Carbonate Mineral Dissolution:

6007

Reaction Rates and Mechanisms

Literature Summary

Funded by Minnesota Legislature Appropriation for Environmental Cooperative Research

June 30, 2001

Minnesota Department of Natural Resources Division of Lands and Minerals Saint Paul, MN

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Daniel Doctor Emmelyn Leopold Kim Lapakko

Minnesota Department of Natural Resources Division of Lands and Minerals Reclamation Section

500 Lafayette Road Saint Paul, MN 55155-4045 (651) 296-4807 1525 3rd Avenue East Hibbing, MN 55746 (218) 262-6767

EXECUTIVE SUMMARY

In order to better understand how the dissolution of different mineral types affects mine waste drainage quality, the Minnesota Department of Natural Resources, Division of Lands and Minerals (MN DNR) has been conducting an ongoing literature review of mineral dissolution rates and mechanisms. Much of the work to date has dealt with oxidative dissolution of iron sulfides (Leopold and Lapakko 2001a,b). Subsequent efforts have focused on acid neutralizing reactions associated with the dissolution of silicate and carbonate minerals.

This document focuses specifically on the acid neutralizing capacity of carbonate minerals with regard to their kinetic rates of dissolution. While many different carbonate minerals have been identified worldwide, only a few are found in the potentially minable rock types in Minnesota (i.e., Duluth Complex and Archean Greenstone belts). The five minerals considered here are calcite, aragonite, dolomite, magnesite and siderite. The references listed in this document were judged to provide the most pertinent information regarding carbonate dissolution rates at ambient temperatures, pressures, and pHs expected in waste drainages. Although some mechanistic information is included, a comprehensive, detailed discussion of carbonate mineral dissolution mechanisms is beyond the scope of this document.

Aragonite and calcite were the most reactive of the five target carbonate minerals at pH 6 and temperature of 25 °C. Under these conditions, the dissolution rates (expressed as -log rate in mol·cm⁻²·s⁻¹) of the minerals considered in this study decreased in the order: aragonite (9.4) \rightarrow calcite (9.6) \rightarrow dolomite (10.8) \rightarrow siderite (12.5) \rightarrow magnesite (13.4).

The current state of knowledge regarding the mechanisms of carbonate dissolution supports a model of mixed kinetics dependent primarily upon the pH of the solution. Rates of dissolution of the mono-metallic carbonates are generally first-order dependent upon pH in the acidic regime (pH < 5), while dolomite exhibits a fractional (<1) order of dependence on pH. For all of the carbonate minerals reviewed, dissolution rates decrease in the near neutral pH regime, and become independent of pH. This change is attributed to a shift in controlling mechanism from transport-control of dissolved constituents in solution to and from reactive sites, to one of surface reaction-control. Near chemical equilibrium, the rates of dissolution become affected by the chemical affinity of the system, and the simultaneous back-reaction (mineral precipitation) significantly affects the dissolution rate in this regime. It is important to note that the rate of dissolution can be strongly influenced by the presence of foreign ions or other inhibitors, which can significantly reduce the rate of carbonate dissolution, and may in fact be the controlling factor on the overall rate of dissolution in many cases.

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1. INTRODUCTION

In mining areas, problematic drainages (i.e. waters containing high levels of acidity and/or metals) can develop when reactive mine wastes are left exposed to the atmosphere. The quality of water draining from a reactive mine waste is determined by the relative abundance and reaction rates of acid producing and acid neutralizing minerals found within the waste material. Acid is produced as a result of the oxidation of iron sulfide minerals (Nelson, 1978; Stumm and Morgan, 1981). The most effective minerals for neutralizing acid are calcium and magnesium carbonates, although silicate minerals may provide limited buffering capacity as well.

To better understand how the dissolution of different mineral types affects drainage quality, the Minnesota Department of Natural Resources, Division of Lands and Minerals (MN DNR) has been conducting an ongoing literature review of mineral dissolution rates and mechanisms. Understanding the relative dissolution rates of specific minerals provides the background necessary to evaluate current developments relevant to environmental waste management. It also creates a foundation for calculating chemical release rates in laboratory dissolutions tests, and comparison of these rates to those of various rock types reported in the literature. Understanding the mechanisms by which specific minerals weather provides a framework through which results from laboratory dissolution tests can be interpreted.

Much of the work to date has dealt with oxidative dissolution of iron sulfides (Leopold and Lapakko 2001a,b). Subsequent efforts have focused on acid neutralizing reactions associated with the dissolution of carbonate and silicate minerals. This document will focus specifically on the dissolution rates and acid neutralizing capability of some common carbonate minerals.

1.1 Mining Potential in the Duluth Complex

Minnesota has an extensive mining industry and potential for mineral expansion and diversification. Potential for base and precious metal development is associated with Minnesota's Precambrian rocks, specifically the Duluth Complex and Archean metavolcanics and metasedimentary formations. The Duluth Complex is a massive gabbroic intrusion in northeastern Minnesota containing low grade copper and nickel sulfides, titanium oxides, and platinum group elements (PGEs). It has been estimated that the Duluth Complex contains copper-nickel resources of 4.4 billion tons (Minnesota Environmental Quality Board, 1979). It has also been developed as a source of dimension stone.

Operational-scale Duluth Complex rock stockpiles are present at LTV Steel Mining Company's (previously Erie Mining Company) Dunka Mine, a full-scale open pit taconite operation near Babbitt, MN. The Dunka open pit intersects the geological contact between the Duluth Complex and the Biwabik Iron Formation, and removal of Duluth Complex rock was required to mine the underlying taconite. More than 50 million tons of the sulfide-bearing Duluth Complex rock is stored at the site in stockpiles, which cover 320 acres.

Current interest in the Duluth Complex formation centers on its potential for base metals and PGEs. Several mining companies and interested parties are currently engaged in exploration activities in the Duluth Complex. Two companies, PolyMet Mining Corp. and Cominco American Inc., are conducting preliminary feasability studies for base metals in the Duluth Complex. PolyMet has been drilling at the Dunka Road site. They've collected a bulk sample on which they are testing their hydrometallurgical process. Cominco does not currently hold the appropriate leases to begin drilling. However, they are interested in obtaining a bulk sample for process tests this summer. Other exploration interests in the area include BPI Inc. (base metals, Carleton Co.), Lehmann Exploration Management Inc. and Impala Mining (PGEs and gold near Birch Lake), Wallbridge America Corp. (PGEs from Filson Creek), Royal Standard Minerals Inc.(PGEs, Waterhand Deposit), and Platnex Inc. (PGEs just south of AMAX).

1.2. Mining Potential in Archean Greenstone Formations

The Archean metavolcanic and metasedimentary formations, or greenstone belts, of Minnesota extend north into Canada, where they have yielded substantial mineral production. These formations are potential hosts for gold, zinc-copper massive sulfides with various by-products, and magmatic sulfide deposits containing copper, nickel, and PGEs. Recent exploration of greenstone belt metasedimentary formations has focused on gold, base metals, and silver-cobalt-copper deposits.

1.3. Field and Laboratory Dissolution Studies Conducted by the MN DNR

In 1976, the Regional Copper-Nickel Study was formed in response to public concerns for the environmental impact of copper-nickel mining. The final summary report was completed in 1979 (Minnesota Environmental Quality Board, 1979). The field investigations conducted included operational scale studies at the Dunka Mine, pilot scale studies at the AMAX exploration site, and monitoring of a bulk sample site. The pilot and operational scale studies at AMAX and Dunka, respectively, were continued by the MN DNR (Lapakko et al., 1998). In addition, extensive laboratory testing has also been conducted on blast hole samples from the Dunka Mine and drill core from the AMAX site, to better understand dissolution of Duluth Complex rock (Lapakko et al., 1998). The objective of these studies was to examine drainage water quality produced by these rocks. Rigorous examination of the mineral dissolution reactions which produced the observed water quality was beyond the scope of these studies.

Hydrothermal quartz carbonate tailings from greenstone belts in Canada have been subjected to laboratory dissolution experiments since 1991 (Lapakko, 1991, 1993; Lapakko et al., 1999). This study has been conducted in three phases. The first phase involved geochemical characterization of the tailings and initiation of dissolution testing (Lapakko, 1991). During the second phase it was concluded that the tailings collected for the study provided the best available approximation of tailings which might be generated if a gold or titanium mine were developed at a greenstone belt exploration site in Minnesota (Lapakko 1993). The third phase of the project, which is still in progress, focuses on the long-term dissolution behavior of these tailings as well as leached sample analyses.

One aspect of current research within the MN DNR Reclamation Section is to evaluate strategies to prevent and control problematic mine drainages. To meet this goal, a laboratory dissolution study on Archean greenstones from the Soudan underground mine in northern Minnesota was initiated in January 2000. These greenstones were also used in predictive and mitigative field experiments conducted at the MN DNR field research facility in Hibbing, MN. These tests began in the summer of 2000.

In summary, understanding carbonate mineral dissolution rates and mechanisms will aid in the interpretation of a large body of data that has been collected over the last twenty years. Furthermore, this information will allow for extrapolation to future mine waste and water quality issues.

1.4. Scope and Objectives

An extensive volume of literature has been published on the subject of carbonate dissolution. The literature on carbonate mineral dissolution kinetics does not specifically address the problem of remediation of acid rock drainage nor of the dissolution of iron-bearing carbonates in particular. With few notable exceptions, kinetic considerations are all but ignored when the usage of carbonates to remediate acid rock drainage is discussed. Our goal, therefore, is to utilize the more general information available on the dissolution rates of carbonate minerals to infer the rates of dissolution of the carbonates present in the Duluth Complex and Archean greenstone rocks. The references listed in this document were judged to provide the most relevant information on carbonate mineral dissolution rates under typical environmental conditions. Additional references regarding carbonate mineral dissolution are included in a bibliography in Appendix 2. This document will also serve as a foundation for future literature searches and reviews.

The purpose of this document is three-fold. The first objective is to enumerate the carbonate minerals found within potentially mineable rock types in Minnesota, namely the Duluth Complex formation and Archean greenstone belts. Second, it summarizes laboratory dissolution rates of these minerals at ambient temperatures and pressures. Although some mechanistic information is included, a comprehensive, detailed discussion of carbonate mineral dissolution mechanisms is beyond the scope of this document. Finally, literature compiled during this effort will be used to expand a literature database maintained by the Lands and Minerals Reclamation Section.

