reference: Ferric Iron-Bearing Sediments as a Mineral Trap for CO_2 Sequestration: Iron Reduction Using Sulfur-Bearing Waste Gas	

Table 5.1. (contd)

Reference	Sites or Conditions Studied	Computer Code(s) Used for Geochemical Reaction Modeling
Pruess et al. (2004); Pruess et al. (2002)	Problem 5 in Pruess et al. (2004) addresses geochemical effects of CO_2 injection into glauconitic sandstone	TOUGHREAC, FLOTRAN, CHEM-TOUGH2
	Title of Reference: Code Intercomparison Builds Confidence in Numerical Simulation Models for Geologic Disposal of CO_2	
Saylor and Zerai (2004)	Rose Run Sandstone, Ohio	Geochemist's Workbench
	Title of Reference: Injection and Trapping of Carbon Dioxide in Deep Saline Aquifers	
White et al. (2005)	White Rim Sandstone, Colorado Plateau, Utah	ChemTOUGH
	Title of Reference: Simulation of Reactive Transport of Injected CO_2 on the Colorado Plateau, Utah, USA	
Xu et al. (2003)	Gulf Coast sediment of the United States	TOUGHREACT
	Title of Reference: Reactive Geochemical Transport Simulation to Study Mineral Trapping for CO_2 Disposal in Deep Arenaceous Formations	
Xu et al. (2004)	Glauconitic sandstone aquifer from the Alberta Sedimentary Basin, Gulf Coast sediment of the United States, dunite (monomineralic rock consisting essentially of olivine)	TOUGHREACT
	Title of Reference: Numerical Simulation of CO_2 Disposal by Mineral Trapping in Deep Aquifers	
Xu et al. (2005)	Sandstone and shale layers representative of Texas Gulf Coast sediment of the United States	TOUGHREACT
	Title of Reference: Mineral Sequestration of Carbon Dioxide in a Sandstone-Shale System	
Xu et al. (2006)	Gulf Coast sediment of the United States	TOUGHREACT
	Title of Reference: TOUGHREACT - A Simulation Program for Non-Isothermal Multiphase Reactive Geochemical Transport in Variably Saturated Geologic Media: Applications to Geothermal Injectivity and CO_2 Geological Sequestration	
Xu et al. (2007)	Co-injection of H_2S or SO_2 with CO_2 into an arkose formation as typically encountered in Gulf Coast aquifers of the United States	TOUGHREACT
	Title of Reference: Numerical Modeling of Injection and Mineral Trapping of CO_2 with H_2S and SO_2 in a Sandstone Formation	
Zerai et al. (2006)	Rose Run Sandstone, Ohio	Geochemist's Workbench
	Title of Reference: Computer Simulation of CO_2 Trapped through Mineral Precipitation in the Rose Run Sandstone, Ohio	

Table 5.1. (contd)

Reference	Sites or Conditions Studied	Computer Code(s) Used for Geochemical Reaction Modeling
Zhang et al. (2009)	Songliao Basin, China - proposed injection formation is saline sandstone formation (quartz, kaolinite, illite, chlorite, calcite, plagioclase, and lesser amounts of K-feldspar, zeolite, pyrite, and anhydrite)	TOUGHREACT
	Title of Reference: Long-Term Variations of CO_2 Trapped in Different Mechanisms in Deep Saline Formations: A Case Study of the Songliao Basin, China	
Zwingmann et al. (2005)	Modeling done prior to CO_2 injection; Haizume Formation, Niigata Basin, Japan – injection formation is sedimentary formation (quartz, plagioclase, feldspar, pyroxene, and clays) covered by a mudstone seal	EQ3/EQ6
	Title of Reference: Preinjection Characterisation and Evaluation of CO_2 Sequestration Potential in the Haizume Formation, Niigata Basin, Japan. Geochemical Modelling of Water-Minerals-CO_2 Interaction	

Table 5.2. Studies of Mineral Characterization Data and/or Geochemical Analyses at CO_2 Field Injection Sites

Reference	Site(s) Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Alfredsson and Gislason (2009) (abstract only)	Basaltic Rock: Chemistry of the Rocks and Waters at the Injection Site, Hellisheidi, southwestern Iceland	None discussed	Yes	PHREEQC
	Title of Reference: CarbFix - CO_2 Sequestration in Basaltic Rock: Chemistry of the Rocks and Waters at the Injection Site, Hellisheidi, SW-Iceland			
Assayag et al. (2009)	Lamont-Doherty Earth observatory test site (New York, United States) – injection at contract between dolerites and underlying Newark Basin metamorphosed sediments	None discussed	None discussed	
	Title of Reference: Water-Rock Interactions during a CO_2 Injection Field-Test: Implications on Host Rock Dissolution and Alteration Effects			
Assayag et al. (2008) (abstract only)	Lamont-Doherty Earth observatory test site (New York, United States) – injection at contract between dolerites and underlying Newark Basin metamorphosed sediments	None discussed	None discussed	
	Title of Reference: CO_2 Ionic Trapping by Water-Rock Interactions during a Push-Pull Test in a Basaltic-Metasedimentary Aquifer			
Carey et al. (2007)	Carbonation of oilwell cement; SACROC Unit reservoir (continuous CO_2-flooding operation) (see Carey and Lichtner [2007] in Table 5.1) in the Cisco and Canyon formations with the Wolfcamp shale forming the caprock, in the Permian Basin in West Texas, United States	Limestone reservoir is mostly calcite with lesser ankerite; carbonated cement contains calcite and aragonite; vein-fillings at cement-casing interface contain calcite and aragonite; carbonates at cement-shale interface include calcite, aragonite, and vaterite (and possibly dawsonite); matrix of shale fragment zone contains the carbonates calcite, aragonite, and dolomite	Yes	FLOTRAN
	Title of Reference: Analysis and Performance of Oil Well Cement with 30 Years of CO_2 Exposure from the SACROC Unit, West Texas, USA			

Table 5.2. (contd)

Reference	Site(s) Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Emberley et al. (2004)	Weyburn Oil Field, Saskatchewan, Canada	None discussed	Yes	Not identified
	Title of Reference: Geochemical Monitoring of Fluid-Rock Interaction and CO_2 Storage at the Weyburn CO_2-Injection Enhanced Oil Recovery Site, Saskatchewan, Canada			
Emberley et al. (2005)	Weyburn Oil Field, Saskatchewan, Canada	None discussed	Yes	SOLMINEQ.88
	Title of Reference: Monitoring of Fluid-Rock Interaction and CO_2 Storage Through Produced Fluid Sampling at the Weyburn CO_2-Injection Enhanced Oil Recovery Site, Saskatchewan, Canada			
Gislason et al. (2009) (abstract only)	Overview – field, laboratory and modeling studies of basalt at the Hellisheidi, Injection Site in southwestern Iceland	None discussed	Yes	Not identified
	Title of Reference: The Carbfix Project: Mineral CO_2 Sequestration into Basalt			
Gislason et al. (2010)	Overview – field, laboratory and modeling studies of basalt at the Hellisheidi, Injection Site in southwestern Iceland	None discussed	Yes	Not identified
	Title of Reference: Mineral Sequestration of Carbon Dioxide in Basalt: A Pre-injection Overview of the Carbfix Project			
Goldberg et al. (2008)	Review of the feasibility of CO_2 sequestration in deep sea basalts such as Juan de Fuca ridge	None discussed	None discussed	
	Title of Reference: Carbon Dioxide Sequestration in Deep-Sea Basalt			
Kharaka et al. (2006a)	Sandstone sections of the Frio Formation pilot site, Texas, United States	None discussed	Yes	SOLMINEQ
	Title of Reference: Gas-Water-Rock Interactions in Frio Formation Following CO_2 Injection: Implications for the Storage of Greenhouse Gases in Sedimentary Basins			
Kharaka et al.(2006b)	Sandstone sections of the Frio Formation pilot site, Texas, United States	None discussed	Yes	SOLMINEQ
	Title of Reference: Gas-Water-Rock Interactions in Sedimentary Basins: CO_2 Sequestration in the Frio Formation, Texas, USA			
Kharaka et al. (2007) (abstract only)	Sandstone sections of the Frio Formation pilot site, Texas, United States	None discussed	Yes	Not identified
	Title of Reference: Potential Environmental Issues of CO_2 Storage in Saline Aquifers: Geochemical Results from the Frio Brine Pilot Tests, Texas, USA			

Table 5.2. (contd)

Reference	Site(s) Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Machel (2005)	Nisku Q-Pool in Alberta, Canada	Formation has dolomite with minor amounts of calcite	None discussed	
	Title of Reference: Geological and Hydrogeological Evaluation of the Nisku Q-Pool in Alberta, Canada, for H_2S and/or CO_2 Storage			
Mani et al. (2008)	Review of the feasibility of CO_2 sequestration in ultramafic rocks of Kolar and Chitradurga greenstone belts in India	None discussed	None discussed	
	Title of Reference: Assessment of Carbon Dioxide Sequestration Potential of Ultramafic Rocks in the Greenstone Belts of Southern India			
Mito et al. (2008)	Sandstone bed (Minami-Nagaoka gas field) of the Haizume Formation at Nagaoka, Japan	Calcite observed in original reservoir rock; characterization of specific carbonate mineral products were not identified	Yes	PHREEQC, ChemTOUGH
	Title of Reference: Case Study of Geochemical Reactions at the Nagaoka CO_2 Injection Site, Japan			
Raistrick et al. (2006)	Weyburn CO_2 Monitoring and Storage Project, Saskatchewan, Canada	None discussed	Yes	SOLMINEQ.88
	Title of Reference: Using Chemical and Isotopic Data to Quantify Ionic Trapping of Injected Carbon Dioxide in Oil Field Brines			
Ueda et al. (2007) (abstract only)	Ogachi HDR (Hot-Dry Rock) Site, northeast Japan	None discussed	None discussed	
	Title of Reference: Preliminary Geochemical Results on the CO_2 Georeactor Sequestration Test at the Ogachi HDR Site			
Ueda et al. (2008) (abstract only)	Ogachi HDR (Hot-Dry Rock) Site, northeast Japan	Precipitation inferred from in situ analyses	None discussed	
	Title of Reference: Geochemical Results on the CO_2 Georeactor Sequestration Tests at the Ogachi Hot Dry Rock Site, NE Japan			

Table 5.2. (contd)

Reference	Site(s) Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Ueda et al. (2009) (abstract only)	Ogachi HDR (Hot-Dry Rock) Site, northeast Japan	Calcite precipitation inferred from in situ analyses	None discussed	
	Title of Reference: Geochemical Monitoring of Calcite Precipitation during CO_2 Injection into the Ogachi Hot Dry Rock Site			
Westrich et al. (2002)	Depleted oil reservoir in the Queen Formation sandstone in the West Pearl Queen Field in southeast New Mexico Overview of studies and proposed measurements – field injection site with planned modeling, laboratory tests, and other activities	None discussed	Yes	Not identified
	Title of Reference: Sequestration of CO_2 in a Depleted Oil Reservoir: An Overview			

Table 5.3. Studies of Mineral Characterization Data and/or Geochemical Analyses from Sites Considered Possible Natural Analogues for Carbonate Processes Associated CO_2 Injection and Sequestration

Reference	Study	Sites Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Baines and Worden (2004)	Natural analogue	Carbonate reservoirs – Blue Whale and Dolphin in the Da Nang Basin offshore Vietnam; quartzose sandstone reservoirs – Miller and Magnus fields in the UK North Sea; red bed sandstone reservoirs – Bravo Dome in New Mexico and Vert le Grand in Paris Basin.	Blue Whale and Dolphin – have marine carbonate cements, early diagenetic vugs have ferroan (Fe-bearing) calcite, calcite late post-vug filling and late diagenetic dolomite cement at Dolphin. Miller and Magnus – early diagenetic assemblages include non- and weakly ferroan calcite cement; late stages include ferroan dolomite or ankerite cement; ferroan dolomite followed by non-ferroan calcite at Miller. Bravo Dome – final cements have ferroan dolomite and siderite. Vert le Grand – carbonate cements include ferroan dolomite, saddle dolomite, and ferroan calcite.	Yes	Geochemist's Workbench
	Title of Reference: The Long-Term Fate of CO_2 in the Subsurface: Natural Analogues for CO_2 Storage				
Beinlich et al. (2009) (abstract only)	Sample characterization	Serpentinized peridotite clasts in conglomerate from the Solund Devonian Basin in southwestern Norway	Calcite	None discussed	
	Title of Reference: CO_2 Sequestration and Extreme Mg Leaching in Serpentinized Peridotite Clasts of the Solund Devonian Basin, SW-Norway				

Table 5.3. (contd)

Reference	Study	Sites Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Boschi et al. (2009)	Sample characterization	Magnesite deposits of Malentrata in Tuscany, Italy, which were derived from serpentinite silicification–carbonation of an ophiolite	Early formation of Fe-poor magnesite followed by Fe-rich magnesite and dolomite cementing the early brecciated magnesite vein	None discussed	
	Title of Reference: Enhanced CO_2-Mineral Sequestration by Cyclic Hydraulic Fracturing and Si-Rich Fluid Infiltration into Serpentinites at Malentrata (Tuscany, Italy)				
Bruno et al. (2009) (abstract only)	Review	Naturally occurring CO_2 abundances in Spain	None discussed	Yes	Not identified
	Title of Reference: Trace Element Behaviour in Connection to the Geological Storage of CO_2: Lessons from Natural Analogues				
Flaathen and Gislason (2007)	Natural analogue and possible field injection site	Groundwater beneath Mt. Hekla Volcano, Iceland	None discussed	Yes	PHREEQC
	Title of Reference: The Groundwater Beneath Hekla Volcano, Iceland; A Natural Analogue for CO_2 Sequestration				
Flaathen et al. (2009)	Natural analogue and possible field injection site	Spring water samples surrounding Mt. Hekla Volcano, Iceland	None discussed	Yes	PHREEQC
	Title of Reference: Chemical Evolution of the Mt. Hekla, Iceland, Groundwaters: A Natural Analogue for CO_2 Sequestration in Basaltic Rocks				
Hansen et al. (2005)	Natural analogue	Carbonated serpentinite (listwanite) at Atlin, British Columbia	Magnesite	None discussed	
	Title of Reference: Carbonated Serpentinite (Listwanite) at Atlin, British Columbia: A Geological Analogue to Carbon Dioxide Sequestration				

Table 5.3. (contd)

Reference	Study	Sites Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Haszeldine et al. (2005)	Natural analogue (overview)	Natural examples – United Kingdom oilfields; natural exhumed examples – Colorado Plateau; modern CO_2 leakage up faults – Salt Wash, Utah and Springerville-St. Johns, Arizona, United States; ancient CO_2 paleo-trap – Moab Anticline, Utah, United States	None discussed	No	
	Title of Reference: Natural Geochemical Analogues for Carbon Dioxide Storage in Deep Geological Porous Reservoirs, a United Kingdom Perspective				
Hövelmann and Austrheim (2009) (abstract only)	Sample characterization	Peridotite clasts from Solund and Fensfjorden Devonian basins of southwestern Norway	Calcite	None discussed	
	Title of Reference: Guidelines for Experiments on CO_2 Sequestration in Peridotites based on a Natural Example				
Matter and Kelemen (2009) (abstract only)	Sample characterization	Natural carbonation of peridotite from ophiolite in Oman	None mentioned	None discussed	
	Title of Reference: Enhanced In Situ Carbonation of Peridotite for Permanent CO_2 Storage				
May (2005)	Natural analogue	Rhenish Massif, western Germany and Belgium	Siderite (most abundant carbonate), dolomite-ankerite, and calcite occur in altered rocks	Yes	PHREEQC
	Title of Reference: Alteration of Wall Rocks by CO_2-Rich Water Ascending in Fault Zones: Natural Analogues for Reactions Induced by CO_2 Migrating along Faults in Siliciclastic Reservoir and Cap Rocks				

Table 5.3. (contd)

Reference	Study	Sites Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Michael and Buschkuehle (2006)	Natural analogue	Sandstones in Halfway Formation at West Stoddart, British Columbia	Presence of fine-grained carbonate cements	Yes	GAMSPATH
	Title of Reference: Acid-Gas Injection at West Stoddart, British Columbia: An Analogue for the Detailed Hydrogeological Characterization of a CO_2 Sequestration Site				
Moore et al. (2005)	Natural analogue	Springerville-St. Johns Field, Arizona, and New Mexico, United States	Dissolution of authigenic carbonate cement (dolomite) and formation of dawsonite	Yes	Geochemist's Workbench
	Title of Reference: Mineralogical and Geochemical Consequences of the Long-Term Presence of CO_2 in Natural Reservoirs: An Example from the Springerville-St. Johns Field, Arizona, and New Mexico, USA				
Pauwels et al. (2007)	Natural analogue	Montmiral CO_2 accumulation, southeastern France	Dissolution of ferroan dolomite and presence of minor ankerite	Yes	SCALE; PHREEQC
	Title of Reference: Chemistry of Fluids from a Natural Analogue for a Geological CO_2 Storage Site (Montmiral, France): Lessons for CO_2-Water-Rock Interaction Assessment and Monitoring				
Pearce et al. (1996)	Natural analogue (review of information) and experimental fluid-rock experiments	Analogue site – Tubb Sandstones of Bravo Dome CO_2-field, New Mexico; laboratory experiments with anhydrite, Mercia Mudstone, and Sherwood Sandstone from United Kingdom	Tubb Sandstones – dolomite as lithoclasts and cement with ferroan dolomite overgrowths, and calcite in some samples as intergranular cement Anhydrite, mudstone, and sandstone experiments – dissolution of dolomite and precipitation of secondary calcite	None discussed	
	Title of Reference: Natural Occurrences as Analogues for the Geological Disposal of Carbon Dioxide				

Table 5.3. (contd)

