# A distributed activation energy model for clumped isotope bond reordering in carbonates

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#### Abstract

Carbonate clumped isotopes ([?]47) have become a widely applied method for paleothermometry, with applicationsspanning many environmental settings over hundreds of millions of years. However, [?]47-based paleothermometry can be complicated by closure temperature-like behavior whereby C-O bonds are reset at elevated diagenetic or metamorphic temperatures, sometimes without obvious mineral alteration. Laboratory studies have constrained this phenomenon by heating well-characterized materials at various temperatures, observing temporal [?]47 evolution, and fitting results to kinetic models with prescribed C-O bond reordering mechanisms. While informative, these models are inflexible regarding the nature of isotope exchange, leading to potential uncertainties when extrapolated to geologic timescales. Here, we propose a "disordered" kinetic framework to circumvent this issue by modeling C–O bond reordering as a continuum of first-order processes occurring in parallel at different rates. We show theoretically that all previous models are specific cases of disordered kinetics; thus, our approach reconciles the transient defect/equilibrium defect and paired reaction-diffusion models. We estimate the rate coefficient distributions from published heating experiment data by finding a regularized inverse solution that best fits each [?]47 timeseries. Importantly, this approach does not assume a particular mechanism or energy distribution a priori. Resulting distributions are well-approximated as lognormal for all experiments on calcite or dolomite; aragonite experiments require more complex distributions. Presuming lognormal rate coefficient distributions and Arrhenius-like temperature dependence yields an underlying activation energy, E, distribution that is Gaussian with a mean value of  $\mu E$  = 224.3±27.6 kJ mol-1 and a standard deviation of  $\sigma E$  = 17.4  $\pm$  0.7 kJ mol-1 (+-1 $\sigma$  uncertainty; n = 24) for calcite and  $\mu E = 230.3 \pm 47.7$  kJ mol-1 and  $\sigma E = 14.8 \pm 2.2$  kJ mol-1 (n = 4) for dolomite. These model results are adaptable to other minerals and may provide a basis for future experiments whereby the nature of carbonate C-O bonds is altered (e.g., by inducing mechanical strain or cation substitution). Finally, we apply our results to geologically relevant heating/cooling histories and suggest that previous models underestimate low-temperature alteration but overestimate [?]47 blocking temperatures.

# 1 Highlights

# <sup>2</sup> A disordered kinetic model for clumped isotope bond reordering in carbonates

- <sup>3</sup> Jordon D. Hemingway, Gregory A. Henkes
- Clumped isotope reordering kinetics arise from random-walk <sup>18</sup>O diffusion
- Carbonate clumped isotope bond reordering is modeled using disordered kinetics
- All previous models are shown to be specific cases of disordered kinetics
- Calcite & dolomite rate coefficient distributions are well-approximated as lognormal
- Disordered kinetics improves *t*-*T* predictions of natural samples

#### A disordered kinetic model for clumped isotope bond reordering in carbonates 9

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#### Abstract 14

Carbonate clumped isotopes ( $\Delta_{47}$ ) have become a widely applied method for paleothermometry, with applications 15 spanning many environmental settings over hundreds of millions of years. However,  $\Delta_{47}$ -based paleothermometry 16 can be complicated by closure temperature-like behavior whereby C-O bonds are reset at elevated diagenetic or 17 metamorphic temperatures, sometimes without obvious mineral alteration. Laboratory studies have constrained this 18 phenomenon by heating well-characterized materials at various temperatures, observing temporal  $\Delta_{47}$  evolution, and 19 fitting results to kinetic models with prescribed C-O bond reordering mechanisms. While informative, these models 20 are inflexible regarding the nature of isotope exchange, leading to potential uncertainties when extrapolated to geologic 21 timescales. Here, we instead propose that observed reordering rates arise naturally from random-walk <sup>18</sup>O diffusion 22 through the carbonate lattice, and we develop a "disordered" kinetic framework that treats C-O bond reordering as 23 continuum of first-order processes occurring in parallel at different rates. We show theoretically that all previous а 24 models are specific cases of disordered kinetics; thus, our approach reconciles the transient defect/equilibrium defect 25 and paired reaction-diffusion models. We estimate the rate coefficient distributions from published heating experi-26 ment data by finding a regularized inverse solution that best fits each  $\Delta_{47}$  timeseries without assuming a particular 27 functional form a priori. Resulting distributions are well-approximated as lognormal for all experiments on calcite or 28 dolomite; aragonite experiments require more complex distributions that are consistent with a change in oxygen bond-29 ing environment during the transition to calcite. Presuming lognormal rate coefficient distributions and Arrhenius-like 30 temperature dependence yields an underlying activation energy, E, distribution that is Gaussian with a mean value of 31  $\mu_E = 224.3 \pm 27.6 \text{ kJ mol}^{-1}$  and a standard deviation of  $\sigma_E = 17.4 \pm 0.7 \text{ kJ mol}^{-1} (\pm 1\sigma \text{ uncertainty}; n = 24)$  for calcite 32 and  $\mu_E = 230.3 \pm 47.7 \text{ kJ mol}^{-1}$  and  $\sigma_E = 14.8 \pm 2.2 \text{ kJ mol}^{-1}$  (n = 4) for dolomite. These model results are adaptable 33 to other minerals and may provide a basis for future experiments whereby the nature of carbonate C-O bonds is al-34 tered (e.g., by inducing mechanical strain or cation substitution). Finally, we apply our results to geologically relevant 35 heating/cooling histories and suggest that previous models underestimate low-temperature alteration but overestimate 36

 $\Delta_{47}$  blocking temperatures. 37

Keywords: activation energy model, carbonate, apparent equilibrium temperature, clumped isotopes, solid-state 38

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#### 40 1. Introduction

Carbonate clumped isotope ratios (reported as  $\Delta_{47}$ ) are a valuable paleothermometer because they have been 41 shown—empirically and experimentally—to solve the underdetermination problem with carbonate-water oxygen iso-42 tope exchange thermometry (Eiler, 2011). This apparent panacea, however, comes with caveats. Specifically, clumped 43 isotopes are subject to alteration during diagenetic dissolution-reprecipitation of the original carbonate, both in water-44 buffered and rock-buffered settings (e.g., Ryb and Eiler, 2018; Shenton et al., 2015), and by internal, diffusion-driven 45 isotope exchange reactions within the solid mineral lattice at elevated temperatures—so-called "solid-state clumped 46 isotope bond reordering" (Dennis and Schrag, 2010; Passey and Henkes, 2012; Stolper and Eiler, 2015; Brenner et al., 47 2018; Lloyd et al., 2018; Chen et al., 2019). 48

Bond reordering has been observed or hypothesized to affect carbonates from many geologic contexts on Earth. 49 Empirical evidence comes from two main sources: (i) carbonatites, where  $\Delta_{47}$ -derived temperatures,  $T(\Delta_{47})$ , are con-50 sistently much lower than inferred igneous crystallization temperatures (Dennis and Schrag, 2010; Stolper and Eiler, 51 2015; Fosu et al., 2020), and (ii) marbles and sedimentary rock alteration along dikes, where  $T(\Delta_{47})$  systematically 52 increases closer to the heat source (Finnegan et al., 2011; Lloyd et al., 2017; Ryb et al., 2017). Furthermore, bond 53 reordering has been invoked to explain elevated  $T(\Delta_{47})$  in deeply buried paleoclimate archives (e.g., shells) that are 54 petrographically and geochemically well-preserved (e.g., Shenton et al., 2015; Henkes et al., 2014, 2018). Predicting 55 the impact of bond reordering on measured  $\Delta_{47}$  values is thus critically important for properly interpreting clumped 56 isotope paleotemperature records, particularly in older archives that may have been exposed to higher diagenetic 57 temperatures (Henkes et al., 2018). 58

<sup>59</sup> Quantifying bond reordering necessitates kinetic models that both satisfy experimental tests and are amenable to <sup>60</sup> a wide range of geologic applications. This has been achieved in the laboratory by heating the same mineralogically <sup>61</sup> pure carbonate material at multiple temperatures for discrete time intervals. From these studies, it is possible to <sup>62</sup> observe  $\Delta_{47}$  evolution without obvious physical or isotopic changes to the reactant (i.e., decarbonation or mineral-<sup>63</sup> gas/mineral-liquid isotope exchange). By assuming first-order kinetics and Arrhenius-like temperature dependence, <sup>64</sup> one can utilize heating experiment results to estimate *E*, the underlying activation energy of clumped isotope bond <sup>65</sup> reordering, and  $k_0$ , the Arrhenius pre-exponential factor (Passey and Henkes, 2012; Stolper and Eiler, 2015). Given

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Figure 1: Crystal structures of (**A**) calcite and (**B**) aragonite, each showing two unit cells projected onto the (001) plane. Carbon (grays), oxygen (reds), and calcium (greens) atoms are shaded according to their distance along the *c* axis. Isotopically substituted oxygens ( $^{18}O$ ) and carbons ( $^{13}C$ ) are shown in gold and blue, respectively. Also included are representations of crystal lattice defects that may influence oxygen bonding environments and clumped isotope reordering rates: calcium substitutions (e.g., Mg<sup>2+</sup> or Sr<sup>2+</sup>; purple), oxygen vacancies (open circles), and interstitial atoms (hexagons). Interactions between an <sup>18</sup>O atom and neighboring defects are highlighted with pink lines, whereas bond distances (in Angstroms) between an <sup>18</sup>O atom and all nearest neighbor O atoms are highlighted with light blue lines (Markgraf and Reeder, 1985; De Villiers, 1971). For aragonite, O1 type oxygens are outlined in dotted lines, whereas O2 type oxygens are outlined in solid lines. Dolomite crystal structure is similar to that of calcite but with the *c*/6 calcium replaced by magnesium.

these experimentally determined Arrhenius parameters,  $\Delta_{47}$  evolution due to bond reordering can then be estimated for any carbonate sample that has experienced any specified time-temperature (*t*-*T*) history (Passey and Henkes, 2012; Stolper and Eiler, 2015).

However, nearly all heating experiments to date are complicated by the presence of an early, rapid change in  $\Delta_{47}$ 69 that appears to deviate from exponential decay predicted by first-order kinetics (Passey and Henkes, 2012; Henkes 70 et al., 2014; Stolper and Eiler, 2015; Lloyd et al., 2018). While initially ignored, these early data points have prompted 71 the development of two alternative bond reordering models. First, the "transient defect/equilibrium defect" model 72 of Henkes et al. (2014) posits that non-first order behavior results from the simultaneous reaction of two defect 73 populations: one that follows first-order kinetics and a second whose concentration decreases with prolonged heating. 74 Despite its presence, Passey and Henkes (2012) and Henkes et al. (2014) argue that the nature of this transient defect 75 pool is ambiguous and likely annealed in many geologic contexts. Second, the "paired reaction-diffusion" model of 76 Stolper and Eiler (2015) treats the early, rapid change in experimental  $\Delta_{47}$  as the result of interactions between pairs of 77 neighboring, singly substituted carbonate groups; these groups can then diffuse through the crystal lattice according 78 to first-order kinetics. This model is intuitive and capable of capturing  $\Delta_{47}$  changes in most experimental datasets 79 but is inflexible and disregards the contribution of lattice defects or other extrinsic factors that may promote isotope 80 exchange. Importantly, both models prescribe C–O bond reordering mechanisms a priori, potentially leading to large 81



Figure 2: The random walk bond reordering model: (A) Potential energy wells for oxygen atoms vibrating about their zero-point energies (ZPE; thick gold lines) in two neighboring CO<sub>3</sub> groups. At the molecular level, diffusion occurs when an oxygen atom "jumps" from one CO<sub>3</sub> group i to a neighboring group j (blue dotted line); a jump requires that the activation energy barrier  $E_{i,j}$  is overcome. If an <sup>18</sup>O atom (gold circle) jumps <sup>13</sup>C-containing group (blue circle), then the ZPE of the resulting clump is lower than that for the initial state and the reaction is to a neighboring thermodynamically favored. (B) Conceptual diagram of the model setup. A grid of  $n_c$  carbon atoms is created, each with a random probability of being isotopically substituted (blue circles) that is equal to the natural abundance of  $^{13}C$  (assumed  $\delta^{13}C = 0$  %). An  $^{18}O$  atom (gold circle) is then "seeded" onto the grid; r<sub>i</sub>, the probability of initially being associated with carbon atom i, follows a uniform distribution but is increased by a factor of  $R^{47,0}/R^{*47}$ , the initial  $\Delta_{47}$  value, for all <sup>13</sup>C atoms. At each time step  $t_k$ , the <sup>18</sup>O atom can "jump" to any of its neighboring carbon atoms with a total probability p such that  $p = \sum q_{i,j}$ , where  $q_{i,j}$  is the probability of jumping to neighboring carbon atom j;  $q_{i,j}$  decreases as the square of the distance between the two carbon atoms and is increased by a factor of  $R^{47,eq}/R^{47}$ , the equilibrium  $\Delta_{47}$  value, for all neighboring <sup>13</sup>C atoms. An example random walk is shown with the dotted gold (no clump formed at  $t_k$ ) and blue (clump formed at  $t_k$ ) trajectory. The random walk process is repeated  $n_0$  times for a given carbon grid; uncertainty is determined by recreating the carbon grid  $n_{\text{iter}}$  times for a total of  $n_0 \times n_{\text{iter}}$  random walks. (C) Model results showing  $G(t_k)$ , the normalized deviation from equilibrium at each time step, as a function of  $\langle J \rangle$ , the ensemble averaged number of jumps per <sup>18</sup>O atom.  $\langle J \rangle = pt_k$  is nondimensional time such that  $\langle J \rangle = 1$  is the mean life of an exponential decay reaction with rate constant k = p (dotted black line). The model shown here (blue line and shaded region) was initialized with  $d_{i,i}$  for calcite (see Fig. 1),  $R^{47,0}/R^{*47} = 1.01$ ,  $R^{47,eq}/R^{*47} = 1.0025$ , p = 0.1,  $n_C = 10^4$ ,  $n_O = 10^6$ ,  $n_{iter} = 10^3$ , and  $n_t = 25$ . Also shown is the predicted  $G(t_k)$  evolution using the best-fit lognormal disordered kinetics solution (solid black line; Section. 4.1).

uncertainties when extrapolated to geologic t-T histories.

