THE INFLUENCE OF PARENT-SOLUTION CHEMISTRY ON THE PRECIPITATION OF Pb-CARBONATES AT 25 °C, 1 BAR TOTAL PRESSURE

by

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A thesis submitted to McGill University in partial fulfilment of the requirements of the degree of Master's of Science

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Abstract

The influence of parent-solution chemistry on the precipitation of various Pbcarbonate phases (cerussite, PbCO_{3(s)}; hydrocerussite, Pb₃(CO₃)₂(OH)_{2(s)}; and phosgenite, Pb₂(CO₃)Cl_{2(s)}) is studied at 25 °C, 1 bar total pressure in the systems Pb(NO₃)₂-CO₂-H₂O and PbCl₂-CO₂-H₂O. Analysis of both fresh and aged (8 and 16 days), fine-grained Pb-carbonate precipitates resulting from the addition of 0.035 M Pb-bearing (PbCl₂ or Pb(NO₃)₂) into 0.035 M C-bearing (NaHCO₃ and Na₂CO₃) reagents (or *vice versa*) by powder X-ray diffraction and variable-pressure scanning electron microscopy reveals that: 1) a potential relationship exists between crystal morphology and aqueous speciation (*i.e.* in the presence of NO₃⁻ and Cl⁻); and 2) solid-phase interconversions between cerussite \leftrightarrow hydrocerussite and cerussite \leftrightarrow phosgenite readily occurs until equilibrium conditions are achieved in a period of time < 8 days. Further, the precipitation conditions corresponding to various morphologies and habits of cerussite (prismatic, bladed, platy-hexagonal) and phosgenite (tabular, intergrown) is documented.

Résumé

L'influence des propriétés chimiques de la solution-mère sur la précipitation de certaines phases de carbonate de plomb (cérussite, PbCO_{3(s)}; hydrocérussite, Pb₃(CO₃)₂(OH)_{2(s)}; and phosgénite, Pb₂(CO₃)Cl_{2(s)}) est documentée à 25 °C, 1 bar de pression totale dans les systèmes Pb(NO₃)₂-CO₂-H₂O et PbCl₂-CO₂-H₂O. Les analyses, par diffraction de rayons-X et microscopie électronique à pression variable, des précipités fraiches et âgées (de 8 et 16 jours) résultant d'une combinaison d'une solution de 0.035 M de Pb et 0.035 M de C (NaHCO₃ ou Na₂CO₃) ou *vice versa* indiquent: 1) une relation potentielle entre la morphologie des précipités et la spéciation aqueuse ou la nature des ions Cl⁻ et NO₃⁻ durant la précipitation; et 2) la conversion entre les phases solides cérussite \leftrightarrow hydro cérussite et cérussite \leftrightarrow phosgénite s'èffectue jusqu'à l'atteinte de l'équilibre, en moins que 8 jours. De plus, les conditions de précipitation menant à différentes habitus de cérussite (prismatique, hexagonale-plate, et en lamelle) et phosgénite (tabulaire et entrecroisés) sont documentées.

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Chapter 1:

Introduction

1.1. General

The introduction of lead (Pb) to the natural environment results primarily from anthropogenic activities such as mining and smelting, use of biosolids as agricultural fertilizer, and use of antiknock gasoline additives such as trimethyl and tetraethyl Pb; Pb derived from natural geologic sources is of relatively minor environmental significance (Brannvall et al., 2001). Once introduced into the terrestrial environment, Pb can severely compromise the local ecosystem and groundwater supply and, as such, is listed as a priority water pollutant by the USEPA (e.g. USEPA, 2004). Concerns surrounding Pb contamination are amplified due to its toxicity at low levels, potential long-term health effects, and long residence time in soils (e.g. Wang et al., 1995). A complete understanding of the behaviour of Pb in natural systems under various geochemical conditions (i.e. pH, Eh, and ionic strength) is required to accurately predict its activity, bioavailability, and mobility in the subsurface. Despite the large amount of research directed towards this goal in the recent past (e.g. Bilinksi and Schindler, 1982; Taylor and Lopata, 1984; Badawy et al., 2002; Godelitsas et al., 2003b), the complex geochemical behaviour of Pb in aqueous solutions remains only moderately understood.

The solubility, lability, and bioavailability of Pb introduced into the subsurface can be affected and controlled by several geochemical processes, including: 1) specific adsorption at the surface of pre-existing minerals (*e.g.*

montmorillonite: Strawn and Sparks, 1999; amorphous quartz: Elzinga and Sparks, 2002; calcite: Rouff et al., 2004); 2) adsorption to organic matter (*e.g.* Turpeinen et al., 2000); 3) precipitation of Pb-bearing compounds (Bilinksi and Schindler, 1982; Badawy et al., 2002); 4) co-precipitation with other phases (*e.g.* Curti et al., 2004); and 5) heterogeneous precipitation on the surface of pre-existing minerals (calcite: Godselitsas et al., 2003*a*,*b*; Rouff et al., 2004, apatite: Traina and Laperche, 1999). A list of Pb minerals of potential environmental significance is presented in Table 1.1 along with pertinent thermodynamic data for comparison.

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Interactions between Pb and the carbonate system can potentially control the subsurface mobility and bioavailability of Pb, either by direct precipitation of Pbcarbonates or interaction with other carbonate phases, particularly calcite due to its geological ubiquity. Lead-carbonates are known to readily precipitate (Bilinksi and Schindler, 1982; Taylor and Lopata, 1984) at low temperatures with a variety of stoichiometries; in addition to the stoichiometrically simple PbCO₃ (cerussite), other Pb-carbonates, such as $Pb_3(CO_3)_2(OH)_{2(s)}$ (hydrocerussite), $Pb_2(CO_3)Cl_{2(s)}$ (phosgenite), and $Pb_{10}O(OH)_6(CO_3)_{6(s)}$ (plumbonacrite) may also play a role. Lead interactions with calcite, either by co-precipitation as a trace component or surface adsorption/precipitation, are also potentially important.

This study employs a laboratory-based, experimental approach to investigate the effect of parent-solution geochemistry (counter-ion speciation, pH, and saturation/precipitation kinetics) on precipitation of Pb-carbonate phases at 25 °C, 1

Table 1.1. Selected cl containing mineral phas	iemical and thermodynamic es of environmental interest	information of nat at 25 °C and 1 ba	urally forming Pb- r (10 ⁵ Pascal) total
Name	Formula	∆G _f (kJ/mol)	logK _{sp}
Oxides and Hydroxides:			· ·
Litharge	РЬО	-189.198 ⁽⁶⁾	-12.9 ⁽³⁾
Massicot	РЬО	-188.361 ⁽⁶⁾	-15.2 ⁽⁷⁾
Lead hydroxide	Pb(OH) ₂	-452.483 ⁽⁶⁾	+8.15 ⁽⁸⁾
Carbonates:	1	· · · · · · · · · · · · · · · · · · ·	<u> </u>
Cerussite	PbCO ₃	-628.0 ⁽¹⁾	-12.8 ⁽³⁾
	an a	-625.34 ⁽¹⁾	$-12.15\pm0.05^{(2)}$
Hydrocerussite	Pb ₃ (CO ₃) ₂ (OH) ₂	-1705 ⁽¹⁾	-44.08 ⁽²⁾
		-1699.8±0.05 ⁽⁴⁾	
Plumbonacrite	Pb ₁₀ O(OH) ₆ (CO ₃) ₆	-5310 ⁽¹⁾	
Phosgenite	Pb ₂ (CO ₃)Cl ₂	-954.11 ⁽⁵⁾	-19.81 ⁽⁶⁾
Barstowite	$Pb_4(CO_3)Cl_6 \cdot (H_2O)$	N/D	N/D
Sulphides:	J	_ I	
Galena	PbS	-95.85 ⁽⁵⁾	-27.5 ⁽³⁾
Sulfates:	J,		
Anglesite	PbSO ₄	-813.80 ⁽⁵⁾	-7.7 ⁽³⁾
Phosphates:			
Pyromorphite	Pb ₅ (PO ₄) ₃ Cl	-3811.55 ⁽⁵⁾	-84.4 ⁽³⁾
Corkite	$PbFe_3(PO_4)(SO_4)(OH)_6$	N/D	-112.6 ⁽³⁾
Hindsalite	PbAl ₃ (PO ₄)(SO ₄)(OH) ₆	N/D	-99.1 ⁽³⁾
Plumbogummite	PbAl ₃ (PO ₄) ₂ (OH) ₅ · H ₂ O	N/D	-99.39 ⁽⁴⁾
Hydroxy-	Pb ₅ (PO ₄) ₃ OH	-3798.15 ⁽⁵⁾	-76.8 ⁽³⁾
pyromorphite			
Fluoro-pyromorphite	Pb ₅ (PO ₄) ₃ F	-3895.64 ⁽⁵⁾	-71.6 ⁽³⁾
Bromo-pyromorphite	Pb ₅ (PO ₄) ₃ Br	N/D	-78.6 ⁽³⁾
	Pb(H ₂ PO ₄)	-2356.77 ⁽⁵⁾	-9.85 ⁽⁵⁾

ND = No data. References: (1) Taylor and Lopata (1984); (2) Bilinski and Schindler (1982); (3) Ruby et al. (1994) and references therein; (4) Mercy et al. (1998); (5) Lindsay (1979); (6) see Pina et al. (2000); (7) calculated from: PbO_(massicot) + H₂O \leftrightarrow Pb²⁺ + 2H₂O with data from Robie et al. (1979); (8) calculated from: Pb(OH)_{2(s)} + 2H⁺ \leftrightarrow Pb²⁺ + 2H₂O (see Parkhurst and Apello, 1999). bar total pressure. The effects of two particular counter-ions (Cl⁻ and NO₃⁻) and their associated aqueous species are investigated.

1.2. Lead carbonates

1.2.1. Mineralogy

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During the course of this study, three mineral phases were observed to precipitate: cerussite, hydrocerussite, and phosgenite. In order to place them in a proper geologic and mineralogical context, the following section discusses pertinent aspects of their crystal chemistry and crystallographic habit.

1.2.1.1. Cerussite

Cerussite, PbCO_{3(s)}, is an orthorhombic carbonate, crystallizing in the space group *Pmcn*. Structurally, cerussite, as well as all other orthorhombic carbonates, is composed of layers of pseudohexagonally-arranged metal atoms parallel to (001) with an ABAB layer sequence along the *c*-axis; within metal layers, alternate atoms are displaced approximately ± 0.05 Å out of the plane. Between each metal layer is a layer of CO₃ groups, pseudohexagonally arranged within the *ab* plane and 'corrugated' because of differing heights along *c*. Each CO₃ group is surrounded by six metal atoms, and each metal atom is nine-coordinated, yielding the structural formula ^[IX]A^[III]C^[IV]O₃. Six of the Pb-O bonds are to the oxygens at the edges of three separate CO₃ groups; (Speer, 1983). Cerussite crystals may assume several different morphologies depending on the conditions of crystallization. Franke et al. (1981) determined that with increasing pressure during crystallization, the following systematic variation in crystal habit is observed: pseudo-hexagonal prismatic crystals (< 200 bar), pseudohexagonal dipyramidal crystals (200-500 bars), pseudohexagonal tabular crystals (500 – 1000 bars), and massive-grained crystals (1000 to 1500 bars). Typical cerussite forms are $\{010\}, \{110\}, and \{021\}.$

1.2.1.2. Hydrocerussite

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trigonal hydroxycarbonate $Pb_3(CO_3)_2(OH)_{2(s)}$ is Hydrocerussite, а crystallizing in the space group R3m. Structurally, hydrocerussite is composed of hexagonal sheets of Pb atoms, stacked along the *c*-axis in the sequence BAABAA. Layer A is composed of Pb and CO₃ and can be considered as interpenetrating hexagonal nets of Pb and CO_3 groups; layer B is composed of Pb and OH and is subject to static disorder. Lead in layer A is 10-coordinated by 9 O atoms from CO₃ groups and 1 OH, whereas the Pb in layer B is 6-coordinated to 6 O atoms from CO_3 groups (Martinetto et al., 2002). The double-layer, AA, is essentially the cerussite structure and forms the structural 'backbone' of hydrocerussite; this is also observed in other Pb-carbonate minerals as well, such as macphersonite, plumbonacrite, leadhillite, and susannite (Krivovichev and Burns, 2000a,b,c). Hydrocerussite crystals commonly have platy, micaceous crystals with forms being {112}, {114}, and {001}.

1.2.1.3. Phosgenite

Phosgenite, $Pb_2(CO_3)Cl_{2(s)}$, is a tetragonal mineral crystallizing in the space group *P4/mbm*. Structurally, the Pb and Cl atoms define layers parallel to (001); these sheets are connected by CO₃ groups. The carbonate groups have the usual trigonal shape and lie in {110} mirror planes. Lead is coordinated by five Cl and four O atoms. Typical phosgenite crystal forms are {011}, {110}, {111}, and {001} (see Pina et al., 1996, and references therein).

1.2.2. Geology and geochemistry

Despite the wide variety of Pb-carbonate minerals (see Table 1.1), cerussite and hydrocerussite are the most geologically abundant; they commonly occur as supergene Pb ores formed by the interaction of carbonated waters and galena. Accordingly, the activity of Pb in most geologic systems will be controlled by the solubility of cerussite and hydrocerussite (Bilinski and Schindler, 1982; Mercy et al., 1998). However, particular aspects of the paragenesis, which will be shown to be intrinsically related to the relative solubilities of these two phases, remain poorly understood. As the occurrence of hydrocerussite is rare compared to cerussite in natural environments (Garrels, 1957; Mercy et al., 1998), it is reasonable to assume that cerussite is stable relative to hydrocerussite. Nevertheless, assessing the relative stability of these minerals in solution through thermodynamic calculations, particularly in solutions exposed to atmospheric P_{CO2} , is complicated by uncertainty of available thermodynamic data. The thermodynamic stability constants derived from classical solubility experiments are highly sensitive to the aqueous speciation

model chosen to interpret the data (Bilinksi and Schindler, 1982; Mercy et al., 1998). The reaction of key importance that links the two phases is as follows:

(Eqn. 1.1)
$$3PbCO_{3(s)} + H_2O_{(l)} \leftrightarrow Pb_3(CO_3)_2(OH)_{2(s)} + CO_{2(g)}$$

(Eqn. 1.2) $K_{rxn} = \{\text{products}\}/\{\text{reactants}\}$

As the equilibrium constant for Eqn. 1.1, K_{rxn} , is equal to P_{CO2} ($\approx fCO_2$ at low T and P), it is clear that the relative stabilities of cerussite and hydrocerussite will largely be controlled by the P_{CO2} of the solution. It is problematic, however, that the estimates of the equilibrium constant closely straddle the atmospheric P_{CO2} value of $10^{-3.5}$ atm (currently approaching $10^{-3.42}$ atm); thus small uncertainties in calculated ΔG^{o}_{f} for cerussite and hydrocerussite result in different projected mineral stabilities.

Bilinski and Schindler (1982) assessed the relative stability of cerussite and hydrocerussite in terms of homogeneous/heterogeneous solubility reactions and aqueous complexation relationships within the system Pb²⁺-CO₂-H₂O at 25°C, I = 0.3M; the geochemical behaviour of this system is largely controlled by Eqns 1.3 to 1.5 (Table 1.2). The extremely small K for reaction Eqn. 1.6 indicates that PbO_(s) is of virtually no importance as a solubility-controlling phase in the presence of CO₂. In this system, thermodynamic calculations corrected by the authors to account for the presence of aqueous species such as HCO₃⁻, CO₃²⁻, Pb(OH)_n⁽²⁻ⁿ⁾, and Pb(CO₃)_n⁽²⁻²ⁿ⁾ yield an equilibrium constant for Eqn. 1.1 of $K = P_{CO2} = 10^{-2.82}$, implying hydrocerussite is stable under atmospheric conditions; omitting such corrections yields an equilibrium constant of $K = P_{CO2} = 10^{-4.80}$, implying cerussite, rather than

hydrocerussite, is stable under atmospheric conditions. In fact, paragenetic evidence (Garrels, 1957) reveals that it is unreasonable for hydrocerussite to be the predominant, stable phase under atmospheric conditions, which suggests an inconsistency in the speciation model used.

Taylor and Lopata (1984) experimentally investigated the solubility and stability relationships of mineral phases in the system PbO-CO₂-H₂O by direct measurement of equilibrium P_{CO2} values for equations 1.1, 1.7, and 1.8; these values are then combined with previously published thermodynamic data for PbO_(s) in order to recalculate the values of ΔG°_{f} , and thus logK_{sp}, for cerussite, hydrocerussite, and plumbonacrite (Table 1.3), thus by-passing the problem of the aqueous speciation model encountered by Bilinski and Schindler (1982).

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Integration of these thermodynamic values by Taylor and Lopata (1984) over $[C]_{tot}$ and pH space suggests that, for natural waters of high total carbon concentration (*i.e.* log $[C]_{tot} > -4$), stability fields are narrow for litharge (12 < pH < 14) and plumbonacrite (11< pH < 13), but broader for hydrocerussite (8 < pH < 12) and cerussite (4 < pH < 9). Furthermore, the thermodynamic data of Taylor and Lopata (1984) contradict those of Bilinksi and Schindler (1982), indicating that in natural waters equilibrated with atmospheric P_{CO2} , cerussite is the most stable phase; however, only a slight depletion in P_{CO2} would be necessary to shift the stability fields and reverse these relative stabilities.

The relative stabilities of cerussite and hydrocerussite were again investigated by Mercy et al. (1998) who used an electrochemical cell to measure the solubility of

Table 1.2. Governing chemical reactions in the system $Pb^{2+}-CO_2-H_2O_2$, as defined by Bilinski and Schindler (1982).		
Eqn.		LogK
1.3	$Pb^{2^+} + CO_3^{2^-} = Pb(CO_3)^0_{(aq)}$	5.40 ± 0.10
1.4	$PbCO_{3(s)} + 2H^{+} = Pb^{2+} + CO_{2(g)} + H_2O$	5.20 ± 0.03
1.5	$Pb(CO_3)_{0.67}(OH)_{0.67} + 2H^+ = Pb^{2+} + 0.67CO_2 + 1.33H_2O$	6.80 ± 0.20
-		6.11 ± 0.10
1.6	$PbO_{(s)} + H_2O = Pb^{2+} + 2OH^{-}$	-15.30

Table 1984)	1.3. Important solid phase interconversion in the system PbO-CO ₂ -H ₂ O	(Taylor and Lopata,
Eqn.		LogK
1.7	$1/6 Pb_{10}O(OH)_6(CO_3)_{6(s)} \leftrightarrow 5/3PbO_{(s)} + CO_{2(g)} + 1/2H_2O_{(l)}$	10 ^{-4.9}
1.8	$5Pb_3(OH)_2(CO_3)_{2(s)} \leftrightarrow 3/2Pb_{10}O(OH)_6(CO_3)_{6(s)} + CO_{2(g)} + 1/2H_2O$	10 ^{-2.9}

hydrocerussite at 25 °C, 1 bar. The result, ΔG°_{f} (hydrocerussite) = -1699.8 ± 1.6 kJ/mol, corresponds to the value reported by Taylor and Lopata (1984). Nevertheless, despite a more dependable value for ΔG°_{f} (hydrocerussite), the true K for Eqn. 1.1 remains unknown, as estimates of ΔG°_{f} (cerussite), inaccessible by electrochemical cell measurements, vary between -635.38 kJ/mol (Robie et al., 1979) and -628.0 kJ/mol (Taylor and Lopata, 1984). Calculation of the equilibrium constant for Eqn. 1.1, using the former ΔG°_{f} yields $K_{eq} = 10^{-4.7} = P_{CO2}$.

Mercy et al. (1998) report that in a solution open to the atmosphere, hydrocerussite is always more soluble than cerussite and, thus, unstable; conversely, in systems closed to the atmosphere, the P_{CO2} is more variable and a reversal of the relative stabilities of the two phases occurs as pH increases. Assuming the system had equilibrated with the atmosphere prior to closure, hydrocerussite becomes more stable than cerussite at pH > 7. Irrespective of the system being open or closed to the atmosphere, in a system dominated by either cerussite or hydrocerussite, the equilibrium Pb activity remains relatively invariant with any given pH; Pb concentrations vary within a narrow range, $5.8 < -\log[Pb]_{tot} < 6.6$, as P_{CO2} varies between 10^{-3} and 10^5 Pa, although the position of the solubility minima migrates from pH ≈ 10 to 6.5 (Taylor and Lopata, 1984).

1.2.3. Chemistry of phosgenite \leftrightarrow cerussite reactions

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The crystallization and, therefore, stability of phosgenite and cerussite is strongly controlled by the pH of the parent-solution; although the specific values depend on the chloride content of the solution (Edwards et al., 1992). As a result of changing pH conditions, phosgenite has been observed to transform to cerussite by a solvent-mediated dissolution-recrystallization mechanism (Pina et al., 1996; 2000). This transformation is structurally-controlled and results in the following epitaxial relationships: $<110>_{ph} \parallel [001]_{cer}, <110>_{ph} \parallel [100]_{cer}, and <math><001>_{ph} \parallel [010]_{cer}$. During the transformation process, the stronger Pb-CO₃ bonds are preserved while the weaker Pb-Cl bonds are broken, allowing for the release of Cl atoms from the lattice. *In situ* inspection of the reaction process by atomic force microscopy (Pina et al., 2000) reveals that cerussite nucleates on the (001) surface of phosgenite as crystals of pseudohexagonal tabular habit. As crystal growth proceeds, cerussite morphology is defined by {010} as the main form, and {110} and {100} as secondary forms.

A notable feature of the phosgenite-cerussite transition is the autocatalytic character of the reaction, whereby the rate of phosgenite dissolution is proportional to the rate of cerussite crystal growth (Pina et al., 2000). The growth of cerussite nuclei results in undersaturation of the solution with respect to phosgenite, resulting in an increased rate of dissolution and a corresponding increase in the rate of cerussite growth. This mechanism can result in a stationary, nonequilibrium state (*i.e.* steady state) where the concentration of the reactants and products are invariant in time while the system remains far from equilibrium; this state can occur because the low solubility of the two phases ensures that growth and dissolution occurs at high supersaturation levels. This autocatalytic reaction explains the ready dissolution of phosgenite, which is sparingly soluble, $\log K_{sp} = -19.81$.

1.3. Pb²⁺ interactions with calcite in solution

As calcite is, by far, the most ubiquitous carbonate mineral on Earth, its interactions with the Pb^{2+} ion will have considerable control on the Pb^{2+} activity and its bioavailability. Interactions can occur by several mechanisms, including: 1) calcite dissolution leading to homogeneous nucleation of pure Pb-carbonate phases in solution; 2) adsorption/solid-state diffusion on the surface of pre-existing calcite; 3) Ca-Pb cation exchange in the calcite lattice; 4) co-precipitation with growing calcite grains; and 5) heterogeneous nucleation of Pb-carbonate phases (e.g. hydrocerussite, cerussite) on the surface of pre-existing carbonate grains. At sufficiently high metal activities (i.e. 0.005 M), heterogeneous nucleation and subsequent surface precipitation of cerussite and hydrocerussite have been shown to occur on the calcite surface (Godelitsas et al., 2003b; Rouff et al., 2004). Similar mechanisms have been observed at the calcite surface for Hg^{2+} (Godelitsas et al., 2003*a*), Mn^{2+} (Lea et al., 2003), Eu³⁺ (Curti et al., 2004; Lakshtanov and Stipp, 2004), Ba²⁺ (Astilleros et al., 2000), and Sr²⁺ (Astilleros et al., 2003). This study is primarily concerned with characterizing the physical and chemical aspects of minerals that could, if Pb were present, precipitate on the calcite surface. Therefore, the following discussion explores the potential structural relationship between calcite and a Pb-carbonate surface precipitate.

1.3.1. Calcite surface structure and Pb²⁺ sorption processes

On a growing calcite crystal, the {10-14} rhombohedron may contain threeor four-sided hillocks, indicating growth dominated by a dislocation-controlled layerby-layer mechanism; these are bilaterally symmetrical and contain two distinct growth steps, characterized by opposite types of kinks ([441]_{+/+}, [441]_{-/-}) along <441>. The difference in coordination sizes and atomic geometries of the two kink sites, the [441]_{+/+} and [441]_{-/-} sites, favours the incorporation of divalent metals with ionic radii greater than and less than that of Ca²⁺, respectively (Paquette and Reeder, 1995). For comparison, the atomic radii of relevance here are as follows: $^{[VI]}Pb^{2+} =$ 1.19 Å, $^{[IX]}Pb^{2+} = 1.35$ Å, $^{[VI]}Ca^{2+} = 1.00$ Å, $^{[IX]}Ca^{2+} = 1.18$ Å (Shannon, 1976). Therefore, $^{[IX]}Pb$ would be expected to be incorporated in the larger [441]_{+/+} kink site. On the other hand, as the difference in these ionic radii is significantly different, the extent of Pb \leftrightarrow Ca substitution is limited. Further incorporation of Pb into the calcite structure must ultimately result in the growth of a distinct Pb-carbonate phase.

The precipitation of Pb-carbonate phases on the surface of calcium carbonate minerals occurs in solutions of sufficiently high Pb concentration (*i.e.* 0.005 M; Godelitsas et al., 2003*b*; Rouff et al., 2004). Although relatively few studies have examined the physicochemical processes related to this heterogeneous nucleation, they propose structurally-controlled, epitaxial growth mechanisms. In one of the more detailed investigations, Godelitsas et al. (2003*b*), using atomic force microscopy, report the heterogeneous nucleation and subsequent precipitation of tabular, hexagonal, and prismatic Pb-carbonates on the surface of calcite and aragonite in solutions of [Pb]_{tot} \approx 0.005 M after only ~10 minutes. Although both hydrocerussite and cerussite were observed on the calcite surface, only cerussite was observed in epitaxial growth with aragonite.

According to Godelitsas et al. (2003b), the crystalline structure of hydrocerussite may preclude any epitaxial relationship with aragonite. On calcite, however, epitaxial hydrocerussite results because structural units in layer A (composed of Pb²⁺ and CO₃²⁻ and stacked along (001)) are arranged similarly to the same units on the {10-14} plane of calcite. There is no such fit between the structures of hydrocerussite and orthorhombic aragonite.

