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EVALUATING CATION EXCHANGE AS A DRIVER FOR MANGANESE RELEASE DURING CARBONATE DISSOLUTION

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EVALUATING CATION EXCHANGE AS A DRIVER FOR MANGANESE RELEASE DURING CARBONATE DISSOLUTION

A THESIS APPROVED FOR THE
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BY THE COMMITTEE CONSISTING OF

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Acknowledgments

I want to thank my advisor, Dr. Andrew Elwood Madden, for allowing me to work with him for the last 3 years on both undergraduate and then graduate research. I have greatly appreciated his knowledge, expertise, and feedback over the past 3 years. I would also like to thank my other committee members, Dr. Doug Elmore and Dr. Kato Dee, for their advice and feedback on my thesis work, as well as other opportunities I had to work with and learn from them. I want to thank Dr. Preston Larson with the OU Samuel Roberts Noble Microscopy Laboratory for his SEM knowledge and expertise. I greatly appreciated his work with my SEM samples, including looking at samples for me during the shutdown and then limited return to campus as a result of Covid-19, as well as his helpfulness with the interpretation of the images. Thank you to Dr. Shannon Dulin for the laughs, gripe sessions, advice, and for getting me (as she would insist!) my NAGT USGS internship. I would like to thank my family and friends for their patience, encouragement, support, and love as I completed yet another college degree. (Last one, I promise! Maybe. I think…) You all have helped keep me sane (mostly) and motivated on this and every other journey in my life, and I am forever grateful to you for that. Last but not least, I would like to thank (not really) Covid-19. You reminded me that science is, well, science, and an essential part of science is knowing that things do not always go as planned, making adaptability an essential skill for any scientist. In this case, Covid-19-related lab shutdowns meant a slew of changes to my research objectives and methods. The result is a much more modeling-intensive thesis than I would have preferred and a thesis that, for various reasons, does not contain a fair amount of my work I had initially planned to include.

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Abstract

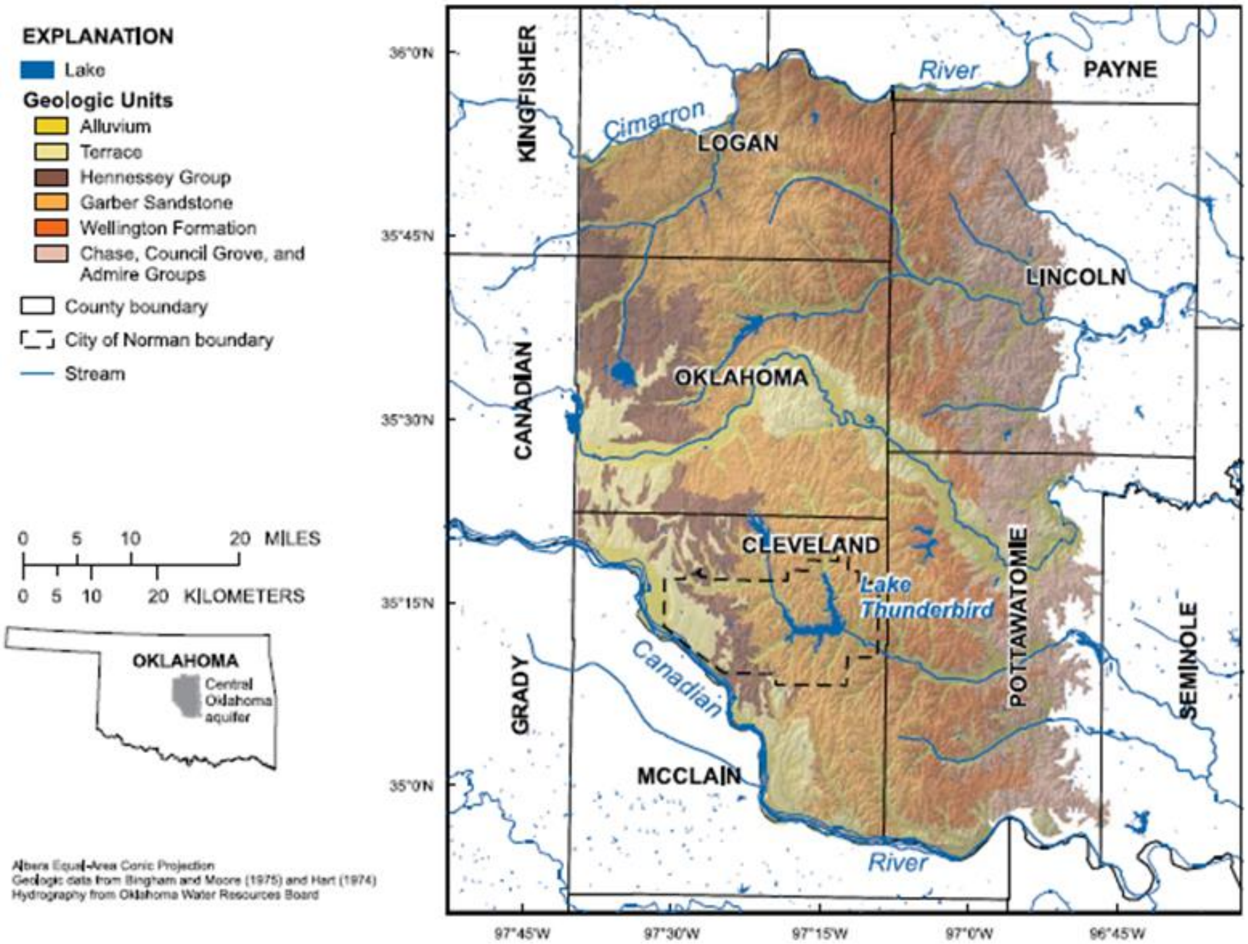
The Central Oklahoma Aquifer (COA) is a heterogeneous siliciclastic aquifer with clays and small amounts of Mn-containing dolomite scattered throughout. Areas of COA groundwater are well-known for the presence of naturally occurring heavy metals, including toxic levels of As, Cr, and U. When leached from aquifer rocks, these metals typically undergo oxidation-reduction reactions to more soluble and, in the case of Cr, more toxic forms. We hypothesized that Mn^{2+} released from dolomite during dissolution is available to serve as a redox couple in these reactions. This study aims to experimentally quantify and geochemically model the role of carbonate dissolution and cation exchange in the release of this Mn^{2+}. Synthetic Mn calcite ± Na-saturated clay was reacted under lower ($pH \approx 6$) and higher ($pH \approx 8$) pH conditions at 25°C and 60°C for 14 days with periodic measurements of pH, alkalinity, and cation concentrations followed by SEM characterization of the final Day 14 reaction products. The experimental samples' aqueous chemistry data provided the basis for PHREEQCI thermodynamic modeling, which was used to calculate and predict solution chemical responses to pH, starting chemistry, type of solid solution, and the presence or absence of exchange. Experimental results were complicated and less straightforward to interpret. Overall, the results of both experimental reactions and modeling predictions indicated carbonate dissolution in the presence of clay/exchanger does result in cation exchange, which then enhances the dissolution of additional carbonates. Temperature and pH tended to have the most significant effect on the extent of dissolution and, therefore, cation concentrations and exchange, though effects of starting chemistry and type of solid solution present were also noted in modeling solutions. Results of experimental reactions and modeling were confirmed by SEM images of final experimental reaction products. These results suggest that aquifer trace element concentrations may be linked to the co-occurrence of Mn carbonates and Na-exchanged clays along recharge flowpaths.

Introduction

Central Oklahoma Aquifer

Overview

The Central Oklahoma Aquifer (COA), known locally as the Garber Wellington Aquifer, underlies approximately 8,000 km^2 in central Oklahoma. It covers part or all of 6 counties and serves as a principal source of drinking water for all communities in central Oklahoma except Oklahoma City.[1,2] (Figure 1) The COA is historically known for high concentrations of heavy metals like chromium (Cr) and arsenic (As) that tend to be concentrated in deeper, more confined regions of the aquifer. In these regions, complex geochemical interactions, including cation exchange, dolomite dissolution, and heavy metal desorption, occur between rocks and groundwater.[3] Dolomite in the aquifer contains manganese (Mn) that must be released upon dolomite dissolution. Because there is a lack of porewater Mn^{2+}, it is believed that these Mn^{2+} ions oxidize and form $Mn^{3+/4+}$ oxides that are then free to interact with heavy metal ions, oxidizing them to more soluble or more toxic (or both) forms. For example, Cr^{3+} may be oxidized to Cr^{6+}, which is the toxic form, or As^{3+} may be oxidized to As^{5+}, which is more soluble. Precisely how much Mn^{2+} is released depends on the extent of dolomite dissolution, which, as hypothesized herein, depends on the extent of cation exchange occurring in the aquifer. In this study, the role of cation exchange in the dissolution and release of Mn^{2+} from Mn-bearing calcite and dolomite will be investigated via laboratory experiments and geochemical modeling. This study's findings will provide insight that may be used in other investigations of both modern and ancient aquifer systems.



Albers Equal-Area Conic Projection
Geologic data from Bingham and Moore (1975) and Hart (1974)
Hydrography from Oklahoma Water Resources Board

Figure 1 – Map of Oklahoma (small map, lower left corner) showing the COA's overall location. The larger map shows the surficial geology of the COA overlain on a county map of central Oklahoma. From Smith et al.[4]

Geologic Setting

A total of 9 lithological units comprise the COA (Figure 2). The average depth to water is 10 m, and the thickness of the freshwater zone within the aquifer is as much as 275 m. However, the base of freshwater is highly variable with location, being considerably deeper on the aquifer's western sides.[1] The uppermost layers consist of Quaternary alluvium and Quaternary terrace deposits found along and adjacent to rivers within the aquifer region. Permian layers consist of the Hennessey Formation, the Garber Sandstone and Wellington Formation, and the Chase, Council Grove, and

Admire groups. The Hennessey Formation is composed of mudstone and siltstone with minor amounts of thin, very fine-grained sandstone beds.[5] It serves as the upper confining unit in the western approximately one-third of the aquifer, the only region where it has not been completely eroded. The Garber Sandstone and the Wellington Formation are lithologically similar and typically grouped. The total thickness of the 2 layers ranges from 355 m to 490 m with a median thickness of 460 m.[1] Both layers contain lenticular beds of fine-grained, cross-bedded sandstone interbedded with siltstone and mudstone and serve as the predominant water-producing units of the COA.[5] The Chase, Council Grove, and Admire Groups are also lithologically similar and typically grouped. Their combined thickness ranges from 170 m to 290 m with a median thickness of 230 m.[1] These units are comprised of mudstone, fine-grained cross-bedded sandstone, and conglomerates.[5] The Pennsylvanian Vanoss Formation serves as the lower confining layer of the aquifer and is composed principally of mudstone with minor amounts of thin, fine-grained sandstone beds.[5] The ancient environment of deposition of the COA has been interpreted as being fluvial and deltaic,[1,5] creating a lithology that exhibits significant lateral and vertical heterogeneity, often over short distances.[1]

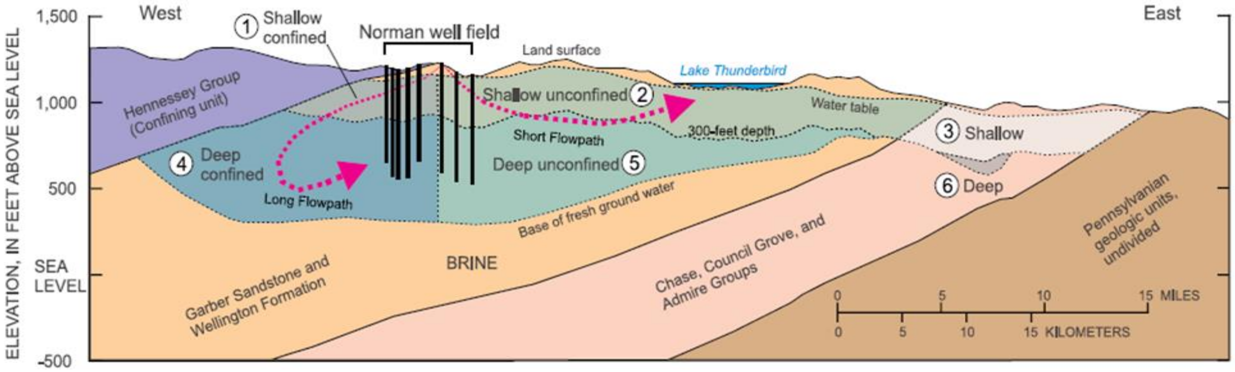


Figure 2 – Cross-section of the COA showing the major lithological units along with shallow versus deep and unconfined versus confined regions. Confined and/or deeper regions have groundwater flowpaths that tend to be much longer. These are the regions where concentrations of heavy metals tend to be the highest. From Smith et al.[4] *(Note extreme vertical exaggeration – actual dip is only about 10 m/km.*[1]*)*

Mineralogy

Principal detrital components of all Permian aquifer layers include quartz and illite, along with relevant minor components that include feldspars, chlorite, and rock fragments, particularly intraclasts of mudstone and dolostone.[5] Sandstones and mudstones throughout the aquifer are mineralogically similar. However, the relative abundance of minerals in each varies with location.[5] Sandstones are primarily sublitharenites with abundant clay matrices, and conglomerates most commonly contain dolostone and mudstone fragments.[5] Kaolinite, illite, illite-smectite, and chlorite are the most abundant clay minerals overall, but smectite-rich mixed-layer clays are commonly found in mudstones of the Chase, Council Grove, and Admire Groups as well as the lower portions of the Garber Sandstone.[5]

Common (relevant) authigenic minerals include sparry dolomite, calcite, hematite, goethite, kaolinite, and Mn oxides, with sparry dolomite being the most common.[5] Sparry dolomite is present as cement, as rhombs within mudstones, and as a replacement for micritic nodules and clasts. It is often found in conjunction with hematite-coated detrital grains or containing inclusions of hematite, goethite, or, less-commonly, kaolinite.[5] Of significant note is the presence of up to 1 weight percent (wt%) Mn within the sparry dolomite.[5] In sample cores obtained by the USGS, Mn oxides were noted in all cores coating dolomite grains as dolomite dissolution occurred.[5]

Geochemistry

Like the lithology and mineralogy, the COA's water chemistry is heterogeneous but tends to show trends with depth. In shallower, unconfined portions of the Garber Wellington, calcium (Ca^{2+}), magnesium (Mg^{2+}), and bicarbonate (HCO^{-}_{3}) are the predominant ions in the water, while in deeper, more confined units of the Garber Wellington and the Chase/Council Grove/Admire Groups the dominating ions are sodium (Na^{+}) and HCO^{-}_{3}.[1] The water chemistry in the deeper portion of the aquifer is a result of dolomite dissolution and cation exchange with clays, predominantly mixed-layer illite-smectite.[1] During cation exchange, Na^{+} in clays is exchanged for aqueous Ca^{2+} and Mg^{2+}, with Ca^{2+} exchange preferred over Mg^{2+}.[6–8] This cation exchange results in undersaturation and further dissolution of dolomite, leading to elevated pH $\geq$8.5 and desorption of heavy metals from iron oxides (discussed below).[4,9] Dissolved oxygen (DO) concentrations are typically >1 mg/L, indicating oxidizing conditions.[1,3] Oxic environments result in oxidation of many of these heavy metal cations, including As ($As^{3+} \rightarrow As^{5+}$), selenium ($Se^{2+} \rightarrow Se^{4+}$ or Se^{6+}), and uranium ($U^{4+} \rightarrow U^{6+}$) from lower, typically less soluble, oxidation states to higher, typically more soluble, oxidation states.[3] Greater solubility of many of these cations has led to concentrations in groundwater that exceed maximum contaminant levels (MCLs). The exceedance of MCLs creates problems for municipalities that rely on the COA for water. One such municipality is the city of Norman, OK, which has had to abandon its use of many wells drilled in confined units due to elevated levels of As.[4] Elevated levels of Cr^{6+} are also known to occur in the COA.[9]

Manganese

Prevalence in Carbonates

Mn is a transition metal with multiple oxidation states, including 2+, 3+, and 4+. However, in ancient sediments not exposed to surface weathering, Mn is almost exclusively found as Mn^{2+}, particularly in anoxic environments that promote the reduction of Mn and other species.[10] Having the same oxidation state as Ca^{2+} and Mg^{2+}, Mn^{2+} can substitute for these ions in carbonates, forming minerals such as rhodochrosite ($MnCO_3$), kutnohorite ($CaMn(CO_3)_2$), manganese calcite ($(Ca,Mn)CO_3$), and manganese dolomite ($(Ca,Mg,Mn)(CO_3)_2$). Such substitutions are apparently quite common. Weber analyzed 300 samples of dolostones collected from locations in North America, Europe, and Asia and found that 98% of the samples contained Mn at an average concentration of ≈240 ppm (range 11-2900 ppm), with even higher concentrations in specific subsets of dolostones (e.g., dolomitic carbonatites, argillaceous dolostones, and hydrothermal dolostones).[11] He also concluded that, based on “low sampling variance…as well as crystallochemical considerations,” the Mn must be contained within the dolomite crystals themselves.[11] For laboratory-synthesized dolomite in the presence of varying amounts of Mn and prepared at 2 different temperatures, Lumsden et al. found that samples contained as much as 16 ppm of Mn.[12] In examining Mn^{2+} partitioning between the Ca and Mg sites in dolomite, Lumsden and Lloyd found that, for 12 samples of dolomite, Mn^{2+} concentrations averaged 133 ppm (range 36-470 ppm).[13] Mn^{2+} substitution has also been found to produce the second most thermodynamically favorable dolomite structure behind Mg^{2+}. Next to Mg^{2+}, the substitution of Mn^{2+} has the lowest Gibbs free energy of formation and results in the least amount of strain on the octahedral dolomite structure compared to other divalent metal cations, e.g., Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}.[14]

Release During Dolomite Dissolution and Cation Exchange

Mass-balance modeling indicates (in agreement with petrographic and isotopic data) that cation exchange dominates in deeper, confined portions of the Garber and Wellington units and portions of the Chase, Council Grove, and Admire Groups where transmissivity is low.[15] During cation exchange, Na^+ in clays is exchanged for Ca^{2+} and Mg^{2+} in the aquifer water via the following reaction, where X< represents an interlayer or surface exchange site of a clay:

$$2Na - X < \; + (Ca^{2+}, Mg^{2+})_{(aq)} \rightleftharpoons Ca, Mg - X < \; + 2Na^{+}_{(aq)}$$

This exchange results in undersaturation of Ca^{2+} and Mg^{2+} in solution, leading to dolomite dissolution with Mn^{2+} release as follows (assuming equal cation proportions):

$$(Ca, Mg, Mn)_2(CO_3)_{2(s)} \; + \; 2H^{+}_{(aq)} \rightleftharpoons \frac{2}{3}Ca^{2+}_{(aq)} \; + \frac{2}{3}Mg^{2+}_{(aq)} \; + \frac{2}{3}Mn^{2+}_{(aq)} \; + \; 2HCO^{-}_{3\,(aq)}$$

Continued cation exchange results in continued dolomite dissolution in a positive feedback loop, producing greater amounts of HCO_3^- and increasing the system's pH. Continued increases of pH to values $\geq$8.5 result in desorption of heavy metals (e.g., chromium, arsenic, and selenium) adsorbed to iron oxides within the aquifer, mobilizing them and potentially increasing their concentrations in groundwater.[3] Mobilization of uranium is also enhanced at elevated pH values.[3]

Link to Heavy Metals

Oxic conditions present throughout the aquifer result in oxidation of the Mn^{2+} previously released from the dolomite, forming $Mn^{3+/4+}$ oxides. These oxides then precipitate as surface coatings on other grains, including dolomite,[5] other metal carbonates (e.g., $MgCO_3$, $MnCO_3$),[16] and iron oxyhydroxides (e.g., goethite, lepidocrocite).[17] Once precipitated, these oxides commonly serve as oxidizing agents or adsorbents for numerous heavy/trace metals, including As,[18–21] Cr,[22–24], U,[25–29] and Se,[30] all of which have shown elevated concentrations in select water samples from the COA.[3] These oxidation and adsorption reactions are highly pH-dependent, with reaction rates that typically increase as pH increases.[17,31] Cation exchange, dolomite dissolution, increasing pH, adsorption/desorption, and redox reactions all serve to create a complex feedback pathway that ultimately results in elevated concentrations of heavy metals within the COA, thereby affecting the quality of drinking water for Central Oklahoma residents.

Relevant Previous Work

U.S. Geological Survey

The USGS has completed a majority of the previous work on the COA as part of the National Water Quality Assessment (NAWQA) Program, examining water quality and potential water quality issues along with the geochemistry and geohydrology of the aquifer. Much of this work has been discussed in the background above, but significant relevant conclusions are included here. Dolomite is present throughout the aquifer and contains up to 1 wt% Mn.[5] Cation exchange is occurring in deeper, confined, clay-rich portions of the aquifer, resulting in the exchange of Na^+ for Ca^{2+} and Mg^{2+}, with Ca^{2+} exchange preferred over Mg^{2+}.[15,31] This cation exchange causes dolomite to dissolve; continued dolomite dissolution results in increased pH values (often $\geq$8.5) within these portions of the aquifer, leading to desorption of heavy metals like Se, Cr, and As.[3,31] With up to 1 wt% Mn, dolomite dissolution should also release Mn^{2+} into the aquifer. However, virtually no Mn is present in aquifer water at deeper levels where dolomite dissolution is occurring.[1] Instead, Mn oxides are common and are associated with dolomite dissolution,[5] suggesting the Mn is being sequestered as oxides. Lastly, concentrations of 4 major heavy elements – Cr, As, Se, and U – have historically been elevated in the aquifer, often above MCLs, particularly in deeper and often more confined portions of the aquifer.[3]

Elwood Madden Research Group

Our research group has done additional work on both the distribution of and mechanisms for elevated Cr concentrations in the COA. Core and outcrop rock samples were analyzed and showed ~1 wt% Mn within dolomite grains in agreement with USGS findings.[5,9] Further analyses revealed that Cr is present primarily as Cr^{3+} substituted for Fe^{3+} in iron (Fe) oxides, and significantly more Cr is found within Fe oxides than in clays.[9]

In addition to core and outcrop samples, historical water chemistry data were also analyzed.[32,33] Using the USGS National Water Information System (NWIS) database (https://waterdata.usgs.gov/nwis), all available data were obtained for all wells within the COA. Geochemical analyses were completed using depth-specific and nondepth-specific data to identify trends in elevated Cr related to depth within the aquifer. From these analyses, we were able to identify trends that provided further evidence supporting the USGS assertion that cation exchange and dolomite dissolution dominate and control the trends seen in heavy metal concentrations in deeper, confined portions of the COA. The first trend used depth-specific data for Cr-bearing samples and showed a Mg/Ca activity ratio of 1.4 for high-Cr (arbitrarily chosen as Cr $\geq$ 20 ppb) samples compared to a Mg/Ca ratio of ~1 for low-Cr (Cr < 20 ppb) samples (Figure 3).[32] A Mg/Ca ratio > 1 indicates greater Mg^{2+} in solution than Ca^{2+}, which would occur during cation exchange with the preferential exchange of Ca^{2+} over Mg^{2+}. High Cr levels lie near this trendline, linking them to greater depths and locations where cation exchange occurs (along with dolomite dissolution, which provides the continuous supply of Ca^{2+} and Mg^{2+}). Additionally, trends exist in plots of Na^{+} versus Mg^{2+} and Na^{+} versus Ca^{2+} activities (Figure 4).[32] Both panels in Figure 4 show that low Cr samples do not follow any specific trends while high Cr samples do. The left panel shows that waters high in Cr have high Mg^{2+} activities (solid line) that decrease to a point where activity remains constant with increased Na^{+} activity. The right panel shows that high Cr waters also have high Ca^{2+} activities (dashed line) that, as with Mg^{2+}, decrease to a point before remaining constant with increasing Na^{+} activity. However, the slope of the Mg^{2+} (solid) line is steeper than the slope of the Ca^{2+} (dashed) line, indicating greater Mg^{2+} activity and, therefore, aqueous concentrations. As in Figure 3, the slopes of the Mg^{2+} and Ca^{2+} lines correspond to a Mg/Ca ratio of 1.4. This information lends further credence to the assumption that cation exchange (along with dolomite dissolution) is occurring.

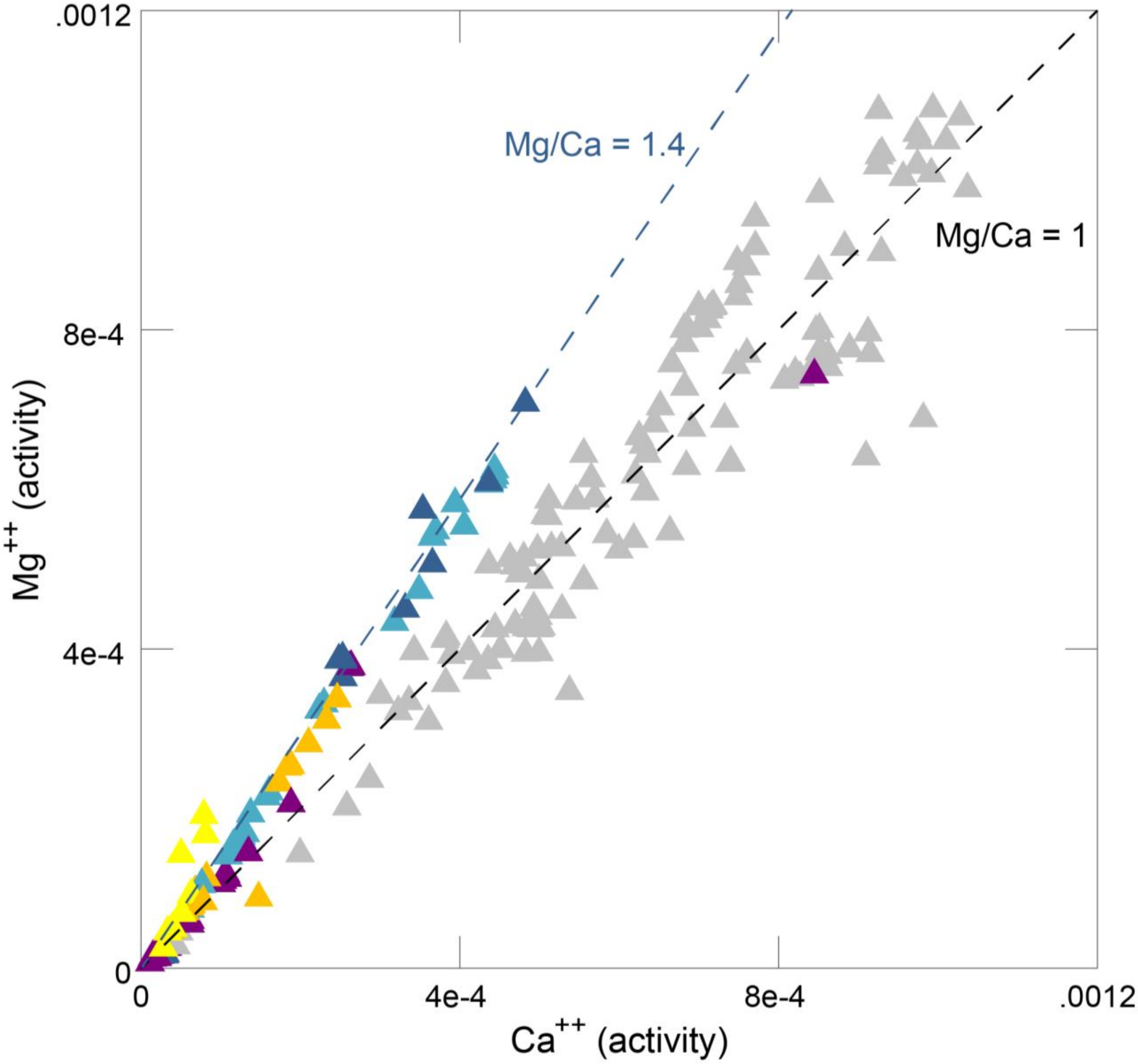


Figure 3 – Plot of Ca^{2+} versus Mg^{2+} activity showing 2 distinct trends in Cr levels with Mg/Ca ratios. Low (<20 ppb) Cr values fall along a trendline where the Mg/Ca ratio is ~1 while elevated (>20 ppb) Cr levels fall closely on a trendline where the Mg/Ca ratio is ~1.4. From Elwood Madden et al.[32]

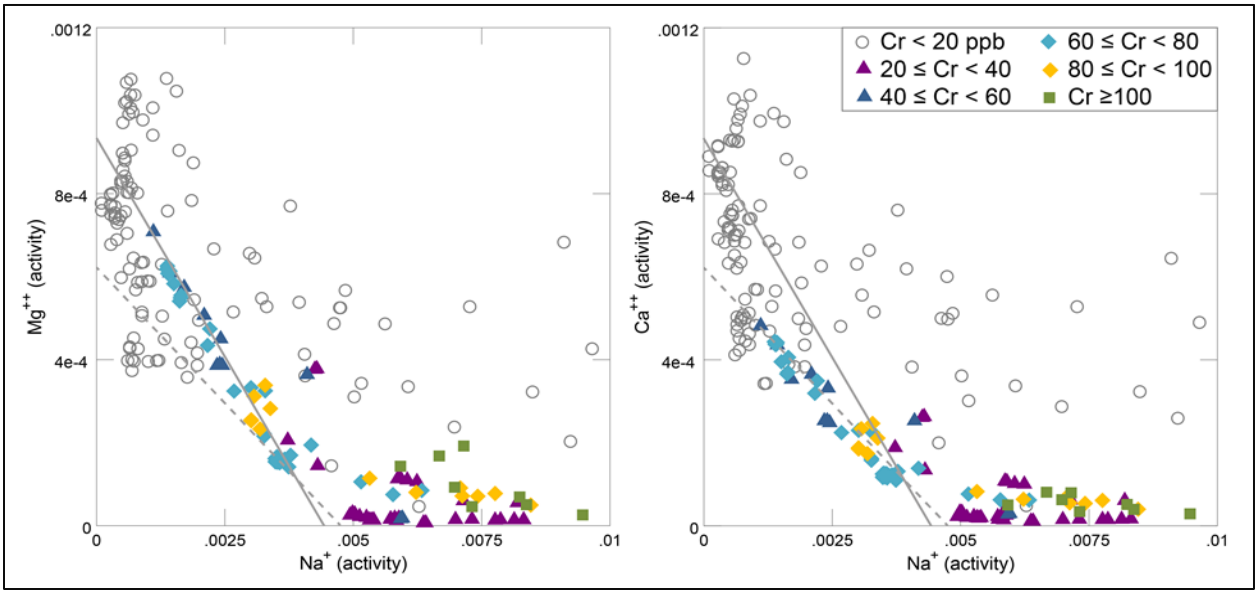


Figure 4 – Na^+ versus Mg^{2+} (left) and Na^+ versus Ca^{2+} (right) activity plots for depth-specific Cr-bearing groundwater samples. The left graph shows high Cr samples associated with high Mg^{2+} activities (solid line) at lower Na^+ activities. The right graph shows high Cr samples associated with high Ca^{2+} activities (dashed line) at lower Na^+ activities. The steeper slope of the Mg^{2+} (solid) line compared to the slope of the Ca^{2+} (dashed) line indicates greater Mg^{2+} activity and, therefore, greater aqueous concentrations. The ratio of the slopes of the 2 lines, signifying the Mg/Ca ratio, is ~1.4. From Elwood Madden et al.[32]

Purpose/Objectives/Hypotheses

Overall Purpose and Objectives

The overall purpose of this study is to experimentally quantify and geochemically model the role of carbonate dissolution and cation exchange in the release of Mn^{2+} from Mn-bearing calcite and dolomite under near-saturated conditions relevant to groundwater. Specific objectives for this study include:

(1) examining the extent of carbonate dissolution and the associated release of Mn^{2+} from synthetic Mn carbonates.

(2) examining the extent of cation exchange between Na^+ from Na-saturated clay and cations (Mn^{2+}, Ca^{2+}, and Mg^{2+}) released upon dissolution of synthetic Mn carbonates.

(3) geochemically modeling carbonate dissolution and solution chemistry evolution using PHREEQCI.

(4) geochemically modeling cation exchange using PHREEQCI.

Of note regarding laboratory experiments is that, because of laboratory closures associated with the rise of COVID-19, Mn carbonate dissolution and exchange experiments were only completed for synthetic Mn calcite. However, PHREEQCI modeling was still completed for Mn carbonates utilizing solid solutions of calcite/rhodochrosite and dolomite/rhodochrosite to represent Mn calcite and Mn dolomite, respectively.

Hypotheses

Hypothesis 1

Mn^{2+}, Ca^{2+}, and Mg^{2+} will be released during the dissolution of Mn-bearing carbonates. However, carbonate dissolution in groundwater aquifers will be limited by equilibrium saturation. In the presence of Na-rich clay, Ca^{2+} exchange will be preferred, followed by the exchange of Mg^{2+} and then Mn^{2+}, allowing carbonate dissolution to continue. The rationale for this hypothesis is that carbonate dissolution results in increased concentrations of Ca^{2+}, Mg^{2+}, and Mn^{2+}. If clays are present, these ions may exchange for monovalent and divalent cations present within the clays. This process should result in increased concentrations of these monovalent or divalent cations – monovalent Na^+ in this case – in solution and decreased concentrations of Ca^{2+}, Mg^{2+}, and Mn^{2+} as they are exchanged. Since Ca^{2+} is preferentially exchanged over Mg^{2+} and Mn^{2+}, decreased Ca^{2+} concentrations should be noted compared to the other 2 ions. Lower concentrations of these divalent cations will cause undersaturation of Mn-bearing carbonates, resulting in continued dissolution and creating a positive feedback loop between cation exchange and carbonate dissolution.

Hypothesis 2

Mn^{2+} ions will be released during carbonate dissolution and will be incorporated onto the surfaces of solid-phase reaction products, where the Mn^{2+} ions may then react with other ions in solution, potentially leading to oxidation of metal cations like Cr^{3+} to Cr^{6+}. The rationale for this hypothesis is that, as carbonates dissolve, ions will be released into solution, making them free to react with each other or other reactants present within the system. Based on a lack of substantial quantities of Mn within groundwater samples of the COA, Mn ions are most likely incorporated onto the surfaces of other minerals/rocks present within the aquifer or precipitated as $Mn^{3+/4+}$ oxides. These Mn ions/minerals are then potentially available to react with other ions in solution, possibly leading to oxidation of metal cations like Cr^{3+} to Cr^{6+}.

Manganese Calcite Experiments

Experimental Methodology

Synthesis and Characterization of Starting Materials

Manganese calcite was anaerobically synthesized using a method loosely adapted from Katsikopoulos et al.,[34] with an overall goal of producing ≈10 g of a solid containing ≈90% Ca and ≈10% Mn (i.e., $Ca_{0.9}Mn_{0.1}CO_3$). A 1 L solution of ultrapure water (UPW) containing 0.09 moles of calcium chloride ($CaCl_2 \cdot 2H_2O$) and 0.01 moles of manganese chloride ($MnCl_2 \cdot 4H_2O$) was prepared, placed on a magnetic stir plate, and stirred vigorously. While stirring vigorously, 0.1 L of a 1 M sodium carbonate (Na_2CO_3)

solution was added. After combining the 2 solutions, the bottle was capped, stirring velocity was reduced, and the mixture was gently stirred for approximately 5 days. The solution was then filtered using a 0.45-micron filter and the resulting precipitate dried at 60°C. Random mount powder XRD (Rigaku Ultima IV X-ray Diffractometer using CuKα radiation at 40 kV and 44mA with a 2-second count time, 0.02°/second step size, and 2θ range of 2-70°) was used to confirm the purity of the sample with pattern interpretation using Jade Pro (MDI, Inc.). Grain size and morphology were characterized via scanning electron microscopy (SEM) (JEOL 840 and Zeiss NEON EsB field-emission SEMs). SEM with Energy Dispersive X-ray Spectroscopy (EDS) analysis revealed submicron-sized particles on Mn calcite grains (see Experimental Results and Figure 7) along with minor amounts of Na (0.2-0.5 wt% in 14/15 locations and 3.2 wt% in 1/15 locations). In an effort to remove these particles and excess Na while avoiding surface reactions with water, the solid portion underwent additional processing via 2 cycles of ultrasonication in 100% ethanol (EtOH) for 15 minutes per cycle followed by 4 cycles of centrifugation in EtOH at 800 rpm for 10 minutes per cycle and decanting.

Experimental Setup

After verifying purity and characterizing grain size and morphology, the synthetic Mn calcite was used in dissolution and exchange reactions performed under various conditions, including acidic (initial pH≈6) or basic (initial pH≈8) pH, room (≈25°C) or high (≈60°C) temperature, and the presence or absence of clay (Table 1). For each sample, 200 mL of either 10 mM MES monohydrate (2-(N-morpholino)ethanesulfonic acid hydrate, pH range 5.5-6.7, pKa 6.1) or EPPS (4-(2-hydroxyethyl)-1-piperazinepropanesulfonic acid, pH range 7.3-8.7, pKa 8.0) buffer solution was added to a 250 mL bottle along with ≈0.5 g of Mn calcite (median 0.4984 ± 0.0017 g (0.33%)). Acidic solutions were adjusted to pH≈6 using 1 M nitric acid (HNO_3), while basic solutions were adjusted to pH≈8 using 1 M potassium hydroxide (KOH). Na bentonite clay was commercially obtained and further reacted by shaking in a 1 M NaCl solution for approximately 24 hours to ensure complete Na saturation. The clay/NaCl solution was centrifuged at 2500-3000 rpm until the supernatant was relatively clear, with the clear supernatant being discarded. UPW was then added to the clay precipitate, and the clay/water solution was shaken vigorously for 30 minutes, followed by centrifugation at 3000 rpm for 45 minutes and decanting of the supernatant. This rinsing process was repeated 3 times for a total of 4 cycles. After rinsing, approximately 0.1333 g of the Na saturated bentonite (calculated based on an amount 20 times the cation exchange capacity (CEC) for bentonite, assuming a CEC of 60 mEq/100 g for smectites in general) was added to the samples highlighted in Table 1, and samples were manually agitated to ensure mixing. Samples were then shaken vigorously on a countertop shaker table (≈25°C) or in an incubator (≈60°C) for the duration of the experiment. Samples were run in duplicate (e.g., MC1A and MC1B) for each set of conditions save for the addition of clay to samples MC4B and MC8B.

Table 1 – Sample Conditions for Mn Calcite Laboratory Experiments

Sample #	**Temp (°C)**	**Buffer (both at 10 mM)**	**Mn Calcite Initial Mass (g)**	**Na-Bentonite Initial Mass (g)**	**Original pH**
MC1A	25	MES	0.5000	0.0000	6.00
MC1B	25	MES	0.4990	0.0000	6.08
MC2A	25	MES	0.4984	0.1334	6.00
MC2B	25	MES	0.4979	0.1329	6.07
MC3A	60	MES	0.4985	0.0000	6.02
MC3B	60	MES	0.4985	0.0000	6.01
MC4A	60	MES	0.4967	0.1330	6.02
MC4B	60	MES	0.4969	0.0000	6.01
MC5A	25	EPPS	0.4985	0.0000	7.96
MC5B	25	EPPS	0.4973	0.0000	7.97
MC6A	25	EPPS	0.4993	0.1321	7.93
MC6B	25	EPPS	0.4981	0.1327	7.98
MC7A	60	EPPS	0.4986	0.0000	8.00
MC7B	60	EPPS	0.4981	0.0000	8.10
MC8A	60	EPPS	0.4974	0.1331	7.97
MC8B	60	EPPS	0.4981	0.0000	8.04

**Shaded rows indicate samples containing Na bentonite.*

Aqueous Sampling and Analysis

Aqueous sampling and pH measurements were conducted for each sample on days 1, 3, 5, 7, and 14. For cations, 5 mL of fluid was withdrawn, filtered with a 0.2-μm syringe filter to remove clays and carbonates and stop the reaction, and diluted to 15 mL with 0.1 M HNO_3. For alkalinity, an additional 5 mL of fluid was withdrawn, filtered with a 0.2-μm syringe filter, and diluted to 20 mL with UPW. Samples were then sent to the Oklahoma State University Soil, Water, and Forage Analytical Laboratory (Stillwater, OK) for measurement of cations (Ca, Na, Mn, Fe, Mg, and K) via ICP-OES (Spectro ARCOS II, Spectro Analytical Instruments, Inc., Germany) as well as assessment of total alkalinity.

Solid Phase Sampling and Analysis

After aqueous sampling was completed on Day 14, samples with no clay were filtered onto a 0.22-μm filter. Each bottle was rinsed with UPW that was also filtered, and then samples were dried at 60°C and stored in airtight vials to prevent oxidation. Samples containing clay were centrifuged at 800 rpm for 10 minutes. The clay fraction was decanted, filtered onto a 0.22-μm filter, dried at 60°C, and preserved for possible future analysis. The residual reacted carbonate was then resuspended with UPW and filtered, dried, and stored in the same manner as the samples with no clay. Carbonate grains of select samples were examined by SEM (JEOL 840 and Zeiss NEON EsB field-emission) to characterize post-reaction grain sizes and morphologies.

