SUPPORTING INFORMATION

Capturing and Labeling CO₂ in a Jar: Mechanochemical ¹⁷O-Enrichment and ssNMR Study of Sodium and Potassium (bi)carbonate Salts

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Materials and Methods

Materials

Carbonyldiimidazole (CDI, TCI, >97% purity) was used as received. Due to its sensitivity to air and humidity, it was systematically stored under Argon and in a fridge. Its purity (lack of hydrolysis) was regularly checked by IR spectroscopy, by verifying the absence of imidazole vibration bands. If impure, a new jar was ordered immediately.

Sodium hydroxide pellets (NaOH, Acros Organics, 98% purity) or micropearls (NaOH, Chem-Lab, 98.5+% purity), and potassium hydroxide pellets (KOH, Sigma-Aldrich, 85% purity), were used as received. These reagents were analyzed by IR and pXRD, revealing the presence of water and carbonate impurities. In the case of NaOH, a more significant hydration was noticed for the micropearls, which explains why this reagent had to be introduced in larger excess in the reactions described below. NaOH educts were stored under air, while KOH, which is more hygroscopic, was stored under Ar.

Labeled water was mainly purchased from Cortecnet or Eurisotop, and used as received. The isotopic compositions provided in the certificates of analysis were as follows:

- $H_2^{18}O$ with 99% enrichment (composition: 99.5% ^{18}O , 0.1% ^{17}O , 0.4% ^{16}O),
- H₂¹⁷O with 40% (composition: 39.30% ¹⁷O, 44.6% ¹⁸O, 16.10% ¹⁶O), 70% (composition: 70.37% ¹⁷O, 3.29% ¹⁸O, 26.34% ¹⁶O), or 90% enrichment (composition: 91.0% ¹⁷O, 1.0% ¹⁸O, 8.0% ¹⁶O).

For the isotope analyses by IRMS (Isotope Ratio Mass Spectrometry), more diluted ¹⁸O-water had to be used (with an ¹⁸O-content \leq 10%), as further detailed below. This water was either purchased from Sigma Aldrich, or prepared from the 99% ¹⁸O-labeled water.

Mechanochemical Syntheses

A Retsch Mixer Mill 400 (MM400) was used for the mechanochemical syntheses. All reactions were performed in 10 mL stainless steel jars with two stainless steel ball bearings (10 mm in diameter), and the joint of the jar was sealed with parafilm during the milling. After milling, the jar was opened and the completion of the reaction was immediately verified by IR.

The CDI-based protocols (**Scheme S1**) were first tested and optimized using ultra-pure water, prior to using ¹⁸O- and ¹⁷O-labeled water. We note that the order of the reagents described below is critical as CDI reacts rapidly with H₂O to form CO₂. Thus, to minimize the interaction of these educts before the milling, the balls were introduced immediately after the water (to try to "cover" the water and occupy more space in the jar), followed by MOH, and then CDI. The

jar was then sealed as fast as possible (to avoid "losing" any CO₂). A video showing what occurs upon introduction of the reagents in the jar is available as supporting information.

In terms of stoichiometries, a 2:1 molar ratio between H_2O and CDI was systematically used (implying a small excess in H_2O), while the amount of base (NaOH or KOH) was adapted case by case, to enable formation of pure bicarbonate or carbonate salts.



Scheme S1. Synthetic approach for the preparation of the ${}^{17}\text{O}/{}^{18}\text{O}$ Na- and K- (bi)carbonate salts. The "box" notation introduced by Michalchuk, Emmerling, *et al.*¹ is used here to describe the milling conditions.

The texture of the product after grinding was found to vary depending on the synthesis and volume of water used, making the crude sample more or less easy to recover. During the work-up, the quantity of absolute EtOH was adapted such that the imidazole by-product was fully removed, while the majority of (bi)carbonate salt was kept. Drying was performed to remove any excess solvent and potential residual water. Once isolated, the samples which had been synthesized using enriched water were stored under argon gas and placed in a fridge.

Further details pertaining to the synthesis of sodium (Na) and potassium (K) (bi)carbonate salts are found below, with examples of the typical masses of educts and products reported in **Table S1**. Each synthesis was repeated multiple times. The error bars on the synthetic yields which are reported at the end of each detailed protocol correspond to an average over 3 independent syntheses (n = 3).

Product	Water	Mass of Hydroxide ^a (mg)	Mass of CDI (mg)	Volume of Water (µL)	Product mass (mg)	Synthetic Yield ^d (%)
	¹⁶ O	45.6^{b}	368.0	80	76	79
NaHCO ₃	17 O	46.2^{b}	376.0	80	75	77
	$^{18}\mathrm{O}$	46.4^{b}	376.9	80	80	82
	^{16}O	140.7^{c}	219.3	48	117	54
Na ₂ CO ₃ •H ₂ O	17 O	140.7^{c}	219.5	48	130	60
	^{18}O	140.7^{c}	219.3	48	125	57
	^{16}O	96.7^{b}	564.8	125	104	60
KHCO ₃	17 O	93.8^{b}	541.7	120	119	71
	^{18}O	96.7^{b}	561.8	125	123	71
K ₂ CO ₃ •1.5H ₂ O	16 O	103.7^{b}	148.8	35	71	47^e
	17 O	110.1^{b}	160.1	35	93	57
	^{18}O	93.3^{b}	135.6	30	78	57

Table S1: Examples of synthesis quantities used in the mechanochemical enrichment of sodium and potassium (bi)carbonate salts.

^a Hydroxides used: NaOH or KOH.

^b Educt introduced as pellets

^c Educt introduced as micropearls.

^d All synthetic yields reported here were calculated taking into consideration the molar mass of *non-labeled* products, because in practice, the exact enrichment level of each product was not measured experimentally (and hence their exact molar mass is uncertain). Nevertheless, these reported yields were calculated to be to the most 3 to 4% higher than the "real" synthetic yields of the enriched products. ^{*e*} The lower synthetic yield for this compound is due to the synthesis being performed on a day with 41% relative humidity, which implies the product was highly deliquescent.

Na₂CO₃·H₂O and Na₂CO₃

H₂O (2 eqv.), NaOH micropearls (2.6 eqv.), and CDI (1 eqv.) were introduced successively into the milling jar in the following order alongside the stainless steel ball bearings: (*i*) H₂O, (*ii*) two 10 mm balls, (*iii*) NaOH, and (*iv*) CDI. The jar was quickly closed, sealed, and the medium milled for 30 minutes at 25 Hz. After milling, the jar was opened and the white paste was scraped using a spatula and transferred on a P4 frit, trying to recover the majority of the product. The rest was recovered with a pipette, by adding absolute EtOH in small fractions to the jar (5 mL in total), which were then added onto the glass frit. The wet precipitate was filtered under dynamic vacuum and washed 3 times with 5 mL of EtOH, followed by 2 x 5 mL Et₂O. The product was left to dry under vacuum for 1 hour. Once dry, the white solid was scraped from the frit onto aluminum foil and transferred to a vial. Average synthetic yield (n = 3): 57 ± 3 %. Typical amount isolated (for quantities in **Table S1**): *ca.* 120 mg.

To obtain anhydrous Na₂CO₃, the monohydrate salt was transferred into a vial, and a heat treatment was performed at 100°C during *ca*. 3 hours in an oven under air. Average synthetic yield (n = 3): 90 \pm 7 %. Typical amount isolated (when heat-treating 75 mg of monohydrate): *ca*. 60 mg.

Specific comments related to $Na_2CO_3 \cdot H_2O$ synthesis:

The amount of NaOH micropearls was optimized step by step; a small excess was eventually used (2.6 eqv. instead of 2.0 eqv.) due to hydrated nature of this precursor. The pXRD characterizations of the final product showed that the only crystalline phase was Na₂CO₃·H₂O, and ²³Na solid state NMR analyses (including using 2D MQMAS analyses) did not reveal any signals other than those of the monohydrate (data not shown here, but available upon request). When using NaOH pellets instead of micropearls, it was found that the phase-pure monohydrate could be collected using only 2.0 eqv. of base.

In a small number of cases, the texture of the product after the grinding step was slightly more liquid, and the isolated product was then found to contain both Na₂CO₃·H₂O and a yet-unidentified phase (which exhibits a strong peak on the X-ray diffraction powder pattern at $2\theta \approx 6.4^{\circ}$, when working with a Cu K α wavelength). The origin of the formation of the latter phase is still unclear. When heated at 100 °C for 3 hours, this mixture quantitatively led to a phase-pure form of Na₂CO₃.

