

Article

Limits of Gas-Only Carbon-Budget Inference: Synthetic Gas–Water–Calcite Benchmarks for Quaternary Outgassing

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Abstract

Quaternary carbon-budget reconstructions combine gas observations with groundwater chemistry and dated carbonate deposits, which record different compartments and timescales. We examine the equilibrium partitioning step underlying such interpretations using an independent ideal-dilute calculation and 95 PHREEQC (pH–redox–equilibrium in C) cases in synthetic gas–water–calcite systems. At 25 °C, changing the headspace-to-water ratio from 0.01 to 10 L kg^{−1} changed the gas fraction of a 10 mmol carbon input in 1 kg water from 0.0118 to 0.9214. A strong-base-to-carbon ratio of one reduced the 1 L-headspace gas fraction from 0.5436 to 0.00892. At that ratio, increasing calcium availability could raise both mineral storage and residual gas expression. A non-limiting CO₂ reservoir and a finite pressure-constrained bubble produced aqueous states indistinguishable at the reported precision under different carbon-budget constraints; the same finite inventory partitioned differently at fixed volume. Four selected phase classifications persisted across three databases. These results identify conditional limits of gas-only inventory inference, not corrections to published palaeofluxes. Application to dated travertines additionally requires water throughput, source attribution, preservation and chronology. The calculations provide reproducible equilibrium benchmarks and a framework for identifying missing constraints before phase-selective observations are combined into Quaternary carbon budgets.

Keywords: CO₂ partitioning; gas–water equilibrium; finite headspace; dissolved inorganic carbon; calcite precipitation; PHREEQC; volcanic outgassing; Quaternary

1. Introduction

Two systems can contain the same amount of carbon yet display very different gas signals. Carbon may remain dissolved in water, enter a carbonate mineral, or occupy the available gas space. Measuring one of these compartments does not, by itself, measure their sum. This simple distinction matters when volcanic, hydrothermal and tectonic carbon is assessed from gas surveys, spring waters and carbonate deposits [1–3]. It also requires a distinction between an inventory, the amount of carbon present, and a flux, the amount crossing a boundary per unit time. A soil-gas chamber measures a flux, whereas the calculations presented here describe equilibrium inventories and phase fractions. No transport law is assumed between them.

For Quaternary research, the problem extends beyond present-day volcanic monitoring. Dated travertines preserve part of a carbon-transfer system over intervals that can be much longer than a gas survey. Their volumes, composition and chronology have been used to reconstruct geogenic CO₂ release in central Italy [4,5]. Such inversions require an explicit



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connection between preserved mineral carbon and the carbon that escaped or remained in water. At Tivoli, published reconstructions already identify preservation losses and degassing before spring emergence as reasons that the inferred release is a minimum [5]. Interpreting each estimate therefore requires an explicit compartment, system boundary and time interval.

The temporal connection is also palaeoenvironmental. The Late Pleistocene Lapis Tiburtinus succession has been used to relate carbonate isotope variations to climate and groundwater-level changes [6]. At Semproniano, dated carbonate veins and associated travertines record episodic Pleistocene fluid discharge and its environmental context [7]. These studies show why an archive can reflect hydrological and depositional controls as well as carbon supply. They do not imply that local geogenic emissions caused the climatic changes. Our equilibrium model does not simulate archive formation through time; it isolates one prerequisite for interpreting an archive or observation: how a prescribed carbon inventory is distributed among the phases that may be sampled.

Modern observations supply complementary evidence. Gas monitoring resolves changes in concentration, composition and flux [8,9], while young groundwater can carry lithospheric volatiles outside conspicuous discharge zones [10]. Studies of the Eifel–Ardennes region and central–southern Italian springs likewise examine groundwater-mediated carbon transfer [11,12]. Mechanical storage and transport can filter deep-gas signals before they reach the surface [13]; gas–water–rock reactions can then alter their chemical expression [14,15]. Aqueous dissolved inorganic carbon (DIC) can include both externally supplied carbon and carbon released by host-rock dissolution [16–18]. Source attribution and phase partitioning are thus different questions.

Carbonate reactions further complicate that interpretation. Hydrothermal calcite can retain carbon [19]; alkalinity, gas exchange and mineral reactions jointly regulate carbonate buffering [20,21]. Precipitation from bicarbonate-rich water can also redistribute some conserved carbon towards dissolved CO₂ and gas, rather than simply suppressing gas expression [22,23]. These are established reactions. Similarly, finite dissolution capacity and pressure decline in closed systems have been analysed at low and high pressures [24,25], and finite headspace has recognised effects on carbonate–water measurements [26].

The study develops a controlled comparison of finite carbon budgets under alternative chemical and gas-boundary constraints. PHREEQC (pH–redox–equilibrium in C), version 3.8.6-17100 (U.S. Geological Survey, Reston, VA, USA) supplies the database-based calculations [27]. Existing applications address basalt carbonation, geothermal phase separation and reactive transport [28–30]; its gas equations and database limitations are separately documented [31–33]. We combine prescribed finite inventories, explicit gas–aqueous–calcite closure, independently implemented ideal-dilute benchmarks, and three non-equivalent gas constraints. This construction allows a direct test of how much an inference changes when chemistry or the gas boundary is changed without silently changing the meaning of the carbon budget. The methodological contribution lies in this integrated comparison and its independent checks, building on the established reactions and software capabilities.

The experiments vary headspace-to-water geometry, strong-base capacity, calcium supply, gas boundary condition, temperature and thermodynamic database. Carbon provenance, precipitation kinetics and wet multicomponent gases are not varied; they are outside the model. The primary use is to test phase accounting and expose underconstrained gas-only interpretations before constructing a site-specific model. The following distinction guides the paper:

Observation, inventory and archive. A gas observation samples a phase; a finite inventory sums the carbon in the connected compartments; a dated carbonate archive records accumulated and preserved deposition. Moving between these

quantities requires additional information. The present calculations resolve the equilibrium partitioning step, not the complete reconstruction of a Quaternary carbon flux.

The Methods specify the model and a modular experiment map. The Results separate geometric, chemical and boundary-condition effects. The Discussion relates those findings to dated carbonate examples, identifies constraints needed for their interpretation, and distinguishes model verification from field validation. Detailed algorithmic specifications are collected in Supplementary Methods S2 so that the main narrative remains accessible without sacrificing reproducibility.

2. Materials and Methods

2.1. Model Definition and Assumptions

2.1.1. Finite Control Volume and Carbon Balance

Consider a closed equilibrium control volume containing a water mass M_w , a gas headspace of volume V_g , and, where allowed, precipitated calcite. A finite amount $N_{C,in}$ of carbon is introduced as CO_2 . In the core cases, the initial water contains no carbon and no carbonate mineral is present. Carbon conservation is therefore

$$N_{C,in} = N_C^g + N_C^{aq} + N_C^{min}, \quad (1)$$

where N_C^g is gas-phase carbon, N_C^{aq} is total aqueous inorganic carbon, and N_C^{min} is carbon stored in precipitated calcite. The phase fractions are

$$\phi_g = \frac{N_C^g}{N_{C,in}}, \quad \phi_{aq} = \frac{N_C^{aq}}{N_{C,in}}, \quad \phi_{min} = \frac{N_C^{min}}{N_{C,in}}, \quad (2)$$

so that

$$\phi_g + \phi_{aq} + \phi_{min} = 1 \quad (3)$$

within numerical tolerance.

The term visible is used operationally and only with respect to a gas-only observation window. The non-gas fraction is

$$\phi_{non-gas} = 1 - \phi_g = \phi_{aq} + \phi_{min}. \quad (4)$$

DIC and carbonate minerals are not intrinsically invisible; they are simply absent from a measurement that samples only the gas phase. This definition avoids treating alkalinity or saturation index as carbon reservoirs. Alkalinity is a charge-balance property, and saturation index is a thermodynamic diagnostic. No constitutive relation is assumed between the equilibrium fraction ϕ_g and an accumulation-chamber flux: the former describes phase availability at equilibrium, whereas the latter is a transport rate.

For the finite-inventory cases, the relative carbon closure residual is

$$r_C = \frac{N_C^g + N_C^{aq} + N_C^{min} - N_{C,in}}{N_{C,in}}. \quad (5)$$

The reduced solver is admitted only when $|r_C| \leq 10^{-8}$, the charge residual is below $10^{-10} \text{ mol kg}^{-1}$, and all phase amounts are non-negative.

2.1.2. Reduced Equilibrium Domain

The reduced model is deliberately narrower than a general hydrothermal calculation. Its purpose is verification and mechanism isolation. The assumptions are listed in Table 1, and the notation is summarised in Table 2.

Table 1. Assumptions of the reduced finite-inventory equilibrium model. These assumptions define the benchmark domain. PHREEQC (pH–redox–equilibrium in C) relaxes the ideal-solution and ideal-gas approximations while retaining equilibrium and the synthetic composition.

Item	Assumption and Consequence
Thermodynamic state	Equilibrium at 25 °C; no kinetic rate law, residence time, metastability, or reaction path is interpreted as elapsed physical time.
Gas phase	Single-component CO ₂ gas in a closed fixed-volume headspace; H ₂ O(g), N ₂ , O ₂ , CH ₄ , and other background gases are excluded. In the reduced ideal-gas model, total gas pressure equals p_{CO_2} .
Aqueous phase	Ideal dilute solution containing CO ₂ [*] , HCO ₃ [−] , CO ₃ ^{2−} , H ⁺ , OH [−] , Na ⁺ , Ca ²⁺ , and Cl [−] . Activity coefficients and ion pairs are omitted.
Carbon source	The core water initially contains no carbon, and all modelled carbon is introduced as a prescribed amount of CO ₂ . This construction isolates phase partitioning but is not a natural-source attribution model.
Neutralisation	NaOH-equivalent strong-base capacity provides a controlled acid–base coordinate without adding carbon. It is not intended to represent a complete natural-water composition.
Calcium	CaCl ₂ provides calcium without adding carbon; Cl [−] closes the strong-ion charge balance.
Solid phase	Calcite is initially absent and may only precipitate to equilibrium. Pre-existing calcite dissolution is excluded because it would mix input carbon with host-rock carbon. Nucleation delay, kinetic inhibition, metastable supersaturation, and growth rate are not represented.
Water basis	Constant $M_w = 1$ kg in the reduced grids; PHREEQC starts with $M_{w,0} = 1$ kg and reports its final solvent mass. Headspace volume is varied independently.