Reference	Study	Sites Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Power et al. (2009)	Natural analogue	Hydromagnesite playas of Atlin, British Columbia, Canada	Precipitation of hydromagnesite, nesquehonite, and dypingite and also with depth, ankerite, aragonite, and magnesite	None discussed	
	Title of Reference: The Hydromagnesite Playas of Atlin, British Columbia, Canada: A Biogeochemical Model for CO_2 Sequestration				
Vosteen and May (2007) (abstract only)	Natural analogue	Bunter Sandstone and Rotliegend sediments, Germany	Dissolution of calcite and precipitation of dolomite	Yes	Not identified
	Title of Reference: Identification of Potential Geochemical Reactions in German Subsurface Storage Sites of CO_2				
Watson et al. (2004)	Natural analogue	Siliciclastic reservoir – Ladbroke Grove and Katnook Gas Fields within western Otway Basin, southwestern South Australia	Ferroan carbonate is main mineral product; Pre-CO_2 calcite in Ladbroke Grove dissolved but ankerite and Fe and Mg carbonates precipitated in microspar form	Yes	EQ3NR
	Title of Reference: The Ladbroke Grove-Katnook Carbon Dioxide Natural Laboratory: A Recent CO_2 Accumulation in a Lithic Sandstone Reservoir				
Wilson et al. (2006)	Sample characterization	Chrysotile mine tailings at Clinton Creek, Yukon Territory, and Cassiar, British Columbia, Canada	Nesquehonite, dypingite, hydromagnesite, and sometimes lansfordite	None discussed	
	Title of Reference: Verifying and Quantifying Carbon Fixation in Minerals from Serpentine-Rich Mine Tailings Using the Rietveld Method with X-ray Powder Diffraction Data				

Table 5.3. (contd)

Reference	Study	Sites Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Wilson et al. (2009)	Sample characterization	Chrysotile mine tailings at Clinton Creek, Yukon Territory, and Cassiar, British Columbia, Canada	Nesquehonite, dypingite, hydromagnesite, and sometimes lansfordite	None discussed	
	Title of Reference: Carbon Dioxide Fixation within Mine Wastes of Ultramafic-Hosted Ore Deposits: Examples from the Clinton Creek and Cassiar Chrysotile Deposits, Canada				
Worden (2006)	Natural analogue	Turbidite sandstones of the Lam Formation in Yemen	In sandstones, carbonate cements include ferroan calcite, dawsonite, ferroan dolomite, and siderite	Yes	Geochemist's Workbench
	Title of Reference: Dawsonite Cement in the Triassic Lam Formation, Shabwa Basin, Yemen: A Natural Analogue for a Potential Mineral Product of Subsurface CO_2 Storage for Greenhouse Gas Reduction				

Table 5.4. Published Studies of Laboratory Experiments Designed to Examine the Geochemical Reactions Associated with the Interaction of CO_2-Containing Fluids with Characterized Rock, Single Mineral, or Cement Samples

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Alemu et al. (2009) (abstract only)	Fluid-rock experiments	Shale seal rock from Adventdalen Group which is a proposed CO_2 storage site in Svalbard near Longyearbyen, Norway	None discussed	Yes	PHREEQC
	Title of Reference: Effect of CO_2 Interaction with Svalbard Shale: Implications to Caprock Integrity for Subsurface Sequestration of CO_2				
Andreani et al. (2008)	Fluid-rock experiments	Claystone caprock (argillaceous material) from the Upper Toarcian formation of Tournemire (France); bulk material contains dominantly clay minerals and lesser amounts of calcite, quartz, siderite, and pyrite; clay fraction contains mostly kaolinite, micas (muscovite), interstratified illite/smectite, and chlorite	None identified	None discussed	
	Title of Reference: Changes in Seal Capacity of Fractured Claystone Caprocks Induced by Dissolved and Gaseous CO_2 Seepage				
Andreani et al. (2009)	Fluid-rock experiments	Sintered dunite (olivine)	Formation of magnesite and siderite	None discussed	
	Title of Reference: Experimental Study of Carbon Sequestration Reactions Controlled by the Percolation of CO_2-Rich Brine through Peridotites				

Table 5.4. (contd)

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Andreani et al. (2009)	Fluid-rock experiments	Dunite which contained 97% olivine, 2% diopside, and 1% spinel (chromite)	Two types of alteration features – one with siderite and other with Ca-enriched magnesite in dissolution surface on olivine	None discussed	
	Title of Reference: Experimental Study of Carbon Sequestration Reactions Controlled by the Percolation of CO_2-Rich Brine through Peridotites				
Bachu and Bennion (2009)	Fluid-cement experiments	Class G Portland cement		None discussed	
	Title of Reference: Experimental Assessment of Brine and/or CO_2 Leakage through Well Cements at Reservoir Conditions				
Barlet-Gouédard et al. (2007)	Fluid-cement experiments	Class G Portland cement and a new CO_2-resistant cement	Aragonite, vaterite, and/or calcite	None discussed	
	Title of Reference: Well Technologies for CO_2 Geological Storage: CO_2-Resistant Cement				
Barlet-Gouédard et al. (2009)	Fluid-cement experiments	Portland cement and Schlumberger (composition proprietary) CO_2 resistant cement	Calcium carbonate (no specifics)	None discussed	
	Title of Reference: A Solution against Well Cement Degradation under CO_2 Geological Storage Environment				
Bateman et al. (2005)	Fluid-rock experiments	Starting materials similar to Saline Aquifer CO_2 Storage (SACS) Project, Utsira Formation, North Sea	Dissolution of calcite and dolomite with later precipitation of dolomite	Yes	PRECIP; PHREEQC
	Title of Reference: Large-Scale Column Experiment: Study of CO_2, Porewater, Rock Reactions and Model Test Case				
Béarat et al. (2006)	Fluid-mineral experiments	Olivine $[(Mg_{0.915}\,Fe_{0.085})_2SiO_4]$	Magnesite	None discussed	
	Title of Reference: Carbon Sequestration via Aqueous Olivine Mineral Carbonation: Role of Passivating Layer Formation				

Table 5.4. (contd)

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Bertier et al. (2006)	Fluid-rock experiments	Westphalian and Buntsandstein Sandstones of the Campine Basin, northeast Belgium	Dissolution of ankerite/ dolomite, and precipitation of end-member carbonates (siderite or pure calcite/ aragonite)	None discussed	
	Title of Reference: Experimental Identification of CO_2-Water-Rock Interactions Caused by Sequestration of CO_2 in Westphalian and Buntsandstein Sandstones of the Campine Basin (NE-Belgium)				
Bertier et al. (2007) (abstract only)	Fluid-rock experiments	Sandstone aquifers in the Campine Basin, northeast Belgium	None discussed	Yes	PHREEQE
	Title of Reference: Evaluation of the CO_2-Sequestration Capacity of Sandstone Aquifers in the Campine Basin (NE-Belgium) Based on Autoclave Experiments and Numerical Modelling				
Brunet et al. (2009) (abstract only)	Fluid-cement experiments	Portland cement	Calcite, aragonite, and vaterite	Yes	Not identified
	Title of Reference: Calcium Carbonates Distribution in Experimentally Carbonated Portland Cement Cores				
Busch et al. (2008)	Fluid-rock experiments	Shale sample (Muderong Shale) from Australia, and several clays; shale contains siderite	Siderite present in shale sample; discussion of possible formation of Mg,Fe carbonates	None discussed	
	Title of Reference: Carbon Dioxide Storage Potential of Shales				
Centeno et al. (2005) (abstract only)	Fluid-cement experiments	Oil well cement	None discussed	None discussed	
	Title of Reference: Dissolution of Oil Well Cement in Presence of CO_2/H_2S under HTHP				
Centeno et al. (2007) (abstract only)	Fluid-cement experiments	Class G and H cement	None discussed	None discussed	
	Title of Reference: Durability and Degradation of Oil Well Cement Exposed to a Source of H_2S and CO_2 Gases				

Table 5.4. (contd)

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Centeno et al. (2009) (abstract only)	Fluid-cement experiments	Class G and H cement	Vaterite, aragonite, and calcite	None discussed	
	Title of Reference: SEM-EDS Applications in Mineralogical Phases Study of Oil Well Cements Attacked with H_2S/CO_2 Mixtures				
Charan and Begum (2008) (abstract only)	Fluid-rock experiments	Basalt samples from the Cretaceous Deccan Continental Flood Basalt Province, India	Formation of carbonates; specific mineral phases not mentioned	None discussed	
	Title of Reference: Geological Sequestration of Carbon-Dioxide in Deccan Continental Flood Basalt Province, India				
Charan et al. (2009) (abstract only)	Fluid-rock experiments	Basalt samples from the Cretaceous Deccan Continental Flood Basalt Province, India	Formation of Fe-, C-, and Mg-containing carbonates that matched well with ankerite, calcite, and magnesite	None discussed	
	Title of Reference: Mineral Trapping in Deccan Basalt Province India: Implications for Geological Sequestration of CO_2				
Choi et al. (2009) (abstract only)	Fluid-mineral experiments	Anorthite	None discussed	None discussed	
	Title of Reference: Dissolution of Anorthite under Supercritical CO_2 - Water - Mineral Reaction System at a CO_2 Sequestration Site				
Daval et al. (2009)	Fluid-mineral experiments	Wollastonite	Calcite	Yes	CHESS
	Title of Reference: Carbonation of Ca-Bearing Silicates, the Case of Wollastonite: Experimental Investigations and Kinetic Modeling				
Dilmore et al. (2008a)	Fluid solubility experiments	Brine samples from Oriskany Sandstone aquifer, Indiana County, Pennsylvania, United States	None discussed	Yes	CO_2 gas solubility model of Duan and Sun (2003)
	Title of Reference: Sequestration of Dissolved CO_2 in the Oriskany Formation				

Table 5.4. (contd)

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Dilmore et al. (2008b)	Fluid-rock experiments	Bauxite	Calcite, magnesite, and dawsonite	Yes	EQ3/EQ6
	Title of Reference: Sequestration of CO_2 in Mixtures of Bauxite Residue and Saline Wastewater				
Dufaud et al. (2009)	Fluid-mineral experiments	Olivines, orthopyroxenes, and serpentines (chrysotile)	Magnesite	None discussed	
	Title of Reference: Experimental Study of Mg-Rich Silicates Carbonation at 400 and 500 °C and 1 kbar				
Dupraz et al. (2007) (abstract only)	Fluid-biomineralization experiments	Carbonate mineral formation by microorganisms	Nucleation of carbonates on bacteria followed by the embedding of the cells within the carbonate crystals	Yes	Chess 3.6
	Title of Reference: A Bacterial Model for Studying Interactions between Microorganisms and CO_2 Injected in the Subsurface				
Dupraz et al. (2008) (abstract only)	Fluid-biomineralization experiments	Mineral formation by microorganisms	Nucleation and growth studies; specific phase not listed	Yes	Not identified
	Title of Reference: Experimental Study of Biomineralization Processes Relevant to CO_2 Geological Sequestration				
Dupraz et al. (2009a)	Fluid-biomineralization experiments	Carbonate formation by microorganisms	Aragonite, calcite, and vaterite	None discussed	
	Title of Reference: Experimental Approach of CO_2 Biomineralization in Deep Saline Aquifers				
Dupraz et al. (2009b)	Fluid-biomineralization experiments	Carbonate formation by microorganisms	Precipitation of Log Mg calcite with small amounts of vaterite and aragonite	Yes	CHESS
	Title of Reference: Experimental and Numerical Modeling of Bacterially Induced pH Increase and Calcite Precipitation in Saline Aquifers				
Fernandez-Bastero et al. (2008)	Fluid-mineral experiments	Glauconite particles	None	None discussed	
	Title of Reference: Kinetic and Structural Constraints during Glauconite Dissolution: Implications for Mineral Disposal of CO_2				

Table 5.4. (contd)

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Frost et al. (2008a)	Characterization measurements	Coalingite and brugnatellite	Coalingite and brugnatellite	None discussed	
	Title of Reference: Infrared and Infrared Emission Spectroscopic Study of Selected Magnesium Carbonate Minerals Containing Ferric Iron - Implications for the Geosequestration of Greenhouse Gases				
Frost et al. (2008b)	Characterization measurements	Artinite, brugnatellite, and dypingite	Artinite, brugnatellite, and dypingite	None discussed	
	Title of Reference: Thermal Stability of Artinite, Dypingite and Brugnatellite - Implications for the Geosequestration of Green House Gases				
Garcia et al. (2008) (abstract only)	Fluid-mineral experiments	Pure minerals – olivine, anorthite, and augite	Olivine reacted to form magnesite, anorthite to form calcite, and augite to form siderite and calcite	None discussed	
	Title of Reference: Basic Minerals for Carbon Dioxide Sequestration: Potential and Quantification				
Gudbrandsson et al. (2009) (abstract only)	Fluid-rock dissolution rate experiments	Basalt from a dyke on Stapafell Mountain on Reykjanes peninsula in Iceland	None discussed	None discussed	
	Title of Reference: Dissolution Rates of Crystalline Basalt as a Function of Temperature and Solution Composition				
Guichet et al. (2005) (abstract only)	Fluid-rock experiments	Porous limestones from Lavous, France	Cores are pure essentially calcite	Yes	DIAPHORE
	Title of Reference: Reactive Transport Experiments and Modelling of CO_2 Sequestration in Deep Aquifers				
Gunter et al. (1997)	Fluid-rock experiments	Glauconitic sandstone from Alberta Sedimentary Basin, Canada	No carbonate minerals detected	Yes	PATHARC.94
	Title of Reference: Aquifer Disposal of CO_2-Rich Greenhouse Gases: Extension of the Time Scale of Experiment for CO_2-Sequestering Reactions by Geochemical Modelling				

Table 5.4. (contd)

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Gysi and Stefánsson (2009) (abstract only)	Fluid-rock experiments	Basalt related to pilot field study in southwestern Iceland	Fe-Mg-Ca-Mn carbonates	Yes	Not identified
	Title of Reference: CO_2-Water-Basalt Interaction: Geochemical Modelling and Experiments				
Hänchen et al. (2008)	Mineral precipitation experiments	Mixing Na_2CO_3 and $MgCl_2$ solutions with CO_2 atmosphere	Nesquehonite, hydromagnesite, magnesite	Yes	EQ3/EQ6
	Title of Reference: Precipitation in the Mg-Carbonate System - Effects of Temperature and CO_2 Pressure				
Hangx and Spiers (2009)	Fluid-mineral experiments	Anorthite and albite	Precipitations of hydrotalcite and some aragonite	None discussed	
	Title of Reference: Reaction of Plagioclase Feldspars with CO_2 under Hydrothermal Conditions				
Iglesias et al. (2008) (abstract only)	Fluid-rock experiments	Subarkose sandstone from the Rio Bonito Formation aquifer in the Paraná Basin, Brazil	Precipitation of calcium and iron carbonates (mineral forms not specified in abstract)	Yes	PHREEQC
	Title of Reference: Experimental and Modeling Studies of CO_2-Water-Rock Interactions in the Rio Bonito Saline Aquifer, Paraná Basin, Brazil				
Izgec et al. (2008a)	Fluid-rock experiments	Cores from carbonate formations from Midyat formation, south east Turkey, and from a quarry, St. Maximim, France	Precipitation of calcite	Yes	STARS, see Izgec et al. (2008b) in Table 2
	Title of Reference: CO_2 Injection into Saline Carbonate Aquifer Formations I: Laboratory Investigation				
Jacquemet et al. (2008)	Fluid-cement experiments	Well cement (crushed) and well casing steel	Precipitation of calcite or aragonite in crushed cement	None discussed	
	Title of Reference: Mineralogical Changes of a Well Cement in Various H_2S-CO_2(-Brine) Fluids at High Pressure and Temperature				
Jarvis et al. (2009)	Fluid-mineral experiments	Olivine (Mg_2SiO_4) containing 8% Fe	Precipitation of magnesite	Yes	EQ3/6
	Title of Reference: Reaction Mechanisms for Enhancing Mineral Sequestration of CO_2				

Table 5.4. (contd)

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Kaszuba et al. (2003)	Fluid-rock experiment	Simulated arkose to represent aquifer and Maplewood Shale (argillaceous share) from Monroe County, New York, United States as the aquitard	Precipitated magnesite (desiccation of brine – by extraction of water from brine into injected $scCO_2$)	None discussed	
	Title of Reference: Carbon Dioxide Reaction Processes in a Model Brine Aquifer at 200°C and 200 Bars: Implications for Geologic Sequestration of Carbon				
Kaszuba et al. (2005)	Fluid-rock experiment	Simulated arkose to represent aquifer and Maplewood Shale (argillaceous share) from Monroe County, New York, United States as the aquitard	Precipitation corroded magnesite followed by siderite	Yes	No details
	Title of Reference: Experimental Evaluation of Mixed Fluid Reactions between Supercritical Carbon Dioxide and NaCl Brine: Relevance to the Integrity of a Geologic Carbon Repository				
Ketzer et al. (2009)	Fluid-rock experiments	Sandstones from the saline reservoir of the Rio Bonito Formation, Paraná Basin in southern Brazil	Samples contained calcite or dolomite; identified precipitation of pure end-member calcite and ferroan calcite	Yes	PHREEQC
	Title of Reference: Water-Rock-CO_2 Interactions in Saline Aquifers Aimed for Carbon Dioxide Storage: Experimental and Numerical Modeling Studies of the Rio Bonito Formation (Permian), Southern Brazil				
Kunieda et al. (2008) (abstract only)	Fluid-cement experiments	Cylinder of Berea sandstone with a center hole filled with oil well cement	Precipitation of aragonite and calcite	None discussed	
	Title of Reference: Experimental Research of Casing Cement Alteration by Interaction with Supercritical CO_2 for Geological Sequestration				

Table 5.4. (contd)

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Kuroda et al. (2008) (abstract only)	Fluid-mineral experiments	Anorthite	Precipitation of calcite	Yes	No details
	Title of Reference: Experimental Research of Plagioclase-Gas-Water Interaction at Hydrothermal Conditions Caused by CO_2 Sequestration				
Kutchko et al. (2007)	Fluid-cement experiments	Class H Portland cement	Calcite	None discussed	
	Title of Reference: Degradation of Well Cement by CO_2 under Geologic Sequestration Conditions				
Kutchko et al. (2008)	Fluid-cement experiments	Class H Portland cement	Calcium carbonate (specific phases not identified) [see Kutchko et al. (2007)]	None discussed	
	Title of Reference: Rate of CO_2 Attack on Hydrated Class H Well Cement under Geologic Sequestration Conditions				
Kutchko et al. (2009)	Fluid-cement experiments	Class H Portland cement amended with Type F flyash	Calcite, aragonite, and vaterite	None discussed	
	Title of Reference: CO_2 Reaction with Hydrated Class H Well Cement under Geologic Sequestration Conditions: Effects of Flyash Admixtures				
Lin et al. (2008)	Fluid-rock and fluid-mineral experiments	Quartz, biotite, and iidate granite	Precipitation of calcite	None discussed	
	Title of Reference: Experimental Evaluation of Interactions in Supercritical CO_2/Water/Rock Minerals System under Geologic CO_2 Sequestration Conditions				
Liu et al. (2003)	Fluid-rock experiments	Iidate Granite from Fukushima Prefecture, Japan; Kimachi Sandstone from Shimane Prefecture, Japan	None discussed	None discussed	
	Title of Reference: CO_2 Injection to Granite and Sandstone in Experimental Rock/Hot Water Systems				

