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^{13}C-^{18}O Bonds in Precipitated Calcite and Aragonite: An *ab Initio* Study

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Abstract

The ^{13}C-^{18}O bonds in carbonates are potential single-phase geo-thermometers. However, their theoretical distributions (noted as Δ_{47}s) in CO_2 degassed from calcite and aragonite with phosphoric acid are unclear. Thus, the isotope reactions of ^{13}C-^{18}O bonds on the growing surfaces of calcite (0001) and aragonite (001) planes were investigated using *ab initio* techniques. It was found that these reactions determined ^{13}C-^{18}O clumped isotope signatures in bulk calcite and aragonite minerals with novel Δ_{47} polynomials:

$$\Delta_{47\text{-calcite}} = -\frac{8.14673\times10^{8}}{T^{4}} - \frac{9.31441\times10^{6}}{T^{3}} + \frac{1.42742\times10^{5}}{T^{2}} - \frac{1.64905\times10^{2}}{T} + 5.65986\times10^{-2} \quad \text{and}$$

$$\Delta_{47\text{-aragonite}} = -\frac{5.81530\times10^{8}}{T^{4}} - \frac{1.18267\times10^{7}}{T^{3}} + \frac{1.50830\times10^{5}}{T^{2}} - \frac{1.71999\times10^{2}}{T} + 5.86981\times10^{-2}$$

for temperatures T ranging from 260 to 1500 K. These theoretical results were in good agreement with the experimental data. In addition, the influence of phosphoric acid on these polynomials was at the level of 0.01‰.

Keywords

^{13}C-^{18}O Bonds, Clumped Isotope, Calcite and Aragonite, *Ab Initio* Calculation

1. Introduction

Since first catching the attention of geochemists in 2004, the ^{13}C-^{18}O bonds in carbonates have become new geo-thermometers. It is first noted that the isotope reaction:

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$$^{12}C^{18}O^{16}O + {}^{13}C^{16}O_2 = {}^{13}C^{18}O^{16}O + {}^{12}C^{16}O_2 \quad (1)$$

is a geo-thermometer if the relative concentration of $^{13}C^{18}O^{16}O$ in the CO_2 (*i.e.* $\Delta_{47}(CO_2)$, see definition in the Methods section) is determined via mass spectrometry (MS) [1] [2]. Ghosh *et al*. (2006) [3] and (2007) [4] then studied multiply substituted carbonate isotopologues in calcite and aragonite minerals:

$$Ca^{12}C^{18}O^{16}O_2 + Ca^{13}C^{16}O_3 = Ca^{13}C^{18}O^{16}O_2 + Ca^{12}C^{16}O_3 \quad (2)$$

by dissolving carbonates with phosphoric acid [5]-[8] and obtaining different $\Delta_{47}(CO_2)$ values at specific temperatures. The authors suggested that the Δ_{47} value reflected the formation temperature T of carbonates and developed polynomials (e.g. $\Delta_{47} = 0.0592\times10^6\times T^2 - 0.02$ in [3]) by fitting their experimental data.

The relationship of the associated variables in the experiment is:

$$\Delta_{47} = \Delta_{63} + y, \quad (3)$$

where y represents the phosphoric acid fractionation factor and Δ_{63} represents the relative concentration of Mass63 in carbonate Mass60 isotopologues (see definition in the Methods section) [9]. The theoretical explanation for observed Δ_{47} values depends on the ability to define Δ_{63} and y; however, the appropriate approach is under debate. Schauble and Eiler (2004) [10], Schauble *et al*. (2006) [11] and Hill *et al*. (2014) [9] (SSH) performed theoretical calculations of $\Delta_{63\text{-SSH}}$s (approximately 0.40‰ for calcite and aragonite at 25˚C) and suggested the phosphoric acid digestion fractionation factor $y_{\text{-SSH}} = 0.20$‰ at 25˚C. The theoretical analysis by Guo *et al*. (2009) [12] provided a value of $y_{\text{--Guo}} = 0.22(3)$‰ (25˚C) for these two minerals. The combination $\Delta_{63\text{-SSH}} + y_{\text{-SSH}}$ (or $y_{\text{--Guo}}$) agrees with the observed Δ_{47} (=0.6460‰ (25˚C) [3]); however, both $y_{\text{--SSH}}$ and $y_{\text{--Guo}}$ are inconsistent with $y \le 0.14$‰, which was recommended by Ghosh *et al*. (2006). Therefore, new strategies for understanding observed values for Δ_{47} are required.

Herein, we described the results of our investigation of the equilibrium reaction (2) at the interfaces between calcite/aragonite crystals and water using *ab initio* techniques. Notably, new Δ_{47} results for ^{13}C-^{18}O bonds in these minerals were obtained. In addition, the influence of the phosphoric acid digestion process on the Δ_{47} signals was discussed.

2. Method

2.1. Carbonate Isotopologues Reacting on Calcite and Aragonite Surfaces

The ^{13}C-^{18}O bonds in carbonates are isotope signals on growing surfaces during precipitation from solution. As shown by crystal growth models (e.g. the "growth entrapment model" [13]-[15] and the "surface kinetic model" [16]), the bulk carbonate crystal records the isotopic information on its growing surface during precipitation from solution. Natural carbonate samples include stalactites and otoliths [4] [17], teeth and bones [18], corals [3], foraminifera and coccoliths, etc. [3] [4] [11] [17]-[22], which are made up of calcite and aragonite.

For clumped ^{13}C-^{18}O isotopes reacted on calcite and aragonite surfaces (**Figure 1(a)** and **Figure 1(b)**, respectively):

$$Ca^{12}C^{18}O^{16}O_2\big| + Ca^{13}C^{16}O_3\big| = Ca^{13}C^{18}O^{16}O_2\big| + Ca^{12}C^{16}O_3\big|, \quad (4)$$

for which the equilibrium constant is noted as K3866| (illustrating the doubly substituted isotopologues $^{13}C^{18}O^{16}O_2^{2-}$ in the reaction):

$$K3866| = \frac{\left[Ca^{13}C^{18}O^{16}O_2\big|\right]\left[Ca^{12}C^{16}O_3\big|\right]}{\left[Ca^{12}C^{18}O^{16}O_2\big|\right]\left[Ca^{13}C^{16}O_3\big|\right]}, \quad (5)$$

where the brackets indicate the concentrations of matter [10] [11], "|" represents the surface, and the ^{13}C-^{18}O clumped bonds in this reaction remain in the calcite or aragonite [13]-[16].

For the isotopologues in the CO_3^{2-} groups of the carbonate minerals:

$$\Delta_{63}\left(CO_3^{2-}\right) = \left(\frac{[\text{Mass63/Mass60}]_{\text{Sample}}}{[\text{Mass63/Mass60}]_{\text{stochastic random}}} - 1\right)\times 1000, \quad (6)$$

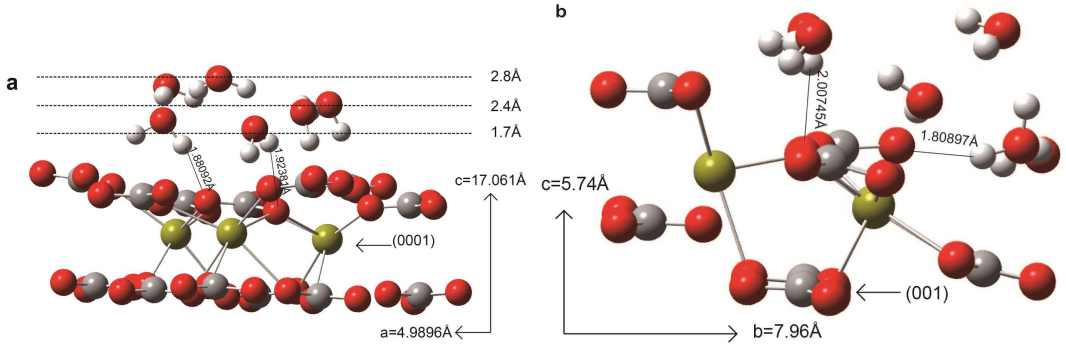

Figure 1. Clusters for the (a) calcite (0001) and (b) aragonite (001) surfaces. The carbonate groups (carbon, grey; oxygen red) of interest are located at the centre of the 1st layers of the solids, and are surrounded by water molecules (hydrogen, white). Also plotted are the lengths of the first 2 shortest Ocarbonate group—Hwater bonds and the thickness of the first 3 water layers perpendicular to the calcite (0001) surface. The effects of the different oxygen sites (not shown) in the groups are also considered in the calculations.

where

$$\text{Mass } 63\ (\text{in amu}) = \text{Mass}\left({}^{12}\text{C}^{16}\text{O}^{17}\text{O}^{18}\text{O}\right) + \text{Mass}\left({}^{12}\text{C}^{17}\text{O}^{17}\text{O}^{17}\text{O}\right) + \text{Mass}\left({}^{13}\text{C}^{16}\text{O}^{17}\text{O}^{17}\text{O}\right) + \text{Mass}\left({}^{13}\text{C}^{16}\text{O}^{16}\text{O}^{18}\text{O}\right)$$

and Mass($^{13}C^{16}O^{16}O^{18}O$) accounts for 94% of the Mass 63 concentration [3] [9] [11] [12].

In physical experiments, the carbonate minerals are dissolved with phosphoric acid to produce CO_2 [3] [4] [20]. For isotopologues of CO_2 degassed from the carbonates:

$$\Delta_{47}\left(\text{CO}_2\right) = \left(\frac{\left[\text{Mass47/Mass44}\right]_{\text{Sample}}}{\left[\text{Mass47/Mass44}\right]_{\text{stochastic random}}} - 1 \right) \times 1000\,, \tag{7}$$

where $\text{Mass } 47\ (\text{in amu}) = \text{Mass}\left({}^{13}\text{C}^{17}\text{O}^{17}\text{O}\right) + \text{Mass}\left({}^{12}\text{C}^{18}\text{O}^{17}\text{O}\right) + \text{Mass}\left({}^{13}\text{C}^{18}\text{O}^{16}\text{O}\right)$, and Mass($^{13}C^{18}O^{16}O$) accounts for 97% of the Mass 47 concentration [1] [2] [10].

2.2. *Ab Initio* Calculations

To investigate reaction (4), the structures of carbonate groups were constructed on calcite (0001) (**Figure 1(a)**) and aragonite (001) (**Figure 1(b)**) surfaces using *ab initio* techniques. Both interfacial clusters [23] [24] had three layers of periodic atoms (calcite, 75; aragonite, 51) to represent each crystal and six water molecules to represent the solution. The atoms in the crystals were terminated with charge points (calcite, 0.333; aragonite, 0.222) [25] at 1 Å along the broken Ca-O bond [26]. The Ca, C and O positions before optimization were the same as those in the lattices, with a = 4.99 Å and c = 17.06 Å for calcite [27] and a = 4.96 Å, b = 7.97 Å and c = 5.74 Å for aragonite [28].

The carbonate groups of interest were located at the centre of each structure and the isotope effect on these carbonate groups from the next-nearest atoms was considered [9] [26] [29]. All of the calculations for these clusters were implemented in the Gaussian09 code [25] using the HF theoretical method [30], and the 6-31G* basis set [31] [32], which are suitable for all of the C, Ca and O elements.

The theoretical equilibrium constant for reaction (4) was calculated using the equation:

$$\text{K3866} = \frac{\text{RPFR}\left(\text{Ca}^{13/12}\text{C}^{18}\text{O}^{16}\text{O}_2\right)}{\text{RPFR}\left(\text{Ca}^{13/12}\text{C}^{16}\text{O}_3\right)}, \tag{8}$$

for which the value of the RPFR (short for reduced partition function ratio [1] [2] [9]-[11] [33] [34]) is given by:

$$\text{RPFR}\left[X^{h/l}E_K\right] = \prod_i^{3N-6} \frac{u_i\left(XE_K^h\right)}{u_i\left(XE_K^l\right)} \frac{\exp\left[-u_i\left(XE_K^h\right)/2\right]}{\exp\left[-u_i\left(XE_K^l\right)/2\right]} \frac{\left\{1-\exp\left[-u_i\left(XE_K^l\right)\right]\right\}}{\left\{1-\exp\left[-u_i\left(XE_K^h\right)\right]\right\}}, \tag{9}$$

where XE_K is the molecule, h and l represent the heavy (^{13}C, ^{18}O) and light (^{12}C, ^{16}O) isotopes for element E and $u = hv_i/kT$, with h representing Planck's constant, v_i the ith frequency of the clusters (see Supplementary Materials) calculated using the Gaussian09 code [25], k is the Boltzmann's constant and T is the temperature (in the range from 260 to 1500 K) (Guo *et al*., 2009; Schauble *et al*., 2006). This temperature range is sufficient for studying the precipitation of calcite and aragonite near 0˚C (the freezing point of water [17]) and 1200˚C (for metamorphic rocks [3]). Note that the symmetry numbers were 1 for both optimized clusters because of their C1 symmetry (see Supplementary Materials).