The data reported in the main text for ${}^{17}O/{}^{18}O$ labeled Na₂CO₃·H₂O correspond to phase-pure forms of the monohydrate.

NaHCO3

H₂O (2 eqv.), NaOH pellets (0.5 eqv.), and CDI (1 eqv.) were introduced successively into the milling jar in the following order alongside the stainless steel ball bearings: (*i*) H₂O, (*ii*) two 10 mm balls, (*iii*) NaOH, and (*iv*) CDI. The jar was quickly closed, sealed, and the medium milled for 30 minutes at 25 Hz. After milling, the jar was opened and then the wet paste was scraped using a spatula to recover the majority of the product on a P4 frit. The rest was recovered with a pipette, by adding absolute EtOH in small fractions to the jar (5 mL in total), which were then added onto the glass frit. The wet precipitate was filtered under dynamic vacuum, and washed 3 times with 5 mL of EtOH, followed by 2 x 5 mL Et₂O. The product was left to dry under vacuum for ca.1 hour. Once dry, the white solid product was scraped from the frit onto aluminum foil and transferred to a vial. Average synthetic yield (n = 3): 79 ± 3 %. Typical amount isolated (for quantities in **Table S1**): *ca.* 80 mg.

Specific comments related to NaHCO₃ synthesis:

For this reaction, a default in the amount of NaOH added was used (0.5 eqv. instead of 1.0 eqv.). This can be explained by the fact that initial tests engaging 1.0 eqv. NaOH led to mixtures of phases, including NaHCO₃, but also Na₃(HCO₃)(CO₃)·2H₂O (Trona). Upon heat treatment at 100 °C for 3 hours, NaHCO₃ also transforms into Na₂CO₃.

$K_2CO_3 \cdot 1.5H_2O$

H₂O (2 eqv.), KOH (2 eqv.), and CDI (1 eqv.) were introduced successively into the milling jar in the following order, alongside the stainless steel ball bearings: (*i*) H₂O, (*ii*) two 10 mm balls, (*iii*) KOH, and (*iv*) CDI. The jar was quickly closed, sealed, and the medium milled for 30 minutes at 25 Hz. After milling, the jar was opened and the sample appeared as a white solid. The contents were scraped using a spatula and transferred onto a P4 frit. Then, 5 x 1 mL fractions of absolute EtOH were used to rinse and recover any remaining precipitate in the jar, which was added on the fritt. The wet precipitate on the glass frit was then washed with 5 x 1 mL fractions of Et₂O. The product was left to dry under dynamic vacuum for 30 minutes. Once dry, the white solid product was scraped from the frit onto aluminum foil, and then transferred to a vial. Average synthetic yield (n = 3): 54 ± 6 %. Typical amount isolated (for quantities in **Table S1**): *ca.* 80 mg.

Specific comments related to K₂CO₃ 1.5H₂O synthesis:

Obtaining K_2CO_3 1.5H₂O in high yield was found to be challenging, especially on days of strong relative humidity (RH > 40%), this compound being highly deliquescent.^{2,3} Several attempts were made to prepare anhydrous K_2CO_3 from K_2CO_3 1.5H₂O, yet the latter product could not be isolated in pure form under the conditions tested.

KHCO3

 H_2O (2 eqv.), KOH (0.5 eqv.), and CDI (1 eqv.) were introduced successively into the milling jar in the following order, alongside the stainless steel ball bearings: (*i*) H_2O , (*ii*) two 10 mm balls, (*iii*) KOH, and (*iv*) CDI. The jar was quickly closed, sealed, and the medium milled for 30 minutes at 25 Hz. After milling, the jar was opened and the sample appeared as a white paste. The contents were scraped and transferred onto a P4 frit. Using a pipette, 5 x 1 mL fractions of absolute EtOH were used to rinse and recover any remaining precipitate from the jar, and added to the P4 frit. The wet precipitate on the glass frit was then washed with 5 x 1 mL fractions of Et₂O. The wet product was left to dry under dynamic vacuum for 30 minutes.

Once dry, the white solid product was scraped from the frit onto aluminum foil and transferred to a vial. Average synthetic yield (n = 3): 67 ± 6 %. Typical amount isolated (for quantities in **Table S1**): *ca.* 115 mg.

Specific comments related to KHCO₃ synthesis:

For this reaction, a default in the amount of KOH added was used (0.5 eqv. instead of 1.0 eqv.). This can be explained by the fact that initial tests using 1.0 eqv. KOH led to mixtures of phases, including KHCO₃, K_2CO_3 1.5H₂O, and a mixed carbonate/bicarbonate salt. Attempts were made to synthesize anhydrous K_2CO_3 by heat-treating KHCO₃, but with no success in isolating a phase-pure compound under the synthetic conditions we tried.

Characterizations

Infra Red spectroscopy

Attenuated total reflectance IR (ATR-IR) analyses were performed either using a Perkin Elmer Spectrum 2 instrument in a range of 400 to 4000 cm⁻¹, or using a Perkin Elmer Spectrum 100 instrument in the range of 650 to 4000 cm⁻¹. Depending on the instrument, 4 or 8 scans were acquired for both the background and sample. IR was used to monitor the course of the reactions, assess the purity of educts and products, and have a first evaluation of the successful enrichment of the final products.

Powder X-ray Diffraction

A Malvern PANalytical X'Pert MPD diffractometer (1.5406 Å Cu K α wavelength, 40kV and 25 mA) was used to acquire powder X-ray diffraction (pXRD) patterns. Samples were placed onto glass plates, and analyzed in a diffraction range of 5° or 10° to 70° 2 θ using a step size of 0.033°, with experimental times of *ca*. 8 to 10 minutes. pXRD was used to assess the purity and crystallinity of the final products, by comparison to reference powder patterns of Na- and K- (bi)carbonates.

Isotope Ratio Mass Spectrometry

Isotopic abundances of ¹⁶O and ¹⁸O in Na-carbonate salts were determined by isotope ratio mass spectrometry (IRMS). Samples were analyzed on a KIEL IV Carbonates apparatus (ThermoFisher Scientific), connected to a Delta V+ Dual Inlet mass spectrometer (ThermoFisher Scientific) of the AETE-ISO analytical platform (OREME, Montpellier, France). As this instrument was designed for Earth Sciences studies, samples had to be

purposely prepared with lower ¹⁸O-levels for these quantifications (see Supplementary Information S1).

Controls of the ¹⁸O enrichment of waters used were performed by CRDS Laser spectroscopy on a Picarro L2130-i analyzer at the LAMA laboratory of Hydrosciences Montpellier, and were used to assess the reaction yields. Further information regarding the precise analysis conditions and enrichment calculations are provided as part of **Supplementary Information S1**. The measured ¹⁸O contents are grouped in **Table S2**.

lubeled wate		emilemient ic	iter of mentals.			
	Labeling	¹⁸ O-labeled	Milling time	¹⁸ O level measured	Maximum ¹⁸ O level	
Entry	macaduma	watan	(MM400.25 Hz)	on the isolated	expected upon full isotopic	
	procedure	water	(MM400, 23 HZ)	product	scrambling	
1	Direct	100/ 180	20	$0.24 \pm 0.01.0$	4.2.0/	
	enrichment	10% "0	30 min	0.24 ± 0.01 %	4.2 %	
2	Direct	100/ 180	00 min	$0.26 \pm 0.01.0$	4 2 0/	
	enrichment	10% 0	90 11111	0.20 ± 0.01 %	4.2 /0	
3	Direct	00% ¹⁸ O	30 min	$0.54 \pm 0.06\%$	30 7 %	
	enrichment	99% U	50 mm	0.34 ± 0.00 %	57.170	
4	CDI	0.63% 180	30 min	$0.38 \pm 0.01.04$	0 37 0⁄ ª	
	reaction	0.0370 0	30 1111	0.38 ± 0.01 70	0.37 70	
5	CDI	1 00% 180	30 min	$0.02 \pm 0.01.04$	0 88 0/ a	
	reaction	1.90% 0	30 1111	0.92 ± 0.01 %	0.88 70	
6	CDI	100/ 180	30 min	datactor saturated ^b	4.2.04	
	reaction	1070 U	50 11111	uciccioi saturateu	4.2 %	

Table S2: ¹⁸O-labeling tests, performed by milling 1 eqv. of Na₂CO₃ with 2 eqv. of ¹⁸O-labeled water, to determine enrichment level by IR-MS.