Table 2. Key notation used in the finite-inventory model and numerical audits. All inventories are expressed as moles of carbon unless otherwise stated.

Symbol	Definition	Unit or Constraint
$N_{\text{C},\text{in}}$	Prescribed finite carbon input	mol C; positive in finite-inventory cases
$N_{\text{C}}^g, N_{\text{C}}^{aq}, N_{\text{C}}^{min}$	Carbon inventories in gas, aqueous, and calcite phases	mol C; non-negative
$\phi_g, \phi_{aq}, \phi_{min}$	Phase fractions relative to $N_{\text{C},\text{in}}$	dimensionless; sum to one in finite closed cases
M_w	Constant water-mass parameter of the reduced model	kg; 1 kg in the reduced grids
$M_{w,0}, M_{w,f}$	Initial and final PHREEQC solvent mass	kg; $M_{w,0} = 1$ kg in the reported cases
V_g	Gas headspace or bubble volume	L
Γ_{gw}	Headspace per unit water mass	L kg ^{−1} ; V_g/M_w in the reduced model
$c_{\text{C},\text{in}}$	Carbon input per unit water mass	mol kg ^{−1} ; $N_{\text{C},\text{in}}/M_w$
A_T	Total alkalinity in the reduced model	mol equivalent kg ^{−1}
m°	Aqueous standard-state molality	1 mol kg ^{−1}
h	Hydrogen-ion activity, a_{H^+}	dimensionless
Π_A	NaOH-equivalent strong-base capacity divided by carbon input	dimensionless
Π_{Ca}	Initial calcium inventory divided by carbon input	dimensionless
K_H^m	Molality-based Henry coefficient defined by Equation (7)	mol kg ^{−1} atm ^{−1}
Λ_H	Geometry–solubility parameter in Equation (11)	dimensionless
$p_{\text{CO}_2}, f_{\text{CO}_2}$	CO ₂ partial pressure and fugacity	atm; not interchangeable for a non-ideal gas
φ_{CO_2}	Gas fugacity coefficient, $f_{\text{CO}_2}/p_{\text{CO}_2}$	dimensionless; distinct from phase fraction ϕ_g
Z	Gas compressibility factor, $PV/(nRT)$	dimensionless; distinct from φ_{CO_2}
$r_{\text{C}}, r_{\text{C}}^{\text{PHR}}$	Reduced-model and PHREEQC carbon-closure residuals (PHR: PHREEQC)	dimensionless

Gas-phase scope.

All reduced and PHREEQC calculations use a single-component CO₂ gas phase. H₂O(g), N₂, O₂, CH₄, and other background gases are not included. Consequently, the fixed-pressure boundary-condition experiment represents a finite pure-CO₂ bubble: while the bubble exists, total gas pressure is determined only by CO₂. The calculated pressures and phase partitions should not be transferred directly to wet or multicomponent natural gases without adding the relevant components and re-evaluating the pressure constraint.

2.1.3. Gas–Water Equilibrium Without Solids

For an ideal gas, with p_{CO_2} in atm, V_g in L and T in K,

$$N_C^g = \frac{p_{\text{CO}_2} V_g}{RT}. \quad (6)$$

Here, CO₂^{*} denotes the conventional sum CO₂(aq) + H₂CO₃. Using the molality-form Henry convention

$$m_{\text{CO}_2^*} = K_H^m p_{\text{CO}_2}, \quad (7)$$

K_H^m has units mol kg^{−1} atm^{−1} and pressure is referenced to 1 atm. The aqueous standard-state molality is denoted by $m^\circ = 1$ mol kg^{−1}. Activities are dimensionless, $h \equiv a_{\text{H}^+}$, and the ideal-dilute approximation is $a_i \simeq m_i / m^\circ$. The acid-dissociation, water, and calcite-equilibrium constants below are written in activity form. The ideal carbonate relations are

$$m_{\text{HCO}_3^-} = \frac{K_1 K_H^m p_{\text{CO}_2}}{h}, \quad m_{\text{CO}_3^{2-}} = \frac{K_1 K_2 K_H^m p_{\text{CO}_2}}{h^2}, \quad (8)$$

where h is hydrogen-ion activity in the ideal approximation. The aqueous carbon inventory is

$$N_C^{aq} = M_w K_H^m p_{\text{CO}_2} \beta_C(h), \quad \beta_C(h) = 1 + \frac{K_1}{h} + \frac{K_1 K_2}{h^2}. \quad (9)$$

For a prescribed total alkalinity A_T , expressed as molar equivalents per kilogram of water, the reduced charge relation is

$$A_T = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m^\circ \frac{K_w}{h} - m^\circ h. \quad (10)$$

Equations (1), (6), (9) and (10) determine p_{CO_2} and h for a closed finite input. Defining

$$\Lambda_H = \frac{M_w K_H^m RT}{V_g}, \quad (11)$$

the gas fraction can be written

$$\phi_g = \frac{1}{1 + \Lambda_H \beta_C(h)}. \quad (12)$$

Equation (12) is exact within the stated ideal model, but it is not a one-parameter closed form because h must also satisfy alkalinity and mass balance. It nevertheless shows why headspace geometry and acid–base speciation cannot be separated. Relations of this type are established for closed gas–brine systems through a finite dissolution-capacity parameter [24,25]; Equation (12) is therefore used as an independently auditable limit rather than claimed as a new closed-system theory.

Define the water-normalised headspace and carbon loading as

$$\Gamma_{gw} = \frac{V_g}{M_w}, \quad c_{C,\text{in}} = \frac{N_{C,\text{in}}}{M_w}, \quad \Lambda_H = \frac{K_H^m RT}{\Gamma_{gw}}. \quad (13)$$

Here Γ_{gw} has units L kg^{-1} and $c_{C,\text{in}}$ has units mol kg^{-1} ; Λ_H is dimensionless. At fixed temperature, composition and boundary type, multiplying M_w , V_g , $N_{C,\text{in}}$, N_A and $N_{Ca,0}$ by the same positive factor preserves molalities, pH, pressure and phase fractions, while phase inventories scale by that factor. For PHREEQC, this transformation applies to the prescribed initial solvent mass $M_{w,0}$ and all initial phase and reaction amounts; the final solvent mass scales accordingly. For a pressure-constrained finite bubble its equilibrium volume also scales. This is an extensivity property of the stated bulk-equilibrium model, which excludes surface and capillary effects. Changing only water mass does not preserve the solution. The 1 kg basis is therefore a normalisation, not a restriction to laboratory-sized systems; transfer requires preservation of both geometry and chemical loading, not Γ_{gw} alone.

2.1.4. Chemical-Capacity Ratios and Calcite Precipitation

The input is normalised by two dimensionless capacities. Let N_A be the number of NaOH equivalents added and $N_{Ca,0}$ the initial calcium supplied as CaCl_2 . In no-solid cases, the imposed strong-base coordinate corresponds to $A_T = N_A/M_w$. Then

$$\Pi_A = \frac{N_A}{N_{C,\text{in}}}, \quad \Pi_{Ca} = \frac{N_{Ca,0}}{N_{C,\text{in}}}. \quad (14)$$

The strong-ion charge balance is

$$m^{\circ}h + m_{\text{Na}^+} + 2m_{\text{Ca}^{2+}} = m^{\circ}\frac{K_w}{h} + m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{Cl}^-}. \quad (15)$$

Sodium and chloride are conservative strong ions in the reduced model:

$$M_w m_{\text{Na}^+} = N_A, \quad M_w m_{\text{Cl}^-} = 2N_{Ca,0}. \quad (16)$$

The factor two follows from the CaCl_2 input. These equalities refer to free-ion molalities only because the reduced species set contains no Na or Cl complexes. In PHREEQC, the corresponding constraints apply to total elemental inventories, summed over all aqueous species. No sodium- or chloride-bearing solid or gas is allowed.

When calcite precipitates, calcium conservation and activity-based saturation require

$$N_{Ca,0} = M_w m_{\text{Ca}^{2+}} + N_C^{\text{min}}, \quad (17)$$

$$a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} = K_{\text{sp,cal}}, \quad a_i \simeq \frac{m_i}{m^{\circ}}. \quad (18)$$

Carbon and calcium conservation impose the strict mass-balance capacity bound

$$0 \leq \phi_{\text{min}} \leq \min(1, \Pi_{Ca}). \quad (19)$$

The NaOH-equivalent coordinate supplies an additional but conditional screening relation. In the synthetic system, precipitation of one mole of calcite lowers total alkalinity by two equivalents, so that

$$M_w A_{T,f} = N_A - 2N_C^{\text{min}}, \quad \phi_{\text{min}} = \frac{\Pi_A - \Pi_{A,f}}{2}, \quad (20)$$

where $A_{T,f}$ is final alkalinity and $\Pi_{A,f} = M_w A_{T,f}/N_{C,\text{in}}$. Only states with $A_{T,f} \geq 0$ therefore satisfy $\phi_{\text{min}} \leq \Pi_A/2$. The ratio $\Pi_A/2$ is a useful screening ceiling within the alkaline branch explored here, not a universal thermodynamic inequality. Neither the strict bound nor the conditional ceiling asserts that all available capacity must be consumed;

residual dissolved species, finite calcite solubility, and gas–water equilibrium generally keep the calculated value below the applicable ceiling.

The same precipitation process can be written in bicarbonate form as



Equation (21) makes clear that calcite precipitation can increase solid carbon while transferring part of the residual dissolved carbon towards CO_2^* and, in a closed gas–water system, towards the gas phase. This stoichiometric coupling is established in carbonate systems and has been treated in lake and speleothem carbon budgets [22,23]. It is retained here as a verification target within a finite-inventory calculation, not as a claim of a new reaction mechanism.

Interpretation of precipitation-only calcite.

Calcite is initially absent, specified as precipitation-only, and allowed to reach thermodynamic equilibrium whenever saturation permits. This construction assumes that a viable nucleation surface or pathway is available. It does not represent induction time, kinetic inhibition, metastable supersaturation, crystal-growth rate, or elapsed reaction time. Calculated mineral fractions are therefore equilibrium precipitation capacities rather than predictions of field precipitation rates.