2. LITERATURE SEARCH METHODS

The MN DNR, Division of Lands and Minerals, Reclamation Section maintains a database of literature pertaining to environmental mine waste characterization, prediction, and management. At present, this database contains roughly 3980 citations. Initial literature searches conducted using this database produced 37 citations using the keywords *carbonate dissolution* and *kinetics*. Of these 37 citations, only 17 were determined to be directly relevant to the purpose of this document. Additional literature searches were conducted using the online journal indexes GeoRef and Geobase. Relevant citations were obtained through the MN DNR library and added to the Division's database. More detailed information on the literature search methods and results can be found in Appendix 2.

3. DESCRIPTION OF EXPERIMENTAL METHODS USED FOR LABORATORY KINETIC STUDIES

This section summarizes methods and briefly describes experimental designs for studying the dissolution rates of carbonate minerals. Among the topics discussed are: the advantages and disadvantages of the experimental approaches, the type of data generated, and a rough guide to the interpretation of those data. Details necessary for designing an experiment are provided in the publications cited.

3.1 Reactors for Kinetic Experiments

3.1.1 Batch reactors:

The most basic form of reactor for conducting kinetic experiments is the batch reactor. This simple design is a container in which fluid and mineral grains are reacted together, and mixed by agitation or stirring (Figure 1). Batch reactors can be either open or closed to the atmosphere. They can also be designed to keep the reaction going under conditions of controlled temperature and pressure, with fixed gas concentrations, or at constant pH ("pH-stat"). The degree of sophistication of the reactor vessel design will depend upon the goals of the experiment.

3.1.2 Flow-through reactors

A variation on the design of a batch reactor, the flow-through reactor allows for the continuous addition of fluid into the reaction vessel, such that the fluid chemistry as well as the total volume of fluid in the reactor vessel are kept constant. Fluid is continually pumped into the vessel at constant flow, and the reaction rate is calculated by comparing the input concentration of the chemical species of interest to its output concentration. A flow-through reactor also allows for the manipulation of the fluid chemistry along the duration of the experiment, if so desired. As with the batch reactor design, mineral grains are maintained in suspension through agitation, stirring, or with a re-circulating secondary flow system that is separate from that used for



Figure 1: A batch reator designed for simple mineral dissolution experiments. Note the outer sleeve allowing for constant temperature, the pH electrode, and the gas inlet to control PCO_2 or other gas fugacities (after Arakaki & Mucci, 1995).

sampling (Figure 2). This latter method of maintaining a well-mixed solution without mechanical means is known as a fluidized-bed reactor, and is described in more detail by Chou and Wollast (1984). The rate of dissolution is obtained by multiplying the flow rate of the renewal solution by the difference in elemental concentrations between the input and output solutions. This rate is subsequently normalized to the total surface area of the solids.



Figure 2: A fluidized bed reactor design: the mixing vessel (1) allows for the chemistry of the solution to be precisely controlled, while pumping the fluid up into the bottom of the reaction vessel (5) keeps the solids in suspension and mixes the solution (after Schenk et al., 1992).

3.1.3 Plug-flow reactor

Also known as the packed bed reactor, this type of design incorporates downward vertical fluid flow through a packed mass of solids, which can be monomineralic or made up of an assemblage of minerals (Figure 3). The advantage of this setup is that it acts as a simulator for weathering of rocks and soils. Although it provides a better approximation to natural scenarios of mineral dissolution, the disadvantage to this type of design is that it is more difficult to interpret due to considerations of pore volumes, wetted vs. total surface area, and residence time of the fluid in contact with the minerals.



Figure 3: A plug flow reactor design: water is periodically added and flows by gravity through columns of packed solids, displacing solutes which are captured in collectors. Interpretation of plug-flow reactor data is complicated by the difficulty in estimating mineral surface area in contact with the fluid, however it is a more realistic simulation of mineral dissolution in mine waste piles (after Poulin et al., 1996)

3.2 Interpretation of the Experimental Data

Experimental data are generated through the analysis of fluid samples taken from the reactor vessel at specified time intervals throughout the duration of the experiment. Changes in fluid chemistry are used to calculate rates of mineral dissolution by monitoring the concentration of the dissolution products over time, and correcting for the removal of samples during the experiment. The rate of reaction is taken as the slope (dc/dt) of the line obtained from a plot of product concentration versus time. The resulting curve may have different slopes corresponding to different intervals of time across the experiment, indicating changing rates of reaction. In the case of rapidly dissolving minerals such as calcite, the rate may also be determined by other methods. For example, some workers have measured the weight loss of single crystals at the conclusion of the experiment. Others have theoretically calculated the number of moles of dissolved mineral from continuous measurements of pH or electrical conductivity.

Regardless of the method, the calculated rate is expressed as the moles of the dissolving phase per unit time, normalized to the mineral surface area. It is most often reported in units of mol·cm⁻²·s⁻¹. Apparent reaction rates will depend upon the component used to calculate the rate. For this reason, it is often useful to compare the rates of release of different chemical components for the same experiment. Once calculated for each interval, the reaction rates can be plotted against different experimental variables, such as surface area, pH, temperature, pressure, or stirring rates. These plots can be used to evaluate the dependence or independence of reaction rates on specific parameters. For example, it is often useful to examine the rate dependence upon the activity of the hydrogen ion (a_{H+}) . If a plot of reaction rate versus a_{H+} (or -log of the rate versus pH) yields a statistically significant correlation, the slope of this line will indicate the order of dependence of the rate upon H⁺, and the intercept will yield the rate constant (Sverdrup, 1990). In the case where the plot yields a slope of 1, the reaction is first-order dependent upon pH. The reaction order suggests a reaction mechanism related to the parameter of interest. In this way, one can attempt to define parameter-specific reaction mechanisms.

It has been noted that the rate of dissolution of calcite is also affected by the ratio of the volume of fluid to the surface area of the solids (V/A), such that with increasingV/A ratio, the rate of dissolution decreases as an artifact of experimental design. Eisenlohr et al. (1999) attribute this phenomenon to inhibitors such as aluminosilicates which are intrinsic impurities in the crystal structure, and that build-up on the mineral surface as dissolution proceeds. The more dissolution that is required to track changes in fluid chemistry during the experiment, the more the inhibitors have an effect of retarding the overall rate.

4. ENUMERATION OF CARBONATE MINERALS

One objective of this document is to enumerate the carbonate minerals found within potentially mineable metal-bearing rocktypes in Minnesota (Table 1). At present, these rock types are the

Duluth Complex formation and Archean greenstone belts, which consist of basaltic rocks, rhyolitic volcanics, and meta-sedimentary rocks (LaBerge, 1994).

The minerals which will be discussed in this document are: calcite, aragonite, dolomite, magnesite, and siderite. Calcite $(CaCO_3)$ is often reported to occur in each of the rock types of interest without the notable occurrence of other carbonate minerals. Although ankerite $(CaFe(CO_3))$ is present in the rocks of interest, no literature has been found to date regarding the study of its dissolution kinetics.

It is important to note that most carbonate minerals form solid solution series whereby significant proportions of different metal ions can substitute into the crystalline structure of the minerals. For example, a complete solid solution series exists between dolomite (CaMg(CO₃)) and ankerite (CaFe(CO₃)) such that any balanced proportion of Fe_x to Mg_{1-x} can be present in the mineral structure, with the dominant metal defining the mineral name. Complete solid solution series also exist between siderite (FeCO₃) and magnesite (MgCO₃), and between siderite (FeCO₃) and rhodochrosite (MnCO₃). In contrast, only an incomplete solid solution exists between the calcium and magnesium carbonates. The formation of dolomite occurs instead at a pure Ca:Mg ratio of 1:1, with limited substitution outside of this ratio. Nonetheless, it is important to note that carbonate minerals are rarely pure end-members of these solid solutions, and it is common to find other metals present in these minerals as impurities. Therefore, we can usually expect to find some iron incorporated into the structures of all the non-ferrous carbonate minerals in minor or trace amounts.

Mineral	Duluth Complex ^{1,2}	Archean Greenstones ^{3,4,5}
Calcite	~	~
Aragonite		
Dolomite		~
Magnesite		
Siderite		~
Ankerite		~

Table 1.	Carbonate minerals reported to be present in Duluth Complex and Archean
	greenstone belts.

¹Stevenson et al. (1979) ²Miller (1993) ³Minnesota Geologic Survey (1972) ⁴Frey (1997) ⁵Mattson (2000)

5. DISSOLUTIÓN KINETICS OF CARBONATE MINERALS

Carbonate kinetics research spans several decades, due mainly to the widespread occurrence of carbonate minerals and their relatively fast dissolution and precipitation kinetics. Experimental studies have primarily been conducted in simple solutions of low ionic strength using calcite crystals as the reactant solids. A major objective of these studies was to determine the relative importance of reactant transport versus chemical reaction at the mineral surface on rates of calcite dissolution (Morse, 1983). Later work extended to investigations of aragonite and dolomite dissolution kinetics. Little work has been done on other metal carbonate minerals, however some literature does exist for magnesite and siderite.

5.1. Mechanisms of Carbonate Mineral Dissolution

Carbonate minerals dissolve rapidly in relation to the majority of minerals (i.e. silicates). The rates at which the carbonate minerals dissolve increases with increasing acidity. Therefore, pH is a controlling variable in the dissolution kinetics of all carbonate minerals. The partial pressure of carbon dioxide (PCO_2) of the system is a second controlling variable, due to the fact that dissolved carbon dioxide creates acidity in water and partially controls the distribution of dissolved inorganic carbon species in solution.

In general, there is a linear relationship between the rate of carbonate dissolution and pH for values of pH between 1 and 4. Above pH of approximately 4, the rates of carbonate mineral dissolution become progressively slower with increasing pH, until a rate plateau is reached between pH 5 and 8, whereby the change in the dissolution rate with a change in pH is slight or insignificant. If the solution is allowed to evolve in the presence of carbonate minerals above pH 8, most natural waters will be at or near saturation with respect to the carbonate minerals, and the rate of subsequent dissolution will be very slow and countered by the back reaction (or precipitation) of the mineral.