Table 5.4. (contd)

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Luquot and Gouze (2009)	Fluid-rock experiments	Oolitic limestone from the Mondeville formation in the Paris Basin in France	Initial samples contained Mg-calcite ($Ca_{0.99}Mg_{0.01}CO_3$); precipitation occurred of Mg-calcite of composition $Ca_{0.92}Mg_{0.08}CO_3$ at the oolith surfaces	Yes	CHESS
	Title of Reference: Experimental Determination of Porosity and Permeability Changes Induced by Injection of CO_2 into Carbonate Rocks				
Martinez et al. (2007) (abstract only)	Fluid-biomineral experiments	Carbonate mineral formation by hotosynthetic cyanobacteria	None discussed	None discussed	
	Title of Reference: Characterization of Carbonate Mineral Formation by Cyanobacteria and the Implications in CO_2 Sequestration				
McGrail et al. (2006)	Fluid-rock experiments	Basalt	Precipitation of calcite that underwent phase transition to ankerite with extended time	Yes	EQ3NR
	Title of Reference: Potential for Carbon Dioxide Sequestration in Flood Basalts				
McKelvy et al. (2004)	Characterization studies and fluid-rock experiments	Lizardite as the model serpentine material	Magnesite	None discussed	
	Title of Reference: Exploration of the Role of Heat Activation in Enhancing Serpentine Carbon Sequestration Reactions				
Mitchell et al. (2008) (abstract only)	Biomineralization and biofilm barrier experiments	Mineral formation by biofilms	Calcium carbonate; specific form not identified	None discussed	
	Title of Reference: Microbially Enhanced Carbonate Mineralization and the Geologic Containment of CO_2				
Mitchell et al. (2009)	Biofilm formation experiments	Berea sandstone	None discussed	None discussed	
	Title of Reference: Biofilm Enhanced Geologic Sequestration of Supercritical CO_2				

Table 5.4. (contd)

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Mito et al. (2008)	Fluid-rock experiments and field sample study	Sandstone bed (Minami-Nagaoka gas field) of the Haizume Formation at Nagaoka, Japan	Calcite observed in original reservoir rock; characterization of specific carbonate mineral products were not identified	Yes	PHREEQC, ChemTOUGH
	Title of Reference: Case Study of Geochemical Reactions at the Nagaoka CO_2 Injection Site, Japan				
Noiriel et al. (2009)	Fluid-rock experiments	Limestone from a borehole drilled in the Campos Basin in Mallorca, Balearic Islands, Spain	Limestone contains only calcite, which occurred in two forms - micrite grains and sparite crystals which have different trace element signatures	None discussed	
	Title of Reference: Changes in Reactive Surface Area during Limestone Dissolution: An Experimental and Modelling Study				
Palandri et al. (2005)	Fluid-mineral experiments	Hematite (reduction of Fe^{III} to Fe^{II})	Precipitation of siderite and dawsonite	Yes	CHILLER
	Title of Reference: Ferric Iron in Sediments as a Novel CO_2 Mineral Trap: CO_2-SO_2 Reaction with Hematite				
Park and Fan (2004)	Fluid-rock experiments	Serpentine	Precipitation of magnesium carbonate	None discussed	
	Title of Reference: CO_2 Mineral Sequestration: Physically Activated Dissolution of Serpentine and pH Swing Process				
Prasad et al. (2009)	Fluid-rock experiments	Picritic basalts from Deccan basalts in India	Precipitation of ankerite	None discussed	
	Title of Reference: Geological Sequestration of Carbon Dioxide in Deccan Basalts: Preliminary Laboratory Study				
Regnault et al. (2009)	Fluid-mineral(cement) experiments	Portlandite because it is a main component of borehole cement	Calcite	Yes	Not identified
	Title of Reference: Experimental Measurement of Portlandite Carbonation Kinetics with Supercritical CO_2				

Table 5.4. (contd)

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Rimmelé et al. (2008)	Fluid-cement experiments	Class G Portland cement	Calcite and aragonite	None discussed	
	Title of Reference: Heterogeneous Porosity Distribution in Portland Cement Exposed to CO_2-Rich Fluids				
Rosenbauer et al. (2005)	Fluid–rock experiments	Limestone; plagioclase-rich arkosic sandstone	Dissolution of calcite and dolomitization of limestone	Yes	SOLMINEQ99, CHILLER, SOLVEQ
	Title of Reference: Experimental Investigation of CO_2-Brine-Rock Interactions at Elevated Temperature and Pressure: Implications for CO_2 Sequestration in Deep-Saline Aquifers				
Rosenbauer and Bischoff (2009) (abstract only)	Fluid-rock experiments	Basalt	None discussed	Yes	Not identified
	Title of Reference: CO_2 Sequestration by Basalt: Experimental studies and Geochemical Modeling				
Sass et al. (2001)	Fluid-rock and fluid-mineral experiments	Mt. Simon sandstone (potential reservoir), Eau Claire shale, and Rome dolomite (caprock for Mt. Simon), Ohio; pure minerals (high Ca plagioclase, anorthite, glauconite, kaolinite, montmorillonite)	No carbonate precipitation observed	Yes	PHRQPITZ, PHREEQC
	Title of Reference: Geochemical Evaluation of Carbon Dioxide Sequestration in Saline Formations - Final Technical Report				
Sass et al. (2002)	Fluid-mineral experiments	Pure minerals (glauconite and anorthite)	No carbonate precipitation observed	Yes	Not identified
	Title of Reference: Interaction of Rock Minerals with Carbon Dioxide and Brine: A Hydrothermal Investigation				
Schaef and McGrail (2009)	Fluid-rock experiments	Basalt samples from Grand Ronde Basalt Formation collected near Vantage, Washington	None discussed	Yes	EQ3NR
	Title of Reference: Dissolution of Columbia River Basalt Under Mildly Acidic Conditions as a Function of Temperature: Experimental Results Relevant to the Geological Sequestration of Carbon Dioxide				

Table 5.4. (contd)

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Schaef et al. (2010)	Fluid-rock experiments	Basalt samples from Columbia River basalt from Grande Ronde Formation in Washington; Newark Basin in South Carolina; Deccan basalt from Khandala Formation in India; and Karoo Formation in South Africa	Precipitation of Ca carbonates (including calcite) also containing Mg, Fe, and Mn; and precipitation of rhodochrosite	Yes	EQ3/EQ6
	Title of Reference: Carbonate Mineralization of Volcanic Province Basalts				
Scherer et al. (2005)	Fluid-rock-cement experiments	Cylinders of Chass H Portland cement inside holes along long axes of cylinders of Salem limestone or Berea sandstone	None dsicusssed; work in progress	Yes	EQ3/EQ6
	Title of Reference: Leakage of CO_2 through Abandoned Wells: Role of Corrosion of Cement				
Schulze et al. (2004)	Fluid-rock experiments	Serpentine	Precipitation of magnesite	None discussed	
	Title of Reference: Characterization of Carbonated Serpentine using XPS and TEM				
Shilobreeva and Martinez (2007) (abstract only)	Fluid-rock experiments	Basalt	None discussed	None discussed	
	Title of Reference: CO_2-Water-Basalt Interactions: Experimental and Mineralogical Study				
Shiraki and Dunn (2000)	Fluid-rock experiments	Tensleep Formation sandstone, Wyoming,	Dissolution of dolomite cement	Yes	SOLMINEQ.88
	Title of Reference: Experimental Study on Water-Rock Interactions during CO_2 Flooding in the Tensleep Formation, Wyoming, USA				
Soong et al. (2004)	Fluid-mineral experiments	Brine samples from the Oriskany Formation in Indiana County, Pennsylvania	Precipitation of calcite	Yes	PHREEQC
	Title of Reference: Experimental and Simulation Studies on Mineral Trapping of CO2 with Brine				

Table 5.4. (contd)

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Stefánsson and Gysi (2008) (abstract only)	Fluid-rock experiments	Basalt	Mg-Fe and Mg-Ca carbonates form during early low pH stage; then with increase in pH, precipitation of calcite dominates	Yes	No details
	Title of Reference: CO_2-Basalt Interaction - Numerical Simulation and Experimental Study				
Sterpenich et al. (2009);	Fluid-rock experiments	Lavoux oolitic limestone from southwestern area of the Paris Basin, France	Oolitic limestone consisted of calcite	Yes	CHESS
	Title of Reference: Experimental Ageing of Oolitic Limestones under CO_2 Storage Conditions: Petrographical and Chemical Evidence				
Stockmann et al. (2008)	Fluid-mineral experiments	Diopside and basaltic glass	Proposed precipitation of calcite on surfaces of diopside and basaltic glass particles	Yes	PHREEQC
	Title of Reference: Dissolution of Diopside and Basaltic Glass: The Effect of Carbonate Coating				
Stockmann et al. (2009) (abstract only)	Fluid-rock experiments	Basaltic glass	Calcite	None discussed	
	Title of Reference: Can Carbonate Coatings Inhibit In Situ Mineral Carbonation?				
Suto et al. (2007)	Fluid-rock experiments	Granite	None discussed	Yes	SOLVEQ
	Title of Reference: Initial Behavior of Granite in Response to Injection of CO_2-Saturated Fluid				
Teir et al. (2009)	Fluid-mineral experiments	Serpentine ore	Hydromagnesite	None discussed	
	Title of Reference: Fixation of Carbon Dioxide by Producing Hydromagnesite from Serpentinite				
Testemale et al. (2009)	Mineral dissolution experiments	Siderite	None	Yes	CHESS
	Title of Reference: An X-ray Absorption Study of the Dissolution of Siderite at 300 Bar between 50 °C and 100 °C				

Table 5.4. (contd)

Reference	Type of Laboratory Study	Sites or Materials Studied	Carbonate Minerals and Reactions Physically Observed	Was Geochemical Reaction Modeling Used?	Computer Codes Used for Geochemical Reaction Modeling
Wigand et al. (2008)	Fluid–rock experiments-	Sandstone (lithic arkose) from Bunter Sandstone Formation	Dissolution of dolomite cement, but no carbonate formation was observed	Yes	PHREEQC
	Title of Reference: Geochemical Effects of CO_2 Sequestration in Sandstones under Simulated In Situ Conditions of Deep Saline Aquifers				
Wigand et al. (2009)	Fluid-cement/rock experiments	Composite consisting of the dry class G Portland well cement and illite-rich shale of the Wolfcamp Formation in West Texas	Calcite, aragonite, and vaterite	Yes	Geochemist's Workbench
	Title of Reference: Geochemical Effects of CO_2 Sequestration on Fractured Wellbore Cement at the Cement/Caprock Interface				
Wolf et al. (2004)	Fluid–rock experiments	Serpentine containing primarily 1T lizardite with minor clino-chrysotile	Precipitation of magnesite	None discussed	
	Title of Reference: In Situ Observation of CO_2 Sequestration Reactions Using a Novel Microreaction System				

6.0 Geochemical Reaction Models and Thermodynamic Databases Used to Study CO_2 Sequestration Processes

6.1 Computer Models

The references in Tables 5.1 through 5.4 were first examined to identify the names of any coupled fluid transport and geochemical models and/or dedicated geochemical models (i.e., no coupled fluid transport) that were used in these CO_2 sequestration studies. The modeling typically involved the prediction of geochemical changes in fluid and mineral compositions from different scenarios of CO_2 injection and sequestration or interpretation of geochemical reactions that occurred in laboratory experiments or at site studies of CO_2 sequestration. Table 6.1 lists the names of geochemical reaction models that were used in the studies in Tables 5.1 through 5.4 to evaluate the geochemistry of CO_2 sequestration in those systems. The information in Table 6.1 is cross-referenced to the studies in Tables 5.1 through 5.4. When possible, Table 5.4 also includes brief information regarding the main source for the thermodynamic database used for each geochemical reaction model. The purpose of tabulating this information is to identify common sources that had been used for development of their thermodynamic database files. In many, if not most cases, code developers rely on thermodynamic database files taken from well-established geochemical reaction codes and/or published sources of tabulated thermodynamic constants as the principle source(s) for their own thermodynamic databases.

Table 6.1. Names of Geochemical Reaction Models Used in the Modeling, Site, and Laboratory CO_2 Sequestration Studies Listed in Tables 5.1 through 5.4

Computer Code or Software Package	Thermodynamic Database Information	Studies that Identify Use of Computer Code or Software Package	Notes
ChemTOUGH	--	White et al. (2005)	White et al. (2005) identified use of SOLTHERM database (Reed and Palandri 2006).
CHEM-TOUGH2	--	Pruess et al. (2004)	--
CHESS Testemale et al. (2009)	--	Daval et al. (2009); Dupraz et al. (2007, 2009b); ; Lagneau et al. (2005); Luquot and Gouze (2009); Sterpenich et al. (2009); Testemale et al. (2009)	Dupraz et al. (2009b) cites van der Lee and Lomenech (2004) as source of thermodynamic database.
CHILLER	The CHILLER thermodynamic database is based on the mineral data of Holland and Powell (1998) and aqueous species data derived from the SUPCRT92 database from Johnson et al. (1992).	Palandri and Kharaka (2005); Palandri et al. (2005); Rosenbauer et al. (2005)	--
CRUNCH	Knauss et al. (2005) identified use of the LLNL-EQ3/EQ6 database.	Knauss et al. (2005)	--
DIAPHORE	Le Gallo et al. (1998) identified database as coming from the KINDISP code as described in Madé et al. (1994).	Brosse et al. (2005); Guichet et al. (2005)	Brosse et al. (2005) list the $\log K_{r,298}°$ values used for calculations.
EQ3/EQ6 (also includes EQ3NR)	Software has its own database that is based the current version of SUPCRT92 database (Johnson et al. 1992) and other sources identified in database file.	Cipolli et al. (2004); Dilmore et al. (2008b); Hänchen et al. (2008); Jarvis et al. (2009); McGrail et al. (2006); Schaef and McGrail (2009); Schaef et al. (2010); Watson et al. (2004); Zwingmann et al. (2005)	--
FLOTRAN	LLNL-EQ3/EQ6	Carey and Lichtner (2007); Carey et al. (2007); Pruess et al. (2004)	--

Table 6.1. (contd)

Computer Code or Software Package	Thermodynamic Database Information	Studies that Identify Use of Computer Code or Software Package	Notes
GAMSPATH (This code is the most recent version of PATHARC)	The GAMSPATH thermodynamic database is based on values derived from SUPCRT92 database (Johnson et al. 1992).	Buschkuehle and Perkins (2004); Michael and Buschkuehle (2006); Palandri and Kharaka (2005)	--
GEM-GHG	--	Ozah et al. (2005)	--
Geochemist's Workbench	User may select from three datasets. These include those from LLNL-EQ3/EQ6, MINTEQ, PHREEQC, and WATEQ4F codes.	Allen et al. (2005); Baines and Worden (2004); Moore et al. (2005); Saylor and Zerai (2004); Wigand et al. (2009); Worden (2006); Zerai et al. (2006)	Baines and Worden (2004), Moore et al. (2005), and Worden (2006) identified the use of the LLNL-EQ3/EQ6 database.
NUFT-GEMBOCHS-Xtol toolbox (NUFT)	Johnson et al. (2001) identified the use of the most current version of the SUPCRT92 database (Johnson et al. 1992)	Johnson et al. (2001); Johnson et al. (2004)	--
PATHARC.94		Gunter et al. (1997; 2000)	--
PHREEQC	USGS distributes the code with three datasets. These include those from PHREEQC, WATEQ4F, and MINTEQ codes. Others (see last column) have reported use of LLNL-EQ3/EQ6 database with PHREEQC.	Alemu et al. (2009); Alfredsson and Gislason (2009); Allen et al. (2005); Bateman et al. (2005); Bertier et al. (2007); Cantucci et al. (2009b); Flaathen and Gislason (2007); Flaathen et al. (2009); Gaus et al. (2005); Gysi and Stefánson (2008); Iglesias et al. (2008); Kervévan et al. (2005); Ketzer et al. (2009); May (2005); Mito et al. (2008); Mito and Nakagawa (2009); Pauwels et al. (2007); Sass et al. (2001); Soong et al. (2004); Stockmann et al. (2008); Wigand et al. (2008)	Bateman et al. (2005); Gaus et al. (2005); Ketzer et al. (2009); Pauwels et al. (2007); Sass et al. (2001); and Wigand et al. (2008) identify use of LLNL-EQ3/EQ6 database. May (2005) used WATEQ4F database.
PHRQPITZ	--	Sass et al. (2001)	--
PRECIP	Bateman et al. (2005) identified use of LLNL-EQ3/EQ6 database.	Bateman et al. (2005)	--
SCALE	Code has its own database.	Pauwels et al. (2007)	--

Table 6.1. (contd)

Computer Code or Software Package	Thermodynamic Database Information	Studies that Identify Use of Computer Code or Software Package	Notes
SCALE2000	Database based on Pitzer parameters. Sources of Pitzer parameters listed in Azaroual et al. (2004).	André et al. (2007); Kervévan et al. (2005)	--
SOLMINEQ	--	Kharaka et al. (2006a, 2006b); Bachu and Adams (2003)	--
SOLMINDB	--	Bachu and Adams (2003)	Modified version of SOLMINEQ (Bachu and Adams 2003)
SOLMINEQ.88	--	Emberley et al. (2005); Raistrick et al. (2006); Shiraki and Dunn (2000)	Shiraki and Dunn (2000) mention corrections to dolomite
SOLMINEQ99	--	Rosenbauer et al. (2005)	--
SOLVEQ	--	Rosenbauer et al. (2005); Suto et al. (2007)	--
STARS	--	Izgec et al. (2008a, 2008b)	--
TOUGHREACT	LLNL-EQ3/6 database with revisions generated by SUPCRT92.	André et al. (2007); Audigane et al. (2007); Cantucci et al. (2009a); Ennis-King and Paterson (2007); Gherardi et al. (2007); Pruess et al. (2004); Xu et al. (2003, 2004, 2005, 2006, 2007) ; Zhang et al. (2009)	Xu et al. (2004, 2005, 2007) describe in detail modifications made to thermodynamic values for certain carbonate minerals.