2.1.5. Gas Boundary Conditions Are Not Interchangeable

The three numerical configurations in Table 3 represent different physical systems. A fixed p_{CO_2} imposed by an equilibrium gas phase supplies or removes carbon as required and behaves as a non-limiting reservoir over the modelled transfer. A finite single-component CO_2 gas phase at fixed total pressure permits gas amount and volume to change while pressure is maintained. A finite single-component CO_2 gas phase at fixed volume represents a closed headspace in which pressure changes as gas dissolves or exsolves [27,31]. Comparisons between these configurations require either matched final pressure or matched total carbon inventory. Treating them as interchangeable would confound boundary-condition effects with chemistry.

Table 3. Gas boundary conditions used in the numerical design. The three configurations are not alternative syntaxes for the same physical system; they encode different carbon constraints.

Configuration	Physical Interpretation	Carbon-Accounting Consequence
Fixed p_{CO_2}	Contact with a non-limiting CO_2 reservoir over the modelled transfer	Carbon may enter or leave until equilibrium is reached; the final local inventory is an output, not a prescribed constant.
Fixed total pressure	Finite single-component CO_2 bubble maintained at prescribed total pressure	Gas amount and volume may change; pressure matching does not guarantee inventory matching.
Fixed volume	Closed finite single-component CO_2 headspace of prescribed volume	Total carbon is conserved and p_{CO_2} responds to dissolution, exsolution, and reaction.

2.2. Computational Implementation and Verification

The numerical design comprised one smoke test and six scientific modules. Table 4 provides the computational-experiment map before the individual solvers, parameter grids, and audit criteria are described. Each scientific module isolates a distinct control on phase partitioning or tests a specific aspect of numerical robustness.

Table 4. Computational experiment map. M0A is a software and output smoke test and is excluded from the 95 scientific calculations. M0–M5 are deterministic equilibrium experiments designed to isolate one class of control at a time. The anchor states are U (unbuffered), B (bicarbonate retention), R (calcite-coupled redistribution), and C (carbonate capture).

Module	Experiment Type and Controlled Design	Cases	Primary Function
M0A	Software smoke test. One fixed-volume gas–water calculation used to test the executable, database loading, gas-phase construction, finite CO ₂ addition, and selected output.	1	Technical admission only; not part of the scientific case count.
M0	Headspace-geometry benchmark. Four headspace volumes (0.01–10 L) crossed with four finite carbon inputs (0.1–100 mmol); unbuffered, fixed-volume, no solids.	16	Quantify geometric control on ϕ_g and benchmark the reduced gas–water solver.
M1	Neutralisation-capacity experiment. Three headspace volumes crossed with six Π_A values at $N_{C,in} = 10$ mmol; no solid phase.	18	Isolate the effect of NaOH-equivalent strong-base capacity on gas–aqueous partitioning.
M2	Calcite-capacity experiment. Six Π_A values crossed with five Π_{Ca} values at $V_g = 1$ L and $N_{C,in} = 10$ mmol; calcite precipitation-only.	30	Quantify equilibrium mineral capacity and redistribution among gas, aqueous, and mineral carbon.
M3	Gas-boundary-condition experiment. Three end members: non-limiting fixed- p_{CO_2} reservoir, finite fixed-total-pressure CO ₂ bubble, and finite fixed-volume CO ₂ headspace.	3	Separate pressure matching from inventory matching and clarify carbon-budget meaning.
M4	Temperature sensitivity. Four anchor states (U, B, R, and C) evaluated at 10, 25, 50, and 75 °C with <code>phreeqc.dat</code> .	16	Test persistence or change of dominant-phase classifications with temperature.
M5	Thermodynamic-database sensitivity. The same four 25 °C anchor states evaluated with <code>phreeqc.dat</code> , <code>wateq4f.dat</code> , and <code>minteq.v4.dat</code> .	12	Test qualitative anchor-state robustness across the three distributed databases.

2.2.1. Independent Reduced Solver

Two Python 3.13.5 implementations provide checks independent of the PHREEQC engine. The gas–water benchmark uses nested bisection: the inner root gives hydrogen-ion activity at trial CO₂ pressure and prescribed alkalinity, and the outer root closes the finite carbon balance. The gas–water–calcite solver instead eliminates pressure explicitly as a function of hydrogen-ion activity on the no-solid branch. It retains that branch when calcium is absent or the calcite saturation ratio is at most $1 + 10^{-8}$. Above this threshold it solves the saturated branch, using the admissible positive root of a quadratic for free calcium and a scalar charge-balance root. Supplementary Methods S2.1–S2.3 give both algorithms, the quadratic coefficients, stable-root formula, brackets, stopping criteria and failure rules exactly as implemented. No coefficients are fitted to PHREEQC results.

The constants at 25 °C are $K_H^m = 0.0339$ mol kg^{−1} atm^{−1}, $K_1 = 10^{-6.35}$, $K_2 = 10^{-10.33}$, $K_w = 10^{-14}$ and $K_{sp,cal} = 10^{-8.48}$, with $R = 0.082057366080960$ L atm mol^{−1} K^{−1} in the executable scripts. These define an ideal-dilute benchmark rather than a replacement for database-specific activities and complexation [34–36]. The source code and comma-separated value (CSV) outputs are supplied in Supplementary Material S1. The role of this benchmark is strongest for conservation, branch logic and limiting behaviour; quantitative calcite results in this paper come from PHREEQC.

2.2.2. Parameter Grids

The two reduced grids are separate Cartesian products, all at 25 °C and $M_w = 1$ kg. The gas–water grid crosses $V_g \in \{0.01, 0.1, 1, 10\}$ L, $N_{C,in} \in \{0.1, 1, 10, 100\}$ mmol and $A_T \in \{0, 1, 10\}$ mmol kg^{−1}, giving $4 \times 4 \times 3 = 48$ cases. The calcite grid crosses $V_g \in \{0.1, 1, 10\}$ L, $N_{C,in} \in \{1, 10, 50\}$ mmol, $\Pi_A \in \{0, 0.5, 1, 2, 3, 4\}$ and $\Pi_{Ca} \in \{0, 0.25, 0.5, 1, 2\}$, giving $3 \times 3 \times 6 \times 5 = 270$ states. The distinct 95-case PHREEQC programme is enumerated

in Table 4; complete grids and units are repeated in Supplementary Methods S2.4. None is a statistical sample of natural systems.

M3A used a 10 mol CO₂ reservoir, more than two orders of magnitude larger than the modelled transfer, so it was non-limiting over the calculation but not mathematically infinite. M3B and M3C shared an initial 1.22327 L CO₂ volume at 1 atm and 298.15 K. This volume was chosen using $V = n_{\text{nom}}RT/P$ for a nominal 50.0000 mmol ideal gas. Peng–Robinson instead gives $n_0 = PV/(ZRT) = 50.2776769$ mmol ($Z \simeq 0.994477$). The difference is an initialisation offset, not carbon created during equilibration. All M3B–M3C closure denominators and phase fractions use n_0 , the actual initialised inventory. In these cases $N_{\text{C,in}}$ in the general balance denotes that inventory. The M4 and M5 anchor states were unbuffered gas–water partitioning (U: $\Pi_A = 0$, $\Pi_{\text{Ca}} = 0$), bicarbonate retention (B: $\Pi_A = 1$, $\Pi_{\text{Ca}} = 0$), calcite precipitation with gas-phase redistribution (R: $\Pi_A = 1$, $\Pi_{\text{Ca}} = 1$), and carbonate capture (C: $\Pi_A = 2$, $\Pi_{\text{Ca}} = 1$). M5 is a limited comparison of these four states rather than a full-grid thermodynamic-database uncertainty analysis.

All grids are controlled mechanism tests. Frequencies of regime occurrence have no probabilistic meaning, and the numerical boundaries should not be read as natural thresholds without site-specific chemistry and hydrology.

2.2.3. PHREEQC Implementation and Audit Criteria

The database-based equilibrium calculations used the PHREEQC release identified in the Introduction; the independent reduced calculations used the Python solvers described above. For reproducibility, all nine normalised inputs were rerun in a new Windows directory with the batch executable `phreeqc.exe` 3.8.6.17100. The exact Secure Hash Algorithm 256-bit (SHA-256) identities of `phreeqc.dat`, `wateq4f.dat`, and `minteq.v4.dat`, together with the complete clean-run outputs, tab-separated value (TSV) selected-output files, and manifest, are archived in the Supplementary Materials. The database required for each job was confirmed from the Database file: header written in its complete .pqo output. The 83 primary M0–M4 cases used `phreeqc.dat`; M5 additionally used the distributed `wateq4f.dat` and `minteq.v4.dat` files while preserving the same input definitions. Database choice is part of the thermodynamic model because the distributed files differ in species, reactions, activity treatments, and intended ranges of use [32,33]. The core finite-inventory runs used an initial solvent mass $M_{w,0} = 1$ kg with no carbon, a fixed-volume single-component CO₂ headspace, and a finite REACTION input.

The final PHREEQC solvent mass ranges from 0.99991750 to 1.00018016 kg across the archived cases. Aqueous inventories use the actual final mass through TOTMOLE, rather than multiplying final molalities by a fixed 1 kg. The reduced model retains a constant water-mass parameter. The proportional-scaling argument therefore concerns the prescribed initial system and all input amounts together.

Sodium without an added counter-anion represented NaOH-equivalent strong-base capacity; calcium was supplied as CaCl₂. In PHREEQC inputs written as `pH 7.0 charge`, the charge qualifier instructs the initial-solution calculation to adjust pH to achieve electroneutrality; 7.0 is therefore an initial estimate rather than a fixed pH constraint. These are synthetic capacity coordinates rather than reconstructions of a natural recharge composition. Calcite was initially absent and, where enabled, was specified as precipitation-only so that mineral carbon could be attributed to the imposed CO₂ input. Because gas-pressure functions are not reported identically across the three database files, M5 comparisons were restricted to pH, phase inventories, phase fractions, fugacity, saturation, and mass-balance diagnostics; all M5 gas fugacities were below 0.14 atm. The input value $pe = 4$ was retained only as a default PHREEQC initialisation. No redox-sensitive component total or redox reaction enters the declared carbon–calcium model, and pe was neither varied nor inter-

puted. Temperature calculations from 10 to 75 °C are treated as structural sensitivity tests within the selected databases; execution at a given temperature does not establish uniform thermodynamic accuracy across database files or their recommended domains of use.