In solutions of $[Pb^{2^+}]_{initial} \approx 0.005$ M (Godelitsas et al., 2003*b*), rhombic etch pits on the calcite surface, which result from dissolution of calcite crystals upon introduction into Pb-enriched distilled water, are rapidly broadened and further transformed into elongated, asymmetric ovals, suggesting that, under these conditions, there may be no preferential incorporation/sorption of Pb²⁺ ions between large and small sites. Shortly after, nucleation occurs inside the elongated oval etch pits and later onto the neighboring microterraces and edges of microsteps, leading to growth of Pb-carbonate crystals and aggregates of cerussite and hydrocerussite crystals of different sizes and morphologies.

The geochemical factors determining the physical morphology of the precipitating Pb-carbonate phases remains poorly understood. Whereas Godelitsas et al. (2003*b*) report the presence of pseudo-hexagonal, tabular cerussite crystals on the surfaces of calcite and aragonite, Pina et al. (2000) observed the presence of pseudohexagonal, tabular cerussite crystals produced by autocatalytic processes on the surface of large (5 mm²) phosgenite crystals that were allowed to react in a fluid cell at 25 °C with a dissolving solution of de-ionized water and Na₂CO₃ (0 – 25 μ mol/L). Conversely, Franke et al. (1981) state that, under ambient atmospheric

conditions, cerussite shows a typical columnar prismatic habit, and only crystals developed at T = 200 °C and 500 < P < 1000 bars developed the pseudohexagonal form. Thus, it appears that morphology cannot be used as an absolute determinative factor for crystal identification for Pb-carbonate crystals that nucleate either by heterogeneous or homogeneous processes.

1.4. Objectives of study

The principal objective of this study is to amplify the knowledge of solid and liquid phase behaviour in Pb-carbonate systems through investigation of the thermodynamic and kinetic evolution of parent-solutions in the systems CO_2 -H₂O-PbCl₂ and CO_2 -H₂O-Pb(NO₃)₂ as the precipitation of Pb-carbonate phases was induced (at 25°C, 1 bar total pressure) in a number of experimental scenarios. The study also investigated: 1) the relationship between parent-solution chemistry and the species of precipitating Pb-carbonate; 2) the relative effect of two counter ion species (Cl⁻ and NO₃⁻) on crystal morphology, and crystal size of the precipitates; and 3) the potential solid-solid interconversions and the resulting morphological differences upon aging of the precipitates. Ultimately, this information could be used to enhance further efforts in modeling the thermodynamics of Pb-calcite interactions.

Chapter 2:

Experimental and Analytical Procedures

2.1. Experimental systems investigated

Precipitation of Pb-carbonate minerals (cerussite, hydrocerussite, and phosgenite) was induced under ambient conditions in an open atmosphere. A 975 Harvard Diffusion Pump was used to inject 50 ml of Na₂CO₃ or NaHCO₃ solution into 50 ml of PbCl₂ or PbNO₃ solution in a reaction beaker, and vice versa. The contents of the 200 ml cylindrical, Pyrex[®] reaction vessel were continually stirred with a VWR 6-holder Orbital Shaker at 215 rpm (Figure 2.1). The experimental conditions and solution/titrant concentrations are specified in Table 2.1. Each experimental reaction was performed at three different injection rates (Table 2.2) to examine the expression of precipitation kinetics on the resulting precipitate composition, mineralogy and morphology. Further, a second (and third) set of experiments was repeated at the lowest injection rate (0.5 ml/min) and allowed to age for 8 (and 16) days in a 120 ml glass bottle, sealed from the atmosphere and shaken This allowed for an investigation of the solid-phase vigorously each day. interconversion and stability of the precipitates.

2.2. Reagent solution preparation

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Four separate solutions (PbCl₂, Pb(NO₃)₂, Na₂CO₃, and NaHCO₃) were prepared using reagent-grade chemicals purchased from VWR Scientific. A weighed


Figure 2.1. Schematic illustration of basic experimental set-up used in all precipitation experiments.

Table 2.1. Experimental systems									
	Reaction	n Pathw	$[Pb_{(aq)}] \approx [C_{tot}]$	pH _{initial}					
(1)	PbCl ₂	\rightarrow	NaHCO ₃	0.035	8.6				
(2)	PbCl ₂	\rightarrow	Na ₂ CO ₃	0.035	10.9				
(3)	NaHCO ₃	\rightarrow	PbCl ₂	0.035	4.8				
(4)	Na ₂ CO ₃	\rightarrow	PbCl ₂	0.035	4.9				
(5)	$Pb(NO_3)_2$	\rightarrow	NaHCO ₃	0.035	8.6				
(6)	$Pb(NO_3)_2$	\rightarrow	Na ₂ CO ₃	0.035	10.9				
(7)	NaHCO ₃	\rightarrow	$Pb(NO_3)_2$	0.035	4.2				
(8)	Na ₂ CO ₃	\rightarrow	$Pb(NO_3)_2$	0.035	4.2				

Tabl	e 2.2. Inject	ion rates
	Injection	Total Injection
	Rate	Time
	(ml/min)	(hrs)
(1)	15.4	0.054
(2)	2.8	0.29
(3)	0.6	1.6

amount of salt (either Na₂CO_{3(s)}·10H₂O, NaHCO_{3(s)}, or PbCl_{2(s)}) was dissolved in double-distilled water (i.e. $\Sigma CO_2 \approx 0$ M) to $[Pb^{2+}]_{tot} \approx 0.035$ M or total dissolved inorganic carbon concentration (ΣCO_2) ≈ 0.035 M. The composition of all solutions was set to $[Pb^{2+}]_{tot} = \sum CO_2$ to allow for the precipitation of stoichiometric PbCO_{3(s)}. The PbCl₂ solution concentration corresponds to 80% saturation with respect to the solid ($K_{sp(25 \circ C)} = 1.7 \times 10^{-5}$; CRC Handbook of Chemistry & Physics, 2005), thus reducing the risk of unwanted precipitation during storage of the reagent solution and providing for enough precipitate for various analyses upon mixing of the The Pb(NO₃)₂ solution was also prepared at the same experimental reagents. concentration, although this solution was highly undersaturated (solubility of $Pb(NO_3)_{2(s)}$ (at 25 °C) = 597 g/L_{H2O}; CRC Handbook of Chemistry and Physics, 2005). Upon the appropriate dilution, the [Pb]_{tot} of the initial solutions was verified using a Perkin-Elmer[®] AAnalyst 800 atomic absorption spectrometer using an airacetylene flame, and calibrated against external standards (1, 5, 10, 15, 20, and 30 ppm) prepared in matrix-matched solutions (reproducible to ± 1 ppm). The $\sum CO_2$ of the carbonate solutions was determined before all experiments using a UIC Coulometrics coulometer, with results reproducible to $\sim 2.49 \text{ x } 10^{-7} \text{ mol C/g.}$

2.3. Monitoring of experimental systems

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Changes in pH were monitored throughout each experiment at specific time intervals, typically every 10 to 60 seconds, depending on the rate of reagent injection. All pH data were collected using Radiometer GK2401C Red Rod Combination pH- electrodes connected to an ELIT 9804 4-channel pH/Ion analyzer. The electrodes were calibrated daily using NIST-traceable buffer solutions of pH 4.00, 7.00, and 10.00 at 25 °C. Data were recorded automatically on a desktop PC. Further, at the end of the aged experiments (both 8 and 16 days), the $\sum CO_2$ of the bulk solution was determined by coulometry.

2.4. Recovery and analysis of precipitates by XRD and SEM

2.4.1. Solid/liquid separation

For all experiments, the precipitate and mixed reagents were separated by filtration through a 0.45 μ m Millipore[®] HA filter, rinsed with Milli-Q[®] water and allowed to dry at ambient temperature for several days, in an open atmosphere. Samples were stored in a covered, plastic dish for several days, prior to analysis.

2.4.2. Powder X-ray diffraction

Identification of solid phases present in the precipitate was carried out using a Rigaku (D/Max 2400 Automated Powder Diffractometer) X-ray powder diffractometer with CuK α radiation. The samples were placed on slurry mounts and scanned between $5 < 2\theta < 100$ at a scan speed of 20 2 θ /min and a step size of 0.02 2 θ at 40 Volts / 180 Amps (Note: three samples were analyzed by a Siemens Diffractometer D5000, using the same procedure and MoK α radiation at UQAM, due to a malfunction in the Rigaku machine at McGill University). MDI Jade 6.5

software was used for XRD data processing; the background was automatically stripped and all profiles were set to fixed-slit geometry.

Powder X-ray diffractometry provided phase identification and detected qualitative trends at different injection rates and upon aging of the precipitates. The XRD patterns of Pb-carbonate minerals, in particular cerussite and hydrocerussite, are too similar to evaluate their proportions quantitatively in a mixture, a problem discussed in further detail by Frost et al. (2003). Nevertheless, synthetic hydrocerussite and cerussite were purchased from VWR[®] Scientific in order to construct a peak height/area calibration curve. However, unlike the hydrocerussite generated by the experiments, the commercially acquired hydrocerussite did not adequately match any of the available JCPDS files and a functional curve could not be constructed.

2.4.3. Scanning electron microscope imaging

Visual examination of the resulting precipitates using a Hitachi S3000-N Variable Pressure Scanning Electron Microscope (VP-SEM) allows for documentation of crystal size and morphology. A sub-sample of each experimental precipitate was mounted on individual half-inch diameter stainless steel mounts with double-sided carbon tape. All samples were analyzed without any type of conductive coating. Samples were imaged in secondary-electron mode, at an accelerating voltage of 10.0 to 20.9 kV. The instrument was set to variable pressure mode (140 Pa) in order to enhance image resolution and quality. An INCA electron-dispersive spectrometer (EDS) was used to detect the presence of chlorine in single crystals, thus distinguishing phosgenite from other Pb-carbonate phases (results not shown).

2.5. Aqueous speciation and saturation index calculations

All speciation and mineral saturation condition modeling was done using PHREEQC-I vr.2.10.0.0 software (Parkhurst and Apello, 1999), available from the U.S. Geological Survey website at http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqci/. When required (see Section 3.2.1), P_{CO2} values were calculated from Ct and pH using PHREEQC-I.

Chapter 3:

Results

3.1. Mineralogy

3.1.1. XRD diffractograms

The results of the X-ray powder diffractometry for the eight experimental systems are presented in Table 3.1 (fresh precipitates) and Table 3.2 (aged precipitates); diffractograms are presented throughout the text. Results indicate that experimental precipitates consist of a combination of one or two crystalline phases (cerussite, cerussite-hydrocerussite, or cerussite-phosgenite). The patterns were matched to JCPDS files 47-1734 (cerussite), 13-0131 (hydrocerussite), and 09-0494 (phosgenite) using the following peaks for phase identification: cerussite: $2\theta = 24.8828$ (d₁₁₁) and 25.526 (d₀₂₁); hydrocerussite: $2\theta = 11.134$ (d₀₀₃), 20.967 (d₀₁₂), and 27.143 (d₀₁₅); phosgenite: $2\theta = 20.036$ (d₀₀₂), 24.435 (d₂₁₀), and 31.798 (d₂₁₂).

Typical limits of detection for powder XRD range between 2 and 5% by weight. Unfortunately, failure to construct reliable calibration curves prevented derivation of a more accurate number; nevertheless, it should be noted that the limit of detection should be similar for cerussite, hydrocerussite, and phosgenite, due to the similarity in Relative Intensity Ratios (RIR = $I/I_{corundum}$), which are 11.20, 10.29, and 10.49, respectively.

3.1.1.1. A note on calibrating to standards

An unsuccessful attempt was made to construct an XRD peak height/area calibration curve using known amounts of cerussite, $PbCO_{3(s)}$, and hydrocerussite,

VWR Scientific[©]. The obtained from commercial $Pb_3(CO_3)_2(OH)_{2(s)},$ $Pb_3(CO_3)_2(OH)_{2(s)}$ failed to match any of the available JCPDS files for hydrocerussite (i.e. 75-0991, 13-0131, and 10-0401). No other source was sought, as it was presumed that this problem would exist in most commercial products. Consequently, it was not possible in this study to extract quantitative phase abundance data on the basis of XRD data; however, comparing changes in peak height ratios of different phases allows estimation of relative changes in phase abundances, assuming a relatively uniform distribution of crystal sizes. Further, examination of the XRD diffractograms reveals a sporadic variation in peak intensity for the $2\theta = 43.571$ (*hkl*) = (d₂₂₁) cerussite peak (e.g. Figures 3.19, 3.21, and 3.23) that fails to correlate with systematic changes in relative phase abundance or crystal size. The exact mechanism responsible for controlling this behaviour is unknown, however possible mechanisms include crystal size, slurry mount thickness, and crystal alignment.

3.2. Aged and non-aged experiments

3.2.1. Chemical and mineralogical results

Resulting precipitate mineralogy from fresh experiments is presented in Table 3.1, and pH data collected throughout each experimental run are presented in Figures 3.1 to 3.8. Mineralogical and chemical data collected after aging precipitates resulting from reagent injection at the slowest studied rate (0.5 ml/min) are presented in Table 3.2. For comparison, the post-aging pH data are also presented in Figures 3.1 to 3.8.

Table 3.1. Mineral phases identified by XRD in fresh precipitates								
Reagent addition	IR	pH	pH ₁	pH _F	Phases	identifi	ed by	
sequence	ml/min	C-sol	Pb-sol		XRD	Contraction of the second s		
The state of the state		-	4.41	States .	Cet	HC	Ph-second	
Ingertation and a light		and the second			XRD	XRD	XRD	
$PbCl_2 \rightarrow NaHCO_3$	0.5	~8.6	4.0-4.1	5.05	X			
$PbCl_2 \rightarrow NaHCO_3$	2.8	~8.6	4.0-4.1	4.48	X			
$PbCl_2 \rightarrow NaHCO_3$	15.4	~8.6	4.0-4.1	4.30	×			
$NaHCO_3 \rightarrow PbCl_2$	0.5	~8.6	4.0-4.1	5.8	X		X	
$NaHCO_3 \rightarrow PbCl_2$	2.8	~8.6	4.0-4.1	5.27	X		X	
$NaHCO_3 \rightarrow PbCl_2$	15.4	~8.6	4.0-4.1	4.71	×		X	
$PbCl_2 \rightarrow Na_2CO_3$	0.5	~11	4.0-4.1	6.92	X	X		
$PbCl_2 \rightarrow Na_2CO_3$	2.8	~11	4.0-4.1	6.37	X	X		
$PbCl_2 \rightarrow Na_2CO_3$	15.4	~11	4.0-4.1	6.30	X	×		
$Na_2CO_3 \rightarrow PbCl_2$	0.5	~11	4.0-4.1	9.51	×	X		
$Na_2CO_3 \rightarrow PbCl_2$	2.8	~11	4.0-4.1	8.52	×	×		
$Na_2CO_3 \rightarrow PbCl_2$	15.4	~11	4.0-4.1	5.45	X	X		
$Pb(NO_3)_2 \rightarrow NaHCO_3$	0.5	~8.6	4.6-4.7	4.90	X			
$Pb(NO_3)_2 \rightarrow NaHCO_3$	2.8	~8.6	4.6-4.7	4.70	X			
$Pb(NO_3)_2 \rightarrow NaHCO_3$	15.4	~8.6	4.6-4.7	4.63	X			
$NaHCO_3 \rightarrow Pb(NO_3)_2$	0.5	~8.6	4.6-4.7	4.46	X			
$NaHCO_3 \rightarrow Pb(NO_3)_2$	2.8	~8.6	4.6-4.7	4.40	X			
$NaHCO_3 \rightarrow Pb(NO_3)_2$	15.4	~8.6	4.6-4.7	4.22	×			
$Pb(NO_3)_2 \rightarrow Na_2CO_3$	0.5	~11	4.6-4.7	6.94	X	X		
$Pb(NO_3)_2 \rightarrow Na_2CO_3$	2.8	~11	4.6-4.7	6.73	X	X		
$Pb(NO_3)_2 \rightarrow Na_2CO_3$	15.4	~11	4.6-4.7	6.33	X	×		
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$Na_2CO_3 \rightarrow Pb(NO_3)_2$	0.5	~11	4.6-4.7	9.35	×			
$Na_2CO_3 \rightarrow Pb(NO_3)_2$	2.8	~11	4.6-4.7	9.29	X			
$Na_2CO_3 \rightarrow Pb(NO_3)_2$	15.4	~11	4.6-4.7	9.15	X			

Ce = cerussite, Hc = hydrocerussite, Ph = phosgenite, pH_I = initial pH of solution, pH_F = final pH of solution.

Table 3.2. Chemical and mineralogical results of aged (8 and 16 days) precipitation experiments											
	IR	Age	pH _{INITIAL} C- solution	pH _{INTTIAL} Pb- solution	pH _{FINAL}	End ∑CO2	End P _{CO2}	End [Pb] _{tot}	Çe	Hc	Ph
	ml/ min	days	ing and a second second			mmol/L	Pa	mmol/L			
Method	1 1.	1.12-1						AA	XRD	XRD	XRD
$PbCl_2 \rightarrow NaHCO_3$	0.5	8	8.45	4.05	4.62	0.87	2510	0.408	×		X
$PbCl_2 \rightarrow NaHCO_3$	0.5	16	8.48	4.05	4.64	0.99	2850	0.386	×		X
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$NaHCO_3 \rightarrow PbCl_2$	0.5	8	8.47	4.03	4.63	1.50	4350	0.311	×		X
$NaHCO_3 \rightarrow PbCl_2$	0.5	16	8.48	4.05	4.62	1.28	3700	0.349	×		×
$PbCl_2 \rightarrow Na_2CO_3$	0.5	8	11.07	4.02	9.33	5.03	14.4	BDL	X	×	
$PbCl_2 \rightarrow Na_2CO_3$	0.5	16	11.00	4.12	9.37	5.16	13.5	BDL	×	×	
			11.00	4.02		4.64					
$Na_2CO_3 \rightarrow PbCl_2$	0.5	8	11.00	4.03	9.32	4.64	13.6	BDL	X		
$Na_2CO_3 \rightarrow PbCl_2$	0.5	16	10.97	4.09	9.33	4.80	13.9	BDL	×	×	
$Pb(NO) \rightarrow NeHCO$	0.5	8	8 22	4.60	A 20	0.74	2160	1.84			ļ
$Pb(NO_3)_2 \rightarrow N_2HCO_3$	0.5	16	8.56	4 72	4.29	0.74	2530	1.04	X		
	1 0.0		0.00			0.07	2330	1.70	<u> </u>		<u> </u>
$NaHCO_3 \rightarrow Pb(NO_3)_2$	0.5	8	8.30	4.72	4.20	1.20	3480	1.89	×		
$NaHCO_3 \rightarrow Pb(NO_3)_2$	0.5	16	8.39	4.67	4.19	1.50	4330	1.76	×		<u> </u>
$Pb(NO_3)_2 \rightarrow Na_2CO_3$	0.5	8	11.07	4.79	8.71	1.04	13.4	BDL	×	×	
$Pb(NO_3)_2 \rightarrow Na_2CO_3$	0.5	16	11.04	4.50	8.74	1.13	13.7	BDL	×	X	
$Na_2CO_3 \rightarrow Pb(NO_3)_2$	0.5	8	11.07	4.72	8.81	0.85	8.0	BDL	×		
$Na_2CO_3 \rightarrow Pb(NO_3)_2$	0.5	16	11.03	4.65	8.85	1.32	12.2	BDL	×		

IR = Injection rate; BDL = below detection limit; Ce = cerussite; Hc = hydrocerussite; Ph = phosgenite



Figure 3.1. Evolution of solution pH during injection phase of experimental system $PbCl_2 \rightarrow NaHCO_3$.



Figure 3.2. Evolution of solution pH during injection phase of experimental system NaHCO₃ \rightarrow PbCl₂.



Figure 3.3. Evolution of solution pH during injection phase of experimental system $PbCl_2 \rightarrow Na_2CO_3$.



Figure 3.4. Evolution of solution pH during injection phase of experimental system $Na_2CO_3 \rightarrow PbCl_2$.



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Figure 3.5. Evolution of solution pH during injection phase of experimental system $Pb(NO_3)_2 \rightarrow NaHCO_3$.



Figure 3.6. Evolution of solution pH during injection phase of experimental system NaHCO₃ \rightarrow Pb(NO₃)₂.



Figure 3.7. Evolution of solution pH during injection phase of experimental system $Pb(NO_3)_2 \rightarrow Na_2CO_3$.



Figure 3.8. Evolution of solution pH during injection phase of experimental system $Na_2CO_3 \rightarrow Pb(NO_3)_2$.

3.2.2. Results of precipitate analysis

3.2.2.1. $PbCl_2 \rightarrow NaHCO_3$

At all injection rates, cerussite is the only phase detected by XRD (Figure 3.9) in the fresh reaction products. At the lowest injection rate (Figure 3.10A), the cerussite is prismatic and shows a bimodal size distribution with large (5-10 long, 1 μ m across) and small (1 by 0.5 μ m) stubbier, prismatic crystals. The smaller crystals appear to be aggregated on the sides of the larger crystals. At intermediate and fast injection rates (Figure 3.10B-C), the crystalline aggregates consist of a unimodal distribution of prisms (1 by 0.5 μ m) without any notable trend in size with injection rate.

In aged precipitates, cerussite and phosgenite are detected by XRD (Figure 3.11). The cerussite crystals are present as subhedral prisms $(2 - 5 \text{ by} < 1 \mu \text{m})$ and lack the notable bi-modal distribution of aligned crystals. Phosgenite grains are large $(5 - 20 \mu \text{m})$, euhedral to subhedral, tabular, tetragonal crystals; which consistently display rounded edges (Figure 3.12B-C).

3.2.2.2. $NaHCO_3 \rightarrow PbCl_2$

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At all injection rates, phosgenite and cerussite are detected by XRD (Figure 3.13) in the fresh reaction products. At the lowest injection rate (Figure 3.14A), the cerussite occurs as bladed crystals $(5 - 10 \text{ by} < 1 \mu \text{m})$ whereas phosgenite occurs as tabular tetragonal crystals (3 by 3 by 1 μ m) in randomly-orientated intergrowths. At the intermediate injection rate (Figure 3.14B), phosgenite crystals retain their tabular, tetragonal habit but show parallel intergrowths along (100) and (010), commonly

creating large (5 – 10 μ m across), platy clusters. Cerussite crystals are bladed (10 by 1 μ m) and twinned, occasionally showing interpenetration at ~ 60 degrees. At the fast injection rate (Figure 3.14C), phosgenite crystals occur with two distinct habits: 1) a similar tabular habit, size and parallel intergrowth pattern to that observed with the lower injection rates; and 2) a small equant tabular habit (1-2 μ m).

In aged precipitates, cerussite and phosgenite are detected by XRD (Figure 3.15). Cerussite crystals are present as subhedral prisms $(5 - 15 \text{ by} \sim 1 \mu \text{m})$ and often show interpenetration at ~60 degrees; phosgenite crystals are euhedral and rectangular $(1-2 \mu \text{m})$, and frequently occur as aggregates of crystals, extending/stacking predominantly in the (100) and (010) directions (Figure 3.16B-C).

3.2.2.3. $PbCl_2 \rightarrow Na_2CO_3$

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At all injection rates, hydrocerussite and cerussite are detected by XRD (Figure 3.17) in the fresh reaction products; however, all the crystals are anhedral and equant, and therefore the phases cannot be distinguished morphologically. The average crystal size of the precipitates decreases with increasing injection rate, from $\sim 1 \ \mu m$ at the lowest injection rate (Figure 3.18A) to $\sim 0.5 \ \mu m$ at the intermediate injection rate (Figure 3.18B) to $\sim 0.1 \ \mu m$ at the highest injection rate (Figure 3.18C).

In aged precipitates, cerussite and hydrocerussite are detected by XRD (Figure 3.19); however, the two phases cannot be distinguished by morphology. Crystal shapes (Figure 3.20B-C) range from stout, euhedral to subhedral prisms (1-2 by < 1 μ m) to equant, subhedral crystals with no recognizable crystal form (< 0.5 μ m in across).

3.2.2.4. $Na_2CO_3 \rightarrow PbCl_2$

At all injection rates, cerussite and hydrocerussite are detected by XRD (Figure 3.21) in the fresh reaction products. Cerussite crystals are present with two distinct morphologies: 1) prismatic (5-10 long by < 1 μ m; Figure 3.22A); and 2) platy, pseudohexagonal crystals (1-5 μ m, Figure 3.22B), commonly occurring in aggregates ranging in size from 10 to 20 μ m. Hydrocerussite is indistinguishable by SEM and, as suggested by the small XRD peak heights, present in relatively small quantities. This is in contrast to the very different habits observed in Figure 3.22, which, at first glance, suggest two different phases. At higher injection rates (Figure 3.22C-D), cerussite and hydrocerussite occur as indistinguishable, anhedral crystals with average sizes declining slightly from ~1 μ m at the injection rate of 2.8 ml/min, to <0.5 μ m at the injection rate of 15.4 ml/min.

In aged precipitates, cerussite and hydrocerussite are detected by XRD (Figure 3.23). As in the fresh reaction products, aged cerussite crystals are present in two distinct habits (Figure 3.24C-D): 1) large, subhedral prisms $(10 - 20 \ \mu m \ long, 2 - 5 \ \mu m \ wide)$, showing pseudohexagonal twinning; and 2) euhedral, platy, pseudohexagonal crystals $(1 - 2 \ \mu m)$. Hydrocerussite, although identified by XRD, cannot be visually distinguished in SEM images.

3.2.2.5. $Pb(NO_3)_2 \rightarrow NaHCO_3$

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At all injection rates, cerussite is the only phase detected by XRD (Figure 3.25) in the fresh reaction products. At the lowest injection rate (Figure 3.26A), cerussite is present as both prismatic (5-10 by $\sim 1 \ \mu$ m) and subhedral, blocky (2-3 μ m)

crystals. At the intermediate injection rate (Figure 3.26B), cerussite is present as subhedral, blocky crystals (~1 μ m across) whereas at the highest injection rate (Figure 3.26C), cerussite occurs as anhedral, blocky crystals (~ 0.5 μ m across).