6.2 Principal Sources Containing Thermodynamic Data for Carbonate Species

Common sources of thermodynamic databases used with the geochemical reaction models listed in Table 6.1 were reviewed to identify the carbonate gaseous, aqueous, and mineral species and associated thermodynamic data included in those sources. Several published compilations of thermodynamic values that are well known and commonly used by the geosciences community were also reviewed for this information. These databases and published compilations of thermodynamic data include the following:

- Thermodynamic database file for the EQ3/EQ6 geochemical model
- Thermodynamic database file for the MINTEQ2 geochemical model
- Thermodynamic database file for the PHREEQC geochemical model
- Holland and Powell (1998) – *An Internally Consistent Thermodynamic Data Set for Phases of Petrological Interest*

- Hummel et al. (2002) – *Nagra/PSI Chemical Thermodynamic Data Base 01/01*
- Nordstrom et al. (1990) – "Revised Chemical Equilibrium Data for Major Water-Mineral Reactions and Their Limitations" in *Chemical Modeling in Aqueous Systems II*
- M. H. Reed (University of Oregon, Eugene, Oregon) – SOLTHERM database of equilibria constants (personal communication, January 31, 2008)
- Robie and Hemingway (1995) – *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar (10^5 Pascals) Pressure and at Higher Temperatures* (U.S. Geological Survey Bulletin 2131)
- Smith et al. (2004) – NIST Standard Reference Database 46 (*NIST Critically Selected Stability Constants of Metal Complexes Database. Version 8 for Windows*)
- Woods and Garrels (1987) – *Thermodynamic Values at Low Temperature for Natural Inorganic Materials: An Uncritical Summary*.

For carbonate species containing elements other than C, O, and H, we focused our database reviews on thermodynamic data available for carbonate species that contain common alkali and alkaline-earth elements, and Fe and Mn. It was assumed that these elements would be the most important elements on a concentration basis in aquifer systems, or have the largest potential impact (besides S) on redox reactions associated with CO_2 sequestration in such systems. The database reviews did not compile information available for carbonate aqueous species and minerals that contain elements, such as Ba, Sr, Cd, Cu, Pb, Zn, rare earth elements, Hg, and radionuclides such as U, Pu, and Am.

6.3 Availability of Thermodynamic Data for CO_2 and CH_4 Gases and Carbonate-Containing Aqueous Species and Minerals in Identified Databases and Compilations

Results of our reviews of the thermodynamic databases and published compilations of thermodynamic data listed above are shown in Tables 6.2, 6.3, and 6.4, respectively. The carbonate species and types of thermodynamic data available for each carbonate species are listed in Tables 6.2 through 6.4 according to the reference sources listed above. If a source does not list a particular carbonate species, then that source is not included for that species. Table 6.2 contains thermodynamic data available for pure CO_2 and CH_4 gases, Table 6.3 contains thermodynamic data available for carbonate aqueous species, and Table 6.4 contains thermodynamic data available for carbonate-containing minerals.

The types of thermodynamic parameters tabulated for compounds vary between the different database sources. Depending on the database, the thermodynamic parameters may include values for the following:

- $\Delta_f G_{298}^\circ$
- $\Delta_f H_{298}^\circ$
- S_{298}°
- $\Delta_r H_T^\circ$
- analytical expression for temperature dependence of C_p° at and above 298 K

- log $K_{r,298}°$
- analytical expression for temperature dependence of log $K_{r,T}°$
- log $K_{r,T}°$ values estimated or extrapolated at a series of temperatures such as 298 K (25°C), 323 K (50°C), 373 K (100°C), 423 K (150°C), 473 K (200°C), 523 K (250°C), 573 K (300°C), and 623 K (350°C).

The equations used to derive the $\Delta_fG_{298}°$, and log $K_{r,298}°$ values and $\Delta_fG_T°$, and log $K_{r,T}°$ at higher temperatures are provided in Section 3.0.

Values of $\Delta_fG_{298}°$ and/or log $K_{r,298}°$ were available for essentially all of the compounds in Tables 6.2 through 6.4. Log $K_{r,T}°$ or heat capacity values at temperatures above 298 K were available for less than approximately one-third of these compounds. For those compounds that do not have high-temperature heat capacity data, the tabulated high-temperature log $K_{r,T}°$ are likely based on extrapolation methods that relied on thermodynamic properties reported at 298 K (25°C). Because the temperatures of host formations that will be used for CO_2 injection and sequestration, and the supporting geochemical reaction modeling studies will range between 50ºC to 100°C or greater, the lack of high-temperature thermodynamic values for key carbonate compounds, especially minerals, will likely impact the accuracy of some modeling calculations.

Values listed in the cited sources for the thermodynamic parameters in Tables 6.2 through 6.4 were not tabulated because this would lead to the necessity of having to compare and explain the differences that exist for thermodynamic values for a particular carbonate compound. To complete an evaluation at that level, one would need to know what the original database manager used for the thermodynamic values for all the ancillary elements and species and in the case of thermodynamic values listed for high temperature, the extrapolation methods to back calculate to the original source values. This is a daunting task, and may not be feasible because records of the calculations and database source values may not have been maintained, sufficiently documented, or be readily available.

The tabulated log $K_{r,298}°$ and $\Delta_rH_{298}°$ values are listed to the same number of significant figures as given in the cited source. The log $K_{r,298}°$ and $\Delta_rH_{298}°$ values are based on dissociation reactions for the specified compounds, which are written in terms of HCO_3^- and H^+/H_2O. The log K_r,298° and $\Delta_rH_{298}°$ values for $CH_4(g)$ and $CH_4°(aq)$ are based on their dissociation reactions written in terms of HCO_3^-, H^+/H_2O, and e^- [not $O_2°(aq)$]. If different basis species (e.g., CO_3^{2-}) were used in the cited source, the log K_r,298° and $\Delta_rH_{298}°$ values given in the source were converted to the HCO_3^- and H^+/H_2O basis species using the appropriate log K_r,298° and $\Delta_rH_{298}°$ values listed in that same source.

Table 6.2. Thermodynamic Data Available for CO_2 and CH_4 Gases

Formula for Carbonate Compound	**$\Delta_f G_{298}°$ (kJ/mol)**	**$\Delta_f H_{298}°$ (kJ/mol)**	**$S_{298}°$ (J/mol·K)**	**log $K_{r,298}°$**	**$\Delta_r H_{298}°$ (kJ/mol)**	**Other Values Included in Source**	**Listed Values Taken from Following Source and References Therein**
CO_2(g)	-394.30	-393.51	213.70	--	--	Analytical expression for temperature dependence of $C_p°$	Holland and Powell (1998)
	-394.371	-393.510	213.785	-7.820	-10.875	--	Hummel et al. (2002)
	--	--	--	-7.820	-10.874	Analytical expression for log $K_{r,T}°$ as a function of temperature	Nordstrom et al. (1990)
	--	--	--	-7.818	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K (25, 50, 100, 150, 200, 250, 300, and 350°C); analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]
	-394.4	-393.5	213.8	--	--	Analytical expression for temperature dependence of $C_p°$ to 2200 K (1927°C) and $\Delta_f G_T°$, $\Delta_f H_T°$, and $S_T°$ values up to 1800 K (1527°C)	Robie and Hemingway (1995)

Table 6.2. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
$CO_2(g)$	--	--	--	-7.818	-10.54	log $K_{r,T}$ listed at one or more values of temperature and ionic strength	Smith et al. (2004)
	-394.4 -394.4 -394.4 -394.4 -394.4 -394.4 -394.4	-393.5 -393.5 -393.5 -393.5 -393.5 -393.5 -393.5	213.6 213.6 213.7 213.8 213.7 213.7	--	--	--	Woods and Garrels (1987)
	-394.36	-393.51	213.74	-7.8136	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	-7.820	-10.874	Analytical expression for log $K_{r,T}°$ as a function of temperature	PHREEQC
	--	--	--	-7.8180	-10.5400	--	MINTEQA2
$CH_4(g)$	-50.66	-74.81	186.26	--	--	Analytical expression for temperature dependence of $C_p°$	Holland and Powell (1998)
	-50.721	-74.810	--	-30.705	242.085	--	Hummel et al. (2002)
	--	--	--	-30.686	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]

Table 6.2. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}^\circ$ (kJ/mol)	$\Delta_f H_{298}^\circ$ (kJ/mol)	S_{298}° (J/mol·K)	log $K_{r,298}^\circ$	$\Delta_r H_{298}^\circ$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
$CH_4(g)$	-50.7	-74.8	186.26	--	--	Analytical expression for temperature dependence of C_p° and $\Delta_f G_T^\circ$, $\Delta_f H_T^\circ$, and S_T° values up to 1800 K (1527°C)	Robie and Hemingway (1995)
	-50.8 -50.8 -50.7 -50.7 -50.7	-74.8 -74.8 -74.8 -74.8 -74.8	186.2 186.2 186.3 186.2 186.3	--	--	--	Woods and Garrels (1987)
	-50.718	-74.810	186.26	-30.677	--	log $K_{r,T}^\circ$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	-33.602	226.375	--	PHREEQC
	--	--	--	-30.7162	242.5330	--	MINTEQA2

(a) Reed MH. 2008. "SOLTHERM Database of Equilibria Constants." Personal communication, University of Oregon, Eugene, January 31, 2008.

Table 6.3. Thermodynamic Data Available for Aqueous Carbonate Species

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
$CO_2°$(aq)	-385.992	-413.494	119.360	-6.352	9.109	--	Hummel et al. (2002)
	--	--	--	-6.352	9.109	Analytical expression for log $K_{r,T}°$ as a function of temperature	Nordstrom et al. (1990)
	--	--	--	-6.345	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K (25, 50, 100, 150, 200, 250, 300, and 350°C); analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]
	-386.2 -386.0 -386.0 -386.0	-412.9 -413.8 -413.8 -413.8	121,3 120.9 117.6 120.9	--	--	--	Woods and Garrels (1987)
	-385.974	-413.798	117.57	-6.3447	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	-6.352	9.110	Analytical expression for log $K_{r,T}°$ as a function of temperature	PHREEQC

Table 6.3. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
$CH_4°(aq)$	-34.413	-88.607	--	-27.849	255.882	--	Hummel et al. (2002)
	--	--	--	-27.827	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]
	-34.45	-87.906	87.822	-27.827	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	-30.742	240.49	--	PHREEQC
CO_3^{2-}	--	-675.23	-50.00	--	--	$C_p°$	Holland and Powell (1998)
	-527.917	-675.314	-50.000	10.329	-14.901	--	Hummel et al. (2002)
	--	--	--	10.329	-14.899	Analytical expression for log $K_{r,T}°$ as a function of temperature	Nordstrom et al. (1990)
	--	--	--	10.329	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]
	-527.0	-675.2	-50.0	--	--	--	Robie and Hemingway (1995)

Table 6.3. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
CO_3^{2-}	--	--	--	10.329	-14.6	log $K_{r,T}$ and $\Delta_r H_T$ listed at one or more values of temperature and ionic strength	Smith et al. (2004) (used CO_3^{2-} as basis species)
	-528.1	-676.2	-53.1	--	--	--	Woods and Garrels (1987)
	-527.9	-677.1	-56.9				
	-527.9	-677.1	-56.9				
	-527.8	-677.1	-56.9				
	-527.9	-677.1					
	-527.9	-677.1	-56.9				
	-527.983	-675.235	-49.999	10.3288	--	log $K_{r,T}°$ values also at 273, 323, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	10.3290	-14.6000	--	MINTEQA2
	--	--	--	10.329	-14.90	Analytical expression for log $K_{r,T}°$ as a function of temperature	PHREEQC
HCO_3^-	-586.875	-690.215	98.400	--	--	--	Hummel et al. (2002)
	--	--	--	See CO_3^{2-}	--	--	Nordstrom et al. (1990)
	-586.8	-689.9	98.4	--	--	--	Robie and Hemingway (1995)

Table 6.3. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
HCO_3^-	--	--	--	See CO_3^{2-}	--	--	Smith et al. (2004)
	-587.0 -586.8 -586.8 -586.8 -586.8	-691.1 -692.0 -692.0 -692.0 -692.0	95.0 91.2 91.2 91.2	--	--	--	Woods and Garrels (1987)
	-586.940	-689.933	98.450	--	--	--	EQ3/EQ6
	--	--	--	See CO_3^{2-}	--	--	MINTEQA2
	--	--	--	See CO_3^{2-}	--	--	PHREEQC
$H_2CO_3°(aq)$	-623.2	-699.7	184.7	--	--	--	Robie and Hemingway (1995)
	--	--	--	-6.352	9.160	log $K_{r,T}$ and $\Delta_r H_T$ listed at one or more values of temperature and ionic strength	Smith et al. (2004)
	-623.4 -623.2 -623.2 -623.1 -623.2 -623.2	-689.7 -699.6 -699.6 -699.6 -699.6 -699.6	191.2 187.4 187.0 187.4 187.4	--	--	--	Woods and Garrels (1987)
	--	--	--	-6.3520	9.1600	--	MINTEQA2

Table 6.3. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}^\circ$ (kJ/mol)	$\Delta_f H_{298}^\circ$ (kJ/mol)	S_{298}° (J/mol·K)	log $K_{r,298}^\circ$	$\Delta_r H_{298}^\circ$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
$CaCO_3^\circ(aq)$	-1099.127	-1203.482	--	7.105	-29.733	--	Hummel et al. (2002)
	--	--	--	7.105	-29.732	Analytical expression for log $K_{r,T}^\circ$ as a function of temperature	Nordstrom et al. (1990)
	--	--	--	7.002	--	log $K_{r,T}^\circ$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}^\circ$ as a function of temperature	M. H. Reed[(a)]
	--	--	--	7.11	-29.6	log $K_{r,T}$ listed at one or more values of ionic strength	Smith et al. (2004)
	-1099.4 -1098.9 -1098.9	--	--	--	--	--	Woods and Garrels (1987)
	-1099.76	-1202.44	10.46	7.0017	--	log $K_{r,T}^\circ$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	7.1290	-30.6000	--	MINTEQA2
	--	--	--	7.105	-29.730	Analytical expression for log $K_{r,T}^\circ$ as a function of temperature	PHREEQC

Table 6.3. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}^\circ$ (kJ/mol)	$\Delta_f H_{298}^\circ$ (kJ/mol)	S_{298}° (J/mol·K)	log $K_{r,298}^\circ$	$\Delta_r H_{298}^\circ$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
$CaHCO_3^+$	-1145.992	-1221.952	--	-1.106	-11.263	--	Hummel et al. (2002)
	--	--	--	-1.106	-11.25	Analytical expression for log $K_{r,T}^\circ$ as a function of temperature	Nordstrom et al. (1990)
	--	--	--	-1.047	--	log $K_{r,T}^\circ$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}^\circ$ as a function of temperature	MH Reed(a)
	--	--	--	-1.20	-19.0	--	Smith et al. (2004)
	-1145.0	--	--	--	--	--	Woods and Garrels (1987)
	-1145.70	-1231.56	66.944	-1.0467	--	log $K_{r,T}^\circ$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	-1.2700	-20.0000	--	MINTEQA2
	--	--	--	-1.106	-11.256	Analytical expression for log $K_{r,T}^\circ$ as a function of temperature	PHREEQC
$Fe^{II}CO_3^\circ(aq)$	-631.818	--	--	5.949	--	--	Hummel et al. (2002)
	--	--	--	5.95	--	--	Nordstrom et al. (1990)
	-646.487	--	--	5.5988	--	--	EQ3/EQ6
	--	--	--	5.949	--	--	PHREEQC

Table 6.3. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
$Fe^{III}CO_3^+$	-600.701	-789.722	-358.569	0.6088	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
$Fe^{II}HCO_3^+$	-677.191	--	--	-2.000	--	--	Hummel et al. (2002)
	--	--	--	-2.000	--	--	Nordstrom et al. (1990)
	--	--	--	-1.10	--	--	Smith et al. (2004)
	-693.971	--	--	-2.7200	--	--	EQ3/EQ6
	--	--	--	-1.1000	--	--	MINTEQA2
	--	--	--	-2.0	--	--	PHREEQC
$MgCO_3°(aq)$	-1000.300	-1130.963	--	7.349	-26.252	--	Hummel et al. (2002)
	--	--	--	7.35	-26.250	Analytical expression for log $K_{r,T}°$ as a function of temperature	Nordstrom et al. (1990)
	--	--	--	7.350	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]
	--	--	--	7.41	-24.6	log $K_{r,T}$ listed at one or more values of ionic strength	Smith et al. (2004)

Table 6.3. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}^\circ$ (kJ/mol)	$\Delta_f H_{298}^\circ$ (kJ/mol)	S_{298}° (J/mol·K)	log $K_{r,298}^\circ$	$\Delta_r H_{298}^\circ$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
$MgCO_3^\circ(aq)$	-1003.5 -1002.5 -99.3 -1002.5	--	--	--	--	--	Woods and Garrels (1987)
	-998.972	-1132.07	-100.42	7.3499	--	log $K_{r,T}^\circ$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	7.4090	-26.6000	--	MINTEQA2
	--	--	--	7.349	-26.25	Analytical expression for log $K_{r,T}^\circ$ as a function of temperature	PHREEQC
$MgHCO_3^+$	-1048.347	-1153.927	--	-1.068	-3.288	--	Hummel et al. (2002)
	--	--	--	-1.01	-5.0	--	Smith et al. (2004)
	--	--	--	-1.07	-3.31	Analytical expression for log $K_{r,T}^\circ$ as a function of temperature	Nordstrom et al. (1990)
	--	--	--	-1.036	--	log $K_{r,T}^\circ$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}^\circ$ as a function of temperature	MH Reed(a)
	-1049.7 -1050.6 -1047.2 -1211.5	--	--	--	--	--	Woods and Garrels (1987)