^a For the CDI protocols, the ¹⁸O-measured contents are very similar (even very slightly higher) to the values calculated for a full isotopic scrambling. Further analyses of isotope contents in ¹⁸O-labeled Na₂CO₃ phases would be needed to rationalize this, which is beyond the scope of the current work. ^b No quantitative measurement could be achieved on this sample on the IRMS instrument used, due to the saturation of the detector.

¹³C solution NMR

¹³C solution NMR spectra were recorded at 14.1 T [$v_0(^1H) = 600.272$ MHz and $v_0(^{13}C) = 150.964$ MHz] on an Avance III Bruker spectrometer, using a TCI prodigy cryoprobe. For the analysis, *ca.* 50 mg of ¹⁸O-enriched Na₂CO₃ was dissolved in *ca.* 500 µL of D₂O (containing a small amount of DSS as an internal reference, with the R-Si(CH₃)₃ peak set to 0 ppm in ¹³C). The NMR tube was prepared just before the NMR analysis, to avoid any significant back-exchange between the labeled oxygens of the carbonates and the non-labeled ones from D₂O. The analysis was performed using the "zgig" pulse sequence, using an acquisition time of *ca*. 5.5 s (to avoid FID truncation), and a recycle delay of 6 s. A total of 600 transients were added.

¹³C Solid-State NMR

¹³C solid-state NMR (ssNMR) magic angle spinning (MAS) spectra were recorded at 14.1 T [$v_0(^1\text{H}) = 599.765$ MHz and $v_0(^{13}\text{C}) = 150.810$ MHz] (600 MHz instrument) on a Varian VNMRS spectrometer using a 3.2 mm HXY probe with samples packed into 3.2 mm outer diameter (o.d.) zirconia pencil rotors. The sample temperatures are estimated to be 280 K. Most spectra were acquired using a ¹H-¹³C variable-amplitude cross polarization (VACP)⁴ sequence at a spinning rate of $v_{rot} = 10$ to 12 kHz, with SPINAL-64^{5.6} ¹H decoupling during acquisition (50 kHz RF). Only the ¹³C NMR spectrum of Na₂CO₃ was acquired using a direct excitation (one pulse) experiment. Further experimental acquisition parameters can be found in **Table S3**. All ¹³C chemical shifts were referenced to adamantane (high frequency peak at δ_{iso} = 38.5 ppm with respect to neat TMS).

at 14.1 T at the ICGM (Montpellier, France). Spectra are shown in Figure S11 .							
Sample	$Na_2CO_3^{a}$	$Na_2CO_3 \cdot H_2O^b$	NaHCO ₃ ^b	$K_2CO_3 \cdot 1.5H_2O^b$	KHCO ₃ ^b		
Pulse Sequence	One pulse	VACP	VACP	VACP	VACP		
Spinning rate (kHz)	10	10	10	12	10		
Regulated temperature (K)	273	273	273	273	273		
Estimated sample temperature (K)	280	280	280	280	280		
Number of scans	8	356	256	512	32		
Experimental time (min)	8	6	45	45	30		
Recycle delay (s)	60	1	10	5	60		
Contact time (ms)	-	2	2	1	2		
¹ H $\pi/2$ pulse width (µs)	-	3.33	3.33	3.33	3.33		
1 H $\pi/2$ pulse rf (kHz)	-	75	75	75	75		
¹ H rf decoupling field (kHz)	-	50	50	50	50		
Dwell time (μ s)	15	15	15	5	15		
Spectral width (ppm)	220	220	220	660	220		
Acquisition length (ms)	10	50	50	20	50		

Table S3: Experimental ¹³C MAS ssNMR acquisition parameters for experiments conducted at 14.1 T at the ICGM (Montpellier, France). Spectra are shown in **Figure S11**.

^{*a*} A commercially labeled Na₂¹³CO₃ sample was purchased from Eurisotop (with 99% ¹³C enrichment); it was preheated at 100°C for 3 hours, prior to analysis, to ensure the absence of any monohydrate impurity. It was then analysed using a Bloch decay (one pulse) experiment, with a ¹³C $\pi/2$ excitation pulse of 5 µs (rf = 50 kHz). ^{*b*} Samples prepared using 99% H₂¹⁸O.

¹⁷O Solid-State NMR

¹⁷O ssNMR 1D and 2D MAS spectra were recorded at various NMR facilities (*i.e.*, ICGM in Montpellier, IMEC University of Lille in Villeneuve d'Ascq, CRMN Lyon in Villeurbanne, and NHMFL in Tallahassee), using different magnetic fields (B_0 = 14.1 T, 18.8 T, and 28.2 T), and measurement temperatures (between *ca*. 105 K and 370 K). General details

regarding the field, facility, and accompanying experiments can be found below, while the sample temperatures and acquisition parameters are summarized in the ESI **Tables S4** to **S8**. A double frequency sweep (DFS) was applied to enhance the sensitivity of ¹⁷O MAS spectra by a factor of *ca*. 2 to 3 fold.^{7,8} For samples containing protons, SPINAL-64 ¹H decoupling was applied during acquisition, using a radio frequency of 75 kHz to 100 kHz.

Experiments at 14.1 T were conducted at the ICGM (Montpellier, France) and the National High Magnetic Field Lab (NHMFL, Tallahassee, Florida). At ICGM $[v_0(^{1}H) = 599.765 \text{ MHz}, v_0(^{17}O) = 81.307 \text{ MHz}], ^{17}O \text{ NMR spectra were recorded on a Varian VNMRS spectrometer using a 3.2 mm triple-resonance HXY Varian probe with samples packed into 3.2 mm o.d. zirconia rotors with Torlon drive tips and caps. Samples were spun at a rate of <math>v_{rot} = 16$ kHz or 20 kHz with the sample temperatures estimated to be between 250 K to 370 K, and most spectra were acquired using a one pulse or DFS enhanced Hahn echo pulse sequence with a $\pi/2$ solid pulse of 2 μ s, followed by a 4 μ s π pulse, and using an echo delay of one rotor period (unless stated differently). At NHMFL $[v_0(^{1}H) = 600.486 \text{ MHz}, v_0(^{17}O) = 81.405 \text{ MHz}], ^{17}O \text{ NMR spectra were recorded on a Bruker Avance NEO spectrometer using a custom-built low-temperature 3.2 mm HXY MAS-DNP probe with samples packed into sapphire rotors with Vespel drive caps. Samples were spun at a rate of <math>v_{rot} = 10$ or 11 kHz at *ca*. 105 K, and spectra were acquired using similar acquisition conditions as at higher temperature. ¹⁷O chemical shifts were referenced directly to tap water at 0 ppm.^a

Experiments at 18.8 T [$v_0(^1\text{H}) = 799.700 \text{ MHz}$, $v_0(^{17}\text{O}) = 108.411 \text{ MHz}$] were conducted at the CRMN Lyon (Villeurbanne, France). ¹⁷O NMR spectra were recorded on an Avance NEO spectrometer using a 3.2 mm triple-resonance HXY ultra-low temperature DNP Bruker probe, with samples packed into 3.2 mm o.d. zirconia rotors with Vespel drive tips, using a spinning rate of $v_{rot} = 12.5$ kHz, and regulating near room temperature. Spectra were acquired using either a DFS-enhanced Bloch decay (one pulse) or Hahn echo pulse sequence with a $\pi/2$ solid pulse of 2.8 µs (followed in the case of the echo by a π pulse of 5.6 µs with an echo delay of one rotor period), both with and without ¹H decoupling. ¹⁷O chemical shifts were referenced directly to tap water at 0 ppm.^a

Experiments at 28.2 T [$v_0(^1\text{H}) = 1200.540 \text{ MHz}$; $v_0(^{17}\text{O}) = 162.751 \text{ MHz}$] were conducted at the IMEC (Villeneuve d'Ascq, France). ¹⁷O NMR spectra were recorded on an Avance NEO spectrometer using a 1.3 mm double-resonance HX Bruker probe with samples packed into 1.3 mm o.d. zirconia rotors with Vespel drive tips, using a spinning rate of $v_{rot} = 50$

^a The ¹⁷O NMR spectrum of D₂O was recorded, and found to be shifted by *ca.* -2.7 ppm compared to tap water.