Experimental Results

Results of XRD and SEM Characterization of Starting Materials

XRD results (Figure 5) of the synthesized Mn calcite showed the highest peak intensities (in decreasing order of intensity) occurring at d-spacings (2θ degrees) of 3.0216 Å (29.539°), 2.2782 Å (39.524°), 1.8667 Å (48.742°), 2.0888 Å (43.280°), 1.8997 Å (47.842°), 2.4900 Å (36.041°), and 3.8470 Å (23.101°). Pure calcite reference peaks coinciding with the above peaks occur at approximately 3.036 Å, 2.285 Å, 1.875 Å, 2.095 Å, 1.913 Å, 2.495 Å, and 3.855 Å, as indicated by the solid black lines in Figure 5.[35,36] No other database matches were found for the observed peaks, including other forms of calcite (e.g., vaterite) or Mn oxides. Of note was the slight shift of peaks for the Mn calcite samples to the right toward lower d-spacing (higher 2θ) values, which was consistent with Mn-containing calcite.[35,37] Based on these results, the synthesized sample was deemed pure Mn calcite and suitable for proposed experimental reactions.

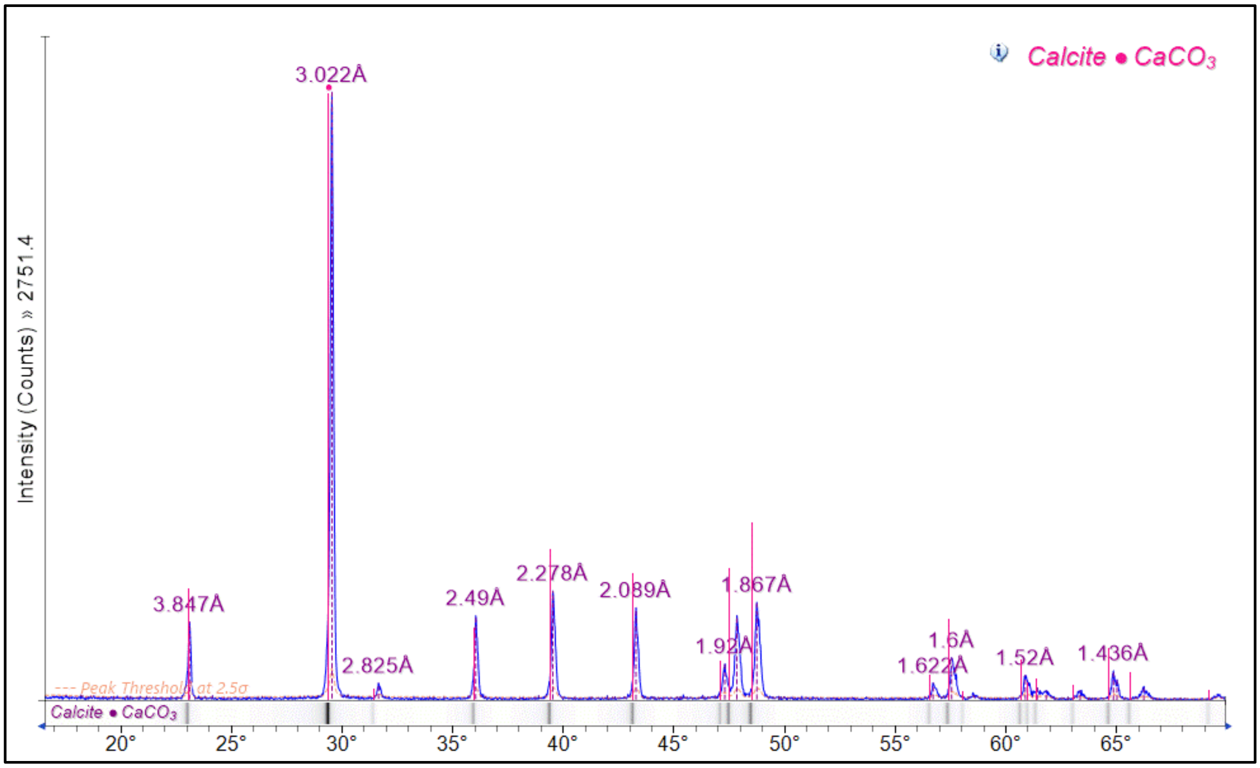


Figure 5 – XRD pattern of synthetic, unreacted Mn calcite. Blue tracing is the synthetic Mn calcite sample pattern, while vertical black bars indicate peaks for pure (no Mn) calcite. Note the slight shift right to higher angles (2θ) and lower d-spacing values for Mn calcite compared to pure calcite, similar to those observed in Zhang et al.[37]

SEM characterization revealed grain sizes that were all <50 μm in diameter, with nearly all grains having diameters <20 μm (Figure 6). Figure 7 contains representative images of unreacted Mn calcite grains at higher magnifications. Unreacted grains appeared as intergrowths of equant subgrains growing in a step-like fashion with smooth, continuous faces and sharp, continuous boundaries. Mn calcite grains also had distinct, submicron-sized particles on their surfaces that were believed to be remnant NaCl synthesis products based on the presence of small amounts of Na in all EDS spectra (below). These particles were the reason for additional rinsing with EtOH before further use in experiments.

EDS spectra were obtained at 15 different locations on grains in a field of view approximately 175 µm by 235 µm. Elements present in all spectra included O, Ca, C, Mn, and Na. Cl was present in only 1 spectrum coincident with a wt% of Na that was significantly higher than at other locations (3.2 wt% versus an average 0.33 wt% for the other 14 locations); weight percentages of other elements at this location were deemed similar to those elsewhere. Iridium (Ir) was also present at all locations, but this was expected since it was used to coat all samples for SEM viewing. Average wt% values for the 4 elements common to Mn calcite are provided in Table 2. Spectra confirmed the presence of Mn in calcite grains at an average of 7% ($(Ca_{0.93}Mn_{0.07})CO_3$). This amount was slightly less than the intended experimental goal of 10%. However, it was still deemed sufficient for experimental purposes considering Mn exists at a concentration of only about 1% ($(Ca_{0.99}Mn_{0.01})CO_3$) within the COA.

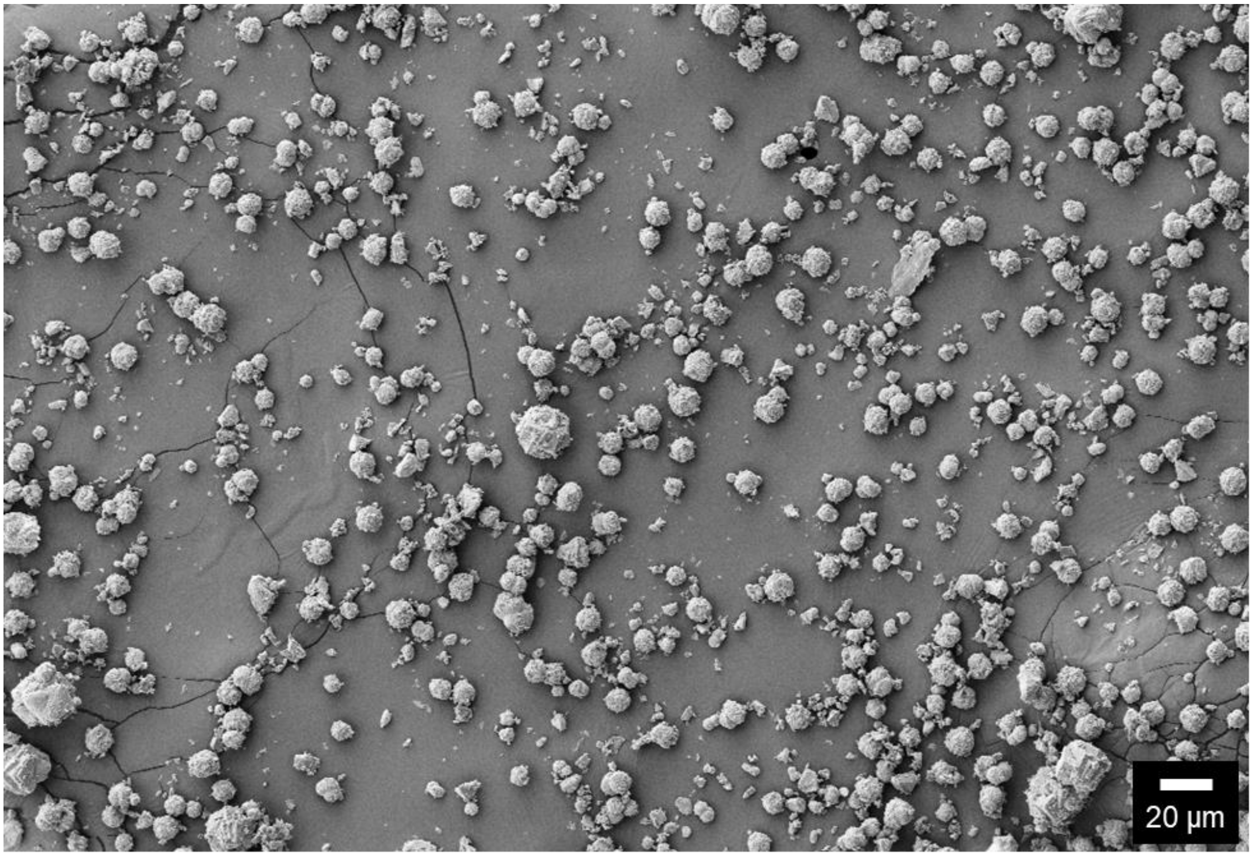


Figure 6 - SEM image of synthetic Mn calcite grains at 250x. Note that nearly all grains had diameters of <20 µm.

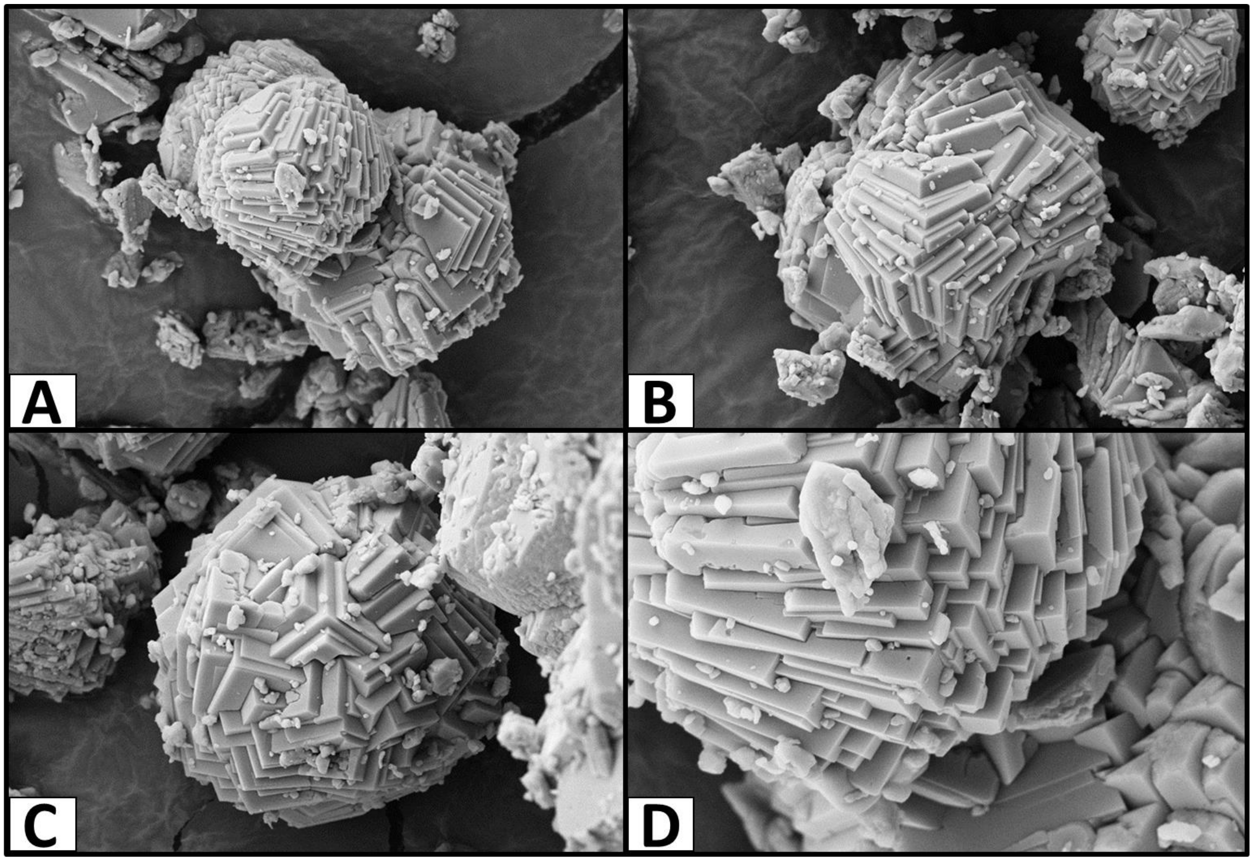


Figure 7 - SEM images of synthesized Mn calcite. A (top left) is at 5000x, B (top right) is at 6000x, C (bottom left) is at 7000x, and D (bottom right; enlarged view of A) is at 15000x.

Table 2 - Average values obtained for 15 EDS spectra during SEM analysis of synthesized Mn calcite

Element	Average Wt%	Wt% Range	Average # Moles
O	53.4	44.0 - 59.7	3.34
Ca	25.3	19.0 - 39.2	0.63
C	16.5	11.3 - 20.5	1.37
Mn	3.9	2.1 - 6.4	0.07

pH, Alkalinity, and Aqueous Chemistry of Reaction Solutions

Full ICP-OES results are reported in Appendix 1. Note that several parameters were reported as “less than” a given value. For analytical purposes, the “less than” value was assumed to be the actual value for the given parameter – e.g., if a value was reported as “<0.5,” then 0.5 was the value used in subsequent analyses. At the time of testing, Fe, Mg, and K were also included to serve as a baseline for anticipated, but never completed, experiments. Those results have been included in Appendix 1 for completion purposes but are not reported or discussed elsewhere.

pH

Benchtop pH values measured in the lab at the time of sample collection (versus at the time of ICP analysis by the lab at OSU) are displayed in Figure 8. The average benchtop pH of acidic samples increased from pH 6.03 (range 6.00-6.07) on Day 0 to pH 7.07 (range 6.93-7.21) by Day 14, or an average ΔpH of (+)1.04 units (range 0.85-1.15). pH increased continuously, though at varying rates, over the entire 14-day period for all samples. The steepest increases occurred from Day 0 to Day 1, and overall rates were higher for Days 0 to 7 compared to Days 7 to 14, with noticeable inflection points at Day 7 for most samples. Samples MC1A and MC1B (room temperature, no clay) had the lowest overall ΔpH and final pH. The 3 clay samples had 3 of the 4 highest final pH values as well as a slightly higher overall ΔpH compared to the 5 samples without clay (ΔpH = (+)1.09 versus (+)1.01). No other associations between temperature and/or the presence or absence of clay were noted.

For basic samples, average pH values exhibited a negligible overall change, decreasing from pH 7.99 (range 7.93-8.10) on Day 0 to pH 7.97 (range 7.88-8.03) on Day 14, or an average ΔpH = (-)0.02 units (range (-)0.07 to (+)0.04). All basic pH values were within ±0.12 units of the target pH of 8.00 for the entire duration of the experiments. Slight increases to Day 5 were noted in 3 of 4 room-temperature samples, including both clay samples, before all 4 room-temperature samples slowly decreased to Day 14. All 4 high-temperature samples showed a slight decrease in pH from Day 1 to Day 3 before increasing again by Day 5 and then remaining steady or slightly decreasing to Day 14. No other distinct similarities or differences were observed for temperature and/or the inclusion or exclusion of clay.

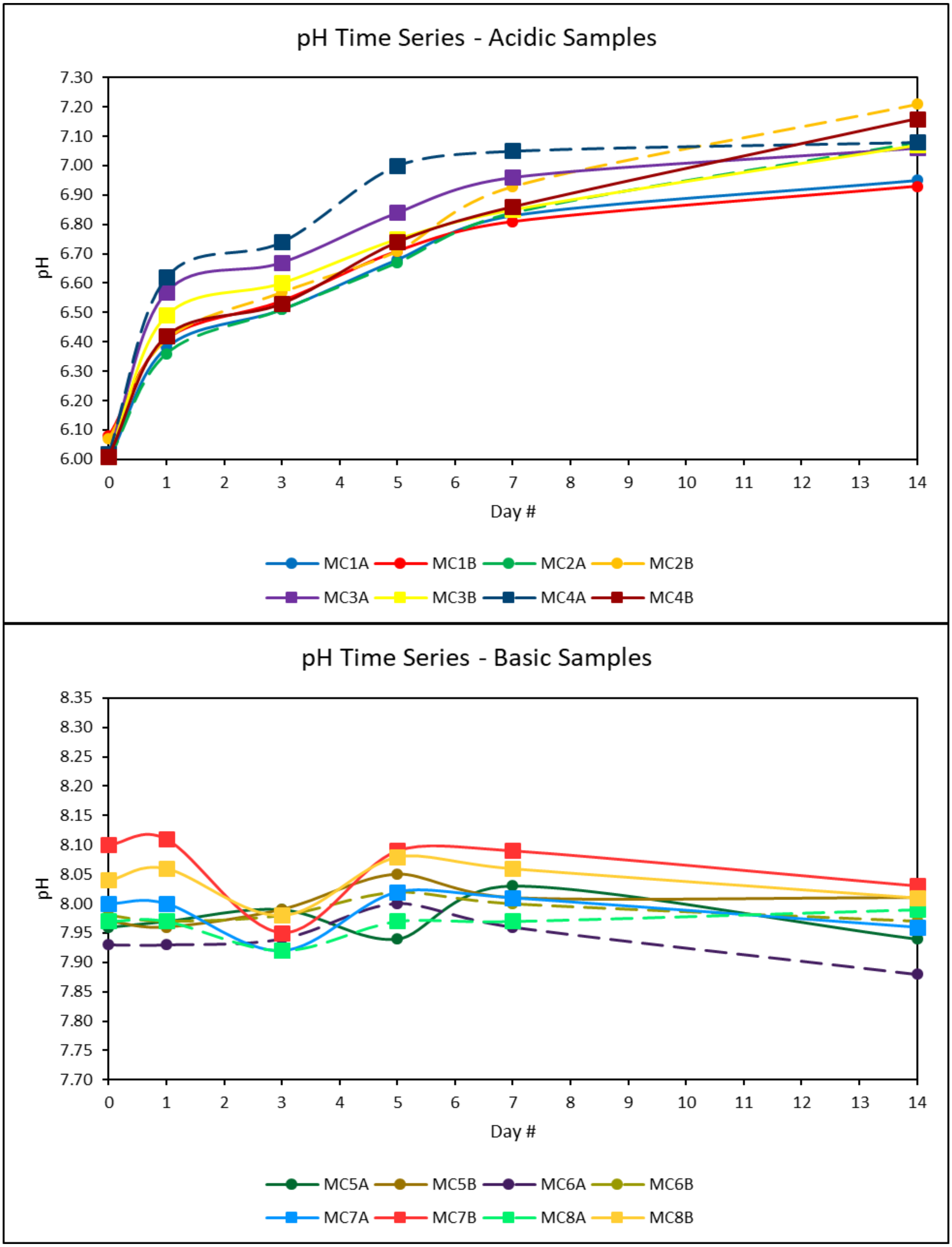


Figure 8 - pH time series. Solid lines represent samples without clay, and dashed lines represent samples containing clay. Round markers represent samples at 25°C, while square markers represent samples at 60°C.

Alkalinity

Alkalinity values are displayed graphically in Figure 9. Except for 1 basic sample on Day 5, acidic samples had higher alkalinities than basic samples on all sampling days. For acidic samples, those at room temperature had higher values than those at high temperature. Acidic samples tended to follow a general trend of decreasing until Day 5 then increasing to Day 7. All 4 room-temperature samples and the high-temperature sample with clay then remained steady or decreased to Day 14, while the 3 high-temperature samples without clay increased. The average Day 1 and Day 14 concentrations for the room-temperature samples were 516.79 mg $CaCO_3$/L (range 502.52-525.68) and 507.23 mg $CaCO_3$/L (range 494.48-516.08), respectively, while those for high-temperature samples were 472.24 mg $CaCO_3$/L (range 461.16-483.80) and 475.07 mg $CaCO_3$/L (range 467.44-484.12), respectively. Room-temperature samples showed an overall decrease in alkalinity of (-)9.56 mg $CaCO_3$/L, with clay samples decreasing less than samples without clay. High-temperature samples exhibited a slight overall increase of (+)2.83 mg $CaCO_3$/L, with values for samples without clay increasing while the value for the single sample with clay decreased. The high-temperature clay sample had higher alkalinity values until approximately Day 11.5 and showed less overall variation throughout the study compared to the other high-temperature samples. Otherwise, no significant differences were noted between samples with and without clay.

Alkalinity trends in basic samples were more variable than trends in acidic samples. Most samples tended to decrease to Day 3, remain steady or increase to Day 5, and increase from Day 7 to Day 14. Other than sample 8A (high temperature with clay) on Day 5, concentrations were relatively similar throughout the study, with no real differences noted between samples based on temperature or the presence or absence of clay. Room-temperature samples had an average alkalinity of 402.62 mg $CaCO_3$/L (range 388.84-415.52) on Day 1 and 407.54 mg $CaCO_3$/L (range 389.48-416.68) on Day 14, or an average change of (+)4.92 mg $CaCO_3$/L, with clay-containing samples increasing more than samples without clay. Average alkalinities for high-temperature samples were 398.35 mg $CaCO_3$/L (range 382.88-408.12) on Day 1 and 395.68 mg $CaCO_3$/L (range 386.32-402.04) on Day 14, or an average change of (-)2.67, with the value for the clay-containing sample increasing. In contrast, the values for the samples without clay decreased. Other than the small difference in change from Day 1 to Day 14, no other significant differences were noted between samples based on temperature. For the 3 clay-containing samples, 2 (1 room temperature, 1 high temperature) had the lowest alkalinities on all but Day 5 of the study. However, differences between the 2 clay samples and the lowest sample without clay were generally small (<20 mg $CaCO_3$/L on Day 1, <10 mg $CaCO_3$/L on other days). Of note for both the acidic and basic samples was that many of the averages were skewed by a single reading; overall changes were still relatively small, with 15 of 16 samples having overall alkalinity changes of less than ±20 mg $CaCO_3$/L.

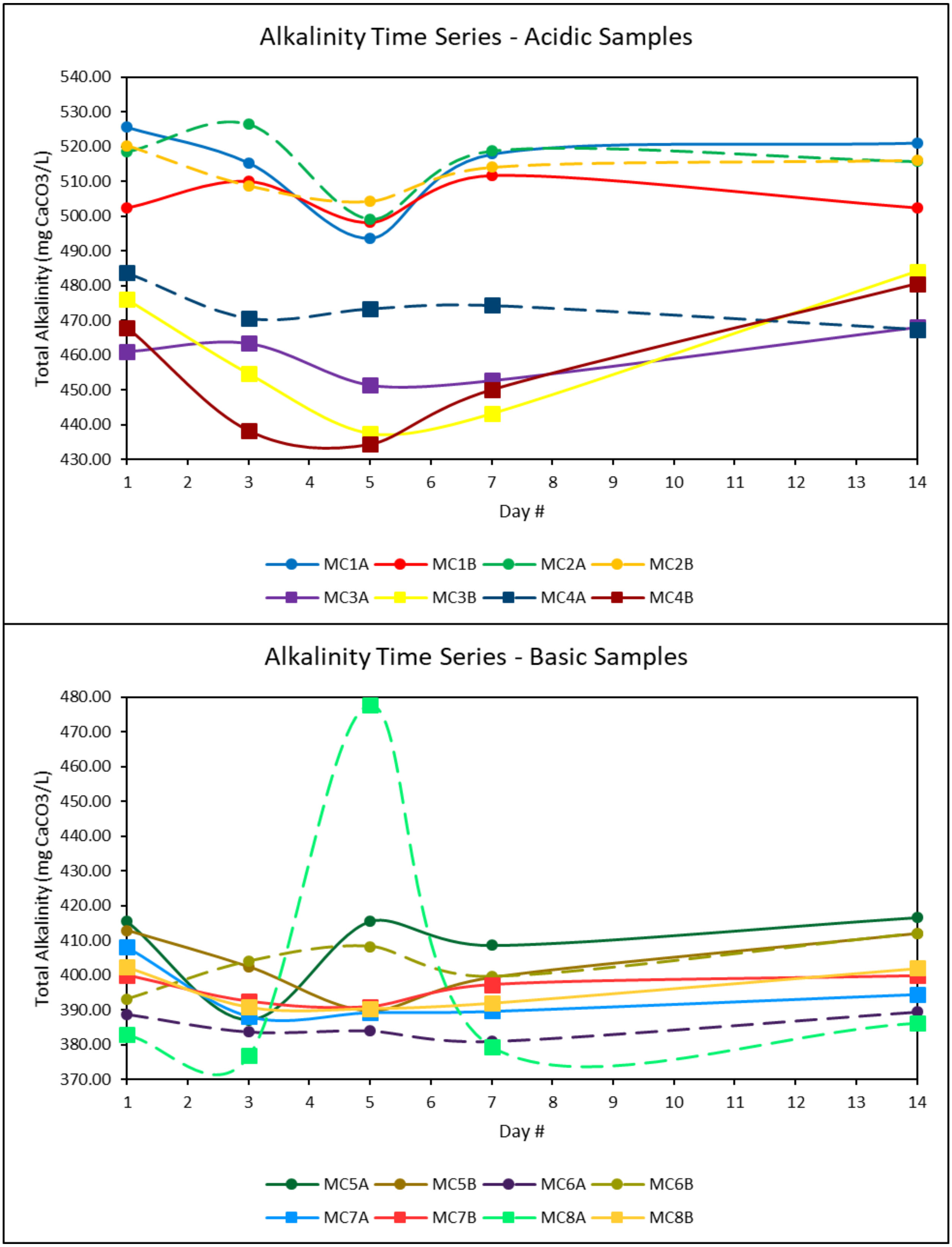


Figure 9 - Alkalinity time series. Solid lines represent samples without clay, and dashed lines represent samples containing clay. Round markers represent samples at 25°C, while square markers represent samples at 60°C.

Calcium

Calcium concentrations are shown in Figure 10. Overall, acidic samples exhibited calcium concentrations that were approximately an order of magnitude greater than basic samples for the entire 14-day period. The average Day 1 concentration for acidic samples was 13.832 mmol/L (range 12.192-15.001 mmol/L). All 8 samples showed increases to peak concentrations at Day 5, decreases to Day 7, then remained steady or increased to Day 14, though final concentrations were lower than on Day 1 (Day 14 average 13.070 mmol/L, range 11.306-15.012 mmol/L; average ΔCa = (-)0.762 mmol/L for Day 1 to Day 14). While all samples showed the same overall trends, room-temperature samples typically had lower overall Ca concentrations throughout the study than high-temperature samples as well as greater overall decreases from Day 1 to Day 14 (ΔCa = (-)1.058 mmol/L versus ΔCa = (-)0.466 mmol/L for high temperature). The 3 samples with clay had 3 of the 4 lowest Ca levels at multiple points during the study, including Days 1 and 14. Additionally, the 3 samples showed an average decrease from Day 1 to Day 14 of more than double that of the 5 samples with no clay (clay ΔCa = (-)1.156 mmol/L; no clay ΔCa = (-)0.526 mmol/L). The 2 room-temperature clay samples decreased more than any of the other samples, and the 1 high-temperature clay sample decreased more than the 3 high-temperature samples without clay. The high-temperature clay sample had a lower Ca concentration than the 3 high-temperature samples without clay at all points, while the 2 room-temperature clay samples were similar to the 2 room-temperature samples without clay.

Basic samples showed a lower overall range than acidic samples, exhibiting a difference of <1 mmol/L between the lowest and highest values over the 14-day study period. For basic samples, trends were more challenging to discern, particularly before Day 7, and did not appear distinct for any particular variable. Increases were seen in 3 of 8 samples to Day 3 followed by decreases to Day 7; 4 of 8 decreased to Day 3, increased to Day 5, then decreased to Day 7; and the remaining sample decreased continuously to Day 7. After Day 7, all 8 samples remained relatively stable, typically changing by <0.100 mmol/L. However, all 8 samples showed decreased overall Ca concentrations, decreasing from an average of 1.371 mmol/L (range 1.017-1.762 mmol/L) on Day 1 to an average of 1.044 mmol/L (range 0.786-1.251 mmol/L) on Day 14, or an average ΔCa = (-)0.328 mmol/L. Room-temperature samples had higher overall concentrations at all points after approximately 4.5 days, while high-temperature samples showed a slightly greater average change from Day 1 to Day 14 (ΔCa = (-)0.335 mmol/L versus ΔCa = (-)0.320 mmol/L for room-temperature samples). Over the 14 days, the 3 samples with clay decreased more than the 5 samples without (average ΔCa = (-)0.445 mmol/L versus (-)0.257 mmol/L). The 2 room-temperature clay samples had lower Ca concentrations than the 2 room-temperature samples without clay at all points after approximately 2.5 days. Before Day 5, the high-temperature clay sample had a higher Ca concentration than the 3 samples without, after which its concentrations fell between the highest and lowest values.

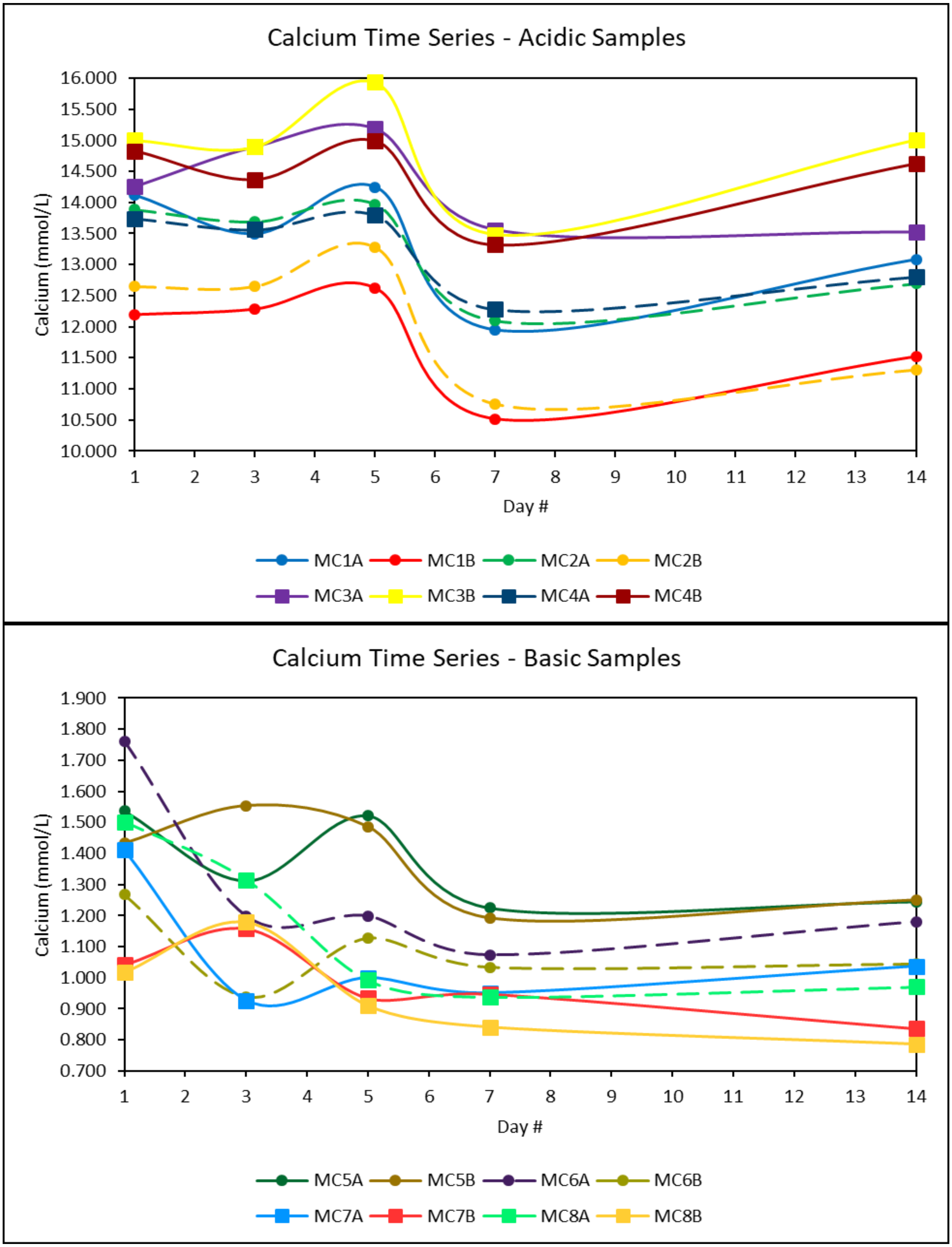


Figure 10 - Calcium time series. Solid lines represent samples without clay, and dashed lines represent samples containing clay. Round markers represent samples at 25°C, while square markers represent samples at 60°C.

Sodium

Sodium concentration trends are displayed in Figure 11. Concentrations in all acidic samples were at least 2-4 times higher than all basic samples at all points during the study. Save for Day 1, all acidic samples followed the same general trend of slight changes to Day 3, increasing to Day 5, decreasing to Day 7, then increasing afterward. Two samples without clay (1 room temperature, 1 high temperature) showed markedly elevated concentrations on Day 1 relative to other samples without clay. However, the 2 sample concentrations decreased rapidly by Day 3 to within the same range as the other samples without clay. Other than these 2 samples on Day 1, samples containing clay all had higher Na values than samples without clay for the duration of the experiment. The average Day 1 concentration for samples with clay was 1.090 mmol/L (range 1.062-1.109), while that for samples without clay (excluding the 2 abnormally elevated samples) was 0.827 mmol/L (range 0.822-0.830). All samples showed an average decrease overall from Day 1 to Day 14, with Day 14 concentrations for samples with clay averaging 0.956 mmol/L (range 0.926-0.981; ΔNa = (-)0.134) and samples without clay (all 5 samples included) averaging 0.766 mmol/L (range 0.731-0.818; ΔNa = (-)0.061). No apparent distinction between room-temperature and high-temperature samples, either including or excluding the presence of clay, was noted.

Basic samples showed somewhat less predictable trends than acidic samples. Room-temperature samples remained stable or decreased to Day 3, increased to Day 5, then decreased to Day 7. Samples with clay then increased through Day 14, while samples without clay continued decreasing. High-temperature samples tended to rapidly increase to Day 3, rapidly decrease to Day 5, then decrease at a much lower rate through Day 14. Except for Day 3, there were no notable differences between samples from the 2 temperature regimes. As with acidic samples, Na concentrations in basic samples with clay were all noticeably higher than in samples without clay. The average Day 1 concentration for samples with clay was 0.292 mmol/L (range 0.246-0.327), while that for samples without clay was 0.012 mmol/L (range <0.012-0.013). Day 14 concentrations averaged 0.186 mmol/L (range 0.165-0.207) for samples with clay versus 0.010 mmol/L (range 0.006-0.017) for samples without clay, and all samples showed an overall decrease in Na concentrations for the study period (ΔNa = (-)0.106 and (-)0.002 for samples with and without clay, respectively). A large number of concentrations for samples without clay were reported as “less than” (60% of room temperature and 80% of high temperature), with the largest of these “less than” concentrations being <0.027 mmol/L, so average concentrations and ΔNa could be even lower for these samples. Except for Day 3, there did not appear to be a difference between the room-temperature and high-temperature samples with clay.

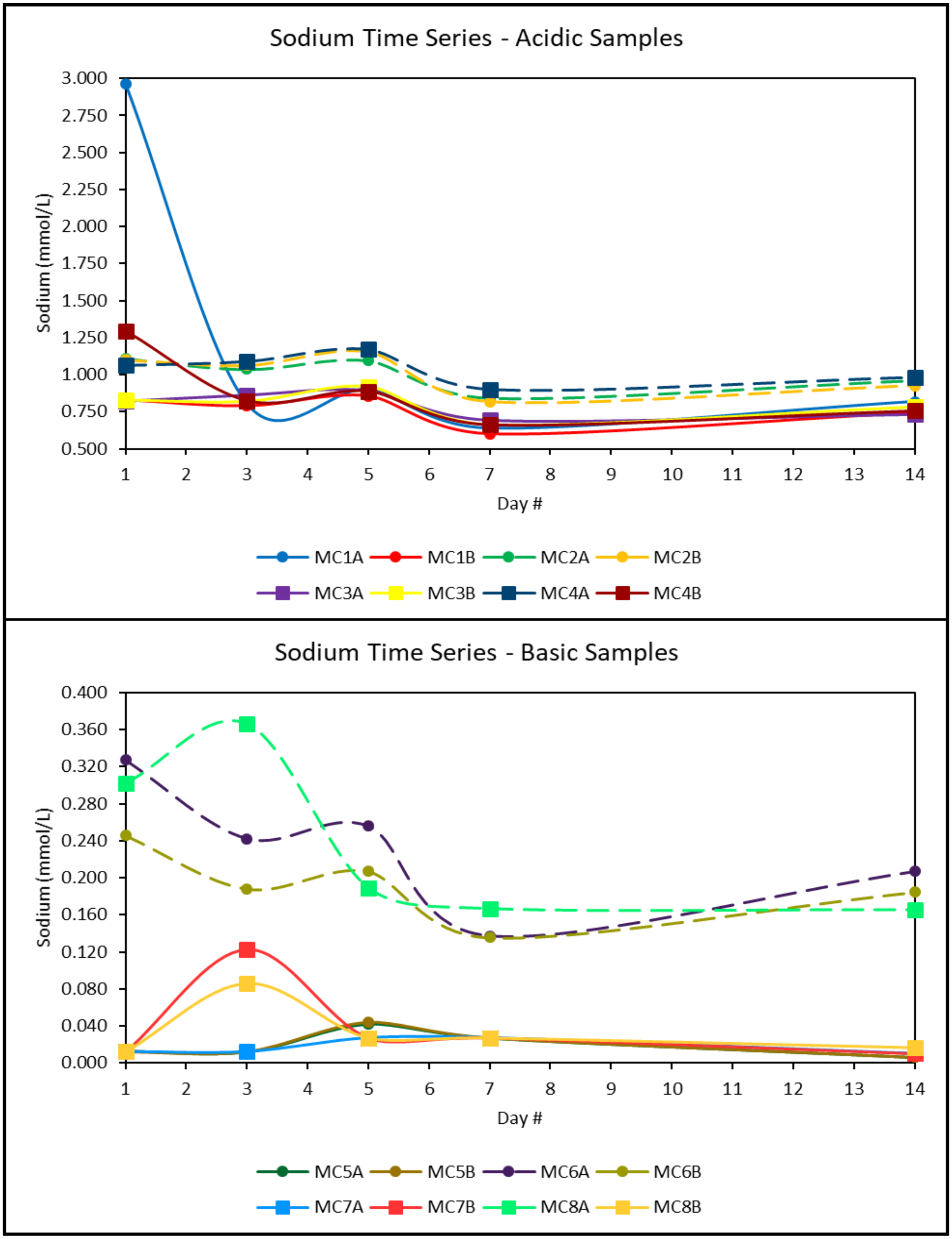


Figure 11 - Sodium time series. Solid lines represent samples without clay, and dashed lines represent samples containing clay. Round markers represent samples at 25°C, while square markers represent samples at 60°C.

Manganese

Concerning Mn (Figure 12), acidic samples had concentrations that were typically at least an order of magnitude greater than basic samples. Similar trends were seen in 6 of 8 samples, with steady or slightly increasing concentrations to Day 5, decreasing concentrations to Day 7, and then concentrations that remained steady or slightly increased to Day 14, including all 4 room-temperature samples and the high-temperature sample with clay. Samples 3B and 4B (high temperature, no clay) both showed dramatic drops over the 14 days relative to the other acidic samples, with a ΔMn = (-)0.932 mmol/L (3B) and (-)1.237 mmol/L (4B) compared to an average ΔMn = (-)0.128 for the other 6 samples. The average Day 1 concentration for all 8 samples was 1.545 mmol/L (range 1.404-1.685), while the average Day 14 concentration for the 6 typical samples was 1.382 mmol/L (range 1.269-1.490). Other than the 2 high-temperature samples previously mentioned, there appeared to be no other association between temperature and Mn concentrations. Regarding clay, the only noticeable difference appeared to be that the 3 samples with clay had an average Day 1 to Day 14 decrease approximately double that of the 3 samples (excluding 3B and 4B) without clay, with the clay samples having an average ΔMn = (-)0.173 compared to (-)0.084 for the samples without clay.

For the basic samples, 3 of the 4 high-temperature samples were reported as having <0.000, <0.006, or <0.009 parts per million (ppm) Mn, which translates to concentrations of 0.000, <0.109, or <0.164 μmol/L. These concentrations were more than 300 times lower than the lowest concentration in any room-temperature sample at any point during the 14-day timeframe. The fourth high-temperature (and clay-containing) sample had higher concentrations reported for Days 1 and 3, but these concentrations were 10-12 times less than the lowest room-temperature concentration reported on the same day; from Day 5 onward, values for this sample were also reported as being <0.164 µmol/L. Room-temperature basic samples showed an overall decrease in Mn concentration from an average of 123 µmol/L (range 110-129) on Day 1 to an average of 67 µmol/L (range 53-87) on Day 14, or an average ΔMn = (-)56 µmol/L. There were 2 room-temperature samples (1 with clay, 1 without) that showed decreases to Day 3, slight (≈5 µmol/L) increases to Day 5, then decreases through Day 14. The other 2 samples decreased continuously to Day 7, after which 1 sample (with clay) remained steady while the other (no clay) continued decreasing. The only difference noted between room-temperature samples with and without clay was that the 2 samples with clay decreased less on average over the 14 days than the 2 samples without clay (clay ΔMn = (-)45 µmol/L; no clay ΔMn = (-)68 µmol/L).