In aged precipitates, cerussite is the only phase identified by XRD (Figure 3.27). Cerussite crystals are subhedral and prismatic with a similar size distribution to that of the fresh precipitates (ranging from 1 by 2 to 1 by 7 μ m; Figure 3.28B-C).

3.2.2.6. $NaHCO_3 \rightarrow Pb(NO_3)_2$

At all injection rates, cerussite is the only phase detected by XRD (Figure 3.29) in the fresh reaction products. Cerussite shows a decrease in crystal size with increasing injection rate from 10 - 15 by 1 μ m (Figure 3.30A), to 5 - 10 by 0.5 μ m (Figure 3.30B), and 3.5 by 0.1 μ m (Figure 3.30C).

In aged precipitates, cerussite is the only mineral detected by XRD (Figure 3.31) and occurs as euhedral, prismatic crystals, 5-10 by < 1 μ m (Figure 3.32).

3.2.2.7. $Pb(NO_3)_2 \rightarrow Na_2CO_3$

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At all injection rates, hydrocerussite and cerussite are detected by XRD (Figure 3.33) in the fresh reaction products; both minerals are present as anhedral crystals and cannot be distinguished on the basis of morphology. The average crystal size decreases with increasing injection rate from ~ 1 μ m (Figure 3.34A) to 0.5 μ m (Figure 3.34B) to 0.1 μ m (Figure 3.34C).

In aged precipitates, hydrocerussite and cerussite are detected by XRD (Figure 3.35). These phases cannot be distinguished morphologically; all crystals are anhedral to subhedral and equant, with diameters of $\sim 1 \ \mu m$ (Figure 3.36B-C).

3.2.2.8. $Na_2CO_3 \rightarrow Pb(NO_3)_2$

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At all injection rates, cerussite is the only phase identified by XRD (Figure 3.37) in the fresh reaction products. The crystals are euhedral, prismatic and decrease in size with increasing injection rate from 5-10 μ m (Figure 3.38A), to 3-5 μ m (Figure 3.38B), to ~1 μ m (Figure 3.38C).

In aged precipitates, cerussite is the only phase identified by XRD (Figure 3.39B-C). Cerussite crystals are present as euhedral, prismatic crystals (5 – 10 μ m by < 1 μ m) and are occasionally present in star-shaped clusters, similar to those seen in the fresh precipitates (Figure 3.40).

3.3. General trends in mineral abundance, crystal size, and morphology

3.3.1. Differences between aged and non-aged precipitates

There are few noticeable differences in mineralogy, crystal size, and crystal morphology between samples that were filtered immediately upon termination of the reagent injection process (*i.e.* fresh precipitates) and those that were allowed to age for either 8 or 16 days, save perhaps a slight increase in size. Certain exceptions are: 1) in the system PbCl₂ \rightarrow NaHCO₃, phosgenite is detected only after aging the fresh precipitate (Figures 3.11 and 3.12); 2) in the system Na₂CO₃ \rightarrow PbCl₂, XRD data show an increase in hydrocerussite abundance (as revealed by an increase of the Hc/Ce peak height ratios) between fresh and aged precipitate (Figure 3.23); 3) in the system $Pb(NO_3)_2 \rightarrow Na_2CO_3$, XRD data show a decrease in hydrocerussite abundance (as revealed by a decrease of the Hc/Ce peak height ratios, as noted in Fig. 3.35 caption) with aging and the aged solution pH is nearly 2 units higher (~9.5) than that of the parental solution immediately after mixing of the reagents (~7.2; Figure 3.7); and 4) in the system $PbCl_2 \rightarrow Na_2CO_3$, the aged solution pH is nearly 3 units higher (~9.5) than that of the fresh solution (~6; Figure 3.3). In addition, there are no apparent, systematic differences, in any of the studied systems, between samples allowed to age either 8 or 16 days.

3.3.2. Trends in crystal sizes

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Among the precipitates examined, there are two noteworthy trends pertaining to crystal size. First, in nearly all systems investigated, the average crystal size of the precipitates decreases with increasing injection rate. One exception to this, however, is the crystallization of phosgenite in the system NaHCO₃ \rightarrow PbCl₂, which shows a less obvious decrease in crystal size with injection rate. Also, it appears that this trend is less pronounced in Cl-bearing systems than in NO₃-bearing systems (*e.g.* Figures 3.14 and 3.30). Second, crystals nucleating and growing at high and low pH tend to be smaller and larger, respectively. Two experimental systems, PbCl₂ \rightarrow NaHCO₃ and Pb(NO₃)₂ \rightarrow NaHCO₃, show the broadest range in pH during the injection phase (see Figures 3.1 and 3.5); this appears to correspond to the broadest range in crystal size observed (Figures 3.10 and 3.26).

3.3.3. Compositional trends in precipitates as a function of injection rate

As discussed previously, the quantification of mineral abundances in precipitates was precluded by the inability to construct a reliable XRD calibration curve (see Section 3.1.1.1); nevertheless, systematic changes in peak heights in XRD diffractograms suggest changes in mineral abundance ratios with increasing injection rate. In the system NaHCO₃ \rightarrow PbCl₂, which produces phosgenite and cerussite (Table 3.1), the decrease in Ce/Ph peak height ratios with increasing injection rate suggests an increase in the amount of phosgenite (Figure 3.13). In the systems PbCl₂ \rightarrow Na₂CO₃ (Figure 3.17), Na₂CO₃ \rightarrow PbCl₂ (Figure 3.21), and Pb(NO₃)₂ \rightarrow Na₂CO₃ (Figure 3.33), all of which precipitate cerussite and hydrocerussite, the decrease in Ce/Hc peak height ratios with increasing injection rate suggests an increase in the abundance of hydrocerussite relative to cerussite.

3.3.4. Cerussite

Several systematic differences are observed when comparing the crystal morphology of cerussite precipitated in nitrate- vs. chloride-dominated solutions. First, examination of experimental systems NaHCO₃ \rightarrow Pb(NO₃)₂ and Na₂CO₃ \rightarrow Pb(NO₃)₂ reveals that cerussite crystals are euhedral at all injection rates (*e.g.* Figures 3.30 and 3.38); conversely, in the experimental system Na₂CO₃ \rightarrow PbCl₂, resulting cerussite crystals are anhedral to subhedral at IR = 2.8 and 15.4 ml/min (Figure 3.22). Second, the habits of cerussite crystals precipitated by the systems Na₂CO₃ \rightarrow PbCl₂ and NaHCO₃ \rightarrow PbCl₂ (Figure 3.14) show a more bladed nature than when precipitated in nitrate-dominated systems (e.g., Figure 3.30). Third, there is a unique cerussite crystal morphology that is observed only in the system $Na_2CO_3 \rightarrow PbCl_2$ (IR = 0.5 ml/min); in addition to the prism commonly observed, platy, hexagonal cerussite is present (Figure 3.22). The data fail to provide a valid explanation for the presence of this anomalous habit; speculatively, it may be the result of pseudomorphism after hydrocerussite.

3.3.5. Hydrocerussite

In all the studied reactions, irrespective of the injection rates, hydrocerussite crystals are fine-grained and anhedral and, thus, difficult to visually distinguish by SEM and discuss.

3.3.6. Phosgenite

Phosgenite precipitation was observed only in the systems NaHCO₃ \rightarrow PbCl₂ (during injection, at all rates) and PbCl₂ \rightarrow NaHCO₃ (during the aging process only). The morphology of phosgenite crystals appears to be highly dependent upon injection rate and growth kinetics. Crystals resulting from growth at the lowest injection rate show intergrowths in several axial directions (Figure 3.14A) whereas at the two highest injection rates (Figure 3.14B and C), intergrowths are strongly favoured along the (100) and (010) directions. The later suggests that at higher injection rates, growth in these directions offers the most efficient mechanism of overcoming the kinetic nucleation barrier in addition to minimizing surface free energy. It should be noted that the fit between the collected and JCPDS XRD profiles is the least satisfactory for phosgenite at the highest injection rate (see Figures 3.13C and 3.14C), suggesting the presence of another, kinetically-favoured, metastable phase. Possibilities for this second phase include lead hydroxide (Pb(OH)₂) and plumbonacrite (Pb₁₀O(OH)₆(CO₃)₆), but the presence of another, kinetically-favoured, metastable phase cannot be ruled out. Comparison of the powder diffraction patterns of these, and other Pb, minerals (see Appendix I) reveals that a considerable degree of similarity between major peak positions and illustrates that potential ambiguity that could result when trying to conclusively differentiate between these phases if even a modest amount of peak shifting were to occur.

3.4. Visual observations regarding precipitation rate

Irrespective of the experimental system investigated, precipitation was observed to occur almost immediately following the addition of even the smallest amount of reagent. Due to the high nucleation rate, abundance of nuclei, and consequently microscopic grain size of the precipitates, visual identification of mineral phase(s) was impossible.



Figure 3.9. Fixed-slit XRD diffractograms of the fresh precipitate (cerussite) produced by the experimental system $PbCl_2 \rightarrow NaHCO_3$ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min. IR = injection rate.



Figure 3.10. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh precipitate (cerussite) produced by the experimental system PbCl₂ \rightarrow NaHCO₃ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min.



Figure 3.11. Fixed-slit XRD diffractograms of the fresh and aged precipitate (cerussite and phosgenite) produced by the experimental system $PbCl_2 \rightarrow NaHCO_3$: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days. Note the appearance of phosgenite with aging. Ce = cerussite (Ce* refers to $2\theta = 24.8$, 25.5 doublet); Ph = phosgenite; IR = injection rate.



Figure 3.12. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh and aged precipitate (cerussite and phosgenite) produced by the experimental system PbCl₂ \rightarrow NaHCO₃: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days. Ce = cerussite; Ph = phosgenite.



Figure 3.13. Fixed-slit XRD diffractograms of the fresh precipitate (phosgenite) produced by the experimental system NaHCO₃ \rightarrow PbCl₂ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min. Note the increase in Ph/Ce peak height ratios with injection rate. Ce = cerussite (Ce* refers to 20 = 24.8, 25.5 doublet); Ph = phosgenite; IR = injection rate.



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Figure 3.14. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh precipitate (cerussite and phosgenite) produced by the experimental system NaHCO₃ \rightarrow PbCl₂ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min. Ce = cerussite; Ph = phosgenite. Note the appearance of tabular phosgenite at high injection rates in (C).



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Figure 3.15. Fixed-slit XRD diffractograms of the fresh and aged precipitate (cerussite and phosgenite) produced by the experimental system NaHCO₃ \rightarrow PbCl₂: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days. Note consistency in relative abundances with aging. Ce = cerussite (Ce* refers to 20 = 24.8, 25.5 doublet); Ph = phosgenite; IR = injection rate.



Figure 3.16. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh and aged precipitate (cerussite and phosgenite) produced by the experimental system NaHCO₃ \rightarrow PbCl₂: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days. Note the coarsening of cerussite with increased injection rate. Ce = cerussite; Ph = phosgenite.



Figure 3.17. Fixed-slit XRD diffractograms of the fresh precipitate (cerussite and hydrocerussite) produced by the experimental system $PbCl_2 \rightarrow Na_2CO_3$ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min. Note the increase in Hc/Ce peak height ratios with injection rate. Ce = cerussite (Ce* refers to $2\theta = 24.8$, 25.5 doublet); Hc = hydrocerussite; IR = injection rate.


Figure 3.18. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh precipitate (cerussite and hydrocerussite) produced by the experimental system PbCl₂ \rightarrow Na₂CO₃ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min.



Figure 3.19. Fixed-slit XRD diffractograms of the fresh and aged precipitate (cerussite and hydrocerussite) produced by the experimental system $PbCl_2 \rightarrow Na_2CO_3$: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days. Note the consistency in relative phase abundances with aging. Ce = cerussite (Ce* refers to $2\theta = 24.8$, 25.5 doublet); Hc = hydrocerussite; IR = injection rate.



Figure 3.20. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh and aged precipitate (cerussite and hydrocerussite) produced by the experimental system PbCl₂ \rightarrow Na₂CO₃: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days.



Figure 3.21. Fixed-slit XRD diffractograms of the fresh precipitate (cerussite and hydrocerussite) produced by the experimental system $Na_2CO_3 \rightarrow PbCl_2$ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min. Note the increase in Hc/Ce peak height ratios with increased injection rate. Ce = cerussite (Ce* refers to 20 = 24.8, 25.5 doublet); Hc = hydrocerussite; IR = injection rate.







(C)



(B)

(D)

Figure 3.22. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh precipitate (cerussite and hydrocerussite) produced by the experimental system Na₂CO₃ \rightarrow PbCl₂ at injection rates: (A and B) 0.5, and (C) 2.8, and (D) 15.4 ml/min. Note the two habits of cerussite at IR = 0.5 ml/min prismatic (A) and platy (B).



Figure 3.23. Fixed-slit XRD diffractograms of the fresh and aged precipitate (cerussite and hydrocerussite) produced by the experimental system $Na_2CO_3 \rightarrow PbCl_2$: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days. Note the consistency in relative phase abundances with aging. Ce = cerussite (Ce* refers to $2\theta = 24.8$, 25.5 doublet); Hc = hydrocerussite; IR = injection rate.





(B)

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(D)

Figure 3.24. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh and aged precipitate (cerussite and hydrocerussite) produced by the experimental system Na₂CO₃ \rightarrow PbCl₂: (A and B) fresh precipitate (IR = 0.5 ml/min), (C) precipitate aged 8 days, and (D) precipitate aged 16 days.



Figure 3.25. Fixed-slit XRD diffractograms of the fresh precipitate (cerussite) produced by the experimental system $Pb(NO_3)_2 \rightarrow NaHCO_3$ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min. IR = injection rate.



Figure 3.26: VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh precipitate (cerussite) produced by the experimental system Pb(NO₃)₂ \rightarrow NaHCO₃ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min. Note the difference in cerussite crystal sizes in (A).



Figure 3.27. Fixed-slit XRD diffractograms of the fresh and aged precipitate (cerussite) produced by the experimental system $Pb(NO_3)_2 \rightarrow NaHCO_3$: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days.



Figure 3.28. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh and aged precipitate (cerussite) produced by the experimental system Pb(NO₃)₂ \rightarrow NaHCO₃: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days.



Figure 3.29. Fixed-slit XRD diffractograms of the fresh precipitate (cerussite) produced by the experimental system NaHCO₃ \rightarrow Pb(NO₃)₂ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min. IR = injection rate.



Figure 3.30. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh precipitate (cerussite) produced by the experimental system NaHCO₃ \rightarrow Pb(NO₃)₂ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min. Note: 1) although crystal size decreases with injection rate, the crystal habit remains unchanged; and 2) the products of this system show similar crystal habits and trends in crystal size with the system Na₂CO₃ \rightarrow Pb(NO₃)₂ (Figure 3.38).



Figure 3.31. Fixed-slit XRD diffractograms of the fresh and aged precipitate (cerussite) produced by the experimental system $NaHCO_3 \rightarrow Pb(NO_3)_2$: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days. IR = injection rate.



Figure 3.32. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh and aged precipitate (cerussite) produced by the experimental system NaHCO₃ \rightarrow Pb(NO₃)₂: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days. Note that crystal sizes and shapes are far more uniform than in the opposite injection sequence, Pb(NO₃)₂ \rightarrow NaHCO₃ (Figure 3.28).



Figure 3.33. Fixed-slit XRD diffractograms of the fresh precipitate (cerussite and hydrocerussite) produced by the experimental system $Pb(NO_3)_2 \rightarrow Na_2CO_3$ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min. Note the increase in Hc/Ce peak heights with increased injection rate. Ce = cerussite (Ce* refers to $2\theta = 24.8$, 25.5 doublet); Hc = hydrocerussite; IR = injection rate.



Figure 3.34. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh precipitate (cerussite and hydrocerussite) produced by the experimental system Pb(NO₃)₂ \rightarrow Na₂CO₃ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min.



Figure 3.35. Fixed-slit XRD diffractograms of the fresh and aged precipitate (cerussite and hydrocerussite) produced by the experimental system $Pb(NO_3)_2 \rightarrow Na_2CO_3$: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days. Note the decrease in Hc/Ce peak height ratios after aging process. Ce = cerussite (Ce* refers to $2\theta = 24.8$, 25.5 doublet); Hc = hydrocerussite; IR = injection rate.



Figure 3.36. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh and aged precipitate (cerussite and hydrocerussite) produced by the experimental system Pb(NO₃)₂ \rightarrow Na₂CO₃: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days.



Figure 3.37. Fixed-slit XRD diffractograms of the fresh precipitate (cerussite) produced by the experimental system $Na_2CO_3 \rightarrow Pb(NO_3)_2$ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min. IR = injection rate.



Figure 3.38. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh precipitate (cerussite) produced by the experimental system Na₂CO₃ \rightarrow Pb(NO₃)₂ at injection rates: (A) 0.5, (B) 2.8, and (C) 15.4 ml/min. Note the decrease in crystal size without any change of habit, in contrast to the opposite system, Pb(NO₃)₂ \rightarrow Na₂CO₃ (Figure 3.34).



Figure 3.39. Fixed-slit XRD diffractograms of the fresh and aged precipitate (cerussite) produced by the experimental system $Na_2CO_3 \rightarrow Pb(NO_3)_2$: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days. IR = injection rate.



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Figure 3.40. VP-SEM (140 Pa) images at 3.5 k magnification (scale bar = 10 μ m) of the fresh and aged precipitate (cerussite) produced by the experimental system Na₂CO₃ \rightarrow Pb(NO₃)₂: (A) fresh precipitate (IR = 0.5 ml/min), (B) precipitate aged 8 days, and (C) precipitate aged 16 days.

Chapter 4:

Discussion

4.1. Chemical reactions controlling the system Pb²⁺-CO₂-H₂O

The chemical evolution of the systems under investigation during the reagent injection phase is controlled predominantly by three categories of chemical reactions: 1) those governing the speciation of the carbonate system (Eqn. 4.1 to 4.3); 2) those resulting in the nucleation, precipitation, and thermodynamic equilibrium of solid Pb-carbonate phases (Eqn. 4.4 to 4.13), including back reactions between early precipitates and the residual parent-solutions (Eqn. 4.16 to 4.19); and 3) those controlling the distribution of the aqueous species listed in Table 4.1.

The carbonate system is defined by the following reactions and mass action laws (from Stumm and Morgan, 1996):

(Eqn. 4.1)	$\mathrm{CO}_{2(\mathrm{g})} + \mathrm{H}_2\mathrm{O}_{(\mathrm{l})} \leftrightarrow \mathrm{H}_2\mathrm{CO}_3$
(Eqn. 4.2a)	$H_2CO_3^* \leftrightarrow HCO_3^- + H^+$
(Eqn. 4.2b)	$K^{\circ}_{1} = \{H^{+}\}\{HCO_{3}^{-}\}/\{H_{2}CO_{3}^{*}\} = 10^{-6.35}$

where K°_{1} is a composite constant that describes the first dissociation of carbonic acid at 25°C and 1 bar total pressure, {i} are the activities of the species involved in the reactions, and {H₂CO₃^{*}} = {CO_{2(aq)} + H₂CO₃}.

(Eqn. 4.3a)
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

(Eqn. 4.3b) $K^{\circ}_2 = \{H^+\}\{CO_3^{2-}\}/\{HCO_3^-\} = 10^{-10.33}$

where K°_{2} is the second dissociation constant of carbonic acid at 25°C and 1 bar total pressure.

The Pb-mineral equilibria pertinent to the solids observed in this study are described by:

(Eqn. 4.4)	$Pb^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \leftrightarrow PbCO_{3(s)}$
(Eqn. 4.5)	$Pb^{2+}_{(aq)} + 2HCO_{3}_{(aq)} \leftrightarrow PbCO_{3(s)} + H_2O_{(l)} + CO_{2(aq)}$
(Eqn. 4.6)	$3Pb^{2+} + 2CO_3^{2-}{}_{(aq)} + 2OH^- \leftrightarrow Pb_3(CO_3)_2(OH)_{2(s)}$
(Eqn. 4.7)	$\mathrm{HCO}_{3}^{-} + 2\mathrm{Pb}^{2+} + 2\mathrm{Cl}^{-} \leftrightarrow \mathrm{Pb}_{2}(\mathrm{CO}_{3})\mathrm{Cl}_{2(s)} + \mathrm{H}^{+}$
(Eqn. 4.8)	$2Pb^{2+} + CO_3^{2-}_{(aq)} + 2Cl^- \leftrightarrow Pb_2(CO_3)Cl_{2(s)}$
(Eqn 4.9)	$Pb(OH)_{2(s)} \leftrightarrow Pb^{2+}_{(aq)} + 2OH^{-}$
(Eqn. 4.10)	$\log K_{\rm sp(ce)} = \log \{ {\rm Pb}^{2+} \} + \log \{ {\rm CO}_3^{2-} \} = -13.13$
	(Parkhurst and Appelo, 1999; see Eqn. 4.4)
(Eqn. 4.11)	$\log K_{sp(hc)} = 3\log \{Pb^{2+}\} + 2\log \{CO_3^{2-}\} + 2\log \{OH^{-}\} = -44.08$
	(Bilinksi and Schindler, 1983; see Eqn. 4.6)
(Eqn. 4.12)	$\log K_{sp(ph)} = 2\log \{Pb^{2+}\} + \log \{CO_3^{2-}\} + 2\log \{CI^{-}\} = -19.81$
	(Pina et al., 2000; see Eqn. 4.8)
(Eqn. 4.13)	$\log K_{sp(Pb(OH)2)} = \log \{Pb^{2+}\} - \log \{H^+\}^2 = 8.15$

(Parkhurst and Appelo, 1999; see Eqn. 4.9)

4.2. Thermodynamic modeling of Pb-carbonate precipitation

PHREEQC-I was used to model the chemical and thermodynamic evolution of systems from which cerussite was the sole, detectable precipitate. Separate models were constructed to simulate closed (*i.e.* conservative total inorganic carbon) and open (*i.e.* fixed $P_{CO2} = 10^{-3.5}$ atm) systems. Model input parameters were derived by assuming PbCO_{3(s)} precipitated at a constant rate driven by the injection of the reagent. Thus, during reagent injection, the addition of one molar unit of Pb²⁺ in the closed system results in the removal of one molar unit of total dissolved inorganic carbon (Σ CO₂) and two equivalents of alkalinity. In the open system, the addition of one molar unit of Pb²⁺ resulted in the removal of two equivalents units of alkalinity (Σ Alk; Eqn. 4.14) while P_{CO2} remained constant through exchange with the atmosphere. Assuming that the addition of 1 mole of Pb results in quantitative precipitation of PbCO_{3(s)} is justified by comparing starting and final concentrations of Pb in solution; here, > 99% of the total Pb precipitation in all runs is observed to be removed from solution (see Table 3.2).

The system was simulated for every ~2.5% volume increment of reagent addition. After removal of Pb and inorganic carbon (and/or carbonate alkalinity) according to the above-defined precipitation scenarios, concentrations of all components of the system were corrected for the volume increase caused by reagent injection. The modeling software iteratively refined $[Pb^{2+}]_{tot}$ and $\sum CO_2$ at each reagent addition increment until cerussite saturation had been achieved (*i.e.* SI(cer) = 0.00; Eqn. 4.15); saturation conditions for other Pb-minerals were then calculated using Eqns. 4.9 to 4.13. Aqueous species listed in Table 4.1 were considered in all iterative calculations. The complexity of polymineralic precipitates precludes the simulation of their systems since the relative rates (and abundances) of precipitation, as well as the potential solid-phase interconversion reactions, could not be assessed.

(Eqn. 4.14)
$$Alk = 2[CO_3^{2-}] + [HCO_3^{-}] + [OH^{-}] - [H^{+}]$$

(Eqn. 4.15) $SI = \log(Ion Activity Product/K_{sp})$

4.2.1. Results of cerussite precipitation models

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In general, the observed pH data curves lie within the area bounded by the modeled open and closed systems (Figures 4.1 to 4.4) and are akin to a carbonate alkalinity titration curve (see Stumm and Morgan, 1996). The discrepancy between the starting modeled and observed pH values in Figures 4.3 and 4.4 should be noted; this is presumably due to the fact the initial solution is modeled to be in equilibrium with cerussite. With decreasing injection rate, the experimental data for the systems $PbCl_2 \rightarrow NaHCO_3$ and $Pb(NO_3)_2 \rightarrow NaHCO_3$ approach the open system model, indicating that experiments of slower precipitation rate were more susceptible to greater exchange with atmospheric $CO_{2(g)}$. The general agreement between the modeled and observed pH data suggests that cerussite precipitation maintains the solution at or near cerussite saturation. The abundance of growth surfaces after nucleation, which would occur during the initial injection phase, likely allows growth of the mineral to proceed uninhibited even at low supersaturation levels.

The modeled, closed-system pH, SI, and aqueous speciation evolution during reagent injection are presented in Figures 4.5 to 4.12. In the model output, it can be observed that cerussite saturation tends to suppress supersaturation/saturation with respect to other Pb-minerals, explaining why cerussite is the only phase observed. Moderate (*i.e.* 0 < SI < 1) supersaturation with respect to phosgenite and Pb(OH)_{2(s)} is achieved during the injection phase in systems PbCl₂ \rightarrow NaHCO₃ (Figure 4.5) and Na₂CO₃ \rightarrow Pb(NO₃)₂ (Figure 4.9), respectively. In both cases, neither phosgenite nor

Table 4.1. Aqueous	s species considered in
H ₂ O-Na-CO ₂ -PbCl ₂	Na ₂ CO ₃ -CO ₂ -Pb(NO ₃) ₂
Pb ²⁺	Pb ²⁺
CI	NO_3^-
PbCl ⁺	$Pb(OH)^2$
PbCl ₂ ⁰	Pb(OH) ₃
PbCl ₃ ⁻	Pb(OH) ₄ ²⁻
PbCl ₄ ²⁻	$Pb_2(OH)^{3+}$
$Pb(OH)_2^0$	$Pb(NO_3)^+$
Pb(OH) ₃ ⁻	Pb(OH) ⁺
$Pb(OH)_4^{2-}$	
$Pb_2(OH)^{3+}$	
Pb(OH) ⁺	
$CO_{2(g)}$	$CO_{2(g)}$
CO_{3}^{2-}	CO_{3}^{2}
HCO ₃	HCO ₃
PbHCO ₃ ⁺	PbHCO ₃ ⁺
PbCO ₃ ⁰	PbCO ₃ ^o
$Pb(CO_3)_2^2$	$Pb(CO_3)_2^2$
Na	Na
NaCO ₃	NaCO ₃
$ NaHCO_3^{\circ} $	NaHCO ₃ °
NaOH	NaOH"
[H]	H

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 $Pb(OH)_{2(s)}$ are observed in the final precipitate assemblages, suggesting that either: 1) the activation energy required to induce nucleation of the second phase was not exceeded by the degree of supersaturation; or 2) the 2-5 % detection limit of the XRD prevented identification of the phases.