kHz, and regulating the temperature at *ca*. 250 K. All spectra were acquired using a DFS enhancement. 1D Bloch decay (one pulse) or echo pulse sequences were recorded with a $\pi/2$ solid pulse of 6 µs, followed by a 12 µs π pulse for echo experiments. 2D ¹H-¹⁷O dipolar mediated heteronuclear multiple-quantum coherence (D-HMQC) and dipolar driven insensitive nuclei enhanced by polarization transfer (D-INEPT) spectra were acquired using the *SR*4²₁ (270₀90₁₈₀)⁹ recoupling scheme with a $\pi/2$ pulse of 6 µs and 1.4 µs on ¹⁷O and ¹H, respectively, with the total recoupling time varied from 100 µs to 1000 µs. Spectra were equivalently referenced to match H₂O at 0 ppm.^{10,b}

All spectra were processed using the TopSpin v4.1.4 and ssnake v1.5¹¹ software packages. All analytical simulations of the ¹⁷O NMR parameters were obtained using the quadrupolar fitting module included in ssnake with the uncertainties assessed by bidirectional variation of each parameter. In the figures below, the actual sample temperatures are provided; these were calibrated using KBr.¹² The chemical shift scales are given both in ppm and kHz, to highlight the breadth of the signals according to both units.

at 14.1 T at the ICGM (Montpel	at 14.1 T at the ICGM (Montpellier, France), as shown in Figure 3A and Figure S18.							
Samples	Na ₂ CO ₃	$Na_2CO_3 \cdot H_2O^a$	NaHCO ₃ ^a	$K_2CO_3 \cdot 1.5H_2O$	KHCO ₃			
Pulse Sequence	One pulse	DFS-echo	DFS-echo	DFS-echo	DFS-echo			
Spinning rate (kHz)	16	16	16	20	20			
Regulated temperature (K)	248	-	243	253	253			
Sample temperature (K)	260	308	255	270	270			
Number of scans	1726	10270	200	1024	1024			
Experimental time (h)	0.5	1.5	6.5	0.5	0.5			
Recycle delay (s)	1	0.5	120	2	2			
¹⁷ O $\pi/2$ pulse width (µs)	2	2	2	2	2			
¹⁷ O π pulse width (µs)	4	4	4	4	4			
¹⁷ O solid pulse rf (kHz)	125	125	125	125	125			
Number of rotor periods (echo)	-	1	1	1	1			
Dwell time (µs)	10	10	10	5	10			
Spectral width (kHz)	100	100	100	200	100			
Acquisition length (ms)	20	20	20	20	20			
¹ H decoupling field (kHz)	-	75	75	75	75			
DFS pulse length (µs)	-	400	400	400	400			
DFS pulse rf (kHz)	-	10	10	10	10			
DFS pulse offsets (kHz)	-	200 - 70	200 - 70	200 - 70	200 - 70			

Table S4: Experimental ¹⁷O MAS ssNMR acquisition parameters for experiments conducted at 14.1 T at the ICGM (Montpellier, France), as shown in **Figure 3A** and **Figure S18**.

^{*a*} Longer experimental times needed for analyzing these phases can be explained by the fact they were enriched using 40%-labeled ¹⁷O-water (rather than 70 or 90%).

^b The « universal referencing » procedure was used for referencing the ¹⁷O NMR spectra recorded at 28.2 T. First, the ¹H chemical shift of adamantane was set to $\delta_{iso} = 1.74$ ppm (secondary reference with respect to TMS in CDCl₃). Then, the reference frequency for neat D₂O at $\delta_{iso} = 0.00$ ppm was calculated using the IUPAC factor $\Xi = 13.556457$ (see ref. 9). Finally, ¹⁷O NMR chemical shifts were back-corrected by 4.3 ppm, because non-labeled H₂O had been measured experimentally at 4.3 ppm at the IMEC, after calibration using this procedure).

1 28.2 1 at the INIEC (Vineneuve d'Ascq, France), as shown in Figures 3D and 314.								
Samples	Na ₂ CO ₃	NaHCO ₃ ^a	$K_2CO_3 \cdot 1.5H_2O$	KHCO ₃				
Pulse Sequence	DFS-Onepulse	DFS-echo	DFS-echo	DFS-echo				
Spinning rate (kHz)	50	50	50	50				
Regulated temperature (K)	250	250	250	250				
Sample temperature (K)	297	297	297	297				
Number of scans	1024	256	512	2048				
Experimental time (min)	8	85	4	68				
Recycle delay (s)	0.5	20	0.5	2				
¹⁷ O $\pi/2$ pulse width (µs)	6	6	6	6				
¹⁷ O π pulse width (µs)	—	12	12	12				
¹⁷ O solid pulse rf (kHz)	42	42	42	42				
Number of rotor periods (echo)	-	1	1	1				
Dwell time (µs)	2.5	2.5	2.5	2.5				
Spectral width (kHz)	200	200	200	200				
Acquisition length (ms)	10	10	10	10				
¹ H decoupling field (kHz)	75	75	75	75				
DFS pulse length (µs)	1000	1000	1000	1000				
DFS pulse rf (kHz)	26	26	26	26				
DFS pulse offsets (kHz)	400 - 80	400 - 80	400 - 80	400 - 80				

Table S5: Experimental ¹⁷O MAS ssNMR acquisition parameters for experiments conducted at 28.2 T at the IMEC (Villeneuve d'Ascq, France), as shown in **Figures 3B** and **S14**.

^{*a*} The longer experimental time needed for analyzing this phase can be explained by the fact it was enriched using 40%-labeled ¹⁷O-water (rather than 70 or 90%), and that the recycle delay was long.

Table S6: Experimental ¹⁷O MAS ssNMR acquisition parameters for HMQC/INEPT experiments conducted at 28.2 T at the IMEC (Villeneuve d'Ascq, France), as shown in **Figures S15** and **S16**.

Samples	NaHCO ₃ ^a	KHCO ₃
Pulse Sequence	INEPT ^b	HMQC ^b
Spinning rate (kHz)	50	50
Regulated temperature (K)	250	250
Sample temperature (K)	297	297
Number of scans (F2/F1)	16/18	16/50
Experimental time (min)	48	8
Recycle delay (s)	10	0.5
¹⁷ O $\pi/2$ pulse width (µs)	6	6
¹⁷ O π pulse width (µs)	12	12
¹⁷ O solid pulse rf (kHz)	42	42
Dwell time (µs)	5	5
Spectral width (kHz) (F2/F1)	100/500 ^c	100/10
Acquisition length (ms) (F2/F1)	25/0.48	25/25
Increment in F1 (µs)	2	100
Recoupling Time (µs)	500	400
¹ H decoupling field (kHz)	75	75
DFS pulse length (µs)	1000	1000
DFS pulse rf (kHz)	26	26
DFS pulse offsets (kHz)	400 - 80	400 - 80

^{*a*} This phase was enriched using 40%-labeled ¹⁷O-water (while 90%-labeled ¹⁷O-water was used for KHCO₃).

^{*b*} Spectra were acquired using $SR4_1^2(270_090_{180})^9$ recoupling scheme.

^c Spectrum involuntarily truncated by using an incorrect spectral width of 500 kHz in place of a spectral width equal to the spinning rate 50 kHz.

Table S7: Experimental ¹⁷O MAS ssNMR acquisition parameters for the spectra shown in **Figure S13**: (*i*) room temperature experiments conducted at 18.8 T at the CRMN Lyon (Villeurbanne, France), and (*ii*) the variable-temperature spectra of KHCO₃ acquired at 14.1 T at the ICGM (Montpellier, France).

Samples	NaHCO ₃ ^a	KHCO ₃	NaHCO ₃ ^a	KHCO ₃	KHCO ₃
Field (T)	18.8	18.8	18.8	18.8	14.1
Pulse Sequence	DFS-Onepulse	DFS-Onepulse	DFS-echo	DFS-echo	DFS-echo
Spinning rate (kHz)	12.5	12.5	12.5	12.5	20
Regulated temperature (K)	298	298	298	298	233/313
Estimated sample temperature (K)	310	310	310	310	250/330
Number of scans	10	80	200	80	1024/512
Experimental time (min)	5	3	133	3	34/8.5
Recycle delay (s)	30	2	40	2	2/1
¹⁷ O $\pi/2$ pulse width (µs)	2.5	2.5	2.5	2.5	2
¹⁷ O π pulse width (µs)	/	/	5	5	4
¹⁷ O solid pulse rf (kHz)	100	100	100	100	125
Number of rotor periods (echo)	/	/	2	1	1
Dwell time (μ s)	5	5	5	5	5
Spectral width (kHz)	100	100	100	100	100
Acquisition length (ms)	15	15	15	15	20
¹ H decoupling field (kHz) ^b	75	75	75	75	75
DFS pulse length (μ s)	400	400	400	400	400
DFS pulse rf (kHz)	13	13	13	13	10
DFS pulse offsets (kHz)	200 - 70	200 - 70	200 - 70	200 - 70	200 - 70

^a This phase was enriched using 40%-labeled ¹⁷O-water (while 90%-labeled ¹⁷O-water was used for KHCO₃).