For calculation of the RPFR, a scaling factor (SF) should be used [11] [29] [35] and is predicted by:

$$\mathrm{SF} = \sum_{\mathrm{i}}^{\mathrm{all}} v_i^{\mathrm{theor}} v_i^{\mathrm{expt}} \Big/ \sum_{\mathrm{i}}^{\mathrm{all}} \left(v_i^{\mathrm{theor}}\right)^2, \tag{10}$$

with the values for v_i for the carbonate groups on the calcite (0001) surface presented in **Table 1**. By comparing the listed experimentally observed and theoretically calculated harmonic frequencies obtained using this equation, the value of the SF was determined to be 1.0613 for the HF/6-31G* level in the present study.

The theoretical values for Δ_{63} were then calculated using the equation:

$$\Delta_{63} \cong 1000 \times \left(\mathrm{K3866}\left|-1\right.\right), \tag{11}$$

which provides results with an accuracy of 94% [3] [9] [11] [12]. All of the Δ_{63} values for calcite and aragonite were obtained by averaging the values for three different oxygen sites (O1, O2 and O3) [9] [11] [12] on each of the two surfaces (see Supplementary Materials).

Re-writing Equation (3) gives the present phosphoric acid fractionation factor:

$$y = \Delta_{47} - \Delta_{63}, \tag{12}$$

where Δ_{47} represents the fitted polynomials from [3] [4] [20] and Δ_{63} represents the values obtained using Equation (11).

3. Results

3.1. Optimized Structures and Harmonic Frequencies

The optimized structures for the calcite and aragonite interfaces are in agreement with experimental observations. In the calcite structure, the O atoms in the water molecules were located at 1.70 - 2.80 Å from and perpendicular to the (0001) surface (**Figure 1(a)**); such values agree well with the vertical data for a (10 - 14) surface: 2.2 - 3.2 Å according to a molecular simulation (MD) study [36] and 2.29 - 3.45 Å as determined via X-ray scattering observations [37].

These structures are also consistent with basic theories on crystal surface chemistry. Both the orientation of the atoms and the bond lengths in the clusters (see Supplementary Materials) slightly deviate from the pure crystal lattice positions [27] [28]; this variation is reasonable [38] due to the termination of the periodic atom layers that are connected to molecules [39].

The *ab initio* harmonic vibrational frequencies (in cm^{-1}), and standard C and O elemental masses for the carbonate groups on the calcite (0001) surface are listed in **Table 1**, which also includes experimental vibrational data for carbonate groups on a calcite surface determined via laser Raman spectroscopy and infrared analysis [40]. The calculated vibrations for the symmetric stretch (v_1) and asymmetric stretching (v_3) bands of the carbonate groups are 1211, 1212 and 1213 cm^{-1} (v_{3b}) and are less than the observed values. On the other hand, the calculated out-of-plane bending (v_2) and in-plane-bending (v_4) bands at 988, 779 and 799 cm^{-1} (v_{4b}) are greater than the observed values.

The harmonic frequencies for the CO_3^{2-} groups with different isotopic masses on the calcite surface are presented in **Table 2**. It can be seen from this data that when the heavier ^{13}C substitutes the lighter ^{12}C isotope in $^{x}C^{16}O^{16}O^{16}O^{2-}|$, v_1 does not change; however, v_2, v_4 and v_{4b} decrease by 29, 2 and 2 cm^{-1}, respectively. These trends are in agreement with the corresponding vibrations in bulk calcite [26]. In addition, when heavier (^{13}C, ^{18}O) isotopes substitute lighter (^{12}C, ^{16}O, respectively) isotopes, the asymmetric stretching (v_3 and v_{3b}) bands under interfacial conditions do not change, which is different from the decreasing trends of v_3 and v_{3b} in bulk calcite [26].

Table 1. Vibrational bands (in cm^{-1}) of carbonate groups on the (0001) surface of calcite and the scaling factor (Scott and Radom, 1996).

Source	ν_1	ν_2	ν_3	ν_{3b}	ν_4	ν_{4b}	S.F.
Experiment[a]	1266	901	1438	1438	713	713	--
This study	1211	988	1212	1213	779	799	1.0613

[a]From Forbes *et al*. (2011)

Table 2. Comparison of the frequencies (in cm^{-1}) of carbonate groups on the calcite surface (this study) and in bulk calcite (Rustad *et al*. (2008)) and their ratios (ν_i/ν_1, in unit 1).

Species	ν_1	ν_2	ν_3	ν_{3b}	ν_4	ν_{4b}	V_i/ν_1	ν_2/ν_1	ν_3/ν_1	ν_{3b}/ν_1	ν_4/ν_1	ν_{4b}/ν_1	Source/Level
$^{12}C^{16}O^{16}O^{16}O^{2-}\|$[a]	1211	988	1212	1213	779	799	1.000	0.816	1.001	1.001	0.643	0.660	
$^{12}C^{18}O^{16}O^{16}O^{2-}\|$	1207	984	1212	1213	773	788	1.000	0.815	1.004	1.005	0.640	0.653	This Study HF/6-31G*
$^{13}C^{16}O^{16}O^{16}O^{2-}\|$	1211	959	1212	1213	777	797	1.000	0.792	1.001	1.001	0.642	0.658	
$^{13}C^{18}O^{16}O^{16}O^{2-}\|$	1207	955	1212	1213	773	786	1.000	0.792	1.004	1.005	0.640	0.651	
$^{12}C^{16}O^{16}O^{16}O^{2-}$-icce[b]	1078	823	1478	1478	685	684	1.000	0.763	1.371	1.371	0.635	0.635	Rustad *et al*. (2008) PBE/6-31G*/3-21G
$^{13}C^{16}O^{16}O^{16}O^{2-}$-icce	1078	798	1436	1436	683	682	1.000	0.740	1.332	1.332	0.634	0.633	

[a]| stands for the surface of the crystal; [b]"icce" stands for inner-crystal-chemical environments.

3.2. Values for Δ_{63}, y and Δ_{47} for Both Calcite and Aragonite

The calculated Δ_{63} values are presented in **Figure 2** and **Figure 3** and **Tables 3-6**. In **Table 4**, it can be seen that for calcite at 25˚C, the Δ_{63} values for O2 and O3 are slightly lower (−0.02‰) and higher (0.02‰), respectively, than the mean value (0.65‰), while that of O1 equals the mean value (**Figure 2(a)**). In contrast, for aragonite at 25˚C, the Δ_{63} values for O2 and O3 are slightly higher (0.01‰ and 0.03‰, respectively) than the mean value (0.66‰), whereas that of O3 is lower (−0.04‰) than the mean value (**Figure 2(b)**). The variations in the Δ_{63} values for the different sites are partly due to the varying lengths of the $O_{(\text{in carbonate group})}$-$H_{(\text{in water})}$ bonds, which range from 1.88 to 1.92 Å in calcite (**Figure 1(a)**) and from 1.81 to 2.01 Å in aragonite (**Figure 1(b)**).

The values for the phosphoric acid fractionation factor y (Equation (12)) are shown in **Figure 4** and **Table 5**. For temperatures ranging from 0˚C to 50˚C, the values in the present study were found to be $y_{\text{-G-T-calcite}} = 0.0067\times10^6/T^2 - 0.0829 \quad \left(R^2 = 0.0106\right)$, $y_{\text{-D-T-calcite}} = -0.0187\times10^6/T^2 + 0.1841$ $\left(R^2 = 0.0106\right)$, $y_{\text{-G-T-aragonite}} = 0.0068\times10^6/T^2 - 0.094 \quad \left(R^2 = 0.0109\right)$ and $y_{\text{-G-T-aragonite}} = -0.0187\times10^6/T^2 + 0.1732 \quad \left(R^2 = 0.0109\right)$ (**Figure 4**). These y values were thus on the order of 0.01‰ in this temperature range, which is in good agreement with the value suggested by Ghosh *et al*. (2006) ($y \le 0.14$ ‰). In addition, the $y_{\text{G-T}}$ polynomials determined for both minerals decreased extremely slowly with increasing temperature (approximately −0.0002‰/˚C), which is consistent with the trend reported by Ghosh *et al*. (2006) (−0.016‰/˚C). Note that the slope calculated in the present study for $y_{\text{D-T}}$ was 0.0005‰/˚C.

Because the values for y calculated in the present study are so small:

$$\Delta_{47} \cong \Delta_{63}, \tag{13}$$

where Δ_{63} is given by Equation (11). Equation (13) provides results with an accuracy of 98%$_{\text{-G}}$ (=(abs (0.658 − 0.01)/0.658)) × 100% for calcite at 25˚C in **Table 5**) and 95%$_{\text{-D}}$ (=(abs(0.658 − 0.032)/0.658)) × 100% for calcite at 25˚C in **Table 5**). This equation also demonstrates why both the Δ_{47} and Δ_{63} values calculated in the present study can be placed on the ordinate in **Figure 2**. Furthermore, the Δ_{47} values calculated in this study agreed well with the experimentally determined values for both minerals (**Figure 2**).

3.3. Uncertainty of the Present Predictions

Possible errors in the *ab initio* calculations were first considered. A series of factors influence the accuracy of the calculated K3866| values, including the quality of the exchange density functional and the level of the basis

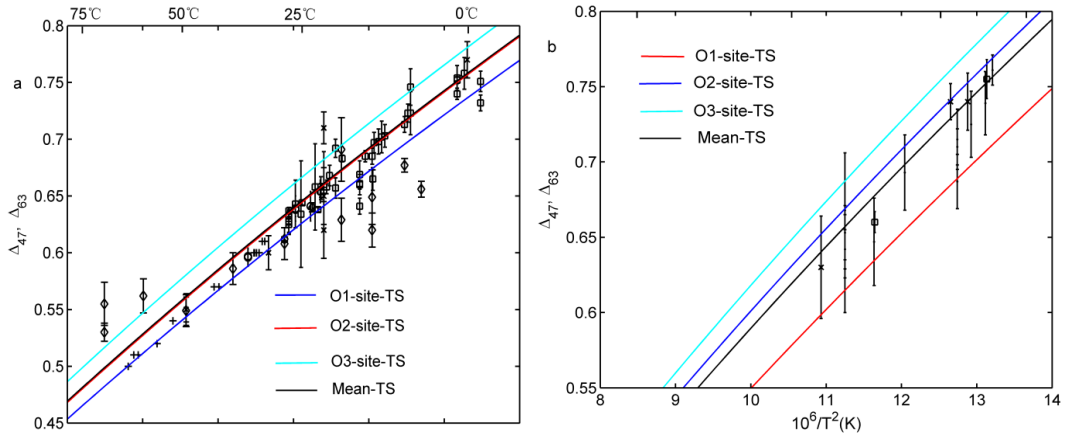

Figure 2. Values for Δ_{47} and Δ_{63} as a function of temperature (K) for (a) calcite and (b) aragonite. The theoretical (this study TS O1, red solid line; TS O2, blue solid line; TS O3, cyan solid line; TS mean, black solid line) and experimental (Ghosh *et al*. (2006), black crosses; Ghosh *et al*. (2007), black dots; Dennis and Schrag (2010), black diamonds; Eagle *et al*. (2010), black circles; Tripati *et al*. (2010), black squares) data are illustrated. The best polynomial fittings for the means of the Δ_{47} and Δ_{63} values for both calcite and aragonite obtained in the present study are shown in **Table 3**.

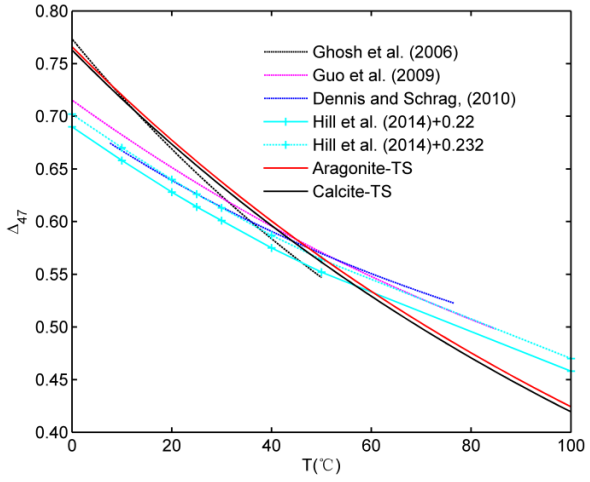

Figure 3. Comparison of this results of the present study (TS, black solid) obtained at the HF/6-31G*/1.0613(SF) level to other theoretical and experimental results for calcite Δ_{47} values from 0˚C to 100˚C. Data points for the data taken from Ghosh *et al*. (2006) (black dashed), Dennis and Schrag (2010) (blue dashed), and combined Guo *et al*. (2009) (cyan dashed) were calculated using their fitted polynomials. The data points for Hill *et al*. (2014) at the B3LYP/6-311++G(2d,dp)(un-scaled) level were illustrated by adding the experimental *y* (0.232 ± 0.015‰) (cross solid) and theoretical *y* (0.220‰, Guo *et al*., 2009) (cross dashed) values. Also shown are the results for $\Delta_{47\text{-aragonite}}$ obtained in the present study (red solid line).

set; thus, the harmonic frequencies, as well as the error of the scaling factor and the Teller-Redlich product rule [41] [42] used in Equation (9). The use of the Teller-Redlich product rule simplifies the calculation of the RPFR [33] [34] with an uncertainty of less than 10^{-5}, as shown in previous theoretical calculations [11] [26] [29] [43]. The standard error for the SF = 1.0613 was not determined because only one experimental vibrational spectrum [40] has been published. The quality of the theoretical method and the level of the basis set consist of systemic errors in the harmonic frequencies; however, it is clear that the systemic errors are partially cancelled out due to the division of the two RPFRs during calculation of the K3866| values [11].