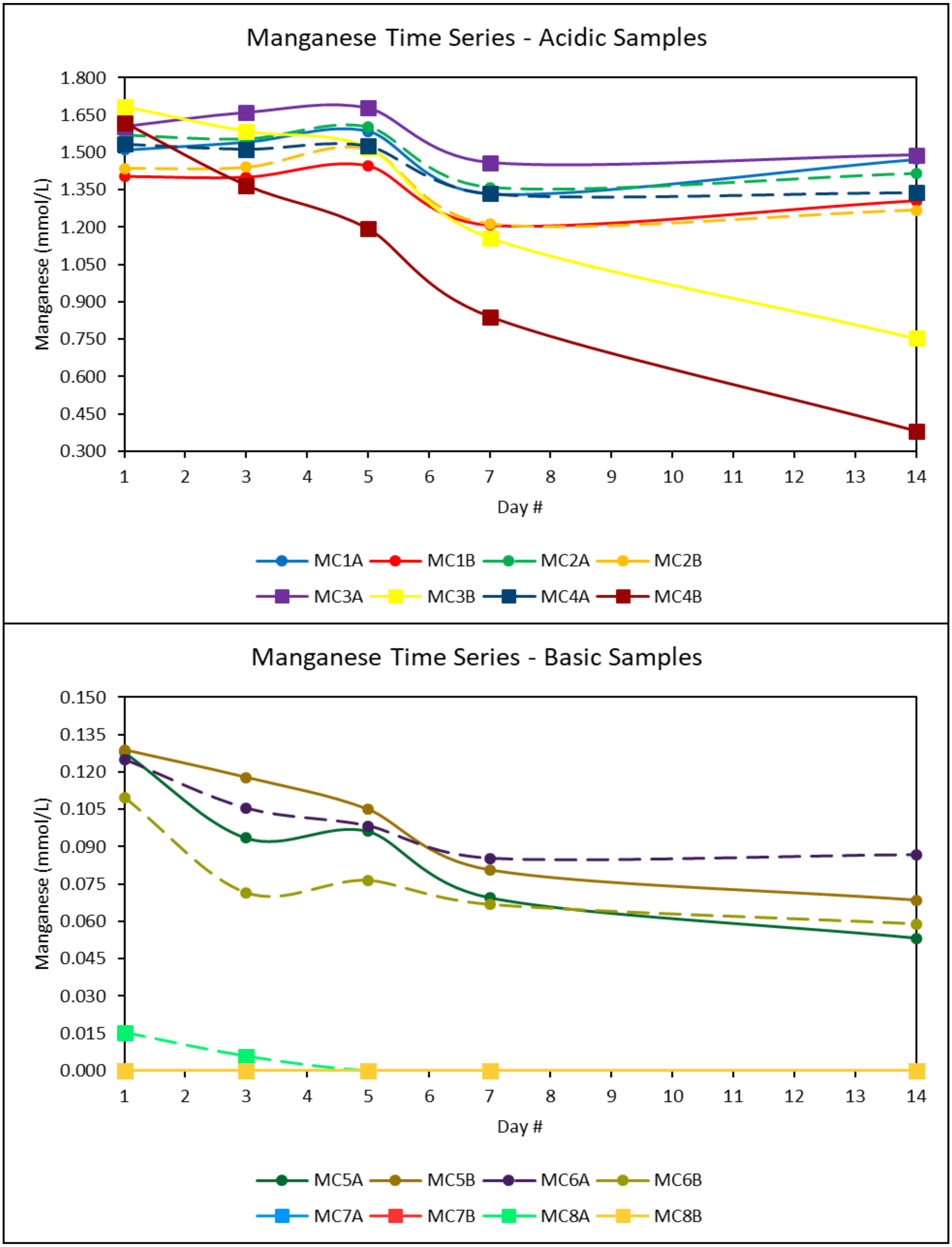
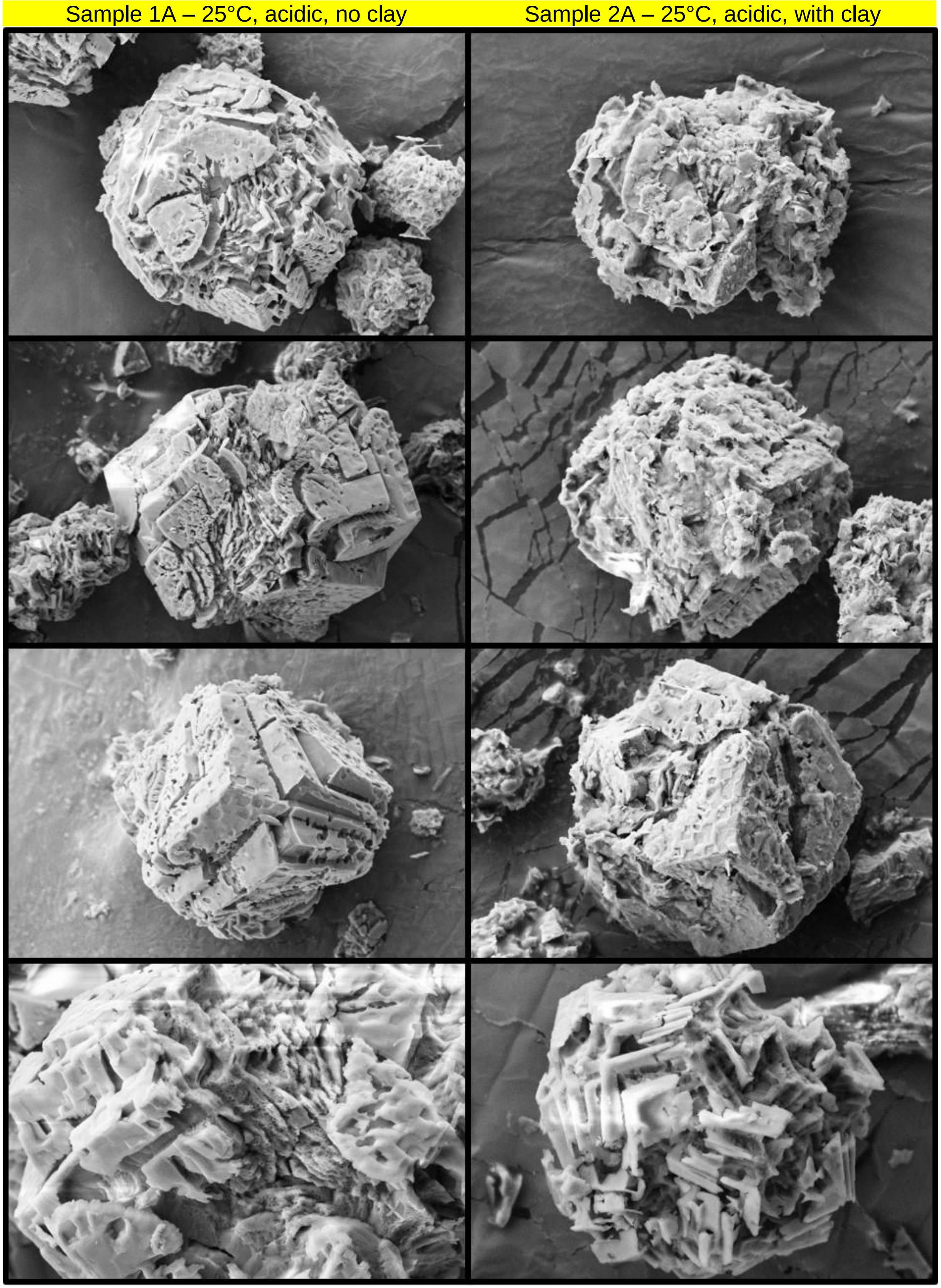


Figure 12 - Manganese time series. Solid lines represent samples without clay, and dashed lines represent samples containing clay. Round markers represent samples at 25°C, while square markers represent samples at 60°C.

SEM Characterization of Final Solid Products

Solid-phase reaction products of 8 samples (one of each pair of samples 1-8) were examined via SEM at the end of the 14-day experiments, with comparison images shown in Figure 13 through Figure 16. Compared to unreacted Mn calcite grains, reacted grains exhibited significantly more dissolution characteristics, including etch pits of various sizes and depths on crystal faces as well as crevices and cracks at crystal interfaces. There was significant erosion of crystal margins, resulting in more rounded edges and discontinuous, indistinct boundaries between crystals compared to the sharp, distinct margins and boundaries seen in unreacted grains. Reacted grains, particularly those of basic samples, also showed secondary precipitation, whereas unreacted grains did not.

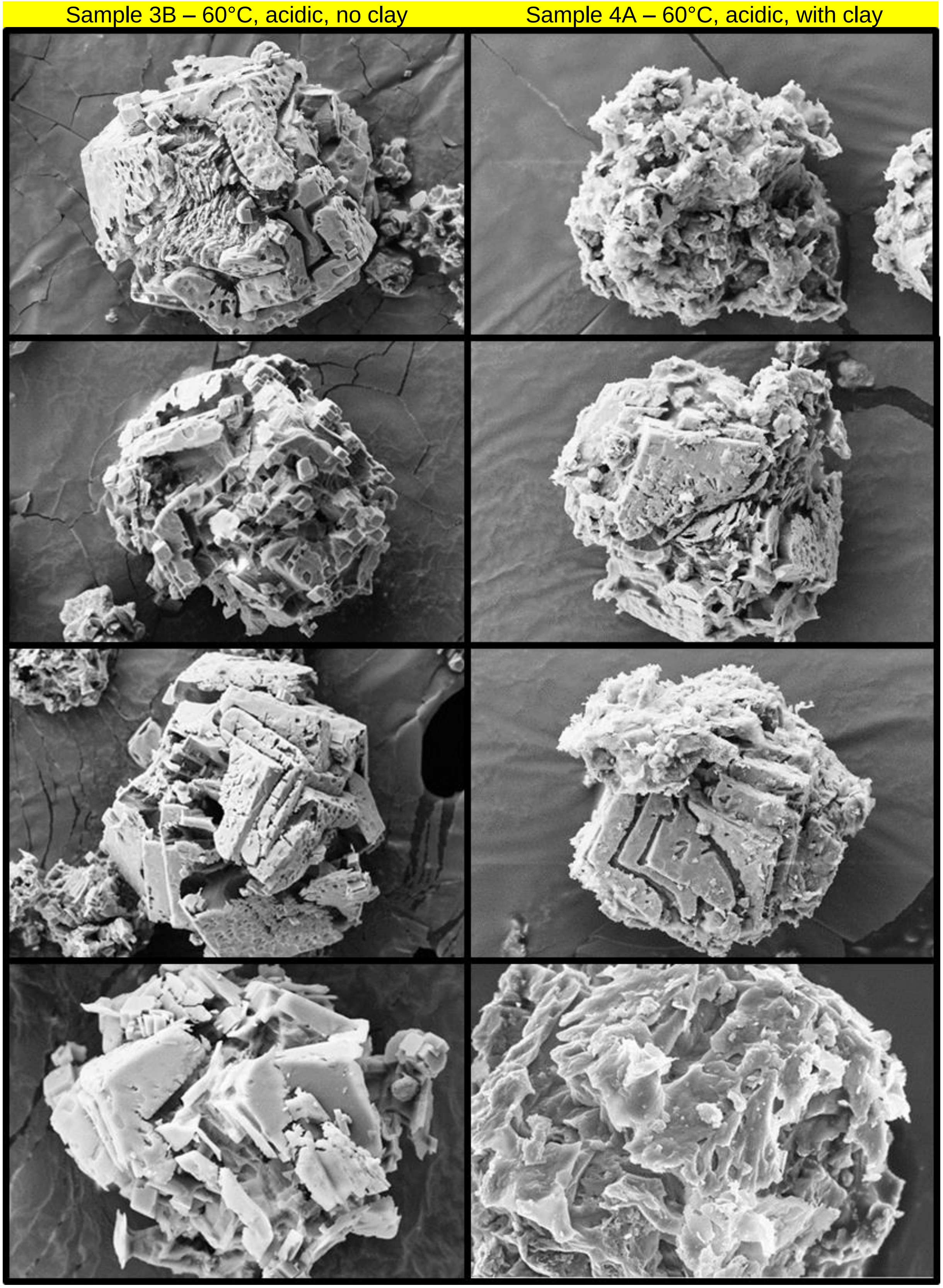
Comparison of grain characteristics among reacted samples was somewhat less evident compared to unreacted grains, thus confidence levels have been provided for each observation. Overall, acidic samples appeared to show significantly greater dissolution features than basic samples (high confidence). High-temperature samples appeared to exhibit more significant precipitation (high confidence) and dissolution (particularly acidic samples; low confidence) compared to the corresponding (acidic or basic) room-temperature samples. Regarding clay, precipitation appeared to be more significant in samples without clay than in samples with clay (high confidence). Conversely, dissolution in clay-containing samples appeared to be greater than in samples with no clay (low confidence). Carbonate precipitation was noted in both acidic and basic samples and, as previously mentioned, appeared to be greater in samples without clay. Larger rhombs were found on Mn calcite grain surfaces in acidic samples, such as in Sample 3B (acidic, high temperature, no clay; Figure 14, left), while (generally) much smaller rhombs and other shapes were found on the surfaces of Mn calcite grains in basic samples (e.g., Samples 5A and 7A – basic, low and high temperature, no clay; Figure 15, left, and Figure 16, left). In addition to rhombs and other shapes, acicular structures were also noted, with small amounts occurring in Sample 1A and more significant amounts in Sample 7A (Figure 17 shows 2 SEM images of Sample 7A, but features were noted in all images obtained of Sample 7A). For this sample (7A), EDS spectra were obtained at 6 different locations on a cluster of these needle-like structures. Results indicated the presence of Mn (average 30.8 wt%; range 21.7-41.7), C (average 19.5 wt%; range 14.3-26.7), O (average 30.0 wt%; range 21.6-42.9), and Ca (average 19.8 wt%; range 11.3-34.7), with no other elements indicated, confirming that these features were some variant of Mn-containing carbonate (likely Mn calcite or rhodochrosite). Confidence in the definitive presence of other similarities or differences between samples was too low to include herein.



Sample 1A – 25°C, acidic, no clay

Sample 2A – 25°C, acidic, with clay

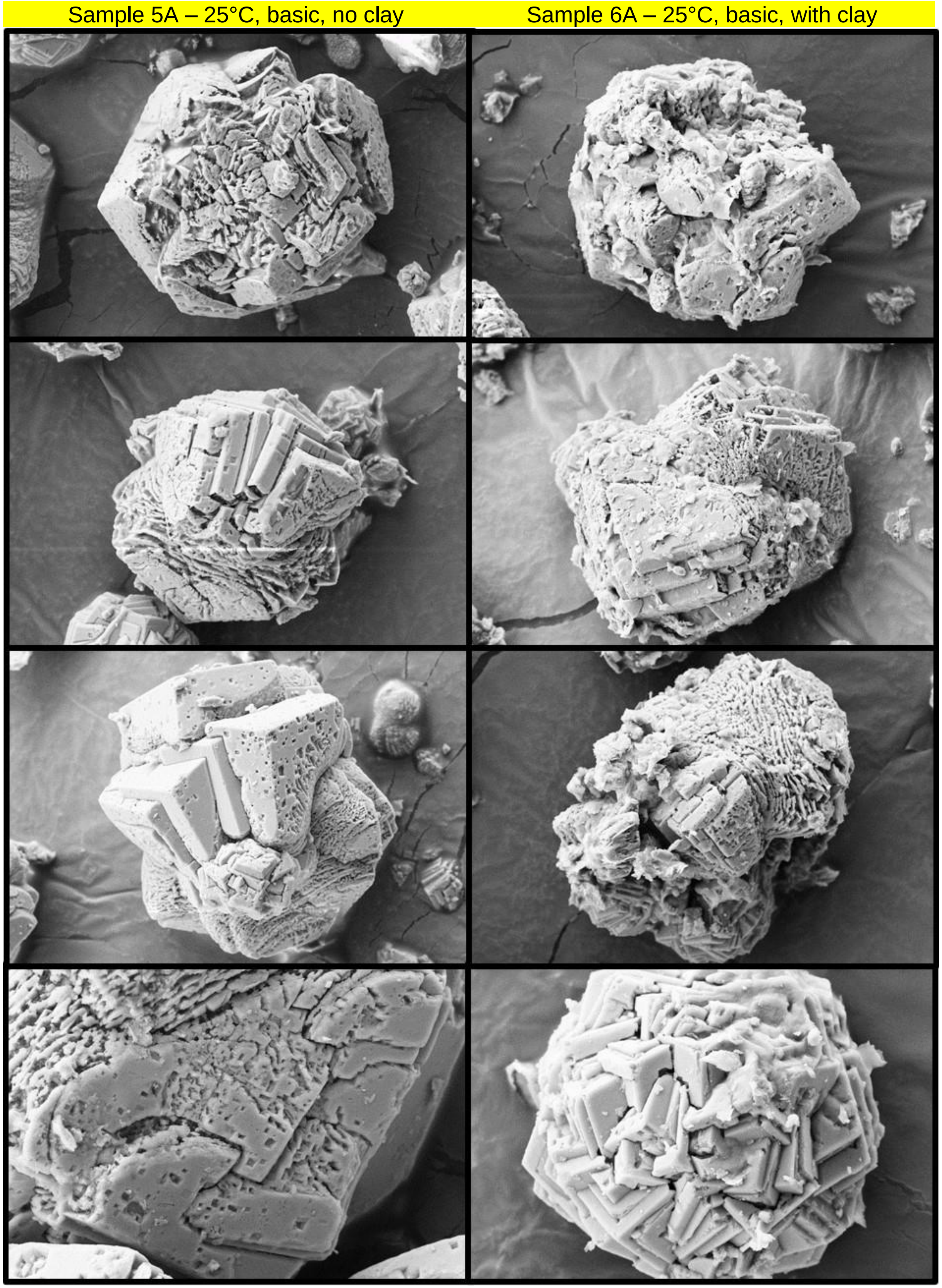
Figure 13 - SEM images of final experimental products for Samples 1A and 2A. The top 3 images on each side are at 3,500X magnification, while the bottom image on each side is at 8,500X magnification.



Sample 3B – 60°C, acidic, no clay

Sample 4A – 60°C, acidic, with clay

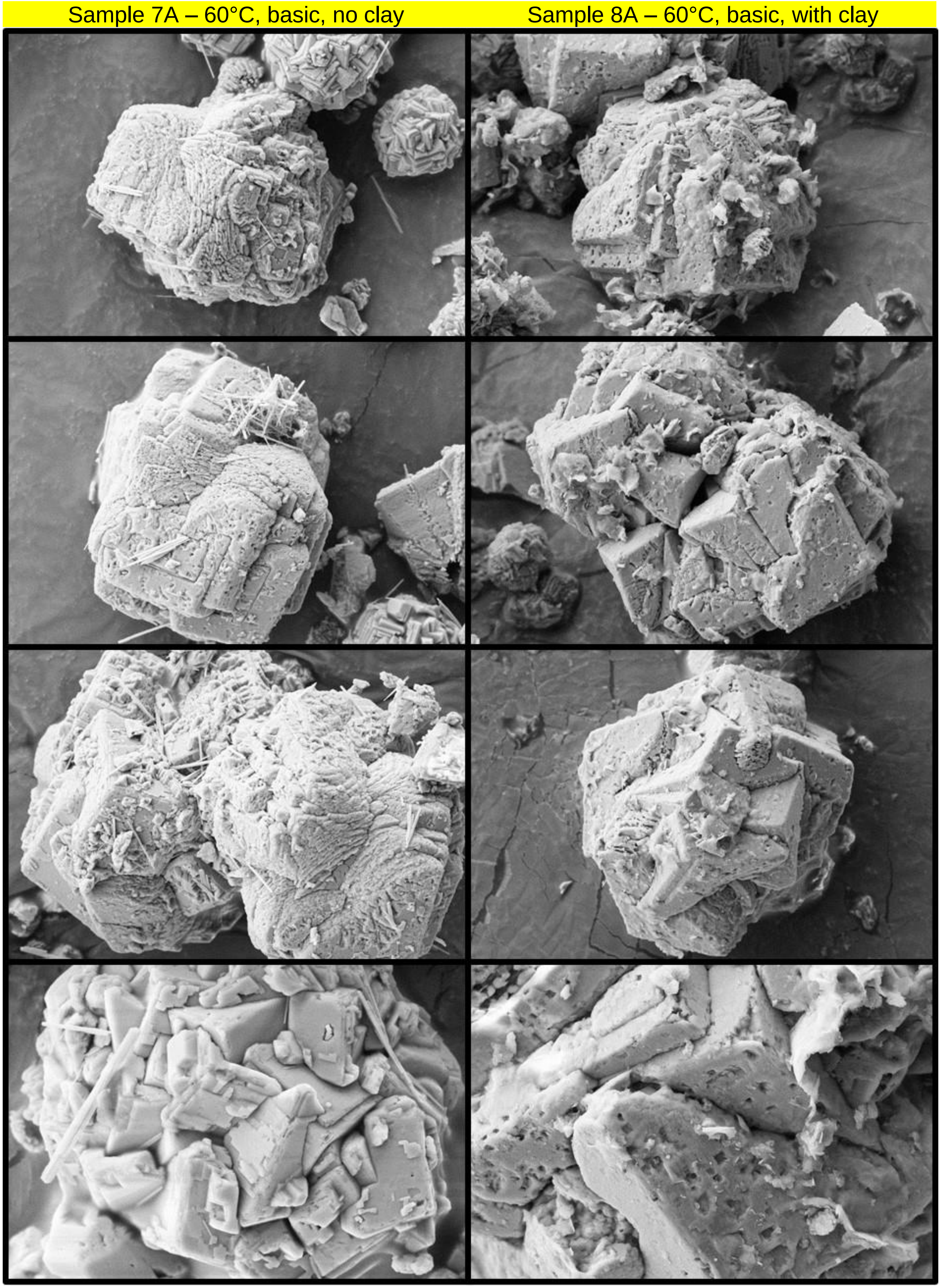
Figure 14 - SEM images of final experimental products for Samples 3B and 4A. The top 3 images on each side are at 3,500X magnification, while the bottom image on each side is at 8,500X magnification.



Sample 5A – 25°C, basic, no clay

Sample 6A – 25°C, basic, with clay

Figure 15 - SEM images of final experimental products for Samples 5A and 6A. The top 3 images on each side are at 3,500X magnification, while the bottom image on each side is at 8,500X magnification.


Sample 7A – 60°C, basic, no clay

Sample 8A – 60°C, basic, with clay

Figure 16 - SEM images of final experimental products for Samples 7A and 8A. The top 3 images on each side are at 3,500X magnification, while the bottom image on each side is at 8,500X magnification.

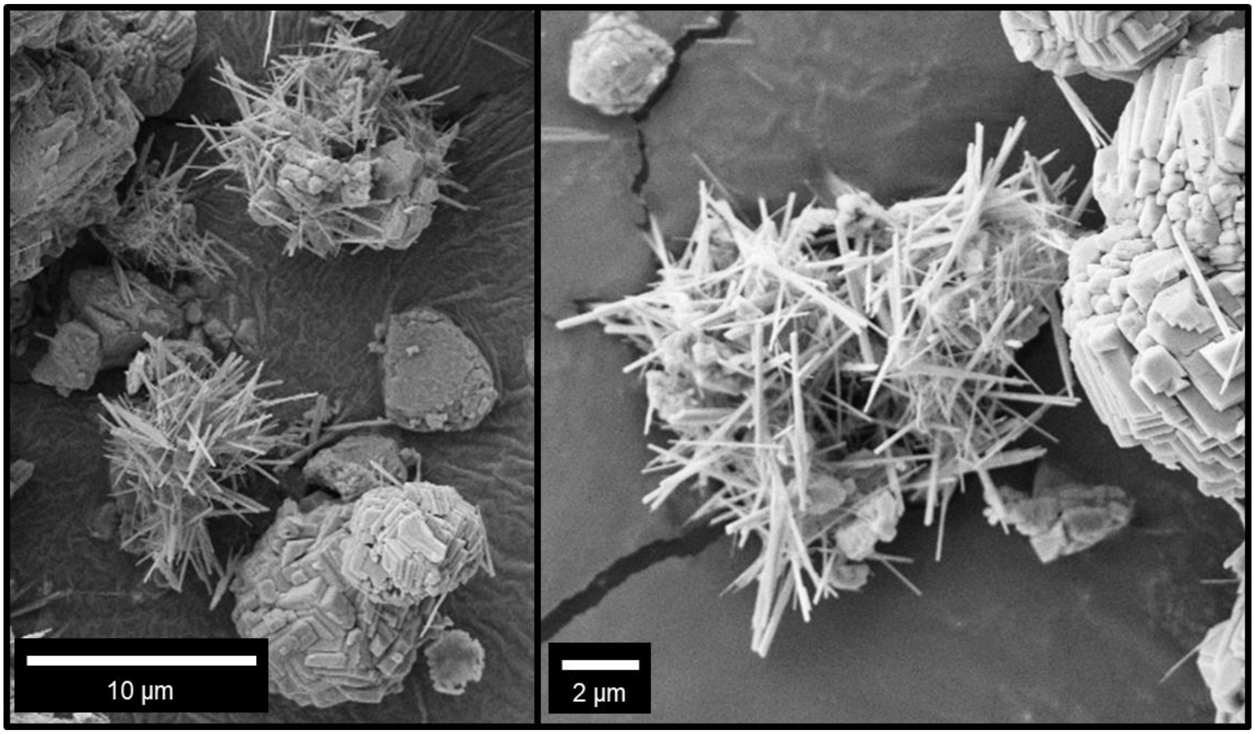


Figure 17 - SEM images of Sample 7A at 1500X (left) and 3000X (right), both showing the acicular structures identified as Mn carbonate by EDS.

Discussion of Experimental Results

pH, Alkalinity, and Aqueous Chemistry of Reaction Solutions

Overall, pH values increased from near 6.00 to around 7.00 for all the acidic samples, whereas the basic samples remained near the target pH of 8.00 for the duration of the experiment. For the acidic samples, there appeared to be at least some degree of association with the presence of clay, with clay-containing samples having 3 of the 4 highest final pH and 3 of the 4 highest ΔpH values. Temperature also appeared to have a slight effect on ΔpH but not final pH, again with 3 of the 4 highest ΔpH values belonging to samples with clay. For basic samples, the small (±0.12 units) difference from the target pH of 8.00 for all samples for the study's duration was deemed insignificant. Neither temperature differences nor the presence or absence of clay appeared to affect pH values significantly. Though acidic samples continuously increased throughout the study, most slopes had become noticeably lower by Day 7. Increasing pH in acidic samples was an expected effect of increased carbonate dissolution, which resulted in increasing amounts of HCO_3^- as CO_3^{2-} combined with H^+, removing H^+ from the system. This process slowed and resulted in smaller slopes as increasing amounts of HCO_3^- formed. By a pH of 8, nearly 98% of the carbonate species in a system is HCO_3^-,[38] so pH values for acidic samples would likely have continued to rise, albeit more slowly, until stabilizing near a pH of 8. The large amount of HCO_3^- present at pH 8 was also likely why the basic samples showed little pH change during the study.

In general, alkalinity changes were small ($\leq$20 mg $CaCO_3$/L) for 15 of the 16 samples, and single values tended to skew averages and changes. This skewing effect made it somewhat difficult to discern any significant trends, though particular characteristics were still noticeable. Overall, alkalinity values were greater in acidic samples than in basic samples, which would be expected with more extensive carbonate dissolution seen at lower pH values. Acidic room-temperature samples had higher alkalinities than acidic high-temperature samples, which would also be expected since carbonate solubility and, therefore, dissolution are more significant at lower temperatures. For basic samples, alkalinities showed little overall changes from Day 1 to Day 14. However, room-temperature samples were typically slightly higher than high-temperature samples, again indicating the effect of increased dissolution at lower temperatures. The presence of clay did not appear to affect alkalinities in either acidic or basic samples, with concentrations in clay-containing samples interspersed with those lacking clay throughout the 14-day study period. These interspersed values suggested that cation exchange did not have a significant effect on alkalinity values.

For Ca, acidic samples had concentrations approximately an order of magnitude greater than most basic samples for the entire study. Greater concentrations in acidic solutions would again be expected with increased carbonate dissolution that should occur at lower pH values. Aqueous Ca in both acidic and basic samples decreased overall from Day 1 to Day 14, which would be expected in the presence of cation exchange, precipitation, or both. Evidence supporting a role for cation exchange here may be seen by comparing changes in Ca concentrations in samples with and without clay. In this case, both acidic and basic clay-containing samples generally had greater overall decreases in Ca than samples without clay, suggesting at least some degree of cation exchange in the clay-containing samples that was absent in samples without clay. This fact continued to be true when samples with and without clay were broken down by temperature. Regarding temperature, the acidic room-temperature samples generally had lower Ca compared to high-temperature samples. In contrast, basic room-temperature samples all had higher concentrations than high-temperature samples (after approximately Day 4.5). Typically, as seen with the basic samples, one would expect the room-temperature samples to have greater dissolution than the high-temperature samples, which means Ca concentrations should be greater. However, for the acidic samples, this was not the case. The most likely explanation for this is precipitation, as observed with the formation of the acicular structures seen in Samples 1A (low temperature acidic) and 7A (high temperature basic). Precipitation also makes sense given that neither Sample 1A nor 7A contained clay, so cation exchange could not have resulted in the reduced Ca concentrations.

For experimental samples, the expected source of Na was the Na-saturated clay found in clay-containing samples. However, 2 other sources of Na were possible as contaminants – remnant particles not fully removed during rinsing of the synthetic Mn calcite and as dissolved ions not fully removed in the UPW. Concentrations in each sample revealed at least some contaminant Na in all samples since Na was detected even in samples without clay. However, other than 2 (likely) anomalous values for 2 acidic samples on Day 1, the remaining acidic Na concentrations followed similar trends for the study's duration, as did all of the basic concentrations. As such, despite some degree of contamination, concentrations were reliable and representative of the samples. Save for Day 1, acidic samples consistently had concentrations at least 2-4 times greater than basic concentrations on the same day. This concentration difference was consistent even in samples without clay. As a result, the most likely explanation was that the excess Na was with the Mn calcite (likely dissolved from solid Na_2CO_3) and, like the Mn calcite, dissolved to a greater extent under acidic conditions. This explanation further seems to be the most plausible since the UPW was obtained from the same source simultaneously for all samples (and would be expected to have little, if any, Na present). Additionally, Mn calcite in all the samples was synthesized as a single batch, meaning the amount of contaminant Na should be similar for all samples. Other than on Day 3 for basic samples, there did not appear to be any distinct effects of temperature on Na concentrations. The one factor that defined differences in the samples, both acidic and basic, was the presence of clay. Samples with clay had distinctly higher Na concentrations compared to those without as well as larger overall decreases. These higher concentrations are appropriate with exchange, where Na^+ is released from the clay as Ca^{2+}, Mg^{2+}, and Mn^{2+} are taken up. The larger overall decreases in clay samples were unexpected and will require further experimentation to understand conclusively.

As with other parameters, Mn concentrations in acidic samples were significantly greater than those in basic samples, with all but 2 of the high-temperature acidic samples having concentrations at least an order of magnitude greater for the study duration. Again, this was to be expected with greater dissolution seen in samples with lower pH values. For the acidic samples, 6 of 8 samples followed similar trends, while 2 of the high-temperature, no clay samples (Samples 3B and 4B) continuously decreased to a much greater extent than the other samples. Sample 3B was viewed in the SEM (Figure 14) and did appear to have some reprecipitation of Mn calcite that might explain this trend. Other possibilities include the precipitation of Mn oxides that were too small to visualize or adsorption of Mn to carbonate surfaces. In basic samples, room-temperature samples had higher concentrations compared to high-temperature samples, as expected. In fact, 3 of the 4 high-temperature samples had sub-nanomolar concentrations for the entire study, while the remaining clay-containing sample had measurable concentrations on Days 1 and 3 and then decreased to sub-nanomolar concentrations as well. Both acidic and basic samples showed overall decreases in concentration. In samples without clay, this suggests reprecipitation of Mn calcite with or without Mn adsorption and/or Mn oxide formation. These same processes are also plausible in samples with clay. However, the 3 acidic clay samples all decreased more than twice as much as non-clay samples, suggesting a role for cation exchange as well. The 2 basic room-temperature samples with clay decreased less than those without clay, which was not expected. However, this does line up with SEM observations of greater precipitation in samples without clay and greater dissolution in samples with clay, which could result in higher Mn concentrations in clay-containing samples.

SEM Characterization of Final Solid Products

Final solid phase products helped further characterize the results of experimental reactions. As expected, acidic samples appeared to undergo greater dissolution than basic samples, with more pronounced etch pits, crevices, cracks, rounded edges, and indistinct margins noted in SEM images of acidic samples (Figure 13 and Figure 14). Experimental chemistries confirmed these findings, with greater aqueous concentrations of Mn calcite dissolution products (Ca^{2+}, Mn^{2+}, and alkalinity) seen in acidic samples compared to basic samples. For temperature, both acidic and basic high-temperature samples, particularly those without clay, appeared to have greater precipitation than room-temperature samples. SEM evidence of this was seen in Sample 3B (Figure 14, left), which appeared to have a significant amount of secondary Mn calcite rhombs on the surfaces of existing Mn calcite grains, and in Sample 7A (Figure 16, left, and Figure 17), which had significant precipitation of acicular Mn calcite. Greater precipitation would be expected at higher versus lower temperatures, as supported by alkalinities, basic Ca concentrations, basic Mn concentrations, and 2 of the 4 acidic Mn concentrations, all of which were lower in high-temperature samples. However, acidic Ca concentrations and the 2 remaining acidic Mn concentrations did not support this observation regardless whether or not exchange was occurring. One possible explanation for the basic samples is that Mn concentrations were closer to equilibrium and, thus, were preferentially precipitating Mn carbonates (e.g., $MnCO_3$) over Mn calcite ($(Ca,Mn)CO_3$) or pure $CaCO_3$. The 2 acidic solutions had lower and continually decreasing Mn concentrations but increasing Ca concentrations. One explanation for this could be the preferential oxidation of Mn and Mn oxide precipitation, which would remove Mn from the solution while leaving Ca levels unaffected. Such a trend can be seen in the Mn time series figure (Figure 12), where samples 3B and 4B have significantly lower Day 14 Mn concentrations compared to other samples. One noticeable difference was that acidic high-temperature samples actually appeared to show greater dissolution than acidic room-temperature samples, as noted by the larger number and size of crevices, cracks, and etch pits in Samples 3B and 4A (Figure 14) compared to 1A and 2A (Figure 13). Such differences were consistent with the higher Ca concentrations seen in acidic high-temperature samples, though one would also expect alkalinity and Mn to have been higher as well. Samples with and without clay also showed distinct trends, where samples with clay tended to show greater dissolution while samples without clay tended to show greater precipitation. These trends agree with the hypothesis that the presence of clay should result in the increased dissolution of carbonates as cation exchange removes incorporated divalent cations (Ca^{2+}, Mg^{2+}, Mn^{2+}) from the solution. Based on the above results and expected reactions, one would ideally see the most significant degree of precipitation in high-temperature basic samples with no clay. Acicular precipitates indicate rapid growth parallel to the c-axis of carbonates,[37,39] and such structures were not present in the original, unreacted Mn calcite. These features were, however, found in significant quantities in Sample 7A (basic, high temperature, no clay), thus supporting the idea that the most significant degree of precipitation occurred under these conditions.

Geochemical Modeling of Mn Carbonate Dissolution and Cation Exchange

Modeling Methodology

PHREEQC batch reaction modeling of cation exchange was conducted using PHREEQC Interactive, or PHREEQCI, from the USGS (64-bit, version 3.5.0.14000, released 14 February 2019). PHREEQCI is a Windows-based graphical user interface (GUI) with all the original PHREEQC program capabilities but without the traditional requirements for knowledge of – and coding with – the C++ programming language. Laboratory experiments provided the basis for input data and the conceptual approach used in modeling. Model solutions consisted of the following combinations, creating a total of 8 different solutions for modeling (Table 3): Day 0 or Day 1 laboratory-measured geochemical parameters; solid solutions comprised of either calcite/rhodochrosite or dolomite/rhodochrosite; and the inclusion or omission of exchange reactions using Na clay (e.g., Na smectite). Concentrations of O_2 and CO_2 were fixed in equilibrium with the atmosphere using log partial pressure O_2 = -0.7 and log partial pressure CO_2 = -3.39 (equivalent to ≈407 ppm). All solutions included K^+ and Cl^- in order to introduce a species (Cl^-) for charge balancing. Adding Cl^- alone resulted in solutions failing to converge, whereas adding both K^+ and Cl^- rectified this issue; K^+ and Cl^- were chosen since neither ion participates in reactions of interest in this study. Temperatures were fixed at their assigned experimental values (25°C or 60°C), and pH was fixed at Day 0 or Day 1 laboratory-measured values using HNO_3. Solid solutions were fixed at 0.99 moles of either calcite or dolomite and 0.01 moles of rhodochrosite, representing the ≈1 wt% Mn found in Mn dolomite in the COA. NaX, representing Na clay, was added to each solution in a stepwise manner from 20 to 500 millimoles in 20-millimole increments (25 steps total). However, only 4 of the 8 solutions contained the “Exchange” keyword block, so cation exchange was only modeled in those 4 solutions, leaving the other 4 solutions as control solutions with no cation exchange. Only samples 1A, 3A, 5A, and 7A were included in each model, representing 1 sample for each set of temperature/pH conditions in the laboratory experiments, so that processing times were limited. The PHREEQCI Wateq4f database was used for all models since it contained the necessary Mn species. PHREEQCI input files for each of the 8 solutions are provided in Appendix 2. Parameters examined in the results and subsequent analyses included alkalinity, cations (Ca^{2+}, Mn^{2+}, Na^{+}, Mg^{2+}, and Mg/Ca ratios), aqueous distribution of Mn species, and saturation indices of predicted precipitates for Mn compounds.

Table 3 - Characteristics of solutions used for PHREEQCI batch reaction modeling.

	Day 0 Geochemistry		Day 1 Geochemistry	
Exchange Modeling	Calcite/ Rhodochrosite Solid Solution	Dolomite/ Rhodochrosite Solid Solution	Calcite/ Rhodochrosite Solid Solution	Dolomite/ Rhodochrosite Solid Solution
No Exchange Modeling	Calcite/ Rhodochrosite Solid Solution	Dolomite/ Rhodochrosite Solid Solution	Calcite/ Rhodochrosite Solid Solution	Dolomite/ Rhodochrosite Solid Solution

Modeling Results

Batch reaction modeling results are summarized below, with full results provided in Appendix 3 and summary statistical averages provided in Appendix 4. Because one of the overarching objectives is to relate modeling results to expected reactions in the COA, only results for Samples 1A (acidic, 25°C) and 5A (basic, 25°C) are detailed below since their temperatures are much closer to expected aquifer temperatures (average ≈17.4°C; range ≈15.5-20.5°C)[1,40] compared to the 60°C samples. Additionally, results are presented primarily with respect to the presence or absence of NaX exchange in line with the study's primary objective investigating the effects of cation exchange. Since cation concentrations were low (< 500 mmol/kg for Na, orders of magnitude lower for others) and only room-temperature samples were used, it was assumed that molality and molarity were approximately equal. As such, all cation concentrations have been converted to mmol/L (millimolar) and alkalinity concentrations to mg $CaCO_3$/L for comparison with experimental results (reported as ppm and mg $CaCO_3$/L). For each of the results sections below, "initial" values indicate the initial calculated values after the addition of 20 mmol NaX (the first incremental step for each solution), while "final" values indicate the final calculated values after the addition of 500 mmol NaX (the last incremental step for each solution).

Alkalinity

Sample 1A (25°C, acidic)

Alkalinity results are presented in Figure 18. For models based on Sample 1A, the average initial alkalinity was 1750.44 mg $CaCO_3$/L (range 1620.69-1900.13) for the 4 exchange solutions compared to 506.75 mg $CaCO_3$/L (range 285.81-730.73) for the 4 solutions with no exchange, while the average final values were 2530.75 mg $CaCO_3$/L (range 2378.74-2698.77) and 744.02 mg $CaCO_3$/L (range 470.12-1026.93) for exchange and no exchange, respectively. While solutions with exchange had average initial and final alkalinities that were ≈3.5 times greater than averages for solutions without exchange, overall changes were similar at 44.7% with exchange versus 49.4% without exchange.

A comparison of starting chemistries revealed that Day 0 exchange solutions had average initial and final alkalinity values that were nearly 3 times higher than the initial and final values for Day 0 solutions without exchange. However, average overall changes for the 2 were similar, with Day 0 exchange increasing 43.2% while Day 0 without exchange increased 45.0%. The difference in initial and final alkalinities was even more remarkable for Day 1 solutions, with alkalinities that were more than 4 times higher for exchange versus no exchange. Again, however, the overall average changes were similar, with Day 1 exchange solutions increasing by 46.1% while solutions with no exchange increased slightly more at 53.8%. For Day 0 versus Day 1 exchange solutions, no real distinction can be made between the average initial and final values and overall changes, as all 3 were similar for both starting chemistries. For solutions without exchange, Day 0 initial and final average values were ≈1.5 times higher than Day 1 values, but the Day 1 average overall change was about 9% higher than that for Day 0.