^b Spectra were also acquired under identical acquisition conditions with the ¹H decoupling off.

Table S8: Experimental ¹⁷O MAS ssNMR acquisition parameters for ultra-low temperature experiments conducted at 14.1 T, at the NHMFL (Tallahassee, Florida), as shown in **Figure S18**.

Samples	Na ₂ CO ₃	$Na_2CO_3 \cdot H_2O^a$	NaHCO ₃ ^a	$K_2CO_3 \cdot 1.5H_2O$	KHCO ₃
Pulse Sequence	DFS-echo	DFS-echo	DFS-echo	DFS-echo	DFS-echo
Spinning rate (kHz)	11	10	11	11	11
Approx. regulated temperature (K)	100	100	100	100	100
Estimated sample temperature (K)	105	105	105	105	105
Number of scans	256	256	128	1024	64
Experimental time (h)	1.3	17	17	17	0.5
Recycle delay (s)	18.2	240	480	60	30
¹⁷ O $\pi/2$ pulse width (µs)	2	2	2	2	2
¹⁷ O π pulse width (µs)	4	4	4	4	4
¹⁷ O solid pulse rf (kHz)	125	125	125	125	125
Number of rotor periods (echo)	1	1	1	1	1
Dwell time (μ s)	3.1	3.1	3.1	3.1	3.1
Spectral width (kHz)	160	160	160	160	160
Acquisition length (ms)	6.5	6.5	6.5	6.5	6.5
¹ H decoupling field (kHz)	100	100	100	100	100
DFS pulse length (μ s)	667	667	667	667	667
DFS pulse rf (kHz)	6	6	6	6	6
DFS pulse offsets (kHz)	200 - 80	200 - 80	200 - 80	200 - 80	200 - 80

^{*a*} Longer experimental times needed for analyzing these phases can be explained by the fact they were enriched using 40%-labeled ¹⁷O-water (rather than 70 or 90%), and that the recycle delays were long.

Computational Details

Geometry optimizations on the reported crystal structures of Na- and K- (bi)carbonate salts^{13–17} were carried out using the Vienna *ab initio* simulation package (VASP)^{18–20}. The revised Perdew-Burke-Erzenhof (rPBE)²¹ generalized gradient approximation (GGA) functional was used, with an energy cut-off of 400 eV, a Monkhorst-Pack k-space grid size chosen to obtain a unit cell with cubic symmetry, and employing Grimme's D3 dispersion correction.²² All atom (All Rel) positions were optimized, while keeping the unit cell fixed.

Subsequent NMR calculations of the NMR parameters, the electric field gradient (EFG) tensor parameters (*i.e.*, C_Q and η_Q) and chemical shieldings (σ_{calc}) were performed on VASP geometry optimized structural models, using plane-wave density functional theory (DFT), as implemented in the QUANTUM-ESPRESSO (QE) software.²³ The NMR parameters were computed using the GIPAW approach,²⁴ with the PBE²⁵ GGA functional, norm conserving pseudopotentials in the Kleinman-Bylander form to describe the valence electrons,²⁶ an energy cut-off of 80 Ry, and a k-space grid as reported in supporting information (**Table S9**).

The calculated ¹⁷O NMR parameters for fully-relaxed structural models of Na- and K-(bi)carbonates are provided in **Table S9**. The quadrupolar moment of -2.558 fm^2 was used for the calculation of the ¹⁷O quadrupolar coupling constants (C_Q).²⁷ The ¹⁷O isotropic chemical shifts δ_{iso} were estimated from the calculated isotropic shieldings σ_{iso} , using, as a first approximation, the following equation: $\delta_{iso} \approx -(\sigma_{iso} - \sigma_{ref})$. Here, a σ_{ref} value of 228 ppm was used, as in a recent publication.²⁸ Structures and further computational details are available upon request.

	ICOD	Oxvgen		GIPAW-DFT calculated values			
	number	Site # (.cif file)	k-space grid	σ _{iso} (ppm)	$\delta_{iso}{}^a$ (ppm)	C_Q^b (MHz)	η_Q^c
Na CO	169120	01	255	69.2	158.8	-7.87	0.96
INa ₂ CO ₃	108129	02	3X3X3	71.3	156.8	7.98	0.99
		03		54.3	173.7	-7.97	0.85
Na ₂ CO ₃ ·H ₂ O	1852	01	3x2x4	59.8	168.2	-7.93	0.80
		O2		61.3	166.7	7.98	0.98
		01		65.5	169.7	8.18	0.88
NaHCO ₃	18183	02	5x2x3	58.3	162.5	-7.83	0.75
		03		99.2	128.8	-8.50	0.46
		01		28.7	199.3	8.20	0.88
$K_2CO_3 \cdot 1.5H_2O$	54765	02	2x2x4	39.5	188.5	-8.00	1.00
		03		49.2	178.8	-8.02	0.83
		01		45.0	183.0	8.26	0.81
KHCO3	2325	02	1x3x6	49.7	178.3	-7.98	0.71
		03	-	94.19	133.8	-8.35	0.38

Table S9: Calculated ¹⁷O NMR parameters for Na- and K- (bi)carbonate salts. DFT calculations were performed using the GIPAW approach, on fully-relaxed structural models of each phase.

^{*a*} The isotropic chemical shift, δ_{iso} , was estimated as $\delta_{iso} \approx -(\sigma_{iso} - \sigma_{ref})$, with $\sigma_{ref} = 228$ ppm. ^{*b*} The quadrupolar coupling constant, C_Q , is defined as $C_Q = eQV_{33}/h$, where the principal components of the EFG tensor, V_{33} , V_{22} , and V_{11} , are defined such that $|V_{33}| \ge |V_{22}| \ge |V_{11}|$. It is not possible to determine the sign of C_Q from experimental ¹⁷O NMR spectra; however, it can be determined from computation.

^c The asymmetry parameter, η_Q , is defined as $\eta_Q = (V_{22} - V_{11})/V_{33}$.

Supplementary Information S1: Quantification of ¹⁸O content in Na-carbonates by Isotope Ratio Mass Spectrometry (IRMS)

Synthesis of ¹⁸O-enriched Na₂CO₃ phases for IRMS analyses

In view of mass spectrometry analyses, Na₂CO₃ samples were enriched by ball milling using ¹⁸O-labeled water, using 2 synthetic approaches:

- 1- *Direct milling* of Na₂CO₃ in presence of 2 eqv. of ¹⁸O-enriched water (followed by drying at 100 °C to remove the excess of water);
- 2- Milling of CDI in presence of 2 eqv. of NaOH and of 2 eqv. of ¹⁸O-enriched water (as in Scheme S1, followed by drying at 100 °C to remove the excess of water).

In both cases, because of the MS instrument specifications (optimized for natural samples, and hence not for materials with high ¹⁸O-enrichments), the maximum ¹⁸O abundance measurable is *ca*. 1%. Hence, diluted ¹⁸O-solutions (with *ca*. 0.5, 2, and 10% ¹⁸O-enrichment) had to be prepared to perform the labeling reactions, to be able to quantify the ¹⁸O-enrichment levels on the products. The exact isotopic composition of these diluted waters was determined as described below.

¹⁸O-labeling contents of enriched waters used: isotopic measurement procedure

Oxygen isotope ratios (${}^{18}R={}^{18}O/{}^{16}O$) in the water molecule were determined by laser absorption spectroscopy on a Picarro L2130-i Cavity Ring Down Spectrometer at the LAMA laboratory of Hydrosciences Montpellier. The output of ${}^{18}O$ -contents was expressed as delta values with respect to the Standard Mean Ocean Water (SMOW) isotopic ratio, as defined in equation (1).

$$\delta^{18}O = ([{}^{18}R_{sample}/{}^{18}R_{standard}] - 1) \times 1000\%$$
(1)

where ${}^{18}R$ is the ${}^{18}O/{}^{16}O$ isotopic ratio.