The agreement between observed and modeled data (open and closed systems) for the system Na₂CO₃ \rightarrow Pb(NO₃)₂ is poor in comparison to that of other models; the data consistently disagree by about -1 pH unit with both open and closed system models (Figure 4.3). Throughout the injection process, the supersaturation with respect to Pb(OH)_{2(s)} may have resulted in precipitation/dissolution of this phase, thus preventing the pH of the system from evolving as modeled (*i.e.* with cerussite the only precipitating, chemistry-controlling phase). Another explanation for the discrepancy in pH may be the ability of NO₃⁻ to inhibit the growth of cerussite through temporary adsorption at surface sites that would otherwise bind to CO₃²⁻ groups during crystal growth (see Section 4.2.3).

Saturation index diagrams for < 1 % of reagent injection are provided (Figures 4.6, 4.8, 4.10, and 4.12) to illustrate: 1) that the solution reached oversaturation with respect to cerussite with injection of a very small amount of reagent; 2) that failure to precipitate cerussite leads to improbable levels of supersaturation (*i.e.* SI(cer) \approx 2-3), and 3) as in models depicting the complete injection process, cerussite saturation-control of the solution prevents supersaturation with respect to all other mineral phases.

The SI indices for Pb-carbonate phases (withholding cerussite precipitation) are presented in Figures 4.6C, 4.8C, 4.10C, and 4.12C. Comparison of these figures

allows theorizing about crystal nucleation rates, assuming that: 1) the number of nuclei is proportional to the degree of supersaturation; and 2) the majority of nucleation occurred within the early stages of reagent injection. Given this, the decrease in average crystal size with injection rate suggests that a higher degree of supersaturation is achieved, thus resulting in a greater number of nuclei, and the continued growth of which, during reagent injection, results in a smaller average crystal size.

This is in contrast to the observed, broad range of crystal sizes present in precipitates of the system $PbCl_2 \rightarrow NaHCO_3$ and $Pb(NO_3)_2 \rightarrow NaHCO_3$, which suggests that nucleation may have occurred at more than one point in time during reagent injection (Figures 3.10 and 3.26). This is possibly due to the loss of $CO_{2(g)}$ to the atmosphere, which significantly increases the pH above that of the closed-system scenario, inducing repeated nucleation events, as suggested by the range of crystal sizes visible at the slowest injection rate.

A greater degree of cerussite and hydrocerussite saturation is achieved in high pH experiments at all injection rates (*i.e.* PbCl₂, Pb(NO₃)₂ \rightarrow NaHCO₃) as compared to low pH experiments (NaHCO₃, Na₂CO₃ \rightarrow Pb(NO₃)₂ (cf. Figures. 4.1 to 4.4). In the former, SI(cer) \approx 2 and SI(hc) \approx 3 are achieved upon 1% of reagent addition, whereas in the latter, SI(cer) \approx 1.5 and SI(hc) \approx 1 result. Given the observation that average crystal sizes are smaller when precipitation occurs at high pH in the parentsolutions (see Section 3.3.2), this relationship suggests higher nucleation rates at high pH.

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Figure 4.1. Comparison of open and closed cerussite-saturated model simulations and experimental pH data at all injection rates for the system $PbCl_2 \rightarrow NaHCO_3$.



Figure 4.2. Comparison of open and closed cerussite-saturated model simulations and experimental pH data at all injection rates for the system $Pb(NO_3)_2 \rightarrow NaHCO_3$.



Figure 4.3. Comparison of open and closed cerussite-saturated model simulations and experimental pH data at all injection rates for the system $Na_2CO_3 \rightarrow Pb(NO_3)_2$.



Figure 4.4. Comparison of open and closed cerussite-saturated model simulations and experimental pH data at all injection rates for the system $NaHCO_3 \rightarrow Pb(NO_3)_2$.

Figure 4.5. Results of closed-system saturation modeling for the experimental system $PbCl_2 \rightarrow NaHCO_3$: (A) pH curve; (B) saturation indices; and (C) distribution of aqueous species. Note supersaturation with respect to phosgenite towards the end of the injection phase, leading to secondary growth of this mineral during the aging process.

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Figure 4.6. Evolution of the SI for the closed-system $PbCl_2 \rightarrow NaHCO_3$: (A) complete experiment; (B) < 1 % PbCl₂ injection with cerussite saturation index set to 0.00; (C) < 1 % PbCl₂ injection without any saturation control (*i.e.* withholding precipitation).

Figure 4.7. Results of closed-system saturation modeling for the experimental system $Pb(NO_3)_2 \rightarrow NaHCO_3$: (A) pH curve; (B) saturation indices; and (C) distribution of aqueous species. Note the continuous undersaturation of the solution with respect to all other phases during the injection process.

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% Pb(NO₃)₂ Injected



Figure 4.8. Evolution of the SI for the closed system $Pb(NO_3)_2 \rightarrow NaHCO_3$: (A) complete experiment; (B) < 1 % $Pb(NO_3)_2$ injection with cerussite saturation index set to 0.00; (C) < 1 % $Pb(NO_3)_2$ injection without any saturation control (*i.e.* withholding precipitation).

Figure 4.9. Results of closed-system saturation modeling for the experimental system $Na_2CO_3 \rightarrow Pb(NO_3)_2$: (A) pH curve; (B) saturation indices; and (C) distribution of aqueous species. Note the eventual supersaturation of the solution with respect to $Pb(OH)_{2(s)}$ and hydrocerussite, despite the fact that these phases were not detected in either the fresh or aged precipitates.

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Figure 4.10. Evolution of the SI for the closed system $Na_2CO_3 \rightarrow Pb(NO_3)_2$: (A) complete experiment; (B) < 1 % Na_2CO_3 injection with cerussite saturation index set to 0.00; (C) < 1 % Na_2CO_3 injection without any saturation control (*i.e.* withholding precipitation).

Figure 4.11. Results of cerussite-saturation model simulation for the closed system NaHCO₃ \rightarrow Pb(NO₃)₂: (A) pH curve; (B) saturation indices; and (C) distribution of aqueous species. Note the constant undersaturation of the solution with respect to all other Pb-phases during the injection process.





Figure 4.12. Evolution of the SI for the closed system NaHCO₃ \rightarrow Pb(NO₃)₂: (A) complete experiment; (B) < 1 % NaHCO₃ injection with cerussite saturation index set to 0.00; (C) < 1 % NaHCO₃ injection without any saturation control (*i.e.* withholding precipitation).

4.2.2. A note on the systems $PbCl_2 \rightarrow Na_2CO_3$ and $Pb(NO_3)_2 \rightarrow Na_2CO_3$

As previously noted, the polymineralic character of the precipitates resulting from the experimental systems $PbCl_2 \rightarrow Na_2CO_3$ and $Pb(NO_3)_2 \rightarrow Na_2CO_3$ precludes the elaboration of reliable simulations. To illustrate that during reagent injection, the solution achieves saturation with respect to cerussite and hydrocerussite almost simultaneously, thus explaining why both phases are observed in the final precipitate assemblages, the saturation index diagrams (withholding precipitation) for these two experimental systems are presented in Figure 4.13. Although supersaturation with respect to $Pb(OH)_{2(s)}$ is reached before that of cerussite and hydrocerussite, this phase was not observed in the diffractograms.

4.2.3. Aqueous speciation of the $Pb(NO_3)_2$ and $PbCl_2$ solutions before and during mineral precipitation

Observations made in section 3.3.4 outline systematic differences in crystal shape and habit of cerussite crystals grown in either chloride- or nitrate-dominated solutions. These observations suggest potential differential influence of Cl⁻ and NO₃⁻ species during the nucleation and growth processes that could modify the resulting precipitate mineralogy and morphology.

Speciation of the initial lead solutions is presented in Table 4.2 to illustrate the general similarity between species distributions in the two solutions, as evidenced by the nearly identical $\{Pb^{2+}\}_{free}$ in both systems as well as the consistency in the ratios of complexes and main ions (*i.e.* $\{Pb^{2+}\}:\{PbNO_3^+(aq)\}:\{NO_3^-(aq)\} \approx \{Pb^{2+}(aq)\}:\{PbCl_n^{(2-n)}\}:\{Cl_{(aq)}\}\}$). This would be the approximate distribution of



(B)

Figure 4.13. Saturation index diagrams (withholding precipitation) for the systems (A) $Pb(NO_3)_2 \rightarrow Na_2CO_3$ and (B) $PbCl_2 \rightarrow Na_2CO_3$. Note the nearly simultaneous (*i.e.* within 0.1 %) saturation with respect to cerussite and hydrocerussite in both experiments (boxed area).

species during crystal growth in experimental systems such as Na₂CO₃, NaHCO₃ \rightarrow PbCl₂ and Na₂CO₃, NaHCO₃ \rightarrow PbCl₂. Further, comparing the two systems over a wide range of pH in cerussite-saturated solutions (Figure 4.14), it is observed that there is considerable similarity between the activities of Pb²⁺, Pb(OH)_n²⁻ⁿ, PbCl_n²⁻ⁿ, and PbNO₃⁺ complexes. The dramatic shift in aqueous complex speciation with pH suggests that the aqueous environment during crystal precipitation would be drastically different depending on pH.

Although the charge difference would preclude extensive substitution of NO₃⁻ for CO₃²⁻ ions in the bulk cerussite lattice, similarities in bond geometry and size (Table 4.3) may favour the adsorption of NO₃⁻ groups at CO₃²⁻ surface sites of a growing crystal. A potential affinity of NO₃⁻ for surface sites of CO₃²⁻ groups is consistent with the isostructural nature of PbCO_{3(s)} / KNO_{3(s)} and CaCO_{3(s)} / NaNO_{3(s)} (see Swainson et al., 1998; Harris, 1999; and Liu et al., 2001). Conversely, due to the simpler steric configuration and higher charge density (relative to a nitrate ion), the chloride ion would not be as sensitive to the surface-structural configuration and different faces on the growing crystal. Multiple Pb — Cl bonds would have to be broken for the Pb to be incorporated in the lattice of the growing crystal phase, presumably a more complex and energy-demanding process than in the case of PbNO₃⁺ incorporation.

Thus, the potential difference in site-specificity adsorption affinity suggests that both NO_3^+ and Cl^- species could modify the nucleation and growth of Pb-carbonate crystals differently. These effects may be enhanced at low pH, where the concentration of complexes such as Pb^{2+} , $PbCl_n^{(2-n)}$ and $PbNO_3^+$ are predominant

Table 4.2. (A) $PbCl_2$ at 25°C and	Species activi and (B) Pb(N(1 bar total pre	ties in a 0.035 $D_3)_2$ (charge-bassure.	M solution of alanced to pH)				
(A)	(B)					
pН	4.64	pH	4.75				
	Log(act)		Log(act)				
Pb ²⁺	-1.99	Pb ²⁺	-2.12				
NO3 ⁻	-1.33	Cl	-1.38				
PbNO ₃ ⁺	-2.15	PbC1 ⁺	-1.90				
		PbCl ₂	-3.07				
		PbCl ₃ ⁻	-4.55				
		PbCl ₄ ²⁻	-6.25				
	·	$\sum PbCl_n^{(2-n)}$	-1.87				
PbOH ⁺	-5.06	PbOH ⁺	-5.08				
Pb(OH) ₂	-9.83	Pb(OH) ₂	-9.73				
Pb(OH) ₃ ⁻	-16.14	Pb(OH) ₃ ⁻	-15.92				
Pb(OH) ₄ ²⁻	-23.14	Pb(OH) ₄ ²⁻	-22.81				
Pb ₂ OH ³⁺	-5.71	Pb ₂ OH ³⁺	-5.84				
OH-	-9.36	OH	-9.25				
H ⁺	-4.64	H^+	-4.75				

Table 4.3. Comparison of basic crystallographic parameters for cerussite (PbCO _{3(s)}) and niter (KNO _{3(s)}) (both orthorhombic) at 25 °C and 1bar total pressure									
PbCO ₃	(Sahl, 1974)	KNO _{3(s)} (N	immo and Lucas, 1973)						
C-0	Å	N-O	Å						
-O(1)	1.30	-O(1)	1.241(2)						
-O(2)	1.26	-O(2)	1.246(1)						
<i>a</i> =	5.1800(7)	<i>a</i> =	5.4142						
<i>b</i> =	8.492(3)	<i>b</i> =	9.1659						
<i>c</i> =	6.134(3)	<i>c</i> =	6.4309						



Figure 4.14. Aqueous complex species and activities in solutions of (A) $0.035 \text{ M Pb}(NO_3)_2$ and (B) $0.035 \text{ M Pb}Cl_2$ solutions in equilibrium with cerussite (charge-balanced by addition of Na₂CO₃, closed with respect to atmosphere) as a function of pH. Note: All activities of bicarbonato and carbonato complexes were all < 10^{-6} and are not included.

(Figures 4.5C and 4.7C). The observation that coarse euhedral and small anhedral crystals are more often observed in $PbNO_3^+$ - and $PbCl^+$ dominated growth solutions, respectively, suggests that NO_3^+ complexes may be superior nucleation inhibitors to $PbCl_n^{(2-n)}$ complexes.

4.3. Aging experiments

4.3.1. A note on aging experiments and model data

The pH values recorded at the end of all the aging experiments are presented in Figures 4.1 to 4.4. These fall either within, or close to, the theoretical data envelope created by the open and closed system pH curves.

4.3.2. Comparison of fresh and aged precipitates: indication of system disequilibrium?

The small difference in solution pH, mineralogy, and crystal morphology of most precipitates post-aging indicates that only minor chemical changes occurred between the time of complete reagent injection and the termination of the aging process. Further, it is important to note that there are no significant differences in either solution chemistry or crystal sizes/morphologies between precipitates allowed to age for either 8 or 16 days (see Table 3.2), indicating that a state of equilibrium was likely reached in less than 8 days.

Notable exceptions, however, are the systems $PbCl_2 \rightarrow Na_2CO_3$ (Figure 3.3) and $Pb(NO_3)_2 \rightarrow Na_2CO_3$ (Figure 3.7), in which a shift of almost 2-3 pH units was observed upon aging of the fresh precipitates and residual parent-solutions, indicating possible interconversion between cerussite, hydrocerussite and the parent-solution; as the aged solutions where closed to the atmosphere upon termination of injection, the effect of atmospheric $CO_{2(g)}$ exchange is nil. Interconversion is further supported by the notable increase in aged Ce/Hc peak height ratios, when comparing diffractograms of fresh and aged precipitates, in the system $Pb(NO_3)_2 \rightarrow Na_2CO_3$ (Figure 3.35); however, no such difference is observed in the diffractograms of the system $PbCl_2 \rightarrow Na_2CO_3$ (Figure 3.19).

Corresponding SEM images fail to show a visible change in crystal morphology and size, indicating that the bulk chemical reorganization that occurred upon aging was likely small. The systems $Pb(NO_3)_2 \rightarrow Na_2CO_3$ and $PbCl_2 \rightarrow$ Na_2CO_3 also yield the most finely-grained precipitate. Presumably, the cerussite \leftrightarrow hydrocerussite interconversions would be more pronounced on the mineral surfaces; therefore, the availability of high surface area should promote interconversion. It should be noted that the resolution of the SEM image is insufficient to detect any phase changes at the surface of minerals.

The only experimental system to show mineralogical differences between the fresh and aged precipitates is the system $PbCl_2 \rightarrow NaHCO_3$, where phosgenite is observed to precipitate only upon aging (Figure 3.12). Modeling cerussite precipitation for the system $PbCl_2 \rightarrow NaHCO_3$ (Figure 4.5) reveals that during the last 40% of the injection process, the solution becomes supersaturated with respect



Figure 4.15. Saturation index diagram (withholding precipitation) for the experimental system NaHCO₃ \rightarrow PbCl₂ (which results in extensive precipitation of phosgenite in both fresh and aged experiments). Note that saturation is achieved with respect to phosgenite at extremely low amounts of NaHCO₃ injection and that the degree of supersaturation rapidly achieves nearly 1000X (SI \approx 3) with less than 1 % of the NaHCO₃ solution injected. Ce = cerussite, Hc = hydrocerussite, Ph = phosgenite.

to phosgenite (SI \approx 1), yet this phase was not detected by XRD or SEM in the fresh precipitate. The moderate degree of supersaturation with respect to phosgenite is likely insufficient to overcome the energy-barrier required to induce phosgenite nucleation and subsequent precipitation. This evidence of a kinetic barrier to phosgenite nucleation is consistent with the tendency of multiple crystals to grow as parallel intergrowths (Figure 3.14) rather than to nucleate separately; this could act to bypass the nucleation energy barrier. This situation is much different in the opposite experimental scenario (*i.e.* NaHCO₃ \rightarrow PbCl₂) where phosgenite supersaturation is reached with injection of < 1% of the NaHCO₃ reagent, resulting in precipitation during injection (see Figure 4.15).

4.3.3. Conditions of equilibrium

4.3.3.1. Equilibrium between cerussite and hydrocerussite

In Chapter 1, various parameters and conditions of chemical equilibrium between cerussite \leftrightarrow phosgenite and cerussite \leftrightarrow hydrocerussite were discussed. For cerussite \leftrightarrow hydrocerussite equilibrium, the pertinent chemical reaction and mass action laws are:

(Eqn. 4.16) $3PbCO_{3(s)} + H_2O_{(1)} \leftrightarrow Pb_3(CO_3)_2(OH)_{2(s)} + CO_{2(g)}$ (Eqn. 4.17) $K_{rxn} = P_{CO2}$

where $K_{\text{rxn}} = P_{\text{CO2}} \approx 14$ Pa (Taylor and Lopata, 1984).

In aged precipitates of systems PbCl₂ \rightarrow Na₂CO₃, Na₂CO₃ \rightarrow PbCl₂, Pb(NO₃)₂ \rightarrow Na₂CO₃, and Na₂CO₃ \rightarrow Pb(NO₃)₂, the calculated, average P_{CO2} is 12.8 Pa (see Eqn. 2.1), which is in close agreement with the equilibrium value proposed by Taylor and Lopata (1984). Chemical equilibrium is also suggested by convergence of pH in aged experiments where the same reactants were mixed in opposite order (see Table 3.2). In all the above-mentioned aged systems, with the exception of the system Na₂CO₃ \rightarrow Pb(NO₃)₂ that contains only cerussite, both hydrocerussite and cerussite are observed in XRD diffractograms; the attainment of the equilibrium P_{CO2} in the system Na₂CO₃ \rightarrow Pb(NO₃)₂ suggests that hydrocerussite may be present but is below the limit of XRD detection. The results in Table 3.2 also suggest that at pH values of ~5, the instability of hydrocerussite relative to cerussite precludes interconversion.

It should be noted that in only one system, $Na_2CO3 \rightarrow PbCl_2$, is there an obvious textural distinction between the growth habits. However, as discussed in Section 3.2.2.4, it is difficult to identify the phases represented by each habit; in the fresh precipitates, both habits are present, but only cerussite is identified by XRD. Nevertheless, the change in habit ratios upon aging (see Figure 3.24), may make this system particularly well-suited to a more quantitative investigation into the relative stability and interconversion between cerussite and hydrocerussite. However, such a study is beyond the scope of this work.

4.3.3.2. Equilibrium between cerussite and phosgenite

The close agreement in pH (4.63 \pm 0.1) and P_{CO2} in both phosgenite- and cerussite-producing systems implies that a reproducible equilibrium condition resulting from the interconversion of phosgenite and cerussite was achieved. Equilibrium between these two phases is represented by:

(Eqn. 4.18)
$$Pb_2(CO_3)Cl_{2(s)} \leftrightarrow PbCO_{3(s)} + Pb^{2+}_{(aq)} + 2Cl_{(aq)}$$

(Eqn. 4.19) $K_{rxn} = [Pb^{2+}_{(aq)}][Cl_{(aq)}]^2$

The data required to assess the cerussite \leftrightarrow phosgenite equilibrium condition, particularly [Cl⁻]_{final} are unavailable.

Chapter 5:

Conclusions and Recommendations

5.1. Significant results

Analysis of Pb-carbonate precipitates (cerussite, hydrocerussite, and phosgenite) generated by this study in the systems $PbCl_2-CO_2-H_2O$ and $Pb(NO_3)_2-CO_2-H_2O$ by XRD and SEM reveals that:

- (1) The kinetics of Pb-carbonate nucleation and growth (cerussite, hydrocerussite, and phosgenite) are sufficiently rapid to prevent the extensive supersaturation generated by reagent addition in both Cl⁻ and NO_3^- -dominated solutions:
- (2) Thermodynamic modeling of experimental systems in which cerussite is the only precipitate suggests that the solution is maintained at cerussite saturation (SI(cer) \approx 0) during the reagent injection process. Modeling also shows that cerussite-saturated solutions prevent extensive supersaturation with respect to other phases during the reagent injection process and that cerussite saturation/supersaturation is achieved follwing < ~0.5 % of reagent injection:
- (3) The observed range of crystal sizes in the system Pb \rightarrow NaHCO₃ suggests repeated nucleation events, induced by loss of CO_{2(g)} to the atmosphere, or

sluggish nucleation kinetics in the HCO_3^- -rich systems relative to $CO_3^{2^-}$ -rich systems.

- (4) The crystal size of the resulting precipitate (cerussite, hydrocerussite, phosgenite) decreases with reagent injection rate, suggesting more prolific nucleation is induced by the higher degree of supersaturation achieved in the initial part of the experiment:
- (5) SEM examination of the cerussite reveals potential relationships between morphology (prismatic, bladed, platy hexagonal) and the parent-solution speciation during crystallization in the systems PbCl₂-CO₂-H₂O and Pb(NO₃)₂-CO₂-H₂O. This may be due to the differences in crystal growth mechanism (*i.e.* layered *vs.* two-dimensional) and in site-specific and non site-specific adsorption affinity of NO₃⁻ and Cl⁻ complexes, respectively:
- (6) At 25 °C, 1 bar, three phosgenite habits are observed in this study: 1) blocky, tetragonal crystals; 2) short, tabular crystals; and 3) large rounded, tabular crystals. Crystals of habit (1) tend to occur as intergrowths along (100) and (010). Habit (2) is observed to precipitate only at very high precipitation rates and conditions of supersaturation (as suggested by a high injection rate). Habit (3) is observed to form in aged solutions, presumably when the rate of precipitation was slow:

(7) Equilibrium between hydrocerussite, cerussite, and the aqueous solution is achieved through solid-phase interconversion (as observed by $K_{eq} \approx 14$ Pa $CO_{2(g)}$) in less than 8 days. Equilibrium between cerussite, phosgenite, and the aqueous solution is also achieved by solid-phase interconversion in less than 8 days. Further, hydrocerussite appears to precipitate only in parent-solution with pH values > ~9.

5.2. Recommendations for further work

Future work should be directed towards the following areas:

(1) Investigation into the potential relationship between aqueous speciation in the parent-solution and growing Pb-carbonate crystal mineralogy and habit. Of particular interest are the potential modifications to cerussite crystal morphology and habit that may result from the binding of NO₃⁻ and Cl⁻ to the crystal surface during growth. Key issues requiring further attention are: 1) differences in surface adsorption mechanisms between $PbCl_n^{(2-n)}(aq)$ and $PbNO_3^+(aq)$; 2) the extent to which NO₃⁻ may substitute for CO_3^{2-} into the crystal lattice during growth of the carbonate crystal; and 3) the extent to which this mechanism would differ between various species of Pb-carbonate minerals:

(2) Investigation into potential variations in Pb-carbonate mineral crystallography as a function of chemical growth environment and kinetics. This study noted: 1) deviations between the available JCPDS files and observed diffractograms; and 2) a seemingly sporadic shift in the intensity of the cerussite, $2\theta = 43.571$ (*hkl*) = (d₂₂₁) peak; the exact cause of this peak intensity variation is unknown. These observations may underlie differences in atomic coordination that may be due to chemical environment during crystal growth and/or kinetics.

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Appendix 1

Comparison of PDF files for all minerals in the system $Pb-CO_2-H_2O$.

All diffraction data are presented in CuK α radiation.





Appendix 2

Complete numerical output generated by PHREEQC-I modeling for both closed and open systems.