An examination of the solid solution used showed that dolomite/rhodochrosite exchange solutions had average initial and final alkalinities that were 12-15% higher than those for calcite/rhodochrosite exchange solutions. However, average changes between the 2 were similar at 45.6% (calcite/rhodochrosite) and 43.7% (dolomite/rhodochrosite). Compared to solutions with exchange, both types of solid solutions with no exchange had average initial and final alkalinities that were 3 (dolomite/rhodochrosite) to 4 (calcite/rhodochrosite) times lower. Calcite/rhodochrosite solid solutions with no exchange had a higher average change (57.0%; range 49.5-64.5) compared to dolomite/rhodochrosite (41.8%; range 40.5-43.0). The average alkalinity change for calcite/rhodochrosite without exchange was also correspondingly higher than that with exchange, while solid solutions of dolomite/rhodochrosite were similar both with and without exchange.

Sample 5A (25°C, basic)

The average initial alkalinity value for solutions with exchange was 954.68 mg $CaCO_3$/L (range 757.95-1126.42), while the average final value was 1330.64 mg $CaCO_3$/L (range 1116.46-1525.66). For solutions without exchange, these averages were ≈8 times lower at 124.45 mg $CaCO_3$/L (initial average; range 13.73-326.59) and 157.37 mg $CaCO_3$/L (final average; range 31.81-331.76). While average alkalinities were higher in solutions with exchange, these solutions had a lower overall average change of 40.1% (range 35.3-47.3) compared to the average change for solutions with no exchange (67.9%; range 1.6-131.7), though solutions with no exchange did exhibit a much broader variation in change.

Comparison of Day 0 starting chemistries showed that solutions with exchange had average initial and final alkalinities that were more than 10-fold higher than those without exchange. However, Day 0 solutions without exchange experienced an overall average change that was double that of solutions with exchange, increasing by 69.2%

(range 66.6-71.8) compared to only 35.4% (range 35.3-35.4) with exchange. Though to a lesser degree, significant alkalinity differences were also present for solutions with Day 1 starting chemistries, with exchange solutions having ≈5-7 times greater initial and final values compared to solutions without exchange. The overall change was also significantly different, with exchange solutions having a 44.8% change (range 42.3-47.3) compared to 66.7% (range 1.6-131.7) for no exchange, though the variation was also significant for no exchange. Day 0 initial and final alkalinities were ≈20-30% higher for solutions with exchange compared to Day 1 solutions with exchange, but the average change was higher for Day 1 exchange solutions by almost 10% (44.8% versus 35.4%). For solutions with no exchange, Day 1 initial concentrations were more than double those for Day 0, while final concentrations were nearly 40% higher. However, overall average changes were similar, though, again, the range was extensive for the Day 1 solutions.

For solid solutions, calcite/rhodochrosite solutions with exchange exhibited more than a 20-fold higher initial average concentration and more than a 15-fold higher final average concentration versus calcite/rhodochrosite solutions with no exchange. The difference in the average change between the 2 was also significant, with no exchange experiencing a 101.7% (range 71.8-131.7) increase compared to only 41.3% (range 35.3-47.3) with exchange. Differences were less for the subset of dolomite/rhodochrosite, with exchange solutions having initial and final concentrations that were only 5 and 7 times greater, respectively, than solutions without exchange. However, the 2 had similar average overall changes (exchange = 38.9%, range 35.4-42.3; no exchange = 34.1%, range 1.6-66.6). Of note for both sets of solid solutions was the wide variability in change for solutions with no exchange. The differences were less contrasting for exchange solutions, with dolomite/rhodochrosite solutions having initial and final alkalinities that were <15% greater than those for calcite/rhodochrosite solutions and with average changes that were more similar as well. A comparison of the 2 solid solutions without exchange showed that dolomite/rhodochrosite solutions had initial and final alkalinities that were 3-4 times higher than those for calcite/rhodochrosite. Though the variability was large, the average overall change for dolomite/rhodochrosite was only about one-third that of calcite-rhodochrosite.

Comparing Samples 1A and 5A, it is clear that both initial and final alkalinity values were significantly larger for acidic Sample 1A compared to basic Sample 5A. These differences were particularly noted when comparing acidic solutions with no exchange to basic solutions with no exchange, where acidic solutions often had alkalinities that were 3-10 times greater compared to their basic counterparts. Even solutions with exchange often saw alkalinities that were 1.5-2 times higher in the acidic solutions compared to basic solutions. Overall changes also tended to be more similar for acidic solutions with and without exchange compared to basic solutions with and without exchange, where, again, basic solutions with no exchange tended to have a wider variability than basic solutions with exchange or any of the acidic solutions.

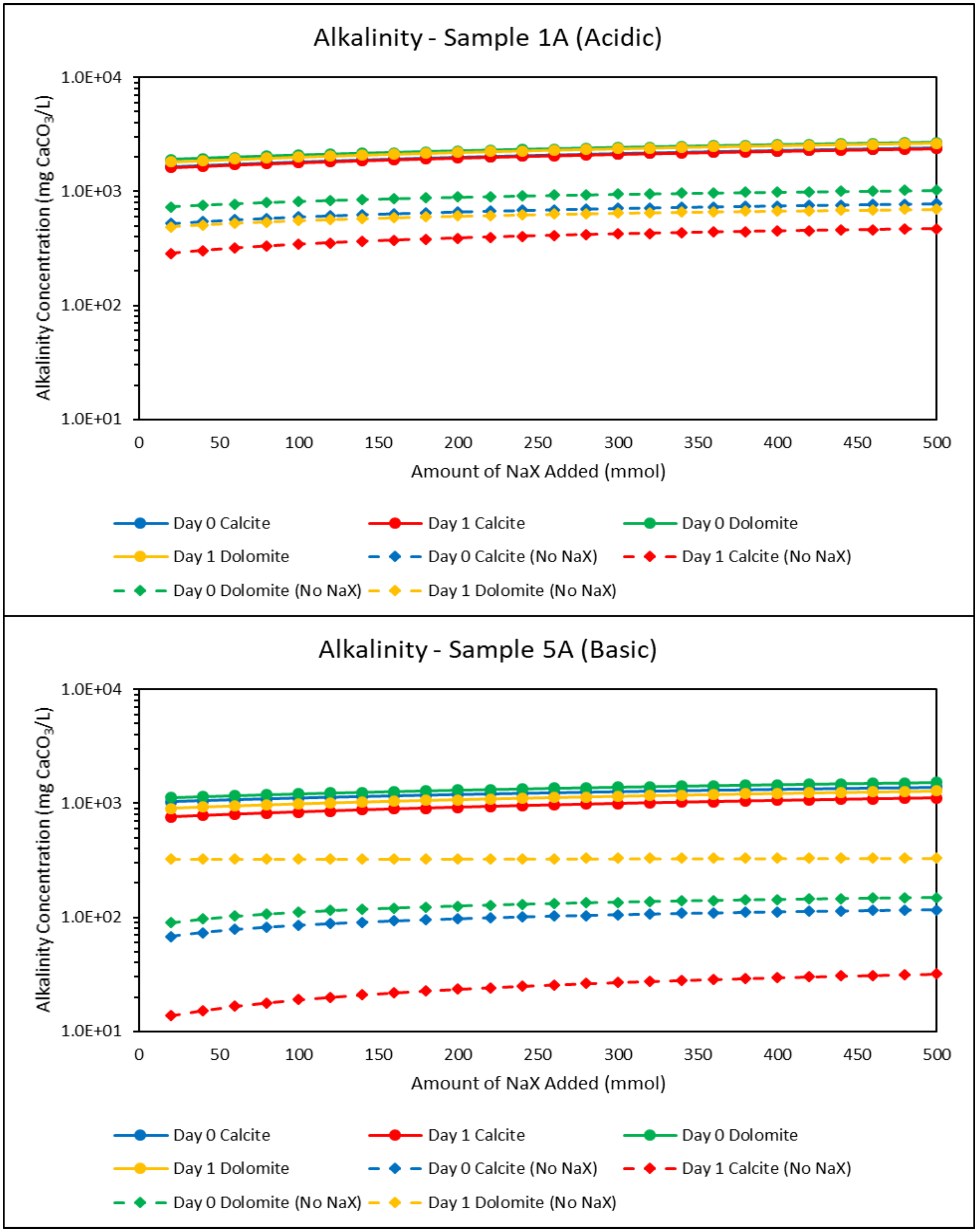


Figure 18 - Summary results of alkalinity concentrations with the incremental addition of NaX from batch reaction modeling. The top graph is Sample 1A (acidic), and the bottom graph is Sample 5A (basic). Solid lines with circles indicate samples with exchange, while dashed lines with diamonds indicate samples without exchange. Note that scales are logarithmic and identical for both Sample 1A and Sample 5A. Concentrations have been converted from Eq/kg (PHREEQCI output) to mg $CaCO_3$/L.

Calcium

Sample 1A (25°C, acidic)

Modeling results for Ca are presented graphically in Figure 19. For Sample 1A, the average initial value for the 4 solutions with exchange was 6.122 mmol/L (range 3.189-10.409), whereas that for solutions without exchange was 20.123 mmol/L (range 17.313-26.312). The average final values were 4.848 mmol/L (range 2.385-8.349) for solutions with exchange versus 24.263 mmol/L (range 21.163-32.963) for solutions without. The result was an average ΔCa = (-)21.5% for exchange compared to 20.2% with no exchange. The average initial and final concentrations for the solutions with no exchange were ≈3-5 times greater than those for the solutions with exchange.

Exchange solutions with Day 0 starting chemistries had ≈2.5 times higher initial and final Ca values than solutions with Day 1 starting chemistries. However, overall changes were similar, with an average ΔCa = (-)20.1% for Day 0 chemistries versus (-)22.9% for Day 1 chemistries. No distinction can be made between initial and final values for Day 0 and Day 1 chemistries for solutions with no exchange save for the Day 0 calcite/rhodochrosite solution had ≈50% higher initial, final, and overall Ca values compared to the other 3 solutions. As with the exchange solutions, average changes were similar for Day 0 versus Day 1 chemistries, with a ΔCa = (+)22.1% for Day 0 versus (+)18.2% for Day 1. Day 0 solutions with no exchange had ≈2.5-4 times higher initial and final Ca concentrations than Day 0 solutions with exchange. This effect was even larger for Day 1 solutions, where those with no exchange had ≈5-8 times higher concentrations than those with exchange. Solutions with no exchange had positive ΔCa values, whereas solutions with exchange all had negative ΔCa values.

Comparing solid solutions, exchange solutions with calcite/rhodochrosite had average initial and final values that were 40-45% higher compared to solutions with dolomite/rhodochrosite, but the average ΔCa values were similar at (-)20.2% (calcite/rhodochrosite) and (-)22.9% (dolomite/rhodochrosite). For solutions with no exchange, the average initial and final values for calcite/rhodochrosite were again greater (≈20-30%) compared to dolomite/rhodochrosite solutions, and the ΔCa was also higher at 25.1% for calcite/rhodochrosite versus 15.3% for dolomite/rhodochrosite. Both calcite/rhodochrosite and dolomite/rhodochrosite solutions had initial and final concentrations ≈3-5 times greater for solutions with no exchange than solutions with exchange. As with Day 0 versus Day 1 chemistries, average ΔCa values were again negative for solutions with exchange and positive for solutions without.

Sample 5A (25°C, basic)

For Sample 5A, the 4 exchange solutions had average initial and final Ca concentrations of 0.130 mmol/L (range 0.076-0.173) and 0.099 mmol/L (range 0.064-0.118), respectively, with an average ΔCa = (-)22.0%. The solutions with no exchange had average initial (6.106 mmol/L; range 0.891-14.149) and final (6.537 mmol/L; range 1.445-14.101) concentrations that were ≈45-65 times greater than those for the solutions with exchange as well as a positive average ΔCa (33.3%). However, the range of initial, final, and ΔCa values was highly variable compared to solutions with exchange.

For solutions with exchange, Day 0 starting chemistries had initial and final average concentrations that were 50-60% lower than those for Day 1 chemistries. Day 0 ΔCa values were also less than Day 1 values ((-)16.1% versus (-)28.0%, respectively), but both solution chemistries still showed overall decreases in Ca concentrations. For solutions without exchange, Day 0 chemistries were a magnitude of order less than those for Day 1. However, Day 0 chemistries showed a much greater average ΔCa of 64.9% versus only 1.7% for Day 1. A comparison of concentrations for Day 0 solutions revealed Ca levels that were a magnitude of order greater for solutions without exchange versus solutions with exchange. Average ΔCa values were also vastly different, with exchange solutions decreasing while solutions without exchange increased. For Day 1 solutions, the concentration difference was even more remarkable, with solutions with no exchange having concentrations 2 orders of magnitude greater than solutions with exchange. Changes in concentrations were smaller than for Day 0 solutions, with Day 1 exchange solutions decreasing by 23-33% while solutions without exchange showed little overall change.

Results based on solid solutions showed that initial and final concentrations for exchange solutions were similar for both calcite/rhodochrosite and dolomite/rhodochrosite, as were average ΔCa values ((-)19.7% for calcite/rhodochrosite and (-)24.3% for dolomite/rhodochrosite). Initial and final concentrations for solutions without exchange were ≈50-60% greater for dolomite/rhodochrosite versus calcite/rhodochrosite, but overall changes were similar (ΔCa = 35.7% for calcite/rhodochrosite and 31.0% for dolomite/rhodochrosite). Initial and final concentrations for calcite/rhodochrosite solutions without exchange were ≈30-50 times greater than calcite/rhodochrosite solutions with exchange. The differences for dolomite/rhodochrosite solutions were even more remarkable, with solutions without exchange having concentrations ≈60-80 times greater than those with exchange.

Examining the differences between models based on Sample 1A and 5A, it was clear that initial and final concentrations for models with basic pH were significantly less than those for acidic pH regardless of the starting chemistry, type of solid solution, or presence or absence of exchange. Values for ΔCa were typically similar for both acidic and basic solutions with exchange; for solutions without exchange, values tended to be higher and vary more widely for basic solutions, particularly when considering the 4 no-exchange solutions together or with respect to solid solution type.

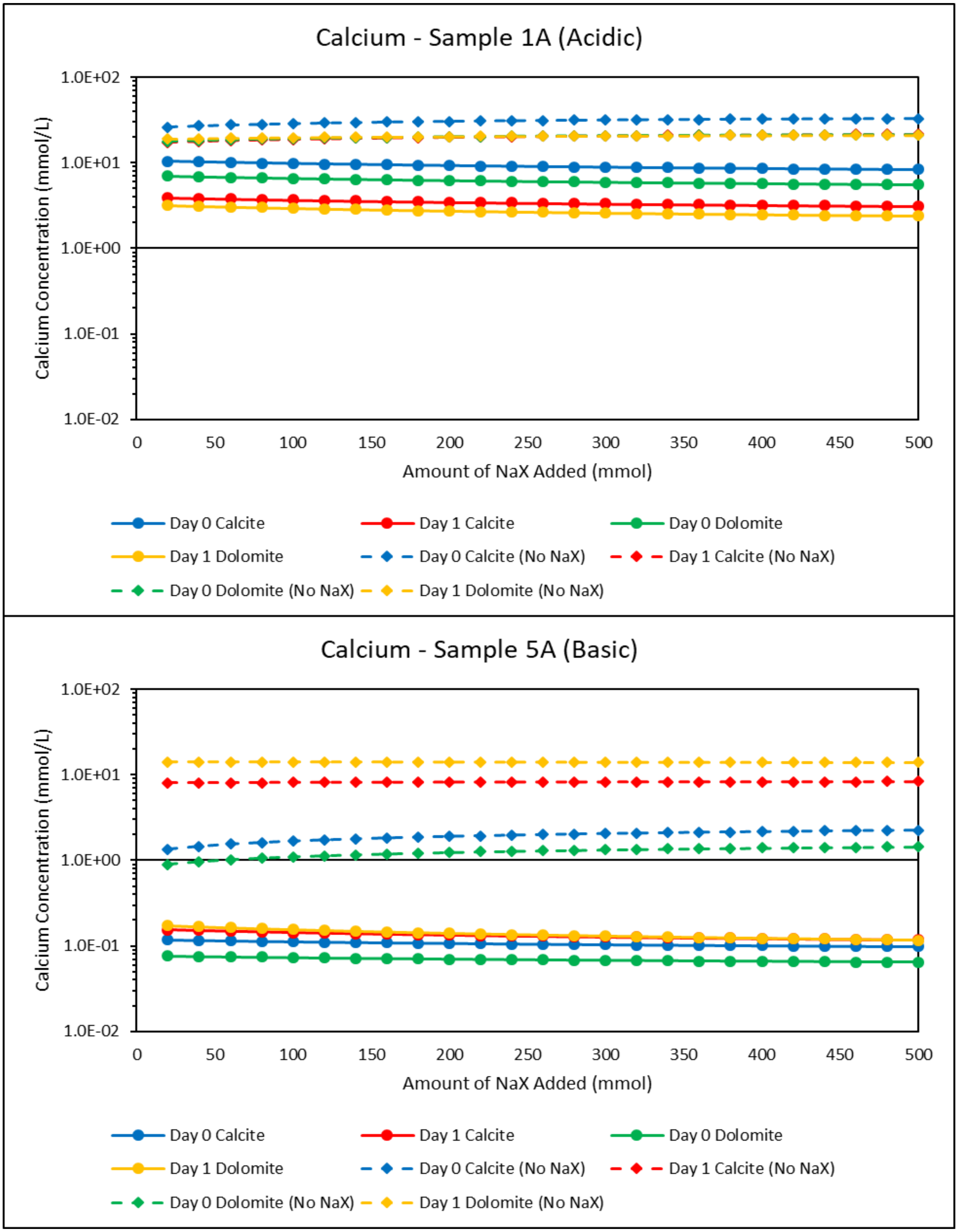


Figure 19 - Summary results of Ca concentrations with the incremental addition of NaX from batch reaction modeling. The top graph is Sample 1A (acidic), and the bottom graph is Sample 5A (basic). Solid lines with circles indicate samples with exchange, while dashed lines with diamonds indicate samples without exchange. Note that scales are logarithmic and identical for both Sample 1A and Sample 5A.

Manganese

Sample 1A (25°C, acidic)

Modeled Mn concentrations are shown in Figure *20*. For solutions with no exchange, 3 of the 4 initial and all 4 final Mn concentrations were higher compared to solutions with exchange. Average initial and final values were $5.883\text{x}10^{-4}$ mmol/L (range $3.837\text{x}10^{-4}$-$7.729\text{x}10^{-4}$) and $8.274\text{x}10^{-4}$ mmol/L (range $5.575\text{x}10^{-4}$-$1.092\text{x}10^{-3}$), respectively, for solutions with no exchange compared to initial and final values of $3.087\text{x}10^{-4}$ mmol/L (range $1.859\text{x}10^{-4}$-$4.411\text{x}10^{-4}$) and $2.861\text{x}10^{-4}$ mmol/L (range $1.702\text{x}10^{-4}$-$4.127\text{x}10^{-4}$), respectively, for solutions with exchange. Average ΔMn concentrations were positive (41.0%; range 38.5-45.3) for solutions without exchange but negative ((-)7.6%; range (-)6.4-(-)8.4) for solutions with exchange.

Based on starting chemistries, results revealed initial and final Day 0 Mn concentrations that were more than 2 times greater than the initial and final Day 1 values for solutions with exchange and ≈1.5 times greater for solutions without exchange. Despite these differences, both Day 0 and Day 1 solutions with exchange had similar average overall changes in Mn concentrations, with Day 0 ΔMn = (-)7.0% (range (-)6.4-(-)7.5) and Day 1 ΔMn = (-)8.2% (range (-)8.1-(-)8.4). Changes were also similar between Day 0 and Day 1 solutions with no exchange, where Day 0 increased an average of 39.9% (range 38.5-41.2) while Day 1 increased an average of 42.2% (range 39.2-45.3). A greater contrast existed between solutions with and without exchange. Day 0 solutions without exchange exhibited average initial and final concentrations that were ≈1.5 and ≈2.5 times higher, respectively, than corresponding values for solutions with exchange, while Day 1 solutions without exchange had even larger differences at ≈2.5 and ≈4 times greater, respectively, compared to Day 1 solutions with exchange. Overall changes were also significantly different, with exchange solutions having decreased Mn concentrations compared to increasing concentrations for solutions without exchange.

A comparison of solid solutions revealed that calcite/rhodochrosite exchange solutions had slightly higher average initial and final Mn concentrations than exchange solutions with dolomite/rhodochrosite, though the difference was small (≈6-8%). Average changes in Mn were similar, with calcite/rhodochrosite changing by (-)7.2% (range (-)6.4-(-)8.1) and dolomite/rhodochrosite by (-)7.9% (range (-)7.5-(-)8.4). Calcite/rhodochrosite solutions without exchange also had higher average initial and final concentrations than dolomite/rhodochrosite solutions with no exchange, though the difference was larger (≈27%) than solutions with exchange. However, average ΔMn values were similar at 40.2% (range 39.2-41.2) and 41.9% (38.5-45.3) for calcite/rhodochrosite and dolomite/rhodochrosite, respectively. An examination of like solution types showed that calcite/rhodochrosite solutions without exchange had approximately double and triple the initial and final concentrations, respectively, of calcite/rhodochrosite solutions with exchange. Dolomite/rhodochrosite solutions had differences that were similar (though slightly lower at ≈1.7 and 2.7 times) to the calcite/rhodochrosite solutions. Clear differences were again apparent between solutions with and without exchange regardless of solid solution type for average changes in Mn, with exchange solutions showing small overall decreases while solutions without exchange showed moderate increases.

Sample 5A (25°C, basic)

For basic Sample 5A, all initial and final Mn concentrations were greater for solutions without exchange versus solutions with exchange. The average initial Mn concentration for solutions without exchange was 7.810×10^{-5} mmol/L (range 1.917×10^{-5}-2.243×10^{-4}), while that for solutions with exchange was 1.144×10^{-5} mmol/L (range 1.011×10^{-5}-1.293×10^{-5}). Average final concentrations were 1.027×10^{-4} mmol/L (range 3.347×10^{-5}-2.590×10^{-4}) for solutions without exchange compared to 1.080×10^{-5} mmol/L (range 9.714×10^{-6}-1.195×10^{-5}) for solutions with exchange. As with Sample 1A, average overall changes were again positive (ΔMn = 58.2%; range 15.5-74.6), though to a larger degree, for solutions without exchange compared to negative (ΔMn = (-)5.5%; range (-)3.9-(-)7.6) for solutions with exchange.

Regarding starting chemistries, Day 1 exchange solutions had initial and final average concentrations that were ≈20-25% greater than Day 0 exchange solutions. Despite greater average concentrations for Day 1 solutions, the average ΔMn values were similar for the 2 chemistries at (-)3.9% (range (-)3.9-(-)4.0) for Day 0 and (-)7.0% (range (-)6.4-(-)7.6) for Day 1. For solutions without exchange, the Day 1 average initial Mn concentration was ≈3.5 times greater than that for Day 0, and the final Mn concentration was ≈2.5 times greater. The average ΔMn for Day 1 was only 45.0% (range 15.5-74.6) compared to 71.4% (range 70.8-72.1) for Day 0. Day 0 solutions with exchange had initial concentrations that were ≈3.5 times less than those without exchange, while final concentrations were ≈6 times lower. For Day 1 solutions with exchange, the difference was even greater, with average initial and final concentrations that were at least an order of magnitude less than Day 1 solutions without exchange.

The average ΔMn was also slightly negative for exchange solutions compared to (generally) large positive values for solutions without exchange. However, of note for solutions with no exchange was the skewing effect of the Day 1 calcite/rhodochrosite solution. This solution had modeled initial and final concentrations that were ≈7-12 times and ≈4-8 times greater, respectively, than the other 3 solutions and a ΔMn of only 15.5% compared to 70-75% for the other 3 solutions.

Examination of calcite/rhodochrosite and dolomite/rhodochrosite solid solutions with exchange revealed similar (within ≈3-4%) average initial and final Mn concentrations along with similar average changes in concentrations (calcite/rhodochrosite ΔMn = (-)5.7%, range (-)3.9-(-)7.6; dolomite/rhodochrosite ΔMn = (-)5.2%, range (-)4.0-(-)6.0). The differences in solid solutions were greater for solutions without exchange, with average initial and final concentrations nearly 4-5 times higher for calcite/rhodochrosite versus dolomite/rhodochrosite. Despite the greater average concentrations, calcite/rhodochrosite solutions only showed an average ΔMn of 43.8% (range 15.5-72.1) compared to 72.7% (range 70.8-74.6) with dolomite/rhodochrosite. However, the calcite/rhodochrosite averages were again skewed because of 1 sample (Day 1 calcite/rhodochrosite with no exchange) having much higher concentrations and a lower ΔMn than the other 3 samples (combined for both solid solutions). This difference was further highlighted when comparing calcite/rhodochrosite solutions with and without exchange. Solutions without exchange had ≈11 and ≈15 times higher average initial and final, respectively, Mn concentrations than solutions with exchange. Comparison of dolomite/rhodochrosite solutions with and without exchange also showed that solutions with no exchange had greater initial and final average concentrations, though the differences were much smaller (≈2.2 and ≈4 times, respectively) compared to calcite/rhodochrosite. As with the acidic sample, there was also a stark contrast in overall changes, with exchange solutions decreasing slightly while solutions with no exchange showed large increases(>70%, excluding the Day 1 calcite/rhodochrosite solution).

A comparison of acidic and basic samples showed that 7 of 8 basic solutions had average initial and final Mn concentrations that were more than an order of magnitude lower than acidic solutions, with many exchange solutions more than 20 times lower. Average ΔMn values were negative and similar for both acidic and basic solutions with exchange of both solid solution types. For solutions without exchange, acidic solutions, when not considering the basic Day 1 calcite/rhodochrosite solution, had ΔMn values that were nearly half those of basic solutions (40-42% versus 70-75%). Both acidic and basic calcite/rhodochrosite solutions had higher overall Mn concentrations than corresponding dolomite/rhodochrosite solutions, though the differences were not typically large save for basic samples with no exchange.

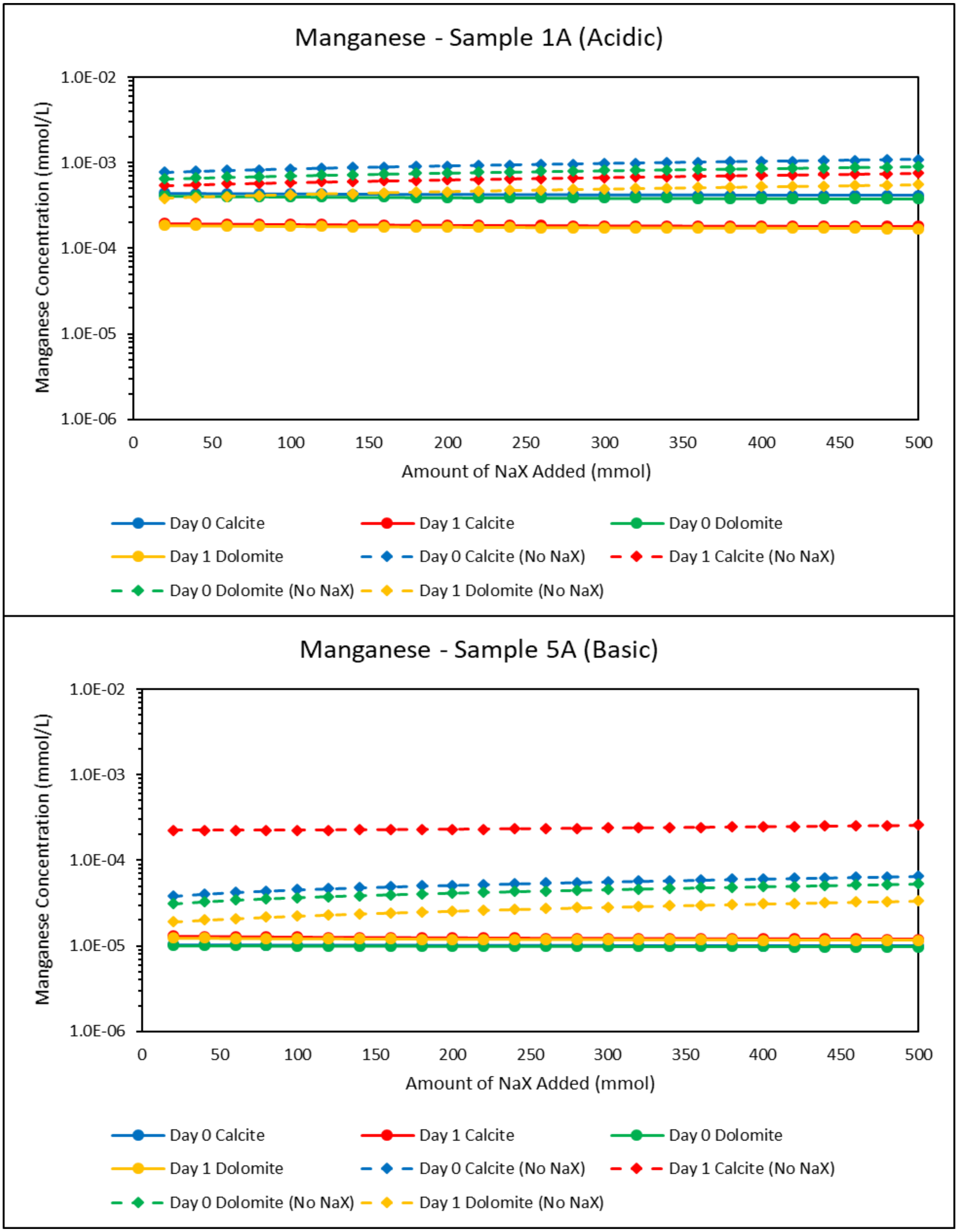


Figure 20 - Summary results of Mn concentrations with the incremental addition of NaX from batch reaction modeling. The top graph is Sample 1A (acidic), and the bottom graph is Sample 5A (basic). Solid lines with circles indicate samples with exchange, while dashed lines with diamonds indicate samples without exchange. Note that scales are logarithmic and identical for both Sample 1A and Sample 5A.

Sodium

Sample 1A (25°C, acidic)

Sodium modeling results are shown in Figure 21. For samples with no exchange, Na concentrations were approximately the same as the amount of NaX being added at each step, and increases were essentially linear (note that Figure 21 is logarithmic). As such, analysis of samples without exchange and comparison to samples with exchange was not possible, so only the results for exchange solutions are presented below. Overall average initial and final Na concentrations were 142.868 mmol/L (range 124.490-161.150) and 207.218 mmol/L (range 174.610-240.760), respectively, with solution concentrations increasing by an average of 44.6% (range 40.3-49.4). For starting chemistries, Day 0 solutions had ≈23% higher initial and ≈29% higher final concentrations compared to Day 1. Overall average changes for the 2 chemistries were similar, though Day 0 increased slightly more with a ΔNa = 48.3% (range 47.3-49.4) compared to ΔNa = 41.0% (range 40.3-41.7) for Day 1. The choice of solid solution also yielded similar initial and final average Na concentrations, with dolomite/rhodochrosite having slightly greater initial (≈5.5%) and final (≈7%) concentrations compared to calcite/rhodochrosite. Overall changes were also similar at 43.8% (range 40.3-47.3) for calcite/rhodochrosite versus 45.5% (range 41.7-49.4) for dolomite/rhodochrosite.

Sample 5A (25°C, basic)

Similar to Sample 1A, Na concentrations for basic Sample 5A also increased linearly, with concentrations again approximating the amount of NaX being added at each step. As with Sample 1A, the results below are only presented for samples with exchange. Overall initial and final sodium concentrations were 55.474 mmol/L (range

50.962-60.956) and 70.804 mmol/L (range 65.754-76.609), respectively, with a ΔNa = 27.7% (range 25.7-29.7). For starting chemistries, Day 1 solutions had ≈10% higher initial and ≈7% higher final Na concentrations than Day 0 solutions, and the average ΔNa values for both were similar at 29.4% (Day 0; range 29.0-29.7) and 26.1% (Day 1; range 25.7-26.4). Solid solutions of dolomite/rhodochrosite had initial and final average concentrations that were both ≈8.6% greater than concentrations for calcite/rhodochrosite, but overall average changes were equivalent for both types of solid solution at 27.7% (range 26.4-29.0 for calcite/rhodochrosite; range 25.7-29.7 for dolomite/rhodochrosite). Comparison of acidic Sample 1A and basic Sample 5A revealed acidic solutions with average initial and final concentrations that were generally 2-3 times greater than basic solutions regardless of starting chemistry or type of solid solution. Additionally, average ΔNa values were ≈55-65% higher for acidic versus basic solutions.

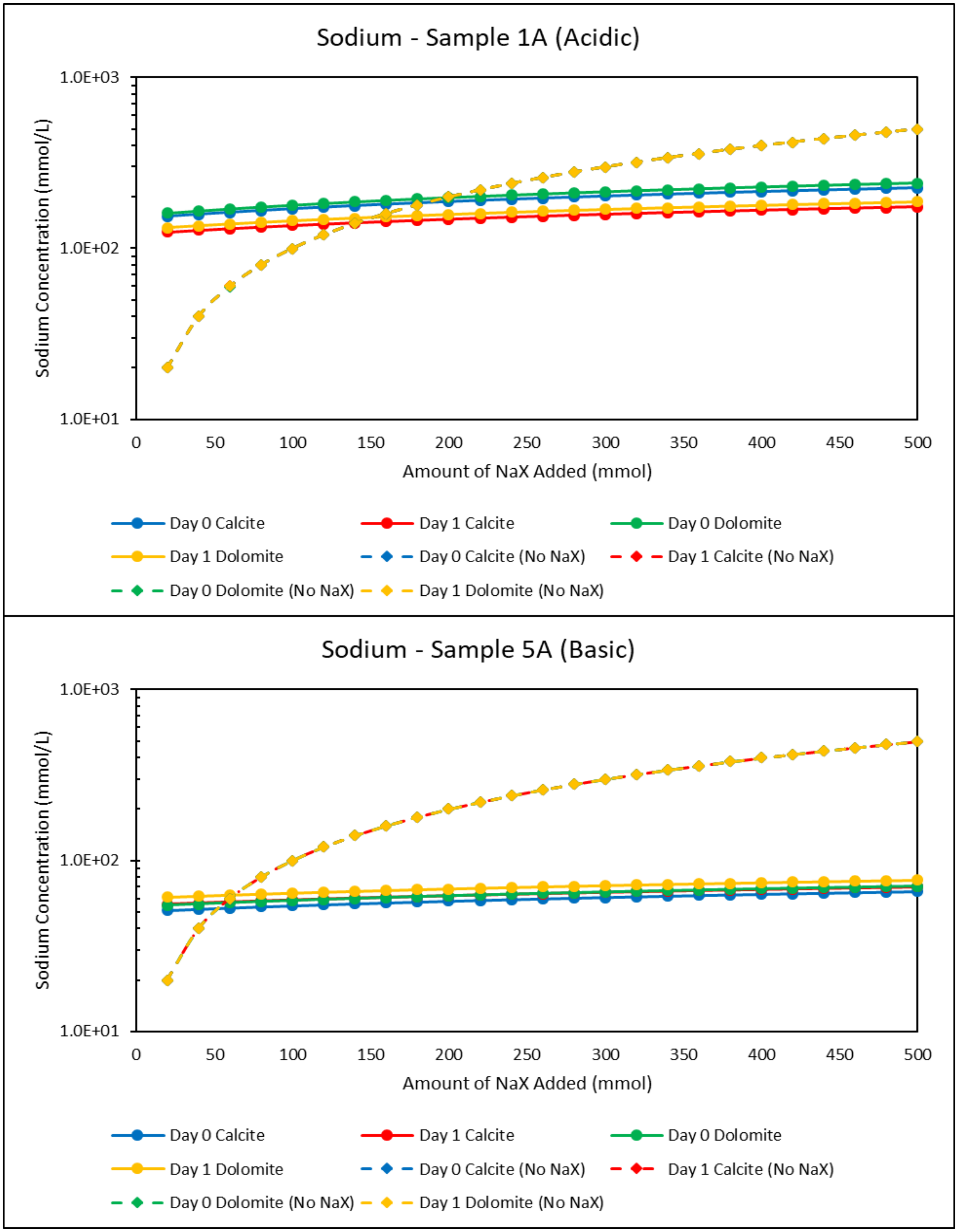


Figure 21 - Summary results of Na concentrations with the incremental addition of NaX from batch reaction modeling. The top graph is Sample 1A (acidic), and the bottom graph is Sample 5A (basic). Solid lines with circles indicate samples with exchange, while dashed lines with diamonds indicate samples without exchange. Note that scales are logarithmic and identical for both Sample 1A and Sample 5A.

Magnesium and Mg/Ca Ratio

Sample 1A (25°C, acidic)

Magnesium and Mg/Ca ratios were calculated for dolomite/rhodochrosite solutions and are shown in Figure 22 and Figure 23. (Since Mg was not artificially added, only solutions with dolomite/rhodochrosite were relevant, and both overall and solid solution-specific results are the same.) Average initial and final Mg concentrations were 11.364 mmol/L (range 4.844-17.884) and 14.191 mmol/L (range 7.097-21.285) for solutions with no exchange. These concentrations were ≈1.8 times and ≈2.7 times greater, respectively, compared to solutions with exchange, which had an average initial concentration of 6.346 mmol/L (range 3.024-9.669) and a final concentration of 5.213 mmol/L (range 2.571-7.854). Average changes were significantly different, as solutions without exchange increased (ΔMg = 32.8%; range 19.0-46.5) while solutions with exchange decreased (ΔMg = (-)16.9%; range (-)15.0-(-)18.8). The Mg/Ca ratio for solutions with exchange was nearly double that of solutions without exchange. Ratios for exchange solutions increased from an average of 1.167 (range 0.948-1.387) to an average of 1.247 (range 1.078-1.417), or an average increase of 7.9% (range 2.2-13.7). For solutions without exchange, ratios increased from an average of 0.628 (range 0.255-1.000) to an average of 0.668 (range 0.335-1.000). This increase was an average of 15.7% (range 0.0-31.4), or approximately double that of exchange solutions. Of note, however, is that the Day 0 starting solution with no exchange exhibited identical initial and final Ca and Mg values, giving it a ratio of 1.000 and, therefore, 0.0% change.

Regarding starting chemistries, since dolomite was the only Mg-containing phase, there was only 1 solution per classification (e.g., Day 0 with exchange, Day 0 without exchange, and so forth), so reported results are for single solutions. The Day 0 solution without exchange had initial and final concentrations that were ≈1.9 and ≈2.7 times greater than the Day 0 solution with exchange and a ΔMg = 19.0% compared to (-)18.8% for no exchange. These concentration trends were also similar for Day 1 with no exchange compared to Day 1 with exchange, though the increase in Mg was even greater for Day 1 with no exchange (46.5% versus (-)15.0). Comparing Day 0 and Day 1 solutions with exchange, initial and final Day 0 concentrations were a little over 3 times higher than Day 1 concentrations, though ΔMg values were similar for both solutions. For Day 0 and Day 1 solutions without exchange, initial and final Day 0 concentrations were ≈3.7 and ≈3 times greater, respectively, than Day 1 concentrations, but the ΔMg for Day 1 was more than double that for Day 0. The initial and final Mg/Ca ratio was greatest for Day 0 with exchange, with values that were ≈39% and ≈42% greater, respectively, than Day 0 without exchange and ≈46% and ≈31% greater, respectively, than Day 1 with exchange. The initial ratio for Day 1 with exchange was ≈3.7 times greater than that for Day 1 without exchange, while the final ratio was ≈3.2 times greater. Compared to Day 0 without exchange, Day 1 without exchange had an initial ratio nearly 4 times lower and a final ratio ≈3 times lower. As mentioned previously, the Day 0 solution with no exchange had no change in the Mg/Ca ratio.

Sample 5A (25°C, basic)

As with acidic solutions, dolomite/rhodochrosite solid solution-specific and overall results were the same. Basic solutions with exchange typically had quite low average Mg concentrations, with an initial value of 0.096 mmol/L (range 0.077-0.115) and a final value of 0.083 mmol/L (range 0.071-0.096). These concentrations were ≈4.5 and ≈9 times less than concentrations for solutions with no exchange. Solutions without exchange had an average initial concentration of 0.449 mmol/L (range 0.008-0.891) and final concentration of 0.739 mmol/L (range 0.033-1.445). The ΔMg was (-)12.0% (range (-)7.4-(-)16.6) for solutions with exchange compared to a positive and much larger ΔMg of 180.8% (range 62.3-299.4) for solutions without exchange. Average initial Mg/Ca ratios for solutions with and without exchange were 0.972 (range 0.443-1.502) and 0.500 (range 0.001-1.000), respectively, while average final ratios were 1.050 (range 0.609-1.491) and 0.501 (range 0.002-1.000), respectively. Ratios for solutions with exchange increased an average of 18.4% (range (-)0.7-37.5), while ratios for solutions without exchange increased 150.4% (range 0.0-300.7). As with the acidic solutions, the Day 0 solution with no exchange had initial and final Ca and Mg values that were the same and, therefore, a Mg/Ca ratio of 1.000. Additionally, change in the ratio for the other solution without exchange was quite small (Mg/Ca increased by 0.001755 units before rounding). There were also more than 2 orders of magnitude difference between concentrations in the 2 solutions with no exchange.