The V-SMOW scale calibration of the raw results was performed by measuring 3 known natural isotopic standards, and a series of controlled enriched solutions up to $\delta^{18}O=+122\%$, showing a striking linearity of the results obtained in the enriched range (data available on demand).

All delta values for the water molecule were expressed relative to the V-SMOW scale, and the ¹⁸R isotopic ratios were back-calculated using equation (2).

$$^{18}R = {}^{18}R_{\text{SMOW}} \times (\delta^{18}O/1000\% + 1)$$
 (2)

with ${}^{18}R_{SMOW} = 0.002005$.

These water compositions were then used to calculate the maximum enrichment levels expected for the ¹⁸O-labeled Na₂CO₃ phases (**Table S2**, **p S9**, last column).

¹⁸O-labeling contents of the enriched Na₂CO₃ salts: isotopic measurement procedure

IRMS measurements of the oxygen isotopic composition in the solid Na₂CO₃ salts were performed using a standard methodology in Earth Sciences,^{29,30} based on the comparison of the mass spectra of the CO₂ released from the Na-carbonate sample by chemical reaction (acidic treatment using 105% H₃PO₄), and of a reference CO₂ gas of known isotopic composition. A total of 8 cycles of comparisons were performed per analysis, the result being given as an average over these cycles, after removal of eventual outlying values using a Sigma test.

All standards and samples were precisely weighed using a SARTORIUS CUBIS II Type MCA3.6P-2S00-M balance (precision: 0.001 mg for a maximum weight of 1.1 g) (AETE-ISO), and introduced in glass vials (which had been previously thoroughly cleaned in a sonicating bath, and dried at 70°C). Each synthetic Na-carbonate was analysed in triplicate.

Results were normalised with respect to the Vienna Pee Dee Belemnite (V-PDB) standard, and expressed using the $\delta^{18}O$ (‰) notation, following equation (1).

Two standards of certified isotopic composition, namely calcite IAEA 603 ($\delta^{13}C = +2.46$ ‰, $\delta^{18}O = -2.37$ ‰) and NBS 18 ($\delta^{13}C = -5.014$ ‰, $\delta^{18}O = -23.01$ ‰) were also analyzed daily, and intercalated every 10-15 analyses for normalisation of the measurements on the VPDB scale. A non-certified standard was also regularly tested to evaluate the instrumental drift and verify for the appropriate functioning of the equipment.

The isotopic ratios ${}^{18}R$ of the samples were back-calculated similarly to water (equation (2)), and ${}^{18}O$ atomic percentages (or mixing ratios) presented in **Table S2** are the isotopic ratios expressed in %, using equation (3):

$$\%^{18}0 = {}^{18}R \times 100\% = {}^{18}R_{VPDB} \times (\delta^{18}0/1000\% + 1) \times 100\%$$
 (3)

where δ^{18} O is the isotopic ratio normalized to V-PDB, and ${}^{18}R_{VPDB}$ is the natural abundance ${}^{18}O/{}^{16}O$ isotopic ratio in V-PDB (${}^{18}R_{VPDB} = 0.0020672$).³¹

¹⁸O-labeling contents of the Na-carbonate salts: measured isotopic contents

Results of ¹⁸O measurements on carbonate salts are reported in **Table S2**:

- For samples prepared using the "direct-enrichment" labeling procedure (entries # 1-3), ¹⁸O levels remain low, even when using 99%-¹⁸O enriched water (below 0.6 %).

- For samples prepared using CDI (entries # 4 - 6), significant ¹⁸O labeling was observed, even when starting from diluted ¹⁸O-enriched water (< 2% ¹⁸O), showing the efficiency of the quantitative transformation.













Figure S6: Experimental IR (left) and pXRD (right) patterns for the unlabeled (blue), and ${}^{17}\text{O}/{}^{18}\text{O}$ -labeled (green and red, respectively) products of purified NaHCO₃. The dashed line in black in the IR spectra denotes a key vibration band in the blue spectrum at ~1350 cm⁻¹ (corresponding to a composite mode " δ OH & v₅" according to previous literature),^{32,33} which is shifted in the green and red spectra, indicating the product is labeled.



Figure S7: Experimental IR (left) and pXRD (right) patterns for the unlabeled (blue), and ${}^{17}O/{}^{18}O$ -labeled (green and red, respectively) products of purified Na₂CO₃·H₂O. The dashed line in black in the IR spectra denotes a key vibration band in the blue spectrum at ~1432 cm⁻¹, which is shifted in the green and red spectra, indicating the product is labeled.



Figure S8: Experimental IR (left) and pXRD (right) patterns for the unlabeled (blue), and ${}^{17}\text{O}/{}^{18}\text{O}$ -labeled (green and red, respectively) products of purified Na₂CO₃. The dashed line in black in the IR spectra denotes a key vibration band in the blue spectrum at ~1422 cm⁻¹, which is shifted in the green and red spectra, indicating the product is labeled.



Figure S9: Experimental IR (left) and pXRD (right) patterns for the unlabeled (blue), and ${}^{17}\text{O}/{}^{18}\text{O}$ -labeled (green and red, respectively) products of purified KHCO₃. The dashed line in black in the IR spectra denotes a key vibration band in the blue spectrum at ~1621 cm⁻¹ (tentatively assigned to 2 v₂ according to previous literature,³² but also close to v₆, *i.e.* v_{as}CO₃),^{32,34} which is shifted in the green and red spectra, indicating the product is indeed labeled.



Figure S10: Experimental IR (left) and pXRD (right) patterns for the unlabeled (blue), and ${}^{17}\text{O}/{}^{18}\text{O}$ -labeled (green and red, respectively) products of purified K₂CO₃·1.5H₂O. A zoom into the region showing bands typical of the carbonate isotopologues can be found in main text.



(600 MHz instrument) of ¹⁸O enriched Na and K (bi)carbonate salts (4 top spectra, recorded on the ¹⁸O-labeled samples). For Na₂CO₃, the sample analyzed here was purchased as enriched with 99% ¹³C, and acquired at 14.1 T using a simple Bloch decay sequence, with no ¹H decoupling. Arrows indicate the ¹³C chemical shifts, with those of the bicarbonate salts resonating at lower frequencies than those of the carbonate salts.

The sample temperatures are *ca*. 280 K in these analyses. Further details on acquisition parameters are reported in the **ESI Table S3**.

The chemical shifts found here for K_2CO_3 ·1.5H₂O and KHCO₃ are in fair agreement with previously reported data.^{35,36}



By noting %(I_i) the relative proportion (in %) of the integral of isotopologue *i* (with i = 0, 1, 2, or 3), and considering the ¹⁸O content of each isotopologue, the average ¹⁸O-level in the enriched Na₂CO₃ was calculated as follows:

- From the IR integrals: $\%(^{18}O) = \%(I_0) \times 0 + \%(I_1) \times 0.33 + \%(I_2) \times 0.66 + \%(I_3) \times 1$ $\%(^{18}O) = 31.70 \times 0 + 37.26 \times 0.33 + 27.97 \times 0.66 + 3.07 \times 1$ $\%(^{18}O) = 33.8$
- From the ¹³C solution NMR integrals: %(¹⁸O) = %(I₀) × 0 + %(I₁) × 0.33 + %(I₂) × 0.66 + %(I₃) × 1 %(¹⁸O) = 37.22 × 0 + 41.50 × 0.33 + 18.47 × 0.66 + 2.81 × 1 %(¹⁸O) = 28.7

Overall, based on these analyses, when starting from 99% ¹⁸O-water, the ¹⁸O enrichment level achieved in Na₂CO₃ is *ca.* 30%.

Hence, by extrapolation, if we assume there are no isotope effects during the labeling procedure used, the following enrichments can be calculated for the ¹⁷O-labeled products:

- *ca.* 27% ¹⁷O, when starting from 90% ¹⁷O-labeled water;
- ca. 21% ¹⁷O, when starting from 70% ¹⁷O-labeled water;
- *ca.* 12% 17 O, when starting from 40% 17 O-labeled water.