For simple carbonates, the elementary mechanistic reactions taking place simultaneously during the dissolution process are:

(1)
$$MeCO_3 + H^+ \Leftrightarrow Me^{2+} + HCO_3^-$$

(2)
$$MeCO_3 + H_2CO_3^* \Leftrightarrow Me^{2+} + 2 HCO_3^-$$

1-

(3)
$$MeCO_3 + H_2O \Leftrightarrow Me^{2+} + HCO_3^- + OH^2$$

where, Me represents the metal ion such as Ca, Mg, Fe, Ba, Sr, Zn, Pb, or Mn (Chou et al., 1989). In this document, we will deal only with the carbonate minerals commonly occuring in the rocks of the Duluth Complex and Archean Greenstones. These carbonates primarily contain the metals Ca, Mg and Fe, with only minor or trace amounts of other metals.

Mineral dissolution occurs as a series of sequential processes, involving both the physical movement of reactants to and from reaction sites, and their chemical interaction at those sites. The slowest of these processes will control the overall rate of reaction, and is therefore defined as the rate-limiting mechanism. For example, some experiments have shown that dissolution rates depend upon the diffusion of ions toward or away from the mineral surface. This can occur when the actual mineral breakdown is faster than the complete mixing within the fluid. Dissolved products can form a barrier to further dissolution simply by building up in concentration within the fluid boundary layer adjacent to the mineral surface. Conversely, the dissolution rate may also be limited by the diffusion of protons toward the surface of the mineral to facilitate dissolution at the crystal surface. In both cases, the rate is described as being transport controlled (Plummer et al., 1978; Sverdrup, 1990). Near equilibrium, detachment of ions from kinks or defects on the crystal surface is the rate-controlling process. In this case the rate is described as surface controlled. Changes in reaction rates are most pronounced in long-duration experiments, when one can observe the system both far from and near to equilibrium.

5.1.1. Calcite/Aragonite

The rate of dissolution of CaCO₃ in aqueous solutions can be conveniently discussed in terms of three pH regimes. At low pH (< 4.0), the dissolution rate is almost directly proportional to the H+ concentration. At higher pH (> 5.5) the dissolution rate is independent of the H+ concentration. Between these two ranges there exists a transitional regime where the H+ dependence varies, and for pure experimental systems PCO_2 is demonstrated to have a controlling influence. These regimes also prescribe regions where the dissolution rate is essentially transport controlled (H+-dependent regime) or controlled by mixed kinetics (H+-independent regime) (Rickard and Sjöberg, 1983).

The transition between the two zones depends upon the rate of transport of H+ to and from the mineral surface. In other words, the hydrodynamics of the system play an important role. At low pH, the more well-mixed the system is, the faster the rate of dissolution will be. At higher pH values, the rate of stirring no longer affects the rate since the dissolution is controlled by the chemical reactions taking place at the mineral surface. For small particles, the dissolution rate will be largely independent of the turbulence of the solution, however for larger particles the hydrodynamics play an increasingly important role.

The work of Plummer et al. (1978) was seminal in rigorously investigating the kinetics of calcium carbonate dissolution. These authors report the following mechanistic rate law for the dissolution of calcite and aragonite:

(4)
$$\mathbf{R} = k_1 a_{\mathrm{H}+} + k_2 a_{\mathrm{H2CO3}}^* + k_3 a_{\mathrm{H2O}} - k_4 a_{\mathrm{Ca}++} a_{\mathrm{HCO3}}^*$$

where k is the rate constant corresponding to each different term in the equation, and a is the activity of the subscripted chemical species (note that k_4 stands for the rate constant of the back-reaction, or precipitation, thus the negative charge on that term). This has been referred to in the literature as the PWP model of calcite dissolution. The rate constants (k_x) are related to the range of pH under which the experiments were conducted. For example, the rate constant k_1 describes the rate of calcite dissolution at low pH values, when the hydrogen ion activity in solution is high with respect to the activity of H₂CO₃* ($a_{H2O}=1$). Thus, in solutions of low pH, the first term in equation 4 dominates the rate expression, and the change in the rate is linear with respect to pH. At higher pH, the rate becomes increasingly dependent upon the second and third terms in the rate expression (equation 4), and finally at near-equilibrium conditions the rate is also influenced by the back-reaction, or calcite precipitation. Plummer et al. (1978) report values for the rate constants in equation 4 under various conditions of temperature and stirring rate (see Appendix 5).

Work done on the kinetics of calcite and aragonite dissolution since the late seventies has essentially confirmed the work of Plummer et al. (1978). Since then, only minor modifications of their model have been suggested, with the primary difference being slightly varying values of the rate constants contained in equation 4.

5.1.2. Dolomite

Busenberg and Plummer (1982) proposed the following rate law for dolomite dissolution:

(5)
$$\mathbf{R} = k_1 a_{\mathrm{H}^+}^n + k_2 a_{\mathrm{H2CO3}^*}^n + k_3$$

A notable difference between the dissolution of dolomite and the dissolution of other carbonates is that the reaction order for dolomite with respect to H⁺ is fractional, i.e., the exponent *n* in equation 5 has a temperature-dependent value that is less than 1. There is some disagreement in the literature about the actual value of *n*. Busenberg and Plummer (1982) reported n = 0.5 for T < 45 °C. Chou et al. (1989), using a fluidized bed reactor, obtained results consistent with equation 5 but with n = 0.75. Gautelier et al. (1999) report a value for n = 0.63 at 25 °C. This fractional order of dependence on H+ activity for dolomite dissolution contrasts with that found for calcite at low pH, where several studies have shown the calcite dissolution rate to be first order dependent on pH. As with calcite, however, the reactions at the dolomite crystal surface become rate-limiting with increasing pH and decreasing availability of hydrogen ions.

5.1.3. Magnesite

The work of Pokrovsky and Schott (1999) showed that dissolution rates of magnesite are pHindependent at 0 < pH < 3, proportional to the activity of H⁺ at 3 < pH < 5, pH-independent again at 5 < pH < 8, and decreasing with increasing pH at pH > 8 and total CO₂ > 0.001 molar. In addition, rates of magnesite dissolution increased significantly with ionic strength in the acidic pH regime ($3 \le pH \le 5$). Surface complexation was shown to play the major role in the dissolution of magnesite, and the following equation was developed to describe magnesite dissolution kinetics overall:

(6)
$$R = [k_{CO3} \{ > CO_3 H^{\circ} \}^m + k_{Mg} \{ > MgOH_2^+ \}^n] \cdot [1 - \exp(-4A/RT)]$$

where $\{>i\}$ stands for the concentration of surface species *i* (in mol·m⁻²), *A* is the chemical affinity of the overal reaction, and, at 25°C, $k_{CO3} = 7.20$, $k_{Mg} = 5.38$ and the exponents *m* and *n* are 3.97 and 3.94, respectively.

5.1.4. Siderite

The mechanisms of siderite dissolution have not been studied to date.

5.2 Inhibitors to Carbonate Mineral Dissolution

There has been much discussion about the role of inhibitor species causing retardation of carbonate mineral dissolution rates, however very few studies have been conducted which directly address this issue. One of the first was by Terjesen et al. (1961), in which various metal ions at concentrations of 10^{-5} molar were tested as inhibitors during calcite dissolution experiments. These authors concluded that the following ions showed inhibiting effects toward calcite dissolution, in order of decreasing effectiveness: Pb²⁺, La²⁺, Y³⁺, Se³⁺, Cd²⁺, Cu²⁺, Au³⁺, Zn²⁺, Ge⁴⁺, Mn²⁺.

More recently, work by Eisenlohr et al. (1999) addressed the problem of intrinsic impurities in natural carbonate rocks (calcite in limestone and marble). Their work showed that during dissolution impurities are released from the calcite matrix and are adsorbed irreversibly to the crystal surface, where they build up and act to retard dissolution. It has been noted that the rate of dissolution of calcite is also affected by the ratio of the volume of fluid to the surface area of the solids (V/A), such that with increasingV/A ratio, the rate of dissolution decreases. Eisenlohr et al. (1999) attribute this phenomenon to a build-up of inhibitors on the mineral surface such as aluminosilicates which are intrinsic impurities in the crystal structure. These impurities were found to be mainly nano-scale complexes aluminosilicates minerals such as kaolinite and mica, with the possibility of other species contributing to the retardation of the dissolution rate.

5.3. Quantified Rates of Carbonate Mineral Dissolution

In general, the dissolution rates of the carbonate minerals discussed in this document are, in order from fastest to slowest: aragonite \rightarrow calcite \rightarrow dolomite \rightarrow siderite \rightarrow magnesite.

5.3.1 Calcite/Aragonite

The rates of calcite and aragonite (CaCO₃) dissolution are the fastest among all the known metal carbonate minerals. For any given pH, aragonite dissolves slightly faster than calcite, due to its greater solubility. At 25 °C, pH = 6, the -log of the rates of calcite and aragonite dissolution are 9.57 and 9.39 mol·cm⁻²·s⁻¹, respectively (Table 2: Busenberg and Plummer, 1986).

pH	Rate Calcite [†]	pH	Rate Aragonite [†]	pH	Rate Dolomite [‡]	pH	Rate Magnesite [§]
2.33	7.44	2.00	7.18	2.08	9.08	2.00	11.58
2.50	7.54	2.50	7.62	2.50	9.21	2.59	11.61
3.00	8.05	3.00	8.10	3.07	9.53	2.98	11.97
3.50	8.53	3.50	8.53			3.52	12.50
4.00	8.91	4.00	8.91	3.88	9.91	4.07	12.22
4.50	9.28	4.50	9.14	4.50	10.20	4.50	13.38
5.00	9.62	4.75	9.32	4.70	10.32		
5.50	9.73	5.50	9.32				
6.00	9.57	6.00	9.39	5.72	10.81	5.0-8.0	13.34
6.70	9.58	6.50	9.52				
7.00	9.62	7.00	9.45				
7.50	9.68	7.50	9.44	7.34	11.35		
8.00	9.60	8.00	9.46	· · · · · · · · · · · · · · ·		·	

Table 2: Summary of carbonate mineral dissolution rates at 25°C with respect to pH (at 0.0 atm PCO₂)*

*All rate values reported as -log dissolution rate in mol·cm⁻²·s⁻¹.

† Data from Busenberg and Plummer, 1986

[‡] Data from Busenberg and Plummer, 1982

§ Data from Pokrovsky and Schott, 1999.

5.3.2 Dolomite

Dolomite (CaMg(CO₃)₂) dissolves at a rate which is slightly more than an order of magnitude slower than calcite. At 25°C, pH = 6, the -log of the rate of dolomite dissolution reported by Busenberg and Plummer (1982) is 10.81 mol·cm⁻²·s⁻¹ (Table 2). Chou et al. (1989) report rate constants k_1 , k_2 , and k_3 for dolomite being 2.6 x 10⁻⁷, 1.0 x 10⁻⁸, and 2.2 x 10⁻¹² mol·cm⁻²·s⁻¹, respectively.