To obviate the need for *a priori* mechanistic assumptions, here we recast clumped isotope bond reordering as a "disordered" kinetic process whereby solid state C–O isotope exchange occurs as a parallel superposition of pseudofirst-order reactions. We show theoretically that all previously published models represent specific cases of disordered kinetics subject to certain constraints. We then relax these constraints and estimate the distributions of rate coefficients that best fit experimental data using a regularized inverse approach. Resulting rate coefficient distributions are generally well-approximated as lognormal, indicating that underlying *E* distributions are Gaussian, consistent with the central limit theorem. Finally, we compare our bond reordering predictions to those of previous models and estimate  $\Delta_{47}$  evolution for examples of geologically relevant heating/cooling histories.

#### 91 2. Conceptual Framework

To motivate the development of our model, we first conceptualize solid-state bond reordering as a random-walk diffusion process occurring within the crystal lattice (Cole and Chakraborty, 2001; Passey and Henkes, 2012). Although new to mineral isotope studies, disordered kinetics have been successfully applied to similar solid-state reactions; in particular, mineral luminescence decay patterns are shown to result from a distribution "trapping sites" that are analogous to the formation of  ${}^{13}C{-}^{18}O$  clumps (Huber, 1985).

For carbonates, <sup>18</sup>O diffusion arises when an oxygen atom randomly "jumps" from one CO<sub>3</sub> group *i* to a neigh-97 boring  $CO_3$  group *j* (Fig. 1; Stolper and Eiler, 2015). Because each atom within a given group vibrates about its 98 zero-point energy (ZPE) such that a jump involves overcoming an activation energy barrier  $E_{i,j}$ , the probability p of a 99 given atom jumping at any given time is small (Cole and Chakraborty, 2001). Following a harmonic oscillator, we as-100 sume  $E_{i,j}$  is inversely proportional to  $d_{i,j}^2$ , the square of the distance between oxygen atoms in neighboring CO<sub>3</sub> groups 101 (Fig. 1). Furthermore, if an <sup>18</sup>O atom from a singly substituted CO<sub>3</sub> group jumps to a neighboring <sup>13</sup>C-containing 102 CO<sub>3</sub> group, the final ZPE of the newly formed clumped group is lower than that of the initial configuration (i.e., it 103 is thermodynamically favored) due to the nonlinear reduction in ZPE (Fig. 2A; Wang et al., 2004). Lattice defects 104 such as vacancies, interstitials, or  $Ca^{2+}$  substitutions likely influence  $E_{i,j}$ , but their presence is not strictly necessary 105 for diffusion within this framework (Fig. 1; Henkes et al., 2014). 106

In statistical mechanical terms, this reduction in ZPE leads to an increase in the probability of following a particular 107 diffusion pathway,  $q_{i,j}$ , when it involves jumping to a neighboring <sup>13</sup>C-containing CO<sub>3</sub> group; the magnitude of this 108 increase is proportional to the ZPE difference between singly and doubly substituted groups and, by extension, to 109 the equilibrium  $\Delta_{47}$  value at a given temperature (Fig. 2B; Schauble et al., 2006). As  $T \to \infty$ , the ZPE difference 110 approaches zero and diffusion becomes truly random (i.e., the reduced partition function ratio between singly- and 111 doubly-substituted CO<sub>3</sub> groups approaches unity; Wang et al., 2004), consistent with the requirement that clumped 112 isotopologues are stochastically distributed in the mineral lattice at high T. Critically, this framework differs from the 113 paired reaction-diffusion model in that we do not treat the "pair-to-clump" transition as a separate chemical reaction 114 that follows unique kinetics ( $k_f$  in Stolper and Eiler, 2015). Rather, we include this as part of the diffusion process and 115 we increase the probability of this diffusion pathway in a manner predicted by statistical mechanics. 116

As shown in Fig. 2C, the random-walk diffusion model described here accurately predicts the observed slowdown in  $\Delta_{47}$  evolution during heating experiments without the need to treat the pair-to-clump transition as a unique chemical reaction or to invoke lattice defects. We interpret this result and predict  $\Delta_{47}$  evolution on geologic timescales by developing the disordered kinetic model for bond reordering.

## 121 3. Methods

# 122 3.1. Data compilation

We compiled results from all published experiments designed to derive the kinetics of solid-state C–O bond reordering. This includes  $\Delta_{47}$  data from 42 experiments using four carbonate minerals: optical and fossil brachiopod calcite (Passey and Henkes, 2012; Henkes et al., 2014; Stolper and Eiler, 2015; Brenner et al., 2018), aragonite (Chen et al., 2019), dolomite (Lloyd et al., 2018), and the carbonate group within apatite (Stolper and Eiler, 2015). All data were generated using near-identical analytical methods either at the California Institute of Technology (see Passey et al., 2010) or at Johns Hopkins University (see Henkes et al., 2013). To summarize, this included carbonate digestion using a 90 °C common phosphoric acid bath, CO<sub>2</sub> purification by cryogenic and He-carrier gas chromatography, and measurement of m/z 44–49 on a Thermo Scientific MAT 253 isotope ratio mass spectrometer. Reported clumped isotope compositions are calculated as

$$\Delta_{47} = \left[ \left( \frac{R^{47}}{R^{*47}} - 1 \right) - \left( \frac{R^{46}}{R^{*46}} - 1 \right) - \left( \frac{R^{45}}{R^{*45}} - 1 \right) \right] \times 1000\%c, \tag{1}$$

where  $R^i$  is the measured ratio of isotopologue *i* relative to  ${}^{12}C^{16}O_2$  and  $R^{*i}$  is the predicted ratio of isotopologue *i* relative to  ${}^{12}C^{16}O_2$  if all isotopes were randomly distributed (Affek and Eiler, 2006).

To perform all calculations in a standardized reference frame, we refer to only published data on the "carbon 134 dioxide equilibrium scale" (Dennis et al., 2011) uncorrected for the fractionation factor between 25 °C and 90 °C 135 phosphoric acid reaction (i.e., CDES<sub>90</sub>; Bonifacie et al., 2017). Study-specific fractionation factors were used to 136 uncorrect all data except those presented in Stolper and Eiler (2015); since no fractionation factor was reported for 137 these experiments, a value of 0.092 % was used to match that reported for other data generated in the same laboratory 138 during the same time period (e.g., Bonifacie et al., 2017). Isotopologue reordering reaction progress should be 139 insensitive to the reported  $\Delta_{47}$  values (i.e., acid or any other standardized correction) so long as equilibrium  $\Delta_{47}$  is 140 reported in the same reference frame. We thus made no attempt to correct for differences in isotope parameters used 141 between studies. 142

Assessing model fits requires knowledge of measurement uncertainty. Here, we use  $\Delta_{47}$  uncertainty reported in each original study without further correction. For samples with replicate measurements, reported uncertainty is the ±1 standard error (s.e.) of all replicates. For samples analyzed only once, reported uncertainty is typically equal to the long-term instrument precision of a suite of standards (Passey et al., 2010; Henkes et al., 2013). In the compiled dataset, uncertainty averages ±0.013 ‰ and never exceeds 0.041 ‰ (n = 355).

<sup>148</sup> All stable isotope data are presented in Table S.1, including: published  $\delta^{13}$ C,  $\delta^{18}$ O, and  $\Delta_{47}$  values;  $\Delta_{47}$  values <sup>149</sup> after conversion to the CDES<sub>90</sub> reference frame; and  $\Delta_{47}$  uncertainty.

#### 150 3.2. Data analysis

<sup>151</sup> Determining C–O bond reordering progress requires knowledge of  $\Delta_{47}^{eq}(T)$ , the equilibrium  $\Delta_{47}$  value at each ex-<sup>152</sup> perimental temperature. We calculate  $\Delta_{47}^{eq}(T)$  using the multiple mineralogy high-temperature *T* vs.  $\Delta_{47}^{eq}(T)$  calibration equation of Bonifacie et al. (2017) (their Eq. 2). However, Lloyd et al. (2018) advocate for the theoretical calibration equation of Schauble et al. (2006) (corrected to CDES<sub>90</sub>) for dolomite reordering experiments since the Bonifacie et al. (2017) calibration over-estimates measured high-temperature dolomite  $\Delta_{47}^{eq}(T)$  values by up to 0.015%. For consistency, we retain the Bonifacie et al. (2017) calibration for all calculations performed herein but discuss in Section 5.3 the degree to which this choice influences resulting activation energy estimates.

All calculations were performed using the 'isotopylog' package in Python 3.7 (Hemingway, 2020). Regularized inversion solutions (Section 4.2.1) were determined using the non-negative least squares algorithm in Lawson and Hanson (1995), whereas lognormal rate distribution solutions (Section 4.2.2) and Arrhenius parameters (Section 4.3), including error estimation, were determined using the Levenberg-Marquardt algorithm for non-linear curve fitting with each data point weighted by the inverse of its analytical variance (Marquardt, 1963). Python scripts to generate all figures and tables are included in the supplementary information.

### 164 4. Theory

Here, we derive the disordered kinetic model and show that it reproduces  $\Delta_{47}$  evolution slowdown observed during 165 random-walk diffusion and in carbonate heating experiments (Section 4.1), and we demonstrate that the "pseudo-166 first-order" (Passey and Henkes, 2012), "transient/equilibrium-defect" (Henkes et al., 2014), and "paired reaction-167 diffusion" (Stolper and Eiler, 2015) models all represent specific cases of disordered kinetics. We further describe how 168 this framework can inform non-monotonic  $\Delta_{47}$  evolution, as has been observed in aragonite heating experiments (Chen 169 et al., 2019). We then outline an inversion approach to determine the rate distributions that best fit experimental data, 170 and we show that these distributions are approximately lognormal (Section 4.2). Finally, we estimate the underlying 171 activation energy distributions using an Arrhenius approach (Section 4.3) and show how to calculate  $\Delta_{47}$  evolution— 172 including uncertainty propagation—over geologically relevant time-temperature histories (Section 4.4). For reference, 173 all mathematical symbols are described in Table S.2. 174

#### 175 4.1. Theoretical derivation

<sup>176</sup> Carbonate isotopologue reordering can be written as

$${}^{12}C^{16}O_3 + {}^{13}C^{18}O^{16}O_2 \xleftarrow[\alpha(T)\kappa(t)]{}^{13}C^{16}O_3 + {}^{12}C^{18}O^{16}O_2,$$
(2)

where  $\kappa(t)$  is the apparent rate coefficient of the "order-to-disorder" reaction at time *t* and  $\alpha(T)$  is the temperaturedependent equilibrium constant (Passey and Henkes, 2012). A general feature of all carbonate isotopologue reordering experiments is that  $\kappa(t)$  decreases with time, either monotonically (apatite, calcite, dolomite; Passey and Henkes, 2012; Henkes et al., 2014; Stolper and Eiler, 2015; Brenner et al., 2018; Lloyd et al., 2018) or after early transient features
have dissipated (aragonite; Chen et al., 2019).

A decreasing apparent rate coefficient can be shown to result from a superposition of multiple reactions, each following a unique rate coefficient *k* (Huber, 1985; Ross and Vlad, 1999). This approach is commonly applied to disordered systems such as organic carbon remineralization (Forney and Rothman, 2012a; Hemingway et al., 2017), fossil fuel pyrolysis (Burnham and Braun, 1999), nonlinear chemical kinetics (Ross and Vlad, 1999), and luminescence decay in crystals (Huber, 1985). Here, we suppose that carbonate  $\Delta_{47}$  evolution during isotopologue reordering similarly follows disordered kinetics. We define the normalized deviation from equilibrium for a subset of material that is associated with a given rate coefficient *k* at time *t* as

$$g(k,t) = \frac{\Delta_{47}(k,t) - \Delta_{47}^{eq}(T)}{\Delta_{47}^0 - \Delta_{47}^{eq}(T)},$$
(3)

where  $\Delta_{47}(k, t)$  is the  $\Delta_{47}$  value of material associated with rate k at time t,  $\Delta_{47}^0$  is the measured  $\Delta_{47}$  value at t = 0, and  $\Delta_{47}^{eq}(T)$  is the temperature-dependent equilibrium  $\Delta_{47}$  value, either measured empirically (e.g., Passey and Henkes, 2012; Bonifacie et al., 2017) or determined theoretically using first-principles estimates of  $\alpha(T)$  (Schauble et al., 2006).