$PbCl_2 \rightarrow NaHCO_2$	- Open System (I	PHREEQC-I Outp	ut)						Second Second	
					log	log	log	log	log	log
% PbCl ₂	pH	∑Alk	[Pb ^{**}] _{TOT}	- 1995	(aPb**)	(aCI)	(aPbCl [*])	(aPbCl ₂)	(aPbCl ₃)	(aPbCL ⁴)
Injected .		meq	M			М	M			
0.00	9.55	3.51E-02	1.99E-05		-10.58					
2.86	9.52	3.22E-02	1.78E-05		-10.53	-2.79	-11.72	-14.31	-17.20	-20.31
5.71	9.50	2.94E-02	1.58E-05		-10.48	-2.50	-11.38	-13.68	-16.28	-19.10
8.57	9.47	2.68E-02	1.39E-05		-10.42	-2.33	-11.16	-13.29	-15.73	-18.38
11.43	9.44	2.43E-02	1.22E-05		-10.36	-2.22	-10.98	-13.00	-15.32	-17.86
14.29	9.41	2.19E-02	1.07E-05		-10.30	-2.13	-10.83	-12.77	-15.00	-17.45
17.14	9.38	1.97E-02	9.24E-06		-10.23	-2.06	-10.70	-12.56	-14.72	-17.11
20.00	9.34	1.75E-02	7.95E-06		-10.16	-2.01	-10.57	-12.37	-14.48	-16.80
22.86	9.30	1.55E-02	6.77E-06		-10.08	-1.96	-10.44	-12.19	-14.25	-16.53
25.71	9.25	1.36E-02	5.72E-06		-9.99	-1.92	-10.30	-12.02	-14.03	-16.27
28.57	9.20	1.17E-02	4.78E-06		-9.89	-1.88	-10.17	-11.85	-13.82	-16.02
31.43	9.15	9.92E-03	3.95E-06		-9.77	-1.85	-10.02	-11.66	-13.61	-15.78
34.29	9.08	8.21E-03	3.22E-06		-9.64	-1.82	-9.85	-11.47	-13.39	-15.52
37.14	9.00	6.58E-03	2.61E-06		-9.47	-1.79	-9.66	-11.26	-13.15	-15.26
40.00	8.89	5.01E-03	2.11E-06		-9.27	-1.77	-9.43	-11.00	-12.87	-14.95
42.86	8.75	3.51E-03	1.73E-06		-8.99	-1.74	-9.14	-10.68	-12.52	-14.59
45.71	8.54	2.06E-03	1.48E-06		-8.56	-1.72	-8.69	-10.21	-12.04	-14.08
48.57	8.07	6.77E-04	1.44E-06		-7.63	-1.71	-7.73	-9.24	-11.05	-13.07
51.43	6.22	1.66E-05	3.39E-04		-3.92	-1.69	-4.01	-5.51	-7.30	-9.31
54.29	5.99	1.62E-05	9.82E-04		-3.46	-1.68	-3.55	-5.03	-6.81	-8.81
57.14	5.89	1.75E-05	1.60E-03		-3.26	-1.67	-3.33	-4.80	-6.57	-8.57
60.00	5.82	1.88E-05	2.20E-03		-3.12	-1.66	-3.19	-4.65	-6.41	-8.40
62.86	5.77	2.01E-05	2.78E-03		-3.03	-1.66	-3.08	-4.54	-6.29	-8.27
65.71	5.74	2.13E-05	3.33E-03		-2.95	-1.65	-3.00	-4.45	-6.20	-8.16
68.57	5.71	2.25E-05	3.87E-03		-2.89	-1.64	-2.93	-4.37	-6.11	-8.07
71.43	5.68	2.36E-05	4.39E-03		-2.84	-1.63	-2.88	-4.31	-6.04	-8.00
74.29	5.66	2.47E-05	4.90E-03		-2.80	-1.63	-2.83	-4.25	-5.98	-7.93
77.14	5.64	2.57E-05	5.38E-03		-2.76	-1.62	-2.78	-4.21	-5.93	-7.87
80.00	5.63	2.67E-05	5.86E-03		-2.73	-1.61	-2.75	-4.16	-5.88	-7.81
82.86	5.61	2.76E-05	6.31E-03		-2.70	-1.61	-2.71	-4.12	-5.83	-7.76
85.71	5.60	2.85E-05	6.76E-03		-2.68	-1.60	-2.68	-4.08	-5.79	-7.71
88.57	5.59	2.93E-05	7.18E-03		-2.65	-1.60	-2.65	-4.05	-5.75	-7.67
91.43	5.58	3.02E-05	7.60E-03		-2.63	-1.59	-2.63	-4.02	-5.71	-7.63
94.29	5.57	3.10E-05	8.01E-03		-2.61	-1.59	-2.60	-3.99	-5.68	-7.59
97.14	5.56	3.17E-05	8.40E-03		-2.59	-1.59	-2.58	-3.97	-5.65	-7.56
100.00	5.55	3.25E-05	8.78E-03		-2.58	-1.58	-2.56	-3.94	-5.62	-7.52

log	log	log	log	log	log	log	log	log	log	log
(aPbOH)	(aPb(OH) ₂)	(aPb(OH) ₃)	(aPb(OH), ')	(aPb ₂ OH ^{**})	(aCO ₂)	log(aCO3 [*])	(aHCO ₃)	(aPbHCO ₃ [*])	(aPbCO ₃)	(aPb(CO ₃) ₂ ")
M	M	M	M	M	M	M	M	M	M	M
-8.74	-8.60	-9.99	-12.08	-17.97	-4.97	-2.55	-1.77	-9.45	-5.89	-5.04
-8.72	-8.60	-10.02	-12.13	-17.90	-4.97	-2.60	-1.80	-9.43	-5.89	-5.09
-8.69	-8.60	-10.04	-12.19	-17.82	-4.97	-2.65	-1.82	-9.40	-5.89	-5.14
-8.66	-8.60	-10.07	-12.24	-17.74	4.97	-2.71	-1.85	-9.37	-5.89	-5.20
-8.63	-8.60	-10.10	-12.30	-17.65		-2.77	-1.88	-9 .34	-5.89	-5.26
-8.60	-8.60	-10.13	-12.36	-17.55	4.97	-2.83	-1.91	-9.31	-5.89	-5.32
-8.57	-8.60	-10.17	-12.43	-17.45	-4.97	-2.90	-1.94	-9.28	-5.89	-5.39
-8.53	-8.60	-10.20	-12.50	-17.34	-4.97	-2.97	-1.98	-9.24	-5.89	-5.46
-8.49	-8.60	-10.24	-12.59	-17.22	4.97	-3.05	-2.02	-9.20	-5.89	-5.54
-8.45	-8.60	-10.29	-12.68	-17.08	-4.97	-3.14	-2.07	-9.16	-5.89	-5.63
-8.39	-8.60	-10.34	-12.78	-16.93	-4.97	-3.24	-2.12	-9.10	-5.89	-5.73
-8.34	-8.60	-10.40	-12.89	-16.76	-4.97	-3.36	-2.17	-9.05	-5.89	-5.85
-8.27	-8.60	-10.46	-13.03	-16.56	-4.97	-3.49	-2.24	-8.98	-5.89	-5.98
-8.19	-8.60	-10.55	-13.19	-16.31	-4.97	-3.66	-2.32	-8.90	-5.89	-6.15
-8.09	-8.60	-10.65	-13.40	-16.00	-4.97	-3.86	-2.43	-8.79	-5.89	-6.35
-7.95	-8.60	-10.79	-13.67	-15.59	-4.97	-4.14	-2.57	-8.66	-5.89	-6.63
-7.73	-8.60	-11.00	-14.10	-14.95	4.97	-4.57	-2.78	-8.44	-5.89	-7.06
-7.26	-8.60	-11.47	-15.04	-13.54	-4.97	-5.50	-3.25	-7.97	-5.89	-7.99
-5.41	-8.60	-13.32	-18.74	-7.98	-4.97	-9.21	-5.10	-6.12	-5.89	-11.70
-5.18	-8.60	-13.55	-19.20	-7.30	-4.97	-9.67	-5.33	-5.89	-5.89	-12.16
-5.08	-8.60	-13.66	-19.41	-6.98	-4.97	-9.87	-5.43	-5.79	-5.89	-12.36
-5.01	-8.60	-13.72	-19.54	-6.79	-4.97	-10.01	-5.50	-5.72	-5.89	-12.50
-4.96	-8.60	-13.77	-19.64	-6.64	-4.97	-10.10	-5.55	-5.67	-5.89	-12.59
-4.93	-8.60	-13.81	-19.71	-6.53	4.97	-10.18	-5.58	-5.64	-5.89	-12.67
-4.90	-8.60	-13.84	-19.77	-6.44	4.97	-10.24	-5.61	-5.61	-5.89	-12.73
-4.87	-8.60	-13.86	-19.82	-6.37	-4.97	-10.29	-5.64	-5.58	-5.89	-12.78
-4.85	-8.60	-13.88	-19.86	-6.30	-4.97	-10.33	-5.66	-5.56	-5.89	-12.82
-4.83	-8.60	-13.90	-19.90	-6.25	-4.97	-10.37	-5.68	-5.54	-5.89	-12.86
-4.82	-8.60	-13.92	-19.93	-6.20	-4.97	-10.40	-5.70	-5.53	-5.89	-12.89
-4.80	-8.60	-13.93	-19.96	-6.15	-4.97	-10.43	-5.71	-5.51	-5.89	-12.92
-4.79	-8.60	-13.94	-19.99	-6.12	-4.97	-10.45	-5.72	-5.50	-5.89	-12.94
_4.78	-8.60	-13.96	-20.01	-6.08	-4.97	-10.48	-5.73	-5.49	-5.89	-12.97
-4.77	-8.60	-13.97	-20.03	-6.05	-4.97	-10.50	-5.74	-5.48	-5.89	-12.99
-4.76	-8.60	-13.98	-20.05	-6.02	-4.97	-10.52	-5.75	-5.47	-5.89	-13.01
4.75	-8.60	-13.99	-20.07	-5.99	-4.97	-10.54	-5.76	-5.46	-5.89	-13.03
-4.74	-8.60	-13.99	-20.09	-5.97	-4.97	-10.55	-5.77	-5.45	-5.89	-13.04

100							n		
log	log	log	log	log	log	SI	SI	SI	SI
(aNa [*])	(aNaCO ₃)	(aNaHCO ₃)	(aNaOH)	(aOH)	(aH [*])	Ce	He	(Pb(OH) _{2(s)})	Ph
M	M	M	M	M	M			144. 199	
-1.56	-2.84	-3.58	-6.19	-4.45	-9.55	0.00	-1.66	0.37	
-1.57	-2.90	-3.61	-6.22	-4.48	-9.52	0.00	-1.66	0.37	-9.43
-1.57	-2.96	-3.65	-6.26	-4.50	-9.50	0.00	-1.66	0.37	-8.80
-1.58	-3.02	-3.68	-6.29	-4.53	-9.47	0.00	-1.66	0.37	-8.41
-1.59	-3.09	-3.72	-6.33	-4.56	-9.44	0.00	-1.66	0.37	-8.12
-1.60	-3.16	-3.76	-6.37	-4.59	-9.41	0.00	-1.66	0.37	-7.89
-1.61	-3.23	-3.80	-6.41	-4.62	-9.38	0.00	-1.66	0.37	-7.68
-1.62	-3.32	-3.85	-6.46	-4.66	-9.34	0.00	-1.66	0.37	-7.49
-1.62	-3.40	-3.89	-6.50	-4.70	-9.30	0.00	-1.66	0.37	-7.31
-1.63	-3.50	-3.95	-6.56	-4.75	-9.25	0.00	-1.66	0.37	-7.14
-1.64	-3.61	-4.00	-6.62	-4.80	-9.20	0.00	-1.66	0.37	-6.96
-1.65	-3.73	-4.07	-6.68	-4.85	-9.15	0.00	-1.66	0.37	-6.78
-1.65	-3.88	-4.15	-6.76	-4.92	-9.08	0.00	-1.66	0.37	-6.59
-1.66	-4.05	-4.23	-6.84	-5.00	-9.00	0.00	-1.66	0.37	-6.37
-1.67	-4.26	-4.34	-6.95	-5.11	-8.89	0.00	-1.66	0.37	-6.12
-1.68	-4.55	-4.49	-7.10	-5.25	-8.75	0.00	-1.66	0.37	-5.80
-1.68	-4.98	-4.71	-7.32	-5.46	-8.54	0.00	-1.66	0.37	-5.33
-1.69	-5.92	-5.19	-7.80	-5.93	-8.07	0.00	-1.66	0.37	-4.36
-1.70	-9.64	-7.05	-9.66	-7.78	-6.22	0.00	-1.66	0.37	-0.63
-1.71	-10.11	-7.29	-9.90	-8.01	-5.99	0.00	-1.66	0.37	-0.15
-1.72	-10.32	-7.40	-10.01	-8.11	-5.89	0.00	-1.66	0.37	0.08
-1.73	-10.46	-7.47	-10.09	-8.18	-5.82	0.00	-1.66	0.37	0.23
-1.73	-10.57	-7.53	-10.14	-8.23	-5.77	0.00	-1.66	0.37	0.34
-1.74	-10.65	-7.58	-10.19	-8.26	-5.74	0.00	-1.66	0.37	0.43
-1.75	-10.72	-7.62	-10.23	-8.29	-5.71	0.00	-1.66	0.37	0.51
-1.76	-10.78	-7.65	-10.26	-8.32	-5.68	0.00	-1.66	0.37	0.57
-1.77	-10.83	-7.68	-10.29	-8.34	-5.66	0.00	-1.66	0.37	0.63
-1.77	-10.87	-7.70	-10.31	-8.36	-5.64	0.00	-1.66	0.37	0.68
-1.78	-10.91	-7.73	-10.34	-8.37	-5.63	0.00	-1.66	0.37	0.72
-1.79	-10.95	-7.75	-10.36	-8.39	-5.61	0.00	-1.66	0.37	0.76
-1.80	-10.98	-7.77	-10.38	-8.40	-5.60	0.00	-1.66	0.37	0.80
-1.80	-11.01	-7.79	-10.40	-8.41	-5.59	0.00	-1.66	0.37	0.83
-1.81	-11.04	-7.81	-10.42	-8.42	-5.58	0.00	-1.66	0.37	0.86
-1.82	-11.07	-7.82	-10.43	-8.43	-5.57	0.00	-1.66	0.37	0.89
-1.83	-11.09	-7.84	-10.45	-8.44	-5.56	0.00	-1.66	0.37	0.91
-1.83	-11.11	-7.85	-10.46	-8.45	-5.55	0.00	-1.66	0.37	0.94

$PbCl_2 \rightarrow NaHCO_3$	- Closed System	(PHREEQC-I Out	put)			1			
				log	log	log	log	log	log
% PbCl ₂	pH	∑Alk	[Pb ^{**}] _{TOT}	(aPb ²⁺)	(aCl)	(aPbCl ⁺)	(aPbCl ₂)	(aPbCl ₃)	(aPbCl4')
Injected		meq	M	M	M	M	M	M	M
0.00	8.13	3.51E-02	2.46E-06	-9.39					
2.86	7.64	3.22E-02	1.67E-06	-8.87	-2.79	-10.06	-12.64	-15.53	-18.64
5.71	7.44	2.94E-02	1.54E-06	-8.63	-2.50	-9.53	-11.83	-14.43	-17.24
8.57	7.25	2.68E-02	1.49E-06	-8.40	-2.33	-9.14	-11.27	-13.70	-16.35
11.43	7.10	2.43E-02	1.49E-06	-8.21	-2.22	-8.83	-10.85	-13.16	-15.70
14.29	6.97	2.19E-02	1.51E-06	-8.04	-2.13	-8.57	-10.50	-12.73	-15.18
17.14	6.86	1.97E-02	1.55E-06	-7.88	-2.06	-8.34	-10.20	-12.37	-14.75
20.00	6.75	1.75E-02	1.61E-06	-7.73	-2.00	-8.13	-9.93	-12.04	-14.36
22.86	6.65	1.55E-02	1.69E-06	-7.57	-1.96	-7.93	-9.68	-11.74	-14.02
25.71	6.55	1.36E-02	1.80E-06	-7.42	-1.91	-7.73	-9.45	-11.46	-13.69
28.57	6.46	1.17E-02	1.95E-06	-7.25	-1.88	-7.53	-9.21	-11.19	-13.38
31.43	6.35	9.92E-03	2.15E-06	-7.08	-1.84	-7.33	-8.97	-10.92	-13.08
34.29	6.24	8.22E-03	2.46E-06	-6.89	-1.82	-7.11	-8.72	-10.64	-12.77
37.14	6.12	6.58E-03	2.95E-06	-6.67	-1.79	-6.86	-8.45	-10.34	-12.45
40.00	5.98	5.02E-03	3.83E-06	-6.42	-1.77	-6.58	-8.15	-10.01	-12.10
42.86	5.81	3.52E-03	5.76E-06	-6.09	-1.74	-6.23	-7.78	-9.62	-11.68
45.71	5.56	2.09E-03	1.19E-05	-5.62	-1.72	-5.74	-7.26	-9.09	-11.13
48.57	5.12	7.95E-04	6.02E-05	-4.76	-1.71	-4.86	-6.37	-8.18	-10.20
51.43	4.65	2.75E-04	4.69E-04	-3.81	-1.69	-3.90	-5.39	-7.18	-9.20
54.29	4.47	1.87E-04	1.07E-03	-3.44	-1.68	-3.53	-5.01	-6.79	-8.79
57.14	4.38	1.54E-04	1.67E-03	-3.25	-1.67	-3.32	-4.80	-6.57	-8.56
60.00	4.32	1.37E-04	2.26E-03	-3.12	-1.66	-3.19	-4.65	-6.41	-8.40
62.86	4.28	1.26E-04	2.83E-03	-3.03	-1.66	-3.08	-4.54	-6.30	-8.27
65.71	4.24	1.18E-04	3.38E-03	-2.96	-1.65	-3.00	-4.45	-6.20	-8.17
68.57	4.22	1.12E-04	3.92E-03	-2.90	-1.64	-2.94	-4.38	-6.12	-8.08
71.43	4.20	1.08E-04	4.44E-03	-2.85	-1.63	-2.88	-4.31	-6.05	-8.00
74.29	4.18	1.04E-04	4.94E-03	-2.80	-1.63	-2.83	-4.26	-5.98	-7.93
77.14	4.16	1.01E-04	5.42E-03	-2.77	-1.62	-2.79	-4.21	-5.93	-7.87
80.00	4.15	9.90E-05	5.89E-03	-2.73	-1.61	-2.75	-4.16	-5.88	-7.81
82.86	4.14	9.69E-05	6.35E-03	-2.71	-1.61	-2.71	-4.12	-5.83	-7.76
85.71	4.13	9.50E-05	6.79E-03	-2.68	-1.60	-2.68	-4.09	-5.79	-7.71
88.57	4.12	9.34E-05	7.22E-03	-2.66	-1.60	-2.66	-4.05	-5.75	-7.67
91.43	4.11	9.20E-05	7.63E-03	-2.64	-1.59	-2.63	-4.02	-5.72	-7.63
94.29	4.13	8.61E-05	8.03E-03	-2.62	-1.59	-2.60	-3.99	-5.68	-7.59
97.14	4.10	8.95E-05	8.43E-03	-2.60	-1.58	-2.58	-3.97	-5.65	-7.56
100.00	4.10	8.85E-05	8.81E-03	-2.58	-1.58	-2.56	-3.94	-5.62	-7.52

	1										
log	log	log	log	log	log	log	log	log	log	log	log
(aPbOH)	(aPb(OH) ₂)	$(aPb(OH)_3)$	(aPb(OH),*)	(aPb ₂ OH ^{**})	(aCO ₂)	log(aCO ₃ *)	(aHCO ₃)	(aPbCO ₃)	(aPb(CO ₃) ₂ *)	(aPbHCO ₃)	(aNa')
M	M 10.05	M 12.0(M	M	M	M	M	M	M	M	M
-8.97	-10.25	-13.06	-16.56	-17.01	-3.32	-3.74	-1.54	-5.89	-6.23	-8.03	-1.54
-8.94	-10.71	-14.01	-18.01	-16.46	-2.86	-4.26	-1.57	-5.89	-6.75	-7.54	-1.55
-8.90	-10.87	-14.37	-18.56	-16.19	-2.70	-4.50	-1.61	-5.89	-6.99	-7.34	-1.56
-8.86	-11.02	-14.71	-19.10	-15.92	-2.55	-4.73	-1.65	-5.89	-7.22	-7.15	-1.57
-8.82	-11.13	-14.97	-19.51	-15.68	-2.44	-4.92	-1.69	-5.89	-7.41	-7.00	-1.58
-8.78	-11.22	-15.19	-19.85	-15.47	-2.35	-5.09	-1.73	-5.89	-7.58	-6.87	-1.59
-8.73	-11.28	-15.37	-20.15	-15.26	-2.29	-5.25	-1.78	-5.89	-7.74	-6.76	-1.60
-8.68	-11.34	-15.53	-20.41	-15.06	-2.23	-5.40	-1.83	-5.89	-7.89	-6.65	-1.61
-8.63	-11.39	-15.68	-20.66	-14.85	-2.18	-5.56	-1.88	-5.89	-8.05	-6.55	-1.62
-8.57	-11.43	-15.81	-20.90	-14.64	-2.14	-5.71	-1.94	-5.89	-8.20	-6.46	-1.62
-8.51	-11.46	-15.95	-21.13	-14.41	-2.11	-5.88	-2.00	-5.89	-8.37	-6.36	-1.63
-8.44	-11.50	-16.08	-21.37	-14.17	-2.07	-6.05	-2.07	-5.89	-8.54	-6.25	-1.64
-8.36	-11.52	-16.22	-21.62	-13.90	-2.05	-6.24	-2.15	-5.89	-8.73	-6.14	-1.65
-8.26	-11.55	-16.37	-21.89	-13.59	-2.02	-6.46	-2.25	-5.89	-8.95	-6.02	-1.66
-8.14	-11.57	-16.53	-22.19	-13.21	-2.00	-6.71	-2.37	-5.89	-9.20	-5.88	-1.67
-7.99	-11.59	-16.73	-22.56	-12.73	-1.98	-7.04	-2.52	-5.89	-9.53	-5.71	-1.67
-7.76	-11.61	-16.99	-23.07	-12.03	-1.96	-7.52	-2.75	-5.89	-10.01	-5.46	-1.68
-7.34	-11.63	-17.45	-23.96	-10.75	-1.94	-8.37	-3.17	-5.89	-10.86	-5.03	-1.69
-6.87	-11.63	-17.92	-24.91	-9.32	-1.94	-9.32	-3.64	-5.89	-11.81	-4.55	-1.70
-6.68	-11.62	-18.09	-25.26	-8.78	-1.95	-9.69	-3.83	-5.89	-12.18	-4.37	-1.71
-6.58	-11.62	-18.18	-25.44	-8.48	-1.95	-9.88	-3.93	-5.89	-12.37	-4.28	-1.72
-6.52	-11.61	-18.23	-25.55	-8.29	-1.96	-10.01	-4.00	-5.89	-12.50	-4.22	-1.73
-6.46	-11.60	-18.27	-25.63	-8.14	-1.97	-10.10	-4.05	-5.89	-12.59	-4.18	-1.73
-6.42	-11.59	-18.29	-25.69	-8.03	-1.98	-10.17	-4.09	-5.89	-12.66	-4.14	-1.74
-6.39	-11.59	-18.31	-25.73	-7.94	-1.99	-10.23	-4.12	-5.89	-12.72	-4.12	-1.75
-6.36	-11.58	-18.32	-25.77	-7.86	-1.99	-10.28	-4.15	-5.89	-12.77	-4.10	-1.76
-6.34	-11.57	-18.33	-25.80	-7.79	-2.00	-10.33	-4.17	-5.89	-12.82	-4.08	-1.77
-6.31	-11.56	-18.34	-25.82	-7.73	-2.01	-10.36	-4.20	-5.89	-12.85	-4.06	-1.77
-6.30	-11.56	-18.35	-25.84	-7.68	-2.01	-10.40	-4.22	-5.89	-12.89	-4.05	-1.78
-6.28	-11.55	-18.35	-25.85	-7.63	-2.02	-10.42	-4.23	-5.89	-12.91	-4.04	-1.79
-6.26	-11.54	-18.35	-25.86	-7.59	-2.03	-10.45	-4.25	-5.89	-12.94	-4.03	-1.80
-6.25	-11.54	-18.36	-25.87	-7.55	-2.03	-10.47	-4.27	-5.89	-12.96	-4.02	-1.80
-6.23	-11.53	-18.36	-25.88	-7.52	-2.04	-10.50	-4.28	-5.89	-12.99	-4.01	-1.81
-6.20	-11.48	-18.28	-25.79	-7.46	-2.10	-10.51	-4.32	-5.89	-13.00	-4.03	-1.82
-6.21	-11.52	-18.36	-25.89	-7.45	-2.05	-10.53	-4.30	-5.89	-13.02	-4.00	-1.83
-6.20	-11.51	-18.35	-25.90	-7.43	-2.06	-10.55	-4.32	-5.89	-13.04	-4.00	-1.83
log	log	log	log	log	SI	SI	SI	SI			
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(aNaCO ₃)	(aNaHCO ₃)	(aNaOH)	(aOH)	(aH [*])	Ce	Hc	(Pb(OH) ₂₍₃₎)	- Ph			
M	M E	M	M	M							
-4.01	-3.33	-7.58	-5.87	-8.13	0.00	-3.31	-1.28				
-4.54	-3.37	-8.09	-6.36	-7.64	0.00	-3.77	-1.74	-7.76			
-4.78	-3.42	-8.29	-6.56	-7.44	0.00	-3.93	-1.90	-6.95			
-5.02	-3.47	-8.50	-6.75	-7.25	0.00	-4.08	-2.05	-6.39			
-5.23	-3.52	-8.66	-6.90	-7.10	0.00	-4.19	-2.16	-5.97			
-5.41	-3.57	-8.79	-7.03	-6.97	0.00	-4.28	-2.25	-5.62			
-5.58	-3.63	-8.92	-7.14	-6.86	0.00	-4.34	-2.31	-5.32			
-5.74	-3.68	-9.03	-7.25	-6.75	0.00	-4.40	-2.37	-5.05			
-5.90	-3.75	-9.14	-7.35	-6.65	0.00	-4.45	-2.42	-4.80			
-6.07	-3.81	-9.25	-7.45	-6.55	0.00	-4.49	-2.46	-4.57			
-6.24	-3.89	-9.36	-7.54	-6.46	0.00	-4.52	-2.49	-4.33			
-6.42	-3.96	-9.47	-7.65	-6.35	0.00	-4.56	-2.53	-4.09			
-6.62	-4.05	-9.59	-7.76	-6.24	0.00	-4.58	-2.55	-3.84			
-6.85	-4.16	-9.72	-7.88	-6.12	0.00	-4.61	-2.58	-3.57			
-7.11	-4.28	-9.87	-8.02	-5.98	0.00	-4.63	-2.60	-3.27			
-7.45	-4.45	-10.05	-8.19	-5.81	0.00	-4.65	-2.62	-2.90			
-7.93	-4.68	-10.30	-8.44	-5.56	0.00	-4.67	-2.64	-2.38			
-8.79	-5.11	-10.75	-8.88	-5.12	0.00	-4.69	-2.66	-1.49			
-9.75	-5.59	-11.23	-9.35	-4.65	0.00	-4.69	-2.66	-0.51			
-10.13	-5.79	-11.42	-9.53	-4.47	0.00	-4.68	-2.65	-0.13			
-10.33	-5.90	-11.52	-9.62	-4.38	0.00	-4.67	-2.65	0.08			
-10.46	-5.97	-11.59	-9.68	-4.32	0.00	-4.67	-2.64	0.23			
-10.57	-6.03	-11.64	-9.72	-4.28	0.00	-4.66	-2.63	0.34			
-10.65	-6.08	-11.68	-9.76	-4.24	0.00	-4.65	-2.62	0.43			
-10.72	-6.12	-11.72	-9.78	-4.22	0.00	-4.64	-2.61	0.50			
-10.77	-6.16	-11.75	-9.80	-4.20	0.00	-4.64	-2.61	0.57			
-10.82	-6.19	-11.77	-9.82	-4.18	0.00	-4.63	-2.60	0.62			
-10.87	-6.22	-11.79	-9.84	-4.16	0.00	-4.62	-2.59	0.67			
-10.91	-6.25	-11.81	-9.85	-4.15	0.00	-4.61	-2.59	0.72			
-10.94	-6.27	-11.83	-9.86	-4.14	0.00	-4.61	-2.58	0.76			
-10.98	-6.30	-11.85	-9.87	-4.13	0.00	-4.60	-2.57	0.79			
-11.01	-6.32	-11.86	-9.88	-4.12	0.00	-4.59	-2.57	0.83			
-11.04	-6.34	-11.88	-9.89	-4.11	0.00	-4.59	-2.56	0.86			
-11.06	-6.38	-11.87	-9.87	-4.13	0.00	-4.53	-2.50	0.89			
-11.09	-6.38	-11.90	-9.90	-4.10	0.00	-4.57	-2.55	0.91			
-11.11	-6.40	-11.92	-9.90	-4.10	0.00	-4.57	-2.54	0.94			