The uncertainties in the calculated *y* values derive from the accuracies of both the calculated Δ_{63} s values and the experimentally fitted Δ_{47} polynomials. As shown above for Equation (11), the Δ_{63} values obtained using

Table 3. Parameters for the polynomial fitting to calculated best-estimate Δ_{63} and Δ_{47} values (Equation (13)) from different studies and the corresponding temperature ranges (K).

	Items	A	B	C	D	E	Temperature range (K)	Reference
Calcite	$\Delta_{47} \cong \Delta_{63}$	-8.14673×10^{8}	-9.31441×10^{6}	1.42742×10^{5}	-1.64905×10^{2}	5.65986×10^{-2}	260 - 1500	This study
	Δ_{63}	-3.40752×10^{9}	2.36545×10^{7}	-2.63167×10^{3}	−5.85372	0.00000	260 - 1500	Schauble *et al.* (2006)
	Δ_{47}	-1.67298×10^{9}	6.81374×10^{6}	5.13850×10^{4}	-7.78016×10^{1}	3.18281×10^{-2}	273.15 - 1373.15	Hill *et al.* (2014)
	Δ_{47}	-3.33040×10^{9}	2.32415×10^{7}	-2.91282×10^{3}	−5.54043	2.32520×10^{-1}	260 - 1500	Guo *et al.* (2009)
Aragonite	$\Delta_{47} \cong \Delta_{63}$	-5.81530×10^{8}	-1.18267×10^{7}	1.50830×10^{5}	-1.71999×10^{2}	5.86981×10^{-2}	260 - 1500	This study
	Δ_{63}	-3.51109×10^{9}	2.40017×10^{7}	-4.62181×10^{2}	−7.25553	0.00000	260 - 1500	Schauble *et al.* (2006)
	Δ_{47}	-1.57483×10^{9}	5.29223×10^{6}	5.85736×10^{4}	-8.57804×10^{1}	3.46876×10^{-2}	273.15 - 1373.15	Hill *et al.* (2014)
	Δ_{47}	-3.43068×10^{9}	2.35766×10^{7}	-8.06003×10^{2}	−6.90300	2.28930×10^{-1}	260 - 1500	Guo *et al.* (2009)

The form of each fit is $\Delta_{47/63}(T) = A/T^4 + B/T^3 + C/T^2 + D/T + E$. Our polynomials reproduce Δ_{63} within 0.26% for both calcite and aragonite from 260 to 1500 K. Present $\Delta_{47} \cong \Delta_{63}$ is given by Equation (13) within 0.01‰.

Table 4. Site-specific effects of Δ_{63} in the present study.

Mineral	Site	0˚C	25˚C	50˚C	75˚C	100˚C
Calcite	O1	0.76	0.65	0.56	0.48	0.42
	O2	0.74	0.63	0.54	0.47	0.41
	O3	0.79	0.67	0.58	0.50	0.44
	Mean	0.76	0.65	0.56	0.48	0.42
Aragonite	O1	0.72	0.62	0.53	0.45	0.39
	O2	0.78	0.67	0.58	0.50	0.43
	O3	0.80	0.69	0.59	0.52	0.45
	Mean	0.77	0.66	0.57	0.49	0.42

the calculated K3866| values have an accuracy within 0.03‰. The external precision of the $\Delta_{47\text{-G}}$ values is 0.01‰ - 0.02‰, with a related temperature precision of ±2˚C [3], and the run-to-run reproducibility and internal counting statistics in [20] were 0.029‰ and 0.012‰, respectively. That is, the accuracies of the experimental Δ_{47} values are at the level of 0.01‰. Therefore, the errors in the *y* values determined in the present study are on the order of 0.01‰, and the precision of the temperature is ±2˚C [3] [4] [9] [12] [20].

3.4. Fractionations for $^{13/12}$C, $^{18/16}$O and $^{14/12}$C

The accuracy of the calculated results obtained in the present study was then evaluated by comparing the calculated and experimentally obtained $^{13/12}$C and $^{18/16}$O fractionations for calcite and aragonite. For RPFR($^{13/12}C_{\text{-calcite}}$) at 25˚C (**Table 6** and **Table 7**), the estimated value of 1.2761 was greater than previously reported results (e.g. 1.2037 [44], 1.1973 [45], 1.20430 [11], 1.1994 [26] and 1.2078 [9]). The calculated value of 1.2785 for RPFR($^{13/12}C_{\text{-aragonite}}$) at 25˚C, was also greater than previously reported results (e.g. 1.20669 [11], 1.2014 [26] and 1.2110 [9]). In contrast, the calculated value of −1.9‰ for $\Delta^{13}C_{\text{Calcite-Aragonite}} = 1000 \times \ln(\text{RPFR}(^{13/12}C_{\text{-calcite}})/\text{RPFR}(^{13/12}C_{\text{-aragontie}}))$ was in good agreement with the value reported previously for low-temperature equilibrium experiments (−1.7 ± 0.4‰, 25˚C) [46] [47].

For RPFR($^{18/16}O_{\text{-calcite}}$) at 25˚C, is the calculated value of 1.1355 was again larger than previously reported results (e.g. 1.1018 [48], 1.1040 [44], 1.10328 [11] and 1.1060 [9]). The calculated value of 1.1394 for RPFR($^{18/16}O_{\text{-aragonite}}$) at 25˚C was also larger than previously reported results (e.g. 1.098 [48], 1.10319 [11], 1.0737 [49] and 1.1075 [9]). On the other hand, the calculated value for $\Delta^{18}O_{\text{Calcite-Aragonite}}$ of −3.4‰ at 25˚C, was less than the experimentally obtained results (−0.6‰ [31] [50] and −1.4‰ at 25˚C, [49]). The difference in the magnitudes of the Δ^{18}O valued may be due to the influence of the acid fractionation factor (1.01107 and 1.01049 for calcite and aragonite, respectively) [11] [51].

The present results may be applied to the study of the climate history of the Paleozoic, Precambrian and Ce-

Table 5. Comparison of Δ_{47}, Δ_{63} and y for different experimental and theoretical predictions. The Δ_{47} and Δ_{63} values for the data taken from Ghosh *et al*. (2006), Guo *et al*. (2009), Schauble *et al*. (2006), Dennis and Schrag (2010) and Hill *et al*. (2014) were calculated from their fitted polynomials, and the corresponding *y* values were copied from these references. The Δ_{63}-T values in the present paper were calculated at the HF/6-31G* level with a scaling factor of 1.0613, and our *y* values were calculated using the equation Δ_{47} (published)-$\Delta_{63\text{-}T}$. For a detailed comparison, the Δ_{47} values at specific temperatures taken from Ghosh *et al*. (2006) and our results are illustrated. See discussions in the text.

Source	Ghosh *et al*. (2006)			Combined Guo *et al*. (2009) with Schauble *et al*. (2006)			Dennis and Schrag (2010)			Hill *et al*. (2014)					
Type	Experiments			Theoretical prediction			Experiments			Theoretical prediction at B3LYP/6-311++G(2d,2p) (unscaled)					
T (˚C)	Δ47	Δ63	*y*	Δ47	Δ63-c[a]	*y*	Δ47	Δ63	*y*	Δ47-c	Δ63-c	*y*	Δ47-c	Δ63-c	*y*
0	0.773			0.724	0.492		-			0.702	0.470		0.690	0.470	
10	0.718			0.690	0.458		0.667			0.670	0.438		0.658	0.438	
20	0.669			0.658	0.427		0.639			0.640	0.408		0.628	0.408	
25	0.646	-	≤0.14	0.643	0.412	0.22	0.626	-	0.22	0.626	0.394	0.232	0.614	0.394	0.22
30	0.624			0.629	0.398		0.614			0.613	0.381		0.601	0.381	
40	0.584			0.601	0.370		0.591			0.587	0.355		0.575	0.355	
50	0.547			0.576	0.345		0.57			0.564	0.332		0.552	0.332	
100	-			0.476	0.245		-			0.470	0.238		0.458	0.238	

[a]The subscript "c" represents calcite.

Source	This study										
Type	Theoretical prediction at HF/6-31G*/1.0613 (SF)										
	Δ47-exp-G[a] (˚C)	Δ63-c	y-G-T-c	Δ63-a[b]	y-G-T-a	T (˚C)	Δ47-exp-D[c]	Δ63-c	y-D-T-c	Δ63-a	y-D-T-a
	0.770(1)	0.758	0.012	0.761	0.009	0	-	0.763	-	0.766	-
	-	-	-	-	-	10	0.677	0.717	−0.040	0.720	−0.043
	0.669(23)	0.661	0.008	0.665	0.004	20	0.660	0.673	−0.013	0.677	−0.017
	-	-	-	-	-	25	0.640	0.653	−0.013	0.657	−0.017
	0.624(33)	0.622	0.002	0.626	−0.002	30	0.624	0.633	−0.009	0.638	−0.014
	-	-	-	-	-	40	0.586	0.596	−0.010	0.601	−0.015
	0.550(50)	0.561	-0.011	0.566	−0.016	50	0.549	0.561	−0.012	0.566	−0.017
	-	-	-	-	-	100	-	0.419	-	0.424	-

[a]The subscripts "exp" and "G" stand for experimental and Ghosh *et al*. (2006), respectively; [b]the subscript "a" represents aragonite; [c]the subscript "D" represents Dennis and Schrag (2010).

Source	This study									
Type	Theoretical prediction at HF/6-31G*/1.0613 (SF)									
T (˚C)	Δ47-fit-G[a]	Δ63-c	y-G-T-c	Δ63-a	y-G-T-a	Δ47-fit-D	Δ63-c	y-D-T-c	Δ63-a	y-D-T-a
0	0.773	0.763	0.010	0.766	0.007	-	0.763	-	0.766	-
10	0.718	0.717	0.001	0.720	–0.002	0.667	0.717	–0.050	0.720	–0.053
20	0.669	0.673	–0.004	0.677	–0.008	0.639	0.673	–0.034	0.677	–0.038
25	0.646	0.653	–0.007	0.657	–0.011	0.626	0.653	–0.027	0.657	–0.031
30	0.624	0.633	–0.009	0.638	–0.014	0.614	0.633	–0.019	0.638	–0.024
40	0.584	0.596	–0.012	0.601	–0.017	0.591	0.596	–0.005	0.601	–0.010
50	0.547	0.561	–0.014	0.566	–0.019	0.570	0.561	0.009	0.566	0.004
100	-	0.419	-	0.424	-	-	0.419	-	0.424	-

[a]The subscript "fit" represents the fitted polynomials from corresponding works.

nozoic [17], including the variation of the ^{14}C concentration in atmosphere in the Quaternary Period [52]. Thus, polynomials for the RPFR($^{14/12}C$) for calcite and aragonite were determined and are provided in **Table 6** and **Table 7**.

Table 6. Parameters for the polynomial fitting to the calculated best-estimate RPFRs for $^{13/12}C$, $^{18/16}O$ and $^{14/12}C$ in calcite and aragonite from 260 to 1500 K.

Mineral	RPFR	A	B	C	D	E
Calcite	$^{13/12}C$	6.91375×10^8	-8.27353×10^6	4.52610×10^4	−2.56409	1.00012
	$^{18/16}O$	2.12160×10^8	-3.00179×10^6	2.02866×10^4	−2.00347	1.00043
	$^{14/12}C$	1.15968×10^9	-1.27842×10^7	8.26906×10^4	−5.28487	1.00064
Aragonite	$^{13/12}C$	7.00201×10^8	-8.34641×10^6	4.55477×10^4	−2.29694	1.00002
	$^{18/16}O$	2.20951×10^8	-3.10683×10^6	2.08805×10^4	−2.00014	1.00042
	$^{14/12}C$	1.17816×10^9	-1.29108×10^7	8.32912×10^4	−4.87379	1.00049

The form of each fit is RPFR (T) = A/T4 + B/T3 + C/T2 + D/T + E. These reproduce RPFR within 1.10‰ ($^{13/12}C$), 0.14‰ ($^{18/16}O$), 1.5‰ ($^{14/12}C$) for calcite and within 1.2‰ ($^{13/12}C$), 0.16‰ ($^{18/16}O$), 1.5‰ ($^{14/12}C$) for aragonite from 260 to 1500 K.

Table 7. RPFRs for $^{13/12}C$, $^{18/16}O$ and $^{14/12}C$ in calcite and aragonite at 25˚C.