Following Passey and Henkes (2012), we show in Appendix A that g(k, t) evolves with time as

$$g(k,t) = e^{-kt}.$$
(4)

That is, g(k, t) follows first-order kinetics. We similarly define the normalized deviation from equilibrium for the bulk sample at time *t* as

$$G(t) = \frac{\Delta_{47}(t) - \Delta_{47}^{\rm eq}(T)}{\Delta_{47}^{0} - \Delta_{47}^{\rm eq}(T)},$$
(5)

where  $\Delta_{47}(t)$  is the measured  $\Delta_{47}$  value at time *t*. G(t) evolves as a superposition of first-order reactions:

$$G(t) = \int_0^\infty p(k)g(k,t)dk,$$
(6)

where p(k) is the fraction of total material initially associated with rate coefficient k such that  $p(k) \ge 0$  for all k and

$$\int_0^\infty p(k) \equiv 1. \tag{7}$$

That is, p(k) forms a probability density function (pdf). Substituting Eq. 4 into Eq. 6 yields

$$G(t) = \int_0^\infty p(k)e^{-kt}dk,$$
(8)

which defines the Laplace transform of p(k) (Hansen, 1994; Forney and Rothman, 2012a). Because the superposition of parallel first-order reactions is itself first order, it follows that

$$\frac{dG(t)}{dt} = -\kappa(t)G(t),\tag{9}$$

where  $\kappa(t)$  is the apparent rate coefficient at time t (Eq. 1). Combining Eqs. 8 and 9 yields

$$\kappa(t) = \frac{\int_0^\infty kp(k)e^{-kt}dk}{\int_0^\infty p(k)e^{-kt}dk},\tag{10}$$

which defines the arithmetic mean of *k* weighted by  $p(k)e^{-kt}$ . Equation 10 states that small *k* values become more heavily weighted with increasing *t* since  $e^{-kt}$  approaches zero most rapidly for large *k*. Put differently,  $\kappa(t)$  must decrease with time for any distribution of p(k) other than a single delta function [in which case  $\kappa(t)$  is constant; see Section 4.1.1]. The observed decrease in  $\kappa(t)$ , which prompted the development of the transient/equilibrium-defect (Henkes et al., 2014) and paired reaction-diffusion (Stolper and Eiler, 2015) models, is thus a natural consequence of disordered kinetics. We now demonstrate that Eq. 8 can describe all previous isotopologue reordering models given the right choice of p(k).

# 209 4.1.1. Relationship to previous models: Passey and Henkes (2012)

We first consider the "pseudo-first-order" model, which supposes that reordering after some critical time point  $t_{cr}$ follows a single first-order reaction with rate constant  $k_c$ . This is written mathematically as a delta function, which has the properties

$$\delta(k - k_c) = \begin{cases} \infty, & \text{if } k = k_c \\ 0, & \text{otherwise} \end{cases}$$
(11)

213 and

$$\int_{-\infty}^{\infty} \delta(k - k_c) dk = 1.$$
<sup>(12)</sup>

Reaction progress for  $t < t_{cr}$  is ignored since it is hypothesized to include "transient defects," the loss of which is 214 assumed to be an artifact of experimental heating. We thus define  $\tau = t - t_{cr}$  and  $p(k) = \delta(k - k_c)$ . Equation 8 becomes 215

$$G(\tau) = \int_0^\infty \delta(k - k_c) e^{-k\tau} dk,$$
  
=  $e^{-k_c \tau},$  (13)

which is identical to governing equation of Passey and Henkes (2012) (their Eq. 3). It can be similarly shown from 216 Eq. 10 that  $\kappa(\tau) = k_c$  for all  $\tau$ , as expected. 217

#### 4.1.2. Relationship to previous models: Henkes et al. (2014) 218

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Next, we consider the "transient defect/equilibrium defect" model. This is an extension of the pseudo-first-order 219 model that includes transient defect reaction progress when  $t < t_{cr}$ . Henkes et al. (2014) state that G(t) follows a 220 first-order reaction (Eq. 9) with an apparent rate constant that evolves as (their Eq. A.11) 221

$$\kappa(t) = k_c + k_d e^{-k_2 t}.$$
(14)

Transient defects are assumed to react with rate  $k_d$  and anneal with time following a first-order reaction governed by 222  $k_2$  where  $k_2 \sim 1/t_{\rm cr}$ . It can be seen from Eq. 14 that  $\kappa(t) = k_c$  when  $t \gg t_{\rm cr}$ , as in the pseudo-first-order model.

Comparing Eqs. 10 and 14, it is apparent that the transient defect/equilibrium defect model follows a parallel 224 superposition of first-order reactions with a distribution p(k) that satisfies 225

$$\frac{\int_{0}^{\infty} kp(k)e^{-kt}dk}{\int_{0}^{\infty} p(k)e^{-kt}dk} = k_{c} + k_{d}e^{-k_{2}t}.$$
(15)

Finding p(k) involves solving the inverse Laplace transform, which in this case does not conform to a particular 226 function that can be derived analytically (see Section 4.2, below). Nonetheless, as an example, we show the p(k)227 distribution that satisfies Eq. 15 for optical calcite heated at 425 °C in Fig. S.1. 228

## 4.1.3. Relationship to previous models: Stolper and Eiler (2015)

Finally, we consider the "paired reaction-diffusion" model, which treats  $\Delta_{47}$  evolution as a serial reaction between "clumps", "pairs", and "singletons". Equation 2 can be rewritten as

$${}^{12}\mathrm{C}^{16}\mathrm{O}_3 + {}^{13}\mathrm{C}^{18}\mathrm{O}^{16}\mathrm{O}_2 \xleftarrow[\alpha_1(T)\kappa_1(t)]{\kappa_1(t)} p$$

$$\xrightarrow{\kappa_{\rm pd}(t)}_{\alpha_{\rm pd}(T)\kappa_{\rm pd}(t)} ({}^{13}{\rm C}^{16}{\rm O}_3)_s + ({}^{12}{\rm C}^{18}{\rm O}^{16}{\rm O}_2)_s, \quad (16)$$

where p denotes "paired" <sup>13</sup>C<sup>16</sup>O<sub>3</sub> groups immediately adjacent to <sup>12</sup>C<sup>18</sup>O<sup>16</sup>O<sub>2</sub> groups, the subscript "*s*" denotes "singleton" <sup>13</sup>C<sup>16</sup>O<sub>3</sub> or <sup>12</sup>C<sup>18</sup>O<sup>16</sup>O<sub>2</sub> groups that do not neighbor any other isotopically substituted group, and pd denotes "pair diffusion". As in Stolper and Eiler (2015), we assume each step of the reaction is described by a single unique rate constant  $\kappa_1(t) = k_1$  and  $\kappa_{pd}(t) = k_{pd}$  and equilibrium constant  $\alpha_1(T)$  and  $\alpha_{pd}(T)$ . Equation 16 describes a system of paired first-order ordinary differential equations.

Two reactions occurring in series can be treated as a superposition of reactions occurring in parallel (Forney and Rothman, 2014). Specifically for this system, we show in Appendix B that G(t) evolves as

$$G(t) = \sum_{i=1}^{2} r(\lambda_i) e^{-\lambda_i t},$$
(17)

where  $\lambda_i \propto k_1, k_{pd}$  are the eigenvalues of the reaction system and and  $r(\lambda_i)$  represents  $p(k_i)$  projected onto its eigenvectors. The paired reaction-diffusion model is thus a specific case of disordered kinetics. Unlike p(k) however, in general  $r(\lambda)$  need not be non-negative since eigenvectors can contain negative entries. Relaxing this constraint can additionally explain non-monotonic G(t) evolution seen in aragonite heating experiments (Chen et al., 2019).

#### 241 4.1.4. Relaxing the non-negativity constraint

It has recently been observed in isotopologue reordering experiments of aragonite that  $\Delta_{47}$  does not monotonically approach  $\Delta_{47}^{eq}$  but rather increases transiently prior to decreasing (Chen et al., 2019). This was interpreted to reflect an initial excess of pairs that rapidly back-react to form clumps on timescales shorter than that of singleton diffusion [i.e., if  $\alpha_1(T)\kappa_1(t) \gtrsim \kappa_2(t)$ ]. This phenomenon is consistent with serial disordered reactions.

<sup>246</sup> We show in Appendix C that, in general,

$$G(t) = \int_0^\infty r(\lambda) e^{-\lambda t} d\lambda,$$
(18)

which is the continuous version of Eq. 17 that allows  $\kappa_1(t)$  and  $\kappa_{pd}(t)$  to evolve with time. That is, we suppose that

each step in Eq. 16 is itself described by a superposition of first-order reactions that progress at different rates; this is predicted by our random-walk diffusion conceptualization (Fig. 2) and follows from the assumption in Chen et al. (2019) that the activation energy of reaction between a given CO<sub>3</sub> group and any of its neighbors need not be identical. Again recognizing that  $r(\lambda)$  is a projection of p(k) onto the eigenvectors of the reaction system, it follows that a  $r(\lambda)$ distribution containing significant negative area can lead to transient increases in G(t) with time.

<sup>253</sup> Negative  $r(\lambda)$  may be a general feature of serial and feedback systems in which some processes occur at much <sup>254</sup> faster rates than others. Negative  $r(\lambda)$  has also been observed in organic matter respiration experiments (Forney and <sup>255</sup> Rothman, 2014) and was interpreted to reflect a lag phase between serial reactions, analogous to the proposed lag <sup>256</sup> prior to the aragonite-to-calcite phase transition observed in Chen et al. (2019).

#### 257 4.2. Fitting experimental data

Previous models derive rate equations after making assumptions about the system of reordering reactions; for example, that transient defects anneal exponentially (Henkes et al., 2014) or that clumps react with pairs in series (Stolper and Eiler, 2015). This prescribes the form of the p(k) distribution *a priori*. Here, we instead use an inverse approach to find the p(k) distribution that best fits observed data without any *a priori* assumptions about the reordering mechanism; we then compare this solution to a theoretically justified pdf to estimate a functional form of p(k).

#### 263 4.2.1. Finding the inverse solution

Since we expect *k* to vary over many orders of magnitude (Passey and Henkes, 2012; Henkes et al., 2014; Stolper and Eiler, 2015; Brenner et al., 2018; Lloyd et al., 2018), we perform a change of variables from *k* to v = ln(k). This facilitates the extraction of underlying activation energy distributions since  $E \propto ln(k)$ . Probability is conserved, so  $p(k)dk = \rho(v)dv$  and Eq. 8 becomes

$$G(t) = \int_{-\infty}^{\infty} \rho(v) e^{-e^{v}t} dv.$$
<sup>(19)</sup>

<sup>268</sup> As shown in Appendix D, this can be written in matrix from as

$$\mathbf{G} = \mathbf{A}\boldsymbol{\rho},\tag{20}$$

where **G** is the length  $n_t$  vector of measured time-series G(t) values,  $\rho$  is the length  $n_v$  vector of  $\rho(v)$  values, and **A** is the  $n_t \times n_v$  Laplace transform operator matrix. Although  $\rho$  can be directly calculated as  $\rho = \mathbf{A}^{-1}\mathbf{G}$ , this solution is highly sensitive to noise at the level of  $\Delta_{47}$  analytical uncertainty and could lead to negative  $\rho(v)$  that is mathematically possible but physically unreasonable (Forney and Rothman, 2012b; Hemingway et al., 2017). In mathematical terms, Eq. 20 is ill posed (Hansen, 1994).



Figure 3: Examples of the disordered kinetic model for optical calcite (MGB-CC-1) isotopologue reordering experiments performed at (top) 385, (middle) 425, and (bottom) 475 °C (data from Passey and Henkes, 2012). Panels **A**, **D**, and **G** show the Tikhonov regularization L-curve for each experiment (solid black line), including the best-fit  $\omega$  value (gray circle). Panels **B**, **E**, and **H** show the pdf of  $\nu$  for each experiment, including the best-fit regularized inverse solution (dotted black line) and the lognormal solution (solid blue line). Panels **C**, **F**, and **I** show the measured  $\Delta_{47}$  values and the modeled  $\Delta_{47}$  evolution as predicted by the best-fit regularized inverse solution (dotted black line) and the lognormal solution (solid blue line). Shaded blue region is the propagated  $\pm 1\sigma$  uncertainty of the lognormal solution. For reference, reaction progress for each experiment is also shown by converting  $\Delta_{47}$  to G(t). The observed left-skewed regularized inverse solution at lower temperature and right-skewed regularized inverse solution at higher temperature is a general feature of most experiments included in this study (Section 5.1). rgh = roughness; rmse = root mean square error, min = minutes.

We use Tikhonov regularization to find the optimal solution that minimizes  $\rho(\nu)$  complexity (determined by the intensity of fluctuations; termed "roughness") while maximizing solution accuracy and ensuring that  $\rho(\nu) \ge 0$ . Following Forney and Rothman (2012b), we calculate roughness as the  $n_{\nu} \times n_{\nu}$  bi-diagonal first-derivative operator matrix,

<sup>277</sup> **R** (Appendix D). The regularized inverse solution is found by including the roughness term in a constrained least



Figure 4: Rate distribution results for optical calcite (MGB-CC-1) isotopologue reordering experiments (data from Passey and Henkes, 2012). Best-fit lognormal rate distributions  $\rho(\nu)$  are shown for each experimental temperature (see Table S.3 for distribution statistics). Distributions generally become narrower and shift toward faster rates with increasing temperature, as predicted by Eq. 27 if isotopologue reordering follows an underlying Gaussian distribution of activation energies.