Like acidic solutions, basic solutions also had only 1 solution per classification. The Day 0 solution without exchange had initial and final concentrations that were nearly 8 and 15 times greater, respectively, than the Day 0 solution with exchange and a positive ΔMg of 62.3% compared to (-)16.6% for exchange. The opposite effect was true for the Day 1 solutions, where the exchange solution had an initial concentration nearly 10 times higher and a final concentration more than double the solution with no exchange. Mg concentrations again decreased for exchange with a ΔMg = (-)7.4% compared to an increase of 299.4% for the solutions without exchange. Comparison of

Day 0 and Day 1 solutions with exchange showed initial and final concentrations that were ≈50% and ≈35% lower, respectively, for Day 1 versus Day 0, and Day 1 also had a lower decrease in concentrations versus Day 0 ((-)7.4% versus (-)16.6%). For the 2 solutions with no exchange, Day 0 had an initial concentration that was more than 2 orders of magnitude greater and a final concentration that was more than 40 times greater than those for Day 1, though the overall change for Day 0 was nearly 5 times less. The initial and final Mg/Ca ratios for Day 0 with exchange were both ≈1.5 times greater than for Day 0 with no exchange, and the exchange ratio changed by only (-)0.7% while the ratio for no exchange remained unchanged. Compared to Day 1 with exchange, the initial and final ratios for the Day 0 solution with exchange increased nearly 3.5 and 2.5 times, respectively, though the ΔMg was much higher for Day 1 (37.5%). The Day 1 solution with exchange had an initial ratio that was ≈443 times greater and a final ratio that was over 300 times greater compared to Day 1 with no exchange. The Day 0 and Day 1 solutions with no exchange were vastly different due to the very low Mg concentrations for the Day 1 solution, which produced initial and final Mg/Ca ratios over 1000 and nearly 500 times greater in Day 0 versus Day 1.

Overall, comparisons of acidic versus basic samples revealed that acidic solutions had average Mg concentrations that were generally much higher than basic solutions, often by more than an order of magnitude. Changes in Mg concentrations were negative and similar for both acidic and basic solutions with exchange. However, for solutions without exchange, these changes were positive in both acidic and basic solutions, though basic solutions typically showed larger increases. Other than Day 0 solutions with exchange, acidic solutions typically had higher Mg/Ca ratios than basic solutions, though basic solutions tended to have greater increases in ratios than acidic solutions. For both the acidic and basic solutions, Day 0 solutions with exchange were the only solutions with Mg/Ca ratios near or above 1.4.

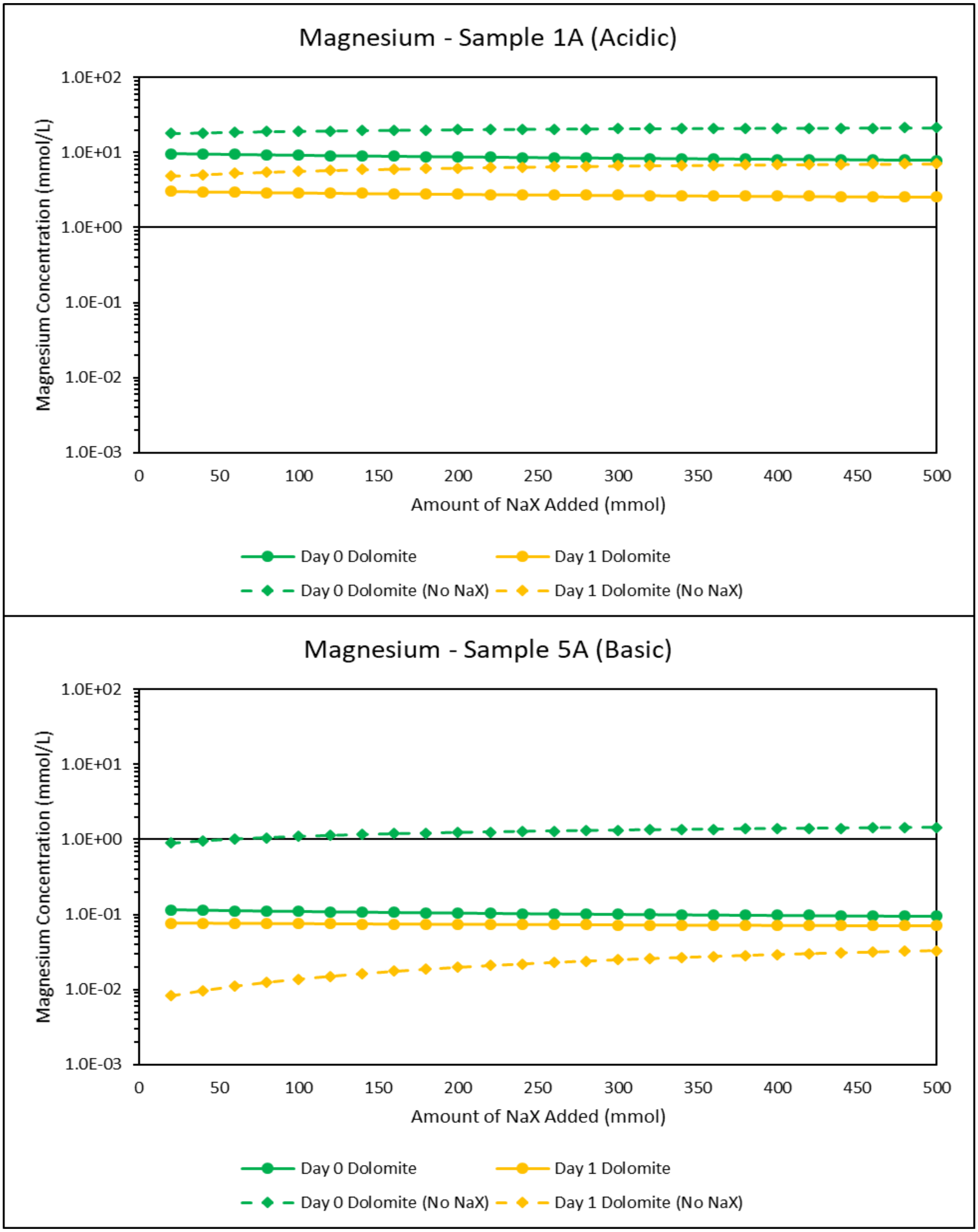


Figure 22 - Summary results of Mg concentrations with the incremental addition of NaX from batch reaction modeling for the 4 model solutions containing dolomite/rhodochrosite solid solution. The top graph is Sample 1A (acidic), and the bottom graph is Sample 5A (basic). Solid lines with circles indicate samples with exchange, while dashed lines with diamonds indicate samples without exchange. Note that scales are logarithmic and identical for both Sample 1A and Sample 5A.

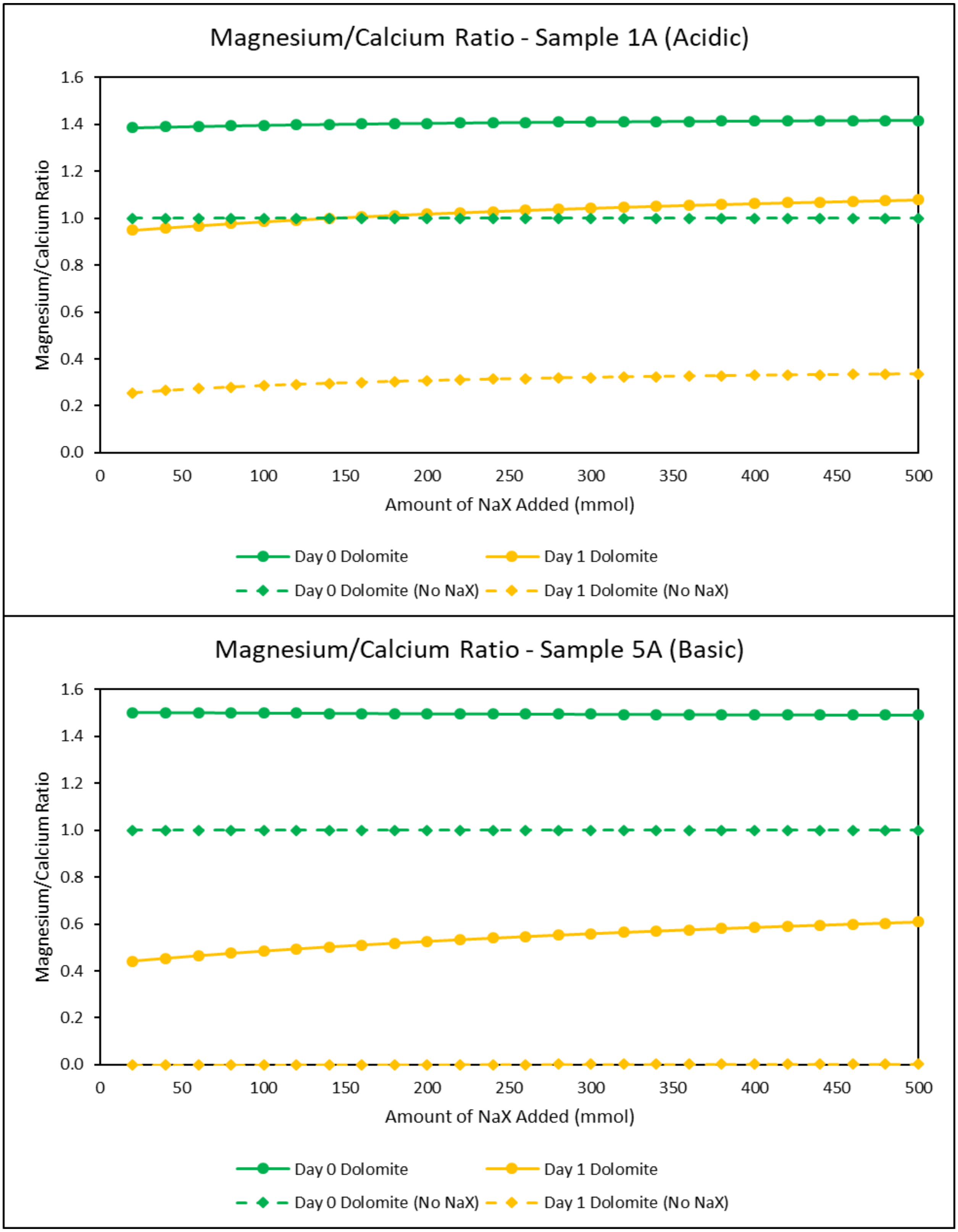


Figure 23 - Summary Mg/Ca ratios with the incremental addition of NaX from batch reaction modeling for the 4 model solutions containing dolomite/rhodochrosite solid solution. The top graph is Sample 1A (acidic), and the bottom graph is Sample 5A (basic). Solid lines with circles indicate samples with exchange, while dashed lines with diamonds indicate samples without exchange.

Aqueous Species Distribution and Saturation Indices for Mn Compounds

PHREEQCI was used to predict the distribution of aqueous Mn species in each of the modeling solutions. Mn^{2+} species were present as $Mn(OH)_3^-$, Mn^{2+}, $MnCO_3$, $MnHCO_3^+$, and $MnOH^+$. Mn^{3+} was present solely as Mn^{3+}, and Mn^{4+} was not predicted in the aqueous form. Mn^{6+} was present as MnO_4^{2-}, and Mn^{7+} was predicted as MnO_4^-. The only species with appreciable concentrations included: Mn^{2+}, with a concentration range of 10^{-6} to 10^{-4} mmol/L (1-100 nanomoles/L) in all solutions; $MnCO_3$, with concentrations in all solutions in the range of 10^{-6} mmol/L; and $MnHCO_3^+$, with concentrations in all solutions in the range of 10^{-6} to 10^{-4} mmol/L. ("All solutions" refers to any solution regardless of pH, starting chemistry, type of solid solution, or presence or absence of exchange.) All other aqueous Mn species were present at concentrations of 10^{-7} or lower (< 1 nanomole/L), with many being several orders of magnitude lower. There were 4 additional Mn^{2+} species present in all solutions – $Mn(NO_3)_2$, $MnCl^+$, $MnCl_2$, and $MnCl_3^-$ – at concentrations up to 10^{-4} mmol/L. However, these 4 species were only present because they were bound to other ions added to fix pH (NO_3^- from HNO_3) and for charge balancing (Cl^- from KCl). These ions (Cl^- and NO_3^-) were chosen for their stated purposes since they were not essential species being investigated in the models.

Based on the ions present in each solution, PHREEQCI also predicted saturation indices for 10 Mn-containing compounds. Nsutite ($(Mn^{4+},Mn^{2+})(O,OH)_2$), birnessite ($(Na,Ca)_{0.5}(Mn^{4+},Mn^{3+})_2O_4\cdot 1.5H_2O$), and pyrolusite ($Mn^{4+}O_2$) were predicted to be saturated in all solutions (again, without regard to pH, starting chemistry, type of solid solution, or the presence or absence of exchange). Hausmannite ($Mn^{2+}Mn^{3+}{}_2O_4$) saturation was predicted in all basic solutions. Bixbyite ($Mn^{3+}{}_2O_3$) and manganite

($Mn^{3+}O(OH)$) were saturated in all solutions with exchange, in basic solutions without exchange, and in both acidic Day 1 solutions with calcite/rhodochrosite (1 with and 1 without exchange). Pyrochroite ($Mn(OH)_2$), both ordered and disordered rhodochrosite ($MnCO_3$), and $MnCl_2 \cdot 4H_2O$ were all predicted to be undersaturated in all solutions.

Modeling Discussion

Modeling results were presented primarily regarding the presence or absence of exchange, as other comparisons tended to be much less informative or representative of trends in the data. For example, using Ca values for Sample 1A, a comparison of Day 0 and Day 1 starting chemistries showed average changes of (-)1.0% for Day 0 compared to (+)2.3% for Day 1 going from 20 millimoles to 500 millimoles of NaX added. In other words, the changes could be interpreted as similar and, thus, insignificant. Realistically, both Day 0 and Day 1 Ca concentrations *with* NaX showed average *decreases* of >20% compared to average *increases* of ≈20% for samples *without* NaX.

Overall, acidic solutions yielded greater concentrations for all parameters related to carbonate dissolution (alkalinity, Ca, Mn, and Mg) compared to basic solutions. As with experimental solutions, this was the expected result since dissolution should be greater at lower pH values. For both acidic and basic solutions, Ca, Mn, and Mg concentrations were all lower in solutions with exchange than in solutions without exchange, and changes in concentration were negative (i.e., decreasing) for solutions with exchange versus positive without. Such trends suggest that cation exchange was indeed occurring, resulting in decreasing ion concentrations in solutions with exchange.

A further breakdown of the solutions based on starting chemistries (Day 0 or Day 1) and solid solution type showed these trends to continue to hold for solutions with exchange.

A comparison of starting chemistries revealed that, for acidic solutions with exchange, Day 0 concentrations of Ca, Mn, and Mg were all greater than Day 1 concentrations, suggesting greater dissolution in Day 0 solutions. This greater dissolution seems plausible since Day 0 solutions had lower pH values compared to Day 1 (6.00 versus 6.38), and greater dissolution should occur at a lower pH. Additionally, concentrations of the 3 ions were already present in Day 1 solutions but not in Day 0 solutions, which may have had an inhibitory effect on dissolution in Day 1 that was not present in Day 0. Both Day 0 and Day 1 exchange solutions had similar negative overall changes in concentration for each ion, suggesting that the extent of cation exchange was similar for each solution regardless of starting chemistry. For acidic samples without exchange, Day 0 concentrations were similar to Day 1 concentrations for Ca and greater for Mn and Mg, while changes in concentrations of each ion were all positive. These concentrations again make sense in light of the lower pH values in Day 0 solutions, resulting in greater dissolution and higher ion concentrations. Additionally, the positive overall change was expected without exchange (or other processes) occurring.

For basic samples with exchange, concentration trends varied for each of the ions mentioned above. For Ca and Mn, Day 1 concentrations were greater than those for Day 0, and both ΔCa and ΔMn were negative. For Mg, Day 0 concentrations were higher than Day 1 concentrations, but overall changes were still negative. Day 1 Ca and Mn concentrations may have been higher since Day 1 solutions already contained quantities of both ions, whereas Day 0 solutions did not. Day 0 Mg concentrations were likely higher because PHREEQCI predicted greater dissolution of the Day 0 dolomite/rhodochrosite solid solution, as evidenced by higher alkalinity values for Day 0 versus Day 1 along with a lower pH for the Day 0 solution. Lower Ca and Mn values, despite higher dissolution, were likely the result of cation exchange combined with the precipitation of Mn calcite, which, as corroborated by SEM images of experimental samples, occurred to a greater extent in basic samples. These same trends in concentrations occurred in basic samples without exchange. However, in this case, concentration changes of all 3 ions were positive since no exchange was occurring. Again, referencing the SEM images of experimental samples, basic samples without clays had even more precipitation than basic samples with clays, as evidenced by SEM images of Sample 7A (Figure 16 and Figure 17), particularly the extensive development of acicular structures that were identified as Mn carbonate. An important note for all samples, both acidic and basic, is the possibility for Mn to oxidize and precipitate as Mn oxides. A greater loss of Mn than Ca could indicate such processes even in the absence of visual confirmation of Mn oxides in precipitates. Such was potentially the case with several of the experimental samples. Looking at Figure 10, acidic samples all showed steady or increasing trends in Ca concentrations at Day 14, as did all but 2 of the basic samples. However, looking at Figure 12, 2 high-temperature acidic samples (3B and 4B, both with no clay) showed continuously decreasing levels of Mn and continued to show downward trends at Day 14 despite trends of increasing Ca. For basic samples, 3 of 4 room-temperature samples also showed downward Day 14 trends in Mn concentrations. All 4 high-temperature samples had minimal (nanomolar) concentrations at Day 14 despite increasing trends in Ca for 2 of the 4 samples. The fact that only some of the samples with decreasing Mn trends had clay indicates that other processes must be occurring, the most likely of which was precipitation of Mn oxides.

Regarding the type of solid solution present, solutions without exchange had significantly greater Ca and Mn concentrations than solutions with exchange for both acidic and basic solutions regardless of solid solution type. Again, this trend was expected, as cation exchange should result in decreased Ca and Mn concentrations as it removes them from the system. In contrast, solutions without exchange would see continued increases unless ions are removed in some other manner (e.g., precipitation or adsorption). Acidic solutions with and without exchange exhibited greater Ca and Mn concentrations in solutions with calcite/rhodochrosite than those with dolomite/rhodochrosite. However, exchange solution concentrations decreased while concentrations in solutions without exchange increased. Basic solutions with exchange had similar Ca and Mn concentrations for calcite/rhodochrosite and dolomite/rhodochrosite, along with negative changes in Ca and Mn concentrations. Basic solutions without exchange, on the other hand, had a greater average Ca concentration for dolomite/rhodochrosite solutions but greater Mn concentrations in solutions with calcite/rhodochrosite, though changes were positive for both ions. Greater concentrations of Ca and Mn in calcite/rhodochrosite solutions should be anticipated regardless of the presence or absence of exchange since calcite is significantly more soluble than dolomite and should undergo greater dissolution. Decreases in Ca and Mn concentrations in solutions with exchange are again expected as cations are removed from solution, with greater removal occurring as greater amounts of NaX exchanger are added. Basic concentrations of Ca and Mn should ideally follow the same trends as those for acidic solutions, though likely producing lower concentrations since dissolution is lower with increased pH. The lower basic Ca concentration noted in the Day 1 calcite/rhodochrosite solution without exchange compared to the Day 1 dolomite/rhodochrosite solution without exchange is not what would be predicted. However, there were only 2 solutions without exchange for each solid solution, 1 for each starting chemistry (Day 0 or Day 1). This low sample size likely confounds analyses, both here and with other geochemistry parameters.

Alkalinity values indicate the extent of carbonate dissolution and, as expected, were greater in acidic solutions versus basic solutions. Additionally, values were greater in both acidic and basic solutions with exchange compared to solutions without regardless of starting chemistry or solid solution. Greater alkalinities and, therefore, greater dissolution in solutions with exchange provides evidence supporting the hypothesis that the presence of clays and exchange enhances carbonate dissolution. Ideally, Day 0 starting solutions should have had greater dissolution and higher alkalinities since initial pH values were lower than in Day 1 solutions. This trend was true for acidic solutions with and without exchange and the basic solutions with exchange. However, the basic solutions without exchange had a higher average alkalinity for Day 1 versus Day 0. This greater average was likely due to the large alkalinity value for the Day 1 dolomite/rhodochrosite solution, which resulted in a higher average alkalinity for Day 1 despite alkalinities for both Day 0 solutions lying between the Day 1 alkalinities (i.e., there was significant overlap of values). For acidic and basic solutions with exchange, both calcite/rhodochrosite and dolomite/rhodochrosite had similar alkalinities and alkalinity values that were greater than for solutions without exchange. This trend again supports the hypothesis that cation exchange enhances dissolution. For solubility, calcite/rhodochrosite should be more soluble and exhibit greater dissolution and higher alkalinities than dolomite/rhodochrosite. However, this was not the case for any of the calcite/rhodochrosite solutions, regardless of the presence or absence of exchange. The most likely explanation for this was that the greater solubility of the calcite/rhodochrosite solid solutions caused equilibrium and then supersaturated conditions to be reached, resulting in precipitation of Mn calcite and lower alkalinity values in calcite/rhodochrosite solutions compared to dolomite/rhodochrosite solutions.

Sodium concentrations in solutions without exchange essentially increased linearly and matched the amount of NaX added to the solution at each increment. As such, comparisons for samples without exchange were not possible, though this did help to verify that the PHREEQCI models were properly set up. For solutions with exchange, Na concentrations and changes were greater for acidic versus basic samples, indicating greater exchange occurring at lower pH values. This trend was expected since carbonate dissolution is greater at lower pH, resulting in greater liberation of divalent cations (Ca^{2+}, Mg^{2+}, and Mn^{2+}) that were then able to displace Na at exchange sites on NaX moieties. This same effect was seen with acidic Day 0 starting chemistries, which also had lower initial pH values compared to Day 1 chemistries. This effect was not seen in basic solutions, where initial pH values were much more similar for Day 0 and Day 1, resulting in similar Na concentrations. For solid solutions, both acidic and basic calcite/rhodochrosite solutions should ideally have had greater Na concentrations owing to the greater solubility of calcite and the resulting release of more divalent cations for exchange. In this case, however, the acidic solutions had similar concentrations for both types of solid solution, while the basic solutions had slightly greater concentrations in the dolomite/rhodochrosite solutions. There was, again, a limited number of samples and a significant overlap of concentrations that likely confounded the interpretation of results with respect to solid solution.

Regarding Mg/Ca ratios, modeling solutions exhibited greater ratios in solutions with exchange than corresponding solutions without exchange. These greater ratios were particularly noteworthy when observing starting chemistries, where the acidic and basic Day 0 solutions of dolomite/rhodochrosite had Mg/Ca ratios near 1.4 and 1.5, respectively. These values are important because ratios near or above 1.4 have been linked to elevated (> 20 ppb) Cr levels in the COA (Figure 3),[32] which has implications for cities like Norman, OK, that use COA groundwater as a source of drinking water for their citizens.

The last modeling topics examined were the aqueous species distributions and saturation indices of Mn compounds. Mn^{2+} was the only aqueous Mn species with any significant concentrations and existed in all solutions in the 1-100 nanomolar range as $Mn^{2+}_{(aq)}$, $MnCO_{3(aq)}$, and $MnHCO_3{}^{+}_{(aq)}$. Mn^{3+}, Mn^{6+}, and Mn^{7+} were all predicted as well, though these concentrations were sub-nanomolar, often by several orders of magnitude. Saturation indices predicted the supersaturation of 3 Mn oxide compounds (nsutite, birnessite, and pyrolusite) in all solutions and 3 other Mn oxides (hausmannite, bixbyite, and manganite) in specific solutions. Each of these 6 oxides contains 1 or more Mn ions (Mn^{2+}, Mn^{3+}, Mn^{4+}) that could potentially precipitate out or adsorb to other mineral surfaces, thereby reducing Mn concentrations in solutions. Additionally, both aqueous ions and Mn oxides may participate in oxidation-reduction reactions, further affecting the solution chemistry. Such oxidation-reduction reactions have important implications in groundwater such as that in the COA, where the mobility and, often, the toxicity of various elements (e.g., As, Cr, Se) are dependent on the oxidation states of the ions and may readily change in the presence of a strong oxidation-reduction agent like Mn. Further, if redox cycling occurs, sub-nanomolar concentrations of ions like Mn may be all that is required to effect noticeable redox changes on other ions.

Conclusions and Future Work

Experiments and models exploring the behavior of Mn-bearing carbonates in solution with and without exchangeable Na-clay revealed a complex time evolution of the geochemical parameters examined. Unexpected results in both experiments and PHREEQCI modeling occurred and were generally believed to be a byproduct of low numbers of samples. An opportunity to perform all of the planned experiments would have provided more results and, thus, permitted a more complete explanation of the data and observed trends. However, the bulk of the data does appear to support the hypothesis that carbonate dissolution releases divalent cations (e.g., Ca^{2+}, Mg^{2+}, and Mn^{2+}) that are then free to undergo cation exchange with clays. This exchange results in decreased concentrations of the divalent cations, resulting in a positive feedback loop whereby more carbonates can dissolve and continue the process. The solution's temperature and pH play a role in the extent of dissolution, with greater dissolution and, therefore, greater alkalinities and divalent cation concentrations seen in the setting of lower pH and lower temperature (since carbonates are anomalously more soluble at lower temperatures). In the presence of Na clays, these divalent cations are exchanged for Na^+, resulting in decreasing aqueous concentrations of divalent cations and increasing concentrations of Na^+. These effects were noted in all experimental samples and modeling solutions containing clay/exchanger regardless of pH or temperature, whereas overall increases in divalent cation concentrations were seen in solutions without clay/exchanger. Of note was that, as seen in SEM images, reprecipitation of products such as Mn carbonates did occur, though the effects of this and other processes (e.g., adsorption) were not quantified. With modeling solutions, the occurrence of cation exchange was not dependent on the starting chemistry of the solutions, though the extent of exchange was affected. This trend was also true for the type of solid solution present in each solution. Lastly, modeling results predicted the formation of numerous aqueous Mn species and saturated Mn compounds. Though concentrations of Mn species were in the nanomolar range or less, these minute concentrations may be all that is required to participate in redox conversions of other metal cations like As and Cr to more soluble and, often, more toxic species. Such conversions are particularly true in Mn cycling and warrant further study to understand better the effects of Mn species in aquifers like the COA. Additionally, precipitation of these Mn oxides, along with Mn carbonates, would undoubtedly affect aqueous Mn concentrations.

Unfortunately, a significant amount of proposed work had to be abandoned when COVID-19 forced the closure of laboratory spaces, leaving several sets of experiments and a more extensive investigation of Mn (hypothesis 2) unaccomplished. The pursuit of additional experiments using other Mn carbonates (e.g., Mn dolomite and rhodochrosite) should help further elucidate the effects of pH, temperature, and the presence or absence of clay on dissolution characteristics and release of Mn^{2+} from Mn carbonates. Inclusion of larger sample numbers, more frequent sampling (e.g., daily, twice daily), and longer study duration will help minimize errors associated with too few sample numbers and large variations in the few samples tested. Also, more frequent SEM characterization and, potentially, other characterizations such as XRD may further help explain many of the trends seen in alkalinity and aqueous ion concentrations (Figure 8 through Figure 12). Varying the amount of clay added to experimental solutions as was done with the incremental addition of NaX in modeling solutions would also be prudent to provide better comparisons between experimental and modeling results. Lastly, a more detailed look at Mn and modeled aqueous distributions and saturation products is critical to a complete understanding of the Mn in an aquifer system such as the COA. In addition to modeling cation exchange, such work should also examine other effects on Mn concentrations and products, including oxidation-reduction reactions, adsorption to other minerals, and possibly even organic matter, including microbial effects on Mn cycling.

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Appendix

Appendix 1 – ICP-OES results for Mn calcite laboratory experiments. Samples highlighted in gray contain clay. Sample #'s shaded in blue are at 25°C, and sample #'s shaded in red are at 60°C. Samples 1-4 are acidic, while samples 5-8 are basic.

Sample #	Temp (°C)	Buffer (both at 10 mM conc.)	Mn Calcite Initial Mass (g)	Na-Bentonite Initial Mass (g)2	Original pH
MC1A	**25**	MES	0.5000	0.0000	6.00
MC1B	**25**	MES	0.4990	0.0000	6.08
MC2A	**25**	MES	0.4984	0.1334	6.00
MC2B	**25**	MES	0.4979	0.1329	6.07
MC3A	**60**	MES	0.4985	0.0000	6.02
MC3B	**60**	MES	0.4985	0.0000	6.01
MC4A	**60**	MES	0.4967	0.1330	6.02
MC4B	**60**	MES	0.4969	0.0000	6.01
MC5A	**25**	EPPS	0.4985	0.0000	7.96
MC5B	**25**	EPPS	0.4973	0.0000	7.97
MC6A	**25**	EPPS	0.4993	0.1321	7.93
MC6B	**25**	EPPS	0.4981	0.1327	7.98
MC7A	**60**	EPPS	0.4986	0.0000	8.00
MC7B	**60**	EPPS	0.4981	0.0000	8.10
MC8A	**60**	EPPS	0.4974	0.1331	7.97
MC8B	**60**	EPPS	0.4981	0.0000	8.04

Appendix 1 – ICP-OES results for Mn calcite laboratory experiments, continued. Samples highlighted in gray contain clay. Sample #'s shaded in blue are at 25°C, and sample #'s shaded in red are at 60°C. Samples 1-4 are acidic, and samples 5-8 are basic.

Sample #	Measured pH (Benchtop)					Measured pH (OSU Laboratory)				
	Day 1	Day 3	Day 5	Day 7	Day 14	Day 1	Day 3	Day 5	Day 7	Day 14
MC1A	6.38	6.51	6.68	6.83	6.95	6.69	6.78	6.95	7.00	6.69
MC1B	6.41	6.54	6.71	6.81	6.93	6.74	6.84	6.98	6.95	6.74
MC2A	6.36	6.51	6.67	6.84	7.08	6.71	6.79	6.91	6.96	6.71
MC2B	6.41	6.57	6.71	6.93	7.21	6.93	6.74	6.94	6.99	6.93
MC3A	6.57	6.67	6.84	6.96	7.06	6.59	6.74	6.85	6.96	6.59
MC3B	6.49	6.60	6.75	6.85	7.07	6.59	6.72	6.79	6.84	6.59
MC4A	6.62	6.74	7.00	7.05	7.08	6.62	6.86	6.94	7.02	6.62
MC4B	6.42	6.53	6.74	6.86	7.16	6.61	6.61	6.75	6.86	6.61
MC5A	7.97	7.99	7.94	8.03	7.94	7.80	7.89	7.87	7.84	7.80
MC5B	7.96	7.99	8.05	8.01	8.01	7.80	7.85	7.87	7.88	7.80
MC6A	7.93	7.94	8.00	7.96	7.88	7.75	7.84	7.78	7.82	7.75
MC6B	7.97	7.98	8.02	8.00	7.97	7.76	7.88	7.82	7.82	7.76
MC7A	8.00	7.92	8.02	8.01	7.96	7.75	7.88	7.81	7.85	7.75
MC7B	8.11	7.95	8.09	8.09	8.03	7.78	7.90	7.94	7.91	7.78
MC8A	7.97	7.92	7.97	7.97	7.99	7.67	7.73	7.86	7.80	7.67
MC8B	8.06	7.98	8.08	8.06	8.01	7.82	7.90	7.93	7.90	7.82

Appendix 1 – ICP-OES results for Mn calcite laboratory experiments, continued. Samples highlighted in gray contain clay. Sample #'s shaded in blue are at 25°C, and sample #'s shaded in red are at 60°C. Samples 1-4 are acidic, and samples 5-8 are basic. Cation values have been converted from ppm (as reported) to mmol/L.

Sample #	Total Alkalinity (mg CaCO3/L)					Calcium (mmol/L)				
	Day 1	Day 3	Day 5	Day 7	Day 14	Day 1	Day 3	Day 5	Day 7	Day 14
MC1A	525.68	515.44	493.72	517.92	494.48	14.116	13.495	14.247	11.955	13.085
MC1B	502.52	510.16	498.32	511.84	502.56	12.192	12.281	12.618	10.517	11.520
MC2A	518.60	526.56	499.16	518.84	515.80	13.882	13.686	13.969	12.096	12.692
MC2B	520.36	508.80	504.28	514.08	516.08	12.644	12.648	13.277	10.755	11.306
MC3A	461.16	463.52	451.48	452.80	468.16	14.252	14.898	15.190	13.558	13.519
MC3B	476.00	454.72	437.56	443.28	484.12	15.001	14.894	15.931	13.484	15.012
MC4A	483.80	470.64	473.40	474.36	467.44	13.744	13.562	13.797	12.279	12.804
MC4B	468.00	438.32	434.40	450.08	480.56	14.826	14.366	14.985	13.322	14.623
MC5A	415.52	387.08	415.56	408.60	416.68	1.537	1.312	1.522	1.225	1.245
MC5B	412.92	402.52	389.84	399.44	412.00	1.433	1.554	1.486	1.193	1.251
MC6A	388.84	383.80	384.08	381.08	389.48	1.762	1.198	1.198	1.073	1.180
MC6B	393.20	404.04	408.28	399.64	412.00	1.268	0.938	1.128	1.034	1.044
MC7A	408.12	388.20	389.32	389.68	394.52	1.411	0.927	1.000	0.951	1.037
MC7B	400.00	392.48	390.92	397.28	399.84	1.042	1.157	0.934	0.947	0.836
MC8A	382.88	376.80	477.64	379.52	386.32	1.502	1.316	0.992	0.938	0.971
MC8B	402.40	390.84	390.40	392.00	402.04	1.017	1.179	0.910	0.841	0.786

*Appendix 1 - ICP-OES results for Mn calcite laboratory experiments, continued. Samples highlighted in gray contain clay. Sample #'s shaded in blue are at 25°C, and sample #'s shaded in red are at 60°C. Samples 1-4 are acidic, and samples 5-8 are basic. Cation values have been converted from ppm (as reported) to mmol/L. * = values that were not zero but were <0.000164 mmol/L (0.164 µmol/L).*

Sample #	**Sodium (mmol/L)**					**Manganese (mmol/L)**				
	Day 1	**Day 3**	**Day 5**	**Day 7**	**Day 14**	**Day 1**	**Day 3**	**Day 5**	**Day 7**	**Day 14**
MC1A	2.964	0.803	0.901	0.637	0.818	1.510	1.541	1.585	1.335	1.472
MC1B	0.830	0.789	0.856	0.599	0.743	1.404	1.401	1.447	1.208	1.307
MC2A	1.109	1.036	1.094	0.844	0.962	1.571	1.555	1.604	1.360	1.416
MC2B	1.100	1.062	1.156	0.816	0.926	1.436	1.441	1.514	1.213	1.269
MC3A	0.822	0.862	0.892	0.692	0.731	1.605	1.661	1.679	1.459	1.490
MC3B	0.828	0.819	0.919	0.662	0.781	1.685	1.585	1.519	1.158	0.753
MC4A	1.062	1.088	1.170	0.899	0.981	1.533	1.513	1.525	1.334	1.338
MC4B	1.295	0.825	0.889	0.662	0.755	1.619	1.368	1.193	0.840	0.382
MC5A	0.013	<0.012	0.042	<0.027	<0.006	0.128	0.093	0.096	0.069	0.053
MC5B	<0.012	0.012	0.044	<0.027	<0.006	0.129	0.118	0.105	0.081	0.069
MC6A	0.327	0.242	0.256	0.137	0.207	0.125	0.105	0.098	0.085	0.087
MC6B	0.246	0.188	0.207	0.135	0.185	0.110	0.071	0.076	0.067	0.059
MC7A	<0.012	<0.012	<0.027	<0.027	<0.010	0.000*	0.000*	0.000*	0.000*	0.000*
MC7B	<0.012	0.123	<0.027	<0.027	<0.010	0.000*	0.000*	0.000*	0.000*	0.000*
MC8A	0.302	0.366	0.189	0.167	0.165	0.015	0.006	0.000*	0.000*	0.000*
MC8B	<0.012	0.086	<0.027	<0.027	0.017	0.000*	0.000*	0.000*	0.000*	0.000*

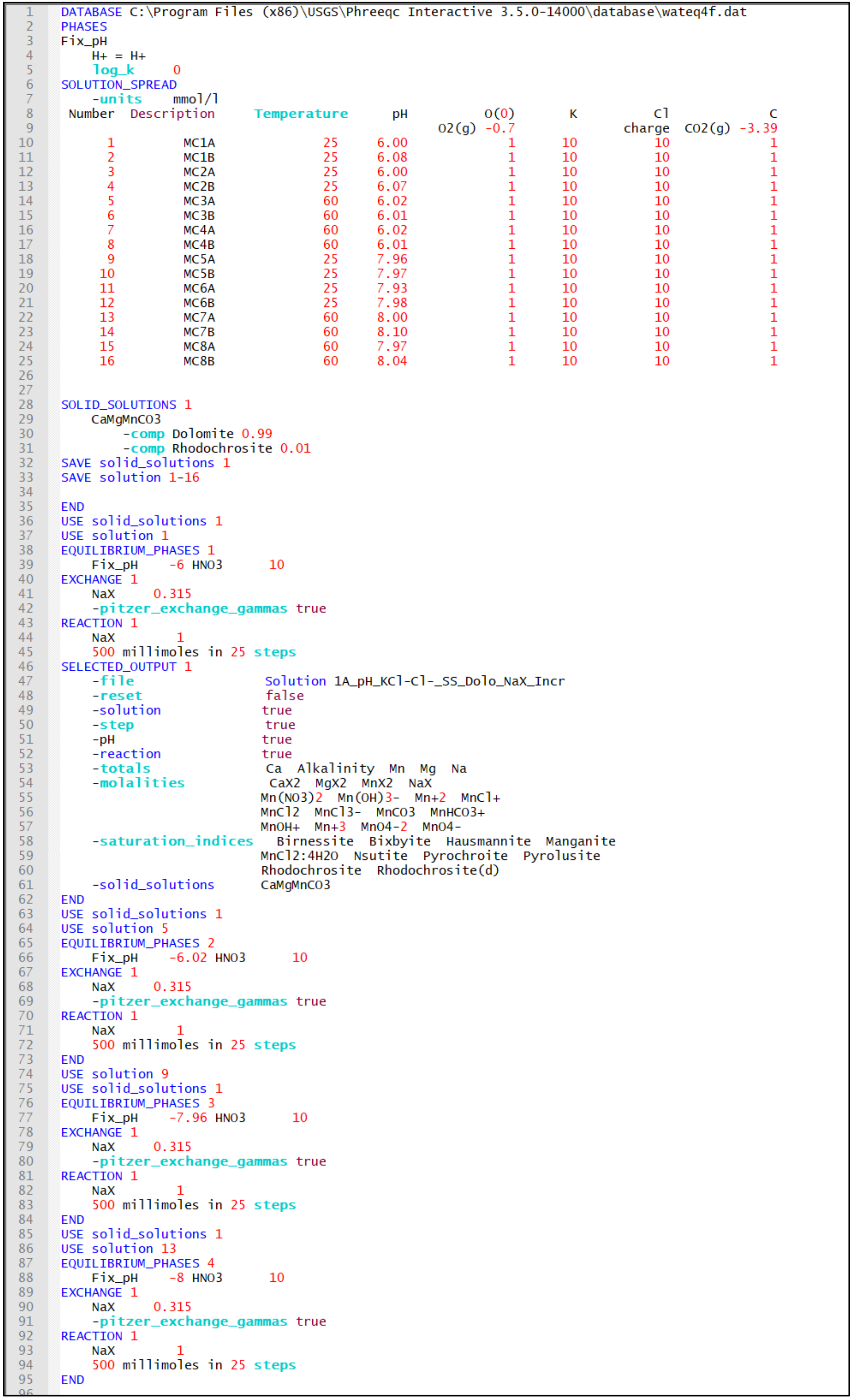
Appendix 1 – ICP-OES results for Mn calcite laboratory experiments, continued. Samples highlighted in gray contain clay. Sample #’s shaded in blue are at 25°C, and sample #’s shaded in red are at 60°C. Samples 1-4 are acidic, and samples 5-8 are basic. Cation values have been converted from ppm (as reported) to mmol/L.

Sample #	Potassium (mmol/L)					Magnesium (mmol/L)				
	Day 1	Day 3	Day 5	Day 7	Day 14	Day 1	Day 3	Day 5	Day 7	Day 14
MC1A	0.241	<0.012	0.183	0.054	0.114	<0.002	<0.002	<0.005	<0.006	<0.007
MC1B	0.147	0.078	0.197	0.053	0.105	<0.002	<0.002	<0.005	<0.006	<0.007
MC2A	0.030	<0.012	0.067	<0.032	<0.011	<0.002	<0.002	<0.005	<0.006	<0.007
MC2B	0.260	0.207	0.320	0.151	0.203	<0.002	<0.002	<0.005	<0.006	<0.007
MC3A	0.015	<0.012	0.092	<0.032	0.020	<0.002	<0.002	<0.005	<0.006	<0.007
MC3B	<0.012	<0.012	0.058	<0.032	<0.011	<0.002	<0.002	<0.005	<0.006	<0.007
MC4A	<0.012	<0.012	0.088	<0.032	<0.011	<0.002	<0.002	<0.005	<0.006	<0.007
MC4B	<0.012	<0.012	0.048	<0.032	<0.011	<0.002	<0.002	<0.005	<0.006	<0.007
MC5A	3.687	3.466	3.926	3.375	3.496	<0.002	<0.002	<0.005	<0.006	<0.007
MC5B	3.679	3.799	3.811	3.256	3.476	<0.002	<0.002	<0.005	<0.006	<0.007
MC6A	3.408	3.143	3.369	2.993	3.303	<0.002	<0.002	<0.006	<0.006	<0.007
MC6B	3.694	2.882	3.487	3.246	3.424	<0.002	<0.002	<0.006	<0.006	<0.006
MC7A	3.937	3.186	3.691	3.490	3.609	<0.002	<0.002	<0.006	<0.006	<0.006
MC7B	4.398	4.660	4.092	4.118	3.936	<0.002	<0.005	<0.006	<0.006	<0.006
MC8A	3.727	3.871	3.345	3.237	3.304	<0.002	<0.005	<0.006	<0.006	<0.006
MC8B	4.469	4.864	4.148	3.903	4.027	<0.002	<0.005	<0.006	<0.006	<0.006

Appendix 1 – ICP-OES results for Mn calcite laboratory experiments, continued. Samples highlighted in gray contain clay. Sample #'s shaded in blue are at 25°C, and sample #'s shaded in red are at 60°C. Samples 1-4 are acidic, and samples 5-8 are basic. Cation values have been converted from ppm (as reported) to mmol/L.