Table 6.3. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
$MgHCO_3^+$	-1046.84	-1153.74	-12.55	-1.0357	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	-1.0100	-4.0000	--	MINTEQA2
	--	--	--	-1.070	-3.310	Analytical expression for log $K_{r,T}°$ as a function of temperature	PHREEQC
$MnCO_3°(aq)$	-783.986	--	--	5.429	--	--	Hummel et al. (2002)
	--	--	--	5.43	--	--	Nordstrom et al. (1990)
	--	--	--	3.820	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	M. H. Reed[(a)]
	--	--	--	5.63	--	log $K_{r,T}$ listed at one or more values of ionic strength	Smith et al. (2004)
	-751.4	-895.0	-136.8	--	--	--	Woods and Garrels (1987)
	-781.810	--	--	5.8088	--	--	EQ3/EQ6
	--	--	--	5.429	--	--	PHREEQC

Table 6.3. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
$MnHCO_3^+$	-826.106	--	--	-1.950	--	--	Hummel et al. (2002)
	--	--	--	-1.95	--	--	Nordstrom et al. (1990)
	--	--	--	-1.30	-4.0	log $K_{r,T}$ listed at one or more values of ionic strength	Smith et al. (2004)
	-820	--	--	--	--	--	Woods and Garrels (1987)
	-820.000	--	--	-0.8816	--	--	EQ3/EQ6
	--	--	--	-1.3000	-4.0000	--	MINTEQA2
	--	--	--	-1.950	--	--	PHREEQC
$NaCO_3^-$	-797.119	-878.375	--	9.059	-52.180	--	Hummel et al. (2002)
	--	--	--	9.06	-52.179	--	Nordstrom et al. (1990)
	--	--	--	9.360	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	M. H. Reed[(a)]
	--	--	--	9.06	--	log $K_{r,T}$ listed at one or more values of ionic strength	Smith et al. (2004)
	-797.2 -792.8	-935.9	-49.8	--	--	--	Woods and Garrels (1987)

Table 6.3. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
$NaCO_3^-$	-792.800	-935.885	-49.800	9.8144	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	9.0590	5.7500	--	MINTEQA2
	--	--	--	9.059	-52.180	--	PHREEQC
$NaHCO_3°(aq)$	-847.401	--	--	0.250	--	--	Hummel et al. (2002)
	--	--	--	0.25	--	--	Nordstrom et al. (1990)
	--	--	--	1.100	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]
	--	--	--	0.3	--	log $K_{r,T}$ listed at one or more values of ionic strength	Smith et al. (2004)
	-848.9 -847.5 -849.7	-930.9 -943.9	155.2 113.8	--	--	--	Woods and Garrels (1987)
	-849.700	-944.007	113.800	-0.1541	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, and 473 K	EQ3/EQ6
	--	--	--	0.2500	13.7301	--	MINTEQA2
	--	--	--	0.25	--	--	PHREEQC

(a) Reed MH. 2008. "SOLTHERM Database of Equilibria Constants." Personal communication, University of Oregon, Eugene, January 31, 2008.

Table 6.4. Thermodynamic Data Available for Carbonate-Containing Minerals

Formula for Carbonate Compound	**$\Delta_f G_{298}^\circ$ (kJ/mol)**	**$\Delta_f H_{298}^\circ$ (kJ/mol)**	**S_{298}° (J/mol·K)**	**log $K_{r,298}^\circ$**	**$\Delta_r H_{298}^\circ$ (kJ/mol)**	**Other Values Included in Source**	**Listed Values Taken from Following Source and References Therein**
Ankerite $Ca(Fe^{II},Mg,Mn^{II})(CO_3)_2$	-1819.29	-1971.50	187.00	--	--	Analytical expression for temperature dependence of C_p°	Holland and Powell (1998)
	--	--	--	-0.311	--	log $K_{r,T}^\circ$ at 298, 323, 373, 423, 473, 523, 573, and 623 K (25, 50, 100, 150, 200, 250, 300, and 350°C); analytical expression for log $K_{r,T}^\circ$ as a function of temperature	MH Reed[(a)]: values for $CaFe^{II}(CO_3)_2$ composition
Aragonite $CaCO_3$	-1128.03	-1207.65	89.50	--	--	Analytical expression for temperature dependence of C_p°	Holland and Powell (1998)
	-1128.306	-1207.480	--	1.933	-25.735	--	Hummel et al. (2002)
	--	--	--	1.993	-25.732	Analytical expression for log $K_{r,T}^\circ$ as a function of temperature	Nordstrom et al. (1990)
	--	--	--	1.954	--	log $K_{r,T}^\circ$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}^\circ$ as a function of temperature	MH Reed[(a)]

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Aragonite $CaCO_3$	-1127.4	-1207.4	88.0	--	--	Analytical expression for temperature dependence of $C_p°$ and $\Delta_f G_T°$, $\Delta_f H_T°$, and $S_T°$ values up to 1000 K (727°C)	Robie and Hemingway (1995)
	--	--	--	2.02	-24.6	--	Smith et al. (2004)
	-1127.7	-1207.0	88.7	--	--	--	Woods and Garrels (1987)
	-1127.4	-1207.0	88.0				
	-1128.5		88.7				
	-1127.8	-1207.4	88.0				
	-1129.2	-1208.0	90.2				
	-1127.8	-1207.1	88.7				
	-1128.2						
	-1129.4						
	-1130.1	-1209.7	87.9				
	-1128.35	-1207.21	90.207	1.9931	--	Log $K_{r,T}°$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	2.0290	-26.6000	--	MINTEQA2
	--	--	--	1.993	-25.730	Analytical expression for log $K_{r,T}°$ as a function of temperature	PHREEQC

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Artinite $Mg_2CO_3(OH)_2{\cdot}3H_2O$	--	--	--	19.656	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]
	-2568.4	-2920.6	232.9	--	--	--	Robie and Hemingway (1995)
	-2568.3 -2568.6	-2920.6 -2920.6	232.9 232.9	--	--	--	Woods and Garrels (1987)
	-2568.62	-2920.61	232.92	19.6560	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	19.9290	-134.8565	--	MINTEQA2
Burkeite $Na_6CO_3(SO_4)_2$	-3592.99	--	--	9.4866	--	--	EQ3/EQ6
Calcite $CaCO_3$	-1128.81	-1207.54	92.50	--	--	Analytical expression for temperature dependence of $C_p°$	Holland and Powell (1998)
	-1129.127	-1208.705	--	1.849	-24.510	--	Hummel et al. (2002)
	--	--	--	1.849	-24.510	Analytical expression for log $K_{r,T}°$ as a function of temperature	Nordstrom et al. (1990)

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}^\circ$ (kJ/mol)	$\Delta_f H_{298}^\circ$ (kJ/mol)	S_{298}° (J/mol·K)	log $K_{r,298}^\circ$	$\Delta_r H_{298}^\circ$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Calcite $CaCO_3$	--	--	--	1.816	--	log $K_{r,T}^\circ$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}^\circ$ as a function of temperature	M. H. Reed[(a)]
	-1128.5	-1207.4	91.7	--	--	Analytical expression for temperature dependence of C_p° and $\Delta_f G_T^\circ$, $\Delta_f H_T^\circ$, and S_T° values up to 1200 K (927°C)	Robie and Hemingway (1995)
	--	--	--	1.85	-24.6	log $K_{r,T}$ listed at one or more values of ionic strength	Smith et al. (2004)
	-1128.8	-1206.9	92.9	--	--	--	Woods and Garrels (1987)
	-1128.3	-1206.8	91.7				
		-1207.7	92.9				
	-1128.8	-1207.4	91.7				
	-1130.1	-1208.2	92.7				
	-1128.8	-1206.9	92.9				
	-1128.8	-1207.4					
	-1129.3						
	-1130.3						
	-1130.6	-1209.0	91.8				
	-1129.18	-1207.30	92.676	1.8487	--	log $K_{r,T}^\circ$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Calcite $CaCO_3$	--	--	--	1.8490	-22.6000	--	MINTEQA2
	--	--	--	1.849	-24.52	Analytical expression for log $K_{r,T}°$ as a function of temperature	PHREEQC
$CaCO_3$ (amorphous solid)	--	--	--	3.94	-31.6	--	Smith et al. (2004)
Dawsonite $NaAlCO_3(OH)_2$	-1782	-1960	131	--	--	--	Bénézeth et al. (2007)
	--	--	--	3.660	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]
	-1786.0	-1964.0	132.0	--	--	Analytical expression for temperature dependence of $C_p°$ and $\Delta_f G_T°$, $\Delta_f H_T°$, and $S_T°$ values up to 500 K (227°C)	Robie and Hemingway (1995)
	-1786.0	-1964.0	132.0	--	--	--	Woods and Garrels (1987)
	-1785.990	-1963.956	132.000	4.3464	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, and 473 K	EQ3/EQ6

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Dolomite (ordered) $CaMg(CO_3)_2$	-2161.51	-2324.56	156.00	--	--	Analytical expression for temperature dependence of $C_p°$	Holland and Powell (1998)
	-2161.565	-2321.148	--	3.568	-69.282	--	Hummel et al. (2002)
	--	--	--	3.57	-69.279	--	Nordstrom et al. (1990)
	--	--	--	3.240	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]
	-2161.3	-2324.5	155.2	--	--	Analytical expression for temperature dependence of $C_p°$ and $\Delta_f G_T°$, $\Delta_f H_T°$, and $S_T°$ values up to 1100 K (827°C)	Robie and Hemingway (1995)
	-2169.3 -2151.9 -2170.0 -2161.7 -2167.2 -2163.4 -2177.8	-2331.7 -2314.6 -2332.7 -2324.5 -2329.9 -2326.3	155.2 155.2 155.2 155.2 155.2	--	--	--	Woods and Garrels (1987)

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}^\circ$ (kJ/mol)	$\Delta_f H_{298}^\circ$ (kJ/mol)	S_{298}° (J/mol·K)	log $K_{r,298}^\circ$	$\Delta_r H_{298}^\circ$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Dolomite[(b)] (ordered) $CaMg(CO_3)_2$	-2166.31	-2328.94	155.18	2.5135	--	log $K_{r,T}^\circ$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	3.568	-69.280	--	PHREEQC: mineral form not specified
	--	--	--	3.5680	-68.7000	--	MINTEQA2
Dolomite (disordered) $CaMg(CO_3)_2$	-2158.425	-2314.228	--	4.118	-76.202	--	Hummel et al. (2002)
	--	--	--	4.12	-76.20	--	Nordstrom et al. (1990)
	--	--	--	4.058	--	log $K_{r,T}^\circ$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}^\circ$ as a function of temperature	MH Reed[(a)]
	-2158.4	-2317.6	166.7	--	--	--	Woods and Garrels (1987)
	-2157.49	-2316.70	166.69	4.0579	--	log $K_{r,T}^\circ$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	4.11800	-75.6000	--	MINTEQA2

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Gaylussite $CaNa_2(CO_3)_2·5H_2O$	-3372.61	--	--	11.1641	--	--	EQ3/EQ6
Huntite $CaMg_3(CO_3)_4$	--	--	--	10.301	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	M. H. Reed[(a)]
	-4203.1	-4529.6	299.5	--	--	--	Robie and Hemingway (1995)
	-4203.4 -4216.2	-4529.6	299.5	--	--	--	Woods and Garrels (1987)
	-4203.71	-4529.60	299.53	10.3010	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	11.3480	-166.1798	--	MINTEQA2
$Mg_4(CO_3)_3(OH)_2·3H_2O$	-4603.3 -4637.1	--	--	--	--	--	Woods and Garrels (1987)
Hydromagnesite $Mg_5(CO_3)_4(OH)_2·4H_2O$	--	--	--	30.854	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]
	-5864.2	-6514.9	503.7	--	--	--	Robie and Hemingway (1995)

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Hydromagnesite $Mg_5(CO_3)_4(OH)_2·4H_2O$	-5864.2 -5864.6	-6514.9 -6514.9	503.7 541.3	--	--	--	Woods and Garrels (1987)
	-5864.66	-6514.86	541.33	30.8539	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	32.5500	-276.8466	--	MINTEQA2
Ikaite $CaCO_3·6H_2O$	-2540.9	-2954.1	370.0	--	--	--	Robie and Hemingway (1995): $\Delta_f G_{298}°$, $\Delta_f H_{298}°$, $S_{298}°$
	--	--	--	2.87	-39.6	--	Smith et al. (2004) (only composition, but not mineral form, specified)
$K_2CO_3·1.5H_2O$	-1431.27	--	--	13.3785	--	--	EQ3/EQ6
$K_8H_4(CO_3)_6·3H_2O$	-1514.032	--	--	27.7099	--	--	EQ3/EQ6
$KNaCO_3·6H_2O$	-596.513	--	--	10.2593	--	--	EQ3/EQ6
K_2CO_3	-1069.0 -1064.0 -1060.6	-1146.1 -1149.8	140.6 155.5	--	--	--	Woods and Garrels (1987)
Kalicinite $KHCO_3$	-207.405	--	--	0.2837	--	--	EQ3/EQ6

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}^\circ$ (kJ/mol)	$\Delta_f H_{298}^\circ$ (kJ/mol)	S_{298}° (J/mol·K)	log $K_{r,298}^\circ$	$\Delta_r H_{298}^\circ$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Kutnahorite $CaMn(CO_3)_2$	-1950.6	--	--	--	--	--	Woods and Garrels (1987)
Lansfordite $MgCO_3 \cdot 5H_2O$	-2200.2 -2201.0 -2199.2	--	--	--	--	--	Woods and Garrels (1987)
	--	--	--	5.79	--	--	Smith et al. (2004) (composition, but not mineral form, specified)
	-2199.200	--	--	4.8409	--	--	EQ3/EQ6
Magnesite $MgCO_3$	-1027.74	-1111.59	65.10	--	--	Analytical expression for temperature dependence of C_p°	Holland and Powell (1998)
	-1030.600	--	--	2.041	--	--	Hummel et al. (2002)
	--	--	--	2.290	--	Log $K_{r,T}^\circ$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}^\circ$ as a function of temperature	MH Reed[(a)]
	-1029.5	-1113.3	65.1	--	--	Analytical expression for temperature dependence of C_p° and $\Delta_f G_T^\circ$, $\Delta_f H_T^\circ$, and S_T° values up to 1000 K (727°C)	Robie and Hemingway (1995)

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Magnesite[(c)] $MgCO_3$	--	--	--	2.87	--	--	Smith et al. (2004) (only specifies composition, but not mineral form)
	-1029 -1012.3 -1029.7 -1029.6 -1029.5 -1027.8 -1012.1 -1027.3	-1113 -1095.8 -1113.1 -1113.2 -1113.3 -1111.4 -1095.8	65.7 65.7 65.7 65.8 65.1 65.7 65.7	--	--	--	Woods and Garrels (1987)
	-1027.83	-1111.40	65.689	2.2936	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	2.8690	5.4000	--	MINTEQA2
Meionite (Al/Si ordered) $Ca_4Al_6Si_6O_{24}CO_3$	-13104.74	-13843.65	752.00	--	--	Analytical expression for temperature dependence of $C_p°$	Holland and Powell (1998)
	--	--	--	77.060	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}^\circ$ (kJ/mol)	$\Delta_f H_{298}^\circ$ (kJ/mol)	S_{298}° (J/mol·K)	log $K_{r,298}^\circ$	$\Delta_r H_{298}^\circ$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Meionite (Al/Si ordered) $Ca_4Al_6Si_6O_{24}CO_3$	-13131.8	-13881.4	715.2	--	--	Analytical expression for temperature dependence of C_p° and $\Delta_f G_T^\circ$, $\Delta_f H_T^\circ$, and S_T° values up to 1200 K (727°C)	Robie and Hemingway (1995)
	-13142.7	-13897.5	691.4	--	--	--	Woods and Garrels (1987)
Monohydrocalcite[(d)] $CaCO_3 \cdot H_2O$	-1361.6	-1498.3	131.1	--	--	--	Robie and Hemingway (1995)
	-1361.3	-1498.3	--	--	--	--	Woods and Garrels (1987)
	--	--	--	2.73	--	--	Smith et al. (2004)
	-1361.600	-1498.290	129.853	2.6824	--	log $K_{r,T}^\circ$ values also at 273, 333, 373, 423, and 473 K	EQ3/EQ6
Na_2CO_3 (likely natrite)	-1045.3	-1129.2	135.0	--	--	--	Robie and Hemingway (1995): (composition, but not mineral form, specified)
	-1047.7 -1047.8 -1044.4	-1130.9 -1131.4 -1130.7	136.0 135.0 135.0	--	--	--	Woods and Garrels (1987)

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}^\circ$ (kJ/mol)	$\Delta_f H_{298}^\circ$ (kJ/mol)	S_{298}° (J/mol·K)	log $K_{r,298}^\circ$	$\Delta_r H_{298}^\circ$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Na_2CO_3 (likely natrite)	-1046.874	-1130.680	134.980	11.1822	--	log $K_{r,T}^\circ$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
$Na_2CO_3 \cdot 7H_2O$	-2714.2 -2715.9	-3200.0	422.2	--	--	--	Woods and Garrels (1987)
	-2714.200	-3199.189	422.200	9.9459	--	log $K_{r,T}^\circ$ values also at 273, 333, 373, 423, and 473 K	EQ3/EQ6
Nahcolite $NaHCO_3$	-851.2	-949.0	102.1	--	--	--	Robie and Hemingway (1995)
	-851.9 -815.9 -851.0	-947.7 -913.4 -950.8	102.1 102.1 101.7	--	--	--	Woods and Garrels (1987)
	-849.461	-947.257	102.09	-0.1118	--	log $K_{r,T}^\circ$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
Natron $Na_2CO_3 \cdot 10H_2O$	-3431.5 -3427.7 -3429.0	-4082.0 -4081.3	564.7 562.7	--	--	--	Woods and Garrels (1987)
	-3427.660	-4079.394	562.700	9.6102	--	log $K_{r,T}^\circ$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	9.0180	51.2771	--	MINTEQA2