Mineral	RPFR	25˚C
Calcite	$^{13/12}C$	1.2761
	$^{18/16}O$	1.1355
	$^{14/12}C$	1.5777
Aragonite	$^{13/12}C$	1.2785
	$^{18/16}O$	1.1394
	$^{14/12}C$	1.5832

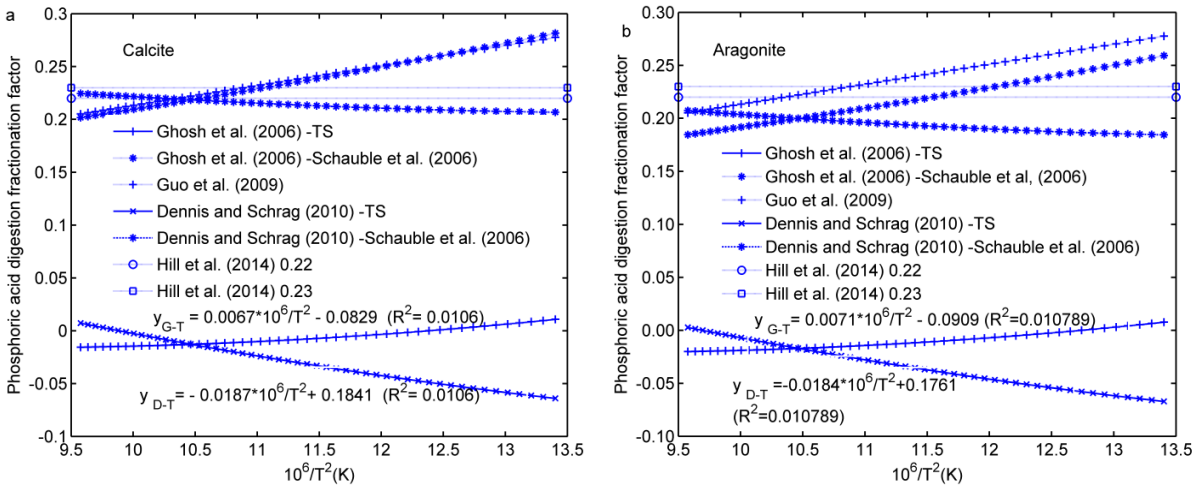

Figure 4. Comparison of the acid digestion fractionation factor *y* for (a) calcite and (b) aragonite for experimental fittings and theoretical results at temperatures from 0˚C to 50˚C. The legends are shown in the middle of both figures. The subscripts "G-T" and "D-T" for our *y* values represent "Ghosh *et al.* (2006)—This work" and "Dennis and Schrag (2010)—This work", respectively. The normals (R^2) of the residuals are also shown. See discussions in the text.

4. Discussion

4.1. Comparison with Previous Studies

Present predictions describe the statistical relationship between observed Δ_{47} values and increasing temperatures. For instance, the Δ_{47} values obtained in the present study are in agreement with those reported in [3] within 0.008‰ (calcite) and 0.004‰ (aragonite) at 23˚C (**Table 5**). This good agreement indicates that the equilibrium isotope reaction (2) occurring on the growing surfaces of these crystals is the source of the experimental Δ_{47} data. The Δ_{47} values calculated in the present study were also in agreement with those reported by Dennis and Schrag (2010) within −0.013‰ (calcite) and −0.017‰ (aragonite) at 25˚C. However, at temperatures above or below 25˚C, the trend in their data is systemically different from that observed for the results obtained in the present study (**Figure 3**). As they stated, the difference may be due to 1) impurities in the precipitated cal-

cite, 2) non-equilibrium isotope fractionation with water, and 3) "inter-lab differences in sample preparation and IRMS analysis". If these factors were to be considered, it is possible that the data would be in better agreement.

The calculated results obtained in the present study were also compared to previously reported theoretical results (**Figure 3**, **Table 3** and **Table 5**). At 25˚C, the present calculated Δ_{63} values of 0.653‰ (calcite) and 0.657‰ (aragonite) were greater than the $\Delta_{63\text{-icce}}$ value (approximately 0.40‰ for both minerals) obtained using lattice dynamics [11] and cluster models [9]. In addition, the calculated Δ_{47} values for calcite systemically deviated from those reported by Guo *et al*. (2009) (**Figure 3**). Furthermore, the y values obtained in the present study were in agreement with [3] but far lower than the conventionally accepted value of 0.22(3)‰ ([9] [12] [20]), regardless of whether $\Delta_{47\text{-fit-G}}$ or $\Delta_{47\text{-fit-D}}$ was used in Equation (12) (**Figure 4** and **Table 5**). This difference is due to different interpretations of the recrystallization process for carbonate samples (see Section 4.2).

Notably, all of the theoretical results obtained in the present study (RPFR($^{13/12}$C), RPFR($^{18/16}$O), K3866|, Δ_{63} and Δ_{47} values) differed from previously reported results. The difference is in part due to the dissimilarity of vibrations (as required in Equation (9)) for carbonate groups at the crystal-water interface (**Figure 1**) and in the inner crystal environment [9] [11] [26]. Examples can be seen in **Table 2**, including the frequencies on the calcite surface at the HF/6-31G* level (this work) and in bulk calcite at the PBE/6-31G*/3-21G level [26]. Note that the frequencies are compared using the $\left(\nu_i/\nu_1\right)$ ratio, because the differences in the magnitudes due to the different calculation levels are cancelled out using this approach, which indicates the property of the *i*th vibration in corresponding clusters. This comparison revealed that: 1) ν_1, ν_2, ν_4 and ν_{4b} on the surface are similar to those in the bulk crystal, whereas the C-O asymmetric stretching vibrations ν_3 and ν_{3b} are very close to ν_1 on the calcite surface, but approximately 1.3 times greater than ν_1 in bulk calcite. As a result, the differences in the results obtained in the present and previous studies are mainly due to the C-O asymmetric stretching vibrations ν_3 and ν_{3b} at the calcite interface.

In addition, the different coordinate atoms (CAs) of the O atoms in the carbonate group in the two different environments also contribute to the difference in the results obtained in the present and previous studies. The CAs of the O atoms include hydrogen, carbon and calcium atoms for both the calcite and aragonite surfaces (**Figure 1**), whereas the CAs for the O atoms in inner crystal environment consist of only carbon and calcium atoms [9]-[11] [26].

4.2. Information behind the Conventional 0.22(3)‰ Value for *y*

In Ghosh *et al*.'s (2006) study, the technical process for analysing the recrystallized $CaCO_3$ from, for example, sample 47413 is shown in **Figure 5**. This process involved seven steps that can be classified as physical or chemical processes. Steps 1, 4 and 6 were physical processes and did not involve chemical reactions and thus were assumed to have little or no influence on the final Δ_{63} and Δ_{47} values.

The remaining four chemical processes play key roles in determining the 0.22(3)‰ value for y. Step 2, which corresponds to the horizontal left arrow in **Figure 6**, includes the reaction:

$$\mathrm{CaCO_3(solid)} \xrightarrow{\text{heat}} \mathrm{CaCO_3(liquid)}, \tag{14}$$

which produces a uniform distribution of different isotopes in the system, but does not change the total chemical composition, including the isotopic Δ_{63} of the system, if a "sealed Pt capsule (ideally without air in it)" is used [3] [4] [12].

In reality, air would be present in the Pt capsules if step 2 in both Ghosh *et al*.'s (2006) and Guo *et al*.'s (2009) experiments was performed in air rather than under a vacuum or atmosphere of a noble gas. In this condition, reactions (15) and (16) below occur during the melting process and contribute to a decrease in the K3866 value.

Steps 3 and 5 involve significant isotopic reactions. Step 3 corresponds to the vertical-down arrow in **Figure 6**. When quenched in air, isotopes in the melted $CaCO_3$ sample (including CO_2, CO and O_2 gases) exchange with gases in the air. Take CO_2 as an example:

$$\mathrm{Ca^{13}CO_3 + {}^{12}CO_2 \Leftrightarrow Ca^{12}CO_3 + {}^{13}CO_2} \tag{15}$$

and

$$\mathrm{CaC^{18}OO_2 + C^{16}OO \Leftrightarrow CaC^{16}OO_2 + C^{18}OO}\,. \tag{16}$$

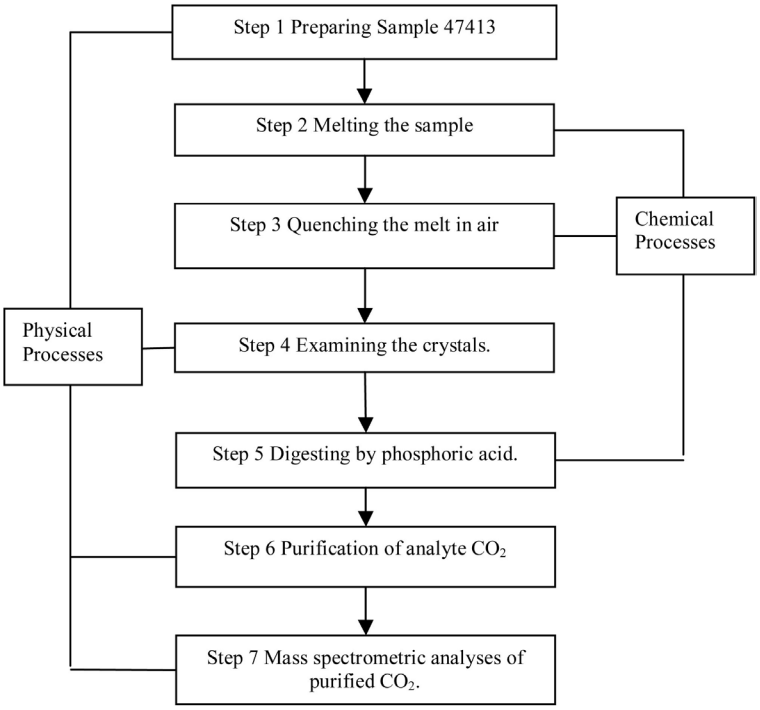

Figure 5. Simplified technical processes for sample 47413 in Ghosh *et al.* (2006). See details for each step in Ghosh *et al*. (2006) and Guo *et al*. (2009). See discussions of the physical (left) and chemical (right) processes in the text.

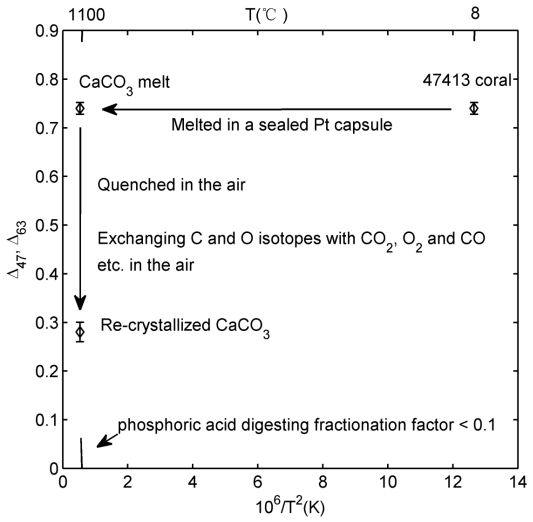

Figure 6. Schematic of the Δ_{63} and Δ_{47}-T paths for the 47413 coral sample during recrystallization. The value for the phosphoric acid digestion fractionation factor in the present study is shown at the bottom of the figure.

Previous experiments (C isotope, [53]; O isotope, [44] [49]) showed that due to these two isotope exchange reactions, calcite is enriched in light ^{12}C and ^{16}O isotopes and loses heavy ^{13}C and ^{18}O isotopes at temperatures above 700˚C, resulting in an increase in the concentration of ^{12}C-^{16}O bonds and a decrease in the concentration of ^{13}C-^{18}O bonds in the sample. Therefore, the values for K3866 (Equation (5)), Δ_{63} (Equation (6)) and Δ_{47} (Equation (7)) decrease. Furthermore, the magnitude of this decline and the extent of the two exchange reactions (Equations (15) and (16)) depend on the concentrations of the isotopes in the CO_2 and the length of the quench-

ing time [54].

When digesting CO_2 from a sample (step 5), phosphoric acid reacts with recrystallized carbonates [5] [8]) and the phosphoric acid fractionation factor is at the level of 0.01‰ according to our calculations. Thus, we suggest that the intercepts (0.28‰, 47413 aragonite coral; 0.22‰, MZ carbonate; 0.14‰, Sigma carb in Ghosh *et al*. (2006) and 0.234, re-crystallized MZ; 0.210, NBS19 standard; 0.243, Sigma carbonate in Guo *et al*. (2009)) represent residual isotope information for the corresponding original $CaCO_3$ samples after reaction with air.

5. Conclusions

Ab initio calculations of ^{13}C-^{18}O clumped isotope reactions on growing surfaces of calcite (0001) and aragonite (001) planes were performed. On the basis of the calculated results, the following conclusions can be drawn:

1) These reactions determine the clumped isotope signatures in bulk carbonate crystals and the corresponding Δ_{47} information after dissolution using phosphoric acid. Over the temperature range from 260 to 1500 K, the calculated Δ_{47} polynomial for calcite was found to be:

$$\Delta_{47\text{-calcite}} = -\frac{8.14673\times10^{8}}{T^{4}} - \frac{9.31441\times10^{6}}{T^{3}} + \frac{1.42742\times10^{5}}{T^{2}} - \frac{1.64905\times10^{2}}{T} + 5.65986\times10^{-2}$$

and that for aragonite:

$$\Delta_{47\text{-aragonite}} = -\frac{5.81530\times10^{8}}{T^{4}} - \frac{1.18267\times10^{7}}{T^{3}} + \frac{1.50830\times10^{5}}{T^{2}} - \frac{1.71999\times10^{2}}{T} + 5.86981\times10^{-2}.$$

2) A comparison of the present results with previously reported experimental data suggests that the phosphoric acid influences the degassing of CO_2 from the carbonates at a level of just 0.01‰. It is therefore thought that the conventional intercept of 0.22(3)‰ is due to C and O isotope reactions between $CaCO_3$ and air.