Sample #	**Iron (mmol/L)**				
	Day 1	**Day 3**	**Day 5**	**Day 7**	**Day 14**
MC1A	0.007	0.001	0.007	0.002	0.006
MC1B	0.009	0.003	0.002	0.002	0.002
MC2A	0.005	0.001	0.001	0.004	0.002
MC2B	0.009	0.005	0.002	0.008	0.002
MC3A	0.002	0.001	0.002	0.002	0.002
MC3B	0.003	0.005	0.002	0.002	0.002
MC4A	0.006	0.001	0.002	0.001	0.003
MC4B	0.005	0.004	0.003	0.002	0.005
MC5A	0.007	0.003	0.003	0.001	0.005
MC5B	0.001	0.003	0.004	0.004	0.002
MC6A	0.003	0.007	0.002	0.001	0.005
MC6B	0.002	0.001	0.002	0.002	0.003
MC7A	0.009	0.004	0.001	0.001	0.003
MC7B	0.002	0.005	0.003	0.004	0.001
MC8A	0.007	0.004	0.002	0.002	0.003
MC8B	0.002	0.003	0.001	0.005	0.001

Appendix 2 – PHREEQCI input files – Day 0 dolomite/rhodochrosite solid solution with NaX exchange

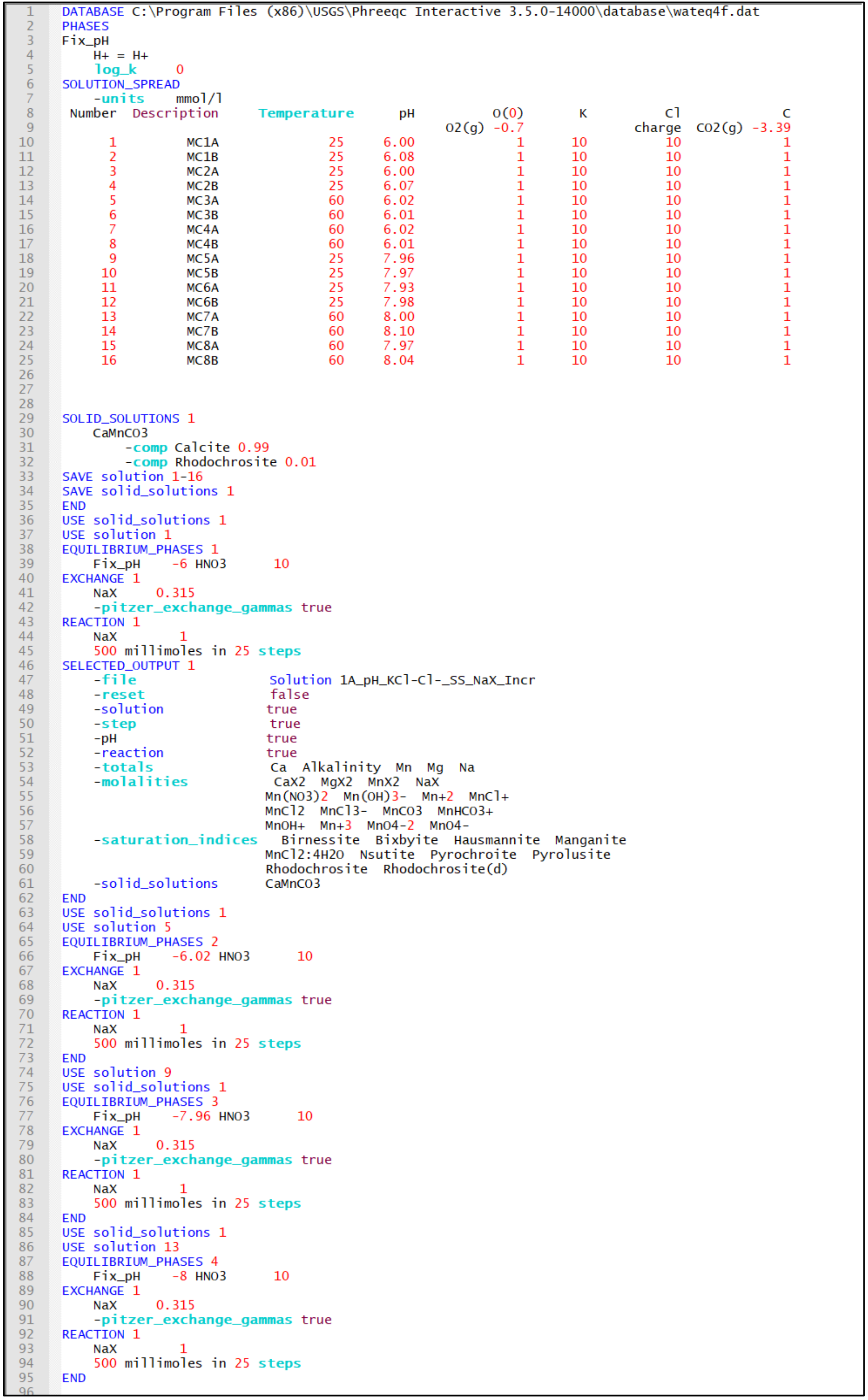


```
DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.5.0-14000\database\wateq4f.dat
PHASES
Fix_pH
    H+ = H+
    log_k      0
SOLUTION_SPREAD
    -units    mmol/l
 Number  Description     Temperature       pH          O(0)       K          Cl              C
                                                 O2(g) -0.7              charge  CO2(g) -3.39
      1         MC1A              25     6.00             1      10          10             1
      2         MC1B              25     6.08             1      10          10             1
      3         MC2A              25     6.00             1      10          10             1
      4         MC2B              25     6.07             1      10          10             1
      5         MC3A              60     6.02             1      10          10             1
      6         MC3B              60     6.01             1      10          10             1
      7         MC4A              60     6.02             1      10          10             1
      8         MC4B              60     6.01             1      10          10             1
      9         MC5A              25     7.96             1      10          10             1
     10         MC5B              25     7.97             1      10          10             1
     11         MC6A              25     7.93             1      10          10             1
     12         MC6B              25     7.98             1      10          10             1
     13         MC7A              60     8.00             1      10          10             1
     14         MC7B              60     8.10             1      10          10             1
     15         MC8A              60     7.97             1      10          10             1
     16         MC8B              60     8.04             1      10          10             1


SOLID_SOLUTIONS 1
    CaMgMnCO3
        -comp Dolomite 0.99
        -comp Rhodochrosite 0.01
SAVE solid_solutions 1
SAVE solution 1-16

END
USE solid_solutions 1
USE solution 1
EQUILIBRIUM_PHASES 1
    Fix_pH    -6 HNO3      10
EXCHANGE 1
    NaX     0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX        1
    500 millimoles in 25 steps
SELECTED_OUTPUT 1
    -file                 Solution 1A_pH_KCl-Cl-_SS_Dolo_NaX_Incr
    -reset                false
    -solution             true
    -step                 true
    -pH                   true
    -reaction             true
    -totals               Ca  Alkalinity  Mn  Mg  Na
    -molalities            CaX2  MgX2  MnX2  NaX
                          Mn(NO3)2  Mn(OH)3-  Mn+2  MnCl+
                          MnCl2  MnCl3-  MnCO3  MnHCO3+
                          MnOH+  Mn+3  MnO4-2  MnO4-
    -saturation_indices     Birnessite  Bixbyite  Hausmannite  Manganite
                          MnCl2:4H2O  Nsutite  Pyrochroite  Pyrolusite
                          Rhodochrosite  Rhodochrosite(d)
    -solid_solutions      CaMgMnCO3
END
USE solid_solutions 1
USE solution 5
EQUILIBRIUM_PHASES 2
    Fix_pH    -6.02 HNO3      10
EXCHANGE 1
    NaX     0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
USE solution 9
USE solid_solutions 1
EQUILIBRIUM_PHASES 3
    Fix_pH    -7.96 HNO3      10
EXCHANGE 1
    NaX     0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
USE solid_solutions 1
USE solution 13
EQUILIBRIUM_PHASES 4
    Fix_pH    -8 HNO3      10
EXCHANGE 1
    NaX     0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
```

Appendix 2 – PHREEQCI input files, continued – Day 0 calcite/rhodochrosite solid solution with NaX exchange

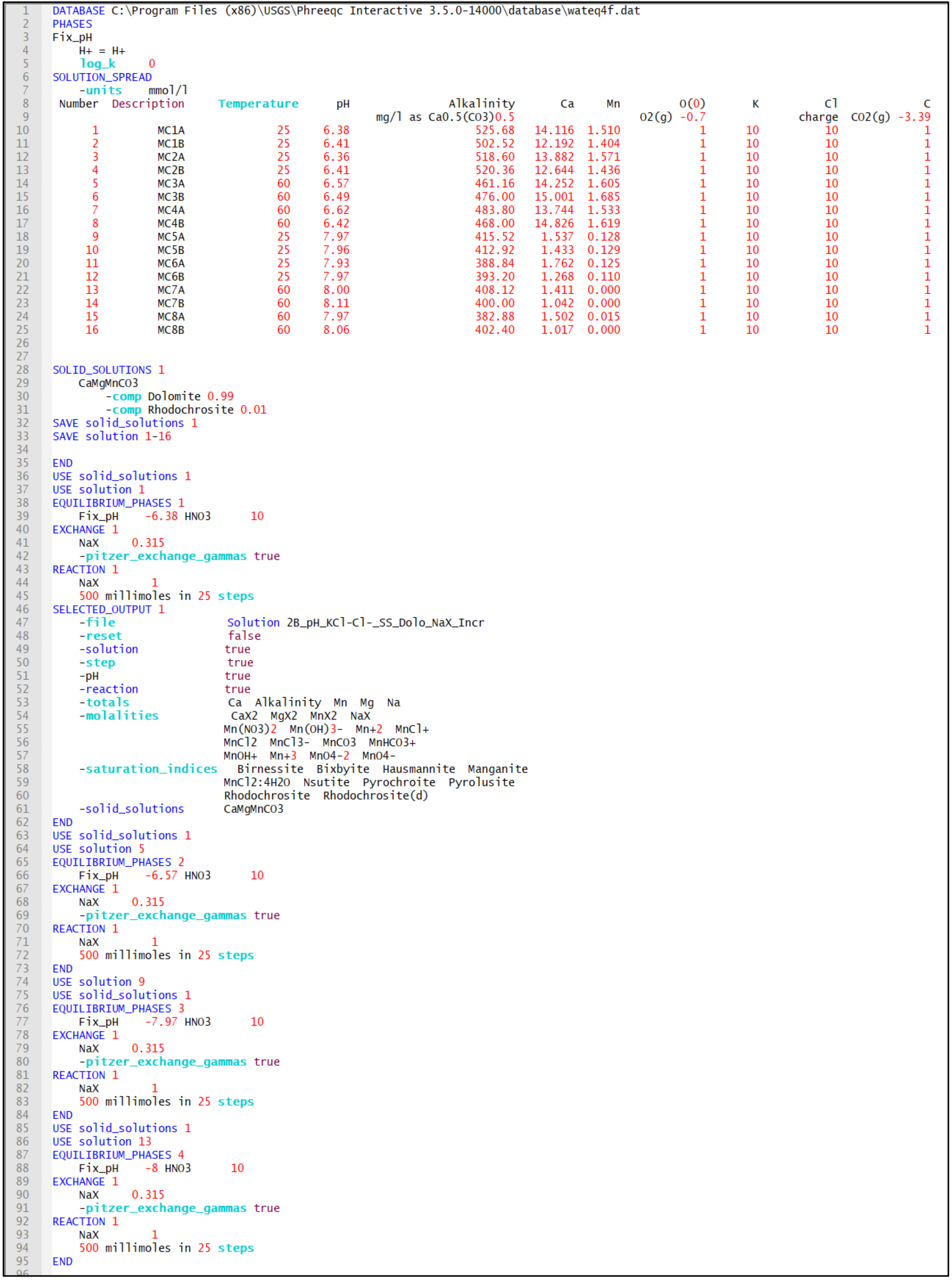


```
DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.5.0-14000\database\wateq4f.dat
PHASES
Fix_pH
    H+ = H+
    log_k     0
SOLUTION_SPREAD
    -units    mmol/l
 Number  Description     Temperature       pH          O(0)       K          Cl             C
                                                 O2(g) -0.7              charge  CO2(g) -3.39
      1         MC1A              25     6.00             1      10          10             1
      2         MC1B              25     6.08             1      10          10             1
      3         MC2A              25     6.00             1      10          10             1
      4         MC2B              25     6.07             1      10          10             1
      5         MC3A              60     6.02             1      10          10             1
      6         MC3B              60     6.01             1      10          10             1
      7         MC4A              60     6.02             1      10          10             1
      8         MC4B              60     6.01             1      10          10             1
      9         MC5A              25     7.96             1      10          10             1
     10         MC5B              25     7.97             1      10          10             1
     11         MC6A              25     7.93             1      10          10             1
     12         MC6B              25     7.98             1      10          10             1
     13         MC7A              60     8.00             1      10          10             1
     14         MC7B              60     8.10             1      10          10             1
     15         MC8A              60     7.97             1      10          10             1
     16         MC8B              60     8.04             1      10          10             1



SOLID_SOLUTIONS 1
    CaMnCO3
        -comp Calcite 0.99
        -comp Rhodochrosite 0.01
SAVE solution 1-16
SAVE solid_solutions 1
END
USE solid_solutions 1
USE solution 1
EQUILIBRIUM_PHASES 1
    Fix_pH    -6 HNO3      10
EXCHANGE 1
    NaX     0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX        1
    500 millimoles in 25 steps
SELECTED_OUTPUT 1
    -file                  Solution 1A_pH_KCl-Cl-_SS_NaX_Incr
    -reset                 false
    -solution             true
    -step                  true
    -pH                   true
    -reaction             true
    -totals                Ca  Alkalinity  Mn  Mg  Na
    -molalities            CaX2  MgX2  MnX2  NaX
                          Mn(NO3)2  Mn(OH)3-  Mn+2  MnCl+
                          MnCl2  MnCl3-  MnCO3  MnHCO3+
                          MnOH+  Mn+3  MnO4-2  MnO4-
    -saturation_indices     Birnessite  Bixbyite  Hausmannite  Manganite
                          MnCl2:4H2O  Nsutite  Pyrochroite  Pyrolusite
                          Rhodochrosite  Rhodochrosite(d)
    -solid_solutions      CaMnCO3
END
USE solid_solutions 1
USE solution 5
EQUILIBRIUM_PHASES 2
    Fix_pH    -6.02 HNO3      10
EXCHANGE 1
    NaX     0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
USE solution 9
USE solid_solutions 1
EQUILIBRIUM_PHASES 3
    Fix_pH    -7.96 HNO3      10
EXCHANGE 1
    NaX     0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
USE solid_solutions 1
USE solution 13
EQUILIBRIUM_PHASES 4
    Fix_pH    -8 HNO3      10
EXCHANGE 1
    NaX     0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
```

Appendix 2 – PHREEQCI input files, continued – Day 1 dolomite/rhodochrosite solid solution with NaX exchange

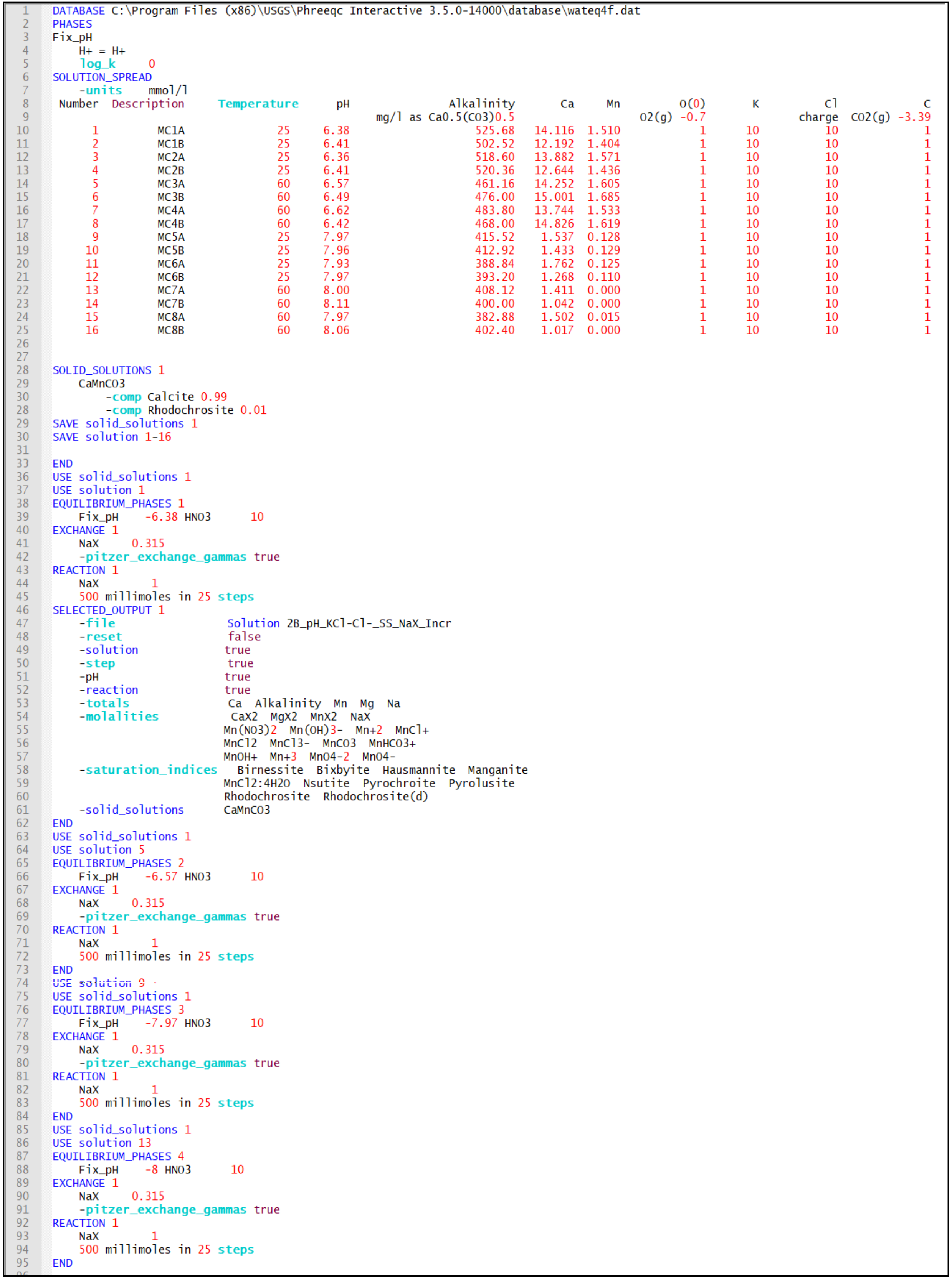


```
DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.5.0-14000\database\wateq4f.dat
PHASES
Fix_pH
    H+ = H+
    log_k     0
SOLUTION_SPREAD
    -units    mmol/l
 Number  Description     Temperature       pH               Alkalinity       Ca     Mn          O(0)          K          Cl             C
                                                 mg/l as Ca0.5(CO3)0.5                   O2(g) -0.7              charge  CO2(g) -3.39
      1         MC1A              25     6.38                   525.68   14.116  1.510            1      10          10             1
      2         MC1B              25     6.41                   502.52   12.192  1.404            1      10          10             1
      3         MC2A              25     6.36                   518.60   13.882  1.571            1      10          10             1
      4         MC2B              25     6.41                   520.36   12.644  1.436            1      10          10             1
      5         MC3A              60     6.57                   461.16   14.252  1.605            1      10          10             1
      6         MC3B              60     6.49                   476.00   15.001  1.685            1      10          10             1
      7         MC4A              60     6.62                   483.80   13.744  1.533            1      10          10             1
      8         MC4B              60     6.42                   468.00   14.826  1.619            1      10          10             1
      9         MC5A              25     7.97                   415.52    1.537  0.128            1      10          10             1
     10         MC5B              25     7.96                   412.92    1.433  0.129            1      10          10             1
     11         MC6A              25     7.93                   388.84    1.762  0.125            1      10          10             1
     12         MC6B              25     7.97                   393.20    1.268  0.110            1      10          10             1
     13         MC7A              60     8.00                   408.12    1.411  0.000            1      10          10             1
     14         MC7B              60     8.11                   400.00    1.042  0.000            1      10          10             1
     15         MC8A              60     7.97                   382.88    1.502  0.015            1      10          10             1
     16         MC8B              60     8.06                   402.40    1.017  0.000            1      10          10             1


SOLID_SOLUTIONS 1
    CaMgMnCO3
        -comp Dolomite 0.99
        -comp Rhodochrosite 0.01
SAVE solid_solutions 1
SAVE solution 1-16

END
USE solid_solutions 1
USE solution 1
EQUILIBRIUM_PHASES 1
    Fix_pH    -6.38 HNO3      10
EXCHANGE 1
    NaX     0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX        1
    500 millimoles in 25 steps
SELECTED_OUTPUT 1
    -file                 Solution 2B_pH_KCl-Cl-_SS_Dolo_NaX_Incr
    -reset                false
    -solution             true
    -step                 true
    -pH                   true
    -reaction             true
    -totals               Ca  Alkalinity  Mn  Mg  Na
    -molalities            CaX2  MgX2  MnX2  NaX
                          Mn(NO3)2  Mn(OH)3-  Mn+2  MnCl+
                          MnCl2  MnCl3-  MnCO3  MnHCO3+
                          MnOH+  Mn+3  MnO4-2  MnO4-
    -saturation_indices     Birnessite  Bixbyite  Hausmannite  Manganite
                          MnCl2:4H2O  Nsutite  Pyrochroite  Pyrolusite
                          Rhodochrosite  Rhodochrosite(d)
    -solid_solutions      CaMgMnCO3
END
USE solid_solutions 1
USE solution 5
EQUILIBRIUM_PHASES 2
    Fix_pH    -6.57 HNO3      10
EXCHANGE 1
    NaX     0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
USE solution 9
USE solid_solutions 1
EQUILIBRIUM_PHASES 3
    Fix_pH    -7.97 HNO3      10
EXCHANGE 1
    NaX     0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
USE solid_solutions 1
USE solution 13
EQUILIBRIUM_PHASES 4
    Fix_pH    -8 HNO3      10
EXCHANGE 1
    NaX     0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
```

Appendix 2 – PHREEQCI input files, continued – Day 1 calcite/rhodochrosite solid solution with NaX exchange

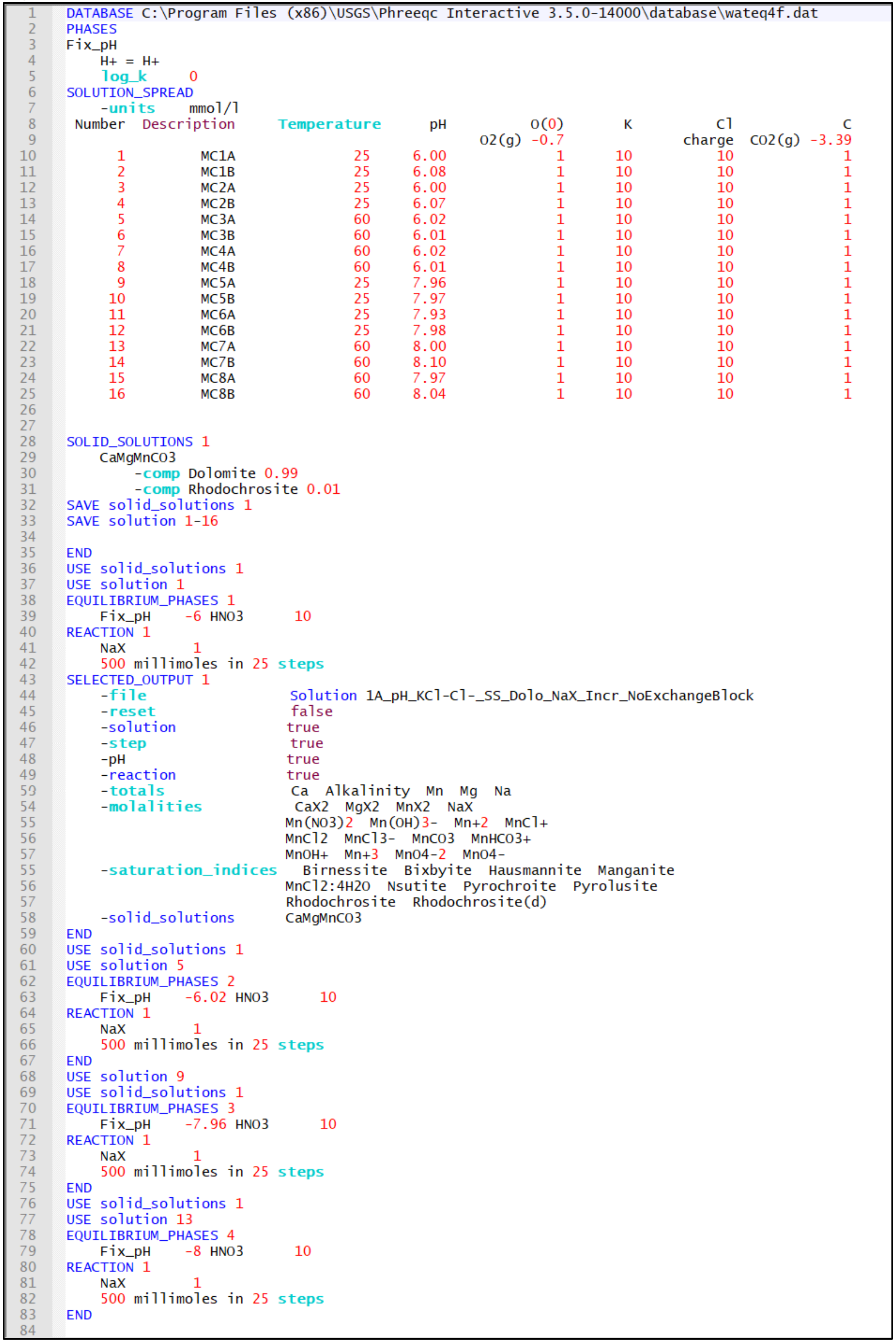


```
DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.5.0-14000\database\wateq4f.dat
PHASES
Fix_pH
    H+ = H+
    log_k     0
SOLUTION_SPREAD
    -units    mmol/l
 Number  Description     Temperature      pH               Alkalinity       Ca     Mn         O(0)       K          Cl             C
                                                 mg/l as Ca0.5(CO3)0.5                   O2(g) -0.7              charge  CO2(g) -3.39
      1         MC1A              25     6.38                   525.68   14.116  1.510            1      10          10             1
      2         MC1B              25     6.41                   502.52   12.192  1.404            1      10          10             1
      3         MC2A              25     6.36                   518.60   13.882  1.571            1      10          10             1
      4         MC2B              25     6.41                   520.36   12.644  1.436            1      10          10             1
      5         MC3A              60     6.57                   461.16   14.252  1.605            1      10          10             1
      6         MC3B              60     6.49                   476.00   15.001  1.685            1      10          10             1
      7         MC4A              60     6.62                   483.80   13.744  1.533            1      10          10             1
      8         MC4B              60     6.42                   468.00   14.826  1.619            1      10          10             1
      9         MC5A              25     7.97                   415.52    1.537  0.128            1      10          10             1
     10         MC5B              25     7.96                   412.92    1.433  0.129            1      10          10             1
     11         MC6A              25     7.93                   388.84    1.762  0.125            1      10          10             1
     12         MC6B              25     7.97                   393.20    1.268  0.110            1      10          10             1
     13         MC7A              60     8.00                   408.12    1.411  0.000            1      10          10             1
     14         MC7B              60     8.11                   400.00    1.042  0.000            1      10          10             1
     15         MC8A              60     7.97                   382.88    1.502  0.015            1      10          10             1
     16         MC8B              60     8.06                   402.40    1.017  0.000            1      10          10             1


SOLID_SOLUTIONS 1
    CaMnCO3
        -comp Calcite 0.99
        -comp Rhodochrosite 0.01
SAVE solid_solutions 1
SAVE solution 1-16

END
USE solid_solutions 1
USE solution 1
EQUILIBRIUM_PHASES 1
    Fix_pH    -6.38 HNO3      10
EXCHANGE 1
    NaX      0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX         1
    500 millimoles in 25 steps
SELECTED_OUTPUT 1
    -file                 Solution 2B_pH_KCl-Cl-_SS_NaX_Incr
    -reset                false
    -solution             true
    -step                 true
    -pH                   true
    -reaction             true
    -totals               Ca  Alkalinity  Mn  Mg  Na
    -molalities            CaX2  MgX2  MnX2  NaX
                          Mn(NO3)2  Mn(OH)3-  Mn+2  MnCl+
                          MnCl2  MnCl3-  MnCO3  MnHCO3+
                          MnOH+  Mn+3  MnO4-2  MnO4-
    -saturation_indices     Birnessite  Bixbyite  Hausmannite  Manganite
                          MnCl2:4H2O  Nsutite  Pyrochroite  Pyrolusite
                          Rhodochrosite  Rhodochrosite(d)
    -solid_solutions      CaMnCO3
END
USE solid_solutions 1
USE solution 5
EQUILIBRIUM_PHASES 2
    Fix_pH    -6.57 HNO3      10
EXCHANGE 1
    NaX      0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX         1
    500 millimoles in 25 steps
END
USE solution 9
USE solid_solutions 1
EQUILIBRIUM_PHASES 3
    Fix_pH    -7.97 HNO3      10
EXCHANGE 1
    NaX      0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX         1
    500 millimoles in 25 steps
END
USE solid_solutions 1
USE solution 13
EQUILIBRIUM_PHASES 4
    Fix_pH    -8 HNO3      10
EXCHANGE 1
    NaX      0.315
    -pitzer_exchange_gammas true
REACTION 1
    NaX         1
    500 millimoles in 25 steps
END
```

Appendix 2 – PHREEQCI input files, continued – Day 0 dolomite/rhodochrosite solid solution without NaX exchange. Note that the only difference compared to files with exchange is the lack of the "Exchange" keyword block for each solution.

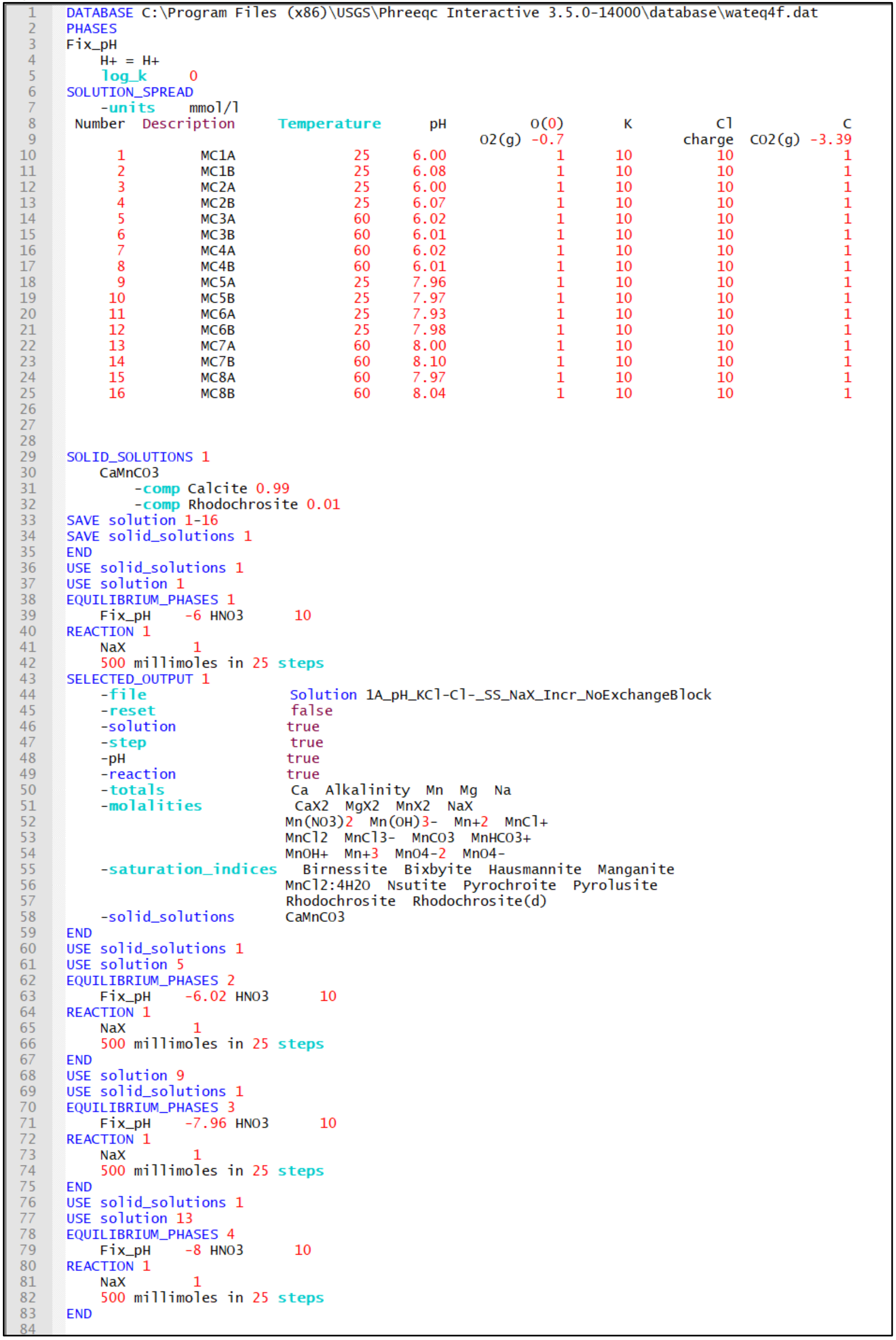


```
DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.5.0-14000\database\wateq4f.dat
PHASES
Fix_pH
    H+ = H+
    log_k      0
SOLUTION_SPREAD
    -units     mmol/l
 Number  Description     Temperature       pH          O(0)        K          Cl             C
                                                 O2(g) -0.7               charge  CO2(g) -3.39
      1         MC1A              25     6.00             1       10          10             1
      2         MC1B              25     6.08             1       10          10             1
      3         MC2A              25     6.00             1       10          10             1
      4         MC2B              25     6.07             1       10          10             1
      5         MC3A              60     6.02             1       10          10             1
      6         MC3B              60     6.01             1       10          10             1
      7         MC4A              60     6.02             1       10          10             1
      8         MC4B              60     6.01             1       10          10             1
      9         MC5A              25     7.96             1       10          10             1
     10         MC5B              25     7.97             1       10          10             1
     11         MC6A              25     7.93             1       10          10             1
     12         MC6B              25     7.98             1       10          10             1
     13         MC7A              60     8.00             1       10          10             1
     14         MC7B              60     8.10             1       10          10             1
     15         MC8A              60     7.97             1       10          10             1
     16         MC8B              60     8.04             1       10          10             1


SOLID_SOLUTIONS 1
    CaMgMnCO3
        -comp Dolomite 0.99
        -comp Rhodochrosite 0.01
SAVE solid_solutions 1
SAVE solution 1-16

END
USE solid_solutions 1
USE solution 1
EQUILIBRIUM_PHASES 1
    Fix_pH    -6 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
SELECTED_OUTPUT 1
    -file                  Solution 1A_pH_KCl-Cl-_SS_Dolo_NaX_Incr_NoExchangeBlock
    -reset                 false
    -solution             true
    -step                  true
    -pH                   true
    -reaction             true
    -totals                Ca  Alkalinity  Mn  Mg  Na
    -molalities            CaX2  MgX2  MnX2  NaX
                          Mn(NO3)2  Mn(OH)3-  Mn+2  MnCl+
                          MnCl2  MnCl3-  MnCO3  MnHCO3+
                          MnOH+  Mn+3  MnO4-2  MnO4-
    -saturation_indices    Birnessite  Bixbyite  Hausmannite  Manganite
                          MnCl2:4H2O  Nsutite  Pyrochroite  Pyrolusite
                          Rhodochrosite  Rhodochrosite(d)
    -solid_solutions      CaMgMnCO3
END
USE solid_solutions 1
USE solution 5
EQUILIBRIUM_PHASES 2
    Fix_pH    -6.02 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
USE solution 9
USE solid_solutions 1
EQUILIBRIUM_PHASES 3
    Fix_pH    -7.96 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
USE solid_solutions 1
USE solution 13
EQUILIBRIUM_PHASES 4
    Fix_pH    -8 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
```

Appendix 2 – PHREEQCI input files, continued – Day 0 calcite/rhodochrosite solid solution without NaX exchange. Note that the only difference compared to files with exchange is the lack of the “Exchange” keyword block for each solution.



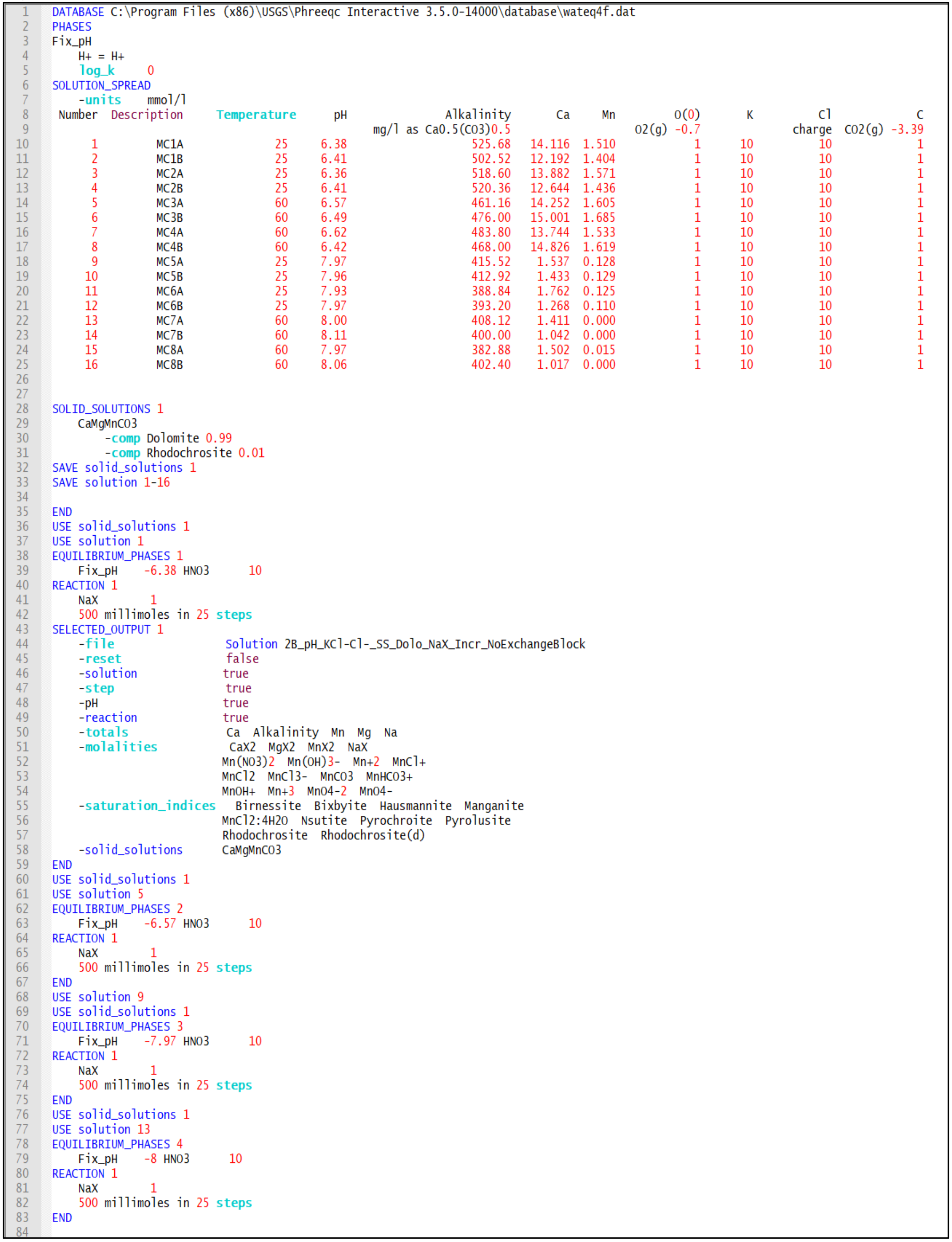
```
DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.5.0-14000\database\wateq4f.dat
PHASES
Fix_pH
    H+ = H+
    log_k      0
SOLUTION_SPREAD
    -units     mmol/l
 Number  Description     Temperature       pH          O(0)       K          Cl             C
                                                 O2(g) -0.7              charge  CO2(g) -3.39
      1         MC1A              25     6.00             1      10          10             1
      2         MC1B              25     6.08             1      10          10             1
      3         MC2A              25     6.00             1      10          10             1
      4         MC2B              25     6.07             1      10          10             1
      5         MC3A              60     6.02             1      10          10             1
      6         MC3B              60     6.01             1      10          10             1
      7         MC4A              60     6.02             1      10          10             1
      8         MC4B              60     6.01             1      10          10             1
      9         MC5A              25     7.96             1      10          10             1
     10         MC5B              25     7.97             1      10          10             1
     11         MC6A              25     7.93             1      10          10             1
     12         MC6B              25     7.98             1      10          10             1
     13         MC7A              60     8.00             1      10          10             1
     14         MC7B              60     8.10             1      10          10             1
     15         MC8A              60     7.97             1      10          10             1
     16         MC8B              60     8.04             1      10          10             1



SOLID_SOLUTIONS 1
    CaMnCO3
        -comp Calcite 0.99
        -comp Rhodochrosite 0.01
SAVE solution 1-16
SAVE solid_solutions 1
END
USE solid_solutions 1
USE solution 1
EQUILIBRIUM_PHASES 1
    Fix_pH    -6 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
SELECTED_OUTPUT 1
    -file                 Solution 1A_pH_KCl-Cl-_SS_NaX_Incr_NoExchangeBlock
    -reset                false
    -solution             true
    -step                 true
    -pH                   true
    -reaction             true
    -totals                Ca  Alkalinity  Mn  Mg  Na
    -molalities            CaX2  MgX2  MnX2  NaX
                          Mn(NO3)2  Mn(OH)3-  Mn+2  MnCl+
                          MnCl2  MnCl3-  MnCO3  MnHCO3+
                          MnOH+  Mn+3  MnO4-2  MnO4-
    -saturation_indices     Birnessite  Bixbyite  Hausmannite  Manganite
                          MnCl2:4H2O  Nsutite  Pyrochroite  Pyrolusite
                          Rhodochrosite  Rhodochrosite(d)
    -solid_solutions      CaMnCO3
END
USE solid_solutions 1
USE solution 5
EQUILIBRIUM_PHASES 2
    Fix_pH    -6.02 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
USE solution 9
USE solid_solutions 1
EQUILIBRIUM_PHASES 3
    Fix_pH    -7.96 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
USE solid_solutions 1
USE solution 13
EQUILIBRIUM_PHASES 4
    Fix_pH    -8 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END

```

Appendix 2 – PHREEQCI input files, continued – Day 1 dolomite/rhodochrosite solid solution without NaX exchange. Note that the only difference compared to files with exchange is the lack of the “Exchange” keyword block for each solution.