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Nesquehonite $MgCO_3·3H_2O$	--	--	--	4.996	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]
	-1723.8	-1977.3	195.6	--	--	--	Robie and Hemingway (1995)
	--	--	--	5.66	--	--	Smith et al. (2004) (composition, but not mineral form, specified)
	-1726.6	-1985.7	159.0	--	--	--	Woods and Garrels (1987)
	-1726.6						
	-1723.7	-1977.3	195.6				
	-1724.0	-1977.2	195.6				
	-1726.1						
	-1723.95	-1977.26	195.64	4.9955	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	5.6590	-38.8312	--	MINTEQA2
Pirssonite $Na_2Ca(CO_3)_2·2H_2O$	-635.794	--	--	11.3230	--	--	EQ3/EQ6

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_fG_{298}°$ (kJ/mol)	$\Delta_fH_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_rH_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Rhodochrosite $MnCO_3$	-817.22	-891.06	98.00	--	--	analytical expression for temperature dependence of $C_p°$	Holland and Powell (1998)
	-819.548	-890.081	--	-0.801	-20.884	--	Hummel et al. (2002)
	--	--	--	-0.80	-20.88	--	Nordstrom et al. (1990)
	--	--	--	0.026	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	M. H. Reed[(a)]
	-819.1	-892.9	98.0	--	--	analytical expression for temperature dependence of $C_p°$ and $\Delta_fG_T°$, $\Delta_fH_T°$, and $S_T°$ values up to 600 K (327°C)	Robie and Hemingway (1995)
	-816.7	-894.1	85.8	--	--	--	Woods and Garrels (1987) (natural sample)
	-815.5	-888.6					
	-816.0	-889.3	100.0				
	-816.1	-889.2	100.0				
	-816.7	-894.1	85.8				
	-815.0	-889.3					
	-818.8						

Table 6.4. (contd)

Formula for Carbonate Compound	**$\Delta_f G_{298}°$ (kJ/mol)**	**$\Delta_f H_{298}°$ (kJ/mol)**	**$S_{298}°$ (J/mol·K)**	**log $K_{r,298}°$**	**$\Delta_r H_{298}°$ (kJ/mol)**	**Other Values Included in Source**	**Listed Values Taken from Following Source and References Therein**
Rhodochrosite $MnCO_3$	--	--	--	-0.67	--	log $K_{r,T}$ listed at one or more values of ionic strength	Smith et al. (2004)
	-816.068	-889.188	99.998	-0.1928	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	-0.2510	-16.4800	--	MINTEQA2
	--	--	--	-0.801	-20.883	--	PHREEQC
Rhodochrosite (synthetic) $MnCO_3$	-815.324	-896.064	--	-0.061	-14.901	--	Hummel et al. (2002)
	--	--	--	-0.061	--	--	Nordstrom et al. (1990)
	-817.6	-895.0	85.6	--	--	--	Woods and Garrels (1987) (form not specified)
	--	--	--	-0.17	--	log $K_{r,T}$ listed at one or more values of ionic strength	Smith et al. (2004) (only specifies composition, but not mineral form)
Rhodochrosite (precipitated) $MnCO_3$	-813.0	-887 -883.2	99.6	--	--	--	Woods and Garrels (1987) (labeled as precipitated form)

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Siderite $FeCO_3$	-680.71	-749.59	109.54	--	--	Analytical expression for temperature dependence for log $K_{r,T}°$ from 298 to 523 K	Bénézeth et al. (2009a)
	-688.16	-761.50	95.00	--	--	Analytical expression for temperature dependence of $C_p°$	Holland and Powell (1998)
	-668.978	-754.037	--	-0.561	-25.278	--	Hummel et al. (2002)
	--	--	--	-0.56	-25.28	--	Nordstrom et al. (1990)
	--	--	--	-1.722	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]
	-682.8	-755.9	95.5	--	--	Analytical expression for temperature dependence of $C_p°$ and $\Delta_f G_T°$, $\Delta_f H_T°$, and $S_T°$ values up to 600 K (327°C)	Robie and Hemingway (1995)
	--	--	--	-0.47	-30.6	log $K_{r,T}$ listed at one or more values of ionic strength	Smith et al. (2004) (only composition, but not mineral form, specified)
	--	--	--	--	--	Analytical expression for temperature dependence for log $K_{r,T}°$ from 298 to 368 K	Sun et al. (2009)

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}^\circ$ (kJ/mol)	$\Delta_f H_{298}^\circ$ (kJ/mol)	S_{298}° (J/mol·K)	log $K_{r,298}^\circ$	$\Delta_r H_{298}^\circ$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Siderite $FeCO_3$	-673.9 -680.3 -679.5	-747.7 -753.1 -752.2	92.9 96.1 96.1	--	--	--	Woods and Garrels (1987)
	-679.540	-749.660	105.02	-0.1920	--	log $K_{r,T}^\circ$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	0.0890	-30.6000	--	MINTEQA2
	--	--	--	-0.561	-25.280	--	PHREEQC
$FeCO_3$ (precipitated form)	-666.467	-764.414	--	-0.121	-14.901	--	Hummel et al. (2002)
	--	--	--	-0.12	--	--	Nordstrom et al. (1990)
Spurrite $Ca_5Si_2O_8CO_3$	-5534.67	-5849.69	330.00	--	--	Analytical expression for temperature dependence of C_p°	Holland and Powell (1998)
	--	--	--	75.201	--	log $K_{r,T}^\circ$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}^\circ$ as a function of temperature	MH Reed[(a)]
	-5525.6	-5840.2	331.0	--	--	Analytical expression for temperature dependence of C_p° and $\Delta_f G_T^\circ$, $\Delta_f H_T^\circ$, and S_T° values up to 1300 K (1027°C)	Robie and Hemingway (1995)

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_fG_{298}°$ (kJ/mol)	$\Delta_fH_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_rH_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Spurrite $Ca_5Si_2O_8CO_3$	-5568.8	-5899.3	270.8	--	--	--	Woods and Garrels (1987)
Thermonatrite $Na_2CO_3{\cdot}H_2O$	-1286.1	-1429.7	168.1	--	--	Analytical expression for temperature dependence of $C_p°$ up to 380 K (107°C)	Robie and Hemingway (1995)
	-1288.7 -1285.3 -1286.0 -1286.6	-1432.0 -1431.3	168.2 168.1	--	--	--	Woods and Garrels (1987)
	-1285.310	-1428.784	168.110	10.9623	--	log $K_{r,T}°$ values also at 273, 333, 373, 423, 473, 523, and 573 K	EQ3/EQ6
	--	--	--	10.9660	-25.0799	--	MINTEQA2
Tilleyite $Ca_5Si_2O_7(CO_3)_2$	-6008.28	-6368.33	390.00	--	--	Analytical expression for temperature dependence of $C_p°$	Holland and Powell (1998)
	--	--	--	53.490	--	log $K_{r,T}°$ at 298, 323, 373, 423, 473, 523, 573, and 623 K; analytical expression for log $K_{r,T}°$ as a function of temperature	MH Reed[(a)]
	-6013.5	-6372.2	394.0	--	--	Analytical expression for temperature dependence of $C_p°$ and $\Delta_fG_T°$, $\Delta_fH_T°$, and $S_T°$ values up to 1200 K (927°C)	Robie and Hemingway (1995)

Table 6.4. (contd)

Formula for Carbonate Compound	$\Delta_f G_{298}°$ (kJ/mol)	$\Delta_f H_{298}°$ (kJ/mol)	$S_{298}°$ (J/mol·K)	log $K_{r,298}°$	$\Delta_r H_{298}°$ (kJ/mol)	Other Values Included in Source	Listed Values Taken from Following Source and References Therein
Tilleyite $Ca_5Si_2O_7(CO_3)_2$	-6009.8	-6371.6	376.7	--	--	--	Woods and Garrels (1987)
Trona $Na_3(CO_3)(HCO_3)·2H_2O$	--	-2682.1	--	--	--	--	Robie and Hemingway (1995)
	-2386.6 -2383.4 -2380.5	-2684.9	301.2	--	--	--	Woods and Garrels (1987)
Trona-K $K_2NaH(CO_3)_2·2H_2O$	-575.740	--	--	11.5891	--	--	EQ3/EQ6
Vaterite $CaCO_3$	-1125.5	--	--	--	--	--	Robie and Hemingway (1995)
	-1125.5	--	--	--	--	--	Woods and Garrels (1987)
	--	--	--	2.42	-29.6	--	Smith et al. (2004)
Wegscheiderite $Na_5(HCO_3)_3CO_3$	--	-3984.0	--	--	--	--	Robie and Hemingway (1995)

(a) Reed MH. 2008. "SOLTHERM Database of Equilibria Constants." Personal communication, University of Oregon, Eugene, January 31, 2008.

(b) Bénézeth et al. (2009b) have determined the solubility product as a function of temperature for a natural sample of dolomite based on solubility measurements from 25ºC to 200°C. Their calculated solubility product values are not listed in their extended abstract.

(c) Bénézeth et al. (2009b) have determined the solubility product as a function of temperature for synthesized magnesite based on solubility measurements from 25ºC to 200°C. Their calculated solubility product values are not listed in their extended abstract.

(d) Munemoto and Fukushi (2009) have determined the solubility product for synthesized monohydrocalcite based on solubility measurements from 5ºC to 40°C. Their calculated value for the solubility product of monohydrocalcite is not listed in their extended abstract.

7.0 Comparison of Carbonate Characterization Data to Known Thermodynamic Data

Table 7.1 lists all the carbonate minerals given in Tables 5.2, 5.3, and 5.4, which were physically identified as being present in the host rock formations at CO_2 injection test sites or natural analogue sites, reaction products of CO_2 injection/intrusion into a host formation, or as mineral reactants or products of laboratory CO_2 fluid-rock/-mineral experiments. Almost all of the carbonates in Table 7.1 were identified in studies of CO_2 natural analogue sites or laboratory CO_2 fluid-rock/-mineral experiments. The carbonate mineralogy obviously must be known for all host formations at sites that are being used or considered for CO_2 injection testing. This mineralogical information was not detailed in the publications (Table 5.2) reviewed for our evaluation but was probably given in references cited by these publications. However, many of the publications listed in Table 5.2 used geochemical reaction modeling to explain CO_2 gas-fluid-rock geochemistry at their sites.

The list of carbonate minerals in Table 7.1 is short and contains typically common carbonate minerals. Except for ferroan and magnesian calcites and ferroan dolomite, data (Table 6.4) are available for the key thermodynamic parameters of the carbonate minerals in Table 7.1. With respect to availability of thermodynamic data, this is good information for those using geochemical reaction modeling techniques to interpret information and results from CO_2 injection and natural analogue sites or laboratory experiments. However, as stated previously, Railsback (1999) noted that in the future, more thorough mineralogical characterization of geological systems affected by anthropogenic activities might show greater diversity of carbonate mineralogy than traditional assumptions would have previously suggested.

Table 7.1. Carbonate Minerals Physically Identified in Host Rock Formations at CO_2 Injection or Natural Analogue Sites, Reaction Products of CO_2 Injection/Intrusion into a Host Formation, or as Mineral Reactants or Products of Laboratory CO_2 Fluid-Rock/-Mineral Experiments

Carbonate Minerals Physically Identified as Being in the Geologic Formation, Products of CO_2 Injection/Intrusion into a Host Formation, or as Reactants or Products of Laboratory Experiments	**Reference and Type of Study**
Ankerite[(a)]	• Bertier et al. (2006) – laboratory fluid-rock experiments • May (2005) – natural analogue • McGrail et al. (2006) – experimental fluid-rock experiments • Pauwels et al. (2007) – natural analogue • Watson et al. (2004) – natural analogue
Aragonite	• Bertier et al. (2006) – laboratory fluid-rock experiments • Jacquemet et al. (2008) – laboratory fluid-rock (cement) experiments
Calcite	• Bateman et al. (2005) – laboratory fluid-rock experiments • Bertier et al. (2006) – laboratory fluid-rock experiments • Guichet et al. (2005) (abstract only) – laboratory fluid-rock experiments • Jacquemet et al. (2008) – laboratory fluid-rock (cement) experiments • Lin et al. (2008) – laboratory fluid-rock and fluid-mineral experiments • Machel (2005) – field injection site • May (2005) – natural analogue • McGrail et al. (2006) – experimental fluid-rock experiments • Michael and Buschkuehle (2006) – natural analogue • Pearce et al. (1996) – natural analogue (review of information) and experimental fluid-rock experiments • Rosenbauer et al. (2005) – laboratory fluid–rock experiments • Vosteen and May (2007) (abstract only) – natural analogue
Calcite, ferroan	• Worden (2006) – natural analogue
Calcite, magnesian	• Park and Fan (2004) – laboratory fluid–rock experiments
Carbonate, ferroan (specific carbonate mineral not identified)	• Watson et al. (2004) – natural analogue
Carbonate, magnesian (specific carbonate mineral not identified)	• Watson et al. (2004) – natural analogue
Dawsonite	• Moore et al. (2005) – natural analogue • Palandri et al. (2005) – experimental fluid-mineral experiments • Worden (2006) – natural analogue

Table 7.1. (contd)

Carbonate Minerals Physically Identified as Being in the Geologic Formation, Products of CO_2 Injection/Intrusion into a Host Formation, or as Reactants or Products of Laboratory Experiments	Reference and Type of Study
Dolomite	• Bateman et al. (2005) – laboratory fluid-rock experiments • Bertier et al. (2006) – laboratory fluid-rock experiments • Machel (2005) – field injection site • May (2005) – natural analogue • Moore et al. (2005) – natural analogue • Pearce et al. (1996) – natural analogue (review of information) and experimental fluid-rock experiments • Rosenbauer et al. (2005) – laboratory fluid–rock experiments • Shiraki and Dunn (2000) – laboratory fluid–rock experiments • Vosteen and May (2007) (abstract only) – natural analogue
Dolomite, ferroan	• Pauwels et al. (2007) – natural analogue • Pearce et al. (1996) – natural analogue (review of information) and experimental fluid-rock experiments • Worden (2006) – natural analogue
Magnesite	• Kaszuba et al. (2003) – laboratory fluid-rock experiments • Kaszuba et al. (2005) – laboratory fluid-rock experiments • Schulze et al. (2004) – laboratory fluid-rock experiments • Wolf et al. (2004) – laboratory fluid-rock experiments
Siderite	• Kaszuba et al. (2003) – laboratory fluid-rock experiments • Kaszuba et al. (2005) – laboratory fluid-rock experiments • Schulze et al. (2004) – laboratory fluid-rock experiments • Wolf et al. (2004) – laboratory fluid-rock experiments
(a) Pure Fe end member ankerite [$Ca(Fe(CO_3)_2$] has not been found in nature or produced in the laboratory (Reeder 1983a).	

8.0 Carbonate Mineral Solid Solutions

Solid solutions (crystal solutions) of different carbonate minerals are common. Carbonate solid solutions are important to understanding the phase relations of carbonates in geochemical systems and thus are important to accurate geochemical reaction modeling of CO_2 sequestration systems and mineral trapping reactions. Theoretical concepts and methods of solid solution thermodynamics needed for modeling aqueous-solid solution geochemical systems are presented in detail by Bruno et al. (2007), Glynn (1990, 2000), Navrotsky (1987), Nordstrom and Munoz (1985), and others, and will therefore not be repeated here. Extensive experimental studies have been completed on the $CaCO_3$-$MgCO_3$, $MgCO_3$-$FeCO_3$, $CaCO_3$-$FeCO_3$, $CaCO_3$-$MnCO_3$, and $CaCO_3$-$SrCO_3$ systems. Glynn (2000) reviews the thermodynamic theory of aqueous solution-solid solution interactions for systems from 0ºC to 100°C, and summarizes the available data on the effects of ionic substitution on the thermodynamic properties of selected rhombohedral (calcite) and orthorhombic (aragonite) carbonate structure solid solutions.

Examples of important carbonate solid solutions include Mg (or magnesian) calcites that involve the random substitution of a range of Mg for Ca in the calcite rhombohedral structure. Magnesian calcites have been the subject of extensive study and research interest. Biogenic calcites may contain up to 30 mol% Mg in solid solution. Magnesian calcites are usually described as either low Mg-calcites with less than 5 mol% Mg, or high Mg-calcites with 5–30 mol% Mg (Appelo and Postma 2005). Mackenzie et al. (1983) and Morse and Mackenzie (1990) review the occurrence of low-temperature magnesian calcites and their chemistry, mineralogy, and composition controls in natural systems.

A complete solid solution also exists in the substitution of Fe^{2+} for Mg^{2+} in the siderite ($FeCO_3$)-magnesite ($MgCO_3$) system. Fe-Mg carbonates are common in sedimentary systems. Chai and Navrotsky (1996b) have studied the synthesis, characterization, and mixing properties of the $(Fe,Mg)CO_3$ solid solution.

Dolomite also exhibits solid solutions. The Ca-to-Mg ratio may vary and substitution of Fe and Mn is common in dolomites. Unlike the siderite-magnesite solid solution series, Fe^{2+} only partially substitutes for Mg^{2+} in dolomite to form ankerite $[Ca(Fe_xMg_{1-x})(CO_3)_2$, where x varies from 0 to 0.7 (Reeder 1983a). The end-member compound $CaFe(CO_3)_2$ does not occur naturally nor has been synthesized in the laboratory (Reeder 1983a). Carbonates within this solid solution range have been called ankerites and ferroan dolomites. These two terms are often used, respectively, to the more and less Fe rich solid-solution phases. The boundary between dolomite and ankerite is arbitrarily set at 20 mol% $CaFe(CO_3)_2$. Chai and Navrotsky (1996a) have studied the synthesis, characterization, and energetics along the dolomite-ankerite join.

It is not possible from the literature reviewed in this report to assess the importance of solid solutions relative to CO_2 sequestration processes and mineral trapping reactions. Solid-solution carbonates were reported in some of the natural analogue and laboratory fluid-rock studies reviewed in our assessment (Table 7.1). These include the identification of ferroan calcite (Worden 2006), magnesian calcite (Park and Fan 2004), ferroan and magnesian carbonates (Watson et al. 2004), and ferroan dolomite (Pauwels et al. 2007; Pearce et al. 1996; Worden 2006). Xu et al. (2004, 2005, 2007) (see Table 5.1) assumed an ideal solution for the dolomite-ankerite $[Ca(Fe_{07}Mg0.3)(CO_3)_2]$ solid solution in their modeling of CO_2 sequestration processes using the reactive geochemical transport code TOUGHREACT. Zwingmann et al. (2005) used the geochemical model EQ3/6 to model CO_2 sequestration in a sandstone formation in

Japan. As part of the initial mineralogical composition they used for the injection formation, Zwingmann et al. (2005) included a calcite solid solution with the composition $(Ca,Mg,Fe,Zn,Sr,Mn)CO_3$, with the six end members being calcite, magnesite, siderite, smithsonite, strontianite, and rhodochrosite. It is not clear from the results of these modeling studies as to the relative importance the carbonate solid solutions had to final modeling results. Given how common such solid solutions are in nature, it is assumed inclusion of carbonate solid solutions would be paramount to accurately modeling CO_2 sequestration systems.

