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Monitoring a Mechanochemical Reaction Reveals the Formation of a New ACC Defect Variant Containing the HCO$_3^-$ Anion Encapsulated by an Amorphous Matrix

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ABSTRACT
Amorphous calcium carbonate (ACC) is an important precursor in the biomineralization of crystalline CaCO$_3$. In nature it serves as a storage material or as permanent structural element, whose lifetime is regulated by an organic matrix. The relevance of ACC in materials science is primarily related to our understanding of CaCO$_3$ crystallization pathways and CaCO$_3$/(bio)polymer nanocomposites. ACC can be synthesized by liquid-liquid phase separation, and it is typically stabilized with macromolecules. We have prepared ACC by milling calcite in a planetary ball mill. Phosphate “impurities” were added in the form of monetite (CaHPO$_4$) to substitute the carbonate anions, thereby stabilizing ACC by substitutional disorder. The phosphate anions do not simply replace the carbonate anions. They undergo shear-driven acid/base and condensation reactions, where stoichiometric (50%) phosphate contents are required for the amorphization to be complete. The phosphate anions generate a strained network that hinders ACC recrystallization kinetically. The amorphization reaction and the structure of BM-ACC were studied by quantitative Fourier transform infrared spectroscopy and solid state $^{31}$P, $^{13}$C, and $^1$H magic angle spinning nuclear magnetic resonance spectroscopy, which are highly sensitive to symmetry changes of the local environment. In the first - and fast - reaction step, the CO$_3^{2-}$
anions are protonated by the HPO$_4^{2-}$ groups. The formation of unprecedented hydrogen carbonate (HCO$_3^-$) and orthophosphate anions appears to be the driving force of the reaction, because the phosphate group has a higher Coulomb energy and the tetrahedral PO$_4^{3-}$ unit can fill space more efficiently. In a competing second - and slow - reaction step, pyrophosphate anions are formed in a condensation reaction. No pyrophosphates are formed at higher carbonate contents. High strain leads to such a large energy barrier that any reaction is suppressed. Our findings aid in the understanding of the mechanochemical amorphization of calcium carbonate and emphasize the effect of impurities for the stabilization of the amorphous phases in general. Our approach allowed the synthesis of new amorphous alkaline earth defect variants containing the unique HCO$_3^-$ anion. Our approach outlines a general strategy to obtain new amorphous solids for a variety of carbonate/phosphate systems that offer promise as biomaterials for bone regeneration.

**INTRODUCTION**

Mechanochemistry has become a tool for the synthesis of new inorganic, organic, and metal–organic compounds. The product range can be extended by using small amounts of solvents or dispersants (liquid-assisted grinding), ionic compounds (ion- and liquid-assisted grinding), or polymers (polymer-assisted grinding) during grinding. Ball-milling is an established strategy for producing out-of-equilibrium structures, and it can be employed for breaking down bulk materials to nano-size. Defect formation on a large scale leads to an amorphization of crystalline solids. Elemental germanium or zeolites show a loss of crystallinity during ball-milling, and changes of extended hydrate networks have been reported for Co$_3$(PO$_4$)$_2$ × 8 H$_2$O. Ball milling can induce an alloying of metals or polymorph changes (e.g., a transformation from the anatase to the rutile phase of TiO$_2$). Similarly, organic compounds mixtures of organic and inorganic compounds undergo structural changes during mechanochemical treatment. This is of particular interest for pharmaceuticals as the higher solubility of amorphous phases enhances the uptake of drugs with poor water solubility. Mechanochemistry is of particular interest for large applications due to its scalability and the reduced use of solvents, which make it a “green chemistry” technique.