5.3.3 Magnesite

Magnesite (MgCO₃) dissolves at a rate which is significantly slower than calcite, by approximately four orders of magnitude. At 25°C, pH = 6, the -log of the rate of magnesite dissolution is 13.34 mol cm⁻²·s⁻¹ (Pokrovsky and Schott, 1999). Table 2 contains rates of magnesite dissolution published by Pokrovsky and Schott (1999) which are in good agreement with the rates obtained by Chou et al. (1989).

5.3.4 Siderite

Siderite (FeCO₃) dissolves at a rate which is also slower than calcite, by approximately three orders of magnitude. For pH = 6, the -log of the rate of siderite dissolution (under anoxic conditions) is 12.50 mol·cm⁻²·s⁻¹ (calculated after the model of Greenberg and Tomson, 1992).

6. DIRECTION OF FUTURE WORK

The scope of this document was largely limited to identification of carbonate minerals relevant to mining in Minnesota and their rates of dissolution. Much work must still be done before these dissolution rates can be applied to mine waste management issues with any confidence. Some of the issues yet to be addressed are listed below:

- Comparison of these dissolution rates to those generated during MN DNR laboratory studies.
- Apply these dissolution rates to MN DNR laboratory dissolution tests and other values reported in the literature.
- Expand the list of "target" minerals to include those found in other, economically viable ores.
- Identify variables that control rates of carbonate mineral dissolution.
- Continue to expand the MN DNR literature database.

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APPENDIX 1

Glossary of Terms



activity The actual reactive concentration of a dissolved ionically charged species in solution. The activity is equivalent to the molar concentration of the species multiplied by its activity coefficient, which is a factor < 1 that accounts for the ionic strength of the solution to correct for interferences due to other ions in solution.

B.E.T. Abbreviation for Brunauer-Emmet-Teller method of determining the surface area of a solid by adsorption of N_2 gas.

flux The release of a chemical species off of the surface of a solid into solution, expressed as moles per unit surface area per time.

free-drift A kinetic experiment in which the pH of the solution is allowed to change freely as the minerals dissolve.

inhibitor A chemical species in solution which slows down the kinetic rate of dissolution of a mineral due to surface adsorption and/or complexation.

pH-stat A kinetic experiment in which the pH of the solution is fixed to a constant value during the experiment via addition of acid or use of a buffer.

point of zero net proton charge (pH_{pznpc}) The proton condition where the mineral surface charge caused by binding of H⁺ or OH⁻ is zero.

rate constant An empirically derived number which, under a specified set of temperature, pressure, and pH conditions, may be used to compare relative rates of mineral dissolution independent of surface area. In mineral dissolution kinetics, the rate consant is represented as k.

rate-limiting step The slowest elementary step of consecutive chemical reactions.

surface reaction-control A mechanistic model which considers chemical reactions occurring at the mineral surface to be rate-limiting.

surface roughness factor (SR) The ratio of the surface area of a mineral determined by the B.E.T. method to that determined geometrically, for a given mass and particle size of mineral solids.

transport-control A mechanistic model which considers the physical transport of ions to and from reactive sites to be rate-limiting.

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APPENDIX 2

Bibliography of Carbonate Dissolution References Reclamation Section Database-Papyrus

List A2.1. Results of literature search of PapyrusTable A2.2. Known Duluth Complex and Archean Greenstone carbonate minerals, with references



List A2.1: Results of literature search of Papyrus using keyword = "*carbonate dissolution*" and keyword = "*kinetics*". Sorted by mineral listed in title and reference number. (Contains 40 references.)

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MINERAL FORMULA		RATE REFERENCE	
Calcite	CaCO3	 #1004 Plummer, Wigley, Parkhurst (1978) #3870 Busenberg & Plummer (1986) #2402 Plummer & Wigley (1976) #303 Sjöberg (1976) #3897 Compton & Unwin (1990) #1115 Wollast (1990) #3894 Arakaki & Mucci (1995) #3971 Baumann & Schultz (1992) #3965 Chou et al. (1989) #3964 Rickard and Sjöberg (1983) #3957 Sjöberg and Rickard (1984) #3972 Dreybrodt (1992) #3963 Morse (1983) 	
Aragonite	CaCO ₃	<u>#1115</u> Wollast (1990) <u>#3965</u> Chou et al. (1989)	
Dolomite	CaMg(CO ₃) ₂	 <u>#3965</u> Chou et al. (1989) <u>#3975</u> Sherman and Barak (2000) <u>#3976</u> Gautelier et al. (1999) 	
Magnesite	MgCO ₃	 #1115 Wollast (1990) #3965 Chou et al. (1989) #3965 Pokrovsky and Scott (1999) 	
Siderite	FeCO ₃	#3900 Greenberg and Tomson (1992)	

 Table A2.2.
 Carbonate minerals references referred to in the document, listed by mineral

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APPENDIX 3

Physical and Chemical Characteristics of Carbonate Minerals Found in Duluth Complex and Archean Greenstone Rocks

Table A3.1.	Physical Characteristics
Table A3.2.	Chemical Characteristics
Table A3.3.	General Occurrence



Mineral	Crystal System	Specific Gravity	Hardness
Calcite Trigonal		2.54	3
Aragonite	Orthorhombic	2.95	3.5 - 4
Dolomite	Trigonal	2.86 -(2.93)	3.5 - 4
Magnesite	Trigonal	2.98-(3.48)	3.5 - 5
Siderite	Trigonal	(3.5)-3.96	3.5 - 4.5

 Table A3.1. Physical Characteristics (Klein and Hurlbut, 1985)

 Table A3.2 Chemical Characteristics (Klein and Hurlbut, 1985)

Mineral	Composition	Trace Elements
Calcite	CaCO ₃	Na, Mg, Sr, Mn, Fe, Cd, Cu, Sb, P, F, Zn, Pb
Aragonite	CaCO ₃	Sr, Pb
Dolomite	CaMg(CO ₃) ₂	Fe, Sr, Mn, Cd, Cu
Magnesite	MgCO ₃	Fe, Sr, Mn, Cd, Cu
Siderite	FeCO ₃	Mn, Mg
Table A3.3. General Mineral Occurrence and Occurrences with Ores (Source: Klein and Hurlbut, 1985)

MINERAL	GENERAL OCCURRENCE	ORE OCCURRENCE
CALCITE	Calcite is one of the most common and widespread minerals. It primarily occurs in extensive sedimentary rock masses in which it is the predominant mineral; <i>limestones</i> are essentially composed entirely of calcite. Though most commonly found in sedimentary rocks, calcite can be found in all rock types, occuring as both a primary and secondary mineral.	Calcite is a common gangue mineral in many sedimentary and metamorphic ore deposits. It is most closely associated with ores of solution origin, precipitated from carbonate-rich groundwaters or hydrothermal fluids. Calcite occurs commonly within fracture fillings and vugs in all rock types. It is common in Mississippi Valley Type ore deposits.
ARAGONITE	The minerals calcite and aragonite are polymorphs of calcium carbonate (CaCO ₃). Aragonite is the biologically precipitated form of calcium carbonate, and is widespread in marine limestones. Calcite is the thermodynamically stable polymorph of calcium carbonate at Earth surface conditions; aragonite is unstable, yet its transformation to calcite is extremely slow, so aragonite is also commonly found. The aragonite crystal structure belongs to the orthorhombic crystal system rather than the trigonal system.	Aragonite is not commonly found in association with ores given its thermodynamic instability. It is precipitated only under a narrow range of conditions represented by low temperature, near-surface environments, particularly marine settings. Mother of pearl and pearls themselves are an economically valuable form of aragonite.
DOLOMITE	The mineral dolomite is a common carbonate mineral. It is a two-component carbonate, consisting of half Ca and Mg metal cations in the pure form of the crystal structure (Ca/Mg = 1:1). Its chemical formula is thus CaMg(CO ₃) ₂ . Dolomite has a similar crystal structure to calcite, but as a result of its chemistry it has very different formation and dissolution kinetics. Dolomite is sparingly soluble in cold dilute acid. It has never been formed in the laboratory under ambient temperature and pressure conditions; rather, a disordered protodolomite solid precipitates. Fe readily substitutes for Mg in dolomite, and can result in the formation of the mineral ankerite, Ca(Mg,Fe ²⁺ ,Mn)(CO ₃) ₂ , for which a complete solid solution exists with dolomite.	Dolomite is a common gangue mineral in many sedimentary and metamorphic ore deposits. It is most closely associated with ores of solution origin, precipitated from carbonate-rich groundwaters or hydrothermal fluids. It is common in Mississippi Valley Type ore deposits.

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MINERAL	GENERAL OCCURRENCE	ORE OCCURRENCE
MAGNESITE	Magnesite occurs as an alteration product of magnesium-rich igneous and metamorphic rocks. It has been found in zones associated with hydrothermal fluids, and also occurs within evaporite deposits. Magnesite is similar to dolomite in being only slightly soluble in cold dilute HCl, however it effervesces in warm acid. Magnesite is unlike dolomite and calcite in that it rarely exhibits twinning.	Magnesite may be found in association with Mg-rich hydrothermal fluids, particularly in regions where these fluids interact with limestones. Numerous localities in the eastern United States show magnesite in association with serpentine, talc, or dolomite rocks. Magnesite is mined in the states of Washington and Nevada.
SIDERITE	The mineral siderite is iron carbonate (FeCO ₃). It has a crystal structure similar to calcite and dolomite. Siderite differs from calcite in its relative insolubility in cold dilute acid, and from magnesite in its common twinning. It commonly occurs in sedimentary rocks, and is a major mineral in clay ironstones.	Siderite is formed by the replacement action of iron-rich solutions upon limestones. It is a common vein mineral associated with various metallic ores, including pyrite, chalcopyrite, tetrahedrite, and galena. Siderite may be common enough to be mined in some cases. Siderite is commonly found in the banded iron formations of the Lake Superior region.