$Pb(NO_3)_2 \rightarrow N$	aHCO ₃ - Oper	System (PHREE)	OC-I Output)									
		1			log	log	log	log	log	log	log	log
% Pb(NO ₁) ₂	pH	ΣAlk	[Pb ²⁺] _{TOT}		(aPb ^{2*})	(aNO ₁)	(aPb(OH).)	(aPb(OH) _h)	(aPb(OH),")	(aPb.OH')	(aPbNO ₃)	(aPbOH)
Injected		meq	M		M	M	M	M	M	M	M	M
0.00	9.55	3.51E-02	1.99E-05	T	-10.58		-8.60	-9.99	-12.08	-17.97		-8.74
2.86	9.52	3.22E-02	1.78E-05		-10.53	-2.79	-8.60	-10.02	-12.13	-17.90	-12.15	-8.72
5.71	9.50	2.94E-02	1.58E-05		-10.48	-2.50	-8.60	-10.04	-12.19	-17.82	-11.81	-8.69
8.57	9.47	2.68E-02	1.39E-05		-10.42	-2.34	-8.60	-10.07	-12.24	-17.73	-11.59	-8.66
11.43	9.44	2.43E-02	1.22E-05		-10.36	-2.22	-8.60	-10.10	-12.30	-17.65	-11.42	-8.63
14.29	9.41	2.19E-02	1.07E-05		-10.30	-2.14	-8.60	-10.13	-12.36	-17.55	-11.27	-8.60
17.14	9.38	1.97E-02	9.24E-06		-10.23	-2.07	-8.60	-10.17	-12.43	-17.45	-11.13	-8.57
20.00	9.34	1.75E-02	7.94E-06		-10.16	-2.01	-8.60	-10.20	-12.50	-17.34	-11.00	-8.53
22.86	9.30	1.55E-02	6.77E-06		-10.08	-1.96	-8.60	-10.24	-12.59	-17.22	-10.87	-8.49
25.71	9.25	1.36E-02	5.72E-06		-9.99	-1.92	-8.60	-10.29	-12.68	-17.08	-10.74	-8.45
28.57	9.20	1.17E-02	4.77E-06		-9.89	-1.88	-8.60	-10.34	-12.78	-16.93	-10.60	-8.39
31.43	9.15	9.91E-03	3.94E-06		-9.77	-1.85	-8.60	-10.40	-12.89	-16.76	-10.45	-8.34
34.29	9.08	8.21E-03	3.22E-06		-9.64	-1.82	-8.60	-10.46	-13.03	-16.56	-10.29	-8.27
37.14	9.00	6.57E-03	2.61E-06		-9.47	-1.79	-8.60	-10.55	-13.19	-16.31	-10.10	-8.19
40.00	8.89	5.01E-03	2.11E-06		-9.27	-1.77	-8.60	-10.65	-13.40	-16.00	-9.87	-8.09
42.86	8.75	3.51E-03	1.73E-06		-8.99	-1.75	-8.60	-10.79	-13.67	-15.59	-9.57	-7.95
45.71	8.54	2.06E-03	1.47E-06		-8.56	-1.73	-8.60	-11.00	-14.10	-14.95	-9.12	-7.73
48.57	8.07	6.76E-04	1.43E-06		-7.63	-1.71	-8.60	-11.47	-15.04	-13.54	-8.17	-7.26
51.43	6.17	1.61E-05	3.39E-04		-3.81	-1.69	-8.60	-13.38	-18.85	-7.82	-4.34	-5.36
54.29	5.94	1.67E-05	9.82E-04		-3.36	-1.68	-8.60	-13.61	-19.31	-7.13	-3.87	-5.13
57.14	5.83	1.85E-05	1.60E-03		-3.15	-1.67	-8.60	-13.71	-19.52	-6.82	-3.65	-5.02
60.00	5.77	2.03E-05	2.20E-03		-3.02	-1.66	-8.60	-13.78	-19.65	-6.62	-3.50	-4.96
62.86	5.72	2.20E-05	2.78E-03		-2.92	-1.65	-8.60	-13.82	-19.74	-6.48	-3.40	-4.91
65.71	5.68	2.36E-05	3.33E-03		-2.84	-1.64	-8.60	-13.86	-19.82	-6.37	-3.32	-4.87
68.57	5.65	2.51E-05	3.87E-03		-2.78	-1.63	-8.60	-13.89	-19.88	-6.28	-3.25	-4.84
71.43	5.63	2.65E-05	4.39E-03		-2.73	-1.62	-8.60	-13.92	-19.93	-6.20	-3.19	-4.82
74.29	5.60	2.79E-05	4.89E-03		-2.69	-1.62	-8.60	-13.94	-19.97	-6.14	-3.14	-4.80
77.14	5.59	2.93E-05	5.38E-03		-2.65	-1.61	-8.60	-13.96	-20.01	-6.08	-3.09	-4.78
80.00	5.57	3.05E-05	5.85E-03		-2.62	-1.60	-8.60	-13.97	-20.04	-6.03	-3.05	-4.76
82.86	5.56	3.18E-05	6.31E-03		-2.59	-1.60	-8.60	-13.99	-20.07	-5.99	-3.02	-4.75
85.71	5.54	3.30E-05	6.75E-03		-2.57	-1.59	-8.60	-14.00	-20.10	-5.95	-2.99	-4.73
88.57	5.53	3.41E-05	7.18E-03		-2.54	-1.58	-8.60	-14.01	-20.12	-5.91	-2.96	-4.72
91.43	5.52	3.52E-05	7.60E-03		-2.52	-1.58	-8.60	-14.02	-20.14	-5.88	-2.93	-4.71
94.29	5.51	3.63E-05	8.00E-03		-2.50	-1.57	-8.60	-14.03	-20.16	-5.85	-2.90	-4.70
97.14	5.50	3.74E-05	8.39E-03		-2.48	-1.57	-8.60	-14.04	-20.18	-5.83	-2.88	-4.69
100.00	5.49	3.84E-05	8.78E-03		-2.47	-1.56	-8.60	-14.05	-20.20	-5.80	-2.86	-4.68

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log	log	log	log	log	log	log	log	log	log	log	log	SI	SI	SI
(aCO ₂)	(aCO ₃ ⁻⁴)	(aHCO ₃)	(aPbHCO ₃ [*])	(aPbCO ₃)	(aPb(CO3)2)	(aNa [†])	(aNaCO ₃)	(aNaHCO ₃)	(aNaOH)	(aOH)	(aH [*])	(Ce)	(Hc)	(Pb(OH) _{2(a)})
M	M	М	M	M	M	M	M	M	М	M	M			
-4.97	-2.55	-1.77	-9.45	-5.89	-5.04	-1.56	-2.84	-3.58	-6.19	-4.45	-9.55	0.00	-1.66	0.37
-4.97	-2.60	-1.80	-9.43	-5.89	-5.09	-1.57	-2.90	-3.61	-6.22	-4.48	-9.52	0.00	-1.66	0.37
-4.97	-2.65	-1.82	-9.40	-5.89	-5.14	-1.57	-2.96	-3.65	-6.26	-4.50	-9.50	0.00	-1.66	0.37
-4.97	-2.71	-1.85	-9.37	-5.89	-5.20	-1.58	-3.02	-3.68	-6.29	-4.53	-9.47	0.00	-1.66	0.37
-4.97	-2.77	-1.88	-9.34	-5.89	-5.26	-1.59	-3.09	-3.72	-6.33	-4.56	-9.44	0.00	-1.66	0.37
-4.97	-2.83	-1.91	-9.31	-5.89	-5.32	-1.60	-3.16	-3.76	-6.37	-4.59	-9.41	0.00	-1.66	0.37
-4.97	-2.90	-1.94	-9.28	-5.89	-5.39	-1.61	-3.23	-3.80	-6.41	-4.62	-9.38	0.00	-1.66	0.37
-4.97	-2.97	-1.98	-9.24	-5.89	-5.46	-1.62	-3.32	-3.85	-6.46	-4.66	-9.34	0.00	-1.66	0.37
-4.97	-3.05	-2.02	-9.20	-5.89	-5.54	-1.62	-3.40	-3.89	-6.50	-4.70	-9.30	0.00	-1.66	0.37
-4.97	-3.14	-2.07	-9.16	-5.89	-5.63	-1.63	-3.50	-3.95	-6.56	-4.75	-9.25	0.00	-1.66	0.37
-4.97	-3.24	-2.12	-9.10	-5.89	-5.73	-1.64	-3.61	-4.01	-6.62	-4.80	-9.20	0.00	-1.66	0.37
-4.97	-3.36	-2.17	-9.05	-5.89	-5.85	-1.65	-3.73	-4.07	-6.68	-4.85	-9.15	0.00	-1.66	0.37
-4.97	-3.49	-2.24	-8.98	-5.89	-5.98	-1.65	-3.88	-4.15	-6.76	-4.92	-9.08	0.00	-1.66	0.37
-4.97	-3.66	-2.32	-8.90	-5.89	-6.15	-1.66	-4.05	-4.23	-6.84	-5.00	-9.00	0.00	-1.66	0.37
-4.97	-3.86	-2.43	-8.79	-5.89	-6.35	-1.67	-4.26	-4.35	-6.96	-5.11	-8.89	0.00	-1.66	0.37
	-4.14	-2.57	-8.66	-5.89	-6.63	-1.68	-4.55	-4.49	-7.10	-5.25	-8.75	0.00	-1.66	0.37
-4.97	-4.57	-2.78	-8.44	-5.89	-7.06	-1.68	-4.98	-4.71	-7.32	-5.46	-8.54	0.00	-1.66	0.37
-4.97	-5.50	-3.25	-7.97	-5.89	-7.99	-1.69	-5.92	-5.19	-7.80	-5.93	-8.07	0.00	-1.66	0.37
-4.97	-9.32	-5.15	-6.07	-5.89	-11.81	-1.70	-9.74	-7.10	-9.71	-7.83	-6.17	0.00	-1.66	0.37
-4.97	-9.77	-5.38	-5.84	-5.89	-12.27	-1.71	-10.21	-7.34	-9.95	-8.06	-5.94	0.00	-1.66	0.37
-4.97	-9.98	-5.49	-5.73	-5.89	-12.47	-1.72	-10.43	-7.46	-10.07	-8.17	-5.83	0.00	-1.66	0.37
-4.97	-10.12	-5.55	-5.67	-5.89	-12.61	-1.73	-10.57	-7.53	-10.14	-8.23	-5.77	0.00	-1.66	0.37
-4.97	-10.21	-5.60	-5.62	-5.89	-12.70	-1.74	-10.68	-7.59	-10.20	-8.28	-5.72	0.00	-1.66	0.37
-4.97	-10.29	-5.64	-5.58	-5.89	-12.78	-1.74	-10.76	-7.63	-10.24	-8.32	-5.68	0.00	-1.66	0.37
-4.97	-10.35	-5.67	-5.55	-5.89	-12.84	-1.75	-10.83	-7.67	-10.28	-8.35	-5.65	0.00	-1.66	0.37
-4.97	-10.40	-5.69	-5.53	-5.89	-12.89	-1.76	-10.89	-7.70	-10.32	-8.37	-5.63	0.00	-1.66	0.37
-4.97	-10.44	-5.72	-5.51	-5.89	-12.93	-1.77	-10.94	-7.73	-10.34	-8.39	-5.61	0.00	-1.66	0.37
-4.97	-10.48	-5.73	-5.49	-5.89	-12.97	-1.78	-10.98	-7.76	-10.37	-8.41	-5.59	0.00	-1.66	0.37
-4.97	-10.51	-5.75	-5.47	-5.89	-13.00	-1.78	-11.02	-7.78	-10.40	-8.43	-5.57	0.00	-1.66	0.37
-4.97	-10.54	-5.76	-5.46	-5.89	-13.03	-1.79	-11.06	-7.81	-10.42	-8.44	-5.56	0.00	-1.66	0.37
-4.97	-10.56	-5.78	-5.44	-5.89	-13.05	-1.80	-11.09	-7.83	-10.44	-8.46	-5.54	0.00	-1.66	0.37
-4.97	-10.59	-5.79	-5.43	-5.89	-13.08	-1.81	-11.12	-7.85	-10.46	-8.47	-5.53	0.00	-1.66	0.37
-4.97	-10.61	-5.80	-5.42	-5.89	-13.10	-1.81	-11.15	-7.86	-10.47	-8.48	-5.52	0.00	-1.66	0.37
-4.97	-10.63	-5.81	-5.41	-5.89	-13.12	-1.82	-11.18	-7.88	-10.49	-8.49	-5.51	0.00	-1.66	0.37
-4.97	-10.65	-5.82	-5.40	-5.89	-13.14	-1.83	-11.20	-7.90	-10.51	-8.50	-5.50	0.00	-1.66	0.37
-4.97	-10.66	-5.83	-5.39	-5.89	-13.15	-1.83	-11.23	-7.91	-10.52	-8.51	-5.49	0.00	-1.66	0.37

$Pb(NO_3)_2 \rightarrow N$	aHCO3 - Clos	ed System (PHREE	QC-I Output)									
				log	log	log	log	log	log	log	log	log
% Pb(NO ₃) ₂	pH	∑Alk	[Pb ^{2*}] _{TOT}	(aPb ^{2*})	(aNO ₃)	(aPb(OH) ₂)	(aPb(OH),)	(aPb(OH) ₄ ⁻²)	(aPb,OH")	(aPbNO ₁ [*])	(aPbOH [*])	(aCO ₂)
Injected		meq	M	M	M	M	M	М	M	M	M	M
0.00	8.13	3.51E-02	2.46E-06	-9.39		-10.25	-13.06	-16.56	-17.01		-8.97	-4.62
2.86	7.64	3.22E-02	1.67E-06	-8.87	-2.79	-10.71	-14.01	-18.01	-16.46	-10.49	-8.94	-2.86
5.71	7.44	2.94E-02	1.54E-06	-8.63	-2.50	-10.87	-14.37	-18.56	-16.19	-9.96	-8.90	-2.70
8.57	7.25	2.68E-02	1.49E-06	-8.40	-2.33	-11.02	-14.71	-19.10	-15.92	-9.57	-8.86	-2.55
11.43	7.10	2.43E-02	1.49E-06	-8.21	-2.22	-11.13	-14.97	-19.51	-15.68	-9.26	-8.82	-2.44
14.29	6.97	2.19E-02	1.51E-06	-8.04	-2.13	-11.22	-15.19	-19.85	-15.47	-9.00	-8.78	-2.35
17.14	6.86	1.97E-02	1.55E-06	-7.88	-2.06	-11.28	-15.37	-20.15	-15.26	-8.77	-8.73	-2.29
20.00	6.75	1.75E-02	1.61E-06	-7.73	-2.01	-11.34	-15.53	-20.41	-15.06	-8.56	-8.68	-2.23
22.86	6.65	1.55E-02	1.68E-06	-7.57	-1.96	-11.39	-15.68	-20.66	-14.85	-8.36	-8.63	-2.18
25.71	6.55	1.36E-02	1.78E-06	 -7.42	-1.92	-11.43	-15.81	-20.90	-14.64	-8.16	-8.57	-2.14
28.57	6.46	1.17E-02	1.92E-06	-7.25	-1.88	-11.46	-15.95	-21.13	-14.41	-7.96	-8.51	-2.11
31.43	6.35	9.91E-03	2.12E-06	 -7.08	-1.85	-11.50	-16.08	-21.37	-14.17	-7.76	-8.44	-2.07
34.29	6.24	8.21E-03	2.40E-06	-6.89	-1.82	-11.52	-16.22	-21.62	-13.90	-7.54	-8.36	-2.05
37.14	6.12	6.58E-03	2.84E-06	 -6.67	-1.79	-11.55	-16.37	-21.89	-13.59	-7.30	-8.26	-2.02
40.00	5.98	5.02E-03	3.63E-06	 -6.42	-1.77	-11.57	-16.53	-22.19	-13.21	-7.01	-8.14	-2.00
42.86	5.81	3.52E-03	5.31E-06	-6.09	-1.75	-11.59	-16.73	-22.56	-12.73	-6.66	-7.99	-1.98
45.71	5.56	2.08E-03	1.05E-05	-5.61	-1.73	-11.61	-16.99	-23.07	-12.03	-6.17	-7.76	-1.96
48.57	5.12	7.78E-04	5.17E-05	-4.74	-1.71	-11.63	-17.45	-23.98	-10.72	-5.28	-7.33	-1.94
51.43	4.60	2.49E-04	4.55E-04	-3.72	-1.69	-11.63	-17.97	-25.00	-9.19	-4.24	-6.82	-1.94
54.29	4.42	1.70E-04	1.06E-03	-3.34	-1.68	-11.62	-18.14	-25.36	-8.62	-3.85	-6.63	-1.95
57.14	4.33	1.41E-04	1.66E-03	-3.15	-1.67	-11.62	-18.23	-25.54	-8.33	-3.65	-6.53	-1.95
60.00	4.27	1.26E-04	2.25E-03	 -3.02	-1.66	-11.61	-18.28	-25.66	-8.13	-3.51	-6.46	-1.96
62.86	4.22	1.16E-04	2.82E-03	 -2.92	-1.65	-11.60	-18.32	-25.74	-7.98	-3.40	-6.41	-1.97
65.71	4.19	1.10E-04	3.38E-03	 -2.85	-1.64	-11.59	-18.34	-25.80	-7.87	-3.32	-6.37	-1.98
68.57	4.16	1.05E-04	3.91E-03	 -2.79	-1.63	-11.58	-18.36	-25.84	-7.77	-3.25	-6.34	-1.99
71.43	4.14	1.01E-04	4.43E-03	-2.74	-1.62	-11.58	-18.38	-25.88	-7.70	-3.19	-6.31	-1.99
74.29	4.12	9.86E-05	4.93E-03	 -2.70	-1.62	-11.57	-18.39	-25.90	-7.63	-3.14	-6.28	-2.00
77.14	4.11	9.62E-05	5.42E-03	-2.66	-1.61	-11.56	-18.39	-25.93	-7.57	-3.10	-6.26	-2.01
80.00	4.10	9.43E-05	5.89E-03	 -2.63	-1.60	-11.56	-18.40	-25.95	-7.52	-3.06	-6.24	-2.01
82.86	4.08	9.26E-05	6.34E-03	 -2.60	-1.60	-11.55	-18.40	-25.96	-7.47	-3.02	-6.22	-2.02
85.71	4.07	9.12E-05	6.78E-03	-2.57	-1.59	-11.54	-18.41	-25.97	-7.43	-2.99	-6.21	-2.03
88.57	4.07	8.99E-05	7.21E-03	-2.55	-1.58	-11.54	-18.41	-25.98	-7.39	-2.96	-6.19	-2.04
91.43	4.06	8.88E-05	7.62E-03	-2.52	-1.58	-11.53	-18.41	-25.99	-7.35	-2.93	-6.18	-2.04
94.29	4.05	8.78E-05	8.03E-03	-2.51	-1.57	-11.52	-18.41	-26.00	-7.32	-2.91	-6.16	-2.05
97.14	4.05	8.69E-05	8.42E-03	-2.49	-1.57	-11.52	-18.41	-26.00	-7.29	-2.88	-6.15	-2.05
100.00	4.04	8.61E-05	8.80E-03	-2.47	-1.56	-11.51	-18.41	-26.01	-7.26	-2.86	-6.14	-2.06

		200											
log	log	log	log	102	log	102	log	log	log	log	SI	SI	ST
(aCO ₃ ⁻²)	(aHCO ₁)	(aPbHCO, [*])	(aPbCO ₁)	(aPb(CO ₁), ²)	(aNa ⁺)	(aNaCO ₁)	(aNaHCO ₁)	(aNaOH)	(aOH)	(aH)	Ce	Hc	(Pb(OH))
M	M	M	M	M	М	M	M	M	М	М			1
-3.74	-1.54	-8.03	-5.89	-6.23	-1.54	-4.01	-3.33	-7.58	-5.87	-8.13	0.00	-3.31	-1.28
-4.26	-1.57	-7.54	-5.89	-6.75	-1.55	-4.54	-3.37	-8.09	-6.36	-7.64	0.00	-3.77	-1.74
-4.50	-1.61	-7.34	-5.89	-6.99	-1.56	-4.78	-3.42	-8.29	-6.56	-7.44	0.00	-3.93	-1.90
-4.73	-1.65	-7.15	-5.89	-7.22	-1.57	-5.02	-3.47	-8.50	-6.75	-7.25	0.00	-4.08	-2.05
-4.92	-1.69	-7.00	-5.89	-7.41	-1.58	-5.23	-3.52	-8.66	-6.90	-7.10	0.00	-4.19	-2.16
-5.09	-1.73	-6.87	-5.89	-7.58	-1.59	-5.41	-3.57	-8.79	-7.03	-6.97	0.00	-4.28	-2.25
-5.25	-1.78	-6.76	-5.89	-7.74	-1.60	-5.58	-3.63	-8.92	-7.14	-6.86	0.00	-4.34	-2.31
-5.40	-1.83	-6.65	-5.89	-7.89	-1.61	-5.74	-3.68	-9.03	-7.25	-6.75	0.00	-4.40	-2.37
-5.56	-1.88	-6.55	-5.89	-8.05	-1.62	-5.90	-3.75	-9.14	-7.35	-6.65	0.00	-4.45	-2.42
	-1.94	-6.46	-5.89	-8.20	-1.62	-6.07	-3.81	-9.25	-7.45	-6.55	0.00	-4.49	-2.46
-5.88	-2.00	-6.36	-5.89	-8.37	-1.63	-6.24	-3.89	-9.36	-7.54	-6.46	0.00	-4.52	-2.49
-6.05	-2.07	-6.25	-5.89	-8.54	-1.64	-6.42	-3.97	-9.47	-7.65	-6.35	0.00	-4.56	-2.53
-6.24	-2.15	-6.14	-5.89	-8.73	-1.65	-6.62	-4.05	-9.59	-7.76	-6.24	0.00	-4.58	-2.55
-6.46	-2.25	-6.02	-5.89	-8.95	-1.66	-6.85	-4.16	-9.72	-7.88	-6.12	0.00	-4.61	-2.58
-6.71	-2.37	-5.88	-5.89	-9.20	-1.67	-7.11	-4.28	-9.87	-8.02	-5.98	0.00	-4.63	-2.60
-7.04	-2.52	-5.71	-5.89	-9.53	-1.68	-7.45	-4.45	-10.05	-8.19	-5.81	0.00	-4.65	-2.62
-7.52	-2.75	-5.46	-5.89	-10.01	-1.68	-7.93	-4.68	-10.30	-8.44	-5.56	0.00	-4.67	-2.64
-8.39	-3.18	-5.02	-5.89	-10.88	1.69	-8.81	-5.12	-10.76	-8.88	-5.12	0.00	-4.69	-2.66
-9.41	-3.69	-4.50	-5.89	-11.90	-1.70	-9.84	-5.64	-11.28	-9.40	-4.60	0.00	-4.69	-2.66
-9.79	-3.88	-4.32	-5.89	-12.28	-1.71	-10.23	-5.84	-11.47	-9.58	-4.42	0.00	-4.68	-2.65
-9.98	-3.98	-4.23	-5.89	-12.47	-1.72	-10.43	-5.95	-11.57	-9.67	-4.33	0.00	-4.67	-2.64
-10.11	-4.05	-4.17	-5.89	-12.60	-1.73	-10.57	-6.03	-11.64	-9.73	-4.27	0.00	-4.67	-2.64
-10.21	-4.10	-4.12	-5.89	-12.70	-1.74	-10.67	-6.09	-11.69	-9.78	-4.22	0.00	-4.66	-2.63
-10.28	-4.14	-4.09	-5.89	-12.77	-1./4	-10.76	-6.14	-11.74	-9.81	-4.19	0.00	-4.65	-2.62
-10.34	-4.18	-4.06	-5.89	-12.83	-1.75	-10.82	-6.18	-11.77	-9.84	-4.16	0.00	-4.64	-2.61
-10.39	-4.20	-4.04	-3.89	-12.88	-1./0	-10.88	-6.22	-11.80	-9.86	-4.14	0.00	-4.64	-2.61
-10.44	4.23	-4.02	-5.89	-12.93	<u>-1.//</u>	-10.93	-6.25	-11.83	-9.88	-4.12	0.00	-4.63	-2.60
-10.47	4.23	-4.01	-3.89	-12.90	-1./8	-10.98	-6.28	-11.85	-9.89	-4.11	0.00	-4.62	-2.59
-10.51	-4.27	-4.00	-5.89	-13.00	-1.78	-11.02	-0.31	-11.8/	-9.90	-4.10	0.00	-4.61	-2.59
-10.55	4.27	-5.99	-3.89	-13.02	-1./9	-11.00	-0.33	-11.89	-9.92	-4.08	0.00	-4.01	-2.58
-10.50	4.32	-5.98	-5.89	-13.03	-1.80	-11.09	-0.30	-11.91	-9.93	-4.07	0.00	-4.60	-2.57
-10.58	-4.32	-3.97	-5.89	-13.07	-1.81	11.12	-0.38	-11.92	-9.93	-4.07	0.00	-4.39	-2.30
-10.63	-4.35	-3.95	-5.89	-13.10	-1.01	-11.13	-0.40	-11.94	-9.94	-4.00	0.00	-4.39	-2.30
-10.64	-4.35	-3.95	-5.89	-13.12	-1.02	-11.10	-0.42	-11.93	-9.93	-4.05	0.00	-4.38	-2.33
-10.64	_4 37	-3.95	-5.89	-13.15	-1.03	-11.20	-0.44	-11.90	-9.93	-4.05	0.00	-4.3/	-2.55
-10.00		-3.74	-3.07	-13.13	L -1.03	-11.22	-0.40	-11.97	-9.90	-4.04	0.00	-4.37	-2.34