Continuous mechanical stress during ball milling was proposed to trigger unusual reactivity and lead to the formation of transient phases that are different from those accessible in conventional solid state reactions. There is limited evidence for or against this hypothesis. Ex situ studies, where the reactants are converted and analyzed after the reaction, provide little information about intermediates, kinetics and dynamics during the mechanochemical reaction itself.
In situ measurements, on the other hand, can provide real-time insight into a ball milling environment.\textsuperscript{22–24} Time-resolved X-ray diffraction with synchrotron radiation (PXRD) is the method of choice for elucidating chemical reaction pathways by the structure determination of intermediates whose existence might be deduced only indirectly otherwise. Diffraction, however, provides meaningful information only for crystalline materials. Non-crystalline solids elude structural analysis with diffraction methods. Only local probes, such as vibrational (IR, Raman) and nuclear magnetic resonance (NMR) spectroscopy or total scattering\textsuperscript{12,16} can aid in the structural analysis. Since solid state transformations are typically diffusion limited and therefore comparatively slow, a step by step analysis can be used to identify transient phases, where “snapshots” are taken at different stages of the reaction.\textsuperscript{25,26} We demonstrate the utility of this approach by unravelling the structure of non-crystalline intermediates from the mechanochemical reaction of calcium carbonate (CaCO\textsubscript{3}) and calcium hydrogenphosphate (monetite, CaHPO\textsubscript{4}).

Calcium carbonate is an important biomineral in ascidians and molluscs, and calcium phosphate is an essential constituent of vertebrate hard tissues (bone, dentine, enamel).\textsuperscript{27–29} The corresponding amorphous polymorphs play a prominent role in biomineralization.\textsuperscript{28,30–33} The transition from amorphous to crystalline phases allows Nature to exert control through ion concentrations (with ion pumps) and organic matrices or molecules.\textsuperscript{34} Many research groups have invested substantial efforts to achieve a deep understanding of the mechanism of biomineralization.\textsuperscript{35} An application-oriented result of the crystallization mechanisms is the use of amorphous calcium carbonate and phosphate for bone grafting materials or nanocomposites.\textsuperscript{36–40} There is a growing interest on the effect of impurities in the local structure of amorphous calcium carbonate (ACC)\textsuperscript{41,42} and amorphous calcium phosphate (ACP).\textsuperscript{43} Organisms control the metastability of ACC by incorporating additives (like Mg\textsuperscript{2+}, PO\textsubscript{4}\textsuperscript{3−} or water).\textsuperscript{43} These impurities have strong effects on the local structure of ACC and ACP, and several studies have been carried out to investigate the effect of additives such as magnesium and phosphate ions on ACC.\textsuperscript{40–43} The local structure in ACC is a matter of debate.\textsuperscript{44} A “protostructuring” of ACC with respect to different crystalline CaCO\textsubscript{3} polymorphs has been proposed,\textsuperscript{45,46} and the concept of “polyamorphism” has been considered for biogenic ACC.\textsuperscript{44} Although the short-range order in ACC is pH dependent\textsuperscript{47} and OH\textsuperscript{−} groups were found to be incorporated in ACC,\textsuperscript{48} there are no indications for the presence of hydrogen carbonate (HCO\textsubscript{3}−) ions in ACC or any hydrated CaCO\textsubscript{3} polymorph.\textsuperscript{49–52} The synthesis and stabilization of ACC have been pursued by freeze-drying,\textsuperscript{53} with polymers\textsuperscript{54} and proteins,\textsuperscript{55} or foreign ions like Mg\textsuperscript{2+}\textsuperscript{56} and phosphate.\textsuperscript{43} These approaches
start from the Ca$^{2+}$ and CO$_3^{2-}$ ion constituents in aqueous solution, and the crystallization process is stopped at the ACC stage by stabilizing the product kinetically.