9.0 Importance of Pitzer Approach to Modeling CO_2 Sequestration Applications

Geochemical modeling of sequestration of CO_2 in deep saline formations has received particular attention because of their widespread extent, large storage capacity, and typically good permeability. Unfortunately, methods such as the Debye-Hückel and Davies equations, commonly used to calculate activity coefficients for aqueous species, are not typically sufficient and will lead to inaccurate modeling results in these high-ionic strength systems. Chemical reactions are written in terms of effective concentrations or activities and not the concentrations of dissolved species. The difference between the activity and dissolved concentration of a dissolved species is by definition expressed as the activity coefficient γ_i. Two general approaches are used in geochemical reaction models to calculate activity coefficients of aqueous species. These methods, their equation forms, the history of their derivation, and their use in calculating activity coefficients are discussed in detail in sources such as Bethke (2008), Langmuir (1997), Marini (2007), and Nordstrom and Munoz (1985), and will not be repeated here. Bethke (2008) and Marini (2007) also provide example calculations to demonstrate the issues related to using these different approaches to calculate geochemical reactions in high-ionic strength solutions.

The first type consists of the Debye-Hückel equation, its variant the Davies equation, and its extended B-dot equation form. This approach treats the activity coefficient of a species as function of the ion size and ionic strength of the solution. These equations are easy to implement and are available in almost all geochemical models. Although this approach takes into account the distribution of species in solution, these particular approaches are, however, typically limited in accuracy to modeling relative dilutions solutions with ionic strengths less than that of seawater. The Debye-Hückel and Davies equation are typically accurate to concentrations of approximately 0.1 and 0.3–0.5 molal, respectively (Bethke 2008), and the references therein. Bethke (2008) lists the accuracy of the B-dot model to ionic strengths of several molal for predicting the activities of Na^+ and Cl^- ions and to approximately 0.3 to 1 molal for the activities of other species.

The second approach involves the use of virial equations. These semi-empirical equations are sometimes called specific interaction equations or Pitzer equations after Kenneth Pitzer (Pitzer 1973) who was primarily responsible for their development. The Pitzer equations are linear algebraic functions of ln γ_i. They differ conceptually from other approaches in that coefficients are used to account for interactions between the individual dissolved components rather than species. This approach is more complicated to apply, requires considerable amounts of data, involves numerous individual parameters, and provides little insight into the distribution of aqueous species (Bethke 2008). The virial method is reviewed in detail in Pitzer (1987) and Weare (1987). A particularly noteworthy implementation of this approach was its use by Harvie et al. (1984) for geochemical modeling mineral solubilities in the Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system to high-ionic strengths. Their implementation of this method is commonly known as the Harvie-Møller-Weare model. The parameters for the Harvie-Møller-Weare model are listed in Weare (1987). Plummer et al. (1988) also includes a large, comprehensive list of virial coefficients. Examples of recent applications of the Pitzer equations to calculations of carbonate mineral solubilities include De Visscher and Vanderdeelen (2003), Gledhill and Morse (2006), and Marion (2001).

Because virial equations can be applied accurately to systems to high-ionic strengths such as brines and highly saline groundwaters, Pitzer equations have been incorporated into several geochemical reactions models. These include the models EQ3/EQ6 (Wolery 1992), Geochemist's Workbench® (Bethke and Yeakel 2007), PHREEQC (Parkhurst 1995), PHRQPITZ (Plummer et al. 1988), and SOLMINEQ.88 (Kharaka et al. 1988).

Given the limitations of the Debye-Hückel and Davies equations for calculating geochemical reactions at high-ionic strengths, application of geochemical models that include the Pitzer equations is important to accurately model CO_2 sequestration in saline formations. However, because redox reactions, especially for the Fe(II)/Fe(III) system, and Al system have not been parameterized for the Pitzer model, use of the Pitzer method currently will not adequately address Fe- or Al-containing geochemical reactions associated with modeling CO_2 field sites and results from fluid-rock experiments. The importance of using Pitzer equations for modeling reactions in saline waters, such as those targeted as possible host formations for CO_2 injection and storage, and the need for parameterization of redox, Fe, and Al species are recognized by most geochemical modelers, but is nonetheless a potential limitation to accurately model such systems.

10.0 Conclusions

Geochemical reaction models require thermodynamic data to calculate the geochemical reactions associated with CO_2 sequestration. Availability of accurate and complete thermodynamic data is certainly a critical data requirement for the successful use of geochemical reaction modeling to CO_2 sequestration field site and laboratory applications (Gaus et al. 2008; Marini 2007).

The results of the literature review indicated that an extensive thermodynamic database exists for CO_2 and CH_4 gases, carbonate aqueous species, and carbonate minerals. Specifically, thermodynamic data exist in databases used for several commonly used geochemical reaction models and/or in published compilations for the following:

Aqueous Species

$CO_2^{\circ}(aq)$
$CH_4^{\circ}(aq)$
CO_3^{2-}
HCO_3^-
$H_2CO_3^{\circ}(aq)$
$CaCO_3^{\circ}(aq)$
$CaHCO_3^+$
$Fe^{II}CO_3^{\circ}(aq)$
$Fe^{III}CO_3^+$
$Fe^{II}HCO_3^+$
$MgCO_3^{\circ}(aq)$
$MgHCO_3^+$
$MnCO_3^{\circ}(aq)$
$MnHCO_3^+$
$NaCO_3^-$
$NaHCO_3^{\circ}(aq)$

Gases

$CO_2(g)$
$CH_4(g)$

Minerals and Related Solids

ankerite $Ca(Fe^{II},Mg,Mn^{II})(CO_3)_2$
aragonite $CaCO_3$
artinite $Mg_2CO_3(OH)_2 \cdot 3H_2O$
burkeite $Na_6CO_3(SO_4)_2$
calcite $CaCO_3$
$CaCO_3(am)$
dawsonite $NaAlCO_3(OH)_2$
dolomite (ordered and disordered) $CaMg(CO_3)_2$
gaylussite $CaNa_2(CO_3)_2 \cdot 5H_2O$
huntite $CaMg_3(CO_3)_4$
$Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$

hydromagnesite $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$
ikaite $CaCO_3 \cdot 6H_2O$
$K_2CO_3 \cdot 1.5H_2O$
$K_8H_4(CO_3)_6 \cdot 3H_2O$
$KNaCO_3 \cdot 6H_2O$
K_2CO_3
kalicinite $KHCO_3$
kutnahorite $CaMn(CO_3)_2$
lansfordite $MgCO_3 \cdot 5H_2O$
magnesite $MgCO_3$
meionite (Al/Si ordered) $Ca_4Al_6Si_6O_{24}CO_3$
monohydrocalcite $CaCO_3 \cdot H_2O$
Na_2CO_3 (likely natrite)
$Na_2CO_3 \cdot 7H_2O$
nahcolite $NaHCO_3$
natron $Na_2CO_3 \cdot 10H_2O$
nesquehonite $MgCO_3 \cdot 3H_2O$
pirssonite $Na_2Ca(CO_3)_2 \cdot 2H_2O$
rhodochrosite $MnCO_3$ (natural and synthetic forms)
siderite $FeCO_3$ (natural and precipitated forms)
spurrite $Ca_5Si_2O_8CO_3$
thermonatrite $Na_2CO_3 \cdot H_2O$
tilleyite $Ca_5Si_2O_7(CO_3)_2$
trona $Na_3H(CO_3)_2 \cdot 2H_2O$
trona-K $K_2NaH(CO_3)_2 \cdot 2H_2O$
vaterite $CaCO_3$
wegscheiderite $Na_5(HCO_3)_3CO_3$

Values of $\Delta_f G_{298}°$ and/or $\log K_{r,298}°$ are available for essentially all of these compounds. $\log K_{r,T}°$ or heat capacity values at temperatures above 298 K exist for less than approximately one-third of these compounds. For those compounds that do not have high-temperature heat capacity data, the tabulated high-temperature $\log K_{r,T}°$ are likely based on extrapolation methods that relied on thermodynamic properties reported at 298 K (25°C). Because the temperatures of host formations that will be used for CO_2 injection and sequestration and of the supporting geochemical reaction modeling studies will be at temperatures in the range of 50ºC to 100°C or greater, the lack of high-temperature thermodynamic values for key carbonate compounds—especially minerals—will likely impact the accuracy of some modeling calculations.

In comparison to the available thermodynamic data for carbonate minerals, the list is short for the carbonate minerals that were described in published studies as being actually present in the host rock formations at CO_2 injection test sites or natural analogue sites, reaction products of CO_2 injection/ intrusion into a host formation, or as mineral reactants or products of laboratory CO_2 fluid-rock/-mineral experiments. Most of the carbonate mineralogical data reported in the literature were from natural analogue site studies and fluid-rock/mineral laboratory experiments.

The list of identified carbonate minerals contains typically common carbonate minerals, including ankerite, aragonite, calcite, ferroan and magnesian calcites, dawsonite, dolomite, ferroan dolomite, magnesite, and siderite. Except for ferroan and magnesian calcites and ferroan dolomite, values are available for the key thermodynamic parameters of the remaining of these carbonate minerals. This suggests that the thermodynamic data for the pure common carbonate minerals is at least adequate for geochemical reaction modeling of CO_2 applications. However, Railsback (1999) noted that more thorough mineralogical characterization in the future might show greater diversity of carbonate mineralogy in geological systems affected by anthropogenic activities.

Carbonate mineral solid solutions are common and have been studied extensively. Examples of important carbonate solid solutions include magnesian calcites that involve substitution of Mg for Ca in the calcite rhombohedral structure. Complete solid solution also exists in the substitution of Fe^{2+} for Mg^{2+} in the siderite ($FeCO_3$)-magnesite ($MgCO_3$) system. Dolomite also exhibits solid solutions. The Ca-to-Mg ratio may vary and substitution of Fe and Mn is common in dolomites. Unlike the siderite-magnesite solid solution series, Fe^{2+} only partially substitutes for Mg^{2+} in dolomite to form ankerite [$Ca(Fe_xMg_{1-x})(CO_3)_2$], where x varies from 0 to 0.7 (Reeder 1983a).

It is not possible from the literature captured by this review to assess the importance of solid solutions to adequately model CO_2 sequestration processes and mineral trapping reactions. Solid-solution carbonates, such as ferroan and magnesian carbonates and ferroan dolomite, were reported in some of the natural analogue and laboratory fluid-rock studies reviewed in our assessment. Solid-solution carbonate models were also used in a few of the geochemical reaction modeling studies identified from our literature review, but it is not clear if their inclusion had an impact on the final modeling results. Given how common carbonate solid solutions are in nature, one would have to assume inclusion of carbonate solid solutions would be paramount to accurately modeling CO_2 sequestration systems.

Two general approaches are used in geochemical reaction models to calculate activity coefficients of aqueous species. The first type consists of the Debye-Hückel equation, its variant the Davies equation, and its extended B-dot equation form. These equations are easy to implement and are available in almost all geochemical models. These equations are, however, typically limited in accuracy to modeling relatively dilute solutions with ionic strengths less than that of seawater. Therefore, their use in modeling sequestration of CO_2 in deep saline formations would likely lead to inaccurate results for these high-ionic strength waters. The second approach involves the use of virial equations, which are sometimes called specific interaction equations or Pitzer equations. This approach is more complicated to apply, requires considerable amounts of data, and involves numerous individual parameters. Pitzer equations can be applied accurately to systems to high-ionic strengths such as brines and highly saline groundwaters, and have been incorporated into several geochemical reactions models, such as EQ3/EQ6 (Wolery 1992), Geochemist's Workbench®, PHREEQC, PHRQPITZ, and SOLMINEQ.88. Given the limitations of the Debye-Hückel and Davies equations for calculating geochemical reactions at high-ionic strengths, application of geochemical models that include the Pitzer equations is important to accurate geochemical reaction modeling in some CO_2 sequestration systems. However, because redox reactions, especially for the Fe(II)/Fe(III) system, and Al system have not been fully parameterized for the Pitzer model, use of the Pitzer method currently will not adequately address Fe- or Al-containing geochemical reactions associated with modeling certain CO_2 sequestration geochemical systems. The importance of using Pitzer equations for modeling reactions in saline waters and the need for parameterization of redox, Fe, and Al species are recognized by modelers, but is nonetheless a potential limitation to accurately model such systems.

11.0 References

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Appendix

Carbonate Minerals

Appendix

Carbonate Minerals

The following tables were prepared from the extensive listing of carbonate-containing minerals compiled by L.B. Railsback (Department of Geology, University of Georgia, Athens, Georgia) with help of J. A. Mandarino (Royal Ontario Museum, Toronto, Ontario, Canada). Railsback's tables are provided online at http://www.gly.uga.edu/railsback/CO3mins_intro.html, as an appendix to the paper authored by Railsback (1999). Railsback notes that many of the carbonate-containing minerals listed in his tables would not be classified as carbonate minerals but derive at least part of their negative charge from CO_3^{2-} or HCO_3^-.

To limit the number of minerals listed in the following tables, we did not include any carbonate-containing minerals tabulated by Railsback (1999), which include As, B, Ba, Bi, Cd, Ce, Co, Cr, Cu, F, Ge, Hg, La, Li, NH_4, Nb, Nd, Ni, Pb, REE, Sr, Ta U, Y Zn, and/or Zr. This was done for the sake of convenience and an assumed lack of importance of such carbonate-species to CO_2 sequestration. However, it should be noted that carbonate-containing minerals containing transition metals and non-carbonate anions may exert important geochemical controls on the solution concentrations and environmental mobility of these metals and non-carbonate anions even though the mineral makes up a small weight percentage of the total mineralogy of the aquifer system.

X-ray diffraction (XRD) is commonly used to identify crystalline compounds, such as minerals which are by definition crystalline, that are present in mineral, sediment, soil, and rock samples from field site and laboratory CO_2 sequestration studies. To determine what minerals are present in a sample, the diffraction peaks in an XRD pattern measured for a sample are compared to the diffraction peaks listed in database patterns for specific minerals of interest. If a sample contains a crystalline compound that does not have an XRD database pattern, it is unlikely the unknown compound will be identified by standard mineral characterization methods. Therefore, to adequately characterize carbonate minerals that might be in samples from field site and laboratory CO_2 sequestration studies, it is essential to know to what extent XRD database patterns may be missing for the carbonate minerals in Tables A.1 through A.8.[1] The carbonate minerals in Tables A.1 through A.8 were therefore checked against the carbonate-containing compounds contained in the mineral powder diffraction files (PDF™) published by the Joint Committee on Powder Diffraction Standards (JCPDS) International Center for Diffraction Data (ICDD). This evaluation revealed that the ICDD database did not have XRD patterns for only 14 minerals in Tables A.1 through A.8.

To determine possible reasons why database patterns did not exist for these minerals, the names and formula given for these 14 carbonate minerals in Tables A.1 through A.8 were then checked against the tabulation of accredited mineral names and formula in Mandarino and Back (2004) and the Internet online mineral database "Athena" at http://un2sg4.unige.ch/athena/mineral/mineral.html. This comparison

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[1] The authors recognize that a crystalline solid compound formed by natural geochemical processes will likely have an accredited mineral name only if its crystallographic system and structural parameters have been determined and therefore its XRD pattern measured and/or calculated. This requirement is derived from the formal definition of a "mineral."

revealed possible explanations why 13 of these 14 carbonate minerals did not have XRD database patterns. These explanations are listed as footnotes in the respective tables in this appendix.

The remaining mineral that did not show up in the search for carbonate minerals in the ICDD mineral database is dashkovaite [$Mg(HCO_3)_2 \cdot 2H_2O$]. A check of online sources and reference literature confirmed that these are, respectively, the accepted name and formula for this mineral as given in Table A.3. A subsequent search of the ICDD mineral database specifically for the name “dashkovaite” determined that a reference pattern existed for this mineral, but the reference pattern listed it as a “magnesium formate hydrate” with the formula $Mg(HCO_2)_2 \cdot 2H_2O$. Apparently the formula for dashkovaite is listed incorrectly in the ICDD database, which explains why it pattern did not show up in the initial ICDD database search for carbonate minerals.

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Table A.1. List of Pure Carbonate Minerals in Which Only CO_3^{2-} Accounts for all the Negative Charge. Table does not include any carbonate-containing minerals tabulated by Railsback (1999), which include As, B, Ba, Bi, Cd, Ce, Co, Cr, Cu, F, Ge, Hg, La, Li, NH_4, Nb, Nd, Ni, Pb, REE, Sr, Ta U, Y Zn, and/or Zr.

Mineral Name	Chemical Formula
Ankerite	$CaFe(CO_3)_2$
Aragonite	$CaCO_3$
Breunnerite(a) (ferroan magnesite)	$(Mg,Fe)CO_3$
Butschliite	$K_2Ca(CO_3)_2$
Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Eitelite	$Na_2Mg(CO_3)_2$
Fairchildite	$K_2Ca(CO_3)_2$
Gregoryite	$(Na,K,Ca)_2CO_3$
Huntite	$Mg_3Ca(CO_3)_4$
Kutnohorite	$CaMn(CO_3)_2$
Magnesite	$MgCO_3$
Magniosiderite(a)	$(Fe,Mg)CO_3$
Natrite	Na_2CO_3
Natrofairchildite	$Na_2Ca(CO_3)_2$
Nyerereite	$Na_2Ca(CO_3)_2$
Oligonite(a) manganoan siderite	$(Fe,Mn)CO_3$
Pistomesite(a)	$(Fe,Mg)CO_3$
Rhodochrosite	$MnCO_3$
Shortite	$Na_2Ca_2(CO_3)_3$
Siderite	$FeCO_3$
Sideroplesite(a)	$(Fe,Mg)CO_3$
Vaterite	$CaCO_3$
Zemkorite	$Na_2Ca(CO_3)_2$

(a) The indicated minerals are solid-solution varieties of siderite or magnesite, and have mineral names that are apparently not accepted. XRD patterns do not exist in the ICDD database for the indicated minerals, and the mineral names are not listed in Mandarino and Back (2004) or the Internet online "Athena" mineral database.