A3.6

APPENDIX 4

Details of Carbonate Dissolution Kinetics Experiments

A4.1.	Table A4.1.1	Characterization and Pre-teatment of Calcite/Aragonite Solid Phases
	Table A4.1.2	Experimental design variables-Calcite/Aragonite
A4.2.	Table A4.2.1	Characterization and Pre-teatment of Dolomite Solid Phases
	Table A4.2.2	Experimental design variables–Dolomite
A4.3.	Table A4.3.1	Characterization and Pre-teatment of Magnesite Solid Phases
	Table A4.3.2	Experimental design variables-Magnesite
A4.4.	Table A4.4.1	Characterization and Pre-teatment of Siderite Solid Phases
	Table A4.4.2	Experimental design variables-Siderite



Table A4.1.1: Characterization and Pre-teatment of Calcite Solid Phases

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*All surface areas were determined by geometric calculation based upon average grain size, unless otherwise indicated in [].

ReferenceMineral CompositionS		Sample Description	Surface Area*	Sample Preparation		
<u>#1004</u> Plummer, Wigley, Parkhurst (1978)	(same as Plummer & Wigley, 1976)	Iceland spar	44.5 cm ² /g (coarse) 96.5 cm ² /g (fine)	Washed in 0.01 N HCl (~10 sec) > DI-H ₂ O > acetone > dried at 100°C.		
<u>#3870</u> Busenberg & Plummer (1986)	#3870 Busenberg & Calcite: Plummer (1986) 0-10 ppm Sr 0-9 ppm Mg Aragonite: 15-940ppm Sr 1-92 ppm Mg		Crystals [Geometric]: 2-10 cm ² Powders [B.E.T.]: 1,900 cm ² /g (calcite) 12,000 cm ² /g (arag.)	Washed in 0.01 N HCl (~10 sec) ≻ DI-H ₂ O ≻acetone≻ dried at 100°C.		
<u>#2402 </u> Plummer & Wigley (1976)	30 ppm Cu 60 ppm Sr 120 ppm Na 190 ppm Mg	Iceland spar	44.5 to 475.5 cm ² /g	N/A		
<u>#303</u> Sjöberg (1976)	N/A	Analytical grade calcite powder	3700 cm ² /g [B.E.T.]	N/A		
<u>#3897</u> Compton & Unwin (1990)	N/A	Iceland spar	7.5 cm^2 (flat crystal surface)	Single crystal: cleaved, polished and acid- etched for 1 min.		
<u>#3894</u> Arakaki & Mucci (1995)	N/A	Non-optical grade Iceland Spar (Wards)	261 cm ² /g mean size=107.5 μm	Wet-sieved		
Baumann & Schultz (1992)	N/A	-Sparry Calcite -Crystalline calcite -Biogenic	Unknown (Packed column)	Washed in 0.01 N HCl (~10 sec) ≻DI-H ₂ O ≻acetone≻ dried at 100°C.		
Chou et al. (1989)	N/A	N/A	300-400 µm size fraction	Ground \gg washed in 1% HCl \gg DI- H ₂ O \gg acetone sonicated \gg dried.		

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Reference	Mineral Composition	Sample Description	Surface Area*	Sample Preparation
Rickard and Sjöberg (1983)	Iceland Spar: Cd = 9 ppm Fe = 11 ppm K = 11 ppm Li = 2 ppm Mg = 6 ppm Mn = 124 ppm Na = 16 ppm Pb = 90 ppm Sr = 189 ppm Carrara Marble: Mg = 5400 ppm Na = 600 ppm Zn = 300 ppm	 Both powders and solid discs were used Iceland Spar calcite (locality unknown) Carrara Marble, Italy 	-Discs had a surface area of 0.7 cm ² (The surface area of the powders was not reported)	N/A
Sjöberg and Rickard (1984)	Same as Rickard and Sjöberg (1983)	Same as Rickard and Sjöberg (1983)	Discs had a surface area of 0.7 cm^2	N/A

*All surface areas were determined by geometric calculation based upon average grain size, unless otherwise indicated in [].

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Reference	Reactor Type	Solution Composition	Duration	Temp (°C) Press (atm)	PCO ₂	рН	Stirring Rate
<u>#1004</u> Plummer, Wigley, Parkhurst (1978)	Batch (pH-stat and free- drift)	CO ₂ -HCl-H ₂ O	up to 7 hrs	5°- 60°C 1 atm	0.0 - 1.0 atm	2.0 to 7.0	800-2750 rpm
<u>#3870</u> Busenberg & Plummer (1986)	Batch (<i>pH-stat</i> and <i>free-</i> drift)	CO ₂ -HCl-H ₂ O- KHCO ₃ -KOH- CaCl ₂	N/A	25°C 1 atm	0, 30, 50, 100%	2.0 to 11.0	260 rpm
<u>#2402</u> Plummer & Wigley (1976)	Batch	CO ₂ -H ₂ O	16 to 49 hrs	25°C 1 atm	0.97 atm (sat'd)	4.0 to 6.0	N/A
<u>#303</u> Sjöberg (1976)	Batch	0.7 M Kcl	N/A	5°- 50°C 1 atm	0.97 atm (sat'd)	8.0 to 10.0	276 rpm
<u>#3897</u> Compton & Unwin (1990)	Flow- through across solid crystal surface	0.25, 050, and 1.0 mM Hcl	several minutes	25°C(?) 1 atm(?)	N/A	< 4.0	N/A
<u>#3894</u> Arakaki & Mucci (1995)	Batch	CO ₂ -H ₂ O	up to 5 hrs	25°C 1 atm	0.97 atm, 30%, 2%, and 0.3%	>4.5	305 -620 rpm
Baumann & Schultz (1992)	Packed column, flow- through	CO ₂ -H ₂ O	N/A	25°C 1 atm	0.97 atm (sat'd)	N/A	N/A

Table A4.1.2: Experimental Design Variables--Calcite

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Reference	Reactor Type	Solution Composition	Duration	Temp (°C) Press (atm)	PCO ₂	рН	Stirring Rate
Chou et al. (1989)	Fluidized bed	HCl-H ₂ O	N/A	25 °C	air equilibrated	4-10	N/A
Rickard and Sjöberg (1983)	-Batch reactor -Rotating disc apparatus	distilled H_2O in N_2 - atmosphere, free of CO_2 pH-stat, HCl used as titrating acid KCl used as an ionic medium (0.1 to 0.7 mol/L)	N/A	25 °C	CO ₂ -free	4-10	Disc rotation rate: 0 to 625 s ⁻¹
Sjöberg and Rickard (1984)	Rotating disc apparatus	Same as Rickard and Sjöberg (1983)	N/A	25 °C	CO ₂ -free	4-10	Disc rotation rate: 0 to 625 s ⁻¹

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Reference	Mineral Composition	Sample Description	Surface Area	S.A. Method	Sample Preparation
Busenberg and Plummer (1982)	$\begin{array}{llllllllllllllllllllllllllllllllllll$	SampleDescriptionAOpaque, whiteBClearCClearDClearEOpaque, whiteFOpaque, whiteGMicroxstl'n, sed.SWhite, gray, opaque	1.8 to 7.1 cm ² (crystal S.A. normally around 3 cm ²)	Geometric	Crystals reacted with 6 M HCl, washed in DI-H ₂ O, dried at 65°C, Seived to between 60 and 140 mesh size.
Chou et al. (1989)	Ca _{0.498} Mg _{0.502} CO ₃ (Contains traces of Fe, Al, Mn, and K)	Sussex, NJ, U.S.A.	100-200 μm size fraction	Geometric	Ground $>$ washed in 1% HCl $>$ rinsed in DI-H ₂ O > acetone sonicated $>dried.$
Gautelier et al. (1999)	$\begin{array}{llllllllllllllllllllllllllllllllllll$	Haute Vallee de l' Aude (France) Polycrystalline white dolomite disks of hydrothermal origin with millimetric grain size.	(Not reported)	Geometric	Disks were ground with 200, 800, and 1200 grit silicon carbide, then with Nylon using silicon oil, and finally cleaned with methyl alcohol.
Sherman and Barak (2000)	$Ca = 20.9 \text{ wt \%} Ca_{1.001}Mg_{0.999}CO_3$ Mg = 12.7 wt % Fe = 0.5 wt % Mn = 0.2 wt % $CO_2 = 63.4 \text{ wt \%}$	Butte, MT, USA (Ward's)	0.25 m ² /g (< 0.25 mm size fraction)	B.E.T.	washed in 0.05 <i>M</i> HCl for 2 min. \gg rinsed in DI-H ₂ O \gg freezedried.

Table A4.2.1: Characterization and Pre-teatment of Dolomite Solid Phases

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Reference	Reactor Type	Solution Composition	Duration	Temp (°C) Press (atm)	PCO ₂	рН	Stirring Rate
Busenberg and Plummer (1982)	Batch , free-drift and pH-stat	pH-adjusted with HCl, KOH, or KHCO ₃ Solution bubbled with CO ₂ -N ₂ gas mixtures	free-drift: 4-5 hrs pH-stat: 15 min to 1 week, (normally 2-48 hrs)	1.5° to 65°C	0 to 1 atm	1-10	260 rpm
Chou et al. (1989)	Fluidized bed	HCl-H ₂ O	N/A	25°C	air- equilibrated	4-10	N/A
Gautelier et al. (1999)	Rotating disk/ mixed flow	HCl-H ₂ O	N/A	25 - 80°C	N/A	-0.5 to 5.0	210, 500 and 1000 rpm
Sherman and Barak (2000)	Batch	Solution bubbled with CO_2 gas	672 days	25°C	0.1 MPa	N/A	N/A

Table A4.2.2: Experimental Design Variables--Dolomite

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Reference	Mineral Composition	Sample Description	Surface Area	S.A. Method	Sample Preparation
Chou et al. (1989)	A: Mg _{0.965} Ca _{0.020} Fe _{0.015} CO ₃ B: MgCO ₃	N/A	50-100 μm size fraction	Geometric	Ground ≻washed in 1% HCl ≻DI-H ₂ O rinse ≻acetone sonicated ≻ dried.
Pokrovsky and Schott (1999)	Less than 0.5 % impurities	Satka (Ural, Russia) ~1cm crystals	50-100 μm size fraction	B.E.T.	Ground $>$ washed in 1% HCl $>$ alcohol sonicated > rinsed in DI-H ₂ O $>$ dried at 60°C

 Table A4.3.1: Characterization and Pre-teatment of Magnesite Solid Phases

 Table A4.3.2: Experimental Design Variables--Magnesite

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Reference	Reactor Type	Solution Composition	Duration	Temp (°C) Press (atm)	PCO ₂	рН	Stirring Rate
Chou et al. (1989)	Fluidized bed	HCl-H ₂ O	N/A	25 °C	air- equilibrated	4-10	N/A
Pokrovsky and Schott (1999)	Mixed-flow	Various: HCl, NaOH, NaHCO ₃ , Na ₂ CO ₃ , NaCl, MgCl ₂ .	Up to ~150 hr.	25 °C	Less than 0.001 atm	1-12	N/A