Mechanochemical treatment of calcium carbonate has been studied before.$^{57-60}$ The transformation of calcite to its high-pressure polymorph aragonite has been reported in a mechanically operated mortar.$^{61}$ The reverse transformation from aragonite to calcite, the thermodynamically stable polymorph, was described later.$^{62}$ Likewise, vaterite can be transformed to calcite mechanochemically.$^{63,64}$ In an earlier study we have shown that amorphous CaCO$_3$ could be prepared by ball milling only, when Na$_2$CO$_3$ (minimum 7.5 mol %) was added to stabilize a metastable ball-milled amorphous calcium carbonate phase (BM-ACC) by cationic defects.$^{65}$ It was, however, not possible to obtain other amorphous alkaline earth metal carbonates for metals other than Ca (e.g. Sr and Ba) by cation “doping” with Sr and Ba. Here we show that amorphous alkaline earth carbonates, in particular amorphous calcium carbonate/calcium hydrogen phosphate (aCCP), amorphous strontium carbonate/calcium hydrogen phosphate (aSCP) and amorphous barium carbonate/calcium hydrogen phosphate (aBCP) can be stabilized by mechanical treatment of crystalline alkaline earth metal carbonates (M = Ca, Sr, Ba, Scheme 1) with CaHPO$_4$.

**Scheme 1.** Summary of the ball-milling experiment

This was achieved for large quantities of materials by grinding in a high-energy planetary ball mill. The amount of monetite was kept constant (1 mmol) and mixed with different amounts of earth alkali carbonates. The composition of the product is expressed in terms of the mole fraction $x$(carbonate) = $n$(CaCO$_3$)/($n$(CaCO$_3$)+$n$(CaHPO$_4$)) (e.g. aCCP (0.2): 1 mmol CaHPO$_4$ and 0.25 mmol CaCO$_3$, i.e. $x$(carbonate)=0.2). Static spin echo delay NMR measurements revealed that even small mole fractions ($x = 0.05$) cause large structural changes.

The process of amorphization was studied *ex situ* by solid-state nuclear magnetic resonance (ssNMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The local structure of the amorphous compounds was probed by ssNMR spectroscopy. Complementary structural information about the local structure motifs revealing the coordination sphere for the alkaline earth cations was derived from the analysis of total scattering data using synchrotron radiation.
The molecular dynamics was derived from X-ray photon correlation spectroscopy (XPCS). An outstanding feature of the amorphous phases is their extraordinary stability and slow crystallization (up to several months), because ACC and BM-ACC crystallize within minutes in contact with humidity. The evaluation of the XPCS data indicates the presence of a highly-strained system in BM-aCCP. This strain due to hydrogen-bonded HCO$_3^-$ groups leads to a large energy barrier that suppresses any further reaction.

RESULTS AND DISCUSSION

Ball Milling Reaction
The milling process was monitored *ex situ* using $^1$H- and $^{31}$P- single pulse excitation (SPE) magic angle spinning solid-state nuclear magnetic resonance spectroscopy ($^{31}$P-MAS-ssNMR) at 10 kHz and FTIR spectroscopy. The full width at half maximum (fwhm) of the NMR signals in crystalline solids is a sensitive measure of the uniformity of the local field and thus suitable to follow the changes during the amorphization process.

The milling process of amorphous calcium carbonate/calcium hydrogen phosphate (aCCP 0.2) was stopped after 10 min, 30 min, 60 min, 240 min and 480 min. Figure 1a shows the $^{31}$P-MAS-ssNMR spectra of aCCP 0.2 as a function of milling time. During the first 30 minutes of milling the two phosphorous resonances at -1.62 and -0.34 ppm are broad but can still be detected. These signals are associated with two different crystallographic environments of the phosphate ion in crystalline CaHPO$_4$. For longer milling times, signal broadening increases due to a loss of crystalline order. The two individual resonances merge indicating complete amorphization. During the milling process the signal shifts to lower field. After 8 h of milling the resonance becomes asymmetric with a maximum at ~ 3 ppm and a broad shoulder at ~ -10 ppm. The appearance of this shoulder indicates the existence of another process besides amorphization.