$NaHCO_1 \rightarrow PI$	b(NO ₃) ₂ - Oper	System (PHREE)	QC-I Output)				200					
				log	log	log	log	log	log	log	log	log
% NaHCO3	pH	ΣAlk	[Pb ^{**}] _{TOT}	(aPb ^{2*})	(aNO ₃)	(aPb(OH)2)	(aPb(OH),)	(aPb(OH)4)	(aPb ₂ OH ^{3*})	(aPbNO ₃)	(aPbOH')	(aCO ₂)
Injected		meq	M	M	M	M	M	M	M	M	М	M
0.00	5.26	1.19E-04	3.54E-02	 -1.99	-1.33	-8.60	-14.29	-20.67	-5.09	-2.15	-4.45	-4.97
2.86	5.26	1.14E-04	3.39E-02	 -2.01	-1.34	-8.60	-14.28	-20.66	-5.11	-2.17	-4.45	-4.97
5.71	5.27	1.10E-04	3.25E-02	-2.02	-1.35	-8.60	-14.27	-20.64	-5.13	-2.20	-4.46	-4.97
8.57	5.28	1.05E-04	3.11E-02	 -2.03	-1.35	-8.60	-14.27	-20.63	-5.15	-2.22	-4.47	-4.97
11.43	5.28	1.01E-04	2.99E-02	-2.05	-1.36	-8.60	-14.26	-20.62	-5.17	-2.24	-4.47	-4.97
14.29	5.29	9.70E-05	2.87E-02	-2.06	-1.37	-8.60	-14.25	-20.61	-5.19	-2.26	-4.48	-4.97
17.14	5.30	9.34E-05	2.75E-02	2.07	-1.38	-8.60	-14.25	-20.59	-5.21	-2.28	-4.49	-4.97
20.00	5.30	8.99E-05	2.64E-02	-2.09	-1.39	-8.60	-14.24	-20.58	-5.23	-2.30	-4.49	-4.97
22.86	5.31	8.66E-05	2.54E-02	-2.10	-1.40	-8.60	-14.23	-20.57	-5.25	-2.32	-4.50	-4.97
25.71	5.31	8.35E-05	2.44E-02	-2.11	-1.40	-8.60	-14.23	-20.55	-5.27	-2.35	-4.51	-4.97
28.57	5.32	8.06E-05	2.35E-02	-2.12	-1.41	-8.60	-14.22	-20.54	-5.29	-2.37	-4.51	-4.97
31.43	5.33	7.78E-05	2.26E-02	-2.14	-1.42	-8.60	-14.22	-20.53	-5.31	-2.39	-4.52	-4.97
34.29	5.33	7.52E-05	2.17E-02	-2.15	-1.43	-8.60	-14.21	-20.52	-5.32	-2.41	-4.53	-4.97
37.14	5.34	7.27E-05	2.09E-02	-2.16	-1.43	-8.60	-14.20	-20.50	-5.34	-2.43	-4.53	-4.97
40.00	5.35	7.03E-05	2.01E-02	-2.17	-1.44	-8.60	-14.20	-20.49	-5.36	-2.45	-4.54	-4.97
42.86	5.35	6.81E-05	1.94E-02	-2.19	-1.45	-8.60	-14.19	-20.48	-5.38	-2.47	-4.54	-4.97
45.71	5.36	6.59E-05	1.86E-02	-2.20	-1.45	-8.60	-14.18	-20.46	-5.40	-2.48	-4.55	-4.97
48.57	5.37	6.39E-05	1.79E-02	-2.21	-1.46	-8.60	-14.18	-20.45	-5.42	-2.50	-4.56	-4.97
51.43	5.37	6.19E-05	1.73E-02	-2.23	-1.47	-8.60	-14.17	-20.44	-5.44	-2.52	-4.56	-4.97
54.29	5.38	6.01E-05	1.66E-02	-2.24	-1.47	-8.60	-14.16	-20.43	-5.46	-2.54	-4.57	-4.97
57.14	5.39	5.83E-05	1.60E-02	-2.25	-1.48	-8.60	-14.16	-20.41	-5.48	-2.56	-4.58	-4.97
60.00	5.39	5.66E-05	1.54E-02	-2.27	-1.49	-8.60	-14.15	-20.40	-5.50	-2.58	-4.58	-4.97
62.86	5.40	5.49E-05	1.48E-02	-2.28	-1.49	-8.60	-14.14	-20.39	-5.52	-2.60	-4.59	-4.97
65.71	5.41	5.34E-05	1.42E-02	-2.29	-1.50	-8.60	-14.14	-20.37	-5.54	-2.62	-4.60	-4.97
68.57	5.41	5.19E-05	1.37E-02	-2.31	-1.50	-8.60	-14.13	-20.36	-5.56	-2.64	-4.60	-4.97
71.43	5.42	5.04E-05	1.32E-02	-2.32	-1.51	-8.60	-14.12	-20.34	-5.58	-2.66	-4.61	-4.97
74.29	5.43	4.90E-05	1.27E-02	-2.33	-1.52	-8.60	-14.12	-20.33	-5.60	-2.68	-4.62	-4.97
77.14	5.43	4.77E-05	1.22E-02	-2.35	-1.52	-8.60	-14.11	-20.32	-5.62	-2.70	-4.62	-4.97
80.00	5.44	4.64E-05	1.17E-02	-2.36	-1.53	-8.60	-14.10	-20.30	-5.64	-2.72	-4.63	-4.97
82.86	5.45	4.51E-05	1.12E-02	 -2.38	-1.53	-8.60	-14.10	-20.29	-5.67	-2.74	-4.64	-4.97
85.71	5.45	4.39E-05	1.08E-02	-2.39	-1.54	-8.60	-14.09	-20.27	-5.69	-2.76	-4.65	-4.97
88.57	5.46	4.27E-05	1.04E-02	-2.41	-1.54	-8.60	-14.08	-20.26	-5.71	-2.78	-4.65	-4.97
91.43	5.47	4.16E-05	9.96E-03	-2.42	-1.55	-8.60	-14.07	-20.24	-5.73	-2.80	-4.66	-4.97
94.29	5.48	4.05E-05	9.55E-03	-2.44	-1.55	-8.60	-14.07	-20.23	-5.75	-2.82	-4.67	-4.97
97.14	5.49	3.94E-05	9.16E-03	-2.45	-1.56	-8.60	-14.06	-20.21	-5.78	-2.84	-4.68	-4.97
100.00	5.49	3.84E-05	8.78E-03	-2.47	-1.56	-8.60	-14.05	-20.20	-5.80	-2.86	-4.68	-4.97

									in the second				-
log	log	log	log	log	log	log	log	log	log	lag	SI	SI	SI
(aCO ₁ ²)	(aHCO ₃)	(aPbHCO,)	(aPbCO ₃)	(aPb(CO ₁), ²)	(aNa')	(aNaCO ₁)	(aNaHCO ₁)	(aNaOH)	(aOH)	(aH)	Ce	Hc	(Pb(OH) ₂₀)
M	M	M	M	М	M	M	M	M	M	M			<u>да ад се се удар</u>
-11.14	-6.06	-5.16	-5.89	-13.63					-8.74	-5.26	0.00	-1.66	0.37
-11.12	-6.06	-5.16	-5.89	-13.61	-3.11	-12.96	-9.42	-12.03	-8.74	-5.26	0.00	-1.66	0.37
-11.11	-6.05	-5.17	-5.89	-13.60	-2.82	-12.66	-9.12	-11.73	-8.73	-5.27	0.00	-1.66	0.37
-11.10	-6.04	-5.18	-5.89	-13.59	-2.65	-12.48	-8.95	-11.56	-8.72	-5.28	0.00	-1.66	0.37
-11.08	-6.04	-5.18	-5.89	-13.57	-2.54	-12.35	-8.83	-11.44	-8.72	-5.28	0.00	-1.66	0.37
-11.07	-6.03	-5.19	-5.89	-13.56	-2.45	-12.25	-8.74	-11.35	-8.71	-5.29	0.00	-1.66	0.37
-11.06	-6.02	-5.20	-5.89	-13.55	-2.38	-12.17	-8.66	-11.27	-8.70	-5.30	0.00	-1.66	0.37
-11.05	-6.02	-5.20	-5.89	-13.54	-2.33	-12.10	-8.60	-11.21	-8.70	-5.30	0.00	-1.66	0.37
-11.03	-6.01	-5.21	-5.89	-13.52	-2.28	-12.04	-8.54	-11.15	-8.69	-5.31	0.00	-1.66	0.37
-11.02	-6.01	-5.22	-5.89	-13.51	-2.24	-11.99	-8.49	-11.10	-8.69	-5.31	0.00	-1.66	0.37
-11.01	-6.00	-5.22	-5.89	-13.50	-2.20	-11.94	-8.45	-11.06	-8.68	-5.32	0.00	-1.66	0.37
-10.99	-5.99	-5.23	-5.89	-13.48	-2.17	-11.89	-8.41	-11.02	-8.67	-5.33	0.00	-1.66	0.37
-10.98	-5.99	-5.24	-5.89	-13.47	-2.14	-11.85	-8.38	-10.99	-8.67	-5.33	0.00	-1.66	0.37
-10.97	-5.98	-5.24	-5.89	-13.46	-2.11	-11.81	-8.34	-10.95	-8.66	-5.34	0.00	-1.66	0.37
-10.96	-5.97	-5.25	-5.89	-13.45	-2.09	-11.77	-8.31	-10.92	-8.65	-5.35	0.00	-1.66	0.37
-10.94	-5.97	-5.25	-5.89	-13.43	-2.07	-11.74	-8.28	-10.89	-8.65	-5.35	0.00	-1.66	0.37
-10.93	-5.96	-5.26	-5.89	-13.42	-2.05	-11.71	-8.26	-10.87	-8.64	-5.36	0.00	-1.66	0.37
-10.92	-5.95	-5.27	-5.89	-13.41	-2.03	-11.68	-8.23	-10.84	-8.63	-5.37	0.00	-1.66	0.37
-10.90	-5.95	-5.27	-5.89	-13.39	-2.01	-11.65	-8.21	-10.82	-8.63	-5.37	0.00	-1.66	0.37
-10.89	-5.94	-5.28	-5.89	-13.38	-2.00	-11.62	-8.19	-10.80	-8.62	-5.38	0.00	-1.66	0.37
-10.88	-5.93	-5.29	-5.89	-13.37	-1.98	-11.59	-8.17	-10.78	-8.61	-5.39	0.00	-1.66	0.37
-10.86	-5.93	-5.29	-5.89	-13.35	-1.97	-11.56	-8.14	-10.76	-8.61	-5.39	0.00	-1.66	0.37
-10.85	-5.92	-5.30	-5.89	-13.34	-1.95	-11.54	-8.12	-10.74	-8.60	-5.40	0.00	-1.66	0.37
-10.84	-5.91	-5.31	-5.89	-13.33	-1.94	-11.51	-8.11	-10.72	-8.59	-5.41	0.00	-1.66	0.37
-10.82	-5.91	-5.31	-5.89	-13.31	-1.93	-11.48	-8.09	-10.70	-8.59	-5.41	0.00	-1.66	0.37
-10.81	-5.90	-5.32	-5.89	-13.30	-1.92	-11.46	-8.07	-10.68	-8.58	-5.42	0.00	-1.66	0.37
-10.80	-5.89	-5.33	-5.89	-13.29	-1.91	-11.44	-8.05	-10.66	-8.57	-5.43	0.00	-1.66	0.37
-10.78	-5.89	-5.33	-5.89	-13.27	-1.90	-11.41	-8.04	-10.65	-8.57	-5.43	0.00	-1.66	0.37
-10.77	-5.88	-5.34	-5.89	-13.26	-1.89	-11.39	-8.02	-10.63	-8.56	-5.44	0.00	-1.66	0.37
-10.75	-5.87	-5.35	-5.89	-13.24	-1.88	-11.36	-8.00	-10.61	-8.55	-5.45	0.00	-1.66	0.37
-10.74	-5.87	-5.36	-5.89	-13.23	-1.87	11.34	-7.99	-10.60	-8.55	-5.45	0.00	-1.66	0.37
-10.73	-5.86	-5.36	-5.89	-13.22	-1.86	-11.32	-7.97	-10.58	-8.54	-5.46	0.00	-1.66	0.37
-10.71	-5.85	-5.37	-5.89	-13.20	-1.86	-11.30	-7.96	-10.57	-8.53	-5.47	0.00	-1.66	0.37
-10.69	-5.84	-5.38	-5.89	-13.18	-1.85		-7.94	-10.55	-8.52	-5.48	0.00	-1.66	0.37
-10.68	-5.84	-5.39	-5.89	-13.17	-1.84	-11.25	-7.93	-10.54	-8.51	-5.49	0.00	-1.66	0.37
-10.66	i -5.83	-5.39	-5.89	-13.15	-1.83	-11.23	-7.91	-10.52	-8.51	-549	I 0.00	-166	037 1

$NaHCO_3 \rightarrow Pl$	b(NO ₃) ₂ - Clos	ed System PHREE	QC-I Output)									
				log	log	log	log	log	log	log	log	log
% NaHCO3	pH	∑Alk	[Pb ^{**}] _{TOT}	(aPb ^{2*})	(aNO ₃)	(aPb(OH))	(aPb(OH),)	(aPb(OH),2)	(aPb,OH")	(aPbNO ₁)	(aPbOH)	(aCO ₃)
Injected		meq	M	M	M	M	М	M	M	М	М	M
0.00	5.07	8.24E-05	3.53E-02	-1.99	-1.33	-8.97	-14.83	-21.40	-5.27	-2.15	-4.63	-4.60
2.86	4.61	4.12E-05	3.38E-02	-2.01	-1.34	-9.91	-16.24	-23.27	-5.76	-2.17	-5.11	-3.66
5.71	4.31	4.30E-05	3.24E-02	-2.02	-1.35	-10.53	-17.16	-24.49	-6.09	-2.20	-5.42	-3.05
8.57	4.23	4.66E-05	3.11E-02	-2.03	-1.35	-10.69	-17.41	-24.82	-6.20	-2.22	-5.51	-2.88
11.43	4.18	4.99E-05	2.98E-02	-2.05	-1.36	-10.81	-17.57	-25.04	-6.27	-2.24	-5.58	-2.76
14.29	4.14	5.28E-05	2.86E-02	-2.06	-1.37	-10.90	-17.70	-25.20	-6.34	-2.26	-5.63	-2.67
17.14	4.11	5.54E-05	2.75E-02	-2.07	-1.38	-10.97	-17.80	-25.33	-6.39	-2.28	-5.67	-2.60
20.00	4.09	5.78E-05	2.64E-02	-2.09	-1.39	-11.03	-17.88	-25.43	-6.44	-2.30	-5.71	-2.54
22.86	4.07	5.99E-05	2.54E-02	-2.10	-1.40	-11.08	-17.94	-25.51	-6.48	-2.32	-5.74	-2.50
25.71	4.06	6.18E-05	2.44E-02	-2.11	-1.40	-11.12	-18.00	-25.58	-6.52	-2.35	-5.76	-2.45
28.57	4.05	6.35E-05	2.35E-02	-2.12	-1.41	-11.15	-18.05	-25.64	-6.56	-2.37	-5.79	-2.42
31.43	4.04	6.50E-05	2.26E-02	-2.14	-1.42	-11.19	-18.09	-25.69	-6.60	-2.39	-5.81	-2.38
34.29	4.03	6.65E-05	2.17E-02	-2.15	-1.43	-11.21	-18.13	-25.74	-6.63	-2.41	-5.83	-2.36
37.14	4.02	6.78E-05	2.09E-02	-2.16	-1.43	-11.24	-18.16	-25.78	-6.66	-2.43	-5.85	-2.33
40.00	4.02	6.90E-05	2.01E-02	-2.18	-1.44	-11.26	-18.19	-25.81	-6.70	-2.45	-5.87	-2.31
42.86	4.01	7.02E-05	1.94E-02	-2.19	-1.45	-11.29	-18.21	-25.84	-6.73	-2.47	-5.89	-2.28
45.71	4.01	7.12E-05	1.86E-02	-2.20	-1.45	-11.31	-18.24	-25.87	-6.75	-2.49	-5.90	-2.26
48.57	4.01	7.23E-05	1.79E-02	-2.21	-1.46	-11.32	-18.26	-25.89	-6.78	-2.51	-5.92	-2.25
51.43	4.00	7.32E-05	1.73E-02	-2.23	-1.47	-11.34	-18.28	-25.91	-6.81	-2.53	-5.93	-2.23
54.29	4.00	7.41E-05	1.66E-02	-2.24	-1.47	-11.36	-18.29	-25.93	-6.84	-2.54	-5.95	-2.21
57.14	4.00	7.50E-05	1.60E-02	-2.25	-1.48	-11.37	-18.31	-25.95	-6.87	-2.56	-5.96	-2.20
60.00	4.00	7.58E-05	1.54E-02	-2.27	-1.49	-11.38	-18.32	-25.96	-6.89	-2.58	-5.98	-2.19
62.86	4.00	7.66E-05	1.48E-02	-2.28	-1.49	-11.40	-18.33	-25.97	-6.92	-2.60	-5.99	-2.17
65.71	4.00	7.74E-05	1.43E-02	-2.29	-1.50	-11.41	-18.34	-25.98	-6.95	-2.62	-6.00	-2.16
68.57	4.01	7.81E-05	1.37E-02	-2.31	-1.50	-11.42	-18.35	-25.99	-6.97	-2.64	-6.01	-2.15
71.43	4.01	7.89E-05	1.32E-02	-2.32	-1.51	-11.43	-18.36	-26.00	-7.00	-2.66	-6.03	-2.14
74.29	4.01	7.96E-05	1.27E-02	-2.34	-1.52	-11.44	-18.37	-26.00	-7.02	-2.68	-6.04	-2.13
77.14	4.01	8.03E-05	1.22E-02	-2.35	-1.52	-11.45	-18.38	-26.01	-7.05	-2.70	-6.05	-2.12
80.00	4.01	8.10E-05	1.17E-02	-2.36	-1.53	-11.46	-18.38	-26.01	-7.08	-2.72	-6.06	-2.11
82.86	4.02	8.17E-05	1.13E-02	-2.38	-1.53	-11.47	-18.39	-26.01	-7.10	-2.74	-6.07	-2.10
85.71	4.02	8.24E-05	1.08E-02	-2.39	-1.54	-11.47	-18.39	-26.01	-7.13	-2.76	-6.08	-2.10
88.57	4.02	8.32E-05	1.04E-02	-2.41	-1.54	11.48	-18.40	-26.02	-7.15	-2.78	-6.10	-2.09
91.43	4.03	8.39E-05	9.98E-03	-2.42	-1.55	-11.49	-18.40	-26.01	-7.18	-2.80	-6.11	-2.08
94.29	4.01	8.89E-05	9.57E-03	-2.44	-1.55	-11.54	-18.47	-26.10	-7.23	-2.82	-6.14	-2.03
97.14	4.04	8.54E-05	9.18E-03	-2.45	-1.56	-11.50	-18.41	-26.01	-7.23	-2.84	-6.13	-2.07
100.00	4.04	8.61E-05	8.80E-03	-2.47	-1.56	-11.51	-18.41	-26.01	-7.26	-2.86	-6.14	-2.06

100				3									
log	log	log	log	log	log	log	log	log	log	log	SI	SI	SI
(aCO ₃ ²)	(aHCO ₁)	(aPbHCO ₃ [*])	(aPbCO ₃)	(aPb(CO ₃) ₂ ²)	(aNa ⁺)	(aNaCO ₃)	(aNaHCO ₂)	(aNaOH)	(aOH)	(aH')	Ce	Hc	(Pb(OH) ₂₍₀)
M	M	M	M	M	M	M	M	M	M	M	2.00		1
-11.14	-5.88	-4.98	-5.89	-13.63					-8.93	-5.07	0.00	-2.02	0.00
-11.12	-5.41	-4.51	-5.89	-13.61	-3.11	-12.96	-8.77	-12.68	-9.39	-4.61	0.00	-2.97	-0.94
-11.11	-5.09	-4.21	-5.89	-13.60	-2.82	-12.66	-8.16	-12.69	-9.69	-4.31	0.00	-3.58	-1.55
-11.10	-5.00	-4.13	-5.89	-13.59	-2.65	-12.48	-7.90	-12.61	-9.77	-4.23	0.00	-3.75	-1.72
-11.08	-4.93	-4.08	-5.89	-13.57	-2.54	-12.35	-7.72	-12.54	-9.82	-4.18	0.00	-3.87	-1.84
-11.07	-4.88	-4.04	-5.89	-13.56	-2.45	-12.26	-7.59	-12.49	-9.86	-4.14	0.00	-3.96	-1.93
-11.06	-4.84	-4.01	-5.89	-13.55	-2.38	-12.17	-7.48	-12.45	-9.89	-4.11	0.00	-4.03	-2.00
-11.05	-4.81	-3.99	-5.89	-13.54	-2.33	-12.10	-7.38	-12.42	-9.91	-4.09	0.00	-4.09	-2.06
-11.03	-4.78	-3.97	-5.89	-13.52	-2.28	-12.04	-7.30	-12.39	-9.93	-4.07	0.00	-4.13	-2.10
-11.02	-4.75	-3.96	-5.89	-13.51	-2.24	-11.99	-7.24	-12.36	-9.94	-4.06	0.00	-4.18	-2.15
-11.01	-4.72	-3.95	-5.89	-13.50	-2.20	11.94	-7.17	-12.34	-9.95	-4.05	0.00	-4.21	-2.18
-10.99	-4.70	-3.94	-5.89	-13.48	-2.17	-11.89	-7.12	-12.31	-9.96	-4.04	0.00	-4.24	-2.22
-10.98	-4.68	-3.93	-5.89	-13.47	-2.14	-11.85	-7.07	-12.29	-9.97	-4.03	0.00	-4.27	-2.24
-10.97	-4.66	-3.92	-5.89	-13.46	-2.11	-11.81	-7.02	-12.27	-9.98	-4.02	0.00	-4.30	-2.27
-10.95	-4.64	-3.92	-5.89	-13.44	-2.09	-11.77	-6.98	-12.25	-9.98	-4.02	0.00	-4.32	-2.29
-10.94	-4.62	-3.91	-5.89	-13.43	-2.07	-11.74	-6.94	-12.24	-9.99	-4.01	0.00	-4.34	-2.32
-10.93	-4.61	-3.91	-5.89	-13.42	-2.05	-11.71	-6.91	-12.22	-9.99	-4.01	0.00	-4.36	-2.34
-10.92	-4.59	-3.91	-5.89	-13.41	-2.03	-11.67	-6.87	-12.20	-9.99	-4.01	0.00	-4.38	-2.35
-10.90	4.58	-3.91	-5.89	-13.39	-2.01	-11.64	-6.84	-12.19	-10.00	-4.00	0.00	-4.40	-2.37
-10.89	-4.56	-3.90	-5.89	-13.38	-2.00	-11.62	-6.81	-12.17	-10.00	-4.00	0.00	-4.41	-2.39
-10.88	-4.55	-3.90	-5.89	-13.37	-1.98	-11.59	-6.78	-12.16	-10.00	-4.00	0.00	-4.43	-2.40
-10.86	-4.54	-3.90	-5.89	-13.35	-1.97	-11.56	-6.75	-12.14	-10.00	-4.00	0.00	-4.44	-2.41
-10.85	-4.52	-3.90	-5.89	-13.34	-1.95	-11.53	-6.73	-12.13	-10.00	-4.00	0.00	-4.45	-2.43
-10.84	-4.51	-3.91	-5.89	-13.33	-1.94	-11.51	-6.70	-12.12	-10.00	-4.00	0.00	-4.47	-2.44
-10.82	-4.50	3.91	-5.89	-13.31	-1.93	-11.48	-6.68	-12.11	-9.99	-4.01	0.00	-4.48	-2.45
-10.81	-4.49	-3.91	-5.89	-13.30	-1.92	-11.46	-6.65	-12.09	-9.99	-4.01	0.00	-4.49	-2.46
-10.79	-4.47	-3.91	-5.89	-13.28	-1.91	-11.43	-6.63	-12.08	-9.99	-4.01	0.00	-4.50	-2.47
-10.78	-4.46	-3.91	5.89	-13.27	-1.90	-11.41	-6.61	-12.07	-9.99	-4.01	0.00	-4.51	-2.48
-10.77	-4.45	-3.92	-5.89	-13.26	-1.89	-11.39	-6.59	-12.06	-9.99	-4.01	0.00	-4.52	-2.49
-10.75	-4.44	-3.92	-5.89	-13.24	-1.88	-11.36	-6.57	-12.04	-9.98	-4.02	0.00	-4.52	-2.50
-10.74	-4.43	-3.92	-5.89	-13.23	-1.87	-11.34	-6.55	-12.03	-9.98	-4.02	0.00	-4.53	-2.50
-10.72	-4.42	3.93	-5.89	-13.21	-1.86	-11.32	-6.53	-12.02	-9.98	-4.02	0.00	-4.54	-2.51
-10.71	-4.41	-3.93	-5.89	-13.20	-1.86	-11.29	-6.51	-12.01	-9.97	-4.03	0.00	-4.55	-2.52
-10.69	-4.37	-3.91	-5.89	-13.18	-1.85	-11.27	-6.47	-12.02	-9.99	-4.01	0.00	-4.60	-2.57
-10.68	4.38	-3.94	-5.89	-13.17	-1.84	-11.25	-6.47	-11.99	-9.96	-4.04	0.00	-4.56	-2.53
-10.66	-4.37	-3.94	-5.89	-13.15	-1.83	-11.22	-6.46	-11.97	-9.96	-4.04	0.00	-4 57	-2 54