278 squares problem:

$$\min_{\rho} \|\mathbf{G} - \mathbf{A}\rho\| + \omega \|\mathbf{R}\rho\| \tag{21}$$

279 subject to the constraints

$$\sum_{j=0}^{n_{\nu}} \rho_j = 1 \text{ and } \rho_j \ge 0 \text{ for } j = 1, \dots, n_{\nu},$$
(22)

where  $\omega$  is a scalar that determines how much to weight roughness  $||\mathbf{R}\rho||$  relative to residual error  $||\mathbf{G} - \mathbf{A}\mathbf{x}||$ . The optimal  $\omega$  is taken as the point of maximum curvature in a log–log plot of residual error vs. roughness, where each point on the curve is calculated by solving Eq. 21 using  $\omega$  values that vary over many orders of magnitude (the socalled "L-curve"; Hansen, 1994). From this optimal point, increasing  $\omega$  greatly increases residual error but has little effect on solution roughness, whereas decreasing  $\omega$  greatly increases roughness but has little effect on residual error (e.g., Fig. 3A, D, G).

#### 286 4.2.2. Finding the lognormal solution

For most calcite, dolomite, and apatite samples, the regularized inverse distribution of  $\rho(v)$  resembles a Gaussian; that is, p(k) is approximately lognormally distributed (e.g., Fig. 3B, E, H). Lognormal p(k) distributions are theoretically justified since they derive naturally from the central limit theorem of multiplicative processes (Montroll and Shlesinger, 1982); they are commonly observed in disordered systems such as organic matter respiration and luminescence decay in minerals (Huber, 1985; Forney and Rothman, 2012a).

To compare with regularized inversion results, we determine the optimal lognormal distribution by setting  $\rho(\nu) \sim$ 

<sup>293</sup>  $\mathcal{N}(\mu_{\nu}, \sigma_{\nu})$  and finding  $\mu_{\nu}$  and  $\sigma_{\nu}$  that best reproduce observed data. That is, we solve

$$\min_{\mu_{\nu},\sigma_{\nu}} \|\mathbf{G} - \mathbf{A}\boldsymbol{\rho}\|,\tag{23}$$

where each entry in  $\rho$  is now subject to the constraint

$$\rho(\nu_i) = \frac{1}{\sqrt{2\pi}\sigma_{\nu}} e^{-(\nu_i - \mu_{\nu})^2/2\sigma_{\nu}^2}, \quad i = 1, \dots, n_{\nu}.$$
(24)

For all isotopologue reordering experiments, optimal lognormal distributions give G(t) evolution estimates that are statistically indistinguishable from regularized inversion fits and are described by a root mean square error that is well within  $\Delta_{47}$  analytical uncertainty (e.g., Fig. 3C, F, I).

Resulting lognormal distributions generally shift toward higher  $\mu_{\nu}$  and lower  $\sigma_{\nu}$  with increasing experimental temperature (Fig. 4). Similar relationships between temperature and bond reordering reaction rates have been observed previously, thus motivating the use of an Arrhenius-like activation energy approach to determine bond reordering temperature dependence (Passey and Henkes, 2012; Henkes et al., 2014; Stolper and Eiler, 2015; Brenner et al., 2018; Lloyd et al., 2018).

### 303 4.3. Determining Activation Energies

Because our ultimate goal is to predict isotopologue reordering over geologic timescales, we extract the underlying reaction energetics to predict reaction rates at any arbitrary temperature. As in previous models (Passey and Henkes, 2012; Henkes et al., 2014; Stolper and Eiler, 2015), we suppose that each rate coefficient k follows the Arrhenius equation

$$k(T) = k_0 e^{-E/RT},\tag{25}$$

where *T* is temperature,  $k_0$  is the Arrhenius pre-exponential factor, *E* is the activation energy of bond reordering for material associated k(T), and *R* is the ideal gas constant. Treating  $k_0$  as constant is strictly inconsistent with transition state theory of chemical reactions, which predicts  $k_0 \propto T$  (Eyring, 1935). However, linear dependence of  $k_0$  on *T* only changes *k* by a factor of ~ 3 over the temperature range of interest for isotopologue reordering ( $\approx 25 - 750$  °C), whereas the exponential term in Eq. 25 varies by many orders of magnitude over this range. Thus, the assumption of constant  $k_0$  negligibly impacts resulting  $\Delta_{47}$  evolution predictions.

We seek p(E), the pdf of E that leads to measured  $\rho(v)$  at a given T. If  $\rho(v) \sim \mathcal{N}(\mu_v, \sigma_v)$ , then we show in



Figure 5: Arrhenius plots showing (A)  $\mu_{\nu}$  and (B)  $\sigma_{\nu}$  as a function of inverse experimental temperature. Arrhenius regression best-fit lines calculated using Eq. 27 for calcite (solid black line) and dolomite (solid blue line) are also shown, including  $\pm 1\sigma$  uncertainty about each regression line (shaded regions). Experiments exhibiting noisy data [i.e.,  $\Delta_{47}(t)$  signal-to-noise < 5] or non-monotonic  $\Delta_{47}(t)$  evolution were excluded from regressions and thus are not shown here (see Sec. 5.3 and Table S.3).

<sup>315</sup> Appendix E that  $p(E) \sim \mathcal{N}(\mu_E, \sigma_E)$  where

$$\mu_E = RT(\nu_0 - \mu_\nu),$$

$$\sigma_E = RT\sigma_\nu,$$
(26)

and  $v_0 = \ln(k_0)$ . Rearranging yields

$$\mu_{\nu} = \nu_0 - \frac{\mu_E}{R} \left( \frac{1}{T} \right),$$

$$\sigma_{\nu} = \frac{\sigma_E}{R} \left( \frac{1}{T} \right).$$
(27)

Equation 27 states that a Gaussian p(E) distribution leads to increasing  $\mu_{\nu}$  and decreasing  $\sigma_{\nu}$  with increasing temperature, as is observed (Fig. 4). Similar to the approach taken in previous models, we fit  $\rho(\nu)$  distributions to a suite of isothermal reordering experiments performed at various temperatures and estimate  $\mu_E$  and  $\sigma_E$  by linearly regressing  $\mu_{\nu}$  and  $\sigma_{\nu}$  against 1/T (Fig. 5).

#### 321 4.4. Reordering on geologic timescales

Finally, we seek to predict  $\Delta_{47}$  evolution for over geologic timescales for any arbitrary *t*-*T* history. No analytical solution exists since *G*(*t*) does not scale linearly with  $\Delta_{47}(t)$  and since *G*(*t*) need not decrease monotonically with *t* (Hemingway et al., 2017); put differently,  $\Delta_{47}(t)$  is free to increase or decrease depending on the specific *t*-*T* history. We therefore numerically estimate  $\Delta_{47}(t)$  evolution following Passey and Henkes (2012). Rewriting Eqs. 5, 19, and 25 in discrete form yields

$$\Delta_{47}(t_i) = \Delta_{47}^{\text{eq}}(T_i) + \left[\Delta_{47}(t_{i-1}) - \Delta_{47}^{\text{eq}}(T_i)\right] \Delta G_i,$$
(28)

327 where

$$\Delta G_{i} = \left[\sum_{j=1}^{n_{E}} \mathcal{N}(\mu_{E}, \sigma_{E}) \exp\left(-\exp\left[\nu_{0} - \frac{E_{j}}{RT(t_{i})}\right] \Delta t\right) \Delta E\right],$$

$$i = 2, \dots, n_{t},$$

$$j = 1, \dots, n_{E},$$
(29)

<sup>328</sup>  $\Delta t$  and  $\Delta E$  are the discrete *t* and *E* steps, and we impose the initial condition  $\Delta_{47}(t_1) = \Delta_{47}^0$ . This is written in matrix <sup>329</sup> form as

$$\begin{aligned} \mathbf{\Delta}_{47} &= \phi(\mathbf{t}, \mathbf{T} | \mathbf{y}), \\ \mathbf{y} &= \left[ \Delta_{47}^0, \mu_E, \sigma_E, \nu_0 \right], \end{aligned} \tag{30}$$

where **t** and **T** are the length  $n_t$  discretized time and temperature vectors,  $\phi$  denotes the function described in Eqs. 28–29 solved at each  $t_i$ ,  $T_i$  given the input parameter values in **y**, and  $\Delta_{47}$  is the length  $n_t$  vector of resulting  $\Delta_{47}$ values.

We additionally propagate  $\Delta_{47}$  uncertainty. Uncertainty is derived from each input parameter in **y**, which contains either analytical error (for  $\Delta_{47}^0$ ) or regression error associated with each Arrhenius plot (for  $\mu_E$ ,  $\sigma_E$ , and  $\nu_0$ ; Fig. 5). We implicitly assume  $\Delta_{47}^{eq}(T_i)$  is perfectly known for all  $T_i$ . This is not strictly true; however,  $\Delta_{47}^{eq}(T)$  error is expected to be minor relative to that of each parameter in **y** given the strong correlation and low uncertainty in T vs.  $\Delta_{47}^{eq}(T)$ calibration equations (Schauble et al., 2006; Passey and Henkes, 2012; Bonifacie et al., 2017; Lloyd et al., 2018).

Some input parameters are highly correlated—in particular,  $\nu_0$  and  $\mu_E$  (Fig. 5). We account for covariance by propagating error using a Taylor expansion approach (Ku, 1966). Specifically, we calculate  $\Delta_{47}$  variance at each  $t_i$  as

$$\boldsymbol{\Sigma}_{\boldsymbol{\Delta}_{47}\boldsymbol{\Delta}_{47}} = \mathbf{J}\boldsymbol{\Sigma}_{\mathbf{yy}}\mathbf{J}^{T},\tag{31}$$

where **J** is the  $n_t \times 4$  Jacobian matrix of  $\phi(\mathbf{t}, \mathbf{T}|\mathbf{y})$ ,  $\Sigma_{\mathbf{yy}}$  is the 4 × 4 covariance matrix of  $\mathbf{y}$ , and  $\Sigma_{\Delta_{47}\Delta_{47}}$  is the resulting  $n_t \times n_t$  covariance matrix of predicted  $\Delta_{47}$  values. The  $\pm 1\sigma$  uncertainty in predicted  $\Delta_{47}$  values is readily determined as  $\sqrt{\text{diag}(\Sigma_{\Delta_{47}\Delta_{47}})}$ .

#### 343 5. Results

#### <sup>344</sup> 5.1. Inverse and lognormal rate distributions

Most calcite, dolomite, and apatite regularized inverse  $\rho(v)$  distributions are unimodal, symmetric, and lead to 345 predicted G(t) evolution with model-data misfit (root-mean-square error, rmse) that is comparable to analytical uncer-346 tainty (Fig. 3, 4; Table S.3). There are two exceptions to this behavior: First, low-temperature experiments ( $\leq 350$  °C) 347 can result in broad, left-skewed  $\rho(v)$  distributions (Fig. 3B); this is most apparent for experiments exhibiting small 34 signals and thus analytical signal-to-noise ratios  $\lesssim 5$ . In extreme cases, left-skewed  $\rho(\nu)$  distributions can extend to 349  $\ll$  -40, equivalent to rates of  $\ll e^{-40}$  min<sup>-1</sup> at these experimental conditions (Fig. S.2). Material associated with ν 350 such slow rates would exhibit bond reordering residence times of  $\gg 10^{11}$  years and thus remains unreacted over exper-351 imental timescales. Second, very high-temperature experiments ( $\gtrsim 500 \,^{\circ}$ C) can lead to right-skewed  $\rho(\nu)$  distributions 352 (Fig. 3H) that extend to  $\nu \gg 10$ , equivalent to rates of  $\gg e^{10} \min^{-1}$ . Material associated with such fast rates would 353 exhibit bond reordering residence times of  $\ll 10^{-5}$  seconds, orders of magnitude shorter than the duration between 354 any two experimental time points and thus not resolvable in any existing dataset. 355

Both left- and right-skew behaviors are mathematically feasible but physically unconstrained; they emerge when 356 some fraction of material is associated with rates that lead to bond reordering on timescales that lie significantly 357 outside of the analytical time window. We therefore omit from further consideration low-temperature experiments 358 with signal-to-noise  $\leq 5$  (n = 4) as well as high-temperature experiments that reach their  $\Delta_{47}^{eq}(T)$  value prior to the first 359 experimental measurement (n = 2), although this choice does not exert a major impact on observed trends. Our final 360 data set includes 24 calcite experiments (spanning 4 studies, 6 calcite types, and 2 pressure/hydration conditions), 1 361 apatite experiment, and 4 dolomite experiments. Regularized inverse  $\rho(v)$  distributions of retained experiments exhibit 362  $\log_{10}$  rmse averaging  $-2.18 \pm 0.22$  %,  $\log_{10}$  roughness averaging  $-2.65 \pm 0.43$ , and  $\log_{10} \omega$  averaging  $0.08 \pm 0.54$ 363 (mean  $\pm$  stdev.; n = 29); this rmse is comparable to the typical analytical uncertainty of ~0.01 % CDES<sub>90</sub> (Table S.2). 364 Lognormal  $\rho(v)$  distributions exhibit average  $\log_{10}$  rmse of  $-2.08 \pm 0.21$  % (mean  $\pm$  stdev.; n = 29) and typically 365 result in G(t) evolutions that are nearly identical to those predicted by regularized inverse solutions (Fig. 3). This 366 similarity holds even for experiments exhibiting left- or right-skewed inverse solutions since any G(t) evolution differ-367 ences resulting from such skew will only manifest outside of the analytical time window. For the entire dataset,  $\mu(\nu)$ 368 averages  $-5.91 \pm 3.25 \ln(\min^{-1})$  and exhibits a strong positive correlation with temperature whereas  $\sigma(v)$  averages 369



Figure 6: Example of the disordered kinetic model for Tazouta aragonite at 300 °C after relaxing the non-negativity constraint (data from Chen et al., 2019). (A) Measured  $\Delta_{47}$  values and modeled  $\Delta_{47}$  evolution as predicted by the best-fit ( $\omega = 0.1$ ) regularized inversion  $r(\lambda)$  distribution shown in **B**. Importantly,  $r(\lambda)$  contains negative area, suggesting aragonite  $\Delta_{47}$  evolution follows serial disordered kinetics that includes a lag phase operating on the timescale of the  $\lambda$  value at which  $r(\lambda)$  reaches its minimum value (here termed  $\lambda_{\text{lag rate}}$ ). (**C**) Predicted  $\lambda_{\text{lag rate}}$  as a function of *T* for a suite of Tazouta aragonite reordering experiments. Predicted  $\lambda_{\text{lag rate}}$  increases with *T* and is roughly equal to the inverse of the time until incipient aragonite-to-calcite transition observed in Chen et al. (2019). For reference, reaction progress is also shown in **A** by converting  $\Delta_{47}$  to G(t).