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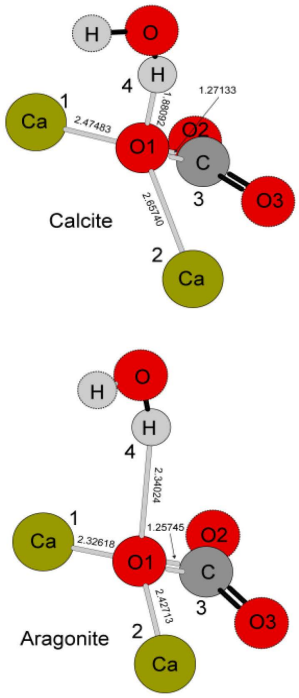
Appendix A. Supplementary Materials

Supplementary Materials can be found in the online version.

This file includes the optimized structures and frequencies for different isotopes of calcite and aragonite at HF/6-31g(d).

Note: the frequencies for calcite in **Table 1** are calculated using the standard masses of the C and O elements, as is required by Scott and Radom, 1996. See details in the reference.

Summarized coordinate atoms of O in the interested carbonate group from the following optimized structures:



The CAs of O atoms are four for both calcite and aragonite. Bonds connecting O atom and its coordinate atoms are labeled in gray. All bond lengths are in unit Å. Three different oxygen sites (O1, O2 and O3) for both clusters are also shown.

Calcite

Optimized structure

C	-0.0230230	0.0007670	-0.4446400
O	0.4617910	-1.1685630	-0.3967090
O	-1.2836860	0.1623270	-0.4144800
O	0.7288450	0.9968490	-0.6315150
Ca	-1.1796140	2.4213900	-1.4197690
Ca	2.7262690	-0.1629330	-1.3789740
Ca	-1.5013110	-2.2980410	-1.3947860
O	6.6810630	-1.2130900	-3.1276730
O	-4.3874590	-5.2876020	-3.1303870
O	-2.3828180	6.4101540	-2.9108600
C	-0.2754310	-5.1617700	0.1913080

O	0.1390190	-2.9999760	-3.0223160
O	-2.2497450	-5.7970080	-2.9695680
O	-0.6523190	-6.3934480	0.3320640
C	-4.5636380	-2.2949640	-0.3904920
O	-4.1999140	-0.1651050	-3.2745190
O	-2.8801880	-3.6960910	-3.0429410
C	-3.1674920	-4.9056350	-3.0269180
O	-1.1664230	-4.2859980	0.0055850
O	-4.3784030	-3.5598870	-0.2440000
O	-5.7769200	-1.8537060	-0.3502480
C	4.2666020	-2.8006590	-0.3448850
O	4.5692300	-0.6493140	-3.0366160
O	2.2471960	-3.5515370	-3.2638800
O	4.4930400	-4.0731380	-0.3433480
O	0.3920450	2.1900710	-3.3436440
O	-2.0668360	-0.7208610	-3.2585870
O	1.6547680	-1.4314100	-3.2477090
C	1.3440560	-2.6478540	-3.1629970
O	0.9471240	-4.9113810	0.2659070
O	3.1361410	-2.3589400	-0.5114570
C	-4.2952320	2.7710240	0.2455700
O	-3.9515380	4.8945710	-3.2127290
O	-2.6665200	1.3765850	-3.0183470
C	-2.9641500	0.1587950	-3.1680420
O	-3.6287250	-1.5386090	-0.6220050
O	-4.6882010	1.5880990	0.3006730
O	-5.1737130	3.7198370	0.3158170
C	4.6006720	2.3358590	0.1858230
O	2.4834930	1.5923220	-3.0917660
O	6.0988860	0.9154360	-3.1600410
C	5.7659620	-0.3182720	-3.0750550
O	5.2803670	-2.0168880	-0.2254650
O	4.2976950	1.1172060	0.0111810
C	0.2746730	5.0886880	-0.3175060
O	-1.8630080	4.2771070	-3.0361700
O	1.9811910	3.7217850	-3.2685370
C	1.6105610	2.4937010	-3.2191400
O	3.7695370	3.2569590	0.2401170
O	0.4322070	3.8806490	-0.4348250
C	-2.7148240	5.1835460	-3.0357640
O	-3.0712680	3.0980310	0.1564520
O	-0.9096860	5.5919710	-0.2155560
O	5.8592190	2.6308380	0.3299360
O	1.2657580	5.9124310	-0.3418320

O	-1.5049420	2.3119750	2.7278940
H	-1.8088750	2.6827930	1.9077160
H	-1.8824040	1.4326430	2.7043390
O	-1.9606090	-2.7767120	3.1322500
H	-2.3246940	-1.9548620	2.8167040
H	-1.0535320	-2.7667590	2.8341590
H	1.1362330	-3.3772950	1.5818770
O	0.9352550	-2.5681990	2.0495070
H	0.8196990	-1.9560540	1.3216630
O	-2.8247080	-0.0875380	1.9322850
H	-3.6081190	0.2892660	1.5359670
H	-2.2510660	-0.1631050	1.1654350
H	0.5826430	1.9428290	2.4758770
O	1.5272880	1.8226250	2.4219010
H	1.7621320	2.0643300	1.5305550
H	2.4077210	-1.3666960	3.0074890
O	2.9750050	-0.6877090	3.3597170
H	2.5652660	0.1300600	3.0830050

^{12}C-^{16}O-^{16}O-^{16}O

30.6544	41.8346	42.7253
53.6617	68.0301	70.1564
78.5847	79.8546	87.8600
97.2758	98.0104	100.9871
105.7885	108.7794	114.7812
115.6602	122.7456	124.6777
129.7366	133.0375	136.6151
141.7599	143.3471	149.4249
153.3454	156.5943	159.3526
165.9855	168.0551	170.3101
174.2787	176.2607	181.6589
184.8070	190.2279	194.5936
196.3730	199.9511	203.9692
207.4377	209.7726	222.3368
228.1494	231.4520	233.8364
234.5392	241.4649	243.9345
246.6461	248.4548	251.2471
264.7378	267.1820	271.9764
273.7314	275.9328	280.3385
280.9214	282.5708	287.8227
291.1314	295.4321	297.3578
301.8462	304.7194	307.0163
314.9027	319.0486	324.6361
326.2658	332.2536	335.1139

341.9809	349.8076	360.3079
365.4962	370.4021	377.8769
380.9912	387.9060	389.7573
396.6841	402.4375	403.4737
406.0564	413.3444	419.0991
421.4648	423.2861	427.6337
438.8009	445.6505	446.4058
449.4633	450.4540	457.7281
461.0814	465.7648	471.5799
474.3527	478.6568	490.4398
497.5874	502.2926	503.0422
514.9460	522.1740	536.8521
553.1607	590.4582	613.0540
616.9678	651.1274	725.2389
767.9069	772.8357	778.9710
781.3630	798.6644	821.3734
825.7894	826.1350	826.4350
826.9117	832.7251	834.7473
836.1825	837.4536	840.9619
842.2231	843.2937	845.0384
846.4536	848.3235	851.0614
852.1290	854.1676	856.0276
856.3232	857.7781	860.0857
867.1921	905.1572	988.1593
1001.8499	1002.9808	1006.8736
1014.1437	1015.5606	1018.2810
1019.7010	1020.6725	1024.1352
1027.0177	1028.4623	1039.7617
1203.3639	1203.9192	1207.4719
1210.8467	1212.0675	1212.5884
1212.9851	1213.4489	1213.6661
1214.1470	1214.9878	1215.5152
1217.3467	1616.4554	1620.8433
1625.0518	1628.3944	1630.6279
1642.7394	1664.4564	1665.9235
1668.5366	1676.5455	1681.6997
1689.1919	1699.3607	1706.9062
1726.6750	1744.3630	1750.0702
1762.9869	1771.1308	1791.6815
1792.4158	1798.2730	1804.7198
1845.1153	1847.7262	1851.7221
1875.5687	1894.0720	1897.8551
1904.0107	1917.3330	1928.2922
3897.6866	3945.2503	3960.5030

3975.6340	3984.9249	4003.4824
4014.1152	4022.6943	4070.1465
4079.8869	4095.3898	4110.3567

^{12}C-^{18}O-^{16}O-^{16}O

30.6252	41.7786	42.6882
53.6153	67.9033	70.0590
78.5605	79.8164	87.8000
97.2409	97.7861	100.9035
105.7267	107.8227	114.6398
115.4961	122.4159	124.5921
129.3606	132.7152	136.3461
141.4591	143.2282	149.0471
152.8865	156.2783	159.1888
165.8883	167.9869	170.0203
174.0532	176.1209	181.4919
184.5366	190.1375	194.3531
196.2625	199.9028	203.8874
207.3763	209.6220	222.0989
227.1419	231.3916	232.8988
233.7263	241.4267	243.1413
246.4970	248.2204	251.0655
264.0542	265.5924	270.5977
273.6466	275.5076	279.9477
280.7585	282.2233	287.4930
290.9634	295.2693	297.2394
301.6646	304.5747	306.9393
314.7891	318.9684	324.6062
326.0217	332.2432	335.0170
341.9752	349.7982	360.2980
365.4901	370.3959	377.8813
380.9932	387.9094	389.7526
396.6899	402.4377	403.4750
406.0468	413.3426	419.0944
421.4613	423.2875	427.5247
438.7884	445.6494	446.3901
449.4442	450.4498	457.7310
461.0836	465.7637	471.5404
474.3589	478.6597	490.4326
497.5781	502.2870	503.0409
514.9484	522.1708	536.8209
553.1594	590.4436	613.0406
616.9659	651.1249	725.1877
761.8619	769.3622	772.8182

780.8139	788.0091	821.3378
825.7869	826.1070	826.4347
826.9030	832.7246	834.7455
836.1797	837.4499	840.9632
842.2227	843.2894	845.0309
846.4534	848.3164	851.0599
852.1266	854.1671	856.0286
856.3227	857.7523	860.0794
866.7383	904.8558	984.1369
1001.8492	1002.9753	1006.8736
1014.1424	1015.5520	1018.2803
1019.6994	1020.6700	1024.1316
1027.0169	1028.4555	1039.7616
1188.4212	1203.3816	1203.9212
1207.4850	1211.8907	1212.5198
1212.8832	1213.4374	1213.5848
1214.1052	1214.9140	1215.5095
1217.3454	1616.4545	1620.8156
1624.8383	1628.3117	1630.3342
1642.0392	1662.4558	1665.3235
1668.5145	1671.9365	1680.9482
1688.2947	1699.3023	1702.0501
1726.6581	1744.1000	1749.8671
1762.9146	1771.1139	1791.6526
1792.4140	1798.1362	1804.7077
1845.0881	1847.6899	1851.6870
1875.4366	1894.0639	1897.7284
1904.0067	1917.1304	1928.2843
3897.6821	3945.2458	3960.5029
3975.6338	3984.9247	4003.4824
4014.1126	4022.6942	4070.1465
4079.8864	4095.3897	4110.3566

^{12}C-^{16}O-^{18}O-^{16}O

30.6299	41.7850	42.6912
53.6219	67.8104	70.0965
78.5541	79.8264	87.7418
96.8790	97.9918	100.7854
105.6947	108.5713	114.6463
115.1848	122.4313	124.3631
129.6400	132.7553	136.4774
141.5227	143.1278	149.1588
152.9029	156.2465	158.9536
165.6887	167.5950	170.0823

174.2431	176.1927	181.4101
184.4705	190.0095	194.0530
196.2425	199.9236	203.7681
207.3403	209.6050	221.9975
228.0155	230.8155	233.3953
234.3567	241.2372	243.6250
246.0924	248.2929	250.6703
264.2250	266.4287	271.6100
273.5614	275.7346	279.7175
280.1790	282.0848	287.2391
290.7042	295.2583	297.3514
301.3654	304.5911	306.8520
314.8668	318.8977	324.6124
326.0439	332.1381	335.0378
341.9282	349.8004	360.2692
365.4390	370.3955	377.8790
380.9918	387.9033	389.7575
396.6924	402.4271	403.4748
406.0545	413.3443	419.0958
421.4586	423.2783	427.4521
438.7914	445.6417	446.3974
449.4448	450.4447	457.7269
461.0861	465.7648	471.5776
474.3581	478.6579	490.4293
497.5875	502.2917	503.0418
514.9518	522.1643	536.8374
553.1536	590.4411	613.0317
616.9554	651.1036	725.2113
762.7547	769.5097	772.8145
780.8952	786.4662	821.2928
825.7870	826.1071	826.4341
826.8992	832.7244	834.7464
836.1764	837.4536	840.9630
842.2225	843.2898	845.0351
846.4520	848.3153	851.0610
852.1257	854.1676	856.0285
856.3220	857.7661	860.0808
867.0355	904.7816	984.0301
1001.8423	1002.9761	1006.8734
1014.1427	1015.5536	1018.2804
1019.6987	1020.6695	1024.1324
1027.0159	1028.4584	1039.7619
1187.7228	1203.3833	1203.9221
1207.4831	1211.8997	1212.5186