$Na_2CO_3 \rightarrow Pbb$	(NO ₃) ₂ - Open	System (PHREEQ	C-I Output)									
10				log	log	log	log	log	log	log	log	log
% Na ₂ CO ₃	рН	ΣAlk	[Pb ²⁺] _{TOT}	(aPb ^{2*})	(aNO ₃)	(aPb(OH) ₂)	(aPb(OH) ₁)	(aPb(OH),')	(aPb ₂ OH ^{2*})	(aPbNO ₃ ⁺)	(aPbOH [*])	(aCO ₃)
Injected		meq	M	- M	M	M	M	M	M	М	M	М
0.00	5.26	1.19E-04	3.54E-02	-1.99	-1.33	-8.60	-14.29	-20.67	-5.09	-2.15	-4.45	-4.97
2.86	5.27	1.13E-04	3.34E-02	-2.01	-1.34	-8.60	-14.28	-20.65	-5.12	-2.18	-4.46	-4.97
5.71	5.28	1.06E-04	3.15E-02	-2.03	-1.34	-8.60	-14.27	-20.63	-5.15	-2.21	-4.47	-4.97
8.57	5.29	1.00E-04	2.97E-02	-2.05	-1.35	-8.60	-14.26	-20.61	-5.18	-2.24	-4.48	-4.97
11.43	5.30	9.46E-05	2.81E-02	-2.07	-1.36	-8.60	-14.25	-20.59	-5.21	-2.26	-4.49	-4.97
14.29	5.31	8.94E-05	2.65E-02	-2.09	-1.37	-8.60	-14.24	-20.57	-5.24	-2.29	-4.50	-4.97
17.14	5.32	8.45E-05	2.50E-02	-2.11	-1.38	-8.60	-14.23	-20.55	-5.27	-2.32	-4.51	-4.97
20.00	5.33	8.00E-05	2.35E-02	-2.14	-1.38	-8.60	-14.22	-20.53	-5.30	-2.35	-4.52	-4.97
22.86	5.34	7.57E-05	2.21E-02	-2.16	-1.39	-8.60	-14.21	-20.51	-5.34	-2.38	-4.53	-4.97
25.71	5.35	7.17E-05	2.08E-02	-2.18	-1.40	-8.60	-14.19	-20.49	-5.37	-2.41	-4.54	-4.97
28.57	5.36	6.79E-05	1.96E-02	-2.20	-1.40	-8.60	-14.18	-20.46	-5.40	-2.43	-4.55	-4.97
31.43	5.37	6.44E-05	1.84E-02	-2.22	-1.41	-8.60	-14.17	-20.44	-5.44	-2.46	-4.56	-4.97
34.29	5.38	6.11E-05	1.72E-02	-2.25	-1.42	-8.60	-14.16	-20.42	-5.47	-2.49	-4.57	-4.97
37.14	5.40	5.79E-05	1.61E-02	-2.27	-1.42	-8.60	-14.15	-20.39	-5.51	-2.52	-4.59	-4.97
40.00	5.41	5.49E-05	1.51E-02	-2.30	-1.43	-8.60	-14.14	-20.37	-5.55	-2.56	-4.60	-4.97
42.86	5.42	5.21E-05	1.41E-02	-2.32	-1.44	-8.60	-14.12	-20.34	-5.58	-2.59	-4.61	-4.97
45.71	5.43	4.94E-05	1.31E-02	-2.35	-1.44	-8.60	-14.11	-20.31	-5.63	-2.62	-4.63	-4.97
48.57	5.45	4.68E-05	1.22E-02	-2.38	-1.45	-8.60	-14.09	-20.29	-5.67	-2.65	-4.64	-4.97
51.43	5.46	4.44E-05	1.13E-02	-2.41	-1.45	-8.60	-14.08	-20.26	-5.71	-2.69	-4.65	-4.97
54.29	5.48	4.20E-05	1.04E-02	-2.44	-1.46	-8.60	-14.06	-20.23	-5.76	-2.73	-4.67	-4.97
57.14	5.49	3.98E-05	9.60E-03	-2.47	-1.46	-8.60	-14.05	-20.19	-5.81	-2.76	-4.69	-4.97
60.00	5.51	3.77E-05	8.80E-03	-2.50	-1.47	-8.60	-14.03	-20.16	-5.86	-2.80	-4.70	-4.97
62.86	5.53	3.56E-05	8.02E-03	-2.54	-1.47	-8.60	-14.01	-20.12	-5.91	-2.85	-4.72	-4.97
65.71	5.55	3.36E-05	7.28E-03	-2.58	-1.48	-8.60	-13.99	-20.09	-5.97	-2.89	-4.74	-4.97
68.57	5.57	3.17E-05	6.56E-03	-2.62	-1.49	-8.60	-13.97	-20.04	-6.03	-2.94	-4.76	-4.97
71.43	5.59	2.99E-05	5.86E-03	-2.67	-1.49	-8.60	-13.95	-20.00	-6.10	-2.99	-4.78	-4.97
74.29	5.62	2.81E-05	5.19E-03	-2.72	-1.50	-8.60	-13.93	-19.95	-6.17	-3.04	-4.81	-4.97
77.14	5.64	2.64E-05	4.54E-03	-2.77	-1.50	-8.60	-13.90	-19.89	-6.26	-3.10	-4.84	-4.97
80.00	5.68	2.47E-05	3.91E-03	-2.83	-1.50	-8.60	-13.87	-19.83	-6.35	-3.17	-4.87	-4.97
82.86	5.71	2.30E-05	3.30E-03	-2.90	-1.51	-8.60	-13.83	-19.76	-6.46	-3.24	-4.90	-4.97
85.71	5.75	2.14E-05	2.71E-03	-2.99	-1.51	-8.60	-13,79	-19.68	-6.58	-3.33	-4.94	-4.97
88.57	5.80	1.98E-05	2.13E-03	-3.09	-1.52	-8.60	-13.74	-19.58	-6.73	-3.43	-4.99	-4.97
91.43	5.87	1.83E-05	1.58E-03	-3.21	-1.52	-8.60	-13.68	-19.45	-6.92	-3.57	-5.06	-4.97
94.29	5.96	1.69E-05	1.04E-03	-3.39	-1.53	-8.60	-13.59	-19.27	-7.19	-3 75	-5.15	-4.97
97.14	6.11	1.63E-05	5.16E-04	-3.70	-1.53	-8.60	-13.43	-18.97	-7.65	-4.06	-5 30	-4.97
100.00	6.83	4.22E-05	2.11E-05	-5.13	-1.54	-8.60	-12.72	-17.53	-9.80	-5.50	-6.02	-4.97

						1.00	100 C						
log	log	log	log	log	log	log	log	log	log	log	SI SI	SI	SI
(aCO3 ⁴)	(aHCO ₃ ')	(aPbHCO ₃ *)	(aPbCO ₃)	(aPb(CO3)2))	(aNa [†])	(aNaCO ₃)	(aNaHCO ₃)	(aNaOH)	(aOH)	(aH*)	(Ce)	(Hc)	(Pb(OH) ₂₍₀)
M	M	M	M	M	M	M	M	M	M	M			
-11.14	-6.06	-5.16	-5.89	-13.63					-8.74	-5.26	0.00	-1.66	0.37
-11.12	-6.05	-5.17	-5.89	-13.61	-2.81	-12.66	-9.11	-11.72	-8.73	-5.27	0.00	-1.66	0.37
-11.10	-6.04	-5.18	-5.89	-13.59	-2.52	-12.35	-8.81	-11.42	-8.72	-5.28	0.00	-1.66	0.37
-11.08	-6.03	-5.19	-5.89	-13.57	-2.35	-12.16	-8.64	-11.25	-8.71	-5.29	0.00	-1.66	0.37
-11.06	-6.02	-5.20	-5.89	-13.55	-2.24	-12.03	-8.51	-11.12	-8.70	-5.30	0.00	-1.66	0.37
-11.04	-6.01	-5.21	-5.89	-13.53	-2.15	-11.92	-8.42	-11.03	-8.69	-5.31	0.00	-1.66	0.37
-11.02	-6.00	-5.22	-5.89	-13.51	-2.08	-11.83	-8.34	-10.95	-8.68	-5.32	0.00	-1.66	0.37
-11.00	-5.99	-5.23	-5.89	-13.49	-2.03	-11.75	-8.27	-10.88	-8.67	-5.33	0.00	-1.66	0.37
-10.97	-5.98	-5.24	-5.89	-13.46	-1.98	-11.68	-8.21	-10.82	-8.66	-5.34	0.00	-1.66	0.37
-10.95	-5.97	-5.25	-5.89	-13.44	-1.94	-11.62	-8.16	-10.77	-8.65	-5.35	0.00	-1.66	0.37
-10.93	-5.96	-5.26	-5.89	-13.42	-1.90	-11.56	-8.11	-10.72	-8.64	-5.36	0.00	-1.66	0.37
-10.91	-5.95	-5.27	-5.89	-13.40	-1.87	-11.50	-8.06	-10.68	-8.63	-5.37	0.00	-1.66	0.37
-10.88	-5.94	-5.28	-5.89	-13.37	-1.84	-11.45	-8.02	-10.63	-8.62	-5.38	0.00	-1.66	0.37
-10.86	-5.93	-5.30	-5.89	-13.35	-1.81	-11.40	-7.99	-10.60	-8.60	-5.40	0.00	-1.66	0.37
-10.83	-5.91	-5.31	-5.89	-13.32	-1.79	-11.35	-7.95	-10.56	-8.59	-5.41	0.00	-1.66	0.37
-10.81	-5.90	-5.32	-5.89	-13.30	-1.76	-11.30	-7.91	-10.52	-8.58	-5.42	0.00	-1.66	0.37
-10.78	-5.89	-5.34	-5.89	-13.27	-1.74	-11.26	-7.88	-10.49	-8.57	-5.43	0.00	-1.66	0.37
-10.75	-5.87	-5.35	-5.89	-13.24	-1.73	-11.21	-7.85	-10.46	-8.55	-5.45	0.00	-1.66	0.37
-10.72	-5.86	-5.36	-5.89	-13.21	-1.71	-11.16	-7.82	-10.43	-8.54	-5.46	0.00	-1.66	0.37
-10.69	-5.84	-5.38	-5.89	-13.18	-1.69	-11.12	-7.78	-10.39	-8.52	-5.48	0.00	-1.66	0.37
-10.66	-5.83	-5.40	-5.89	-13.15	-1.68	-11.07	-7.75	-10.36	-8.51	-5.49	0.00	-1.66	0.37
-10.63	-5.81	-5.41	-5.89	-13.12	-1.66	-11.02	-7.72	-10.33	-8.49	-5.51	0.00	-1.66	0.37
-10.59	-5.79	-5.43	-5.89	-13.08	-1.65	-10.97	-7.69	-10.30	-8.47	-5.53	0.00	-1.66	0.37
-10.55	-5.77	-5.45	-5.89	-13.04	-1.64	-10.92	-7.66	-10.27	-8.45	-5.55	0.00	-1.66	0.37
-10.51	-5.75	-5.47	-5.89	-13.00	-1.63	-10.87	-7.63	-10.24	-8.43	-5.57	0.00	-1.66	0.37
-10.46	-5.73	-5.49	-5.89	-12.95	-1.61	-10.81	-7.59	-10.20	-8.41	-5.59	0.00	-1.66	0.37
-10.41	-5.70	-5.52	-5.89	-12.90	-1.60	-10.75	-7.56	-10.17	-8.38	-5.62	0.00	-1.66	0.37
-10.36	-5.68	-5.55	-5.89	-12.85	-1.59	-10.68	-7.52	-10.13	-8.36	-5.64	0.00	-1.66	0.37
-10.30	-5.64	-5.58	-5.89	-12.79	-1.58	-10.61	-7.48	-10.09	-8.32	-5.68	0.00	-1.66	0.37
-10.23	-5.61	-5.61	-5.89	-12.72	-1.58	-10.53	-7.44	-10.05	-8.29	-5.71	0.00	-1.66	0.37
-10.15	-5.57	-5.65	-5.89	-12.64	-1.57	-10.44	-7.39	-10.00	-8.25	-5.75	0.00	-1.66	0.37
-10.04	-5.52	-5.70	-5.89	-12.53	-1.56	-10.33	-7.33	-9.94	-8.20	-5.80	0.00	-1.66	0.37
-9.92	-5.45	-5.77	-5.89	-12.41	-1.55	-10.20	-7.25	-9.86	-8.13	-5.87	0.00	-1.66	0.37
-9.74	-5.36	-5.86	-5.89	-12.23	-1.54	-10.01	-7.16	-9.77	-8.04	-5.96	0.00	-1.66	0.37
-9.43	-5.21	-6.01	-5.89	-11.92	-1.54	-9.70	-7.00	-9.61	-7.89	-6.11	0.00	-1.66	0.37
-8.00	-4.49	-6.73	-5.89	-10.49	-1.53	-8.26	-6.27	-8.88	-7.17	-6.83	0.00	-1.66	0.37

$Na_2CO_3 \rightarrow Pb$	(NO3)2 - Close	d System (PHREE)	QC-I Output)			1.1							
		200 BC 200 A 400			log	log	log	log	log	log	log	log	log
% Na ₂ CO ₃	pH	∑Alk	[Pb ^{**}] _{TOT}	(a	Pb ^{4*})	(aNO ₃)	(aPb(OH)2)	(aPb(OH) ₂)	(aPb(OH)4 ⁴)	(aPb ₂ OH ²)	(aPbNO ₃ ⁺)	(aPbOH [*])	(aCO ₂)
Injected		meq	M		М	M	M	M	M	M	M	M	М
0.00	5.07	8.24E-05	3.53E-02	-	1.99	-1.33	-8.97	-14.83	-21.40	-5.27	-2.15	-4.63	-4.60
2.86	5.09	7.92E-05	3.34E-02	-	2.01	-1.34	-8.95	-14.79	-21.34	-5.29	-2.18	-4.63	-4.62
5.71	5.11	7.61E-05	3.15E-02	-	2.03	-1.34	-8.93	-14.76	-21.29	-5.31	-2.21	-4.63	-4.64
8.57	5.13	7.32E-05	2.97E-02	-	2.05	-1.35	-8.91	-14.72	-21.23	-5.33	-2.23	-4.63	-4.66
11.43	5.15	7.05E-05	2.80E-02	-	2.07	-1.36	-8.89	-14.68	-21.18	-5.36	-2.26	-4.63	-4.68
14.29	5.17	6.79E-05	2.65E-02	-	2.09	-1.37	-8.88	-14.65	-21.12	-5.38	-2.29	-4.63	-4.69
17.14	5.19	6.54E-05	2.49E-02	-	2.11	-1.38	-8.86	-14.61	-21.07	-5.40	-2.32	-4.64	-4.71
20.00	5.21	6.30E-05	2.35E-02	-	2.13	-1.38	-8.84	-14.58	-21.01	-5.42	-2.35	-4.64	-4.73
22.86	5.23	6.07E-05	2.21E-02	-	2.16	-1.39	-8.83	-14.54	-20.95	-5.45	-2.38	-4.64	-4.74
25.71	5.25	5.85E-05	2.08E-02	-	2.18	-1.40	-8.81	-14.50	-20.90	-5.47	-2.40	-4.64	-4.76
28.57	5.26	5.64E-05	1.96E-02	-	2.20	-1.40	-8.79	-14.47	-20.84	-5.50	-2.43	-4.65	-4.78
31.43	5.28	5.44E-05	1.84E-02	-	2.22	-1.41	-8.78	-14.43	-20.79	-5.52	-2.46	-4.65	-4.79
34.29	5.30	5.25E-05	1.72E-02	-	2.25	-1.42	-8.76	-14.39	-20.73	-5.55	-2.49	-4.65	-4.81
37.14	5.33	5.06E-05	1.61E-02	-	2.27	-1.42	-8.74	-14.36	-20.67	-5.58	-2.52	-4.66	-4.83
40.00	5.35	4.88E-05	1.51E-02	-	2.30	-1.43	-8.73	-14.32	-20.61	-5.61	-2.56	-4.66	-4.84
42.86	5.37	4.71E-05	1.41E-02	-	2.32	-1.44	-8.71	-14.28	-20.56	-5.64	-2.59	-4.67	-4.86
45.71	5.39	4.54E-05	1.31E-02	-	2.35	-1.44	-8.69	-14.24	-20.49	-5.67	-2.62	-4.67	-4.88
48.57	5.41	4.38E-05	1.22E-02	-	2.38	-1.45	-8.67	-14.20	-20.43	-5.70	-2.65	-4.68	-4.90
51.43	5.44	4.22E-05	1.13E-02	-	2.41	-1.45	-8.66	-14.16	-20.37	-5.74	-2.69	-4.68	-4.91
54.29	5.46	4.06E-05	1.04E-02	-	2.44	-1.46	-8.64	-14.12	-20.30	-5.78	-2.73	-4.69	-4.93
57.14	5.48	3.91E-05	9.59E-03	-	2.47	-1.46	-8.62	-14.08	-20.23	-5.82	-2.76	-4.70	-4.95
60.00	5.51	3.76E-05	8.80E-03		2.50	-1.47	-8.60	-14.03	-20.16	-5.86	-2.80	-4.70	-4.97
62.86	5.54	3.62E-05	8.02E-03	-	2.54	-1.47	-8.58	-13.99	-20.09	-5.90	-2.85	-4.71	-4.99
65.71	5.57	3.47E-05	7.28E-03	-	2.58	-1.48	-8.56	-13.94	-20.01	-5.95	-2.89	-4.72	-5.01
68.57	5.60	3.33E-05	6.56E-03	-	2.62	-1.49	-8.54	-13.89	-19.93	-6.00	-2.94	-4.73	-5.03
71.43	5.63	3.19E-05	5.86E-03	-	2.67	-1.49	-8.52	-13.83	-19.84	-6.06	-2.99	-4.74	-5.05
74.29	5.67	3.05E-05	5.19E-03	-	2.72	-1.50	-8.50	-13.77	-19.74	-6.12	-3.04	-4.76	-5.07
77.14	5.71	2.91E-05	4.54E-03	-	2.77	-1.50	-8.47	-13.71	-19.64	-6.19	-3.10	-4.77	-5.10
80.00	5.75	2.77E-05	3.91E-03	-	2.83	-1.50	-8.45	-13.64	-19.52	-6.27	-3.17	-4.79	-5.12
82.86	5.80	2.63E-05	3.30E-03	-	2.90	-1.51	-8.42	-13.55	-19.39	-6.36	-3.24	-4.81	-5.15
85.71	5.86	2.49E-05	2.71E-03		2.99	-1.51	-8.38	-13.46	-19.24	-6.47	-3.33	-4.83	-5.19
88.57	5.93	2.33E-05	2.14E-03	-	3.09	-1.52	-8.34	-13.34	-19.05	-6.60	-3.43	-4.86	-5.23
91.43	6.03	2.17E-05	1.58E-03	-	3.22	-1.52	-8.28	-13.20	-18.81	-6.76	-3.57	-4.90	-5.29
94.29	6.16	2.00E-05	1.04E-03	-	3.40	-1.53	-8.20	-12.99	-18.48	-6.99	-3.75	-4.95	-5.37
97.14	6.38	1.80E-05	5.17E-04		3.70	-1.53	-8.06	-12.62	-17.88	-7.38	-4.06	-5.03	-5.51
100.00	8.30	1.96E-05	9.79E-06	-	5.94	-1.54	-6.46	-9.10	-12.43	-9.94	-6.31	-5.35	-7.11

								1000			•4.00		
log	log	log	log	log	log	log	102	log	log	log	SI	SI	SI
(aCO ₁ ²)	(aHCO ₃)	(aPbHCO ₃ [*])	(aPbCO ₁)	(aPb(CO ₁), ²)	(aNa [†])	(aNaCO ₁)	(aNaHCO ₃)	(aNaOH)	(aOH)	(aH)	(Ce)	(Elc)	(Pb(OH))
М	M	M	M	M	М	М	М	M	M	M			· · · · · · · · · · · · · · · · · · ·
-11.14	-5.88	-4.98	-5.89	-13.63					-8.93	-5.07	0.00	-2.02	0.00
-11.12	-5.88	-4.99	-5.89	-13.61	-2.81	-12.66	-8.94	-11.90	-8.91	-5.09	0.00	-2.01	0.02
-11.10	-5.88	-5.01	-5.89	-13.59	-2.52	-12.35	-8.65	-11.59	-8.89	-5.11	0.00	-1.99	0.04
-11.08	-5.88	-5.03	-5.89	-13.57	-2.35	-12.16	-8.48	-11.40	-8.87	-5.13	0.00	-1.97	0.06
-11.06	-5.88	-5.05	-5.89	-13.55	-2.24	-12.03	-8.37	-11.27	-8.85	-5.15	0.00	-1.95	0.08
-11.04	-5.88	-5.07	-5.89	-13.53	-2.15	-11.92	-8.28	-11.16	-8.83	-5.17	0.00	-1.94	0.09
-11.02	-5.88	-5.09	-5.89	-13.51	-2.08	-11.83	-8.21	-11.08	-8.81	-5.19	0.00	-1.92	0.11
-11.00	-5.87	-5.11	-5.89	-13.49	-2.03	-11.75	-8.15	-11.00	-8.79	-5.21	0.00	-1.90	0.13
-10.97	-5.87	-5.13	-5.89	-13.46	-1.98	-11.68	-8.10	-10.93	-8.77	-5.23	0.00	-1.88	0.14
-10.95	-5.87	-5.15	-5.89	-13.44	-1.94	-11.62	-8.05	-10.87	-8.75	-5.25	0.00	-1.87	0.16
-10.93	-5.87	-5.17	-5.89	-13.42	-1.90	-11.56	-8.01	-10.81	-8.74	-5.27	0.00	-1.85	0.18
-10.91	-5.86	-5.19	-5.89	-13.40	-1.87	-11.50	-7.98	-10.76	-8.72	-5.28	0.00	-1.83	0.19
-10.88	-5.86	-5.21	-5.89	-13.37	-1.84	-11.45	-7.95	-10.71	-8.70	-5.30	0.00	-1.82	0.21
-10.86	-5.86	-5.23	-5.89	-13.35	-1.81	-11.40	-7.92	-10.67	-8.67	-5.33	0.00	-1.80	0.23
-10.83	-5.85	-5.25	-5.89	-13.32	-1.79	-11.35	-7.89	-10.62	-8.65	-5.35	0.00	-1.78	0.24
-10.81	-5.85	-5.27	-5.89	-13.30	-1.76	-11.30	-7.86	-10.58	-8.63	-5.37	0.00	-1.77	0.26
-10.78	-5.84	-5.29	-5.89	-13.27	-1.74	-11.26	-7.84	-10.54	-8.61	-5.39	0.00	-1.75	0.28
-10.75	-5.84	-5.31	-5.89	-13.24	-1.73	-11.21	-7.81	-10.49	-8.59	-5.41	0.00	-1.73	0.30
-10.72	-5.83	-5.34	-5.89	-13.21	-1.71	-11.16	-7.79	-10.45	-8.56	-5.44	0.00	-1.72	0.31
-10.69	-5.82	-5.36	-5.89	-13.18	-1.69	-11.12	-7.77	-10.41	-8.54	-5.46	0.00	-1.70	0.33
-10.66	-5.82	-5.39	-5.89	-13.15	-1.68	-11.07	-7.74	-10.37	-8.52	-5.48	0.00	-1.68	0.35
-10.63	-5.81	-5.41	-5.89	-13.12	-1.66	-11.02	-7.72	-10.33	-8.49	-5.51	0.00	-1.66	0.37
-10.59	-5.80	-5.44	-5.89	-13.08	-1.65	-10.97	-7.70	-10.29	-8.46	-5.54	0.00	-1.64	0.39
-10.55	-5.79	-5.47	-5.89	-13.04	-1.64	-10.92	-7.68	-10.25	-8.43	-5.57	0.00	-1.62	0.41
-10.51	-5.78	-5.50	-5.89	-13.00	-1.63	-10.87	-7.65	-10.21	-8.40	-5.60	0.00	-1.60	0.43
-10.46	-5.77	-5.53	-5.89	-12.95	-1.61	-10.81	-7.63	-10.16	-8.37	-5.63	0.00	-1.58	0.45
-10.41	-5.75	-5.57	-5.89	-12.90	-1.60	-10.75	-7.61	-10.12	-8.33	-5.67	0.00	-1.56	0.47
-10.36	-5.74	-5.61	-5.89	-12.85	-1.59	-10.68	-7.58	-10.07	-8.29	-5.71	0.00	-1.53	0.50
-10.30	-5.72	-5.65	-5.89	-12.79	-1.58	-10.61	-7.56	-10.01	-8.25	-5.75	0.00	-1.51	0.52
-10.23	-5.70	-5.70	-5.89	-12.72	-1.58	-10.53	-7.53	-9.95	-8.20	-5.80	0.00	-1.48	0.55
-10.14	-5.68	-5.76	-5.89	-12.63	-1.57	-10.44	-7.50	-9.88	-8.14	-5.86	0.00	-1.44	0.59
-10.04	-5.65	-5.84	-5.89	-12.53	-1.56	-10.33	-7.46	-9.80	-8.07	-5.93	0.00	-1.40	0.63
-9.92	-5.61	-5.93	-5.89	-12.41	-1.55	-10.20	-7.41	-9.71	-7.97	-6.03	0.00	-1.34	0.69
-9.74	-5.56	-6.06	-5.89	-12.23	-1.54	-10.01	-7.36	-9.57	-7.84	-6.16	0.00	-1.26	0.77
-9.43	-5.48	-6.28	-5.89	-11.92	-1.54	-9.70	-7.27	-9.34	-7.62	-6.38	0.00	-1.12	0.91
-7.19	-5.16	-8.20	-5.89	-9.68	-1 53	-7.45	-6.94	-7.41	-5.70	-8 30	0.00	0.48	2.51