2.93 ± 1.01 ln(min<sup>-1</sup>) and exhibits a strong negative correlation with temperature (Fig. 4-5). Propagated model fit uncertainty is small, with estimated parameter error averaging ±0.35 ln(min<sup>-1</sup>) for  $\mu(\nu)$  and ±0.45 ln(min<sup>-1</sup>) for  $\sigma(\nu)$ .

#### 372 5.1.1. Aragonite inverse rate distributions

Unlike all other carbonate minerals, regularized inverse rate distributions for aragonite heating experiments contain 373 negative area due to the observed transient  $\Delta_{47}$  increase (Fig. 6). This result prevents the inclusion of aragonite 374 results when determining Gaussian E distributions, since this exercise requires that rate distributions are lognormally 375 distributed (Eq. 27). Rather, negative  $r(\lambda)$  implies that aragonite bond reordering follows serial disordered kinetics 376 in which one process is significantly slower than others (i.e., a lag phase; Forney and Rothman, 2014). Observed lag 37 rates increase from  $e^{-8.26}$  min<sup>-1</sup> at 200 °C to  $e^{-5.55}$  min<sup>-1</sup> at 400 °C, indicating a temperature-dependent lag phase (Fig. 378 6). This timescale is roughly equal to the time until incipient aragonite-to-calcite phase transition observed by Chen 379 et al. (2019), implicating phase change as the cause of  $\Delta_{47}$  reordering lag. Importantly, this result does not require 380 the inclusion of arbitrary tuning parameters, as has been done previously ( $d_i$  in Table 2 of Chen et al., 2019), nor 381 the assumption that the pair-to-clump reaction is chemically distinct from diffusion (Stolper and Eiler, 2015). Rather, 382 rapid initial  $\Delta_{47}$  decrease followed by a transient  $\Delta_{47}$  increase is consistent with random-walk diffusion and a transition 383 from aragonite to calcite O-O bond distances (Fig. 1-2). 384

# 385 5.2. Comparison to previous models

Lognormal distributed kientics results in model fits that are comparable to or better than those for both the transient defect/equilibrium model (Henkes et al., 2014) and the paired reaction-diffusion model (Stolper and Eiler, 2015). All



Figure 7: Example model fit comparison for an optical calcite (MGB-CC-1) heating experiment performed at 425 °C showing (**A**) measured and predicted  $\Delta_{47}$  evolution trends and (**B**) predicted – measured  $\Delta_{47}$  evolution misfit for each model (data from Passey and Henkes, 2012). Fit statistics for each model are as follows: transient defect/equilibrium defect (blue; Henkes et al., 2014),  $\log_{10}$  rmse = -1.94; paired reaction-diffusion (orange; Stolper and Eiler, 2015),  $\log_{10}$  rmse = -1.92; lognormal disordered kinetics (red; this study),  $\log_{10}$  rmse = -2.06. Shading in **A** represents model parameter  $\pm 1\sigma$  uncertainty. Model results in **B** are staggered slightly along the *t* axis for error bar visual clarity.

models provide similar model-data misfit rmse values. However, estimated  $\mu(\nu)$  and  $\sigma(\nu)$  uncertainty is considerably less than that predicted for Henkes et al. (2014) and Stolper and Eiler (2015) model parameters, leading to smaller propagated error in G(t) evolution predictions (Fig. 7A).

Furthermore, treating reordering rates as a continuous distribution naturally leads to a gradual slowdown in G(t)391 evolution with time; in contrast, the "kinked" rate slowdown behavior of previous models results from fitting a fi-392 nite set of discrete rates to each experiment (3 for the transient defect/equilibrium defect model; 2 for the paired 393 reaction-diffusion model). This difference in gradual vs. kinked rate slowdown leads to slightly divergent model be-394 havior, evidenced by the differences in predicted – measured  $\Delta_{47}$  evolution between different model types (Fig. 7B). 395 Specifically, both previous models tend to over-predict  $\Delta_{47}$  at intermediate time points and under-predict  $\Delta_{47}$  at late 396 time points; in contrast, the lognormal distributed kinetic model exhibits either the opposite behavior or no trend with 397 time. Although these differences are small and statistically insignificant over the timescales of heating experiments 398 considered here, they may become significant if projected over longer experimental timescales. 399

Table 1: Arrhenius regression activation energy distribution results (Eq. 27) for individual calcite and dolomite sample materials and for the "all calcite" average. Experiments exhibiting noisy data [i.e.,  $\Delta_{47}(t)$  signal-to-noise < 5] or non-monotonic  $\Delta_{47}(t)$  evolution were excluded from these calculations (see Sec. 5.3 and Table S.3). Sample materials are only included here if  $\geq$  3 experiments were retained after this screening procedure. OC = optical calcite; BC = brachiopod shell calcite; SC = spar calcite; D = dolomite; WHP = wet, high-pressure experiments; *n* = number of experiments included in Arrhenius regression.

sample	$\mu_E (\mathrm{kJ}\mathrm{mol}^{-1})$		$v_0 ({\rm min}^{-1})$		$\sigma_E (\mathrm{kJ}\mathrm{mol}^{-1})$		п	data reference
	mean	std. dev.	mean	std. dev.	mean	std. dev.		
Eugui dolomite (D)	230.3	47.7	29.0	6.8	14.8	2.2	4	Lloyd et al. (2018)
MGB-CC-1 (OC)	290.2	27.1	42.7	4.6	20.4	1.8	5	Passey and Henkes (2012)
MGB-CC-1 (OC; WHP)	277.8	40.9	41.2	7.1	13.5	2.7	4	Brenner et al. (2018)
NE-CC-1 (SC)	264.4	16.8	35.6	2.7	24.3	0.8	6	Passey and Henkes (2012)
Mexico calcite (OC)	250.7	13.6	34.2	2.3	15.7	1.7	3	Stolper and Eiler (2015)
WA-CB-13 (BC)	247.4	15.6	35.8	2.6	16.6	0.6	5	Henkes et al. (2014)
All calcite average	224.3	27.6	31.5	4.6	17.4	0.7	24	-

#### 400 5.3. Activation energy distributions

Similar to previous observations, disordered kinetic model parameter values scale linearly with 1/T following 401 Arrhenius-like behavior (Fig. 5). Combining all calcite samples yields a  $\mu_{y}$  Arrhenius regression described by  $\mu_{E}$  = 402 224.3 ± 27.6 kJ mol<sup>-1</sup> and  $v_0 = 31.5 \pm 4.6 \ln(\min^{-1})$  and a  $\sigma_v$  Arrhenius regression described by  $\sigma_E = 17.4 \pm 0.7$ 403 kJ mol<sup>-1</sup> [ $\mu_v$  rmse = 1.3 ln(min<sup>-1</sup>);  $\sigma_v$  rmse = 0.9 ln(min<sup>-1</sup>); n = 24]. Similarly, dolomite experiments yield a  $\mu_v$ 40 Arrhenius regression described by  $\mu_E = 230.3 \pm 47.7 \text{ kJ mol}^{-1}$  and  $\nu_0 = 29.0 \pm 6.8 \ln(\text{min}^{-1})$  and a  $\sigma_{\nu}$  Arrhenius 405 regression described by  $\sigma_E = 14.8 \pm 2.2 \text{ kJ mol}^{-1} [\mu_v \text{ rmse} = 0.5 \ln(\text{min}^{-1}); \sigma_v \text{ rmse} = 0.6 \ln(\text{min}^{-1}); n = 4].$ 406 When separated into individual experimental materials, calculated  $\mu_E$  ranges from a minimum of 230.3 ± 47.7 407 kJ mol<sup>-1</sup> for Eugui dolomite to a maximum of  $290.2 \pm 27.1$  kJ mol<sup>-1</sup> for optical calcite sample MGB-CC-1; similarly, 408  $\sigma_E$  ranges from a minimum of  $14.8 \pm 2.2$  kJ mol<sup>-1</sup> for Eugui dolomite to a maximum of  $24.3 \pm 0.8$  kJ mol<sup>-1</sup> for spar 409 calcite sample NE-CC-1 (Table 1). Although all calculated  $\mu_E$  results are statistically identical (two-tailed t test; 410 > 0.05), the "combined calcite" value appears lower than that for any individual calcite type due to bias caused p 411 by differences in the 1/T ranges spanned by experiments using different calcite types. In contrast to  $\mu_E$ , calculated 412  $\sigma_E$  values exhibit statistically significant differences between sample materials (p < 0.05; Table 1), potentially due to 413 differences in trace element contents, ionic impurities, and/or crystallogrpahic defect concentrations (Fig. 1; Henkes 414 et al., 2014; Lloyd et al., 2018). 415

Arrhenius regression results exhibit a minor dependence on the choice of  $\Delta_{47}^{eq}(T)$  calibration equation (Bonifacie et al., 2017; Lloyd et al., 2018). Specifically, recalculating lognormal disordered kinetic model fits and Arrhenius regression parameters using the  $\Delta_{47}^{eq}(T)$  equation advocated by Lloyd et al. (2018) (their Eq. 4) decreases the "combined calcite"  $\mu_E$  value to 205.5 ± 31.1 kJ mol<sup>-1</sup> and leads to slightly higher rmse values but has little impact on  $\nu_0$  and  $\sigma_E$  $[\mu_v \text{ rmse} = 1.4 \ln(\min^{-1}); \sigma_v \text{ rmse} = 1.5 \ln(\min^{-1}); n = 24;$  Fig. S.3]. In contrast, recalculating dolomite results using



Figure 8: Isotopologue reordering diagnostic plots. (A) Apparent equilibrium temperature,  $T(\Delta_{47})_{ae}$ , for a variety of cooling rates. To generate each line,  $\Delta_{47}$  is initially in equilibrium at an arbitrarily high temperature, which then decreases linearly at a given rate.  $T(\Delta_{47})_{ae}$  at each cooling rate is determined using the calculated apparent equilibrium  $\Delta_{47}$  value for that rate. (B) Time-temperature fields for  $\Delta_{47}$  preservation. To generate each line, material that is initially described by  $T(\Delta_{47}) = 25$  °C is assumed to be instantaneously heated and held at a given temperature; dotted lines indicate the time until incipient (1%) isotopologue reordering, which is conservative and may be below the detection limit given typical precision on natural samples, whereas solid lines indicate the time until complete (99%) isotopologue reordering at that temperature. Colors indicate predictions using the kinetic values for each model as reported in their original publications: blue = transient defect/equilibrium defect (Henkes et al., 2014), orange = paired reaction-diffusion (Stolper and Eiler, 2015), black = dolomite lognormal disordered kinetics (this study), red = calcite lognormal disordered kinetics (this study). Shading in A represents model parameter  $\pm 1\sigma$  uncertainty.

- the Lloyd et al. (2018)  $\Delta_{47}^{\text{eq}}(T)$  equation increases  $\mu_E$  to 258.3 ± 43.7 kJ mol<sup>-1</sup> and  $\sigma_E$  to 20.9 ± 3.4 kJ mol<sup>-1</sup> [ $\mu_v$  rmse = 0.5 ln(min<sup>-1</sup>);  $\sigma_v$  rmse = 0.8 ln(min<sup>-1</sup>); n = 4; Fig. S.3)]. None of these differences in Arrhenius parameters calcu-
- lated using the Bonifacie et al. (2017) or the Lloyd et al. (2018)  $\Delta_{47}^{eq}(T)$  calibration equations is statistically significant
- 424 (two-tailed *t* test; p > 0.05).