The same trend was observed in the $^1$H-MAS-ssNMR spectra (Figure 1b). The $^1$H spectrum of crystalline monetite displays three $^1$H resonances at 12.55, 13.22 and 15.60 ppm associated with different environments of the hydrogen phosphate proton. After 10 min of milling time four additional “solvent” signals can be detected in the $^1$H spectrum: The signal (i) at 1.22 ppm can be assigned to the presence of the cyclohexane as dispersion medium, (ii) the signal at 4.8 ppm
Figure 1. (a) $^{31}$P-MAS-ssNMR spectra of aCCP 0.2 as a function of milling time in comparison to crystalline CaHPO$_4$. (b) $^1$H-MAS-ssNMR spectra of aCCP 0.2 as a function of milling time in comparison to crystalline CaHPO$_4$. The $^1$H spectrum of crystalline CaHPO$_4$ contains three $^1$H resonances at 12.55, 13.22 and 15.60 ppm related with different environments of the hydrogen phosphate group. After 10 min of milling solvent signals (1.22 ppm: cyclohexane, 4.8 ppm: water, 0.88 and 3.52 ppm: ethanol) appear. The signals broaden with milling time. The broad resonance at 11 ppm (8 h) corresponds to a chemical reaction. (c) X-ray powder diffractograms (XRPD) of aCCP 0.5 (black), aSCP 0.5 (red), aBCP 0.5 (blue) after 480 min of milling time. Background measurement is presented in grey. (d) TEM image of aCCP 0.5 and the associated diffraction pattern after 480 min of milling show complete amorphization.

shows the presence of residual water and (iii) the signals at 0.88 and 3.52 ppm are related to ethanol used in the washing step. These resonances remained unaffected even after drying the sample for 8 h at 40 °C in a vacuum oven (Figure S1, Supporting Information). This indicates
that the solvent molecules are encapsulated in nanocavities or in “grain boundaries” of the amorphous structure. Increasing the milling time leads to broadening of all signals, related with a loss of order and/or mobility. The appearance of a broad resonance at 11 ppm after 8 h of milling is attributed to changes in the $^1$H environment leading to higher shielding of the phosphate proton or to a chemical reaction.

Figure 1c shows the X-ray powder diffractograms (XRPD) of the amorphous alkaline earth metal carbonate phosphates (x(carbonate) = 0.5) after 480 min of milling. The loss of all reflections associated with the starting crystalline components and the simultaneous appearance of

![Figure 2. IR spectra of crystalline alkaline earth carbonates and ball-milled amorphous alkaline earth carbonate phosphates (x(Carbonate) = 0.5) after 480 min of milling time. (a) M = Ca, (b) M = Sr, (c) M = Ba. (d) IR reference spectrum of CaHPO$_4$ (monetite).](image)
modulations characteristic for amorphous materials reveal all samples to be “X-ray amorphous”. However, the pure starting materials, MCO₃ (M = Ca, Sr, Ba) and CaHPO₄, cannot be amorphized completely by ball milling (exemplary for CaCO₃ Figure S2a, Supporting Information as well as the Quantification of the remaining crystalline proportion: Table S1). Transmission electron microscopy (TEM) images and the associated diffraction patterns for aCCP 0.5 confirm the complete lack of long-range order. The morphology of the particles (Figure 1d) is very different compared to amorphous carbonates precipitated from solution, and the particles have much larger diameters (up to 1 μm, TEM images of aSCP and aBCP 0.5: Figure S3, Supporting Information.