SELECTED_OUTPUT and USER_PUNCH recorded pH, alkalinity, ionic strength, aqueous carbon, gas carbon, calcite inventory, calcium, carbon and calcium residuals, gas volume, calcite saturation, and CO₂ gas diagnostics. For Peng–Robinson calculations, partial pressure, fugacity coefficient, and fugacity were distinguished as

$$f_{\text{CO}_2} = \varphi_{\text{CO}_2} p_{\text{CO}_2}. \quad (22)$$

The PHREEQC Basic functions PR_P("CO2(g)") and PR_PHI("CO2(g)") were interpreted only for calculations containing an explicit GAS_PHASE; they report p_{CO_2} and φ_{CO_2} , whereas $10^{\text{SI}(\text{CO}_2(\text{g}))}$ reports fugacity, with SI denoting the gas saturation index [27,31]. In M3A, the EQUILIBRIUM_PHASES entry for CO₂(g), with target 0.0 and 10.0 mol available, imposed $\log_{10} p_{\text{CO}_2} = 0$, corresponding to a nominal target $p_{\text{CO}_2} = 1$ atm. Because M3A contains no explicit GAS_PHASE object, PR_P and PR_PHI were not interpreted; the archive reports the nominal pressure target and $f_{\text{CO}_2} = 10^{\text{SI}(\text{CO}_2(\text{g}))}$. For M3B and M3C, PR_P and PR_PHI provide the final gas-phase partial pressure and fugacity coefficient. Carbon closure for finite-inventory PHREEQC cases was evaluated as

$$r_{\text{C}}^{\text{PHR}} = \frac{N_{\text{C}}^{\text{aq}} + N_{\text{C}}^{\text{g}} + N_{\text{C}}^{\text{min}} - N_{\text{C},\text{in}}}{N_{\text{C},\text{in}}}, \quad (23)$$

where the superscript “PHR” denotes the PHREEQC calculation; the corresponding calcium residual was formed from aqueous and calcite calcium. Equation (23) was not applied to M3A because that case was coupled to a non-limiting reservoir and had no prescribed local finite $N_{\text{C},\text{in}}$; reservoir transfer and final aqueous inventory were reported instead. For the no-solid comparison, let superscripts PHR and red denote PHREEQC and the ideal-dilute benchmark. The reported discrepancies are

$$\begin{aligned} E_{\phi} &= |\phi_{\text{g}}^{\text{PHR}} - \phi_{\text{g}}^{\text{red}}|, & E_{\text{pH}} &= |\text{pH}^{\text{PHR}} - \text{pH}^{\text{red}}|, \\ E_f &= \frac{|f^{\text{PHR}} - p^{\text{red}}|}{\max(|p^{\text{red}}|, 10^{-30} \text{ atm})}. \end{aligned} \quad (24)$$

In the ideal gas benchmark $f^{\text{red}} = p^{\text{red}}$. Signed differences in archived tables use PHREEQC minus reduced; admission uses their absolute values. The archived screening limits are $E_{\phi} \leq 0.02$ and $E_{\text{pH}} \leq 0.15$, with $E_f \leq 0.10$ as a supplementary diagnostic when both fugacities are at least 10^{-7} atm. Two percentage points in a phase fraction and 0.15 pH units are conservative comparison limits, small relative to the main regime contrasts but allowing non-ideal activities and additional species omitted from the benchmark. The 10% fugacity limit is likewise a screening convention, not measured uncertainty or a fitted confidence interval. These comparisons do not replace the much tighter mass-balance acceptance tests and are not imposed as a universal agreement requirement on the calcite branch. Below 10^{-7} atm, absolute fugacity differences and signed logarithmic ratios are reported together with the relative discrepancies, phase fractions and pH. Relative differences can be large when the reference fugacity is small even where the absolute amount of gas carbon is negligible; this does not establish numerical round-off as their cause. The threshold is an operational reporting convention, not a physical phase boundary. Definitions and executable checks are provided in Supplementary Methods S2.5.

Raw PR_P and PR_PHI values were retained only for traceability when gas inventory approached zero. In the raw M0A–M1 selected-output files, the legacy heading

pCO2_atm stores $10^{SI(\text{CO}_2(\text{g}))}$ and therefore denotes fugacity rather than Peng–Robinson partial pressure; raw files are preserved unchanged, while derived audit tables use an explicit fugacity label.

Every input, complete text output, selected-output table, provenance record, and audit table for M0A–M5 is retained in the Supplementary Materials. The S2 verifier reconstructs finite carbon balances from the raw phase amounts, recognises both mineral-inventory column names, and checks exported fractions against those amounts. Elemental checks use the solvent mass of each initial and final state. Missing or non-finite required values fail explicitly; exported residuals are not used as substitutes for these checks. Supplementary Methods S2.11 document the verification and the historical M1 volume-column label.

3. Results

3.1. Numerical Admission and Reproduction Tests

The independent reduced calculations passed all admission tests. The maximum absolute relative carbon residual was 9.37×10^{-10} in the 48-case gas–water benchmark and 4.34×10^{-16} in the 270-state calcite grid; the global maximum therefore remained more than one order of magnitude below the 10^{-8} tolerance. The maximum absolute charge residual in the calcite grid was $9.99 \times 10^{-15} \text{ mol kg}^{-1}$. The executed PHREEQC programme contained 95 deterministic equilibrium cases plus the M0A smoke test. Across all finite-inventory M0–M5 cases, the largest absolute relative carbon residual was 2.76×10^{-11} ; M3A was excluded because its local carbon inventory was not prescribed, and its 34.005 mmol aqueous inventory was supplied by the non-limiting reservoir. Calcium closure in all calcium-bearing M2, M4, and M5 cases was exact to the precision written in the selected output, and no negative phase inventory or unintended calcite dissolution occurred.

The 16 M0 cases passed the archived benchmark tolerances. The maximum absolute difference between PHREEQC and the reduced solution was 0.002433 for ϕ_g , 0.002505 pH units, and 1.03% for CO_2 fugacity. In M1, the maximum $|\Delta\phi_g|$ was 0.002923 and the maximum $|\Delta\text{pH}|$ was 0.1324. All 12 comparisons for which both calculations yielded $f_{\text{CO}_2} \geq 10^{-7} \text{ atm}$ ($\Pi_A \leq 2$) had relative fugacity differences no greater than 0.0940. In the six $\Pi_A = 3\text{--}4$ cases, PHREEQC fugacity was 2.54×10^{-9} to $1.01 \times 10^{-8} \text{ atm}$. The relative differences were approximately 24–26%, although the maximum absolute difference was only $3.19 \times 10^{-9} \text{ atm}$; the signed $\log_{10}$ fugacity ratios ranged from -0.1335 to -0.1191 . These are non-zero model discrepancies at very small fugacities, not evidence of a mass-balance failure or a demonstrated floating-point instability. They remain explicitly reported but are not used as standalone admission failures below the reporting threshold; phase-fraction, pH and conservation checks are assessed separately. A strict clean rerun completed all nine jobs with PHREEQC 3.8.6-17100 and the intended database in every case. The raw-table verifier accepts all 96 archived final states, including the separately treated reservoir case, and rejects the seven intentionally corrupted M2 test tables. These tests operate on disposable copies and do not change the numerical evidence. Detailed comparisons, identifiers, checksums and verification outputs are provided in Supplementary Material S2.

3.2. Headspace Geometry Controls Gas Expression

The reduced gas–water solution and the 16 PHREEQC M0 anchor points are compared in Figure 1. Across inputs from 0.1 to 100 mmol, a 0.01 L headspace retained only 0.0111–0.0122 of the carbon as gas, whereas a 10 L headspace retained 0.9062–0.9228. The 0.1 and 1 L cases occupied intermediate ranges of 0.1007–0.1098 and 0.5217–0.5483, respectively. For a 10 mmol input, ϕ_g increased from 0.01182 at 0.01 L to 0.92145 at 10 L.

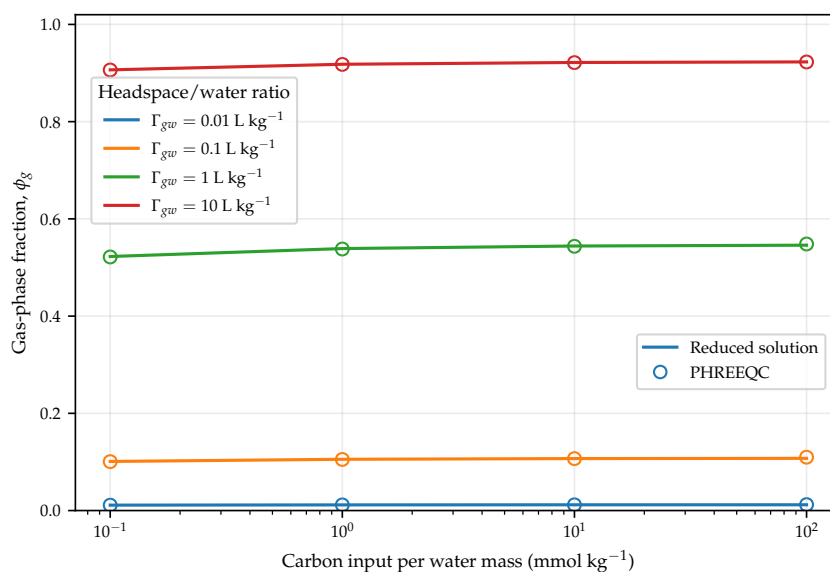


Figure 1. Gas-phase fraction of a finite CO₂-derived carbon input in an unbuffered closed gas–water system at 25 °C. The reduced model uses constant $M_w = 1$ kg; PHREEQC starts from $M_{w,0} = 1$ kg. Lines are the independent reduced solution; open circles are PHREEQC (pH–redox–equilibrium in C) M0 results. The legend reports headspace volume per kilogram of the prescribed water basis, and the abscissa reports carbon input on the same basis. For PHREEQC this normalisation uses $M_{w,0}$. Transfer to another water mass requires proportional scaling of all extensive quantities, as specified in Equation (13).

The same prescribed input can therefore be predominantly aqueous in a water-rich, small-headspace domain and predominantly gaseous in a large connected void. Within each headspace series, the effect of input magnitude is weak relative to the geometric capacity contrast over the tested range.