Reference	Mineral Composition	Sample Description	Surface Area (cm²/g)	S.A. Method	Sample Preparation
Greenberg and Tomson (1992)	FeCO3	Synthetic	5.92 x 10 ⁴ 9.17 x 10 ³	Geometric	Synthetically grown xstals, washed in deoxygenated water, heated in an oil bath at 70.00°C for 1 weak

 Table A4.4.1: Characterization and Pre-teatment of Siderite Solid Phases

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Reference	Reactor Type	Solution Composition	Duration	Temp (°C) Press (atm)	PCO ₂	рН	Stirring Rate
Greenberg and Tomson (1992)	Batch	Deoxygenated water and CO.	20-30 min	26°C	1.96	N/A	N/A
10hison (1992)		water and etc ₂		60°C	1.82		

APPENDIX 5

Reported Carbonate Mineral Dissolution Rates

- A5.1 Table A5.1.1: Calcite/Aragonite Rate Data Table A5.1.2: pH, PCO₂ and Calcite Dissolution Rates Table A5.1.3: pH, PCO₂, and Aragonite Dissolution Rates
- A5.2 Table A5.2.1: Dolomite Rate Data Table A5.2.2: pH, PCO₂ and Dolomite Dissolution Rates
- A5.3 Table A5.3.1: Magnesite Rate Data Table A5.3.2: pH, Ionic strength and Magnesite Dissolution Rates
- A5.4 Table A5.4.1: Siderite Rate Data Table A5.4.2: Spreadsheet calculation of siderite dissolution rates vs. pH



Reference	Experiment or Literature Review?	Rate data	(-log ı	rate in	mol∙cn	n ⁻² ·s ⁻¹)		Rate determined by	Activation Energy (kJ/mol)
<u>#1115</u> Wollast,	Review		<u>k</u> 1	<u>k</u> ,	<u>k</u> 3	<u>k.</u> 3	Reference	pH, PCO ₂	N/A
1990		Calcite						change, and	
		Powders	4.29	7.47	9.93		Plummer et al. (1978)	theoretical Ca	
		Single xstal	5.06	7.32	9.63		Busenberg & Plummer (1986)	release	
		Powders	4.05	7.30	10.19	1.73	Chou et al. (1989)		
		Powders				2.39	Nancollas & Reddy (1971)		
		Powders				1.82 to 1.93	Inskeep & Bloom (1985)		
		Aragonite			0.44	• • •			
		Single xstal	5.06	7.32	9.46	2.38	Busenberg & Plummer (1986)		
		Powders	3.92	7.40	10.00	1.78	Chou et al (1989)		
<u>#1004</u> Plummer, Wigley, Parkhurst (1978)	Experimental (2 <ph<7)< td=""><td>6.5 to 11.0 (depending t</td><td>)* upon pH</td><td>I, PCO₂,</td><td>and stirr</td><td>ing rate)</td><td></td><td><i>pH-stat</i>: moles of HCl titrated</td><td>$k_1 = 8.4$ $k_2 = 41.8$ $k_3 = 6.3$ (for</td></ph<7)<>	6.5 to 11.0 (depending t)* upon pH	I, PCO ₂ ,	and stirr	ing rate)		<i>pH-stat</i> : moles of HCl titrated	$k_1 = 8.4$ $k_2 = 41.8$ $k_3 = 6.3$ (for
								free-drift:	T < 25°C)
								calculated Ca	= 7.9 (for
								release based	T > 25°C)
								on pH and	$k_4 = N/A$
								PCO ₂	

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Table A5.1.1: Calcite/Aragonite Rate Data

Reference	Experiment or Literature Review?	Rate data (-log	rate in mol·cm ⁻	⁻² ·s ⁻¹)		Rate determined by	Activation Energy (kJ/mol)
<u>#3870</u> Busenberg & Plummer (1986)	Experimental (2 <ph<11)< td=""><td>$k_{1} = \frac{CALCITE}{5.06}$ $k_{2} = 7.32$ $k_{3} = 9.63$</td><td>ARAGONITE 5.06 7.32 9.46</td><td></td><td></td><td><i>pH-stat</i>: -weight of crystals - measured Ca release <i>free-drift</i>: changes in pH, or Ca release rate</td><td>N/A</td></ph<11)<>	$k_{1} = \frac{CALCITE}{5.06}$ $k_{2} = 7.32$ $k_{3} = 9.63$	ARAGONITE 5.06 7.32 9.46			<i>pH-stat</i> : -weight of crystals - measured Ca release <i>free-drift</i> : changes in pH, or Ca release rate	N/A
<u>#3894</u> Arakaki & Mucci (1995)	Experimental (4.5 <ph<7)< td=""><td><u>-Log diss. Rate</u> 8.50 to 11.00* 9.00 to 11.00* 10.00 to 11.00*</td><td><u>Pco</u>₂ 1 atm 0.3 atm 0.02 atm</td><td><u>pH range</u> 4.5 to 6 5.0 to 6 6.0 to 7</td><td><u>e</u> 5.0 5.5 7.0</td><td>measured changes in pH, PCO₂</td><td>N/A</td></ph<7)<>	<u>-Log diss. Rate</u> 8.50 to 11.00* 9.00 to 11.00* 10.00 to 11.00*	<u>Pco</u> ₂ 1 atm 0.3 atm 0.02 atm	<u>pH range</u> 4.5 to 6 5.0 to 6 6.0 to 7	<u>e</u> 5.0 5.5 7.0	measured changes in pH, PCO ₂	N/A
Baumann & Schultz (1992)	Experimental (plug-flow reactor)	<u>-Log diss. Rate</u> 9.00 to 11.00* 9.60 to 11.00* 10.12 to 11.00* 10.70 to 11.30*	Flow velocity 1.15 cm/s 1.51 cm/s 0.47 cm/s 0.005 cm/s	PCO ₂ 5 0.75 atm 0.05 atm 0.006 atm 0.008 atm	Sample Porous calcite Sparry calcite Sparry calcite Biogenic carb.	measured change in solution conductivity, leading to theoretically calculated Ca release	N/A
Dreybrodt (1992)	Theoretical 10° C, p CO ₂ =30Pa	10.04 to 11.00* (for magnitude <i>slower</i>)	or turbulent water f	flow; rates for la	minar flow are 1 order of	N/A	N/A

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Reference	Experiment or Literature Review?	Rate data (-log rate in mol·cm ⁻² ·	s⁻¹)		Rate determined by	Activation Energy (kJ/mol)
Morse (1983)	Review (0.5 <ph<7)< td=""><td>6.0 to 9.5* (depending upon pH, PCO₂</td><td>)</td><td></td><td>N/A</td><td>N/A</td></ph<7)<>	6.0 to 9.5* (depending upon pH, PCO ₂)		N/A	N/A
Rickard and Sjöberg (1983)	Experimental	-Log diss. Rate (25°)† Ionic Strength 9.00 to 10.00* 0.1 9.82 to 9.07* 0.7 9.02 to 9.32* 0.7 8.65 to 9.20* 0.7	<u>pH</u> 9.8 9.8 8.4 8.4	<u>Sample</u> Iceland Spar Carrara Marble Iceland Spar Carrara Marble	N/A	N/A
Sjöberg and Rickard (1984)	Experimental	-Log diss. Rate (25°)† Ionic Strength 6.40 to 7.12* 0.1 6.82 to 7.30* 0.1 7.60 to 8.00* 0.1	<u>pH</u> 2.00 2.46 2.96	<u>Sample</u> Iceland Spar Iceland Spar Iceland Spar	N/A	N/A

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*Rate graphically determined from a published figure, or re-calculated from published data. †Rates depend on rotation speed of calcite disc.

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Table A5.1.2 : Mineral dissolution rates for CALCITE (-log rate in mol·cm⁻²·s⁻¹) at different pH and **PCO₂**:

(Data were taken from Busenberg and Plummer, 1986. All experiments performed at 25°C. Not all rate data are reported here due to space considerations. For additional rate data, see the original reference.) *Average of several runs conducted at the same pH, PCO₂.

pH	0 atm	рН	0.1 atm	pН	0.5 atm	pН	1.0 atm
2.33	7.44	3.16	8.04	2.47	7.55	2.69	7.69
2.50	7.54	3.27	8.10	2.70	7.68	2.74	7.86
2.65	7.77	3.50	8.46	2.82	7.87	3.00	7.99
2.84	8.00	3.77	8.52	3.03	8.02	3.19	8.17
3.00	8.05	4.00	8.81	3.49	8.39	3.50	8.40
3.25	8.25	4.23	8.96	3.91	8.62	3.75	8.57
3.40	8.47	4.47	9.13	4.31	8.78	4.00	8.63
3.50	8.53	4.72	9.28	4.63	8.95	4.25	8.66
3.75	8.64	5.00	9.43	4.89	9.02	4.50	8.79
3.85	8.72	5.20	9.37	5.25	9.16	4.73	8.81
4.00	8.91	5.51	9.55	5.38	9.15	5.00	8.93*
4.19	9.18	5.78	9.52	5.54	9.21	5.26	8.98
4.30	9.16	6.00	9.59	5.67	9.25	5.50	9.01*
4.50	9.28	6.27	9.59*	5.73	9.23	5.74	9.02
4.75	9.53	6.54	9.53	5.85	9.25	6.01	9.12
5.00	9.62	6.66	9.62*	6.04	9.26	6.21	9.08
5.35	9.70	6.84	9.64	6.28	9.25	6.49	9.14*
5.50	9.73	7.05	9.56	6.50	9.37	6.74	9.22*
5.75	6.68	7.22	9.64	6.75	9.39	7.00	9.41*
6.00	9.57	7.50	9.66	7.07	9.46	7.25	9.58
6.20	9.75	7.68	9.91	7.29	9.61	7.55	10.12
6.70	9.58	7.80	10.15	7.48	10.06	7.72	10.23
7.00	9.62	8.04	10.25	7.69	10.16		
7.20	9.66	8.28	10.60	7.87	10.46		

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pН	0 atm	pН	0.1 atm	pН	0.5 atm	pH	1.0 atm
7.50	9.68						
7.75	9.56						
8.00	9.60						
8.20	9.57						
8.60	9.73						
9.00	9.69						
9.45	9.78						
10.01	9.83						
10.55	9.79						
11.04	9.94						
11.18	9.85						