#### 425 6. Discussion

#### 426 6.1. Model results, implication, and application

This disordered kinetic model provides a generalizable framework of carbonate isotopologue bond reordering. Importantly, previous models (Henkes et al., 2014; Stolper and Eiler, 2015) can be treated as specific cases of disordered kinetics. The finding that  $\mu_E$  for the "all calcite average" appears slightly lower than  $\mu_E$  for dolomite (although within uncertainty) is consistent with the conclusions of Lloyd et al. (2018) (their Fig. 5) and implies that observed

differences between calcite and dolomite from the same metamorphic system are driven, at least in part, by differen-431 tial isotopologue reordering behavior during the same thermal history. There were not enough heating experiments on 432 carbonate groups in apatite that met our screening criteria to derive  $\mu_E$  and  $\sigma_E$  values (see Sec. 5.1). We nonetheless 433 find that apatite  $\mu_{\nu}$  is lower than calcite but identical to dolomite at equivalent experimental temperatures, whereas 434 apatite  $\sigma_{y}$  appears to be slightly lower than any observed calcite or dolomite value (Fig. 5). This result is consistent 435 with the original conclusions of Stolper and Eiler (2015) that experimental heating and empirical carbonatite results 436 for apatite are at odds. Differences between calcite and apatite kinetics, and similarities with dolomite, necessitate 437 additional heating experiments and possible model refinements to accommodate exchange with phosphatic oxygen. 438

Future studies that include independently constrained thermal histories will provide important natural tests of 439 laboratory-derived kinetics. For example,  $\Delta_{47}$  measurements on carbonatites result in  $T(\Delta_{47})$  values far below the 440 canonically known temperatures of crystallization (Dennis and Schrag, 2010). Akin to the concept of closure tem-441 perature in thermochronology (Dodson, 1973), this "apparent equilibrium"  $\Delta_{47}$ -derived temperature, or  $T(\Delta_{47})_{ae}$ , has 442 been shown to depend on geologic cooling rate (Passey and Henkes, 2012). While  $T(\Delta_{47})_{ae}$  measurements may pro-443 vide a useful geospeedometer, cooling rate predictions are sensitive to the choice of bond reordering kinetic model 444 (Fig. 8A). All models predict similar  $T(\Delta_{47})_{ae}$  values of  $\approx 100$  to 200 °C for geologic cooling rates between  $10^{-8}$  and 445  $10^{-4}$  °C yr<sup>-1</sup>, broadly consistent with published  $\Delta_{47}$  measurements of carbonatites and marbles (Dennis and Schrag, 446 2010; Stolper and Eiler, 2015; Lloyd et al., 2017). Interestingly, this similarity at slow cooling rates includes both 447 dolomite and calcite predictions. However,  $T(\Delta_{47})_{ae}$  values diverge significantly at faster rates. For a given mineral, the 448 disordered kinetic model presented here always predicts lower  $T(\Delta_{47})_{ae}$  values than both previous models—although 449 these differences are statistically insignificant at the slowest cooling rates—and suggests that calcite  $T(\Delta_{47})_{ae} \gtrsim 400$ 450 °C as the result of isotopologue reordering in natural samples at geologic cooling rates should be rare. 451

The  $\Delta_{47}$  preservation of low-temperature carbonates such as shells, micritic cements, and carbonate nodules can 452 similarly be evaluated in the context of isotopologue reordering. Such materials have been shown to exhibit high 453  $T(\Delta_{47})$  values without any obvious geochemical alteration to the original mineral (Henkes et al., 2014; Stolper and 454 Eiler, 2015); understanding this phenomenon is critical for screening and omitting altered samples from paleoclimate 455 studies (e.g., Henkes et al., 2018). However, the time-temperature history at which reordering is predicted to occur 456 depends on the choice of kinetic model (Fig. 8B). Specifically, the model presented here conforms to previous limits 457 of  $\Delta_{47}$  preservation but results in a left-ward shift for both "incipient" (1%) and "complete" (99%) reordering curves. 458 That is, relative to previous models, ours predicts that less time and/or lower temperatures are needed to reach the same 459 degree of alteration and suggests that previous models overestimate the temperatures at which isotopologue reordering 460 is activated. Observed differences between models may be driven in part by our use of a single calcite Arrhenius 461

regression (Fig. 5) rather than sample-specific (e.g., brachiopod fossil in Henkes et al., 2014) or experiment-specific
curves (e.g., hydrothermal reactions in Brenner et al., 2018). When separated by calcite type, our model conforms
more closely to predictions of Henkes et al. (2014), particularly for brachiopod shell materials (Fig. S.4).



Figure 9: Thermal histories and corresponding model-predicted carbonate  $T(\Delta_{47})$  evolution for two geologic examples from the recent literature: (**A**–**B**) a 1D conductive cooling model of the Amba Dongar carbonatite (Fosu et al., 2020, cooling model adapted from Ehlers (2005) for a 550 °C intrusion 1.9 km in diameter that cools by thermal diffusion with 30 °C country rock with a diffusivity of 38 km<sup>2</sup> Ma<sup>-1</sup>), and (**C**–**D**) modeled thermal history for various sample depths of the Wagon Wheel 1 (WW-1) drill core in the northwestern Green River Basin (Lacroix and Niemi, 2019). Panels **A** and **C** show imposed *t*–*T* histories (color-coded by WW-1 core depth in **C**) whereas panels **B** and **D** show reordering model-predicted  $T(\Delta_{47})$  plotted against imposed model *T*. All models in **B** predict closure temperature-like behavior, whereas the *T*–*T* pathways predicted by the disordered kinetic model in **D** are more complex and exhibit three distinctive features: (i) the temperature of incipient isotopologue bond reordering, (ii) the rate of approach to equilibrium (shown as a dotted 1 : 1 line), and (iii) the final  $T(\Delta_{47})_{ae}$  (shown to the left of the *y*-axis, including ±1 $\sigma$  model uncertainty). Colors in **B** indicate predictions using the kinetic values for each model as reported in their original publications. Published  $T(\Delta_{47})$  values for each geologic scenario are shown shown as: small gray circles = non-replicated measurements from Amba Dongar (population mean and median as large white circle and red line, respectively; Fosu et al., 2020); large grayscale circles = WW-1 measurements color-coded by core depth, including ±1 s.e. measurement uncertainty.

## 465 6.2. Geologic tests

To exemplify how disordered kinetic model predictions might be applied to real geologic systems, we consider thermal histories of two different calcite-containing rocks from the recent literature. The current challenge for any geologic test of clumped isotope bond reordering models is that few natural systems have complete thermal histories that are known independently (e.g., from thermochronology) and have a sufficient number of  $\Delta_{47}$  measurements for a detailed evaluation of measured versus model-predicted results (exceptions include Shenton et al., 2015; Lloyd et al., 2017; Lawson et al., 2018). Here, we select two  $\Delta_{47}$  datasets with relatively well-constrained thermal histories to test <sup>472</sup> model behavior: (i) the Amba Dongar carbonatite complex from the Deccan large igneous province (Gujarat, India;
<sup>473</sup> Fig. 9A; Fosu et al., 2020) and (ii) lacustrine limestones from drill core in the Pinedale Anticline of the Green River
<sup>474</sup> basin (Wyoming, USA; Fig. 9C; Lacroix and Niemi, 2019).

For the first example, the Amba Dongar thermal history described by Fosu et al. (2020) is a linear 10 °C Myr<sup>-1</sup> 475 cooling from a 400 °C emplacement temperature at 65 Ma. This cools the intrusion to ambient rock temperatures 476 by 40 Ma, after which there is no additional heating. As noted by Fosu et al. (2020), actual intrusion cooling rates 477 are typically non-linear and asymptotic, so instead we model Amba Dongar carbonatite cooling using a 1D thermal 478 diffusion model whereby the intrusion cools by conduction with the country rock (Fig. 9A; Ehlers, 2005). This 479 cooling pathway could also represent other geologic settings, including contact metamorphism (Lloyd et al., 2017) 480 and heating of sedimentary rocks adjacent to dikes (Finnegan et al., 2011). Given that the starting temperature is 481 equivalent to the warmest laboratory heating experiments (i.e., complete  $\Delta_{47}$  change within minutes), all kinetic 482 models predict apparent equilibrium temperature behavior. However, each model results in a slightly different  $T(\Delta_{47})_{ae}$ 483 value (Fig. 9B). The calcite disordered kinetic model predicts a lower  $T(\Delta_{47})_{ae}$  and a shorter interval of departure from 484 equilibrium than both previous models, suggesting  $\Delta_{47}$  systematics are more "open" during the cooling of igneous and 485 metamorphic rocks than previously thought. This finding is consistent with the mean and median  $T(\Delta_{47})$  from the 486 best preserved Amba Dongar calciocarbonatites (B. Fosu, personal communication), both of which are lower than 487 previous model predicted  $T(\Delta_{47})$ . The comparison is limited, however, by outlier high  $T(\Delta_{47})$  values that are difficult 488 to interpret without knowing exact sample locations within the intrusion (e.g., samples from the perimeter may have 489 cooled more rapidly than samples from the core). 490

The second example evaluates bond reordering in deeply buried sedimentary carbonates from the northern Green 491 River Basin using modeled thermal histories for different sample depths of the Wagon Wheel 1 (WW-1) drill core 492 (Fig. 9C, D). Burial temperatures in Lacroix and Niemi (2019) are derived from basin modeling that incorporates 493 stratigraphic thickness, lithology, thermal maturity indices, and geothermal gradients. Unlike conductive cooling of 494 the Amba Dongar complex, modeled WW-1  $T(\Delta_{47})$  exhibits complex and varied features (Fig. 9D). We exclude 495 a direct model-model comparison for this example to highlight depth-dependent patterns (previous bond reordering 496 models were explicitly evaluated by Lacroix and Niemi, 2019). The calcite disordered kinetic model near-perfectly 497 predicts  $T(\Delta_{47})$  at WW-1 depths 2253 and 3373 m; this was not the case for all data-model comparisons performed in 498 Lacroix and Niemi (2019). At deeper depths in Fig. 9C and D, our model over-predicts measured  $T(\Delta_{47})$  by  $\approx 20$  °C; 499 however, Lacroix and Niemi (2019) cite burial model error of 18 °C ( $\pm 1\sigma$ ) during peak heating at 28 to 55 Ma. This 500 allows for the possibility of burial model overestimation of peak temperatures at 4543, 4912, and 5476 m, which 501 would reconcile those apparent data-model discrepancies (Fig. 9D). 502

#### 503 6.3. Outlook

The adaptation of disordered kinetic models to describe internal isotopologue reordering in carbonates will en-504 able more targeted future experiments and will provide robust predictions of bond reordering when applied to natural 505 systems. It has been suggested that various carbonate minerals may exhibit unique isotopologue reordering E distri-506 butions, possibly driven by inherent differences in metal-oxide bond strength (Lloyd et al., 2018) or O-O distances 507 between neighboring  $CO_3$  groups (Fig. 1). Accurately constraining these distributions may allow for the derivation of 508 independent cooling rates from the same rock in geologic systems that contain multiple carbonate types (Ryb et al., 509 2017; Lloyd et al., 2017). A mineralogical driver of isotopologue reordering kinetics would predict that one min-510 eralogy can be thermally reset while another, more refractory carbonate may preserve its formation  $\Delta_{47}$  values after 511 experiencing the same thermal history. Additionally, it has been observed that the same carbonate mineralogy (i.e., 512 calcite) may record different  $\Delta_{47}$  signatures after burial (Shenton et al., 2015). While the underlying reason(s) for 513 this phenomenon remain elusive, improvements in error propagation developed here (e.g., Fig. 9D) can provide an 514 empirical means to interrogate such trends. 515

This disordered kinetic framework can be adapted to characterize the reordering kinetics of other, novel mineral 516 isotopologue measurements. For example, sulfate, phosphate, and silicates all contain isotopologue arrangements that 517 include clumps analogous to <sup>13</sup>C-<sup>18</sup>O (e.g., <sup>34</sup>S-<sup>18</sup>O) and/or double heavy isotope substitutions (e.g., <sup>18</sup>O-<sup>18</sup>O) in 518 the oxyanion group; these minerals are likely subject to analogous diffusive bond reordering at elevated temperatures 519 over geologic timescales. Measurement of such isotopologues with sufficient precision to resolve both natural and 520 experimentally induced isotope effects is imminent (Ueno et al., 2019; Neubauer et al., 2020). Furthermore, future 521 carbonate heating experiments should additionally target  ${}^{12}C^{16}O^{18}O_2$  isotopolgue evolution ( $\Delta_{48}$ ) as a complimentary 522 isotopic marker for diffusive C-O bond breakage and reformation in the solid mineral lattice, although analytical 523 signal-to-noise may limit the applicability of this approach (Fiebig et al., 2019). Finally, disordered kinetics may be 524 usefully applied to mineral-pair isotope exchange kinetics and systems where the same elements occupies different intercrystalline sites (e.g., oxyhydroxides; Miller et al., 2020). 526

# 527 7. Conclusion

<sup>528</sup> We show that early, rapid changes in  $\Delta_{47}$  observed during calcite, dolomite, and apatite laboratory heating experi-<sup>529</sup> ments arise from random-walk isotope diffusion through the mineral lattice, and we derive a disordered kinetic model <sup>530</sup> to describe these results. This framework can be extended to describe  $\Delta_{47}$  evolution other minerals, including non-<sup>531</sup> monotonic aragonite evolution (Chen et al., 2019). We show theoretically that two previous models—the transient <sup>532</sup> defect/equilibrium defect model (Sec. 4.1.2; Henkes et al., 2014) and the paired reaction-diffusion model (Sec. 4.1.3;

Stolper and Eiler, 2015)—represent specific cases of disordered kinetics. By fitting published heating experiment  $\Delta_{47}$ 533 data using an inverse approach, we show that isotopologue reordering rate distributions are approximately lognormal, 534 consistent with the central limit theorem. To extrapolate reordering kinetic model results to geologic scenarios, we 535 determine the underlying Gaussian activation energy distributions using an Arrhenius approach, and we apply these 536 results to two real-world geologic examples. Over geologically reasonable linear cooling rates, all isotopologue re-53 ordering models result in  $T(\Delta_{47})_{ae} < 600$  °C, with our model indicating that observed  $T(\Delta_{47})_{ae} > 400$  °C should be 538 rare for calcite. We also suggest that previous models overestimate the  $\Delta_{47}$  preservation threshold for calcite pale-539 otemperature archives (e.g., fossil shells). These differences are minor for incipient isotopologue reordering, which 540 conforms with limits established by Henkes et al. (2014), but are larger for nearly complete resetting of  $\Delta_{47}$ . For 541 complex thermal histories relevant to metamorphic and sedimentary carbonates, we show that the disordered kinetic 542 model yields reductions in error that will be important for empirical tests of model predictions. Lastly, we hypothe-543 size that the disordered kinetic framework should be easily adapted to other current and future mineral isotopologue 544 measurements such as carbonate  ${}^{18}O{-}^{18}O(\Delta_{48})$  and sulfate  ${}^{34}S{-}^{18}O$ . 545

Accompanying this paper is an open-source Python package 'isotopylog' (Hemingway, 2020) that allows for model comparisons, incorporation of new isotopologue reordering experiment data (including from new carbonate mineralogies), and the prediction of  $\Delta_{47}$  during any point of a geologic thermal history.