3.3. Neutralisation Capacity Suppresses Gas Expression

M1 isolated NaOH-equivalent strong-base capacity in the absence of calcium and solids (Figure 2). For $N_{C,in} = 10$ mmol and $V_g = 1$ L, the unbuffered state had $\phi_g = 0.54355$. At $\Pi_A = 0.5$, $\phi_g = 0.27309$; at $\Pi_A = 1$, it fell to 0.008915 while $\phi_{aq} = 0.991085$ and pH was 8.421. At $\Pi_A = 2$, $\phi_g = 2.74 \times 10^{-6}$ and more than 0.999997 of the input was aqueous. The same regime sequence occurred for 0.1 and 10 L headspaces: geometry remained important at low Π_A , whereas chemical capacity dominated as the one- and two-equivalent transitions were approached.

At $\Pi_A \simeq 1$, bicarbonate accounted for approximately 95–97% of aqueous carbon across the three headspaces. Near $\Pi_A = 2$, carbonate became the dominant aqueous species. These are stoichiometric screening transitions in the synthetic strong-ion system, not universal pH thresholds for natural waters.

3.4. Equilibrium Calcite Precipitation Capacity Depends on Neutralisation and Calcium Supply

M2 introduced calcium independently and enabled precipitation-only calcite. No calcite precipitated at $\Pi_A = 0$, even when $\Pi_{Ca} = 2$, because the acidic solution did not attain calcite saturation. At $\Pi_A = 0.5$, precipitation remained weak and required relatively high calcium capacity. At $\Pi_A = 1$, increasing Π_{Ca} from 0 to 2 increased the equilibrium calcite carbon fraction from 0 to 0.33825. At $\Pi_A = 2$, $\phi_{min} = 0.98333$ for $\Pi_{Ca} = 1$ and 0.99772 for $\Pi_{Ca} = 2$. Higher-neutralisation end members approached the strict stoichiometric ceiling $\min(1, \Pi_{Ca})$ (Figure 3).

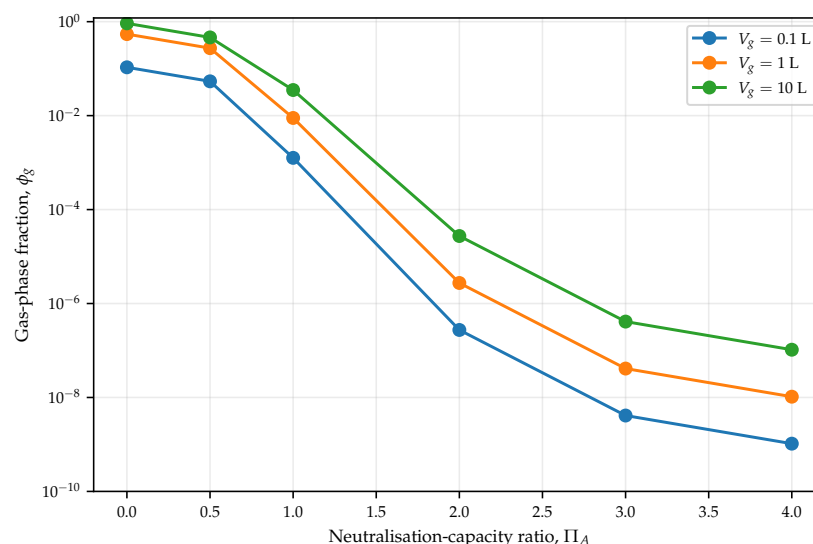


Figure 2. PHREEQC gas-phase fraction as a function of NaOH-equivalent capacity ratio for a 10 mmol input, an initial water mass of 1 kg, and three closed headspace volumes. The logarithmic ordinate resolves the bicarbonate- and carbonate-dominated limits.

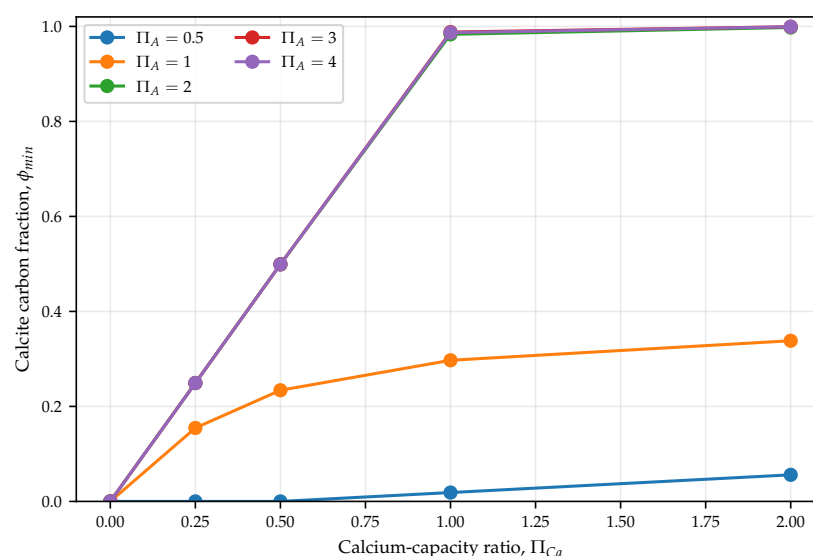


Figure 3. PHREEQC calcite carbon fraction as a function of calcium-capacity ratio for a 10 mmol input, a 1 L headspace, and selected NaOH-equivalent capacity ratios. Calcite was initially absent and precipitation-only.

The database calculation respects the strict mass-balance bound in Equation (19) and the conditional alkaline screening relation in Equation (20). Near $\Pi_A = 1$, the quantitative extent of precipitation is lower than in the ideal reduced model. The difference reflects the aggregate effects of database-specific equilibrium constants, non-ideal activities, additional aqueous species and complexes, and gas non-ideality; the maximum ionic strength in the PHREEQC M2 grid was $0.06766\text{ mol kg}^{-1}$. The reduced solver is therefore an independent mechanistic benchmark, not a quantitative substitute for the database calculation.

3.5. Near the Bicarbonate Transition, Equilibrium Calcite Precipitation Redistributes Mobile Carbon Towards the Gas Phase

The bicarbonate-rich $\Pi_A = 1$ series provides the most demanding verification case (Figure 4). Without calcium, $\phi_g = 0.008915$ and $\phi_{aq} = 0.991085$. At $\Pi_{Ca} = 0.25$, 0.15468 of the input precipitated as calcite and the gas fraction rose to 0.08527. At $\Pi_{Ca} = 1$, the

phase fractions were $(\phi_g, \phi_{aq}, \phi_{min}) = (0.16289, 0.54000, 0.29711)$; at $\Pi_{Ca} = 2$, they were $(0.18572, 0.47603, 0.33825)$. The gas fraction thus increased by a factor of 20.8 relative to the no-calcium state while total carbon remained closed. These values describe an equilibrium capacity state, not a precipitation rate or elapsed reaction time.

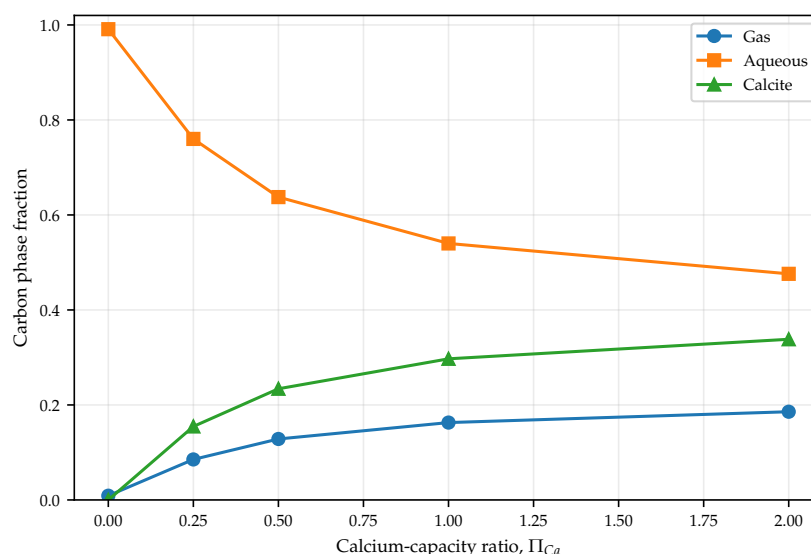


Figure 4. PHREEQC redistribution of a 10 mmol carbon input among gas, aqueous species, and calcite at $\Pi_A = 1$ as calcium capacity increases. The simultaneous increase in gas and calcite fractions is a redistribution of conserved carbon, not carbon production.

The reference for the redistribution ratios is the no-calcium case $\Pi_{Ca} = 0$ at $\Pi_A = 1$, $N_{C,in} = 10$ mmol, $V_g = 1$ L, initial $M_{w,0} = 1$ kg and 25 °C. With $\Delta N_C^\alpha = N_C^\alpha(\Pi_{Ca}) - N_C^\alpha(0)$ for phase α , the precipitating cases give

$$\frac{\Delta N_C^{aq}}{\Delta N_C^{min}} \simeq -1.49 \text{ to } -1.52, \quad \frac{\Delta N_C^g}{\Delta N_C^{min}} \simeq 0.49 \text{ to } 0.52. \quad (25)$$

Here $\Delta N_C^{min} = N_C^{min}(\Pi_{Ca})$ because the reference contains no calcite. The ratios are between equilibrium scenarios with different CaCl_2 inputs, not time derivatives or reaction yields at fixed solution composition. Changing calcium also changes ionic strength and complexation in PHREEQC. Their sum with the unit mineral increment is zero by carbon conservation. The bicarbonate reaction in Equation (21) explains the direction of redistribution, but not a universal numerical gas yield. At $\Pi_A \geq 2$, where calcium was supplied, capture approached the applicable stoichiometric ceiling $\min(1, \Pi_{Ca})$, with negligible gas expression. Supplementary Methods S2.7 tabulate the reference and all four ratios.

Representative PHREEQC states are listed in Table 5.

Table 5. Representative PHREEQC states for $N_{C,in} = 10$ mmol, $V_g = 1$ L, initial $M_{w,0} = 1$ kg, and 25 °C. f_{CO_2} is calculated from the gas saturation index.