**Crystalline starting compounds and amorphous products**

Figure 2 shows FTIR spectra of amorphous alkaline earth metal carbonate phosphates \( x_{\text{Carbonate}} = 0.5 \) with their respective crystalline precursors. All samples show the characteristic vibration modes of the carbonate ion in amorphous solids, in particular for aCCP 0.5: \( ν₂ \approx 862 \text{ and } 836 \text{ cm}^{-1}, ν₃ ≈ 1410 \text{ and } 1493 \text{ cm}^{-1}, ν₄ ≈ 693 \text{ and } 728 \text{ cm}^{-1} \) (Figure 2a). The expected \( ν₁ \) mode of the carbonate ion overlaps with the P-O stretch \( (ν₅ \text{ P-O} ≈ 1010 \text{ cm}^{-1}) \). Overall, the FTIR spectra of the samples are similar (Figure 2a-c). Therefore, we expect that the mechanism leading to amorphization is independent of the cation. However, the different Pearson hardness of the alkaline earth cations (absolute values for Mg²⁺: η=32.5; Ca²⁺: η=19.7; Ba²⁺:η=12.8) leads to slight shifts in the \( ν₂ \) vibration mode to higher wavenumbers and to lower wavenumbers for the \( ν₃ \) and \( ν₄ \) vibration modes, which is consistent with the size of the cations. Therefore, the different charge density of the cations leads to different ionic bond strengths, and bands appear at different positions (i.e. vibrational energies, Table S1, Supporting Information).

For crystalline monetite the bands of the \( ν₅ \text{ P-O(\text{H})} \) stretch at 884.2 cm⁻¹ in crystalline monetite cannot be detected in any of the amorphous products. Possible explanations are (i) strong shifts of the absorption maxima, (ii) strong signal broadening, or (iii) loss of intensity due to chemical transformation. Furthermore, the \( ν₅ \text{ P-O} \) stretch remained broadened in all samples, which is well known for amorphous phosphates. The broad bands at about 3500 cm⁻¹ are assigned to \( ν₅ \text{ O-H stretching modes} \). All spectral bands show a significant broadening due to the loss of long-range order compared to those of the crystalline compounds. The bands at 2931 and 2853 cm⁻¹ indicate that the dispersant medium cyclohexane is occluded in “nanocavities” of the amorphous product. The bands are
characteristic for the asymmetric and symmetric C-H stretch of the CH$_2$ groups in cyclohexane.\textsuperscript{75}

**Phosphate Environment: $^{31}$P NMR Spectroscopy**

The ratio between the starting materials CaCO$_3$ and CaHPO$_4$ has a great effect on the structure of the amorphous products (Figure 3a). The increase of the carbonate content for a milling time of 480 min results in a shift of the $^{31}$P signal of the amorphous product to lower field. For carbonate mole fractions $x > 0.3$ the maximum of the $^{31}$P signal at 1.6 ppm remains unchanged (Figure 3b). Thus, the average phosphorus environment depends on the milling time (Figure 1b) and the carbonate:hydrogen phosphate ratio, especially for low carbonate concentrations. For low carbonate contents a shoulder appears at $\sim$ -9 ppm which decreases with increasing carbonate content and disappears almost completely for $x = 0.66$, i.e. the $^{31}$P resonance becomes symmetric.

![Figure 3.](image)

**Figure 3.** (a) $^{31}$P signals of ball-milled amorphous calcium carbonate phosphates after 480 min of milling time. (b) Signal maxima of ball-milled amorphous calcium carbonate phosphates as a function of the carbonate mole fraction $x_{\text{Carbonate}}$. The ball-milled CaHPO$_4$ after 480 min of ball milling is included additionally. The dashed line represents a trend line.

To further investigate the results of the amorphization process as a function of the carbonate:hydrogen phosphate ratio a TEDOR (Transferred Echo DOuble Resonance) recoupling experiment at 25 kHz MAS was used.\textsuperscript{76} The fast magic angle spinning averages the heteronuclear $^1$H-$^{31}$P dipole-dipole couplings; this leads to a loss of the associated information. To reintroduce the heteronuclear coupling interaction in the TEDOR experiment, 180° pulses are applied in the middle of the rotor period. The spectra are recorded as a function of the recoupling time (rotor period). Those recorded with short recoupling times provide information about the
strongly coupled heteronuclear pairs and those with longer recoupling times reveal information about long range dipolar couplings or about mobile systems where the dipolar interaction is influenced by the motion.