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Table A5.1.3 : Mineral dissolution rates for ARAGONITE (-log rate in mol·cm⁻²·s⁻¹) at different pH and PCO_2 :

pH	0.00 atm	pН	0.285 atm	pН	0.480 atm	pН	0.960 atm
2.00	7.18	3.24	8.23	3.50	8.40	2.25	7.35
2.23	7.35	3.75	8.63	4.06	8.67	2.49	7.59
2.50	7.62	4.07	8.81	4.24	8.78	2.75	7.77
2.77	7.88	4.16	8.85	4.53	8.86	2.99	7.99
3.00	8.10	4.40	8.95	4.60	8.80	3.24	8.25
3.20	8.27	4.60	8.94	4.81	8.98	3.35	8.20
3.40	8.46	4.72	9.02	5.04	8.91	3.50	8.28
3.50	8.53	4.75	9.02	5.24	9.03	3.68	8.42
3.75	8.78	4.96	9.15	5.53	9.11	3.75	8.40
3.80	8.75	5.25	9.17	5.76	9.07	3.92	8.48
4.00	8.91	5.50	9.17	5.82	9.12	4.25	8.61
4.25	9.13	5.76	9.23	6.00	9.13	4.50	8.63
4.50	9.14	5.92	9.23	6.27	9.13	4.75	8.71
4.75	9.32	6.00	9.24	6.50	9.17	4.78	8.75
5.50	9.32	6.03	9.30			5.00	8.74
6.00	9.39	6.14	9.28			5.26	8.79
6.50	9.52	6.26	9.29			5.31	8.85
7.00	9.45	6.35	9.23			5.50	8.90
7.03	9.44	6.52	9.27			5.75	8.92
7.50	9.44	7.00	9.39			5.85	8.85
8.00	9.46					5.95	8.95
8.52	9.49					6.02	8.90
9.00	9.47					6.11	8.96
9.40	9.49					6.25	8.97
9.58	9.50					6.30	9.02

(Data from Busenberg and Plummer, 1986; all experiments performed at 25°C)

pH	0.00 atm	pН	0.285 atm	pH	0.480 atm	pH	0.960 atm
9.79	9.50					6.35	9.02
10.04	9.59					6.51	9.04
10.20	9.65					6.74	9.16
10.22	9.63					6.88	9.24
10.46	9.72					6.99	9.26
10.61	9.73					7.07	9.22
10.84	9.80					7.20	9.37
						7.26	9.48
						7.62	9.63

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Reference	Experiment or Literature Review?	Rate data (-log rate in mol·cm ⁻² ·s ⁻¹)	Rate determined by	Activation Energy (kJ/mol)
Busenberg and Plummer (1982)	Experimental (1 <ph<10) 25 ℃</ph<10) 	-Log diss. Rate* PCO ₂ pH range 8.61 to 11.67 0 atm 1.18 to 9.90 8.95 to 10.11 0.96 atm 2.01 to 5.20 9.40 to 9.84 0.30 atm 2.90 to 4.60 9.91 0.096 atm 4.40 9.91 to 10.12 0.03 atm 4.00 to 4.64 9.92 to 10.33 0.003 atm 3.93 to 5.00	 Weight loss measurements of single xstals Calculated from measured pH, PCO₂ 	$k_1 = 51.9$ to 89.5 $k_2 = 29.3$ to 77.4 $k_3 = 39.9$ to 159 (values depend upon type of dolomite samplesee Table 4 and related discussion in the original article for more info).
Chou et al. (1989)	Experimental (2 <ph<10) 25 ℃</ph<10) 	$k_1 = 6.59$ $k_2 = 8.00$ $k_3 = 11.66$	Measured Ca-release, Alk, pH	N/A
Gautelier et al. (1999)	Experimental (-0.5 <ph<5.0) 25- 80 °C</ph<5.0) 	TempLog Rate (k_1) n_1 257.010.63±0.03 506.290.73±0.03805.750.80±0.03	Measured Ca and Mg release, pH	Activation energy decreases from 46 to 15 kJ/mol with increasing pH from 0 to 5.

Table A5.2.1: Dolomite Rate Data

*See Table A5.2.1 for pH and PCO₂ dependence

pН	0.00 atm	pН	0.003 atm	pН	0.030 atm	pН	0.300 atm	pН	0.960 atm
1.18	8.61	3.93	9.92	4.00	9.91	2.90	9.40	2.01	8.95
2.08	9.08	4.18	10.02	4.40	10.08	3.57	9.64	2.54	9.13
2.25	9.11	4.54	10.21	4.64	10.12	3.84	9.66	3.40	9.45
2.73	9.31	5.00	10.33			4.20	9.77	3.68	9.48
3.07	9.53					4.60	9.84	3.93	9.60
3.88	9.91							4.22	9.65
4.50	10.20							4.72	9.73
4.70	10.32							5.20	10.11
5.72	10.81								
7.34	11.35								
9.09	11.69								
9.90	11.67								

Table A5.2.2: Mineral dissolution rates for DOLOMITE (-log rate in mol·cm⁻²·s⁻¹) at different pH and PCO₂: (Data from Busenberg and Plummer, 1982; all experiments performed at 25°C)

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Reference	Experiment or Literature Review?	Rate data (-log rate in mol·cm ⁻² ·s ⁻¹)	Rate determined by	Activation Energy
Chou et al. (1989)	Experimental	$k_1 = 8.60$ $k_2 = 9.22$ $k_3 = 13.35$ $k_{.3} = 5.35$ (calculated for the back-reaction, or precipitation)	Measured Mg-release, Alk, pH	N/A
Pokrovsky and Schott (1999)	Experimental (1 <ph<12) 25 ℃</ph<12) 	In strongly acidic solutions (pH ≤ 2.5), rates are independent of pH and ionic strength and $\mathbf{R} = 11.61$	Measured Mg-release, pH	up to 42.4 kJ/mol at pH = 5
		At mildly acidic conditions $(3 \le pH \le 5)$ the dissolution rate is proportional to the H ⁺ activity at all ionic strengths, and rates increase significantly with ionic strength.		
		At $5 < pH < 8$, rates are independent of both pH and ionic strength (0.01 \le I \le 0.5 M), and R = 13.34		

Table A5.3.1: Magnesite Rate Data

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Table A5.3.2: Mineral dissolution rates for MAGNESITE (-log rate in mol·cm⁻²·s⁻¹) at different (low) pH and **Ionic Strength** (M):

pН	0.003 M	pН	0.01 M	pН	0.10 <i>M</i>	pН	0.50 M
2.85	12.19	2.00	11.58	1.00	11.56	0.190	11.45
3.28	12.27	2.07	11.63	1.02	11.68	0.264	11.48
3.24	12.34	2.83	11.90	1.05	11.63		
3.52	12.44	2.92	11.96	2.37	11.67*		
3.70	12.58	2.98	11.95*	2.59	11.61		
		3.18	11.98*	3.48	11.84*		
		3.25	11.97	3.69	11.90		
		3.40	12.10	3.75	11.98		
		3.45	12.01	3.80	12.05		
		3.87	12.38	3.90	12.07		
		4.50	13.31*	3.95	12.08		
		4.60	13.53	4.08	12.23		
				4.12	12.26		
				4.15	12.34*		
				4.20	12.47		
		-		4.28	12.55		
				4.34	12.64		
				4.47	12.75		
l				4.50	12.81		

(Data from Pokrovsky and Schott, 1999; all experiments performed at 25°C)

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*Average of several runs conducted at the same pH, Ionic strength.

A5.16

Reference	Experiment or Literature Review?	Rate data** (see discussion below)	Rate determined by	Activation Energy
Greenberg and Tomson (1992)	Experiment	$k_{d}^{1st} = 1.529 \times 10^{-4} (L \cdot m^{-2} \cdot s^{-1})^{*}$ $k_{d}^{2nd} = 2.651 \times 10^{-5} (L \cdot mol^{-1} \cdot m^{-2} \cdot s^{-1})^{\dagger}$	Fe-concentration in the solution	$k_{d}^{1st} = 45.6 \text{ kJ/mol}$ $k_{d}^{2nd} = 43.0 \text{ kJ/mol}$
		*For the first-order rate expression †For the second order rate expression		

Table A5.4.1: Siderite Rate Data

**N.B.: The dissolution rate (or flux of iron from the mineral surface) must be CALCULATED for the conditions of the system of interest by transforming the rate constant given by Greenberg and Tomson into a flux with units of mol $cm^{-2} s^{-1}$. This is done by substituting $k_d(S/V)$ for k into equation 8 from Greenberg and Tomson (1992) to arrive at the expression:

$(V/S) dFe_t/dt = k_d^{1st}(Fe_{ca} - Fe_t)$	where:
	V = Volume of reactor from the experiment (= 0.750 L)
-or-	S = Surface area of the solids from the experiment (= 5.921 m^2)
	$k_{\rm d}^{\rm 1st} = 1.529 \text{ x } 10^{-4} (\text{L} \cdot \text{m}^{-2} \cdot \text{s}^{-1})$
$\mathbf{E}_{\mathrm{bar}} = h \frac{\mathrm{lst}}{\mathrm{E}_{\mathrm{c}}} \mathbf{E}_{\mathrm{c}}$	

 $Flux = k_d^{1st}(Fe_{eq} - Fe_t)$

If the iron concentration in solution is known (or assumed) for a particular time increment (Fe₁), then the flux for that time increment can be calculated once the equilibrium iron concentration in solution has been calculated for the conditions of the system. In other words, one must define the pH, alkalinity (or PCO₂), and temperature of the system, then calculate the iron concentration at equilibrium using the solubility constant for siderite (pK_{sp}=10.780 at 25 °C, Greenberg and Tomson, 1992, Table 2). The equilibrium Fe concentration (at 25 degrees C) can then be determined according to the expressions:

 $[\mathrm{Fe_{eq}}^{2^+}][\mathrm{CO}_3^{-2}] = \mathrm{K}sp = 10^{-10.780}$ $[H_2CO_3^*]/PCO_2 = K_H = 10^{-1.5}$ $[H^{+}][HCO_{3}^{-}]/[H_{2}CO_{3}^{+}] = K_{1} = 10^{-6.3}$ $[H^+][CO_3^{2-}]/[HCO_3^{-}] = K_2 = 10^{-10.3}$

As an example, for an assumed Fe, = 0, the -log dissolution rate (or flux) for siderite is 12.50 mol·cm⁻²·s⁻¹ at pH=6, Alk=1.4 meq/L. This is the maximum flux under these conditions, given that no Fe was assumed to be present in the solution before siderite dissolution began.