Π_A	Π_{Ca}	pH	f_{CO_2} (atm)	ϕ_g	ϕ_{aq}	ϕ_{min}
0	0	4.348	1.328×10^{-1}	0.5436	0.4564	0.0000
1	0	8.421	2.181×10^{-3}	0.00892	0.99108	0.0000
1	0.25	7.286	2.086×10^{-2}	0.08527	0.76006	0.15468
1	0.5	6.987	3.140×10^{-2}	0.12838	0.63759	0.23403
1	1	6.750	3.984×10^{-2}	0.16289	0.54000	0.29711
1	2	6.570	4.541×10^{-2}	0.18572	0.47603	0.33825
2	1	9.936	6.671×10^{-7}	2.73×10^{-6}	0.01667	0.98333

3.6. A Fixed Gas Pressure Is Compatible with Many Total Inventories

The reduced forward calculation in Figure 5 fixes $p_{\text{CO}_2} = 10^{-2}$ atm and calculates the total carbon inventory required for equilibrium. For $V_g = 1$ L, increasing alkalinity from 0 to 1, 10, and 50 mmol kg⁻¹ increased the compatible total inventory from 0.760 to 1.748, 10.717, and 50.017 mmol, respectively. The gas inventory remained 0.409 mmol because pressure and volume were fixed; the additional carbon was stored in aqueous species.

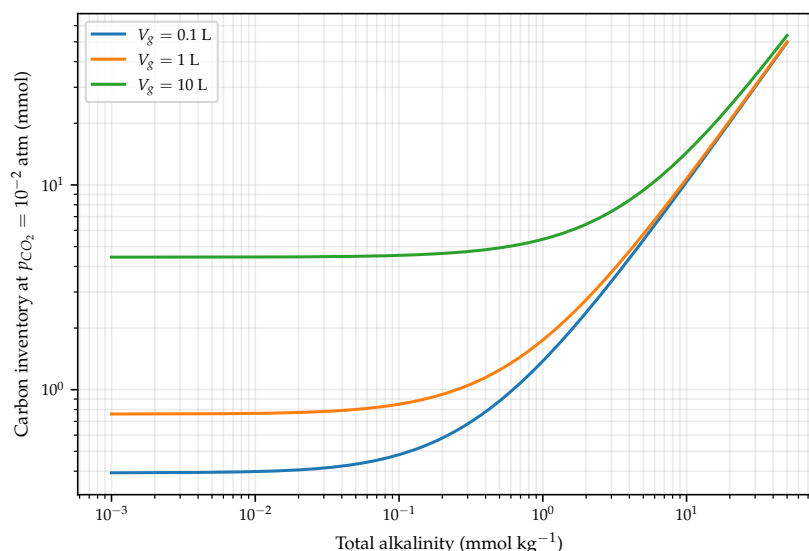


Figure 5. Reduced-model total carbon inventory compatible with fixed $p_{\text{CO}_2} = 10^{-2}$ atm as a function of alkalinity and headspace volume. A gas-phase pressure observation alone does not uniquely determine the total inventory. The logarithmic axis excludes $A_T = 0$: its compatible total inventories are 0.392, 0.760 and 4.439 mmol for $V_g = 0.1$, 1 and 10 L, respectively (1 kg water). Those zero-alkalinity states are retained in the tabulated data.

The inference is one-way. Given geometry, chemistry, and boundary conditions, the forward model determines phase partitioning. Given only a gas pressure, the inverse problem remains non-unique because effective water-to-gas geometry, alkalinity, temperature, and mineral reaction can compensate one another.

3.7. Dominant-Phase Map at 25 °C

Figure 6 classifies the largest PHREEQC phase fraction on the M2 grid. Gas dominance is restricted to the unbuffered row. Aqueous dominance occupies sub-stoichiometric neutralisation states and calcium-limited portions of the grid. Calcite becomes dominant only when both neutralisation and calcium capacities are sufficiently large. To quantify near-degeneracy, define the dominance margin as

$$\Delta_{\text{dom}} = \phi_{\text{largest}} - \phi_{\text{second-largest}} \quad (26)$$

A reporting margin of 0.002 separates unqualified dominant-phase labels from near ties. The three cells at $\Pi_{Ca} = 0.5$, $\Pi_A \geq 2$ are labelled “NT: aqueous–calcite near tie” (NT denotes near tie) rather than assigned unqualified aqueous dominance. Their margins are 0.001608, 0.001649 and 0.001757. This is a descriptive threshold, not a new phase, an uncertainty estimate or a thermodynamic boundary.

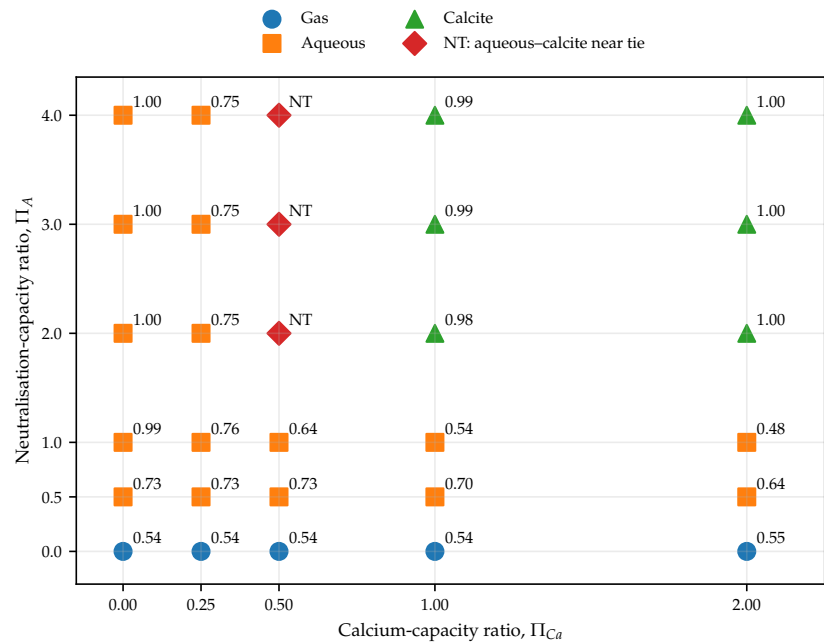


Figure 6. Dominant PHREEQC carbon phase at 25 °C for a 10 mmol input, an initial water mass of 1 kg, and a 1 L single-component CO₂ headspace. Marker shape identifies the largest phase fraction only where the dominance margin in Equation (26) is at least 0.002; annotations report that fraction. Diamonds labelled NT (near tie) mark the three aqueous–calcite near ties at $\Pi_{Ca} = 0.5$, $\Pi_A \geq 2$. No unqualified dominant phase is assigned to them. This discrete synthetic grid is not a universal phase diagram.

3.8. Gas Boundary Conditions Change Both Phase Partitioning and Budget Meaning

M3 compared three single-component CO₂ systems at 25 °C (Table 6; Figure 7). The non-limiting nominal fixed- p_{CO_2} reservoir and the finite fixed-total-pressure bubble reached aqueous states indistinguishable at the reported precision: pH 3.911 and $N_C^{aq} = 34.005$ mmol. Their carbon budgets were nevertheless different. M3A imported that aqueous carbon from a reservoir that remained non-limiting over the transfer, whereas M3B conserved a finite 50.2777 mmol inventory and retained 16.272 mmol in a pure-CO₂ bubble that contracted to 0.3959 L. M3C conserved the same finite pure-CO₂ inventory at fixed volume. Its final state contained 20.347 mmol aqueous carbon and 29.931 mmol gas carbon, with $p_{CO_2} = 0.59666$ atm.

Table 6. Boundary-condition outcomes at 25 °C. The M3A pressure is an imposed nominal target; M3B–M3C give final pressures and share an actual 50.2777 mmol inventory. Gas moles, volume and coefficient are not assigned to M3A, which has no explicit gas-phase object.

Case	pH	N_C^{aq} (mmol)	N_C^g (mmol)	p_{CO_2} (atm)	f_{CO_2} (atm)	φ_{CO_2}	V_g (L)
M3A	3.911	34.005	–	1.000 target	0.994472	–	–
M3B	3.911	34.005	16.272	1.000000	0.994472	0.994472	0.395914
M3C	4.023	20.347	29.931	0.596658	0.594689	0.996700	1.223270

M3A and M3B are nominally pressure-matched at 1 atm, not inventory-matched. Their CO₂ fugacities also agree at the reported precision (0.994472 atm) under the shared temperature, composition and thermodynamic formulation. This agreement is a calculated consequence, not an independently imposed fugacity-matching experiment. For M3A only the nominal target and $10^{SI(CO_2(g))}$ are interpreted; no local bubble or gas-volume estimate is inferred. M3B and M3C, by contrast, are inventory-matched: their different final pressures, fugacities and partitions in Table 6.

The 0.55535% offset from the nominal 50 mmol is explained by the non-ideal initialisation in Section 2.2.2. The archived sum-of-phases versus SYS("C") diagnostic remains below 2.0×10^{-13} . A separate check reconstructs the common initial inventory as $N_{C,0} = V_{g,0}/V_m$, using $V_{g,0} = 1.223270$ L and the M3B gas molar volume $V_m = 24.3302808295$ L mol⁻¹. Because the initial and final M3B gas have the same temperature, pressure and pure-CO₂ composition, this reconstruction is independent of the final phase-inventory sum. It gives $N_{C,0} = 50.277676964452$ mmol and relative residuals below 1.0×10^{-12} for both M3B and M3C. Both diagnostics are reported separately in Supplementary Methods S2.6. Neither the offset nor the non-limiting-reservoir calculation is counted as a finite mass-balance failure.