1212.8806	1213.4362	1213.5891
1214.1047	1214.9097	1215.5082
1217.3457	1616.4232	1620.8360
1624.5128	1627.9509	1630.5923
1642.3787	1660.6805	1665.6475
1668.1751	1670.5313	1681.5131
1687.6223	1699.3540	1706.1139
1726.6698	1744.1842	1749.9372
1762.9667	1771.0735	1791.6781
1792.4065	1798.2540	1804.6480
1845.1109	1847.6219	1851.7119
1875.5221	1894.0634	1897.7779
1903.9533	1917.2241	1928.2219
3897.6762	3945.2482	3960.5029
3975.6339	3984.9248	4003.4824
4014.1141	4022.6933	4070.1463
4079.8867	4095.3895	4110.3565

^{12}C-^{16}O-^{16}O-^{18}O

30.6436	41.8186	42.6877
53.5750	67.9853	70.0846
78.5564	79.7469	87.7935
97.2154	97.7927	100.3748
105.7332	108.7618	114.5370
115.5723	122.6106	124.4828
128.9775	132.6291	136.3520
141.5944	143.0270	148.8424
153.2185	156.3978	159.0100
165.8562	167.3513	170.0729
174.2448	175.9636	181.4730
184.6149	190.1769	194.2736
195.9903	199.7706	203.8194
207.1755	208.9522	222.2114
227.9665	231.4463	233.4878
234.3523	241.3127	243.8819
246.2821	248.1157	250.9270
264.4752	266.9551	271.5927
273.6751	275.7644	279.6379
280.7005	282.3383	286.8207
290.9986	295.0008	297.2610
300.9188	304.5866	306.8509
314.7100	318.8202	324.6353
325.6426	332.1210	335.0209
341.9326	349.7970	360.2645

365.4315	370.3954	377.8789
380.9897	387.8998	389.7558
396.6788	402.4331	403.4377
406.0571	413.2493	419.0890
421.4642	423.2764	427.5838
438.8001	445.6465	446.3942
449.4377	450.4503	457.7263
461.0859	465.7646	471.5726
474.3534	478.6585	490.4100
497.5823	502.2893	503.0428
514.9499	522.1641	536.7713
553.1542	590.4404	613.0163
616.9556	651.1183	725.2054
765.8319	770.8980	772.7902
779.1188	781.9985	821.3377
825.7878	826.0942	826.4344
826.9055	832.7233	834.7461
836.1791	837.4531	840.9637
842.2212	843.2878	845.0344
846.4534	848.3148	851.0604
852.1243	854.1659	856.0282
856.3210	857.7629	860.0822
866.9675	905.0353	984.3458
1001.8493	1002.9804	1006.8735
1014.1435	1015.5542	1018.2805
1019.6995	1020.6687	1024.1306
1027.0172	1028.4595	1039.7618
1188.8671	1203.3795	1203.9228
1207.4837	1211.8959	1212.5229
1212.8777	1213.4379	1213.5862
1214.1002	1214.9165	1215.5087
1217.3457	1616.4163	1620.8362
1624.9370	1628.1001	1630.5047
1642.6665	1663.9225	1665.8198
1668.0024	1674.7926	1681.2726
1687.8569	1695.8459	1699.4934
1726.6692	1744.3236	1749.4479
1762.8647	1771.0261	1791.6661
1792.3916	1798.1558	1804.6633
1845.0821	1847.6763	1851.6774
1875.2705	1894.0683	1897.8455
1903.9608	1917.3144	1928.2808
3897.6821	3945.2475	3960.5028
3975.6339	3984.9245	4003.4823

4014.1146	4022.6937	4070.1464
4079.8868	4095.3891	4110.3566

^{13}C-^{16}O-^{16}O-^{16}O

30.6447	41.8169	42.7134
53.6388	67.9832	70.1278
78.5704	79.8473	87.8359
97.2205	98.0031	100.9208
105.7714	108.7538	114.7478
115.6230	122.6614	124.6338
129.6204	132.9297	136.5717
141.6834	143.3076	149.4065
153.2308	156.4918	159.2742
165.9461	167.9681	170.3092
174.2751	176.2098	181.6562
184.7930	190.2134	194.5800
196.3666	199.9465	203.9533
207.4098	209.7446	222.2756
228.0798	231.4206	233.7790
234.3388	241.4113	243.8262
246.5607	248.4502	251.2404
264.5952	267.0758	271.7943
273.6821	275.8264	280.1978
280.7400	282.3478	287.6960
291.0576	295.3686	297.3483
301.6753	304.6545	306.9702
314.8848	318.9950	324.6119
326.1501	332.2014	335.0535
341.9588	349.8025	360.2980
365.4822	370.3970	377.8785
380.9919	387.9074	389.7571
396.6894	402.4329	403.4717
406.0578	413.3403	419.0959
421.4630	423.2863	427.6147
438.7966	445.6483	446.3943
449.4463	450.4457	457.7261
461.0833	465.7632	471.5504
474.3543	478.6578	490.4258
497.5864	502.2857	503.0398
514.9482	522.1733	536.8377
553.1426	590.4488	613.0108
616.9588	651.1236	725.2217
767.7504	772.8309	777.1261
781.1539	796.5892	821.2825

825.7897	826.1258	826.4344
826.8653	832.7244	834.7410
836.1822	837.4498	840.9623
842.1721	843.2920	845.0333
846.4520	848.3223	851.0613
852.1269	854.1677	856.0275
856.3230	857.7746	860.0848
867.1411	904.3616	959.4713
1001.8310	1002.9591	1006.8679
1014.1436	1015.5324	1018.2781
1019.6951	1020.6555	1024.1230
1027.0146	1028.4510	1039.7608
1203.3619	1203.9181	1207.4700
1210.7572	1212.0571	1212.5762
1212.9776	1213.4474	1213.6601
1214.1443	1214.9839	1215.5117
1217.3466	1615.2884	1617.6832
1620.8494	1626.7374	1628.2718
1636.4177	1645.7012	1658.2247
1666.0943	1668.3044	1671.9939
1683.4834	1687.5117	1699.4135
1726.6485	1743.7375	1748.8629
1762.7192	1770.8996	1791.6168
1792.3712	1797.8860	1804.5145
1845.0369	1847.4506	1851.5802
1874.8745	1894.0544	1897.5641
1903.8683	1916.9614	1928.2110
3897.6511	3945.2303	3960.5022
3975.6333	3984.9235	4003.4822
4014.1083	4022.6924	4070.1462
4079.8865	4095.3888	4110.3565

C-^{18}O-^{16}O-^{16}O

30.6155	41.7612	42.6762
53.5922	67.8562	70.0308
78.5464	79.8093	87.7756
97.1852	97.7787	100.8367
105.7105	107.7969	114.6038
115.4607	122.3333	124.5497
129.2557	132.6023	136.3019
141.3806	143.1991	149.0269
152.7880	156.1871	159.1075
165.8506	167.9000	170.0185
174.0474	176.0722	181.4883

184.5222	190.1227	194.3384
196.2570	199.8982	203.8724
207.3500	209.5940	222.0328
227.0374	231.3669	232.7471
233.6808	241.3757	243.0539
246.4003	248.2172	251.0647
263.8855	265.4130	270.4982
273.5941	275.4562	279.7053
280.6263	282.0910	287.3550
290.9033	295.2133	297.2306
301.4939	304.5206	306.8989
314.7719	318.9190	324.5844
325.9178	332.1929	334.9663
341.9535	349.7936	360.2874
365.4754	370.3913	377.8830
380.9938	387.9109	389.7525
396.6953	402.4331	403.4730
406.0483	413.3383	419.0914
421.4597	423.2877	427.5066
438.7844	445.6473	446.3793
449.4283	450.4421	457.7292
461.0855	465.7621	471.5128
474.3606	478.6607	490.4186
497.5773	502.2805	503.0389
514.9506	522.1701	536.8063
553.1416	590.4339	612.9968
616.9568	651.1214	725.1623
759.7559	769.1671	772.8117
780.7403	786.3399	821.2439
825.7872	826.1011	826.4341
826.8541	832.7239	834.7390
836.1793	837.4453	840.9636
842.1703	843.2877	845.0255
846.4518	848.3157	851.0599
852.1248	854.1670	856.0286
856.3225	857.7484	860.0786
866.6876	903.9455	955.4175
1001.8290	1002.9558	1006.8679
1014.1422	1015.5304	1018.2779
1019.6944	1020.6558	1024.1216
1027.0142	1028.4469	1039.7607
1188.1359	1203.3802	1203.9200
1207.4841	1211.8896	1212.5152
1212.8828	1213.4372	1213.5817

1214.1042	1214.9135	1215.5067
1217.3453	1610.1293	1616.3625
1620.8424	1626.3464	1626.7478
1634.0995	1645.3275	1654.6062
1666.0643	1668.0187	1671.1325
1683.3219	1687.2733	1699.4085
1726.6412	1743.6418	1748.8001
1762.6952	1770.8921	1791.5999
1792.3703	1797.8184	1804.5062
1845.0191	1847.4238	1851.5584
1874.7889	1894.0479	1897.4686
1903.8655	1916.8114	1928.2040
3897.6467	3945.2259	3960.5021
3975.6331	3984.9233	4003.4822
4014.1058	4022.6923	4070.1462
4079.8860	4095.3888	4110.3565

^{13}C-^{16}O-^{18}O-^{16}O

30.6203	41.7671	42.6795
53.5991	67.7633	70.0680
78.5400	79.8194	87.7173
96.8263	97.9866	100.7191
105.6759	108.5456	114.6086
115.1469	122.3558	124.3159
129.5197	132.6529	136.4363
141.4437	143.0992	149.1416
152.7891	156.1443	158.8811
165.6548	167.5213	170.0771
174.2390	176.1425	181.4073
184.4552	189.9953	194.0411
196.2380	199.9190	203.7543
207.3122	209.5810	221.9315
227.9475	230.7720	233.3574
234.1571	241.1691	243.5221
246.0547	248.2958	250.6573
264.0618	266.2733	271.4349
273.5085	275.6439	279.4104
280.0883	282.0053	287.1112
290.6724	295.1992	297.3407
301.2102	304.5336	306.8144
314.8495	318.8476	324.5902
325.9385	332.0950	334.9851
341.9096	349.7953	360.2606
365.4272	370.3909	377.8806

380.9925	387.9047	389.7574
396.6976	402.4232	403.4727
406.0558	413.3402	419.0926
421.4569	423.2786	427.4358
438.7874	445.6398	446.3865
449.4287	450.4371	457.7249
461.0879	465.7632	471.5481
474.3598	478.6589	490.4158
497.5865	502.2849	503.0394
514.9540	522.1636	536.8226
553.1350	590.4311	612.9861
616.9460	651.0992	725.1923
760.7980	769.2204	772.8026
780.8227	784.7413	821.2022
825.7873	826.1015	826.4335
826.8521	832.7238	834.7403
836.1761	837.4500	840.9634
842.1699	843.2883	845.0300
846.4502	848.3147	851.0610
852.1237	854.1676	856.0285
856.3217	857.7627	860.0799
866.9900	903.9302	955.2466
1001.8245	1002.9568	1006.8677
1014.1426	1015.5308	1018.2782
1019.6940	1020.6553	1024.1221
1027.0138	1028.4493	1039.7610
1187.3229	1203.3827	1203.9209
1207.4817	1211.8992	1212.5140
1212.8799	1213.4358	1213.5871
1214.1035	1214.9088	1215.5052
1217.3457	1606.8085	1616.6145
1620.7823	1626.4852	1628.1409
1634.3150	1643.5911	1657.7783
1665.9705	1668.2137	1671.8296
1683.3361	1687.4595	1699.4104
1726.6454	1743.6597	1748.8122
1762.7097	1770.8738	1791.6147
1792.3660	1797.8737	1804.4742
1845.0335	1847.3812	1851.5722
1874.8436	1894.0458	1897.5049
1903.8263	1916.8772	1928.1532
3897.6409	3945.2282	3960.5022
3975.6333	3984.9234	4003.4822
4014.1073	4022.6914	4070.1460

4079.8864	4095.3886	4110.3563
^{13}C-^{16}O-^{16}O-^{18}O		
30.6339	41.8010	42.6759
53.5521	67.9387	70.0561
78.5425	79.7393	87.7693
97.1532	97.7897	100.3123
105.7146	108.7364	114.5020
115.5369	122.5258	124.4459
128.8533	132.5282	136.3042
141.5110	143.0014	148.8289
153.1054	156.3021	158.9289
165.8177	167.2828	170.0659
174.2412	175.9205	181.4692
184.5999	190.1632	194.2587
195.9859	199.7667	203.8055
207.1450	208.9406	222.1529
227.8921	231.4138	233.4261
234.1584	241.2677	243.7675
246.2034	248.1001	250.9230
264.3244	266.8343	271.4195
273.6297	275.6750	279.4451
280.5218	282.1846	286.6824
290.9321	294.9455	297.2528
300.7831	304.5312	306.8209
314.6964	318.7750	324.6105
325.5627	332.0804	334.9738
341.9140	349.7919	360.2557
365.4199	370.3912	377.8806
380.9904	387.9013	389.7558
396.6844	402.4287	403.4365
406.0584	413.2463	419.0860
421.4625	423.2766	427.5663
438.7958	445.6447	446.3824
449.4205	450.4419	457.7245
461.0876	465.7631	471.5431
474.3550	478.6594	490.3973
497.5811	502.2823	503.0405
514.9521	522.1633	536.7567
553.1368	590.4317	612.9753
616.9466	651.1144	725.1838
764.6713	770.2147	772.7600
777.3621	781.5356	821.2479
825.7881	826.0890	826.4338