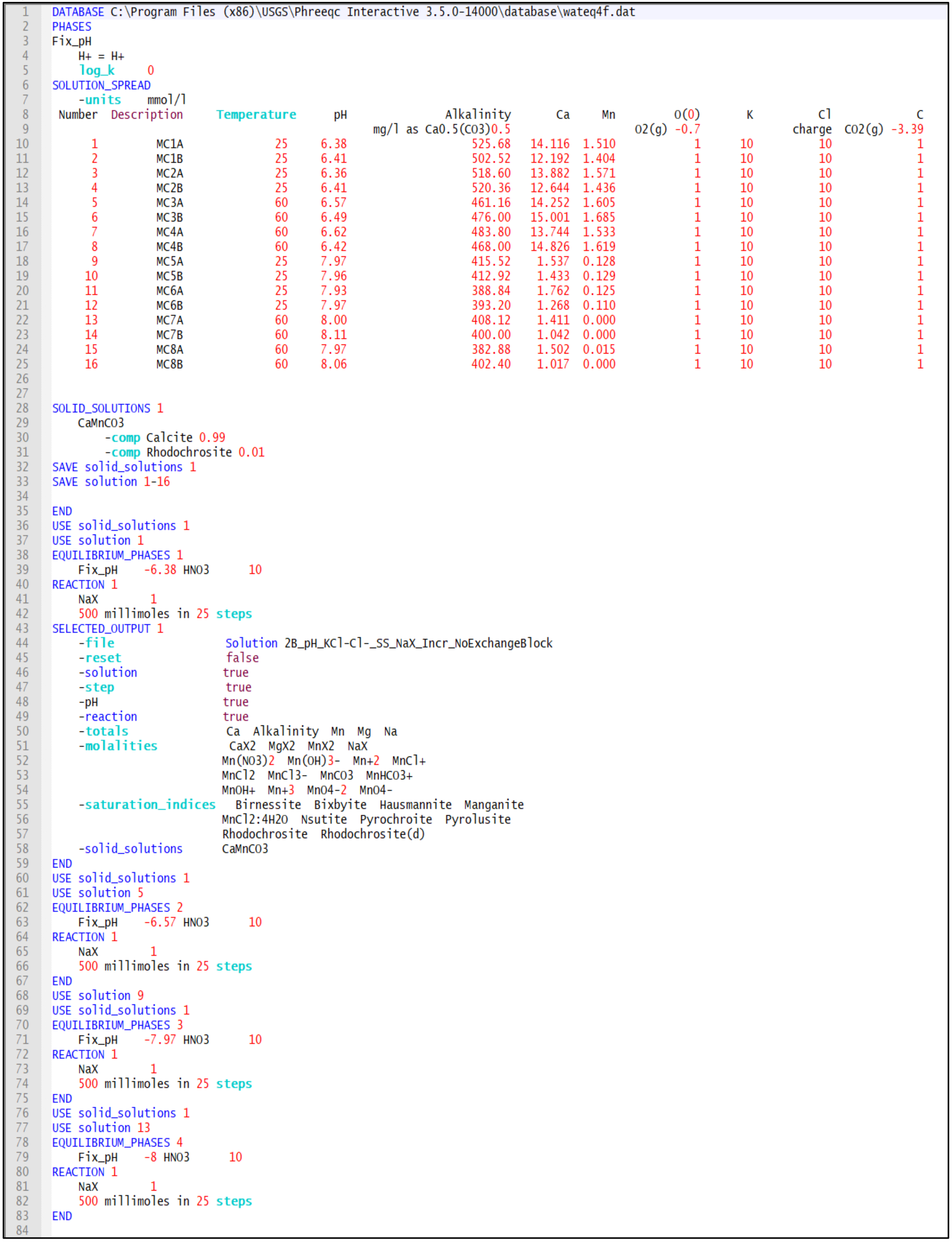


```
DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.5.0-14000\database\wateq4f.dat
PHASES
Fix_pH
    H+ = H+
    log_k     0
SOLUTION_SPREAD
    -units    mmol/l
 Number  Description      Temperature        pH               Alkalinity       Ca     Mn         O(0)       K          Cl            C
                                                 mg/l as Ca0.5(CO3)0.5                   O2(g) -0.7              charge  CO2(g) -3.39
      1         MC1A              25     6.38                   525.68   14.116  1.510            1      10          10             1
      2         MC1B              25     6.41                   502.52   12.192  1.404            1      10          10             1
      3         MC2A              25     6.36                   518.60   13.882  1.571            1      10          10             1
      4         MC2B              25     6.41                   520.36   12.644  1.436            1      10          10             1
      5         MC3A              60     6.57                   461.16   14.252  1.605            1      10          10             1
      6         MC3B              60     6.49                   476.00   15.001  1.685            1      10          10             1
      7         MC4A              60     6.62                   483.80   13.744  1.533            1      10          10             1
      8         MC4B              60     6.42                   468.00   14.826  1.619            1      10          10             1
      9         MC5A              25     7.97                   415.52    1.537  0.128            1      10          10             1
     10         MC5B              25     7.96                   412.92    1.433  0.129            1      10          10             1
     11         MC6A              25     7.93                   388.84    1.762  0.125            1      10          10             1
     12         MC6B              25     7.97                   393.20    1.268  0.110            1      10          10             1
     13         MC7A              60     8.00                   408.12    1.411  0.000            1      10          10             1
     14         MC7B              60     8.11                   400.00    1.042  0.000            1      10          10             1
     15         MC8A              60     7.97                   382.88    1.502  0.015            1      10          10             1
     16         MC8B              60     8.06                   402.40    1.017  0.000            1      10          10             1


SOLID_SOLUTIONS 1
    CaMgMnCO3
        -comp Dolomite 0.99
        -comp Rhodochrosite 0.01
SAVE solid_solutions 1
SAVE solution 1-16

END
USE solid_solutions 1
USE solution 1
EQUILIBRIUM_PHASES 1
    Fix_pH    -6.38 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
SELECTED_OUTPUT 1
    -file                 Solution 2B_pH_KCl-Cl-_SS_Dolo_NaX_Incr_NoExchangeBlock
    -reset                false
    -solution             true
    -step                 true
    -pH                   true
    -reaction             true
    -totals               Ca  Alkalinity  Mn  Mg  Na
    -molalities            CaX2  MgX2  MnX2  NaX
                          Mn(NO3)2  Mn(OH)3-  Mn+2  MnCl+
                          MnCl2  MnCl3-  MnCO3  MnHCO3+
                          MnOH+  Mn+3  MnO4-2  MnO4-
    -saturation_indices     Birnessite  Bixbyite  Hausmannite  Manganite
                          MnCl2:4H2O  Nsutite  Pyrochroite  Pyrolusite
                          Rhodochrosite  Rhodochrosite(d)
    -solid_solutions      CaMgMnCO3
END
USE solid_solutions 1
USE solution 5
EQUILIBRIUM_PHASES 2
    Fix_pH    -6.57 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
USE solution 9
USE solid_solutions 1
EQUILIBRIUM_PHASES 3
    Fix_pH    -7.97 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
USE solid_solutions 1
USE solution 13
EQUILIBRIUM_PHASES 4
    Fix_pH    -8 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
```

Appendix 2 – PHREEQCI input files, continued – Day 1 calcite/rhodochrosite solid solution without NaX exchange. Note that the only difference compared to files with exchange is the lack of the “Exchange” keyword block for each solution.



```
DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.5.0-14000\database\wateq4f.dat
PHASES
Fix_pH
    H+ = H+
    log_k      0
SOLUTION_SPREAD
    -units     mmol/l
 Number  Description     Temperature       pH               Alkalinity       Ca     Mn         O(0)       K          Cl            C
                                                 mg/l as Ca0.5(CO3)0.5                   O2(g) -0.7              charge  CO2(g) -3.39
      1         MC1A              25     6.38                   525.68   14.116  1.510            1      10          10            1
      2         MC1B              25     6.41                   502.52   12.192  1.404            1      10          10            1
      3         MC2A              25     6.36                   518.60   13.882  1.571            1      10          10            1
      4         MC2B              25     6.41                   520.36   12.644  1.436            1      10          10            1
      5         MC3A              60     6.57                   461.16   14.252  1.605            1      10          10            1
      6         MC3B              60     6.49                   476.00   15.001  1.685            1      10          10            1
      7         MC4A              60     6.62                   483.80   13.744  1.533            1      10          10            1
      8         MC4B              60     6.42                   468.00   14.826  1.619            1      10          10            1
      9         MC5A              25     7.97                   415.52    1.537  0.128            1      10          10            1
     10         MC5B              25     7.96                   412.92    1.433  0.129            1      10          10            1
     11         MC6A              25     7.93                   388.84    1.762  0.125            1      10          10            1
     12         MC6B              25     7.97                   393.20    1.268  0.110            1      10          10            1
     13         MC7A              60     8.00                   408.12    1.411  0.000            1      10          10            1
     14         MC7B              60     8.11                   400.00    1.042  0.000            1      10          10            1
     15         MC8A              60     7.97                   382.88    1.502  0.015            1      10          10            1
     16         MC8B              60     8.06                   402.40    1.017  0.000            1      10          10            1


SOLID_SOLUTIONS 1
    CaMnCO3
        -comp Calcite 0.99
        -comp Rhodochrosite 0.01
SAVE solid_solutions 1
SAVE solution 1-16

END
USE solid_solutions 1
USE solution 1
EQUILIBRIUM_PHASES 1
    Fix_pH    -6.38 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
SELECTED_OUTPUT 1
    -file                 Solution 2B_pH_KCl-Cl-_SS_NaX_Incr_NoExchangeBlock
    -reset                false
    -solution             true
    -step                 true
    -pH                   true
    -reaction             true
    -totals               Ca  Alkalinity  Mn  Mg  Na
    -molalities            CaX2  MgX2  MnX2  NaX
                          Mn(NO3)2  Mn(OH)3-  Mn+2  MnCl+
                          MnCl2  MnCl3-  MnCO3  MnHCO3+
                          MnOH+  Mn+3  MnO4-2  MnO4-
    -saturation_indices     Birnessite  Bixbyite  Hausmannite  Manganite
                          MnCl2:4H2O  Nsutite  Pyrochroite  Pyrolusite
                          Rhodochrosite  Rhodochrosite(d)
    -solid_solutions      CaMnCO3
END
USE solid_solutions 1
USE solution 5
EQUILIBRIUM_PHASES 2
    Fix_pH    -6.57 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
USE solution 9
USE solid_solutions 1
EQUILIBRIUM_PHASES 3
    Fix_pH    -7.97 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
USE solid_solutions 1
USE solution 13
EQUILIBRIUM_PHASES 4
    Fix_pH    -8 HNO3      10
REACTION 1
    NaX        1
    500 millimoles in 25 steps
END
```

Appendix 3 – PHREEQCI batch reaction modeling results – exchange block included

Day 0 Calcite/Rhodochrosite Solid Solution, Exchange Block Included

Sample	Step	pH	NaX Added (mmol)	Ca (mmol/L)	Alkalinity (mg $CaCO_3$/L)	Mn (mmol/L)	Mg (mmol/L)	Na (mmol/L)
1A	1	6.00	20	10.409	1658.73	4.411E-04	0.000	153.590
1A	2	6.00	40	10.246	1701.66	4.385E-04	0.000	158.020
1A	3	6.00	60	10.096	1742.95	4.361E-04	0.000	162.240
1A	4	6.00	80	9.958	1782.68	4.340E-04	0.000	166.280
1A	5	6.00	100	9.830	1821.01	4.321E-04	0.000	170.150
1A	6	6.00	120	9.710	1858.00	4.303E-04	0.000	173.870
1A	7	6.00	140	9.599	1893.78	4.287E-04	0.000	177.450
1A	8	6.00	160	9.494	1928.41	4.272E-04	0.000	180.900
1A	9	6.00	180	9.396	1961.94	4.258E-04	0.000	184.230
1A	10	6.00	200	9.304	1994.51	4.245E-04	0.000	187.450
1A	11	6.00	220	9.217	2026.14	4.233E-04	0.000	190.560
1A	12	6.00	240	9.134	2056.92	4.222E-04	0.000	193.580
1A	13	6.00	260	9.056	2086.84	4.212E-04	0.000	196.500
1A	14	6.00	280	8.982	2116.02	4.202E-04	0.000	199.340
1A	15	6.00	300	8.911	2144.44	4.193E-04	0.000	202.100
1A	16	6.00	320	8.843	2172.22	4.185E-04	0.000	204.790
1A	17	6.00	340	8.779	2199.29	4.177E-04	0.000	207.400
1A	18	6.00	360	8.717	2225.76	4.169E-04	0.000	209.950
1A	19	6.00	380	8.658	2251.63	4.162E-04	0.000	212.430
1A	20	6.00	400	8.601	2276.91	4.155E-04	0.000	214.860
1A	21	6.00	420	8.547	2301.68	4.149E-04	0.000	217.220
1A	22	6.00	440	8.495	2325.95	4.143E-04	0.000	219.530
1A	23	6.00	460	8.444	2349.72	4.137E-04	0.000	221.790
1A	24	6.00	480	8.396	2373.04	4.132E-04	0.000	224.000
1A	25	6.00	500	8.349	2395.86	4.127E-04	0.000	226.170
5A	1	7.96	20	0.117	1031.39	1.036E-05	0.000	50.962
5A	2	7.96	40	0.116	1053.10	1.033E-05	0.000	51.852
5A	3	7.96	60	0.114	1073.87	1.030E-05	0.000	52.702
5A	4	7.96	80	0.113	1093.79	1.027E-05	0.000	53.515
5A	5	7.96	100	0.112	1112.86	1.025E-05	0.000	54.295
5A	6	7.96	120	0.111	1131.27	1.022E-05	0.000	55.046
5A	7	7.96	140	0.110	1148.99	1.020E-05	0.000	55.769
5A	8	7.96	160	0.109	1166.10	1.018E-05	0.000	56.466
5A	9	7.96	180	0.108	1182.67	1.016E-05	0.000	57.140
5A	10	7.96	200	0.107	1198.73	1.014E-05	0.000	57.793
5A	11	7.96	220	0.106	1214.29	1.013E-05	0.000	58.426
5A	12	7.96	240	0.105	1229.41	1.011E-05	0.000	59.040
5A	13	7.96	260	0.105	1244.12	1.010E-05	0.000	59.636
5A	14	7.96	280	0.104	1258.43	1.008E-05	0.000	60.216
5A	15	7.96	300	0.103	1272.34	1.007E-05	0.000	60.781
5A	16	7.96	320	0.103	1285.90	1.005E-05	0.000	61.332
5A	17	7.96	340	0.102	1299.17	1.004E-05	0.000	61.869
5A	18	7.96	360	0.102	1312.13	1.003E-05	0.000	62.393
5A	19	7.96	380	0.101	1324.74	1.002E-05	0.000	62.905
5A	20	7.96	400	0.100	1337.15	1.001E-05	0.000	63.405
5A	21	7.96	420	0.100	1349.21	9.998E-06	0.000	63.895
5A	22	7.96	440	0.099	1361.07	9.988E-06	0.000	64.374
5A	23	7.96	460	0.099	1372.68	9.978E-06	0.000	64.843
5A	24	7.96	480	0.098	1384.04	9.969E-06	0.000	65.303
5A	25	7.96	500	0.098	1395.20	9.960E-06	0.000	65.754

Appendix 3 – PHREEQCI batch reaction modeling results, continued – exchange block included

Day 0 Dolomite/Rhodochrosite Solid Solution, Exchange Block Included

Sample	Step	pH	NaX Added (mmol)	Ca (mmol/L)	Alkalinity (mg CaCO3/L)	Mn (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Mg/Ca Ratio
1A	1	6.00	20	6.973	1900.13	4.122E-04	9.669	161.150	1.387
1A	2	6.00	40	6.859	1946.17	4.096E-04	9.531	165.990	1.390
1A	3	6.00	60	6.754	1990.51	4.072E-04	9.404	170.600	1.392
1A	4	6.00	80	6.658	2033.20	4.050E-04	9.285	175.030	1.395
1A	5	6.00	100	6.568	2074.48	4.030E-04	9.175	179.270	1.397
1A	6	6.00	120	6.485	2114.37	4.012E-04	9.071	183.340	1.399
1A	7	6.00	140	6.408	2153.00	3.995E-04	8.974	187.270	1.401
1A	8	6.00	160	6.335	2190.43	3.979E-04	8.883	191.050	1.402
1A	9	6.00	180	6.267	2226.71	3.964E-04	8.796	194.700	1.404
1A	10	6.00	200	6.203	2261.99	3.950E-04	8.715	198.230	1.405
1A	11	6.00	220	6.142	2296.32	3.937E-04	8.638	201.650	1.406
1A	12	6.00	240	6.085	2329.65	3.925E-04	8.564	204.960	1.407
1A	13	6.00	260	6.031	2362.18	3.913E-04	8.494	208.170	1.408
1A	14	6.00	280	5.979	2393.86	3.902E-04	8.428	211.290	1.409
1A	15	6.00	300	5.930	2424.78	3.892E-04	8.364	214.320	1.410
1A	16	6.00	320	5.884	2454.96	3.882E-04	8.303	217.270	1.411
1A	17	6.00	340	5.839	2484.43	3.873E-04	8.245	220.140	1.412
1A	18	6.00	360	5.797	2513.21	3.864E-04	8.189	222.940	1.413
1A	19	6.00	380	5.756	2541.38	3.856E-04	8.136	225.670	1.414
1A	20	6.00	400	5.717	2568.96	3.848E-04	8.085	228.330	1.414
1A	21	6.00	420	5.679	2595.98	3.840E-04	8.035	230.930	1.415
1A	22	6.00	440	5.643	2622.45	3.833E-04	7.987	233.470	1.415
1A	23	6.00	460	5.609	2648.38	3.826E-04	7.941	235.950	1.416
1A	24	6.00	480	5.575	2673.80	3.820E-04	7.897	238.380	1.416
1A	25	6.00	500	5.543	2698.77	3.813E-04	7.854	240.760	1.417
5A	1	7.96	20	0.076	1126.42	1.011E-05	0.115	54.594	1.502
5A	2	7.96	40	0.075	1150.29	1.008E-05	0.113	55.573	1.501
5A	3	7.96	60	0.075	1173.11	1.005E-05	0.112	56.506	1.501
5A	4	7.96	80	0.074	1194.93	1.003E-05	0.111	57.400	1.500
5A	5	7.96	100	0.073	1215.89	1.000E-05	0.110	58.257	1.499
5A	6	7.96	120	0.072	1236.11	9.978E-06	0.108	59.081	1.499
5A	7	7.96	140	0.072	1255.58	9.957E-06	0.107	59.875	1.498
5A	8	7.96	160	0.071	1274.34	9.936E-06	0.106	60.641	1.498
5A	9	7.96	180	0.070	1292.56	9.917E-06	0.106	61.381	1.497
5A	10	7.96	200	0.070	1310.18	9.899E-06	0.105	62.098	1.497
5A	11	7.96	220	0.069	1327.24	9.883E-06	0.104	62.792	1.496
5A	12	7.96	240	0.069	1343.80	9.867E-06	0.103	63.466	1.496
5A	13	7.96	260	0.068	1359.97	9.851E-06	0.102	64.121	1.495
5A	14	7.96	280	0.068	1375.63	9.837E-06	0.102	64.757	1.495
5A	15	7.96	300	0.068	1390.95	9.823E-06	0.101	65.377	1.494
5A	16	7.96	320	0.067	1405.81	9.810E-06	0.100	65.981	1.494
5A	17	7.96	340	0.067	1420.37	9.798E-06	0.100	66.570	1.494
5A	18	7.96	360	0.066	1434.53	9.786E-06	0.099	67.145	1.493
5A	19	7.96	380	0.066	1448.39	9.774E-06	0.099	67.706	1.493
5A	20	7.96	400	0.066	1461.96	9.763E-06	0.098	68.255	1.493
5A	21	7.96	420	0.065	1475.27	9.753E-06	0.098	68.792	1.492
5A	22	7.96	440	0.065	1488.23	9.743E-06	0.097	69.318	1.492
5A	23	7.96	460	0.065	1500.94	9.733E-06	0.097	69.832	1.492
5A	24	7.96	480	0.065	1513.45	9.723E-06	0.096	70.336	1.491
5A	25	7.96	500	0.064	1525.66	9.714E-06	0.096	70.831	1.491

Appendix 3 – PHREEQCI batch reaction modeling results, continued – exchange block included

Day 1 Calcite/Rhodochrosite Solid Solution, Exchange Block Included

Sample	Step	pH	NaX Added (mmol)	Ca (mmol/L)	Alkalinity (mg $CaCO_3$/L)	Mn (mmol/L)	Mg (mmol/L)	Na (mmol/L)
1A	1	6.38	20	3.918	1620.69	1.958E-04	0.000	124.490
1A	2	6.38	40	3.851	1665.83	1.944E-04	0.000	127.560
1A	3	6.38	60	3.791	1709.07	1.931E-04	0.000	130.490
1A	4	6.38	80	3.735	1750.55	1.919E-04	0.000	133.290
1A	5	6.38	100	3.684	1790.39	1.909E-04	0.000	135.970
1A	6	6.38	120	3.637	1828.77	1.899E-04	0.000	138.540
1A	7	6.38	140	3.593	1865.80	1.890E-04	0.000	141.020
1A	8	6.38	160	3.552	1901.53	1.882E-04	0.000	143.400
1A	9	6.38	180	3.514	1936.11	1.874E-04	0.000	145.690
1A	10	6.38	200	3.478	1969.64	1.867E-04	0.000	147.910
1A	11	6.38	220	3.444	2002.12	1.861E-04	0.000	150.060
1A	12	6.38	240	3.412	2033.65	1.855E-04	0.000	152.140
1A	13	6.38	260	3.382	2064.32	1.849E-04	0.000	154.150
1A	14	6.38	280	3.354	2094.15	1.843E-04	0.000	156.110
1A	15	6.38	300	3.326	2123.17	1.838E-04	0.000	158.010
1A	16	6.38	320	3.301	2151.45	1.834E-04	0.000	159.860
1A	17	6.38	340	3.276	2179.07	1.829E-04	0.000	161.660
1A	18	6.38	360	3.253	2206.00	1.825E-04	0.000	163.420
1A	19	6.38	380	3.230	2232.32	1.821E-04	0.000	165.130
1A	20	6.38	400	3.209	2258.04	1.817E-04	0.000	166.800
1A	21	6.38	420	3.188	2283.21	1.813E-04	0.000	168.430
1A	22	6.38	440	3.169	2307.83	1.810E-04	0.000	170.030
1A	23	6.38	460	3.150	2331.95	1.807E-04	0.000	171.590
1A	24	6.38	480	3.132	2355.57	1.804E-04	0.000	173.110
1A	25	6.38	500	3.114	2378.74	1.801E-04	0.000	174.610
5A	1	7.97	20	0.154	757.95	1.293E-05	0.000	55.384
5A	2	7.97	40	0.151	779.37	1.285E-05	0.000	56.266
5A	3	7.97	60	0.148	799.79	1.277E-05	0.000	57.108
5A	4	7.97	80	0.146	819.40	1.270E-05	0.000	57.914
5A	5	7.97	100	0.143	838.22	1.264E-05	0.000	58.686
5A	6	7.97	120	0.141	856.34	1.258E-05	0.000	59.429
5A	7	7.97	140	0.139	873.80	1.252E-05	0.000	60.145
5A	8	7.97	160	0.137	890.67	1.247E-05	0.000	60.835
5A	9	7.97	180	0.136	906.98	1.243E-05	0.000	61.503
5A	10	7.97	200	0.134	922.79	1.238E-05	0.000	62.149
5A	11	7.97	220	0.133	938.11	1.234E-05	0.000	62.774
5A	12	7.97	240	0.131	953.02	1.230E-05	0.000	63.382
5A	13	7.97	260	0.130	967.48	1.227E-05	0.000	63.972
5A	14	7.97	280	0.129	981.59	1.223E-05	0.000	64.546
5A	15	7.97	300	0.127	995.31	1.220E-05	0.000	65.104
5A	16	7.97	320	0.126	1008.72	1.217E-05	0.000	65.649
5A	17	7.97	340	0.125	1021.78	1.214E-05	0.000	66.180
5A	18	7.97	360	0.124	1034.54	1.211E-05	0.000	66.698
5A	19	7.97	380	0.123	1047.00	1.208E-05	0.000	67.204
5A	20	7.97	400	0.122	1059.16	1.206E-05	0.000	67.699
5A	21	7.97	420	0.121	1071.12	1.204E-05	0.000	68.183
5A	22	7.97	440	0.120	1082.78	1.201E-05	0.000	68.656
5A	23	7.97	460	0.120	1094.24	1.199E-05	0.000	69.120
5A	24	7.97	480	0.119	1105.45	1.197E-05	0.000	69.575
5A	25	7.97	500	0.118	1116.46	1.195E-05	0.000	70.021

Appendix 3 – PHREEQCI batch reaction modeling results, continued – exchange block included

Day 1 Dolomite/Rhodochrosite Solid Solution, Exchange Block Included

Sample	Step	pH	NaX Added (mmol)	Ca (mmol/L)	Alkalinity (mg CaCO3/L)	Mn (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Mg/Ca Ratio
1A	1	6.38	20	3.189	1822.22	1.859E-04	3.024	132.240	0.948
1A	2	6.38	40	3.119	1871.21	1.845E-04	2.990	135.620	0.959
1A	3	6.38	60	3.056	1918.15	1.833E-04	2.959	138.840	0.968
1A	4	6.38	80	2.999	1963.24	1.821E-04	2.929	141.910	0.977
1A	5	6.38	100	2.947	2006.57	1.811E-04	2.902	144.860	0.985
1A	6	6.38	120	2.898	2048.41	1.802E-04	2.876	147.690	0.992
1A	7	6.38	140	2.854	2088.74	1.793E-04	2.852	150.400	0.999
1A	8	6.38	160	2.813	2127.73	1.785E-04	2.830	153.020	1.006
1A	9	6.38	180	2.774	2165.46	1.778E-04	2.808	155.550	1.012
1A	10	6.38	200	2.739	2201.99	1.771E-04	2.788	157.980	1.018
1A	11	6.38	220	2.705	2237.47	1.764E-04	2.768	160.340	1.023
1A	12	6.38	240	2.674	2271.95	1.758E-04	2.750	162.630	1.029
1A	13	6.38	260	2.644	2305.43	1.752E-04	2.733	164.850	1.034
1A	14	6.38	280	2.616	2338.06	1.747E-04	2.716	167.000	1.038
1A	15	6.38	300	2.589	2369.79	1.742E-04	2.700	169.090	1.043
1A	16	6.38	320	2.564	2400.76	1.737E-04	2.685	171.120	1.047
1A	17	6.38	340	2.541	2430.94	1.732E-04	2.670	173.100	1.051
1A	18	6.38	360	2.518	2460.46	1.728E-04	2.656	175.030	1.055
1A	19	6.38	380	2.496	2489.24	1.724E-04	2.643	176.910	1.059
1A	20	6.38	400	2.476	2517.41	1.720E-04	2.630	178.750	1.062
1A	21	6.38	420	2.456	2544.99	1.716E-04	2.617	180.540	1.066
1A	22	6.38	440	2.437	2571.96	1.712E-04	2.605	182.290	1.069
1A	23	6.38	460	2.419	2598.33	1.709E-04	2.593	184.010	1.072
1A	24	6.38	480	2.402	2624.25	1.705E-04	2.582	185.680	1.075
1A	25	6.38	500	2.385	2649.63	1.702E-04	2.571	187.330	1.078
5A	1	7.97	20	0.173	902.98	1.237E-05	0.077	60.956	0.443
5A	2	7.97	40	0.168	925.60	1.230E-05	0.076	61.895	0.454
5A	3	7.97	60	0.163	947.21	1.224E-05	0.076	62.791	0.465
5A	4	7.97	80	0.159	968.03	1.219E-05	0.076	63.650	0.475
5A	5	7.97	100	0.155	988.00	1.214E-05	0.075	64.474	0.485
5A	6	7.97	120	0.152	1007.27	1.209E-05	0.075	65.267	0.494
5A	7	7.97	140	0.149	1025.83	1.205E-05	0.075	66.031	0.503
5A	8	7.97	160	0.146	1043.80	1.201E-05	0.074	66.768	0.511
5A	9	7.97	180	0.143	1061.21	1.197E-05	0.074	67.481	0.519
5A	10	7.97	200	0.141	1078.03	1.193E-05	0.074	68.172	0.526
5A	11	7.97	220	0.138	1094.39	1.190E-05	0.074	68.841	0.533
5A	12	7.97	240	0.136	1110.30	1.187E-05	0.073	69.491	0.540
5A	13	7.97	260	0.134	1125.77	1.184E-05	0.073	70.123	0.547
5A	14	7.97	280	0.132	1140.83	1.181E-05	0.073	70.737	0.553
5A	15	7.97	300	0.130	1155.49	1.178E-05	0.073	71.335	0.559
5A	16	7.97	320	0.129	1169.81	1.176E-05	0.073	71.919	0.565
5A	17	7.97	340	0.127	1183.77	1.173E-05	0.072	72.488	0.570
5A	18	7.97	360	0.125	1197.43	1.171E-05	0.072	73.043	0.576
5A	19	7.97	380	0.124	1210.79	1.169E-05	0.072	73.586	0.581
5A	20	7.97	400	0.123	1223.85	1.167E-05	0.072	74.116	0.586
5A	21	7.97	420	0.121	1236.61	1.165E-05	0.072	74.636	0.591
5A	22	7.97	440	0.120	1249.12	1.163E-05	0.071	75.144	0.595
5A	23	7.97	460	0.119	1261.38	1.161E-05	0.071	75.642	0.600
5A	24	7.97	480	0.118	1273.44	1.159E-05	0.071	76.130	0.604
5A	25	7.97	500	0.116	1285.25	1.157E-05	0.071	76.609	0.609

Appendix 3 – PHREEQCI batch reaction modeling results, continued – exchange block NOT included

Day 0 Calcite/Rhodochrosite Solid Solution, Exchange Block NOT Included

Sample	Step	pH	NaX Added (mmol)	Ca (mmol/L)	Alkalinity (mg CaCO3/L)	Mn (mmol/L)	Mg (mmol/L)	Na (mmol/L)
1A	1	6.00	20	26.312	521.60	7.729E-04	0.000	19.990
1A	2	6.00	40	27.080	543.92	7.947E-04	0.000	39.971
1A	3	6.00	60	27.732	563.58	8.142E-04	0.000	59.943
1A	4	6.00	80	28.297	581.30	8.320E-04	0.000	79.907
1A	5	6.00	100	28.794	597.36	8.485E-04	0.000	99.862
1A	6	6.00	120	29.235	612.18	8.641E-04	0.000	119.810
1A	7	6.00	140	29.631	625.89	8.789E-04	0.000	139.750
1A	8	6.00	160	29.987	638.70	8.930E-04	0.000	159.670
1A	9	6.00	180	30.309	650.66	9.066E-04	0.000	179.590
1A	10	6.00	200	30.602	661.92	9.198E-04	0.000	199.510
1A	11	6.00	220	30.870	672.58	9.326E-04	0.000	219.410
1A	12	6.00	240	31.114	682.69	9.450E-04	0.000	239.300
1A	13	6.00	260	31.339	692.29	9.572E-04	0.000	259.190
1A	14	6.00	280	31.544	701.40	9.692E-04	0.000	279.070
1A	15	6.00	300	31.734	710.11	9.810E-04	0.000	298.940
1A	16	6.00	320	31.908	718.42	9.925E-04	0.000	318.800
1A	17	6.00	340	32.068	726.37	1.004E-03	0.000	338.650
1A	18	6.00	360	32.215	734.03	1.015E-03	0.000	358.490
1A	19	6.00	380	32.351	741.34	1.026E-03	0.000	378.330
1A	20	6.00	400	32.476	748.39	1.038E-03	0.000	398.150
1A	21	6.00	420	32.591	755.15	1.049E-03	0.000	417.970
1A	22	6.00	440	32.696	761.65	1.059E-03	0.000	437.780
1A	23	6.00	460	32.793	767.96	1.070E-03	0.000	457.580
1A	24	6.00	480	32.882	774.02	1.081E-03	0.000	477.370
1A	25	6.00	500	32.963	779.82	1.092E-03	0.000	497.160
5A	1	7.96	20	1.347	67.96	3.799E-05	0.000	19.996
5A	2	7.96	40	1.457	73.59	4.035E-05	0.000	39.983
5A	3	7.96	60	1.544	78.06	4.225E-05	0.000	59.961
5A	4	7.96	80	1.616	81.81	4.388E-05	0.000	79.931
5A	5	7.96	100	1.679	85.07	4.535E-05	0.000	99.892
5A	6	7.96	120	1.734	87.97	4.669E-05	0.000	119.840
5A	7	7.96	140	1.783	90.58	4.794E-05	0.000	139.790
5A	8	7.96	160	1.828	92.96	4.912E-05	0.000	159.720
5A	9	7.96	180	1.869	95.14	5.025E-05	0.000	179.650
5A	10	7.96	200	1.906	97.17	5.133E-05	0.000	199.570
5A	11	7.96	220	1.941	99.05	5.237E-05	0.000	219.480
5A	12	7.96	240	1.974	100.81	5.339E-05	0.000	239.380
5A	13	7.96	260	2.004	102.46	5.439E-05	0.000	259.270
5A	14	7.96	280	2.032	104.01	5.536E-05	0.000	279.160
5A	15	7.96	300	2.059	105.48	5.631E-05	0.000	299.030
5A	16	7.96	320	2.084	106.86	5.726E-05	0.000	318.900
5A	17	7.96	340	2.107	108.18	5.819E-05	0.000	338.760
5A	18	7.96	360	2.129	109.43	5.911E-05	0.000	358.610
5A	19	7.96	380	2.150	110.62	6.002E-05	0.000	378.450
5A	20	7.96	400	2.170	111.75	6.092E-05	0.000	398.280
5A	21	7.96	420	2.189	112.84	6.182E-05	0.000	418.100
5A	22	7.96	440	2.207	113.87	6.271E-05	0.000	437.920
5A	23	7.96	460	2.225	114.86	6.361E-05	0.000	457.720
5A	24	7.96	480	2.241	115.81	6.449E-05	0.000	477.520
5A	25	7.96	500	2.256	116.72	6.538E-05	0.000	497.310

Appendix 3 – PHREEQCI batch reaction modeling results, continued – exchange block NOT included

Day 0 Dolomite/Rhodochrosite Solid Solution, Exchange Block NOT Included

Sample	Step	pH	NaX Added (mmol)	Ca (mmol/L)	Alkalinity (mg CaCO3/L)	Mn (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Mg/Ca Ratio
1A	1	6.00	20	17.884	730.73	6.523E-04	17.884	19.988	1.000
1A	2	6.00	40	18.283	755.65	6.681E-04	18.283	39.967	1.000
1A	3	6.00	60	18.625	777.97	6.825E-04	18.625	59.938	1.000
1A	4	6.00	80	18.924	798.14	6.959E-04	18.924	79.899	1.000
1A	5	6.00	100	19.186	816.60	7.086E-04	19.186	99.852	1.000
1A	6	6.00	120	19.420	833.67	7.206E-04	19.420	119.800	1.000
1A	7	6.00	140	19.628	849.53	7.320E-04	19.628	139.730	1.000
1A	8	6.00	160	19.816	864.34	7.431E-04	19.816	159.660	1.000
1A	9	6.00	180	19.985	878.20	7.538E-04	19.985	179.580	1.000
1A	10	6.00	200	20.138	891.32	7.642E-04	20.138	199.490	1.000
1A	11	6.00	220	20.276	903.63	7.744E-04	20.276	219.390	1.000
1A	12	6.00	240	20.402	915.34	7.844E-04	20.402	239.280	1.000
1A	13	6.00	260	20.516	926.45	7.941E-04	20.516	259.170	1.000
1A	14	6.00	280	20.620	937.01	8.037E-04	20.620	279.040	1.000
1A	15	6.00	300	20.715	947.06	8.132E-04	20.715	298.910	1.000
1A	16	6.00	320	20.801	956.62	8.225E-04	20.801	318.770	1.000
1A	17	6.00	340	20.879	965.83	8.318E-04	20.879	338.620	1.000
1A	18	6.00	360	20.950	974.59	8.409E-04	20.950	358.460	1.000
1A	19	6.00	380	21.015	982.99	8.500E-04	21.015	378.290	1.000
1A	20	6.00	400	21.073	991.05	8.590E-04	21.073	398.120	1.000
1A	21	6.00	420	21.125	998.81	8.680E-04	21.125	417.930	1.000
1A	22	6.00	440	21.172	1006.26	8.769E-04	21.172	437.740	1.000
1A	23	6.00	460	21.215	1013.42	8.857E-04	21.215	457.540	1.000
1A	24	6.00	480	21.252	1020.28	8.945E-04	21.252	477.330	1.000
1A	25	6.00	500	21.285	1026.93	9.033E-04	21.285	497.120	1.000
5A	1	7.96	20	0.891	89.54	3.097E-05	0.891	19.996	1.000
5A	2	7.96	40	0.960	96.64	3.281E-05	0.960	39.983	1.000
5A	3	7.96	60	1.014	102.25	3.430E-05	1.014	59.961	1.000
5A	4	7.96	80	1.059	106.94	3.558E-05	1.059	79.931	1.000
5A	5	7.96	100	1.098	111.01	3.674E-05	1.098	99.892	1.000
5A	6	7.96	120	1.132	114.60	3.781E-05	1.132	119.840	1.000
5A	7	7.96	140	1.163	117.83	3.880E-05	1.163	139.790	1.000
5A	8	7.96	160	1.190	120.76	3.975E-05	1.190	159.720	1.000
5A	9	7.96	180	1.215	123.45	4.065E-05	1.215	179.650	1.000
5A	10	7.96	200	1.238	125.92	4.151E-05	1.238	199.570	1.000
5A	11	7.96	220	1.259	128.21	4.236E-05	1.259	219.480	1.000
5A	12	7.96	240	1.279	130.34	4.317E-05	1.279	239.380	1.000
5A	13	7.96	260	1.297	132.34	4.397E-05	1.297	259.270	1.000
5A	14	7.96	280	1.314	134.21	4.476E-05	1.314	279.160	1.000
5A	15	7.96	300	1.330	135.97	4.553E-05	1.330	299.030	1.000
5A	16	7.96	320	1.345	137.62	4.629E-05	1.345	318.900	1.000
5A	17	7.96	340	1.359	139.19	4.705E-05	1.359	338.760	1.000
5A	18	7.96	360	1.372	140.68	4.779E-05	1.372	358.610	1.000
5A	19	7.96	380	1.384	142.08	4.853E-05	1.384	378.450	1.000
5A	20	7.96	400	1.396	143.42	4.927E-05	1.396	398.280	1.000
5A	21	7.96	420	1.407	144.69	5.000E-05	1.407	418.100	1.000
5A	22	7.96	440	1.417	145.90	5.072E-05	1.417	437.920	1.000
5A	23	7.96	460	1.427	147.05	5.145E-05	1.427	457.720	1.000
5A	24	7.96	480	1.436	148.15	5.217E-05	1.436	477.520	1.000
5A	25	7.96	500	1.445	149.20	5.290E-05	1.445	497.310	1.000