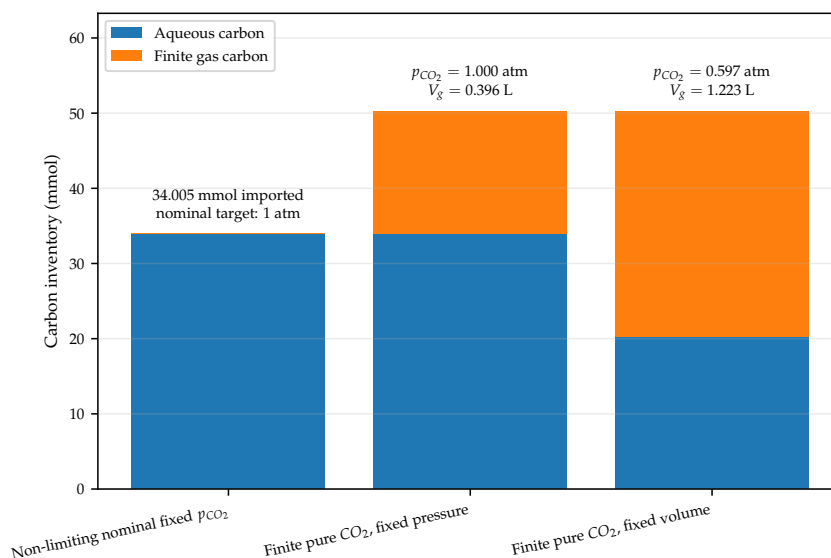


Figure 7. Carbon inventories for three single-component CO₂ boundary-condition end members at 25 °C. M3A uses a non-limiting reservoir with nominal target $p_{\text{CO}_2} = 1$ atm; M3B is a finite pure-CO₂ bubble at fixed total pressure; M3C is a finite pure-CO₂ headspace at fixed volume. M3B and M3C start from the same actual 50.2777 mmol inventory. For M3A, the archive reports the nominal target and $f_{\text{CO}_2} = 10^{SI(\text{CO}_2(\text{g}))}$; PR_P and PR_PHI diagnostics are reported only for M3B and M3C, which contain explicit GAS_PHASE objects. SI denotes the gas saturation index.

Thus, aqueous states indistinguishable at the reported precision do not imply identical carbon budgets, and identical finite inventories do not imply identical phase partitioning. The physical meaning of the gas constraint must be stated before gas or water observations are used to infer inventory.

3.9. Temperature Preserves Some Regimes and Moves Others Across Phase Boundaries

M4 tested four representative states from 10 to 75 °C (Figure 8). In the unbuffered *U* state, ϕ_g increased from 0.44293 at 10 °C to 0.72100 at 75 °C. The dominant phase changed from aqueous at 10 °C to gas at 25 °C and above. In the bicarbonate-retention *B* state, the aqueous fraction remained above 0.980 throughout, although ϕ_g increased from 0.00622 to 0.01991.

The precipitation-coupled *R* state showed the strongest redistribution. Between 10 and 75 °C, ϕ_g increased from 0.11836 to 0.29769 and ϕ_{min} from 0.26476 to 0.41037, while ϕ_{aq} fell from 0.61688 to 0.29194. The dominant phase was aqueous at 10–50 °C and calcite at 75 °C. The carbonate-capture *C* state remained calcite-dominant: calcite retained 0.9811–0.9845 of the input across the full temperature range. Its gas fraction increased from 6.88×10^{-7} to 1.07×10^{-4} but remained negligible in absolute terms.

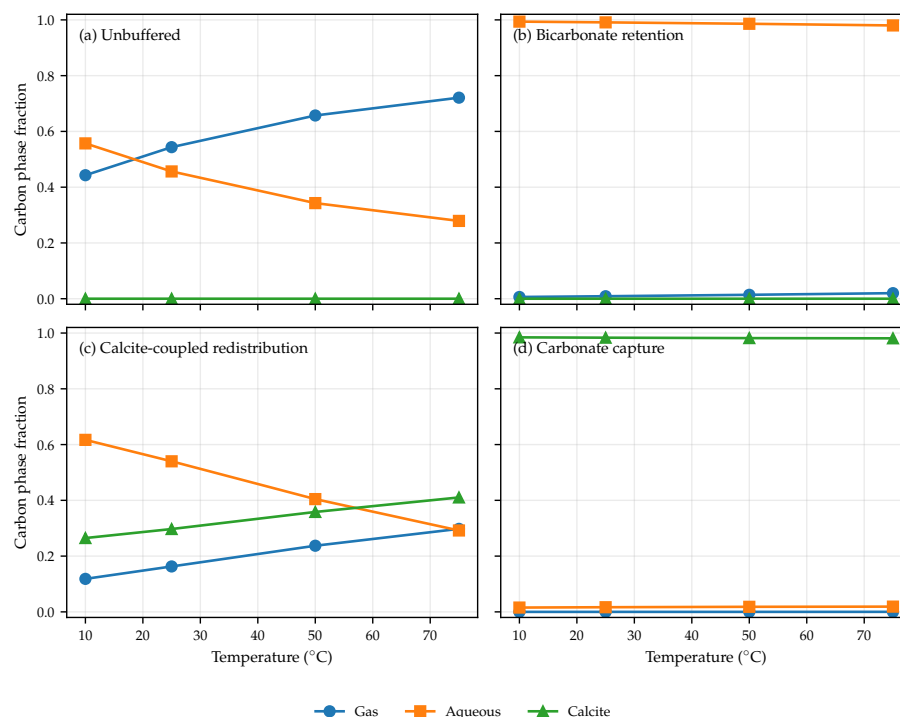


Figure 8. PHREEQC temperature comparison for four representative regimes: (a) *U*, unbuffered gas–water partitioning; (b) *B*, bicarbonate retention without solids; (c) *R*, calcite-coupled gas-phase redistribution; and (d) *C*, carbonate capture. Each system starts with 1 kg water and receives 10 mmol carbon in a 1 L fixed-volume headspace.

Temperature is therefore not a uniform multiplicative correction. It leaves the aqueous-dominant *B* and calcite-dominant *C* classifications intact over the tested interval, but it can move the *U* and *R* states across dominant-phase boundaries. The 25 °C regime map in Figure 6 is consequently a conditional slice rather than a universal phase diagram.

3.10. The Four Anchor States Retain Their Dominant Phases Across the Tested Databases

M5 repeated the *U*, *B*, *R*, and *C* states at 25 °C with `phreeqc.dat`, `wateq4f.dat`, and `minteq.v4.dat` (Figure 9). The dominant phase was unchanged in every comparison: *U* remained gas-dominant, *B* aqueous-dominant, *R* an aqueous-dominant mixed state, and *C* calcite-dominant. All 12 carbon balances closed within 3.17×10^{-12} relative error, and calcium closure was exact to the precision reported for the calcium-bearing states.

The numerical dispersion was smallest in the strongly separated end members and largest in the transition state. Across databases, the gas fraction ranged from 0.54203 to 0.54355 in *U* and from 2.705×10^{-6} to 2.727×10^{-6} in *C*. In *B*, ϕ_g ranged from 0.008915 to 0.009464 and pH from 8.393 to 8.421. The *R* state showed the largest spread: $\phi_g = 0.15641$ – 0.16289 , $\phi_{aq} = 0.54000$ – 0.55712 , and $\phi_{min} = 0.28647$ – 0.29711 . The maximum cross-database range of any phase fraction was therefore 0.01712, associated with the aqueous fraction of *R*.

The test supports a qualitative robustness statement, not database independence of the full parameter surface. All primary M0–M4 grids and numerical phase boundaries remain based on `phreeqc.dat`; M5 establishes only that the four selected anchor-state classifications were unchanged under the tested database substitutions.

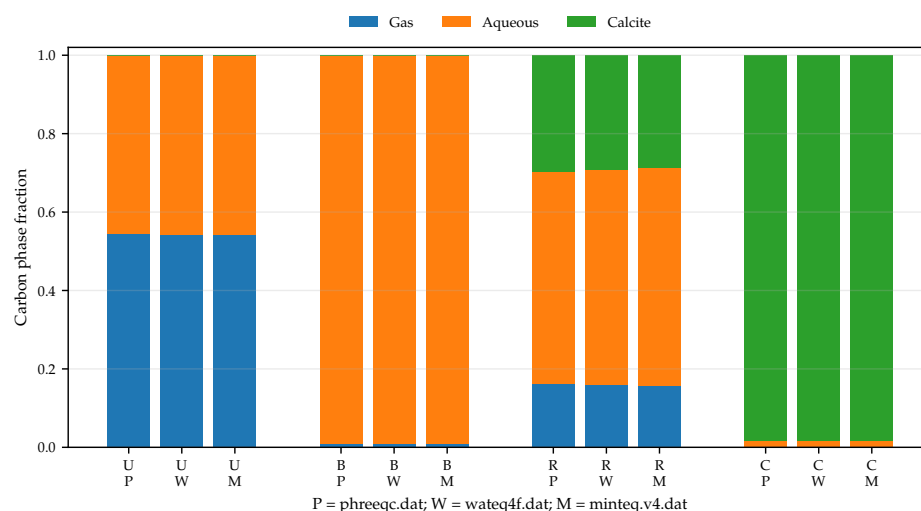


Figure 9. Phase fractions of four 25 °C anchor states calculated with phreeqc.dat, wateq4f.dat, and minteq.v4.dat. P, W, and M denote the three files, respectively. The comparison tests only these four states; it does not establish database independence of the full parameter surface or of the transition boundaries.

4. Discussion

4.1. What a Gas-Only Observation Does and Does Not Constrain

The calculations distinguish a forward problem from an inverse interpretation. With specified geometry, chemical inputs and gas constraint, the forward model calculates the equilibrium compartments. Figure 5 provides a direct counterexample to a unique gas-pressure-to-inventory conversion. At $p_{\text{CO}_2} = 0.01$ atm, $V_g = 1$ L, $M_w = 1$ kg and 25 °C, the same approximately 0.409 mmol gas inventory is compatible with total carbon inventories of approximately 0.760 and 50.017 mmol as alkalinity changes from 0 to 50 mmol kg⁻¹. The approximately 66-fold contrast concerns equilibrium states with the same specified gas observation. It demonstrates conditional non-uniqueness when alkalinity is unconstrained. M3 separately illustrates how gas boundary conditions change the meaning of the budget.

A phase fraction must also be distinguished from a gas observation: ϕ_g is a normalised accounting output that already requires the total inventory in its denominator. A pressure or concentration measurement alone need not provide that denominator.

This result is conditional, not a universal theorem that every natural carbon budget is unidentifiable. Independent measurements or defensible bounds may restrict the compatible systems. Conversely, a list of measured variables does not guarantee uniqueness for an arbitrary reacting and flowing aquifer. The useful question is which alternative budgets remain compatible with the observations and model assumptions. The benchmark supplies controlled examples for testing that question.

Separating carbon compartments is useful outside volcanic settings too. Jiang et al. [37] distinguished inorganic and organic carbon stocks in the Yellow River Delta under land-use change and tidal-barrier construction during 1980–2020. Those stocks followed different trajectories; treating them as a single pool would conceal that distinction. This is a conceptual parallel in carbon accounting, not evidence for the gas–water–calcite mechanism: the present calculations contain no organic carbon or landscape model.

