$^{13}C/^{12}C$ Partitioning during Synthesis of $Na_2Ca(CO_3)_2 \cdot 2H_2O$

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During the synthesis of $Na_2Ca(CO_3)_2 \cdot 2H_2O$ (pirssonite) from aqueous solutions at 60 and 90 °C, ^{13}C is enriched in the solid with respect to the dissolved carbonate species.

Orthorhombic $Na_2Ca(CO_3)_2 \cdot 2H_2O$ **1** may be formed in chemical processes[1,2] and occurs in nature as the mineral pirssonite.[3] Although the determination of the stable isotopic compositions may be useful to resolve the formation conditions of natural and synthetic carbonate solids,[4] no isotope partition experiments involving **1** have been carried out yet. Therefore, $^{13}C/^{12}C$ fractionation during formation of **1** was investigated by synthesis from aqueous solutions.

Compound **1** was synthesized at 60 and 90 °C by the reaction of artificial calcite **2a** [1.2 mmol; $\delta^{13}C = -14.84$‰[†]] or natural aragonite **2b** [1.2 mmol; $\delta^{13}C = 5.03$‰] with freshly prepared aqueous Na_2CO_3 solutions [39 g; 2.88 mol dm^{-3}; $\delta^{13}C = -5.47$‰], as in the method of Bury and Redd.[1] The reaction vessels (40 cm^3), which were continuously rotated at run temperature in an oven, contained polytetrafluoroethylene-coated metal bars to promote the reaction and to prevent coating of **2** by **1**. At the end of each run, the vessel was cooled (H_2O) within a few minutes to room temperature. The solution pH was measured under air-tight conditions, and **1**[‡] was separated rapidly from the solution by ultrafiltration under N_2 pressure, washed and dried. The sum of the final dissolved carbonate species **3** was precipitated quantitatively as $BaCO_3$ **4** in a degassed solution of NaOH and $BaCl_2$ under N_2.

Compound **1** formed in solutions containing dissolved Na^+ and CO_3^{2-} and **2** according to the overall reaction (1). Since

$$CaCO_3 + 2\,Na^+ + CO_3^{2-} + 2\,H_2O \rightarrow Na_2Ca(CO_3)_2 \cdot 2H_2O \quad (1)$$

the sum of the dissolved carbonate species was always in significant excess with respect to **1** and **2**, the isotopic compositions of **1** are nearly independent of the initial $CaCO_3$ and the $^{13}C/^{12}C$ ratios of dissolved carbonate did not change significantly during the interaction process (Table 1). The measured isotope values of **3** compare well with those obtained from mass balance calculations (Table 1). As **3** is essentially carbonate (CO_3^{2-}), α(**1** − **3**)[¶] virtually equals α(**1** − CO_3^{2-}) (Table 2). Taking into account the fractionation factors between the dissolved carbonate species and gaseous CO_2,[5] the α-values in Table 2 are obtained. At 60 and 90 °C, ^{13}C is enriched in **1** with respect to the dissolved carbonate species considered and gaseous CO_2, and the degree of fractionation seems to decrease with increasing temperature. The effect of temperature on the isotope fractionation between **1** and the dissolved carbonate species is significantly smaller than for the calculated solid–gas system.[||]

Table 1 Run conditions and final isotopic compositions during synthesis of **1**.

Starting $CaCO_3$	Conditions	$\delta^{13}C$ (‰) of **1**	$\delta^{13}C$ (‰)[b] of **4**, measured	$\delta^{13}C$ (‰)[b] of **4**, calculated
2a	60 °C; 453 h	−2.45	−5.57	−5.69
2a	90 °C; 144 h	−3.35	−5.73	−5.67
2b	90 °C; 360 h	−3.19	*a*	−5.38

[a] Not determined. [b] See footnote §.

Table 2 Measured and calculated fractionation factors involving **1**

T/°C	α(**1** − **3**)[a]	α(**1** − CO_3^{2-})	α(**1** − HCO_3^-)	α(**1** − CO_2)
60	1.0033	1.0033	1.0031	1.0077
90	1.0023	1.0023	1.0023	1.0045

[a] See footnote §.

In the temperature range used for the present experiments, isotope fractionation has not hitherto been investigated for hydrated carbonates. However, carbon isotope partitioning has been treated theoretically in several studies[6] for the system calcite–CO_2. In the most recent work, Chacko *et al.*[6] obtained α(calcite-CO_2) values of 1.0071 and 1.0047 at 60 and 90 °C, respectively, which are similar to the present experimental results for **1** (Table 2).

The IR spectra were obtained by Dr P.-L. Gehlken.

Received, 23rd February 1994; Com. 4/01116C

Footnotes

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[†] Isotope measurements were carried out on phosphoric acid-liberated CO_2 with a triple collector mass spectrometer and isotope ratios are given in the δ-notation {$\delta^{13}C_A = [(^{13}C/^{12}C)_A/(^{13}C/^{12}C)_{PDB} - 1] \times 1000$; See Hoefs[4]} with respect to the PDB-standard [natural carbonate (belemnitella americana) from the Peedee-formation; see Hoefs[4]].

[‡] **1** was identified by powder XRD and IR spectroscopy.

[§] The isotopic composition of **3** equals that of **4**.

[¶] $\alpha(A\text{-}B) = [\delta^{13}C_A + 1000]/[\delta^{13}C_B + 1000]$.

[||] A similar behaviour seems to occur for $^{18}O/^{16}O$ of the carbonate ion group of **1**.

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