Appendix 3 – PHREEQCI batch reaction modeling results, continued – exchange block NOT included

Day 1 Calcite/Rhodochrosite Solid Solution, Exchange Block NOT Included

Sample	Step	pH	NaX Added (mmol)	Ca (mmol/L)	Alkalinity (mg CaCO3/L)	Mn (mmol/L)	Mg (mmol/L)	Na (mmol/L)
1A	1	6.38	20	17.313	285.81	5.442E-04	0.000	19.994
1A	2	6.38	40	17.791	303.13	5.573E-04	0.000	39.980
1A	3	6.38	60	18.196	318.13	5.691E-04	0.000	59.957
1A	4	6.38	80	18.547	331.42	5.800E-04	0.000	79.925
1A	5	6.38	100	18.857	343.39	5.903E-04	0.000	99.885
1A	6	6.38	120	19.133	354.29	6.002E-04	0.000	119.840
1A	7	6.38	140	19.382	364.30	6.096E-04	0.000	139.780
1A	8	6.38	160	19.608	373.55	6.187E-04	0.000	159.710
1A	9	6.38	180	19.814	382.15	6.276E-04	0.000	179.640
1A	10	6.38	200	20.002	390.19	6.363E-04	0.000	199.550
1A	11	6.38	220	20.176	397.73	6.448E-04	0.000	219.460
1A	12	6.38	240	20.336	404.81	6.532E-04	0.000	239.360
1A	13	6.38	260	20.485	411.50	6.615E-04	0.000	259.250
1A	14	6.38	280	20.622	417.81	6.697E-04	0.000	279.130
1A	15	6.38	300	20.750	423.80	6.778E-04	0.000	299.010
1A	16	6.38	320	20.869	429.49	6.859E-04	0.000	318.870
1A	17	6.38	340	20.980	434.89	6.939E-04	0.000	338.730
1A	18	6.38	360	21.084	440.03	7.019E-04	0.000	358.580
1A	19	6.38	380	21.181	444.94	7.098E-04	0.000	378.420
1A	20	6.38	400	21.271	449.62	7.177E-04	0.000	398.250
1A	21	6.38	420	21.355	454.09	7.257E-04	0.000	418.070
1A	22	6.38	440	21.434	458.36	7.335E-04	0.000	437.880
1A	23	6.38	460	21.508	462.45	7.414E-04	0.000	457.690
1A	24	6.38	480	21.577	466.37	7.493E-04	0.000	477.480
1A	25	6.38	500	21.642	470.12	7.572E-04	0.000	497.270
5A	1	7.97	20	8.039	13.73	2.243E-04	0.000	19.996
5A	2	7.97	40	8.068	15.26	2.237E-04	0.000	39.983
5A	3	7.97	60	8.093	16.61	2.237E-04	0.000	59.961
5A	4	7.97	80	8.115	17.82	2.240E-04	0.000	79.931
5A	5	7.97	100	8.135	18.94	2.246E-04	0.000	99.892
5A	6	7.97	120	8.153	19.96	2.255E-04	0.000	119.840
5A	7	7.97	140	8.170	20.92	2.265E-04	0.000	139.790
5A	8	7.97	160	8.185	21.81	2.276E-04	0.000	159.720
5A	9	7.97	180	8.200	22.65	2.289E-04	0.000	179.650
5A	10	7.97	200	8.213	23.45	2.302E-04	0.000	199.570
5A	11	7.97	220	8.226	24.20	2.317E-04	0.000	219.480
5A	12	7.97	240	8.238	24.92	2.333E-04	0.000	239.380
5A	13	7.97	260	8.249	25.60	2.349E-04	0.000	259.270
5A	14	7.97	280	8.260	26.24	2.366E-04	0.000	279.160
5A	15	7.97	300	8.270	26.86	2.384E-04	0.000	299.030
5A	16	7.97	320	8.279	27.45	2.402E-04	0.000	318.900
5A	17	7.97	340	8.288	28.02	2.421E-04	0.000	338.760
5A	18	7.97	360	8.296	28.56	2.440E-04	0.000	358.610
5A	19	7.97	380	8.304	29.08	2.460E-04	0.000	378.450
5A	20	7.97	400	8.312	29.58	2.481E-04	0.000	398.280
5A	21	7.97	420	8.319	30.06	2.502E-04	0.000	418.100
5A	22	7.97	440	8.326	30.52	2.523E-04	0.000	437.920
5A	23	7.97	460	8.332	30.97	2.545E-04	0.000	457.720
5A	24	7.97	480	8.339	31.40	2.567E-04	0.000	477.520
5A	25	7.97	500	8.344	31.81	2.590E-04	0.000	497.310

Appendix 3 – PHREEQCI batch reaction modeling results, continued exchange block NOT included

Day 1 Dolomite/Rhodochrosite Solid Solution, Exchange Block NOT Included

Sample	Step	pH	NaX Added (mmol)	Ca (mmol/L)	Alkalinity (mg CaCO3/L)	Mn (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Mg/Ca Ratio
1A	1	6.38	20	18.983	488.86	3.837E-04	4.844	19.993	0.255
1A	2	6.38	40	19.224	507.89	3.950E-04	5.088	39.978	0.265
1A	3	6.38	60	19.431	524.65	4.051E-04	5.298	59.954	0.273
1A	4	6.38	80	19.612	539.66	4.145E-04	5.481	79.922	0.279
1A	5	6.38	100	19.772	553.28	4.232E-04	5.645	99.880	0.285
1A	6	6.38	120	19.915	565.79	4.315E-04	5.791	119.830	0.291
1A	7	6.38	140	20.044	577.25	4.394E-04	5.923	139.770	0.295
1A	8	6.38	160	20.160	587.91	4.470E-04	6.042	159.700	0.300
1A	9	6.38	180	20.266	597.86	4.543E-04	6.151	179.630	0.304
1A	10	6.38	200	20.363	607.12	4.615E-04	6.251	199.540	0.307
1A	11	6.38	220	20.452	615.83	4.684E-04	6.343	219.450	0.310
1A	12	6.38	240	20.534	624.04	4.752E-04	6.428	239.350	0.313
1A	13	6.38	260	20.609	631.74	4.819E-04	6.506	259.240	0.316
1A	14	6.38	280	20.678	639.05	4.885E-04	6.578	279.120	0.318
1A	15	6.38	300	20.741	646.01	4.951E-04	6.645	298.990	0.320
1A	16	6.38	320	20.800	652.56	5.015E-04	6.707	318.860	0.322
1A	17	6.38	340	20.855	658.77	5.079E-04	6.764	338.710	0.324
1A	18	6.38	360	20.905	664.72	5.142E-04	6.817	358.560	0.326
1A	19	6.38	380	20.951	670.38	5.205E-04	6.867	378.400	0.328
1A	20	6.38	400	20.994	675.73	5.267E-04	6.912	398.230	0.329
1A	21	6.38	420	21.034	680.89	5.329E-04	6.955	418.050	0.331
1A	22	6.38	440	21.070	685.79	5.391E-04	6.995	437.870	0.332
1A	23	6.38	460	21.104	690.44	5.453E-04	7.031	457.670	0.333
1A	24	6.38	480	21.135	694.95	5.514E-04	7.065	477.470	0.334
1A	25	6.38	500	21.163	699.20	5.575E-04	7.097	497.250	0.335
5A	1	7.97	20	14.149	326.59	1.917E-05	0.008	19.996	0.001
5A	2	7.97	40	14.148	326.46	2.008E-05	0.010	39.983	0.001
5A	3	7.97	60	14.146	326.46	2.092E-05	0.011	59.961	0.001
5A	4	7.97	80	14.145	326.55	2.169E-05	0.012	79.931	0.001
5A	5	7.97	100	14.143	326.69	2.241E-05	0.014	99.892	0.001
5A	6	7.97	120	14.141	326.87	2.310E-05	0.015	119.840	0.001
5A	7	7.97	140	14.139	327.08	2.376E-05	0.016	139.790	0.001
5A	8	7.97	160	14.137	327.30	2.439E-05	0.018	159.720	0.001
5A	9	7.97	180	14.135	327.54	2.501E-05	0.019	179.650	0.001
5A	10	7.97	200	14.134	327.79	2.560E-05	0.020	199.570	0.001
5A	11	7.97	220	14.132	328.05	2.618E-05	0.021	219.480	0.001
5A	12	7.97	240	14.130	328.31	2.675E-05	0.022	239.380	0.002
5A	13	7.97	260	14.128	328.58	2.731E-05	0.023	259.270	0.002
5A	14	7.97	280	14.126	328.85	2.785E-05	0.024	279.160	0.002
5A	15	7.97	300	14.123	329.11	2.839E-05	0.025	299.030	0.002
5A	16	7.97	320	14.121	329.38	2.892E-05	0.026	318.900	0.002
5A	17	7.97	340	14.119	329.65	2.945E-05	0.027	338.760	0.002
5A	18	7.97	360	14.117	329.92	2.996E-05	0.028	358.600	0.002
5A	19	7.97	380	14.115	330.19	3.047E-05	0.028	378.450	0.002
5A	20	7.97	400	14.113	330.45	3.098E-05	0.029	398.280	0.002
5A	21	7.97	420	14.110	330.72	3.149E-05	0.030	418.100	0.002
5A	22	7.97	440	14.108	330.98	3.198E-05	0.031	437.920	0.002
5A	23	7.97	460	14.106	331.24	3.248E-05	0.032	457.720	0.002
5A	24	7.97	480	14.104	331.50	3.297E-05	0.032	477.520	0.002
5A	25	7.97	500	14.101	331.76	3.347E-05	0.033	497.310	0.002

Appendix 4 – Summary statistics and averages of PHREEQCI batch reaction modeling results. The table below contains summary results for all solutions for Sample 1A (acidic, room temperature).

Sample 1A - Acidic

			Ca (mmol/L)	Alkalinity (mg CaCO3/L)	Mn (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Mg/Ca Ratio
Exchange	**Day 0 Calcite/ Rhodochrosite**	**Initial**	10.409	1658.73	4.411E-04		153.590	
		Final	8.349	2395.86	4.127E-04		226.170	
		Change	(-)2.060	737.13	(-)2.842E-05		72.580	
		% Change	(-)19.8	44.4	(-)6.4		47.3	
	Day 1 Calcite/ Rhodochrosite	**Initial**	3.918	1620.69	1.958E-04		124.490	
		Final	3.114	2378.74	1.801E-04		174.610	
		Change	(-)0.804	758.05	(-)1.577E-05		50.120	
		% Change	(-)20.5	46.8	(-)8.1		40.3	
	Day 0 Dolomite/ Rhodochrosite	**Initial**	6.973	1900.13	4.122E-04	9.669	161.150	1.387
		Final	5.543	2698.77	3.813E-04	7.854	240.760	1.417
		Change	(-)1.430	798.64	(-)3.084E-05	(-)1.815	79.610	0.030
		% Change	(-)20.5	42.0	(-)7.5	(-)18.8	49.4	2.2
	Day 1 Dolomite/ Rhodochrosite	**Initial**	3.189	1822.22	1.859E-04	3.024	132.240	0.948
		Final	2.385	2649.63	1.702E-04	2.571	187.330	1.078
		Change	(-)0.804	827.41	(-)1.562E-05	(-)0.453	55.090	0.130
		% Change	(-)25.2	45.4	(-)8.4	(-)15.0	41.7	13.7
No Exchange	**Day 0 Calcite/ Rhodochrosite**	**Initial**	26.312	521.60	7.729E-04		19.990	
		Final	32.963	779.82	1.092E-03		497.160	
		Change	6.651	258.22	3.188E-04		477.170	
		% Change	25.3	49.5	41.2		2387.0	
	Day 1 Calcite/ Rhodochrosite	**Initial**	17.313	285.81	5.442E-04		19.994	
		Final	21.642	470.12	7.572E-04		497.270	
		Change	4.329	184.31	2.131E-04		477.276	
		% Change	25.0	64.5	39.2		2387.1	
	Day 0 Dolomite/ Rhodochrosite	**Initial**	17.884	730.73	6.523E-04	17.884	19.988	1.000
		Final	21.285	1026.93	9.033E-04	21.285	497.120	1.000
		Change	3.401	296.20	2.510E-04	3.401	477.132	0.000
		% Change	19.0	40.5	38.5	19.0	2387.1	0.0
	Day 1 Dolomite/ Rhodochrosite	**Initial**	18.983	488.86	3.837E-04	4.844	19.993	0.255
		Final	21.163	699.20	5.575E-04	7.097	497.250	0.335
		Change	2.180	210.34	1.738E-04	2.253	477.257	0.080
		% Change	11.5	43.0	45.3	46.5	2387.1	31.4

Appendix 4 – Summary statistics and averages of PHREEQCI batch reaction modeling results. The table below contains summary results for all solutions for Sample 5A (basic, room temperature).

Sample 5A - Basic

			Ca (mmol/L)	Alkalinity (mg CaCO3/L)	Mn (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Mg/Ca Ratio
Exchange	**Day 0 Calcite/ Rhodochrosite**	**Initial**	0.117	1031.39	1.036E-05		50.962	
		Final	0.098	1395.20	9.960E-06		65.754	
		Change	(-)0.019	363.81	(-)4.02E-07		14.792	
		% Change	(-)16.2	35.3	(-)3.9		29.0	
	Day 1 Calcite/ Rhodochrosite	**Initial**	0.154	757.95	1.293E-05		55.384	
		Final	0.118	1116.46	1.195E-05		70.021	
		Change	(-)0.036	358.51	(-)9.850E-07		14.637	
		% Change	(-)23.2	47.3	(-)7.6		26.4	
	Day 0 Dolomite/ Rhodochrosite	**Initial**	0.076	1126.42	1.011E-05	0.115	54.594	1.502
		Final	0.064	1525.66	9.714E-06	0.096	70.831	1.491
		Change	(-)0.012	399.24	(-)3.998E-07	(-)0.019	16.237	(-)0.011
		% Change	(-)16.0	35.4	(-)4.0	(-)16.6	29.7	(-)0.7
	Day 1 Dolomite/ Rhodochrosite	**Initial**	0.173	902.98	1.237E-05	0.077	60.956	0.443
		Final	0.116	1285.25	1.157E-05	0.071	76.609	0.609
		Change	(-)0.057	382.28	(-)7.960E-07	(-)0.006	15.653	0.166
		% Change	(-)32.7	42.3	(-)6.4	(-)7.4	25.7	37.5
No Exchange	**Day 0 Calcite/ Rhodochrosite**	**Initial**	1.347	67.96	3.799E-05		19.996	
		Final	2.256	116.72	6.538E-05		497.310	
		Change	0.909	48.76	2.739E-05		477.314	
		% Change	67.5	71.8	72.1		2387.0	
	Day 1 Calcite/ Rhodochrosite	**Initial**	8.039	13.73	2.243E-04		19.996	
		Final	8.344	31.81	2.590E-04		497.310	
		Change	0.305	18.08	3.473E-05		477.314	
		% Change	3.8	131.7	15.5		2387.0	
	Day 0 Dolomite/ Rhodochrosite	**Initial**	0.891	89.54	3.097E-05	0.891	19.996	1.000
		Final	1.445	149.20	5.290E-05	1.445	497.310	1.000
		Change	0.554	59.66	2.192E-05	0.554	477.314	0.000
		% Change	62.3	66.6	70.8	62.3	2387.0	0.0
	Day 1 Dolomite/ Rhodochrosite	**Initial**	14.149	326.59	1.917E-05	0.008	19.996	0.001
		Final	14.101	331.76	3.347E-05	0.033	497.310	0.002
		Change	(-)0.048	5.17	1.430E-05	0.025	477.314	0.002
		% Change	(-)0.3	1.6	74.6	299.4	2387.0	300.7

Appendix 4 – Summary statistics and averages of PHREEQCI batch reaction modeling results, continued. The table below contains overall averages and ranges for all solutions for Sample 1A (acidic, room temperature). N=4 for exchange and n=4 for no exchange for all parameters except Mg (n=2) and Mg/Ca ratio (n=2).

SAMPLE 1A (ACIDIC)

		Ca (mmol/L)	**Alkalinity (mg $CaCO_3$/L)**	**Mn (mmol/L)**	**Mg (mmol/L)**	**Na (mmol/L)**	**Mg/Ca Ratio**
Exchange	**Average Initial**	6.122	1750.44	3.087E-04	6.346	142.868	1.167
	Range	3.189 - 10.409	1620.69 - 1900.13	1.859E-04 - 4.411E-04	3.024 - 9.669	124.490 - 161.150	0.948 - 1.387
	Average Final	4.848	2530.75	2.861E-04	5.213	207.218	1.247
	Range	2.385 - 8.349	2378.74 - 2698.77	1.702E-04 - 4.127E-04	2.571 - 7.854	174.610 - 240.760	1.078 - 1.417
	Average Change	(-)1.274	780.31	(-)2.266E-05	(-)1.134	64.350	0.080
	Range	(-)0.804 - (-)2.060	737.13 - 827.41	(-)1.562E-05 - (-)3.084E-05	(-)0.453 - (-)1.815	50.120 - 79.610	0.030 - 0.130
	Average Change (%)	(-)21.5	44.7	(-)7.6	(-)16.9	44.6	7.9
	Range	(-)19.8 - (-)25.2	42.0 - 46.8	(-)6.4 - (-)8.4	(-)15.0 - (-)18.8	40.3 - 49.4	2.2 - 13.7
No Exchange	**Average Initial**	20.123	506.75	5.883E-04	11.364	19.991	0.628
	Range	17.313 - 26.312	285.81 - 730.73	3.837E-04 - 7.729E-04	4.844 - 17.884	19.988 - 19.994	0.255 - 1.000
	Average Final	24.263	744.02	8.274E-04	14.191	497.200	0.668
	Range	21.163 - 32.963	470.12 - 1026.93	5.575E-04 - 1.092E-03	7.097 - 21.285	497.120 - 497.270	0.335 - 1.000
	Average Change	4.140	237.27	2.392E-04	2.827	477.209	0.040
	Range	2.180 - 6.651	184.31 - 296.20	1.738E-04 - 3.188E-04	2.253 - 3.401	477.132 - 477.276	0.000 - 0.080
	Average Change (%)	20.2	49.4	41.0	32.8	2387.1	15.7
	Range	11.5 - 25.3	40.5 - 64.5	38.5 - 45.3	19.0 - 46.5	2387.0 - 2387.1	0.0 - 31.4

Appendix 4 – Summary statistics and averages of PHREEQCI batch reaction modeling results, continued. The table below contains overall averages and ranges for all solutions for Sample 5A (basic, room temperature). N=4 for exchange and n=4 for no exchange for all parameters except Mg (n=2) and Mg/Ca ratio (n=2).

SAMPLE 5A (BASIC)							
		Ca (mmol/L)	**Alkalinity (mg $CaCO_3$/L)**	**Mn (mmol/L)**	**Mg (mmol/L)**	**Na (mmol/L)**	**Mg/Ca Ratio**
Exchange	**Average Initial**	0.130	954.68	1.144E-05	0.096	55.474	0.972
	Range	0.076 - 0.173	757.95 - 1126.42	1.011E-05 - 1.293E-05	0.077 - 0.115	50.962 - 60.956	0.443 - 1.502
	Average Final	0.099	1330.64	1.080E-05	0.083	70.804	1.050
	Range	0.064 - 0.118	1116.46 - 1525.66	9.714E-06 - 1.195E-05	0.071 - 0.096	65.754 - 76.609	0.609 - 1.491
	Average Change	(-)0.031	375.96	(-)6.458E-07	(-)0.012	15.330	0.077
	Range	(-)0.012 - (-)0.057	358.51 - 399.24	(-)3.998E-07 - (-)9.850E-07	(-)0.006 - (-)0.019	14.637 - 16.237	(-)0.011 - (+)0.166
	Average Change (%)	(-)22.0	40.1	(-)5.5	(-)12.0	27.7	18.4
	Range	(-)16.0 - (-)32.7	35.3 - 47.3	(-)3.9 - (-)7.6	(-)7.4 - (-)16.6	25.7 - 29.7	(-)0.7 - (+)37.5
No Exchange	**Average Initial**	6.106	124.45	7.810E-05	0.449	19.996	0.500
	Range	0.891 - 14.149	13.73 - 326.59	1.917E-05 - 2.243E-04	0.008 - 0.891	19.996 - 19.996	0.001 - 1.000
	Average Final	6.537	157.37	1.027E-04	0.739	497.310	0.501
	Range	1.445 - 14.101	31.81 - 331.76	3.347E-05 - 2.590E-04	0.033 - 1.445	497.310 - 497.310	0.002 - 1.000
	Average Change	0.430	32.92	2.459E-05	0.290	477.314	0.001
	Range	(-)0.048 - (+)0.909	5.17 - 59.66	1.430E-05 - 3.473E-05	0.025 - 0.554	477.314 - 477.314	0.000 - 0.002
	Average Change (%)	33.3	67.9	58.2	180.8	2387.0	150.4
	Range	(-)0.3 - (+)67.5	1.6 - 131.7	15.5 - 74.6	62.3 - 299.4	2387.0 - 2387.0	0.0 - 300.7

Appendix 4 – Summary statistics and averages of PHREEQCI batch reaction modeling results, continued. The table below contains averages and ranges for solutions for Sample 1A (acidic, room temperature) based on starting chemistries (Day 0 or Day 1). N=2 for exchange and n=2 for no exchange for all parameters except Mg (n=1) and Mg/Ca ratio (n=1).

SAMPLE 1A		**Day 0**					
		Ca (mmol/L)	**Alkalinity (mg $CaCO_3$/L)**	**Mn (mmol/L)**	**Mg (mmol/L)**	**Na (mmol/L)**	**Mg/Ca Ratio**
Exchange	**Average Initial**	8.691	1779.43	4.266E-04	9.669	157.370	1.387
	Range	6.973 - 10.409	1658.73 - 1900.13	4.122E-04 - 4.411E-04		153.590 - 161.150	
	Average Final	6.946	2547.31	3.970E-04	7.854	233.465	1.417
	Range	5.543 - 8.349	2395.86 - 2698.77	3.813E-04 - 4.127E-04		226.170 - 240.760	
	Average Change	(-)1.745	767.88	(-)2.963E-05	(-)1.815	76.095	0.030
	Range	(-)1.430 - (-)2.060	737.13 - 798.64	(-)2.842E-05 - (-)3.084E-05		72.580 - 79.610	
	Average Change (%)	(-)20.1	43.2	(-)7.0	(-)18.8	48.3	2.2
	Range	(-)19.8 - (-)20.5	42.0 - 44.4	(-)6.4 - (-)7.5		47.3 - 49.4	
No Exchange	**Average Initial**	22.098	626.16	7.126E-04	17.884	19.989	1.000
	Range	17.884 - 26.312	521.60 - 730.73	6.523E-04 - 7.729E-04		19.988 - 19.990	
	Average Final	27.124	903.38	9.975E-04	21.285	497.140	1.000
	Range	21.285 - 32.963	779.82 - 1026.93	9.033E-04 - 1.092E-03		497.120 - 497.160	
	Average Change	5.026	277.21	2.849E-04	3.401	477.151	0.000
	Range	3.401 - 6.651	258.22 - 296.20	2.510E-04 - 3.188E-04		477.132 - 477.170	
	Average Change (%)	22.1	45.0	39.9	19.0	2387.1	0.0
	Range	19.0 - 25.3	40.5 - 49.5	38.5 - 41.2		2387.0 - 2387.1	

Appendix 4 – Summary statistics and averages of PHREEQCI batch reaction modeling results, continued. The table below contains averages and ranges for solutions for Sample 1A (acidic, room temperature) based on starting chemistries (Day 0 or Day 1). N=2 for exchange and n=2 for no exchange for all parameters except Mg (n=1) and Mg/Ca ratio (n=1).

SAMPLE 1A		Day 1					
		Ca (mmol/L)	Alkalinity (mg $CaCO_3$/L)	Mn (mmol/L)	Mg (mmol/L)	Na (mmol/L)	Mg/Ca Ratio
Exchange	Average Initial	3.553	1721.45	1.908E-04	3.024	128.365	0.948
	Range	3.189 - 3.918	1620.69 - 1822.22	1.859E-04 - 1.958E-04		124.490 - 132.240	
	Average Final	2.750	2514.19	1.751E-04	2.571	180.970	1.078
	Range	2.385 - 3.114	2378.74 - 2649.63	1.702E-04 - 1.801E-04		174.610 - 187.330	
	Average Change	(-)0.804	792.73	(-)1.570E-05	(-)0.453	52.605	0.130
	Range	(-)0.804 - (-)0.804	758.05 - 827.41	(-)1.562E-05 - (-)1.577E-05		50.120 - 55.090	
	Average Change (%)	(-)22.9	46.1	(-)8.2	(-)15.0	41.0	13.7
	Range	(-)20.5 - (-)25.2	45.4 - 46.8	(-)8.1 - (-)8.4		40.3 - 41.7	
No Exchange	Average Initial	18.148	387.34	4.639E-04	4.844	19.994	0.255
	Range	17.313 - 18.983	285.81 - 488.86	3.837E-04 - 5.442E-04		19.993 - 19.994	
	Average Final	21.403	584.66	6.574E-04	7.097	497.260	0.335
	Range	21.163 - 21.642	470.12 - 699.20	5.575E-04 - 7.572E-04		497.250 - 497.270	
	Average Change	3.255	197.32	1.934E-04	2.253	477.267	0.080
	Range	2.180 - 4.329	184.31 - 210.34	1.738E-04 - 2.131E-04		477.257 - 477.276	
	Average Change (%)	18.2	53.8	42.2	46.5	2387.1	31.4
	Range	11.5 - 25.0	43.0 - 64.5	39.2 - 45.3		2387.1 - 2387.1	

Appendix 4 – Summary statistics and averages of PHREEQCI batch reaction modeling results, continued. The table below contains averages and ranges for solutions for Sample 5A (basic, room temperature) based on starting chemistries (Day 0 or Day 1). N=2 for exchange and n=2 for no exchange for all parameters except Mg (n=1) and Mg/Ca ratio (n=1).

SAMPLE 5A		**Day 0**					
		Ca (mmol/L)	**Alkalinity (mg $CaCO_3$/L)**	**Mn (mmol/L)**	**Mg (mmol/L)**	**Na (mmol/L)**	**Mg/Ca Ratio**
Exchange	**Average Initial**	0.097	1078.90	1.024E-05	0.115	52.778	1.502
	Range	0.076 - 0.117	1031.39 - 1126.42	1.011E-05 - 1.036E-05		50.962 - 54.594	
	Average Final	0.081	1460.43	9.837E-06	0.096	68.293	1.491
	Range	0.064 - 0.098	1395.20 - 1525.66	9.714E-06 - 9.960E-06		65.754 - 70.831	
	Average Change	(-)0.016	381.53	(-)4.010E-07	(-)0.019	15.515	(-)0.011
	Range	(-)0.012 - (-)0.019	363.81 - 399.24	(-)3.998E-07 - (-)4.022E-07		14.792 - 16.237	
	Average Change (%)	(-)16.1	35.4	(-)3.9	(-)16.6	29.4	-0.7
	Range	(-)16.0 - (-)16.2	35.3 - 35.4	(-)3.9 - (-)4.0		29.0 - 29.7	
No Exchange	**Average Initial**	1.119	78.75	3.448E-05	0.891	19.996	1.000
	Range	0.891 - 1.347	67.96 - 89.54	3.097E-05 - 3.799E-05		19.996 - 19.996	
	Average Final	1.851	132.96	5.914E-05	1.445	497.310	1.000
	Range	1.445 - 2.256	116.72 - 149.20	5.290E-05 - 6.538E-05		497.310 - 497.310	
	Average Change	0.732	54.21	2.466E-05	0.554	477.314	0.000
	Range	0.554 - 0.909	48.76 - 59.66	2.192E-05 - 2.739E-05		477.314 - 477.314	
	Average Change (%)	64.9	69.2	71.4	62.3	2387.0	0.0
	Range	62.3 - 67.5	66.6 - 71.8	70.8 - 72.1		2387.0 - 2387.0	

Appendix 4 – Summary statistics and averages of PHREEQCI batch reaction modeling results, continued. The table below contains averages and ranges for solutions for Sample 5A (basic, room temperature) based on starting chemistries (Day 0 or Day 1). N=2 for exchange and n=2 for no exchange for all parameters except Mg (n=1) and Mg/Ca ratio (n=1).

SAMPLE 5A		**Day 1**					
		Ca (mmol/L)	**Alkalinity (mg $CaCO_3$/L)**	**Mn (mmol/L)**	**Mg (mmol/L)**	**Na (mmol/L)**	**Mg/Ca Ratio**
Exchange	**Average Initial**	0.163	830.46	1.265E-05	0.077	58.170	0.443
	Range	0.154 - 0.173	757.95 - 902.98	1.237E-05 - 1.293E-05		55.384 - 60.956	
	Average Final	0.117	1200.86	1.176E-05	0.071	73.315	0.609
	Range	0.116 - 0.118	1116.46 - 1285.25	1.157E-05 - 1.195E-05		70.021 - 76.609	
	Average Change	(-)0.046	370.39	(-)8.905E-07	(-)0.006	15.145	0.166
	Range	(-)0.036 - (-)0.057	358.51 - 382.28	(-)7.960E-07 - (-)9.850E-07		14.637 - 15.653	
	Average Change (%)	(-)28.0	44.8	(-)7.0	(-)7.4	26.1	37.5
	Range	(-)23.2 - (-)32.7	42.3 - 47.3	(-)6.4 - (-)7.6		25.7 - 26.4	
No Exchange	**Average Initial**	11.094	170.16	1.217E-04	0.008	19.996	0.001
	Range	8.039 - 14.149	13.73 - 326.59	1.917E-05 - 2.243E-04		19.996 - 19.996	
	Average Final	11.223	181.78	1.462E-04	0.033	497.310	0.002
	Range	8.344 - 14.101	31.81 - 331.76	3.347E-05 - 2.590E-04		497.310 - 497.310	
	Average Change	0.129	11.63	2.451E-05	0.025	477.314	0.002
	Range	(-)0.048 - (+)0.305	5.17 - 18.08	1.430E-05 - 3.473E-05		477.314 - 477.314	
	Average Change (%)	1.7	66.7	45.0	299.4	2387.0	300.7
	Range	(-)0.3 - (+)3.8	1.6 - 131.7	15.5 - 74.6		2387.0 - 2387.0	

Appendix 4 – Summary statistics and averages of PHREEQCI batch reaction modeling results, continued. The table below contains averages and ranges for solutions for Sample 1A (acidic, room temperature) based on the solid solution used (calcite/rhodochrosite or dolomite/rhodochrosite). For calcite/rhodochrosite, n=2 for exchange and n=2 for no exchange for all parameters except Mg (n=0) and Mg/Ca ratio (n=0).

SAMPLE 1A		**Calcite/Rhodochrosite**					
		Ca (mmol/L)	**Alkalinity (mg $CaCO_3$/L)**	**Mn (mmol/L)**	**Mg (mmol/L)**	**Na (mmol/L)**	**Mg/Ca Ratio**
Exchange	**Average Initial**	7.163	1639.71	3.185E-04	N/A	139.040	N/A
	Range	3.918 - 10.409	1620.69 - 1658.73	1.958E-04 - 4.411E-04		124.490 - 153.590	
	Average Final	5.731	2387.30	2.964E-04	N/A	200.390	N/A
	Range	3.114 - 8.349	2378.74 - 2395.86	1.801E-04 - 4.127E-04		174.610 - 226.170	
	Average Change	(-)1.432	747.59	(-)2.210E-05	N/A	61.350	N/A
	Range	(-)0.804 - (-)2.060	737.13 - 758.05	(-)1.577E-05 - (-)2.842E-05		50.120 - 72.580	
	Average Change (%)	(-)20.2	45.6	(-)7.2	N/A	43.8	N/A
	Range	(-)19.8 - (-)20.5	44.4 - 46.8	(-)6.4 - (-)8.1		40.3 - 47.3	
No Exchange	**Average Initial**	21.813	403.70	6.585E-04	N/A	19.992	N/A
	Range	17.313 - 26.312	285.81 - 521.60	5.442E-04 - 7.729E-04		19.990 - 19.994	
	Average Final	27.303	624.97	9.245E-04	N/A	497.215	N/A
	Range	21.642 - 32.963	470.12 - 779.82	7.572E-04 - 1.092E-03		497.160 - 497.270	
	Average Change	5.490	221.27	2.659E-04	N/A	477.223	N/A
	Range	4.329 - 6.651	184.31 - 258.22	2.131E-04 - 3.188E-04		477.170 - 477.276	
	Average Change (%)	25.1	57.0	40.2	N/A	2387.1	N/A
	Range	25.0 - 25.3	49.5 - 64.5	39.2 - 41.2		2387.0 - 2387.1	

Appendix 4 – Summary statistics and averages of PHREEQCI batch reaction modeling results, continued. The table below contains averages and ranges for solutions for Sample 1A (acidic, room temperature) based on the solid solution used (calcite/rhodochrosite or dolomite/rhodochrosite). For dolomite/rhodochrosite, n=2 for exchange and n=2 for no exchange for all parameters, including Mg and Mg/Ca ratio.

SAMPLE 1A		**Dolomite/Rhodochrosite**					
		Ca (mmol/L)	**Alkalinity (mg $CaCO_3$/L)**	**Mn (mmol/L)**	**Mg (mmol/L)**	**Na (mmol/L)**	**Mg/Ca Ratio**
Exchange	**Average Initial**	5.081	1861.17	2.990E-04	6.346	146.695	1.167
	Range	3.189 - 6.973	1822.22 - 1900.13	1.859E-04 - 4.122E-04	3.024 - 9.669	132.240 - 161.150	0.948 - 1.387
	Average Final	3.964	2674.20	2.758E-04	5.213	214.045	1.247
	Range	2.385 - 5.543	2649.63 - 2698.77	1.702E-04 - 3.813E-04	2.571 - 7.854	187.330 - 240.760	1.078 - 1.417
	Average Change	(-)1.117	813.02	(-)2.323E-05	(-)1.134	67.350	0.080
	Range	(-)0.804 - (-)1.430	798.64 - 827.41	(-)1.562E-05 - (-)3.084E-05	(-)0.453 - (-)1.815	55.090 - 79.610	0.030 - 0.130
	Average Change (%)	(-)22.9	43.7	(-)7.9	(-)16.9	45.5	7.9
	Range	(-)20.5 - (-)25.2	42.0 - 45.4	(-)7.5 - (-)8.4	(-)15.0 - (-)18.8	41.7 - 49.4	2.2 - 13.7
No Exchange	**Average Initial**	18.434	609.79	5.180E-04	11.364	19.991	0.628
	Range	17.884 - 18.983	488.86 - 730.73	3.837E-04 - 6.523E-04	4.844 - 17.884	19.988 - 19.993	0.255 - 1.000
	Average Final	21.224	863.07	7.304E-04	14.191	497.185	0.668
	Range	21.163 - 21.285	699.20 - 1026.93	5.575E-04 - 9.033E-04	7.097 - 21.285	497.120 - 497.250	0.335 - 1.000
	Average Change	2.791	253.27	2.124E-04	2.827	477.195	0.040
	Range	2.180 - 3.401	210.34 - 296.20	1.738E-04 - 2.510E-04	2.253 - 3.401	477.132 - 477.257	0.000 - 0.080
	Average Change (%)	15.3	41.8	41.9	32.8	2387.1	15.7
	Range	11.5 - 19.0	40.5 - 43.0	38.5 - 45.3	19.0 - 46.5	2387.1 - 2387.1	0.0 - 31.4

Appendix 4 – Summary statistics and averages of PHREEQCI batch reaction modeling results, continued. The table below contains averages and ranges for solutions for Sample 1A (acidic, room temperature) based on the solid solution used (calcite/rhodochrosite or dolomite/rhodochrosite). For calcite/rhodochrosite, n=2 for exchange and n=2 for no exchange for all parameters except Mg (n=0) and Mg/Ca ratio (n=0).

SAMPLE 5A		**Calcite/Rhodochrosite**					
		Ca (mmol/L)	**Alkalinity (mg $CaCO_3$/L)**	**Mn (mmol/L)**	**Mg (mmol/L)**	**Na (mmol/L)**	**Mg/Ca Ratio**
Exchange	**Average Initial**	0.135	894.67	1.165E-05	N/A	53.173	N/A
	Range	0.117 - 0.154	757.95 - 1031.39	1.036E-05 - 1.293E-05		50.962 - 55.384	
	Average Final	0.108	1255.83	1.095E-05	N/A	67.888	N/A
	Range	0.098 - 0.118	1116.46 - 1395.20	9.960E-06 - 1.195E-05		65.754 - 70.021	
	Average Change	(-)0.027	361.16	(-)6.936E-07	N/A	14.715	N/A
	Range	(-)0.019 - (-)0.036	358.51 - 363.81	(-)4.022E-07 - (-)9.850E-07		14.637 - 14.792	
	Average Change (%)	(-)19.7	41.3	(-)5.7	N/A	27.7	N/A
	Range	(-)16.2 - (-)23.2	35.3 - 47.3	(-)3.9 - (-)7.6		26.4 - 29.0	
No Exchange	**Average Initial**	4.693	40.84	1.311E-04	N/A	19.996	N/A
	Range	1.347 - 8.039	13.73 - 67.96	3.799E-05 - 2.243E-04		19.996 - 19.996	
	Average Final	5.300	74.26	1.622E-04	N/A	497.310	N/A
	Range	2.256 - 8.344	31.81 - 116.72	6.538E-05 - 2.590E-04		497.310 - 497.310	
	Average Change	0.607	33.42	3.106E-05	N/A	477.314	N/A
	Range	0.305 - 0.909	18.08 - 48.76	2.739E-05 - 3.473E-05		477.314 - 477.314	
	Average Change (%)	35.7	101.7	43.8	N/A	2387.0	N/A
	Range	3.8 - 67.5	71.8 - 131.7	15.5 - 72.1		2387.0 - 2387.0	

Appendix 4 – Summary statistics and averages of PHREEQCI batch reaction modeling results, continued. The table below contains averages and ranges for solutions for Sample 1A (acidic, room temperature) based on the solid solution used (calcite/rhodochrosite or dolomite/rhodochrosite). For dolomite/rhodochrosite, n=2 for exchange and n=2 for no exchange for all parameters, including Mg and Mg/Ca ratio.

SAMPLE 5A		**Dolomite/Rhodochrosite**					
		Ca (mmol/L)	**Alkalinity (mg CaCO$_3$/L)**	**Mn (mmol/L)**	**Mg (mmol/L)**	**Na (mmol/L)**	**Mg/Ca Ratio**
Exchange	**Average Initial**	0.125	1014.70	1.124E-05	0.096	57.775	0.972
	Range	0.076 - 0.173	902.98 - 1126.42	1.011E-05 - 1.237E-05	0.077 - 0.115	54.594 - 60.956	0.443 - 1.502
	Average Final	0.090	1405.46	1.064E-05	0.083	73.720	1.050
	Range	0.064 - 0.116	1285.25 - 1525.66	9.714E-06 - 1.157E-05	0.071 - 0.096	70.831 - 76.609	0.609 - 1.491
	Average Change	(-)0.034	390.76	(-)5.979E-07	(-)0.012	15.945	0.077
	Range	(-)0.012 - (-)0.057	382.28 - 399.24	(-)3.998E-07 - (-)7.960E-07	(-)0.006 - (-)0.019	15.653 - 16.237	(-)0.011 - (+)0.166
	Average Change (%)	(-)24.3	38.9	(-)5.2	(-)12.0	27.7	18.4
	Range	(-)16.0 - (-)32.7	35.4 - 42.3	(-)4.0 - (-)6.4	(-)7.4 - (-)16.6	25.7 - 29.7	(-)0.7 - (+)37.5
No Exchange	**Average Initial**	7.520	208.06	2.507E-05	0.449	19.996	0.500
	Range	0.891 - 14.149	89.54 - 326.59	1.917E-05 - 3.097E-05	0.008 - 0.891	19.996 - 19.996	0.001 - 1.000
	Average Final	7.773	240.48	4.318E-05	0.739	497.310	0.501
	Range	1.445 - 14.101	149.20 - 331.76	3.347E-05 - 5.290E-05	0.033 - 1.445	497.310 - 497.310	0.002 - 1.000
	Average Change	0.253	32.42	1.811E-05	0.290	477.314	0.001
	Range	(-)0.048 - (+)0.554	5.17 - 59.66	1.430E-05 - 2.192E-05	0.025 - 0.554	477.314 - 477.314	0.000 - 0.002
	Average Change (%)	31.0	34.1	72.7	180.8	2387.0	150.4
	Range	(-)0.3 - (+)62.3	1.6 - 66.6	70.8 - 74.6	62.3 - 299.4	2387.0 - 2387.0	0.0 - 300.7