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#### 557 Appendix A. Deriving the first-order rate equation

The carbonate isotopologue reordering reaction for material associated with a given rate constant k in a closed system can be written as

$${}^{12}C^{16}O_3(k) + {}^{13}C^{18}O^{16}O_2(k) \xrightarrow[\alpha(T)k]{k}$$

where we have appended each species with (*k*) to emphasize that this reaction only describes the subset of material associated with rate *k*. In all subsequent equations, we replace each species with its atomic mass for convenience. This implicitly ignores contributions to each atomic mass by <sup>17</sup>O-containing isotoplogues since these are negligible (Wang et al., 2004; Schauble et al., 2006). Following Eq. A.1, the derivative of  ${}^{13}C{}^{18}O{}^{16}O{}_{2}$  abundance with respect to time can be written as

$$\frac{d[63](k,t)}{dt} = -k[63](k,t)[60](k,t) + \alpha(T)k[61](k,t)[62](k,t), \quad (A.2)$$

where [*i*] denotes the fractional abundance of atomic mass *i* such that  $\sum_{i=60}^{63} [i] = 1$  (ignoring negligible contributions by other multiply substituted isotopologues; Passey and Henkes, 2012). Similarly following Eq. A.1, we have

$$\alpha(T) = \frac{[60]_{eq}[63]_{eq}}{[61]_{eq}[62]_{eq}},\tag{A.3}$$

where the subscript "eq" denotes equilibrium abundance at temperature *T*; importantly, equilibrium abundances are independent of *k*. Because  ${}^{12}C^{16}O_3$ ,  ${}^{13}C^{16}O_3$  and  ${}^{12}C^{18}O^{16}O_2$  are orders-of-magnitude more abundant than  ${}^{13}C^{18}O^{16}O_2$ (Wang et al., 2004; Affek and Eiler, 2006), we assume that changes in the concentrations of these species are negligible and let

$$[60](k, t) = [60]_{eq},$$

$$[61](k, t) = [61]_{eq},$$

$$[62](k, t) = [62]_{eq}.$$
(A.4)

## 564 Combining Eqs. A.2–A.4 yields

$$\frac{d[63](k,t)}{dt} = -k[60]_{\rm eq} \left\{ [63](k,t) - [63]_{\rm eq} \right\},\tag{A.5}$$

which is a separable first-order differential equation of the form x'(t) = a[x(t) + b]. Because  $[60]_{eq} \approx 1$  (Wang et al., 2004; Affek and Eiler, 2006), we subsume this term into *k*. The fractional abundance of  ${}^{13}C^{18}O^{16}O_2$  at time *t* can thus be determined by integrating Eq. A.5 from an initial time t = 0:

$$\frac{[63](k,t) - [63]_{eq}}{[63]_0 - [63]_{eq}} = e^{-kt},$$
(A.6)

where  $[63]_0$  is the fractional abundance of  ${}^{13}C^{18}O^{16}O_2$  at t = 0. Similar to equilibrium abundances, initial fractional abundances are independent of *k*. Equation A.6 is equivalent to (Passey and Henkes, 2012)

$$\frac{\Delta_{63}(k,t) - \Delta_{63}^{\text{eq}}(T)}{\Delta_{63}^0 - \Delta_{63}^{\text{eq}}(T)} = e^{-kt},\tag{A.7}$$

<sup>570</sup> where, by analogy to Eq. 1,

$$\Delta_{63} = \left[ \left( \frac{R^{63}}{R^{*63}} - 1 \right) - \left( \frac{R^{62}}{R^{*62}} - 1 \right) - \left( \frac{R^{61}}{R^{*61}} - 1 \right) \right] \times 1000\%, \tag{A.8}$$

 $R^{i} = [i]/[60]$ , and  $R^{*i}$  denotes the  $R^{i}$  value for a stochastic isotopologue distribution (Schauble et al., 2006). Following Guo et al. (2009), we let  $\Delta_{63} = \Delta_{47} - \Delta_{47}^{*}$ , where the phosphoric acid fractionation factor  $\Delta_{47}^{*}$  is approximately constant for a given acid digestion temperature. Thus, Eq. A.7 is equal to

$$\frac{\Delta_{47}(k,t) - \Delta_{47}^{\text{eq}}(T)}{\Delta_{47}^0 - \Delta_{47}^{\text{eq}}(T)} = e^{-kt}.$$
(A.9)

Utilizing the definition of g(k, t) from Eq. 3, this can be written as

$$g(k,t) = e^{-kt}. (A.10)$$

Although derivational details differ, this result is identical to that in Appendix A of Passey and Henkes (2012) for bulk  $\Delta_{47}(t)$  evolution assuming a single *k* value.

#### 577 Appendix B. Relationship between reactions in parallel and in series

Stolper and Eiler (2015) treat the carbonate isotopologue reordering reaction as two processes occurring in series: First, neighboring  ${}^{13}C^{18}O^{16}O_2$  and  ${}^{12}C^{16}O_3$  groups react to form a "pair". Then, paired  ${}^{13}C^{16}O_3$  and  ${}^{12}C^{18}O^{16}O_2$ groups diffuse to form "singletons". Following Eq. 16, the derivative of  ${}^{13}C^{18}O^{16}O_2$  and pair abundances with respect to time is

$$\frac{d[63](t)}{dt} = -k_1[60](t)[63](t) + \alpha_1 k_1[p](t), 
\frac{d[p](t)}{dt} = k_1[60](t)[63](t) - (\alpha_1 k_1 + k_{pd})[p](t) 
+ \alpha_{pd} k_{pd}[61]_s(t)[62]_s(t),$$
(B.1)

where [*i*] denotes the fractional abundance of atomic mass *i* and [p] denotes the fractional abundance of pairs such that  $\sum_{i=60}^{63} [i] + [p] = 1$ . As above, we ignore contributions to each atomic mass by <sup>17</sup>O-containing isotopologues (Wang et al., 2004; Schauble et al., 2006). Similarly following Eq. 16, we have

$$\alpha_{1}(T) = \frac{[60]_{eq}[63]_{eq}}{[p]_{eq}},$$

$$\alpha_{pd}(T) = \frac{[p]_{eq}}{[61]_{s,eq}[62]_{s,eq}},$$
(B.2)

where the subscripts "eq" denotes equilibrium abundance at temperature *T* and the subscript "s" denotes singletons. Because  ${}^{12}C^{16}O_3$ ,  $({}^{13}C^{16}O_3)_s$  and  $({}^{12}C^{18}O^{16}O_2)_s$  are orders-of-magnitude more abundant than pairs and  ${}^{13}C^{18}O^{16}O_2$ (Wang et al., 2004; Affek and Eiler, 2006; Stolper and Eiler, 2015), we again assume that changes in the concentrations of these species are negligible and let

$$[60](t) = [60]_{eq},$$

$$[61]_{s}(t) = [61]_{s, eq},$$

$$[62]_{s}(t) = [62]_{s,eq}.$$
(B.3)

589 Furthermore, we use the fact that G(t) is equivalent to

$$G(t) = \frac{[63](t) - [63]_{eq}}{[63]_0 - [63]_{eq}},$$
(B.4)

<sup>590</sup> and we similarly define the reaction progress of pairs as

$$H(t) = \frac{[\mathbf{p}](t) - [\mathbf{p}]_{eq}}{[63]_0 - [63]_{eq}},$$
(B.5)

<sup>591</sup> noting that the upper bound of H(t) depends on [63]<sub>0</sub> and [63]<sub>eq</sub> (i.e., H(t) is not strictly bounded to [0, 1]). By <sup>592</sup> substituting Eqs. B.2–B.5 into Eq. B.1, the derivatives of reaction progress with respect to time can be simplified to

$$\frac{dG(t)}{dt} = -k_1G + \alpha_1k_1H,$$

$$\frac{dH(t)}{dt} = k_1G - (\alpha_1k_1 + k_{\rm pd})H.$$
(B.6)

<sup>593</sup> In matrix from, this becomes

$$\frac{d\mathbf{x}(t)}{dt} = \mathbf{B}\mathbf{x}(t),\tag{B.7}$$

594 where

$$\mathbf{x}(t) = \begin{bmatrix} G(t) \\ H(t) \end{bmatrix}, \quad \mathbf{B} = \begin{bmatrix} -k_1 & \alpha_1 k_1 \\ k_1 & -(\alpha_1 k_1 + k_{pd}) \end{bmatrix}.$$
 (B.8)

<sup>595</sup> The solution to Eq. B.8 is found by assuming solutions exist in the form (Forney and Rothman, 2014)

$$\mathbf{x}(t) = \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} e^{-\lambda t}.$$
 (B.9)

<sup>596</sup> Substituting Eq. B.9 into Eq. B.7 results in the eigenvalue problem

$$-\lambda \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \begin{bmatrix} -k_1 & \alpha_1 k_1 \\ k_1 & -(\alpha_1 k_1 + k_{pd}) \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix},$$
 (B.10)

<sup>597</sup> where  $\lambda$  must satisfy

$$\det\left(\mathbf{B} + \lambda \mathbf{I}\right) = 0,\tag{B.11}$$

and I is the 2×2 identity matrix. Because  $\alpha_1 \gtrsim 1$  and  $(k_1 + k_{pd} + \alpha_1 k_1)^2 > 4k_1k_{pd}$ , Eq. B.11 contains two real solutions,

 $\lambda_1$  and  $\lambda_2$ . Substituting these into Eq. B.10 yields the two eigenvectors,  $\mathbf{u}_1$  and  $\mathbf{u}_2$ . The solution to  $\mathbf{x}(t)$  is thus a superposition of both exponential decays (Forney and Rothman, 2014)

$$\mathbf{x}(t) = f_1 \mathbf{u}_1 e^{-\lambda_1 t} + f_2 \mathbf{u}_2 e^{-\lambda_2 t},\tag{B.12}$$

where the weighting factors  $f_1$  and  $f_2$  can be found by substituting the initial conditions  $G_0$  and  $H_0$  at t = 0 into Eq. B.12;  $G_0 \equiv 1$  by definition whereas  $H_0$  is estimated based on mass spectrometric measurements of [63]<sub>0</sub> and known or assumed *T* vs. [63]<sub>eq</sub> and *T* vs. [p]<sub>eq</sub> relationships (e.g., Eqs. 2 and 17 in Bonifacie et al., 2017; Stolper and Eiler, 2015, respectively). Focusing on G(t), this can be written as

$$G(t) = \sum_{i=1}^{2} r(\lambda_i) e^{-\lambda_i t},$$
(B.13)

where  $r(\lambda_i) = f_i u_{i,1}$  can be though of as  $p(k_i)$  projected onto the eigenvectors (Forney and Rothman, 2014). Therefore, while Eq. 16 defines two reactions in series, the total isotopologue reordering reaction behaves as two reactions occurring in parallel.