4.2. Contribution Relative to Established Equilibrium Models

Published applications of PHREEQC address basalt carbonation and geothermal gas–water–rock interaction [28–30]. Closed-system dissolution and finite-headspace effects also have established analytical treatments [24–26], and the bicarbonate–calcite–CO₂ reaction is

known [22,23]. These established process descriptions supply the thermodynamic basis of the present comparison.

The underlying carbonate equilibria are standard; the added value is their controlled comparison under explicit inventory accounting. The study holds the carbon input finite, reports each final compartment, checks limiting behaviour with independent code, and separates pressure matching from inventory matching. For example, the same initial inventory gives $\phi_g = 0.32365$ in the finite fixed-pressure case and 0.59532 at fixed volume. A pressure-constrained external reservoir can instead reproduce the aqueous state without specifying the local finite inventory. These are different physical questions, not interchangeable software options. The benefit is an auditable test of which inventories remain compatible with a specified observation and set of physical constraints.

4.3. Quaternary Carbon Budgets and Dated Archives

A specifically Quaternary application concerns the reconstruction of past carbon transfer from preserved deposits. Mancini et al. [4] used travertine masses to evaluate geogenic CO₂ release. The Tivoli study [5] related depositional units to degassing and explicitly recognised lower-bound effects from incomplete preservation, pre-emergence gas loss and the sampled exposure. The finite-inventory benchmark complements these lower-bound reconstructions by isolating the relation between the sampled compartment and the other carbon pools.

The temporal context also helps separate supply changes from hydrological controls. In the 150–30 ka (thousands of years ago) Lapis Tiburtinus succession, isotope interpretations link climate and groundwater-level variation to degassing conditions [6]. Semproniano provides a separate dated record of episodic Pleistocene fluid discharge [7]. These examples motivate a distinction between changes in source supply and changes in hydrology, partitioning or preservation. They provide context for the inference problem rather than validation data or a calculation of climatic forcing. Table 7 states what is observed and what the present benchmark can legitimately contribute.

Table 7. Targeted Quaternary examples and the boundary of the present interpretation. Published site results are contextual examples, not validation data or quantities recalculated here. ka denotes thousands of years ago; the age span is written from older to younger.

Example	Observation and Inference	Relevant Additional Constraints
Central Italian travertines [4,5]	Deposit mass, composition and chronology used to infer past geogenic CO ₂ release.	Deposition-to-degassing relation, dissolved export, pre-spring gas loss, erosion and temporal coverage. Equilibrium fractions are not direct palaeoflux conversion factors.
Lapis Tiburtinus, 150–30 ka [6]	Dated carbonate isotope record interpreted with climate and groundwater variation.	Hydrological state and isotope processes in addition to phase accounting. No isotope or climate response is simulated here.
Semproniano, Pleistocene [7]	Dated carbonate vein and travertine record of repeated fluid discharge.	Discharge history, growth duration and preservation; a static inventory does not specify the rate or duration of an event.

The distinction can be written as an accounting requirement, not as a new simulation. For a selected natural control volume, let $N_C(t)$ be its instantaneous carbon stock and let F_{in} and $F_{out,\alpha}$ be carbon rates across its boundary. Then

$$\frac{dN_C}{dt} = F_{in} - \sum_{\alpha} F_{out,\alpha}. \quad (27)$$

Internal gas–water–mineral transfers cancel in this total balance. A preserved deposit, however, records an integral of deposition modified by dissolution, erosion and sampling.

The equilibrium fractions in Equation (2) supply neither those rates nor that preservation history. Likewise, dissolved export requires water discharge and carbon concentration; a snapshot DIC inventory is not its time integral. The system boundary determines whether a mineral deposit is retained stock or exported carbon, and it must not be counted twice.

Consequently, the approximately 0.49–0.52 gas-carbon increase per mole of calcite in our closed-headspace scenario comparison is not a replacement for the bicarbonate reaction's one-to-one CO₂–calcite stoichiometry used in an open degassing reconstruction. The remaining molecular CO₂ can stay dissolved in our closed system, and the scenarios also differ in CaCl₂ supply. A palaeobudget needs a transport and preservation model in addition to the equilibrium step. The defensible use of this study is to identify which unobserved compartments and boundary conditions require constraints before such a reconstruction is interpreted as a total-system budget.

4.4. Practical Use and Independent Constraints

A weak local gas-phase signal alone need not imply a small total carbon inventory. The calculations do not turn that statement into a field-flux estimate. Groundwater studies provide independent evidence of dissolved carbon transfer [10,15,16]; the present model instead helps formulate alternative equilibrium explanations for a phase-selective signal. Table 8 is a practical checklist, not a proven minimal or sufficient measurement set.

Table 8. Information to consider when moving from a phase-selective observation to a site-specific carbon budget. Sufficiency must be tested for the chosen model and control volume.

Observation	Quantity Constrained	Complementary Information
Gas pressure, concentration or composition	Gas-phase state; not a total inventory or a flux by itself	Connected gas/water geometry, gas composition, temperature, openness, and a transport relation if flux is the target.
Spring or aquifer chemistry	Dissolved inorganic carbon (DIC) and aqueous speciation	Alkalinity, pH, major ions, temperature, mixing and source attribution. Discharge and duration are needed for exported amounts.
Dated travertine or calcite	Preserved mineral carbon and depositional chronology	Calcium/alkalinity supply, growth and dissolution, depositional gaps, erosion and pre-depositional gas loss.
Integrated observations	Constraints on several compartments	A common spatial boundary and time interval, uncertainty bounds, and tests of remaining model non-uniqueness.

A practical sequence is to define the target quantity and its spatial and temporal support, identify the sampled phases, constrain chemistry and plausible gas boundaries, and test the remaining alternatives. Where a parameter cannot be measured directly, a justified range can be propagated rather than replaced by a universal conversion factor. The benchmark provides test cases for the equilibrium component of that workflow. It does not demonstrate that every field inverse problem can be solved.

A reduced soil-gas source–transport–observation analysis likewise distinguishes source-related sensitivity from water-state, transport and measurement-support effects [38]. At the station scale, a frequency-selective diagnostic combines flux with paired-depth pressure and temperature measurements to examine environmental and acquisition effects [39]. These complementary synthetic studies address transport and observation design, rather than the finite-inventory equilibrium closure examined here. Source attribution may additionally require isotopes, radiocarbon, helium or inverse geochemical balances [16,40].

4.5. Robustness and Limits of Transfer

Numerical closure, benchmark agreement and field validity are different tests. Small conservation residuals verify accounting but do not eliminate uncertainty in activities, database constants or natural geometry. The reduced calcite solver is not quantitatively interchangeable with PHREEQC: the archived M2 comparisons quantify their differences, while all published mineral fractions and phase labels are PHREEQC outputs. The three near-tie cells are explicitly distinguished from well-separated dominant states.

The temperature experiments combine solubility, acid dissociation, mineral equilibrium, activities and gas non-ideality. The four-state database comparison supports only local persistence of phase classifications, not uncertainty bounds for the complete grid [32,33,41]. The reduced grids fix $M_w = 1$ kg; PHREEQC specifies $M_{w,0} = 1$ kg and uses its calculated final solvent mass. Equation (13) explains proportional rescaling of the prescribed system. The maximum M2 ionic strength is $0.06766 \text{ mol kg}^{-1}$. None of these checks establishes equal thermodynamic accuracy across all temperatures or databases.

The synthetic system contains initially carbon-free water, NaOH-equivalent base, CaCl_2 , pure CO_2 gas and initially absent precipitation-only calcite. It excludes other solids, wet gas mixtures, high salinity, redox, organic or microbial carbon, boiling, nucleation delays, kinetics and reactive transport. Carbon origin is prescribed, not inferred. Calcite amounts are equilibrium capacities conditional on an accessible precipitation pathway, not field growth predictions. Time-dependent hydrothermal storage introduces a separate inference problem. Reduced integer–fractional dynamics and causal Volterra memory-kernel formulations describe delayed transfer and inherited memory over finite observation windows [42,43]. Those processes are outside the present static equilibrium calculation. These boundaries define where the benchmark ends and a site-specific Quaternary reconstruction must begin.

5. Conclusions

A gas-phase observation and a total carbon budget are not interchangeable. In the tested synthetic systems, the same finite carbon input produced very different phase partitions as gas–water geometry, strong-base capacity, calcium supply and the gas constraint changed. For 10 mmol carbon in 1 kg water at 25°C , geometry alone shifted the gas fraction from 0.0118 to 0.9214. Near the bicarbonate transition, calcium addition could increase both calcite and residual gas; under more alkaline conditions with sufficient calcium, calcite retained more than 0.98 of the input. Pressure-matched and inventory-matched comparisons answered different budget questions even when aqueous states were indistinguishable at the reported precision.

The direct inverse counterexample holds gas pressure and volume fixed while compatible total inventories differ by approximately 66-fold over the tested alkalinity range. This is a conditional limitation on inference from a single observed phase. Independent reduced calculations, phase-resolved mass balances and archived PHREEQC outputs make the comparison reproducible. Temperature and the limited database substitutions provide bounded sensitivity checks, and near-tie phase classifications are reported explicitly.

For Quaternary research, the practical value is to separate what a gas measurement, groundwater sample or dated carbonate archive actually constrains. The calculations offer equilibrium benchmarks and identify missing chemical and boundary-condition information. Reconstruction of past release additionally requires chronology, water throughput, source attribution and preservation. We neither recalculate published palaeofluxes nor infer climatic forcing. Keeping these quantities distinct makes phase accounting useful within, rather than a substitute for, site-specific carbon-budget reconstruction.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/quat9050070/s1>. Supplementary Material S1 contains the numerical reproducibility package publicly archived in Zenodo at <https://doi.org/10.5281/zenodo.21788075> (archive verified on 26 September 2026): canonical PHREEQC inputs and outputs, database/executable identities, independent solvers, numerical results and verification scripts. Supplementary Material S2 provides detailed algorithms, explicit parameter grids and metrics, gas diagnostics, redistribution and near-tie tables, figure-generation scripts and verification utilities. S1 and S2 are complementary; S2 is supplied with this manuscript and is separate from the cited Zenodo release.

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