Figure 4. (a) $^1$H-$^{31}$P TEDOR spectrum of ball-milled calcium hydrogen phosphate, recorded at 1, 2, 4, and 6 rotor periods (40, 80, 160 and 240 μs recoupling time respectively) after 480 min of ball milling. (b) $^{31}$P single pulse excitation (SPE) reference spectra of crystalline CaHPO$_4$, Ca$_3$(PO$_4$)$_2$ and Ca$_2$P$_2$O$_7$. (c) TEDOR spectra of amorphous aCCP ($x_{\text{Carbonate}} = 0.2$) after 480 min of ball milling and (d) amorphous aCCP ($x_{\text{Carbonate}} = 0.5$) after 480 min of ball milling as a function of the rotor period, with the respective $^{31}$P single pulse excitation (SPE) spectra.

Neutron diffraction studies on crystalline calcium hydrogen carbonate revealed the presence of two crystallographically distinct phosphate groups. At ambient conditions one half of the
phosphate groups exist as \( \text{HPO}_4^{2-} \) with one O-H group covalently bound to the central P atom while the other half has one proton in a symmetrically bridging hydrogen bond and one proton statistically distributed between two centrosymmetric positions.\(^{73,77,78}\) The existence of two phases – an ordered low temperature and a disordered high temperature phase with a phase transition at about 280 K was suggested.\(^{78}\) Furthermore, the increased \(^1\)H linewidth in low-temperature NMR spectra was assumed to result from a reduced proton mobility.\(^{77}\) The increased temperature for longer milling times would induce disorder and enhance proton transfer, i.e. destabilize the hydrogen bonds. The applied mechanical force would most probably facilitate the transfer of the protons participating in destabilized hydrogen bonds (orange marked signals at -1.7 and -1.6 ppm, Figure 4a and b) to different from the original environments (Figure 4a, signal at -5.5 ppm). This would lead to different phosphorus environments and \(^{31}\)P resonances as observed in the TEDOR spectra (Figure 4) of the ball-milled calcium hydrogen carbonate phosphate. The \(^{31}\)P signal appearing at \(-0.3\) ppm in the crystalline compound is significantly broadened, but its chemical shift is hardly influenced. On the other hand, the sharp \(^{31}\)P resonance at -1.6 ppm in crystalline CaHPO\(_4\) disappears almost completely, and a new signal appears at -5.5 ppm. It may be related with the new environment of the mobile protons and thus lead to different \(^{31}\)P shifts.

Figure 4a shows a typical \(^1\)H-\(^{31}\)P TEDOR spectrum of ball-milled calcium hydrogen phosphate, recorded at 1, 2, 4, and 6 rotor periods (40, 80, 160 and 240 \(\mu\)s recoupling time respectively). Reference spectra of crystalline CaHPO\(_4\), Ca\(_3\)(PO\(_4\))\(_2\) and Ca\(_2\)P\(_2\)O\(_7\) are presented in Figure 4b for comparison. Surprisingly, well defined resonances rather than one broad (amorphous) signal appear in all TEDOR spectra, which implies local order. The \(^{31}\)P SPE reference spectrum is broadened inhomogeneously. In addition, the \(^{31}\)P resonances in the TEDOR spectra (depending on the recoupling time) are shifted by up to \(7.5\) ppm up- and downfield with respect to the signals for crystalline CaHPO\(_4\). These differences - not typical for a simple amorphization - are associated with changes in the chemical (and electronic) environment of the phosphorus atoms when new bonds are formed.