Figure S13: (A-C) Experimental ¹⁷O MAS NMR spectra acquired at 18.8 T (800 MHz instrument) on ¹⁷O enriched KHCO₃ (**A**, top left) and NaHCO₃ (**B**, top right) at a spinning rate of 12.5 kHz and sample temperatures *ca*. 310 K. The spectra were acquired using either a Bloch decay or Hahn echo sequence with a one rotor period echo-delay, and using on resonance ¹H decoupling (75 kHz rf) or not. Representative fits for the spectral regions of C=O (green and blue) and C–OH (purple) are recalled to highlight the discontinuities impacted the most as a result of using ¹H decoupling. The latter arise from ¹⁷O signals from covalently or hydrogen bound protons.

(C) Expanded spectra of KHCO₃ acquired using either a Bloch decay experiment with ¹H decoupling (dashed red), or a Hahn echo sequence with no decoupling (solid black), demonstrating the importance of both the choice of NMR experiment and acquisition conditions for bicarbonates to properly detect the C–OH groups.

(**D**) Experimental ¹⁷O MAS NMR spectra acquired at 14.1 T (600 MHz instrument) on ¹⁷O enriched KHCO₃ at a spinning rate of 20 kHz, and sample temperatures *ca*. 250 K and 330 K, showing the significant change in lineshape in the latter case.

All these comparisons highlight the importance of ¹⁷O NMR acquisition conditions on the study of (bi)carbonate salts, and could explain why the C–OH groups in KHCO₃ were not detected in a recent study.³⁷

Further details on acquisition parameters for the spectra above are provided in the Table S7.







Figure S16: (A) Experimental 2D ¹H-¹/O{¹H} INEPT spectrum acquired at 28.2 T (1.2 GHz instrument) on ¹⁷O enriched NaHCO₃ at a spinning rate of 50 kHz, and sample temperature *ca.* 297 K, using a recoupling time of 500 μ s.^c The experimental 1D ¹⁷O MAS NMR spectrum recorded at the same magnetic field is shown in dashed blue line in the ¹⁷O dimension, for comparison. In the corresponding 2D spectrum, signals of the hydrogen bonded carbonyl oxygen (C=O^{...}H, O2) and hydroxyl oxygen (C–OH, O3) are visible. On the right, a slice extracted along the ¹H dimension is shown, with the experimental spectrum in black and its overall fit shown dashed red (composed of a simulated fit including two ¹⁷O signals, O2 and O3, in green and purple, respectively, with the parameters indicated in the table below). (B) 1D ¹H-¹⁷O{¹H} INEPT spectra, recorded with a recoupling time array from 100 to 800 μ s (increments of 100 μ s). As the recoupling time is increased, the appearance of the signal arising from the H-bonded O2 can be seen to steadily increase, while that for O3 plateaus from 200 to 800 μ s. Further details on acquisition parameters for the displayed spectrum are shown in the **Table S6**.

^c The spectral window along the ¹H dimension was incorrectly set to 500 kHz, corresponding to an increment of 2 μ s during acquisition, thus the spectrum appears poorly resolved in the ¹H dimension.

Table S10: Experimental ¹⁷O NMR parameters for sodium and potassium bicarbonate salts for spectra acquired at 28.2 T with sample temperatures estimated to be 297 K. Quadrupolar parameters are compared to previously reported NQR data acquired at 291 K.³⁸ The values indicated in parentheses correspond to the experimental uncertainty in the last digit(s).

			δ_{iso} (ppm) ^a	C _Q (MHz)	ηϱ
	01	Exp.	175.9 (28)	7.21 (15)	0.83 (9)
NoUCO.	01	Exp.	171.5 (32)	6.58 (25)	1.00 (15)
NahCO ₃	02	NQR		[6.747]	[0.790]
	Exp	Exp.	137.7 (25)	7.65 (20)	0.39 (5)
	03 (OH)	NQR		[-7.749]	[0.370]
	01	Exp.	190.6 (23)	7.30 (15)	0.73 (4)
VUCO.	01	Exp.	178.7 (25)	6.75 (20)	0.64 (5)
KHCU ₃	02	NQR		[6.772]	[0.661]
	02 (011)	Exp.	146.9 (26)	7.30 (15)	0.21 (9)
	U3 (UH)	NQR		[-7.342]	[0.237]

^{*a*} A conservative 2-3 ppm uncertainty in the isotropic chemical shifts is given here, to account for small differences in referencing depending on the methodology used (see materials and methods section for details).



Figure S17: Plots of (A) δ_{iso} vs. $|C_Q|$ and (B) δ_{iso} vs. η_Q for ¹⁷O NMR parameters obtained from experiments (for the two bicarbonate salts, **Figure S14**) and DFT calculations on periodic structural models (for all 5 (bi)carbonate salts, **Table S9**). Data arising from the Naand K- salts are shown in blue and orange, respectively.

The shaded boxes correspond to the C=O and C–OH zones reported in recent DFT computations on hydrated (bi)carbonate clusters.¹⁹ The dashed boxes correspond to the expected C=O and C–OH zones found here (see **Figure S14** and **Table S9**), showing that a larger range of possible ¹⁷O NMR parameters needs to be considered in studies of systems involving carbonates and bicarbonates.



Figure S18: Experimental ¹⁷O{¹H} MAS NMR spectra of Na- and K- (bi)carbonates acquired at $B_0 = 14.1$ T (600 MHz instrument). Sample temperatures and spinning rates are indicated near the spectra. Spectra acquired with the sample temperature *ca*. 105 K: *all* appear as well-defined quadrupolar lineshapes, compared to their counterparts acquired at *ca*. 255 K to 310 K. Spinning sidebands are denoted with an asterisk (*), ¹⁷O NMR signals arising from crystalline water with a dagger (†), and from satellite transitions with a cross (×). Further details on acquisition parameters for displayed spectra are shown in the **Table S4** and **S8**. The complete analysis of these low-temperature spectra will be reported in a forthcoming publication.

Supplementary Information S2: Selective ¹⁷O enrichment of crystalline water in $Na_2CO_3 \cdot H_2O$ and accompanying NMR experimental information.

90% H₂¹⁷O (110 µL, 2 eqv.)^d and anhydrous Na₂CO₃ (325.9 mg, 1 eqv.) were introduced successively into the jar alongside two stainless steel ball bearings. The jar was closed, sealed with parafilm, and the medium was milled for 30 minutes at 25 Hz using a Retsch MM400. After milling, the jar was opened and the white solid product was scraped and dried under dynamic vacuum for 24 hours. Prior to ssNMR experiments, it was analysed by IR and pXRD (**Figure S19**), showing the quantitative formation of Na₂CO₃·H₂O.



In-situ variable temperature (VT) ¹⁷O MAS ssNMR experiments were performed at 14.1 T $[v_0(^1H) = 599.764 \text{ MHz} v_0(^{17}O) = 81.307 \text{ MHz}]$ at the ICGM (Montpellier, France). ¹H and ¹⁷O NMR spectra were recorded in tandem on a Varian VNMRS spectrometer using a 3.2 mm triple-resonance HXY Varian probe with samples packed into 3.2 mm o.d. zirconia rotors with Torlon drive tips and caps. Samples were spun at a rate of $v_{rot} = 20$ kHz with the temperature of the regulating unit varied in a range of 233 K to 353 K. ¹H NMR spectra were acquired using a simple Bloch decay (One pulse) sequence, with a $\pi/2$ excitation pulse of 3.5 µs, a recycle delay of 1 s, and acquiring 4 scans. ¹⁷O NMR spectra were acquired using a DFS enhanced Hahn echo pulse sequence with a $\pi/2$ solid pulse of 2 µs) followed by a π pulse of 4 µs, and using an echo

^d An excess of H₂O was used, to remain in similar stoichiometries to those involved in the labeling procedure involving CDI.

delay of one rotor period. Acquisition parameters for all spectra are listed in the **Table S11** below.

The NMR rotor with the sample was weighed before (650.8 mg) and after ssNMR (650.7 mg), showing no significant weight loss. The sample was re-characterized by IR and pXRD after the ssNMR analyses (**Figure S19**), revealing once more the characteristic signatures of Na_2CO_3 ·H₂O.