826.8574	832.7227	834.7396
836.1788	837.4495	840.9640
842.1678	843.2861	845.0289
846.4517	848.3141	851.0604
852.1226	854.1660	856.0282
856.3208	857.7594	860.0814
866.9144	904.1531	955.6171
1001.8309	1002.9574	1006.8671
1014.1433	1015.5312	1018.2782
1019.6947	1020.6550	1024.1209
1027.0147	1028.4499	1039.7609
1188.7004	1203.3780	1203.9219
1207.4823	1211.8951	1212.5192
1212.8768	1213.4376	1213.5833
1214.0985	1214.9162	1215.5056
1217.3456	1613.5005	1617.3424
1620.5713	1625.5510	1627.2640
1636.2865	1641.6328	1651.6163
1665.8709	1668.2418	1670.5148
1682.9332	1687.4277	1699.4091
1726.6438	1743.7219	1748.6616
1762.6789	1770.8603	1791.6085
1792.3578	1797.8330	1804.4828
1845.0134	1847.4182	1851.5532
1874.6809	1894.0520	1897.5573
1903.8344	1916.9493	1928.2021
3897.6467	3945.2275	3960.5020
3975.6332	3984.9231	4003.4821
4014.1077	4022.6918	4070.1461
4079.8864	4095.3882	4110.3564

Aragonite

Optimized structure

C	-0.1725860	-0.4361650	0.1891690
O	-0.3580990	-0.7200520	1.4171820
O	0.9827230	-0.3613020	-0.3091550
O	-1.1546330	-0.1228010	-0.5309430
Ca	0.0291560	0.5973620	-2.5236760
C	-4.8478800	0.1160510	0.0348820
C	4.8507310	-0.2942410	0.0304710
O	-4.8203830	0.2350890	1.3017600
O	4.8443920	-0.1578690	1.2883860
O	-3.8095300	0.0476960	-0.6131960
O	5.9765090	-0.2333880	-0.5667590

Ca	-2.4292370	0.8686510	1.1434250
Ca	2.4981230	0.5818950	1.1797030
C	0.1192400	2.6853040	-0.0636330
C	5.0659050	2.6203890	-0.0414700
C	-2.5481730	-0.8770530	-3.9559820
C	2.4749360	-1.1056720	-3.9319670
C	-2.2374590	2.1137320	-3.7938370
C	-2.4144880	1.7648180	3.8495390
C	2.4052480	1.9093810	-3.7897580
C	2.5551640	1.5292760	3.8586010
C	-4.8314380	3.0390090	-0.0432470
O	-4.8366850	3.2255000	-1.2858770
O	0.1237200	2.8218300	-1.3080980
O	5.0876340	2.8057720	-1.2849370
O	-2.5271650	-0.6700930	-5.2355360
O	2.4612710	-0.8842810	-5.2100580
O	-2.2537770	1.9301270	-2.5565050
O	-2.3996280	1.8376070	5.1065440
O	2.4072220	1.7170340	-2.5505390
O	2.5484030	1.5825300	5.1241340
O	-5.9128190	3.1606380	0.5851310
O	-0.9694260	2.7385920	0.5722410
O	3.9819230	2.5399440	0.5677420
O	-1.4575320	-1.0431970	-3.3850080
O	3.5887030	-1.2382680	-3.3723340
O	-3.3310380	2.3206750	-4.4145480
O	-3.5060860	1.7178010	3.2312690
O	1.3420930	1.8828670	-4.4398460
O	1.4695970	1.4888880	3.2328460
O	-3.6695360	-0.9327520	-3.3923380
O	1.3739410	-1.1974930	-3.3548590
O	-1.1798130	1.9955970	-4.4444010
O	-1.3373410	1.6362090	3.2179050
O	3.5111160	2.0317180	-4.4104990
O	3.6407320	1.4153350	3.2466040
O	-5.9701150	0.2637130	-0.5543100
O	3.8020360	-0.3185180	-0.6155030
O	-3.7553330	2.8799410	0.5676680
O	1.2061240	2.6194850	0.5740660
O	6.1558240	2.6565930	0.5846940
O	-2.9761310	-2.7781830	-1.0906830
H	-2.3268450	-2.1201500	-0.8674640
H	-3.4212980	-2.3333450	-1.8069360
O	2.0633800	-1.9444060	1.8633330

H	2.3044080	-2.3309430	1.0139680
H	1.1498230	-1.6639770	1.7451220
O	2.5256340	-2.9404810	-0.8683570
H	3.1193110	-2.3001550	-1.2556610
H	1.6983790	-2.6575030	-1.2449200
O	-1.1346410	-1.2014340	4.1823000
H	-0.8001400	-0.8235430	3.3726200
H	-0.8442040	-2.1090680	4.1426300
O	-4.0952810	-0.9430740	4.6684460
H	-3.1543680	-1.0854660	4.5843480
H	-4.3602610	-0.5660950	3.8395380
O	0.1010900	-3.7381450	3.2878560
H	0.9280860	-3.3520060	3.0088000
H	-0.4126850	-3.7949180	2.4907010

^{12}C-^{16}O-^{16}O-^{16}O

25.9731	34.5015	47.0763
63.8670	67.7190	75.2052
89.9886	94.4752	95.9246
105.2157	115.2175	120.9085
125.4642	128.6023	144.2251
147.2381	149.8592	164.2406
165.9676	167.6335	176.9085
187.8815	193.8459	203.2976
208.0605	211.1808	215.0179
216.4792	229.4220	231.3552
240.3244	241.4672	249.0635
260.6808	263.6970	264.9748
266.8514	268.6232	272.6189
273.1160	276.6529	279.7675
283.9349	287.4145	289.9067
290.3693	293.0853	294.3539
295.8610	301.8701	302.6995
306.3095	309.8829	310.3045
313.6831	316.6507	317.4602
321.4651	322.4512	324.3445
328.8436	332.1401	333.6479
334.7521	341.9676	345.0220
347.0002	351.3422	351.8922
356.4367	359.7621	361.7361
365.9039	367.1953	370.7295
374.2581	379.0368	382.8220
384.8617	386.7989	390.6582
393.0677	396.2062	401.2650

402.9481	408.5480	415.9018
416.8047	423.7246	426.4750
428.4585	432.0462	436.2060
439.3298	442.8479	449.6811
459.8785	461.2496	465.1558
469.8212	545.9002	582.2756
585.8348	589.2807	677.3573
680.4194	705.5449	717.4103
764.3707	790.6120	799.8950
809.7247	825.9609	828.8646
832.6103	834.5304	835.2361
837.7872	840.4463	843.3853
848.7781	849.2363	854.0111
857.7909	865.5366	879.0348
884.0962	885.0661	888.7694
898.4870	902.0844	928.2079
952.7464	955.6517	975.8154
979.0761	981.0532	983.1216
987.1558	1000.5169	1001.9932
1005.0093	1014.0580	1016.4581
1021.0028	1023.3920	1052.1681
1213.4553	1217.0936	1225.3937
1237.2786	1242.3009	1244.2865
1251.2708	1252.2309	1253.3695
1256.0450	1260.3111	1263.8601
1634.9713	1648.8909	1673.5442
1697.6825	1708.8977	1713.8158
1727.1305	1732.1685	1746.6296
1767.8376	1773.4514	1779.0698
1788.3774	1788.8961	1792.7631
1802.1618	1815.9982	1820.1427
1835.8807	1838.6103	1843.7019
1858.0228	1864.2083	1868.6079
1874.6660	1884.4103	1890.2343
1897.9880	1905.8027	1915.9212
3804.0086	3865.1703	3975.3986
3998.4775	4009.7939	4023.2087
4034.5287	4071.4975	4098.2953
4106.9224	4120.8056	4136.1211

^{12}C-^{18}O-^{16}O-^{16}O

25.8870	34.2900	47.0705
63.6253	67.4741	74.7104
89.8877	92.9773	95.6080

105.2160	114.8425	120.8036
125.2030	128.4523	144.0605
146.8677	149.8012	164.0635
164.9276	166.4320	176.8285
187.8609	193.7334	203.2894
207.4014	210.9283	214.8173
215.4797	229.4104	231.3212
240.2436	241.4461	248.3863
260.4765	263.5210	264.8589
266.8442	268.4896	272.6269
273.0201	276.0279	279.4343
283.9274	287.1941	289.9059
290.1289	293.0423	293.8668
295.8543	301.7794	302.7057
306.2687	309.8705	310.2820
313.5619	316.6408	317.4141
321.4663	322.3993	324.3273
328.8144	332.0741	333.6274
334.6296	341.9003	345.0196
346.7520	351.2236	351.8586
356.4216	359.6199	361.7351
365.8634	367.1881	370.7185
374.2116	379.0386	382.7285
384.7666	386.7527	390.6380
392.9812	396.0247	401.2560
402.8712	408.5392	415.9042
416.8010	423.7102	426.4671
428.4570	432.0073	436.1876
439.3001	442.8302	449.6689
459.8781	461.2287	465.1547
469.8228	545.8806	582.2765
585.7903	589.2797	677.3566
680.3952	705.5144	717.2451
749.2720	790.3422	799.8901
809.7204	819.9887	825.9704
832.0532	833.2816	834.6209
837.7793	840.4363	843.3042
848.7788	849.1546	854.0072
857.7905	865.5369	879.0356
884.0943	885.0391	888.7695
898.4871	902.0849	928.1744
952.7532	955.6536	973.6363
979.0709	981.0300	983.1200
986.8173	1000.4078	1001.0247

1004.8018	1014.0573	1016.4563
1021.0003	1023.3887	1051.7473
1201.8605	1213.4566	1217.1108
1237.2373	1242.1931	1244.2553
1251.2707	1252.2300	1253.3696
1256.0452	1260.3084	1263.8603
1634.9636	1648.7478	1662.1918
1697.0291	1708.7221	1713.5501
1727.1305	1732.1545	1746.4955
1767.8043	1773.4306	1779.0591
1788.3732	1788.8804	1792.7529
1802.1512	1815.8754	1820.0527
1835.7762	1838.6019	1843.6935
1857.9981	1864.1567	1868.5973
1874.6629	1884.3932	1890.2080
1897.9773	1905.5688	1915.8097
3803.9986	3865.1610	3975.3980
3998.4770	4009.7936	4023.2087
4034.5286	4071.4955	4098.2953
4106.9220	4120.8055	4136.1210

^{12}C-^{16}O-^{18}O-^{16}O

25.9744	34.4556	47.0549
63.8364	67.5474	74.8263
89.9752	94.0697	95.8513
105.0199	115.1382	120.0251
125.0285	128.5336	144.1749
147.1627	149.7815	163.9678
165.5100	166.8565	176.5701
187.3813	193.5296	203.2621
207.8618	211.0282	214.7801
215.3815	229.2873	231.1312
239.7491	241.4518	248.7415
260.6295	263.5568	264.5996
266.8141	268.6175	272.5189
273.0679	276.5225	279.6206
283.7514	287.1821	289.8777
290.2807	292.9606	294.1510
295.7638	301.8030	302.6500
306.1766	309.7952	310.2501
313.6155	316.5437	317.3291
321.3953	322.2772	324.2929
328.8021	331.9393	333.6116
334.5089	341.8366	345.0167

346.3774	350.8042	351.8375
356.4263	359.2600	361.7230
365.8683	367.1908	370.5415
374.2289	379.0385	382.3166
384.6454	386.5706	390.6067
392.9979	395.6436	398.9836
402.5290	408.5182	415.9036
416.7555	423.7070	426.4667
428.2497	432.0398	435.8841
439.1677	442.5902	449.6723
459.8601	461.2345	465.1563
469.8139	545.7458	582.2766
585.7431	589.2776	677.3355
680.4008	705.4026	717.2285
749.7299	790.3510	799.8855
809.7175	818.8624	825.9716
832.0371	833.2154	834.6233
837.7828	840.4363	843.3181
848.7790	849.1561	854.0042
857.7898	865.5355	879.0378
884.0943	885.0499	888.7695
898.4879	902.0845	928.1919
952.7505	955.6531	973.6979
979.0720	981.0314	983.1211
986.8137	1000.3500	1000.8457
1004.7743	1014.0571	1016.4555
1021.0006	1023.3871	1051.8389
1202.4669	1213.4574	1217.1112
1237.2266	1242.2020	1244.2475
1251.2706	1252.2297	1253.3696
1256.0449	1260.3070	1263.8603
1634.8587	1648.8587	1666.4457
1696.6757	1704.3909	1712.8948
1727.1305	1732.1665	1744.3793
1767.5099	1773.4231	1779.0134
1788.3098	1788.6847	1792.6287
1801.9856	1815.9711	1820.0392
1835.8604	1838.5679	1843.6533
1858.0126	1864.1732	1868.4294
1874.6450	1884.3814	1890.1521
1897.8633	1905.3327	1915.8894
3804.0027	3865.1660	3975.3983
3998.4774	4009.7933	4023.2085
4034.5287	4071.4965	4098.2952