# 608 Appendix C. A continuum of paired reaction-diffusion rates

<sup>609</sup> By analogy to Eq. 8, suppose that each step in Eq. 16 is itself described by a parallel superposition of *n* reactions <sup>610</sup> occurring at various rates. This allows  $\kappa_1(t)$  and  $\kappa_{pd}(t)$  in Eq. 16 to evolve with time. It follows that

$$G(t) = \sum_{i=0}^{n} p(k_i)g(k_i, t), \quad H(t) = \sum_{i=0}^{n} q(k_i)h(k_i, t),$$
(C.1)

where  $p(k_i)$  and  $q(k_i)$  are the fractional contributions of each  $k_i$  to G(t) and H(t), respectively, and

$$\sum_{i=1}^{n} p(k_i) \equiv 1, \quad \sum_{i=1}^{n} q(k_i) \equiv 1.$$
(C.2)

#### Equation B.7 can be rewritten for the fraction of material associated with a given k as

$$\frac{dg(k_i,t)}{dt} = -k_i g(k_i,t) + p(k_i) \alpha_1 \sum_{j=1}^n q(k_j) k_j h(k_j,t),$$

$$\frac{dh(k_i,t)}{dt} = q(k_i) \sum_{j=1}^n p(k_j) k_j g(k_j,t) - \left(\alpha_1 \sum_{j=1}^n p(k_j) k_j + k_i\right) h(k_i,t).$$
(C.3)

613 Reaction progress again follows Eq. B.8 but with

$$\mathbf{x}(t) = \begin{bmatrix} \mathbf{g}(t) \\ \mathbf{h}(t) \end{bmatrix},\tag{C.4}$$

614 where

$$\mathbf{g}(t) = [g(k_1, t), g(k_2, t), \dots, g(k_n, t)]^T,$$
  

$$\mathbf{h}(t) = [h(k_1, t), h(k_2, t), \dots, h(k_n, t)]^T,$$
(C.5)

and **B** is now a  $2n \times 2n$  matrix with each row calculated using Eq. C.3. As above,  $\mathbf{x}(t)$  can be found by assuming solutions in the form

$$\mathbf{x}(t) = \begin{vmatrix} u_1 \\ u_2 \\ \vdots \\ u_{2n} \end{vmatrix} e^{-\lambda t}.$$
 (C.6)

There now exist 2*n* solutions with unique eigenvalues and eigenvectors. The overall solution is again a superposition
 of all exponential decays (Forney and Rothman, 2014) calculated as

$$\mathbf{x}(t) = \mathbf{U}e^{-\Lambda t}\mathbf{f},\tag{C.7}$$

where **U** is the  $2n \times 2n$  matrix of eigenvectors, *e* is the matrix exponential, **A** is the  $2n \times 2n$  diagonal matrix of eigenvalues, and **f** is the vector of weighting factors. As above, **f** is found by substituting the initial conditions into Eq. C.7:

$$\mathbf{f} = \mathbf{U}^{-1}\mathbf{x}_0,\tag{C.8}$$

622 where

$$\mathbf{x}_0 = \begin{bmatrix} \mathbf{g}_0 \\ \mathbf{h}_0 \end{bmatrix},\tag{C.9}$$

623 and

$$\mathbf{g}_{0} = G_{0} \left[ p(k_{1}), p(k_{2}), \dots, p(k_{n}) \right]^{T},$$
  

$$\mathbf{h}_{0} = H_{0} \left[ q(k_{1}), q(k_{2}), \dots, q(k_{n}) \right]^{T}.$$
(C.10)

 $G_{24}$   $G_0$  and  $H_0$  are calculated as in Appendix B. Each entry in  $\mathbf{x}(t)$  is thus equal to

$$x_i(t) = f_i \sum_{j=1}^{2n} u_{j,i} e^{-\lambda_i t}.$$
 (C.11)

Again focusing solely on G(t) and recalling that the first *n* rows of  $\mathbf{x}(t)$  correspond to each  $g(k_i, t)$ , Eqs. C.1 and C.11 can be combined to give

$$G(t) = \sum_{i=1}^{n} r(\lambda_i) e^{-\lambda_i t},$$
(C.12)

627 where

$$r(\lambda_i) = p(k_i) f_i \sum_{j=1}^{2n} u_{j,i}.$$
 (C.13)

Equation C.12 is readily written in continuous form as

$$G(t) = \int_0^\infty r(\lambda) e^{-\lambda t}.$$
 (C.14)

Similar to the 2-component case (Appendix B), a system of two reactions in series—each of which following a parallel superposition of first-order reactions at different rates—behaves itself as a superposition of reactions occurring in parallel. A unique feature of serial reactions is that each  $r(\lambda_i)$  can be negative since this represents p(k) projected onto eigenvectors whose entries need not be positive (Eq. C.13).

# 633 Appendix D. Solving the inverse Laplace transform

To numerically estimate  $\rho(\nu)$ , we first discretize *t* and *G*(*t*) into vectors **t** and **G** containing *n<sub>t</sub>* nodes such that each node corresponds to the time of each  $\Delta_{47}$  measurement (Forney and Rothman, 2012b; Hemingway et al., 2017). Importantly, this does not require a uniform time step since  $\Delta_{47}$  reordering experiments are rarely uniformly distributed in time. We similarly discretize *v* into a uniformly spaced vector *v* containing *n<sub>v</sub>* nodes such that

$$\Delta \nu = \frac{\nu_{\rm max} - \nu_{\rm min}}{n_{\nu}},\tag{D.1}$$

where we let  $v_{\min} = -60$  and  $v_{\max} = 20$  based on published data (Passey and Henkes, 2012; Henkes et al., 2014; Stolper and Eiler, 2015; Brenner et al., 2018; Lloyd et al., 2018; Chen et al., 2019).

Equation 19 can be separated into two components: (i)  $\rho(\nu)$  and (ii) the Laplace transform operator  $e^{-e^{\nu}t}$ . We discretize the Laplace transform operator into a  $n_t \times n_{nu}$  matrix **A** such that

$$A_{i,j} = \exp\left[-\exp\left(v_j\right)t_i\right]\Delta v,$$
  

$$i = 1, \dots, n_t,$$
  

$$j = 1, \dots, n_v.$$
  
(D.2)

<sup>642</sup> Finally, we define  $\rho$  to be the unknown, discretized vector of  $\rho(\nu)$  such that

$$\rho_{j} = \frac{1}{\Delta \nu} \int_{\nu_{j} - \frac{1}{2} \Delta \nu}^{\nu_{j} + \frac{1}{2} \Delta \nu} \rho(\nu) d\nu, \quad j = 1, \dots, n_{\nu}.$$
 (D.3)

643 Our model can thus be written in matrix form as

$$\mathbf{G} = \mathbf{A}\boldsymbol{\rho}.\tag{D.4}$$

To find a "smoothed" solution using Tikhonov regularization, we additionally calculate the bi-diagonal first-derivative operator matrix,  $\mathbf{R}$ . That is, we let

$$\left\|\frac{d\rho(\nu)}{d\nu}\right\| = \left[\sum_{j=2}^{n_{\nu}-1} \left(\frac{\rho_{j+1}-\rho_j}{\Delta\nu}\right)^2\right]^{\frac{1}{2}} \equiv \|\mathbf{R}\rho\|,\tag{D.5}$$

where the first and last rows of **R** are set to  $\begin{bmatrix} 1 & 0 \end{bmatrix}$  and  $\begin{bmatrix} 0 & -1 \end{bmatrix}$ , respectively, and **0** is the zero vector of length  $n_v - 1$ . This forces the constraint that  $\rho = 0$  outside of the range  $\nu_{\min} < \nu < \nu_{\max}$  (Forney and Rothman, 2012b).

#### <sup>648</sup> Appendix E. Deriving p(E) from $\rho(v)$

Suppose  $\rho(\nu) \sim \mathcal{N}(\mu_{\nu}, \sigma_{\nu})$  and  $\nu = \nu_0 - E/RT$ , then the pdf of *E* can be readily calculated by change of variables. That is,

$$p(E) = \rho\{\nu(E)\} \left| \frac{d\nu}{dE} \right|,$$

$$= \left( \frac{1}{\sqrt{2\pi}\sigma_{\nu}} \exp\left[ -\frac{(\nu_0 - \frac{E}{RT} - \mu_{\nu})^2}{2\sigma_{\nu}^2} \right] \right) \left| -\frac{1}{RT} \right|.$$
(E.1)

651 If we let

$$\mu_E = RT(\nu_0 - \mu_\nu),$$

$$\sigma_E = RT\sigma_\nu,$$
(E.2)

652 then this simplifies to

$$p(E) = \frac{1}{\sqrt{2\pi\sigma_E}} \exp\left[-\frac{(E - \mu_E)^2}{2\sigma_E^2}\right],$$
(E.3)

which defines a normal distribution with mean  $\mu_E$  and standard deviation  $\sigma_E$ .

# 654 Appendix F. Supplementary data and figures

<sup>655</sup> Supplementary data and figures associated with this article can be found in the online version at http://xxxxxx.

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Table S.1: All heating experiment metadata (sample ID, mineralogy, time, temperature, reference) and stable isotope data ( $\delta^{13}$ C,  $\delta^{18}$ O,  $\Delta_{47}$ ,  $\Delta_{47}$  uncertainty) used in this study. Where applicable,  $\Delta_{47}$  values are presented both in their original reference frame as well as in the CDES<sub>90</sub> reference frame.

Table S.2: Descriptions of all mathematical symbols used throughout this study.

Table S.3: Resulting statistics of regularized inverse (rmse, roughness norm,  $\omega$ ) and lognormal (rmse,  $\mu_{\nu}, \sigma_{\nu}$ ) model fits for all heating experiments used in this study. The non-negativity constraint was relaxed for aragonite experiments [i.e.,  $r(\lambda)$  was fit]; thus, only regularized inverse model fit statistics are included for these experiments.



Figure S.1: Example demonstrating that the "transient defect/equilibrium defect" model (Henkes et al., 2014) is consistent with disordered kinetics. Henkes et al. (2014) *k* values for the model fit to an optical calcite (MGB-CC-1) isotopologue reordering experiment at 425 °C [symbols in **A**; in Henkes et al. (2014) notation; data from their Table B2] were used to generate a  $\Delta_{47}$  evolution trajectory (dotted black line in **B**). The inverse Laplace transform was then determined from this trajectory, leading to the pdf of  $\nu$  in **A** and the corresponding forward-modeled  $\Delta_{47}$  trajectory in **B** (solid blue lines). Both  $\Delta_{47}$  trajectories are identical, demonstrating that the Henkes et al. (2014) model is perfectly recreated by disordered kinetics. For reference, reaction progress is also shown by converting  $\Delta_{47}$  to G(t).



Figure S.2: Same as Fig. 3, but calculated using the spar calcite (NE-CC-1) isotopologue reordering experiment performed at 300 °C (data from Passey and Henkes, 2012). (A) Tikhonov regularization L-curve (solid black line), including the best-fit  $\omega$  value (gray circle). (B) pdf of  $\nu$ , including the best-fit regularized inverse solution (dotted black line) and the lognormal solution (solid blue line). (C) measured  $\Delta_{47}$  values and the modeled  $\Delta_{47}$  evolution as predicted by the best-fit regularized inverse solution (dotted black line) and the lognormal solution (solid blue line). Shaded blue region is the propagated  $\pm 1\sigma$  uncertainty of the lognormal solution. For reference, reaction progress is also shown by converting  $\Delta_{47}$  to G(t). The model fit is poor for this experiment due to the low analytical signal-to-noise ratio, leading to large model uncertainty and an overly broad, left-skewed inverse solution for  $\rho(\nu)$ ; as such, this experiment was omitted from the final dataset. rgh = roughness; rmse = root mean square error, min = minutes.



Figure S.3: Same as Fig. 5, but calculated using the T vs.  $\Delta_{47}^{eq}(T)$  relationship from Lloyd et al. (2018) (their Eq. 4). (A)  $\mu_{\nu}$  and (B)  $\sigma_{\nu}$  as a function of inverse experimental temperature. Arrhenius regression best-fit lines calculated using Eq. 27 for calcite (solid black line) and dolomite (solid blue line) are also shown, including  $\pm 1\sigma$  uncertainty about each regression line (shaded regions). Experiments exhibiting noisy data [i.e.,  $\Delta_{47}(t)$  signal-to-noise < 5] or non-monotonic  $\Delta_{47}(t)$  evolution were excluded from regressions and thus are not shown here (see Sec. 5.3 and Table S.3).



Figure S.4: Time-temperature fields for  $\Delta_{47}$  preservation. Same as Fig. 8B, but calculated here for individual calcite minerals: (A) MGB-CC-1 optical calcite (data from Passey and Henkes, 2012), (B) NE-CC-1 spar calcite (data from Passey and Henkes, 2012), (C) Mexican optical calcite (data from Stolper and Eiler, 2015), (D) WA-CB-13 brachiopod shell calcite (data from Henkes et al., 2014). To generate each line, material that is initially described by  $T(\Delta_{47}) = 25$  °C is assumed to be instantaneously heated and held at a given temperature; dotted lines indicate the time until incipient (1%) isotopologue reordering, which is conservative and may be below the detection limit given typical precision on natural samples, whereas solid lines indicate the time until complete (99%) isotopologue reordering at that temperature. Where available, predictions were generated using kinetic values for each model as reported in their original publications (Henkes et al., 2014; Stolper and Eiler, 2015). In some cases, model parameters for certain minerals have not been previously reported (transient defect/equilibrium defect: NE-CC-1, Mexican optical calcite; paired reaction-diffusion: NE-CC-1) and were calculated here by fitting the original heating experiment data using the 'isotopolog' python package (Hemingway, 2020). blue = transient defect/equilibrium defect (Henkes et al., 2014), orange = paired reaction-diffusion (Stolper and Eiler, 2015), black = lognormal disordered kinetics, hydrothermal conditions (this study; sample MGB-CC-1 only; data from Brenner et al., 2018), red = lognormal disordered kinetics (this study).