Table A.2. List of Pure Carbonate Minerals with H_2O or OH^-. Table does not include any carbonate-containing minerals tabulated by Railsback (1999), which include As, B, Ba, Bi, Cd, Ce, Co, Cr, Cu, F, Ge, Hg, La, Li, NH_4, Nb, Nd, Ni, Pb, REE, Sr, Ta U, Y Zn, and/or Zr.

Mineral Name	Chemical Formula
Barringtonite	$MgCO_3{\cdot}2H_2O$
Baylissite	$K_2Mg(CO_3)_2{\cdot}4H_2O$
Dawsonite	$NaAlCO_3(OH)_2$
Gaylussite	$Na_2Ca(CO_3)_2{\cdot}5H_2O$
Ikaite	$CaCO_3{\cdot}6H_2O$
Lansfordite	$MgCO_3{\cdot}5H_2O$
Monohydrocalcite	$CaCO_3{\cdot}H_2O$
Natron	$Na_2CO_3{\cdot}10H_2O$
Nesquehonite	$MgCO_3{\cdot}3H_2O$
Pirssonite	$Na_2Ca(CO_3)_2{\cdot}2H_2O$
Sergeevite	$Ca_2Mg_{11}(CO_3)_{13}{\cdot}10H_2O$
Thermonatrite	$Na_2CO_3{\cdot}H_2O$

Table A.3. List of Pure Carbonate Minerals in Which Only HCO_3^- Account for all the Negative Charge. Table does not include any carbonate-containing minerals tabulated by Railsback (1999), which include As, B, Ba, Bi, Cd, Ce, Co, Cr, Cu, F, Ge, Hg, La, Li, NH_4, Nb, Nd, Ni, Pb, REE, Sr, Ta U, Y Zn, and/or Zr.

Mineral Name	Chemical Formula
Bicarbonates	
Dashkovaite(a)	$Mg(HCO_3)_2{\cdot}2H_2O$
Kalicinite	$KHCO_3$
Nahcolite	$NaHCO_3$
Trona	$Na_3HCO_3CO_3{\cdot}2H_2O$
Wegscheiderite	$Na_5(HCO_3)_3CO_3$

(a) It is not known why there is no XRD pattern for dashkovaite in the ICDD database. The mineral name and formula listed above are identical to those in Mandarino and Back (2004) and the Internet online "Athena" mineral database.

Table A.4. List of Pure Carbonates with H_2O and OH^-, and Layered Hydroxyl-Carbonate Minerals. Table does not include any carbonate-containing minerals tabulated by Railsback (1999), which include As, B, Ba, Bi, Cd, Ce, Co, Cr, Cu, F, Ge, Hg, La, Li, NH_4, Nb, Nd, Ni, Pb, REE, Sr, Ta U, Y Zn, and/or Zr.

Mineral Name	Chemical Formula
Alumohydrocalcite	$CaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O$
Artinite	$Mg_2CO_3(OH)_2 \cdot 3H_2O$
Brugnatellite	$Mg_6Fe^{3+}CO_3(OH)_{13} \cdot 4H_2O$
Caresite	$Fe_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$
Charmarite	$Mn_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$
Coalingite	$Mg_{10}Fe^{3+}{}_2CO_3(OH)_{24} \cdot 2H_2O$
Desautelsite	$Mg_6Mn^{3+}{}_2CO_3(OH)_{16} \cdot 4H_2O$
Dypingite	$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$
Giorgiosite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$
Hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$
Hydroscarbroite	$Al_{14}(CO_3)_3(OH)_{36} \cdot nH_2O$
Hydrotalcite	$Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$
Indigirite	$Mg_2Al_2(CO_3)_4(OH)_2 \cdot 15H_2O$
Manasseite	$Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$
Para-alumohydrocalcite	$CaAl_2(CO_3)_2(OH)_4 \cdot 6H_2O$
Pokrovskite	$Mg_2CO_3(OH)_2 \cdot 0.5H_2O$
Pyroaurite	$Mg_6Fe^{3+}{}_2CO_3(OH)_{16} \cdot 4H_2O$
Quintinite	$Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$
Scarbroite	$Al_5CO_3(OH)_{13} \cdot 5H_2O$
Sjogrenite	$Mg_6Fe^{3+}{}_2CO_3(OH)_{16} \cdot 4H_2O$
Wermlandite	$Ca_2Mg_{14}(Fe^{3+},Al)_4CO_3(OH)_{42} \cdot 29H_2O$
Yoshikawaite(a)	$Mg_5(CO_3)_4(OH)_2 \cdot 8H_2O$

(a) The indicated mineral may correspond to dypingite (see above in same table). There is no XRD pattern for yoshikawaite in the ICDD database, and yoshikawaite is not listed in Mandarino and Back (2004) or the Internet online "Athena" mineral database.

Table A.5. List of Chloride-Containing Carbonates. Table does not include any carbonate-containing minerals tabulated by Railsback (1999), which include As, B, Ba, Bi, Cd, Ce, Co, Cr, Cu, F, Ge, Hg, La, Li, NH_4, Nb, Nd, Ni, Pb, REE, Sr, Ta U, Y Zn, and/or Zr.

Mineral Name	**Chemical Formula**
Afghanite(a)	$(Na,Ca,K)_8(Si,Al)_{12}O_{24}(SO_4,Cl,CO_3)_3{\cdot}H_2O$
Chlorartinite	$Mg_2(CO_3)Cl(OH){\cdot}3(H_2O)$
Chlormagaluminite	$(MgFe)_4Al_2(OH)_{12}(Cl_2,CO_3){\cdot}2H_2O$
Davyne	$(Na,Ca,K)_8Al_6Si_6O_{24}(Cl,SO_4,CO_3)_{2\text{-}3}$
Defernite	$Ca_3CO_3(OH,Cl)_4{\cdot}H_2O$
Franzinite(a)	$(Na,Ca)_7(Si,Al)_{12}O_{24}(SO_4,CO_3,OH,Cl)_3{\cdot}H_2O$
Hanksite	$Na_{22}K(SO_4)_9(CO_3)_2Cl$
Holdawayite	$Mn_6(CO_3)_2(OH)_7(Cl,OH)$
Liottite(a)	$(Ca,Na)_4(Si,Al)_6O_{12}(SO_4,CO_3,OH,Cl)_2{\cdot}nH_2O$
Microsommite(a)	$(Na,Ca,K)_{7\text{-}8}(Si,Al)_{12}O_{24}(Cl,SO_4,CO_3)_{2\text{-}3}$
Northupite	$Na_3Mg(CO_3)_2Cl$
Sacrofanite(a)	$(Na,Ca,K)_9(Si,Al)_{12}O_{24}[(OH)_2,SO_4,CO_3,Cl_2]_3{\cdot}nH_2O$
Sheldrickite	$NaCa_3(CO_3)_2F_3{\cdot}H_2O$
Tatarskite	$Ca_6Mg_2(SO_4)_2(CO_3)_2Cl_4(OH)_4{\cdot}7H_2O$
Tunisite	$NaCa_2Al_4(CO_3)_4(OH)_8Cl$
Vishnevite(a)	$(Na,Ca,K)_6(Si,Al)_{12}O_{24}(SO_4,CO_3,Cl_2)_{2\text{-}4}{\cdot}nH_2O$

(a) The formula formally accepted for the noted minerals do not contain CO_3. All of the noted minerals are members of the cancrinite mineral group that have the general formula $A_{6\text{-}9}(Si,Al)_{12}O_{24}[(SO_4),(CO_3),Cl_2,(OH)_2]_{2\text{-}4}{\cdot}nH_2O$ where A is Na, Ca, and/or K. The noted mineral names are listed in Mandarino and Back (2004) and the Internet online “Athena” mineral database, but the formula listed in those sources do not include CO_3 as given above. XRD patterns for the indicated minerals do not exist in the ICDD database but the comparison was based on a search of only the carbonate-containing minerals in the ICDD database.

Table A.6. List of Sulfate-Containing Carbonates. Table does not include any carbonate-containing minerals tabulated by Railsback (1999), which include As, B, Ba, Bi, Cd, Ce, Co, Cr, Cu, F, Ge, Hg, La, Li, NH_4, Nb, Nd, Ni, Pb, REE, Sr, Ta U, Y Zn, and/or Zr.

Mineral Name	Chemical Formula
Afghanite[(a)]	$(Na,Ca,K)_8(Si,Al)_{12}O_{24}(SO_4,Cl,CO_3)_3 \cdot H_2O$
Burkeite	$Na_6CO_3(SO_4)_2$
Davyne	$(Na,Ca,K)_8Al_6Si_6O_{24}(Cl,SO_4,CO_3)_{2-3}$
Ferrotychite	$Na_6(Fe,Mn,Mg)_2SO_4(CO_3)_4$
Franzinite[(a)]	$(Na,Ca)_7(Si,Al)_{12}O_{24}(SO_4,CO_3,OH,Cl)_3 \cdot H_2O$
Hanksite	$Na_{22}K(SO_4)_9(CO_3)_2Cl$
Jouravskite	$Ca_3Mn^{4+}(SO_4,CO_3)_2(OH)_6 \cdot 13H_2O$
Latiumite	$K_2Ca_6(Si,Al)_{11}O_{25}(SO_4,CO_3)$
Liottite[(a)]	$(Ca,Na)_4(Si,Al)_6O_{12}(SO_4,CO_3,OH,Cl)_2 \cdot nH_2O$
Manganotychite	$Na_6Mn_2SO_4(CO_3)_4$
Microsommite[(a)]	$(Na,Ca,K)_{7-8}(Si,Al)_{12}O_{24}(Cl,SO_4,CO_3)_{2-3}$
Motukoreaite	$NaMg_{19}Al_{12}(CO_3)_{6.5}(SO_4)_4(OH)_{54} \cdot 28H_2O$
Rapidcreekite	$Ca_2SO_4CO_3 \cdot 4H_2O$
Sacrofanite[(a)]	$(Na,Ca,K)_9(Si,Al)_{12}O_{24}[(OH)_2,SO_4,CO_3,Cl_2]_3 \cdot nH_2O$
Silvialite	$Ca_4Al_6Si_6O_{24}(SO_4)_{0.6}(CO_3)_{0.4}$
Tatarskite	$Ca_6Mg_2(SO_4)_2(CO_3)_2Cl_4(OH)_4 \cdot 7H_2O$
Thaumasite	$Ca_3SiCO_3SO_4(OH)_6 \cdot 12H_2O$
Tuscanite	$K(Ca,Na)_6(Si,Al)_{10}O_{22}[SO_4,CO_3,(OH)_2] \cdot H_2O$
Tychite	$Na_6Mg_2SO_4(CO_3)_4$
Vishnevite[(a)]	$(Na,Ca,K)_6(Si,Al)_{12}O_{24}(SO_4,CO_3,Cl_2)_{2-4} \cdot nH_2O$

(a) The formula formally accepted for the noted minerals do not contain CO_3. All of the noted minerals are members of the cancrinite mineral group that have the general formula $A_{6-9}(Si,Al)_{12}O_{24}[(SO_4),(CO_3),Cl_2,(OH)_2]_{2-4} \cdot nH_2O$ where A is Na, Ca, and/or K. The noted mineral names are listed in Mandarino and Back (2004) and the Internet online "Athena" mineral database, but the formula listed in those sources do not include CO_3 as given above. XRD patterns for the indicated minerals do not exist in the ICDD database but the comparison was based on a search of only the carbonate-containing minerals in the ICDD database.

Table A.7. List of Silicate-Containing Carbonates. Table does not include any carbonate-containing minerals tabulated by Railsback (1999), which include As, B, Ba, Bi, Cd, Ce, Co, Cr, Cu, F, Ge, Hg, La, Li, NH_4, Nb, Nd, Ni, Pb, REE, Sr, Ta U, Y Zn, and/or Zr.

Mineral Name	Chemical Formula
Afghanite[(a)]	$(Na,Ca,K)_8(Si,Al)_{12}O_{24}(SO_4,Cl,CO_3)_3 \cdot H_2O$
Cancrinite	$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2$
Cancrisilite	$Na_7(Al_5Si_7O_{24})CO_3 \cdot 3H_2O$
Carletonite	$KNa_4Ca_4Si_8O_{18}(CO_3)_4(OH,F) \cdot H_2O$
Davyne	$(Na,Ca,K)_8Al_6Si_6O_{24}(Cl,SO_4,CO_3)_{2-3}$
Franzinite[(a)]	$(Na,Ca)_7(Si,Al)_{12}O_{24}(SO_4,CO_3,OH,Cl)_3 \cdot H_2O$
Fukalite	$Ca_4Si_2O_6CO_3(OH,F)_2$
Hydroxycancrinite[(a)]	$Na_8(Al_6Si_6O_{24})(OH,CO_3)_2 \cdot 2H_2O$
Latiumite	$K_2Ca_6(Si,Al)_{11}O_{25}(SO_4,CO_3)$
Liottite[(a)]	$(Ca,Na)_4(Si,Al)_6O_{12}(SO_4,CO_3,OH,Cl)_2 \cdot nH_2O$
Meionite	$Ca_4Al_6Si_6O_{24}CO_3$
Microsommite[(a)]	$(Na,Ca,K)_{7-8}(Si,Al)_{12}O_{24}(Cl,SO_4,CO_3)_{2-3}$
Paraspurrite	$Ca_5Si_2O_8CO_3$
Sacrofanite[(a)]	$(Na,Ca,K)_9(Si,Al)_{12}O_{24}[(OH)_2,SO_4,CO_3,Cl_2]_3 \cdot nH_2O$
Scawtite	$Ca_7Si_6O_{18}CO_3 \cdot 2H_2O$
Silvialite	$Ca_4Al_6Si_6O_{24}(SO_4)_{0.6}(CO_3)_{0.4}$
Spurrite	$Ca_5Si_2O_8CO_3$
Thaumasite	$Ca_3SiCO_3SO_4(OH)_6 \cdot 12H_2O$
Tilleyite	$Ca_5Si_2O_7(CO_3)_2$
Tuscanite	$K(Ca,Na)_6(Si,Al)_{10}O_{22}[SO_4,CO_3,(OH)_2] \cdot H_2O$
Vishnevite[(a)]	$(Na,Ca,K)_6(Si,Al)_{12}O_{24}(SO_4,CO_3,Cl_2)_{2-4} \cdot nH_2O$

(a) The formula formally accepted for the noted minerals do not contain CO_3. All of the noted minerals are members of the cancrinite mineral group that have the general formula $A_{6-9}(Si,Al)_{12}O_{24}[(SO_4),(CO_3),Cl_2,(OH)_2]_{2-4} \cdot nH_2O$ where A is Na, Ca, and/or K. The noted mineral names are listed in Mandarino and Back (2004) and the Internet online "Athena" mineral database, but the formula listed in those sources do not include CO_3 as given above. XRD patterns for the indicated minerals do not exist in the ICDD database but the comparison was based on a search of only the carbonate-containing minerals in the ICDD database.

Table A.8. List of Carbonates that Contain Two or More Other Anions other than CO_3^{2-} or HCO_3^-. Table does not include any carbonate-containing minerals tabulated by Railsback (1999), which include As, B, Ba, Bi, Cd, Ce, Co, Cr, Cu, F, Ge, Hg, La, Li, NH_4, Nb, Nd, Ni, Pb, REE, Sr, Ta U, Y Zn, and/or Zr.

Mineral Name	Chemical Formula
Afghanite[(a)]	$(Na,Ca,K)_8(Si,Al)_{12}O_{24}(SO_4,Cl,CO_3)_3\cdot H_2O$
Davyne	$(Na,Ca,K)_8Al_6Si_6O_{24}(Cl,SO_4,CO_3)_{2\text{-}3}$
Franzinite[(a)]	$(Na,Ca)_7(Si,Al)_{12}O_{24}(SO_4,CO_3,OH,Cl)_3\cdot H_2O$
Hanksite	$Na_{22}K(SO_4)_9(CO_3)_2Cl$
Latiumite	$K_2Ca_6(Si,Al)_{11}O_{25}(SO_4,CO_3)$
Liottite[(a)]	$(Ca,Na)_4(Si,Al)_6O_{12}(SO_4,CO_3,OH,Cl)_2\cdot nH_2O$
Microsommite[(a)]	$(Na,Ca,K)_{7\text{-}8}(Si,Al)_{12}O_{24}(Cl,SO_4,CO_3)_{2\text{-}3}$
Sacrofanite[(a)]	$(Na,Ca,K)_9(Si,Al)_{12}O_{24}[(OH)_2,SO_4,CO_3,Cl_2]_3\cdot nH_2O$
Silvialite	$Ca_4Al_6Si_6O_{24}(SO_4)_{0.6}(CO_3)_{0.4}$
Tatarskite	$Ca_6Mg_2(SO_4)_2(CO_3)_2Cl_4(OH)_4\cdot 7H_2O$
Thaumasite	$Ca_3SiCO_3SO_4(OH)_6\cdot 12H_2O$
Tuscanite	$K(Ca,Na)_6(Si,Al)_{10}O_{22}[SO_4,CO_3,(OH)_2]\cdot H_2O$
Vishnevite[(a)]	$(Na,Ca,K)_6(Si,Al)_{12}O_{24}(SO_4,CO_3,Cl_2)_{2\text{-}4}\cdot nH_2O$

(a) The formula formally accepted for the noted minerals do not contain CO_3. All of the noted minerals are members of the cancrinite mineral group that have the general formula $A_{6\text{-}9}(Si,Al)_{12}O_{24}[(SO_4),(CO_3),Cl_2,(OH)_2]_{2\text{-}4}\cdot nH_2O$ where A is Na, Ca, and/or K. The noted mineral names are listed in Mandarino and Back (2004) and the Internet online "Athena" mineral database, but the formula listed in those sources do not include CO_3 as given above. XRD patterns for the indicated minerals do not exist in the ICDD database but the comparison was based on a search of only the carbonate-containing minerals in the ICDD database.

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