4106.9216	4120.8055	4136.1211
^{12}C-^{16}O-^{16}O-^{18}O		
25.7459	34.3939	46.9274
63.7205	67.2757	74.9717
89.8566	94.0546	95.6922
104.9222	114.5193	120.7340
125.3839	128.5698	144.0145
147.2164	149.6139	163.7647
165.4508	167.5871	176.6463
187.6036	193.8375	203.1957
207.8849	210.7247	214.9742
216.2714	229.2366	231.2884
240.2795	241.4135	248.6376
260.5848	263.5655	264.9289
266.7211	268.4894	272.5484
272.9894	276.4071	279.3308
283.7847	287.1307	289.8451
290.0909	293.0382	293.9301
295.8309	301.7524	302.6535
306.1605	309.8736	310.2707
313.6342	316.4906	317.4436
321.3783	322.3786	324.2128
328.7504	332.0793	333.6287
334.6584	341.8162	345.0106
346.7120	351.2069	351.8409
356.4258	359.4360	361.6972
365.8495	367.1582	370.6021
374.1851	379.0371	381.7357
384.3649	386.5549	390.5209
392.6945	395.0390	399.4915
402.4319	408.4927	415.9036
416.7563	423.6995	426.4737
428.2040	432.0372	435.8567
439.1447	442.5949	449.6435
459.8510	461.2424	465.1537
469.8184	545.8841	582.2757
585.8318	589.2818	677.3291
680.4141	705.4867	717.3837
754.6881	790.5023	799.8798
809.7224	812.1657	825.9680
831.8363	833.1412	834.6155
837.7823	840.4334	843.2883
848.7788	849.1302	854.0066

857.7890	865.5298	879.0382
884.0944	885.0160	888.7691
898.4872	902.0851	928.1844
952.7502	955.6531	973.5563
979.0709	981.0268	983.1171
986.7862	1000.2944	1000.7938
1004.7586	1014.0577	1016.4543
1020.9977	1023.3860	1051.3360
1203.1054	1213.4560	1217.1085
1237.2258	1242.1752	1244.2577
1251.2707	1252.2295	1253.3696
1256.0451	1260.3065	1263.8602
1634.9025	1648.7868	1667.7823
1697.2971	1702.5404	1712.0732
1727.1304	1732.1390	1744.1097
1767.6091	1773.4500	1779.0482
1788.2903	1788.6382	1792.5812
1801.9889	1815.7241	1820.1320
1835.7519	1838.5995	1843.6175
1858.0076	1864.2068	1868.4820
1874.6159	1884.4039	1890.1306
1897.9502	1905.6614	1915.5689
3804.0046	3865.1677	3975.3982
3998.4775	4009.7934	4023.2087
4034.5286	4071.4964	4098.2953
4106.9209	4120.8056	4136.1210

^{13}C-^{16}O-^{16}O-^{16}O

25.9650	34.5038	47.0737
63.8261	67.7109	75.1587
89.9660	94.2972	95.8684
105.1958	115.0567	120.8413
125.3863	128.5869	144.1481
147.2185	149.8454	164.1858
165.8825	167.5015	176.8382
187.7792	193.7926	203.2848
208.0480	211.1392	215.0107
216.4418	229.4011	231.2721
240.2656	241.4643	248.9761
260.6318	263.6125	264.9344
266.8353	268.6007	272.6058
273.0835	276.5120	279.6409
283.8817	287.3003	289.9041
290.2748	293.0638	294.1565

295.8355	301.8253	302.6988
306.2530	309.8708	310.2884
313.6796	316.6386	317.4417
321.4504	322.4335	324.3200
328.8214	332.0963	333.6449
334.6936	341.9022	345.0212
346.8038	351.2342	351.8491
356.4283	359.6059	361.7327
365.8996	367.1900	370.7215
374.2334	379.0366	382.7485
384.7863	386.7776	390.6487
393.0156	396.0850	401.0221
402.8486	408.5408	415.9028
416.8008	423.7162	426.4721
428.4251	432.0386	436.1532
439.2933	442.8023	449.6751
459.8765	461.2443	465.1554
469.8210	545.8841	582.2757
585.8211	589.2808	677.2976
680.4156	705.5186	717.3782
762.1042	790.5578	799.8940
809.7189	825.9541	827.6372
832.4980	834.2609	834.7211
837.7865	840.4428	843.3690
848.7783	849.2081	854.0030
857.7898	865.5337	879.0355
884.0955	885.0604	888.7694
898.4870	902.0849	928.1552
952.7452	953.6830	955.6595
979.0661	980.9778	983.1142
985.7414	996.4059	1000.5706
1004.5141	1014.0565	1016.4544
1020.9940	1023.3814	1051.9867
1213.4548	1217.0925	1225.0403
1237.2772	1242.2974	1244.2851
1251.2708	1252.2309	1253.3696
1256.0448	1260.3112	1263.8602
1629.2138	1634.5685	1649.2175
1674.6186	1696.5036	1711.6736
1727.1304	1732.1130	1740.3403
1767.0910	1773.3840	1778.9465
1787.8954	1788.5065	1792.3836
1801.6916	1815.3662	1819.8402
1835.5199	1838.5185	1843.4883

1857.9479	1864.0744	1868.2099
1874.5583	1884.3285	1889.8976
1897.7669	1904.5279	1915.2632
3803.9670	3865.1452	3975.3966
3998.4772	4009.7907	4023.2087
4034.5281	4071.4905	4098.2951
4106.9177	4120.8054	4136.1210

^{13}C-^{18}O-^{16}O-^{16}O

25.8792	34.2937	47.0679
63.5821	67.4696	74.6628
89.8649	92.8096	95.5696
105.1952	114.6875	120.7309
125.1281	128.4415	143.9851
146.8566	149.7866	163.9929
164.8809	166.2762	176.7599
187.7592	193.6822	203.2762
207.3847	210.8928	214.7954
215.4688	229.3900	231.2411
240.1802	241.4470	248.3065
260.4219	263.4415	264.8235
266.8276	268.4624	272.6142
272.9804	275.8987	279.3195
283.8773	287.0658	289.9008
290.0394	293.0105	293.7333
295.8304	301.7390	302.7052
306.2152	309.8601	310.2675
313.5582	316.6299	317.3989
321.4517	322.3808	324.3035
328.7921	332.0270	333.6240
334.5744	341.8337	345.0188
346.5594	351.1237	351.8241
356.4143	359.4767	361.7316
365.8583	367.1836	370.7100
374.1886	379.0385	382.6439
384.6938	386.7309	390.6277
392.9290	395.9141	401.0058
402.7784	408.5329	415.9052
416.7971	423.7027	426.4645
428.4235	432.0008	436.1342
439.2650	442.7853	449.6636
459.8761	461.2240	465.1544
469.8227	545.8648	582.2765
585.7763	589.2797	677.2971

680.3907	705.4896	717.2003
746.9094	790.2998	799.8888
809.7147	818.3283	825.9697
832.0022	833.2470	834.6186
837.7795	840.4358	843.3018
848.7790	849.1415	853.9989
857.7896	865.5340	879.0363
884.0938	885.0359	888.7695
898.4869	902.0852	928.1219
950.0441	952.7567	955.6572
979.0652	980.9741	983.1132
985.6538	996.1403	1000.5697
1004.5089	1014.0560	1016.4527
1020.9928	1023.3798	1051.5938
1200.9909	1213.4561	1217.1101
1237.2345	1242.1915	1244.2546
1251.2707	1252.2300	1253.3696
1256.0449	1260.3085	1263.8603
1616.7253	1634.4754	1649.1328
1674.1880	1696.3880	1711.6412
1727.1304	1732.1076	1740.3021
1767.0753	1773.3723	1778.9417
1787.8859	1788.5054	1792.3804
1801.6875	1815.2856	1819.7856
1835.4565	1838.5131	1843.4841
1857.9313	1864.0341	1868.2024
1874.5562	1884.3141	1889.8721
1897.7561	1904.3573	1915.1774
3803.9571	3865.1361	3975.3961
3998.4767	4009.7904	4023.2086
4034.5279	4071.4885	4098.2951
4106.9173	4120.8053	4136.1209

^{13}C-^{16}O-^{18}O-^{16}O

25.9660	34.4586	47.0523
63.7953	67.5404	74.7820
89.9527	93.8908	95.7981
105.0012	114.9712	119.9654
124.9474	128.5210	144.0985
147.1436	149.7685	163.9041
165.4628	166.7024	176.5037
187.2883	193.4762	203.2497
207.8488	210.9871	214.7545
215.3738	229.2555	231.0555

239.6908	241.4549	248.6599
260.5791	263.4700	264.5722
266.7978	268.5956	272.5034
273.0363	276.3857	279.4999
283.7045	287.0620	289.8749
290.1898	292.9331	293.9787
295.7430	301.7626	302.6501
306.1226	309.7826	310.2366
313.6128	316.5323	317.3163
321.3795	322.2580	324.2694
328.7807	331.8818	333.6071
334.4561	341.7633	345.0149
346.1820	350.7249	351.8117
356.4190	359.1534	361.7185
365.8632	367.1861	370.5351
374.2071	379.0375	382.1844
384.5738	386.5518	390.5947
392.9432	395.4885	398.7878
402.5074	408.5134	415.9046
416.7534	423.6990	426.4644
428.2232	432.0326	435.8388
439.1393	442.5618	449.6668
459.8587	461.2300	465.1559
469.8140	545.7277	582.2767
585.7282	589.2776	677.2780
680.3970	705.3819	717.1936
747.5122	790.2837	799.8839
809.7110	816.9857	825.9708
831.9875	833.1871	834.6208
837.7829	840.4357	843.3148
848.7791	849.1429	853.9949
857.7887	865.5327	879.0386
884.0940	885.0456	888.7695
898.4878	902.0849	928.1420
949.9176	952.7539	955.6567
979.0658	980.9744	983.1140
985.6369	996.0470	1000.5695
1004.5055	1014.0556	1016.4522
1020.9931	1023.3789	1051.6725
1202.1019	1213.4571	1217.1107
1237.2229	1242.2015	1244.2464
1251.2705	1252.2296	1253.3697
1256.0447	1260.3071	1263.8604
1620.9002	1634.5309	1649.0218

1666.1686	1696.4882	1711.6622
1727.1304	1732.1117	1739.6738
1766.9800	1773.3728	1778.9223
1787.7709	1788.4952	1792.3439
1801.6220	1815.3541	1819.7768
1835.5047	1838.4922	1843.4606
1857.9403	1864.0492	1868.0860
1874.5474	1884.3075	1889.8385
1897.6624	1904.2611	1915.2465
3803.9612	3865.1410	3975.3964
3998.4771	4009.7902	4023.2084
4034.5280	4071.4895	4098.2950
4106.9169	4120.8054	4136.1210

^{13}C-^{16}O-^{16}O-^{18}O

25.7380	34.3950	46.9243
63.6785	67.2703	74.9261
89.8347	93.8606	95.6455
104.9065	114.3603	120.6698
125.3103	128.5550	143.9397
147.1964	149.6033	163.6878
165.4089	167.4501	176.5792
187.5057	193.7841	203.1836
207.8695	210.6893	214.9689
216.2326	229.2122	231.2137
240.2165	241.4129	248.5589
260.5326	263.4802	264.8851
266.7058	268.4646	272.5381
272.9486	276.2570	279.2226
283.7364	287.0037	289.8390
290.0045	293.0091	293.7882
295.8083	301.7137	302.6527
306.1062	309.8627	310.2551
313.6297	316.4785	317.4263
321.3634	322.3607	324.1912
328.7314	332.0336	333.6254
334.6023	341.7442	345.0100
346.5193	351.1059	351.8127
356.4187	359.2987	361.6931
365.8435	367.1544	370.5917
374.1596	379.0365	381.5749
384.3172	386.5415	390.5080
392.6354	394.9403	399.2752
402.4211	408.4899	415.9046

416.7541	423.6927	426.4711
428.1784	432.0303	435.8149
439.1207	442.5684	449.6393
459.8501	461.2376	465.1535
469.8185	545.8679	582.2758
585.8178	589.2818	677.2703
680.4102	705.4545	717.3482
752.7452	790.4358	799.8754
809.7035	809.9745	825.9679
831.8118	833.1298	834.6142
837.7826	840.4332	843.2874
848.7790	849.1199	853.9972
857.7879	865.5261	879.0390
884.0940	885.0132	888.7691
898.4871	902.0854	928.1249
949.6909	952.7540	955.6567
979.0651	980.9721	983.1115
985.6279	996.0218	1000.5690
1004.5040	1014.0562	1016.4513
1020.9912	1023.3780	1051.1328
1202.8471	1213.4555	1217.1076
1237.2221	1242.1743	1244.2573
1251.2706	1252.2294	1253.3696
1256.0448	1260.3065	1263.8603
1622.4937	1634.0653	1649.2085
1663.8661	1696.4127	1711.5884
1727.1304	1732.0999	1739.6502
1767.0270	1773.3831	1778.9376
1787.7383	1788.4909	1792.3216
1801.6232	1815.2239	1819.8329
1835.4418	1838.5114	1843.4439
1857.9380	1864.0734	1868.1264
1874.5259	1884.3233	1889.8280
1897.7377	1904.4540	1915.0235
3803.9630	3865.1426	3975.3962
3998.4772	4009.7903	4023.2086
4034.5279	4071.4894	4098.2951
4106.9162	4120.8054	4136.1210

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