Sample	Na ₂ CO ₃ ·H ₂ O		
Pulse Sequence	DFS-echo		
Spinning rate (kHz)	20		
Regulated temperature (K)	233 to 353		
Sample temperature (K)	250 to 370		
Number of scans	1024		
Experimental time (min)	15		
Recycle delay (s)	1		
¹⁷ O $\pi/2$ pulse width (µs)	2		
¹⁷ O π pulse width (µs)	4		
17 O pulse rf (kHz) ^a	42		
Number of rotor periods (echo)	1		
Dwell time (μ s)	10		
Spectral width (kHz)	100		
Acquisition length (ms)	20		
¹ H decoupling field (kHz)	75		
DFS pulse length (µs)	400		
DFS pulse rf (kHz)	10		
DFS pulse offsets (kHz)	200 - 70		

 Table S11: Acquisition parameters for *in-situ* VT ¹⁷O MAS ssNMR experiments (see Figure S20 A for data).

Additional ¹⁷O NMR experiments were carried out at a later date on a freshly packed sample, after having allowed it to evolve overnight at 370 K (>12 hours), while spinning at 20 kHz. These ¹⁷O NMR spectra were acquired using either (*i*) a Hahn echo with a $\pi/2$ solid pulse of 2 µs followed by a π pulse of 4 µs, and using an echo delay of one rotor period, or (*ii*) a Bloch decay (one pulse) under MAS or static conditions, using $\pi/2$ CT-selective and non-selective pulses, respectively. Additional acquisition parameters for these spectra, which are now shown in **Figure S23**, are listed in the **Tables S12**.

Sample	Na ₂ CO ₃ ·H ₂ O	Na ₂ CO ₃ ·H ₂ O	Na ₂ CO ₃ ·H ₂ O
Pulse Sequence	Hahn-echo	One pulse	One pulse ^{<i>a</i>}
Spinning rate (kHz)	20	20	static
Regulated temperature (K)	353	353	353
Sample temperature (K)	370	370	355
Number of scans	889	4096	124
Experimental time (min)	15	68	2
Recycle delay (s)	1	1	1
¹⁷ O $\pi/2$ pulse width (µs)	2	2	6
¹⁷ O π pulse width (µs)	4	-	-
¹⁷ O pulse rf (kHz)	42	42	42
Number of rotor periods (echo)	1	-	-
Dwell time (μ s)	10	10	10
Spectral width (kHz)	100	100	100
Acquisition length (ms)	20	20	20

Table S12: Acquisition parameters for *in-situ* VT ¹⁷O MAS ssNMR experiments performed after having left the sample evolve overnight (**Figure 4D** in main text, and **Figure S23** in supporting information).

^{*a*} Spectrum acquired using a non-selective or solution $\pi/2$ pulse for ¹⁷O.

Supplementary Information S3: Selective ¹⁸O enrichment of crystalline water in $Na_2CO_3 \cdot H_2O$, and accompanying heating and IR analyses.

 $H_2^{18}O$ (38 µL, 2 eqv., 99% ¹⁸O-labeled) and freshly prepared anhydrous Na₂CO₃ (109.3 mg, 1 eqv.) were introduced successively into a 10 mL stainless steel jar alongside two stainless steel ball bearings. The jar was closed and the joint sealed with parafilm and milled for 30 minutes at 25 Hz using a Retsch MM400. After milling, the jar was opened and the white solid product was scraped and dried under dynamic vacuum overnight. Prior to performing heating experiments, it was analysed by IR showing the presence of Na-carbonate monohydrate (with no detectable ¹⁸O enrichment on the carbonate). Samples were packed into 3.2 mm o.d. zirconia NMR rotors (identical to those used for NMR measurements) and placed into a Memmert UF 30 oven either at \approx 40 °C or 100 °C.

- For the sample heated at 100 °C, the rotor was taken out at various time intervals (17 min, 2 h, 5 h, and 16 h), and analysed by IR using a Perkin Elmer Spectrum 2 instrument in a range of 400 to 4000 cm⁻¹, or using a Perkin Elmer Spectrum 100 instrument in the range of 650 to 4000 cm⁻¹ (with 4 scans for both the background and sample).
- For the sample heated at 40 °C, the rotor was taken out after 16 h of heating and analysed by IR.

In both cases, after heating, no significant change in weight was measured (see **Table S13**), and only the monohydrate phase was observed by IR spectroscopy. IR variations in the ¹⁸O-isotopologue regions are shown in **Figures 4E** in main text, and **Figure S22** in ESI.

Sample	Duration of Sample in Oven (hours)	Weight of Sample and			
		Rotor $(mg)^a$			Oven Regulated
		Before	After	After	Temperature (°C)
		Oven	Oven	IR^{b}	
Sample 1	0.3	643.6	643.4	642.6	≈ 100
Sample 2	2	643.2	643.0	642.5	pprox 100
	5	642.5	642.4	641.7	pprox 100
	16	641.7	641.6	-	≈ 100
Sample 3	0.3	649.7	649.7	649.0	pprox 40
	16	649.0	648.9	-	pprox 40

Table S13: Weight of sample and rotor during *ex-situ* IR experiments of Na₂CO₃·H₂O.

^{*a*} Typical mass of sample in the rotor: 25-30 mg.

^b Weight loss is observed after IR measurement as some sample was taken out of rotor for analysis.



Figure S20:

A/ Full VT range probed during the experimental ¹⁷O{¹H} MAS NMR spectra acquired at $B_0 = 14.1$ T (600 MHz instrument) of Na₂CO₃·H₂O, initially prepared with ¹⁷O-labeling selectively on the water. The spectral regions at which CO₃²⁻ (200 to 40 ppm) and crystalline H₂O (0 to -120 ppm) appear at this field are shown in orange and light blue, respectively. Spectra were recorded using the conditions reported in **Table S11.** Sample temperatures are indicated on the left for each spectrum.

N.B.: Experiments were recorded here using a DFS-echo, which does not allow the detection of small amounts of mobile water by ¹⁷O NMR, while these are visible in the ¹H NMR spectra in **B**.

B/ Preliminary VT ¹H MAS NMR spectra acquired at $B_0 = 14.1$ T of Na₂CO₃·H₂O, initially prepared with ¹⁷O-labeling selectively on the water. The dashed line in black at *ca*. 5.1 ppm (centered on the sharp peak observed in the first spectrum acquired at a sample temperature of 310 K) is indicative of the presence of a small amount of mobile water (at the surface of the crystals); its position shifts depending on the temperature. Sample temperatures are indicated on the left for each spectrum.

N.B.: Experiments were recorded here using a Torlon cap and insert in the rotor, giving rise to a large ¹H background. No subtraction of the residual background signal was done at this stage. A yet-unidentified impurity in the spectra is also denoted with a cross (\times).



dashed red is for a Na₂C^{*}O₃·H₂^{*}O sample enriched with ¹⁷O by ball milling (starting from CDI, NaOH and ¹⁷O-enriched water), and recorded at a similar sample temperature. The spectral regions at which CO_3^{2-} (200 to 40 ppm) and crystalline H₂O (0 to -120 ppm) can appear at this field are shown in orange and light blue, respectively.



Figure S22: Experimental IR of selectively ¹⁸O-labeled samples of Na₂CO₃·H₂¹⁸O, packed inside a 3.2 mm rotor, and heated overnight (16 hours) in an oven at 40 °C and 100 °C. The full spectral width of IR spectra on the left indicate the monohydrate phase remains intact. When zooming into the region between 1150 and 950 cm⁻¹, the IR spectra on the right show that no labeling of the carbonate in the sample occurs when heating overnight at a temperature of 40 °C. However, labeling is observed when heating overnight at 100 °C, as revealed by the appearance of peaks corresponding to the various isotopologues of C¹⁸O₃^{2–} in Na₂CO₃·H₂O (see text for details).



Figure S23: Experimental *in-situ* ¹⁷O NMR spectra of a sample of Na₂CO₃·H₂¹⁷O acquired under various measurement conditions (indicated on right of spectra), after having spun the rotor overnight at 370 K (sample temperature) The bottom spectrum was acquired using a Bloch decay reveals four species (i) two broad resonances for crystalline H₂O (light blue region) and CO_3^{2-} (yellow region) and (ii) two sharper resonances for mobile H₂O (light blue region) and CO_3^{2-} (red region). The middle spectrum was acquired using a Hahn echo shows only the broad resonances assigned to crystalline Na₂CO₃·H₂O. The top spectrum was acquired under static conditions using a non-selective Bloch decay, and shows only the resonances of the most mobile species (in a liquid-like environment). The regulated temperature is the same for all 3 spectra, which explains why the actual sample temperature is lower in the case of the static experiment shown here (no frictional heating). Further details on acquisition parameters are available in **Table S12**.



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