Rate of Siderite Dissolution at 25 C				[H+][HCO3-]/[H2CO3*] = K1 = 10^-6.3					
					[H+][CO3]/[HCO3-] = K2 = 10^-10.25				
					[H2CO3*]/ pC	[H2CO3*]/ pCO2 = KH = 10^-1.5			
log Rate	FLUX	Fe-eq	Fe	pН	H+	Alk (Ct)	K2	Ksp Siderite	
	(mol/cm2/s)	(mol/L)	(mol/L)			(mol/L)			pCO2
-4.50	0.000031945	2.09e+03	0	2	1.00e-02	0.0014	5.01e-11	1.66e-11	1
-5.50	0.000003195	2.09e+02	0	2.5	3.16e-03	0.0014	5.01e-11	1.66e-11	1
-6.50	0.00000319	2.09e+01	0	3	1.00e-03	0.0014	5.01e-11	1.66e-11	1
-7.50	0.00000032	2.09e+00	0	3.5	3.16e-04	0.0014	5.01e-11	1.66e-11	1
-8.50	0.00000003	2.09e-01	0	4	1.00e-04	0.0014	5.01e-11	1.66e-11	1
-9.50	3.19453e-10	2.09e-02	0	4.5	3.16e-05	0.0014	5.01e-11	1.66e-11	1
-10.50	3.19453e-11	2.09e-03	0	5	1.00e-05	0.0014	5.01e-11	1.66e-11	1
-11.50	3.19453e-12	2.09e-04	0	5.5	3.16e-06	0.0014	5.01e-11	1.66e-11	1
-12.50	3.19453e-13	2.09e-05	. 0	6	1.00e-06	0.0014	5.01e-11	1.66e-11	1
-13.50	3.19453e-14	2.09e-06	0	6.5	3.16e-07	0.0014	5.01e-11	1.66e-11	1
-14.50	3.19453e-15	2.09e-07	0	7	1.00e-07	0.0014	5.01e-11	1.66e-11	1
-15.50	3.19453e-16	2.09e-08	0	7.5	3.16e-08	0.0014	5.01e-11	1.66e-11	1
-16.50	3.19453e-17	2.09e-09	0	8	1.00e-08	0.0014	5.01e-11	1.66e-11	1

Table A5.4.2: Spreadsheet calculation of siderite dissolution rates with changing pH at $PCO_2 = 1$.

APPENDIX 6

Reported Carbonate Mineral Dissolution Mechanisms

Table A6.1	Calcite/Aragonite Mechanistic Information
Table A6.2	Dolomite Mechanistic Information
Table A6.3	Magnesite Mechanistic Information



Reference	pH Dependence	Rate Equation	Controlling Variables	Additional Description (transport control vs. surface reaction control, adsorption of inhibitor species, etc.)
<u>#1004</u> Plummer, Wigley, Parkhurst (1978)	pH < 3.5 Rate is linearly dependent upon a_{H+} , independent of PCO ₂ , and is a function of stirring rate (<i>transport</i> <i>controlled</i>) 3.5 < pH < 5.5 Rate is a function of both pH and PCO ₂ 5.5 < pH < 8.0 Rate is function of PCO ₂ , independent of pH (<i>This region represents most of the</i> <i>reaction toward reaching</i> <i>equilibrium</i>)	$\mathbf{R} = \mathbf{k}_{1} \ a_{\text{H}+} + \mathbf{k}_{2} \ a_{\text{H2CO3}} * + \mathbf{k}_{3} \ a_{\text{H2O}} - \mathbf{k}_{4} \ a_{\text{Ca++}} \ a_{\text{HCO3-}}$	 pH PCO₂ stirring rate temperature 	pH < 3.5 Rate is linearly dependent upon a_{H+} , independent of PCO ₂ , and is a function of stirring rate (<i>transport</i> <i>controlled</i>) 3.5 < pH < 5.5 Rate is a function of both pH and PCO ₂ 5.5 < pH < 8.0 Rate is function of PCO ₂ , independent of pH (<i>This region represents most of</i> <i>the reaction toward reaching</i> <i>equilibrium</i>)
#3870 Busenberg & Plummer (1986)	pH < 3.5 Rate is linearly dependent upon a_{H^+} , independent of PCO ₂ 3.5 < pH < 5.5 Rate is a function of only PCO ₂ 5.5 < pH < 8.0 Rate is function of PCO ₂ , independent of pH	(same as Plummer, Wigley, Parkhurst , 1978)	(same as Plummer, Wigley, Parkhurst, 1978)	Aragonite dissolves faster than calcite.

 Table A6.1 : Calcite/Aragonite Mechanistic Information

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Reference	pH Dependence	Rate Equation	Controlling Variables	Additional Description (transport control vs. surface reaction control, adsorption of inhibitor species, etc.)
Rickard and Sjöberg (1983)	Transport-controlled when pH < 5	dc/dt = k'A (1- $\Omega^{1/2}$) where: Ω = saturation index A = surface area (cm ²) -or- dc/dt = k A (a° _{±CaCO3} - a _{±CaCO3}) where: a° _{±CaCO3} = equilibrium activity	Different calcites behave differently according to crystal structure, surface distribution of kinetic sites, and impurities.	 <u>Mixed Kinetic Theory</u>: Rate dependence on relative saturation (Ω) is caused by interplay between transport-dependent and chemically-dependent concentration gradients. Rate can also be expressed in terms of calcium carbonate activity gradient. The reaction is first order and is directly proportional to the gradient between the surface concentration of calcium carbonate and its equilibrium value

Reference	pH Dependence	Rate Equation	Controlling Variables	Additional Description (dissolution of layers, adsorption of H ⁺ , etc)
Busenberg and Plummer (1982)	 Half order dependence on pH at low temperatures In near absence of CO₂, log R is proportional to pH, up to pH 6. Above pH 8 (in near absence of CO₂), log R is constant. The presence of CO₂ causes the rate of dissolution to increase above the values observed for no CO₂. 	$R = k_1 a_{H+}^{n} + k_2 a_{H2CO3}^{n} + k_3 a_{H2O}^{n} - k_4 a_{HCO3}^{n}$ where the exponent $n = 0.5$ for T < 45 °C	The presence of CO_2 increases the rate of dissolution above values observed for no CO_2 . Lack of stirring dependence and high activation energies suggest a <i>chemical</i> , <i>surface-</i> <i>controlled</i> , mechanism for dolomite dissolution	"The forward reaction mechanisms are interpreted as two consecutive steps in three parallel reactions. The first step of the three parallel reactions involves reaction of the CaCO ₃ component of the dolomite with bulk solution (bk) H ⁺ , H ₂ CO ₃ [•] , and H ₂ O. In the second and much slower step, the bulk solution H ⁺ , H ₂ CO ₃ [•] , and H ₂ O react with the MgCO ₃ component of dolomite. The rate limiting step in dissolution is the breakdown of the MgCO ₃ component which leads to the observed half order reaction dependence on H ⁺ , H ₂ CO ₃ [•] , and H ₂ O."

 Table A6.2 : Dolomite Mechanistic Information

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Reference	pH Dependence	Rate Equation	Controlling Variables	Additional Description (dissolution of layers, adsorption of H ⁺ , etc)
Chou et al. (1989)	0.75 order dependence on pH	$\mathbf{R} = \mathbf{k}_{1} a^{n}_{H^{+}} + \mathbf{k}_{2} a^{n}_{H^{2}CO3} + \mathbf{k}_{3}$ where the exponent $\mathbf{n} = 0.75$ at 25°C From kinetic theory, which considers the activity of MgCO ₃ at the mineral surface to be fixed by the equilibrium condition of the reaction: $Mg(CO_{3})_{(s)} + H^{+}_{(bk)} \Rightarrow$ $Mg^{2+}_{(a)} + HCO_{3}^{-}_{(a)}$ another rate equation can be derived: $\mathbf{R} = kK(a_{H^{+}})^{2}/a_{Ca2^{+}} \cdot a_{HCO3^{-}}$	Depends on the formation of surface complexes (<i>surface-controlled</i>)	N/A
Gautelier et al. (1999)	Fractional order of dependence on pH observed as in other previous studies. 0.63 order dependence found at 25 °C	Rates at all temperatures found to be consistent with $\mathbf{R} = \mathbf{k}_1 a^{\mathbf{n}}_{\mathbf{H}+ \text{ surf}}$ where the exponent $\mathbf{n} = 0.63$ at 25 °C	Surface-controlled	N/A

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Reference	pH Dependence	Rate Equation	Controlling Variables:	Additional Description (dissolution of layers, adsorption of H ⁺ , etc)
Chou et al. (1989)	Similar to that of calcite, however the rate is approximately four orders of magnitude slower.	$R_{\text{forward}} = k_1 a_{\text{H}+} + k_2 a_{\text{H2CO3}}^* + k_3 a_{\text{H2O}}$ $R_{\text{back}} = k_{-1} a_{\text{Mg2+}} a_{\text{HCO3-}} + k_{-2} a_{\text{Mg2+}} a_{\text{HCO3-}}^2 + k_{-3} a_{\text{Mg2+}} a_{\text{CO3}^{2-}}^2$	Similar to dolomite	N/A
Pokrovsky and Schott (1999)	Rate is first-order dependent on pH only in mildly acidic solutions (3 < pH < 5). Ionic strength dependence is also strong in this range.	$R = R_{H^{+}} + R_{H2O}$ $R = [k_{CO3} \{ >CO_{3}H^{\circ} \}^{m} + k_{Mg} \{ >MgOH_{2}^{+} \}^{n}] \cdot [1 - \exp(-4A/RT)]$ where, at 25°C, $k_{CO3} = 7.20$ $k_{Mg} = 5.38$ and the exponents <i>m</i> and <i>n</i> are 3.97 and 3.94, respectively.	pH, Ionic strength	"Magnesite dissolution is controlled by surface reactions occurring on both protonated carbonate and hydratred magnesium sites. Hence, the forward reaction rate is proportional to the concentration of two rate- controlling surface species: $>CO_3H^\circ$ and $>MgOH_2^+$."

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Table A6.3 : Magnesite Mechanistic Information

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