In the TEDOR spectra of the aCCP sample (\(x_{\text{Carbonate}} = 0.2\)) (Figure 4c) three resonances appear at 1.8, -2.6 and -9.1 ppm together with a shoulder at \(-5.5\) ppm. The broadened \(^{31}\)P signal at -9.3 ppm and the shoulder at -5.5 ppm are in harmony with the shift range typical for crystalline Ca\(_2\)P\(_2\)O\(_7\).\(^{79}\) Thus, it is likely that pyrophosphate was formed as an intermediate in a condensation reaction during the ball milling process. The other \(^{31}\)P shifts are compatible with hydrogen phosphate or orthophosphate units from the reference spectra. A higher calcium carbonate content (aCCP = \(x_{\text{Carbonate}} = 0.5\)) (Figure 4d) results in a loss of the signal at -9.1 ppm. All other
resonances in the TEDOR spectra are shifted to lower field (i.e. at 0.3, ~2 and 4.0 ppm). By “diluting” the phosphate starting compound with carbonate the mean P–P distance increases, and a condensation reaction is less likely. In addition, new signals appear at low field, in agreement with the results of the $^{31}$P-MAS ssNMR experiments (Figure 3b). Figure S4-8 (Supporting Information) summarize the results of the $^{31}$P NMR and TEDOR experiments for x = 0.2 and 0.5 for different alkaline earth metals.

**Figure 5.** (a) SPE $^{13}$C NMR spectra and (b) $^{13}$C CP NMR spectra of aMCP (M = Ca, Sr, Ba) ($x_{\text{Carbonate}} = 0.2$, $t_{\text{cp}} = 2\text{ms}$) and (c) $^{13}$C CP NMR spectra ($x_{\text{Carbonate}} = 0.5$, $t_{\text{cp}} = 2\text{ms}$) (all spectra: 480 min of ball milling).

**Carbonate Environment: $^{13}$C NMR Spectroscopy**

Ball milling leads to pronounced changes in the $^{31}$P environments. The $^{13}$C environment was probed as a function of the carbonate content and the alkaline earth metal using $^{13}$C SPE, cross-polarization (CP) and heteronuclear correlation (HETCOR) NMR experiments, where two different types of nuclei are correlated via through-space dipole-dipole couplings. Figure 5a shows the SPE $^{13}$C NMR spectra for aCCP, aSCP and aBCP ($x_{\text{Carbonate}} = 0.2$). Figure 5b presents the corresponding $^{13}$C CP NMR spectra and Figure 5c the $^{13}$C CP NMR spectra ($x_{\text{Carbonate}} = 0.5$ content). Two broad resonances appear in all spectra. The first signal at ~168 ppm (full width at half maximum (fwhm): 436 Hz) is typical for amorphous carbonates. The width at half maximum decreases for strontium (aSCP: 390 Hz) and barium ion (aBCP: 379 Hz). This reflects the least ordered local environment in the case of aCCP with decreasing order in the order Ba > Sr > Ca.

The second broad resonance appears at ~162 ppm. Such chemical shifts have been reported by Nebel et al.$^{70}$ for sodium and potassium hydrogen carbonate. Although the existence of alkaline earth metal hydrogen carbonates is well known in solution,$^{80-82}$ there are no reports about alkaline earth metal hydrogen carbonate in the solid state. This is assessed from this resonance which is associated with the hydrogen carbonate chemical environment. Therefore, in line with the data of the $^{31}$P NMR, it can be envisioned that (i) the carbonate group is protonated in an
acid/base reaction by the hydrogen phosphate group or (ii) that this specific “hydrogen carbonate” (bicarbonate) environment is formed by reorganization during the milling process. The $^{13}$C SPE spectra show a 7:1 ratio between the signals of amorphous calcium carbonate and the hydrogen carbonate. The hydrogen carbonate content in the samples increases drastically for the heavier group homologues SrCO$_3$ (2.6:1) and BaCO$_3$ (2.4:1). The fwhm for the resonance at ~162 ppm is 549 Hz for aCCP, 690 Hz for aSCP, and 703 Hz for aBCP. This correlates well with the increasing ionic radii of the alkaline earth metals ($r$(Ca$^{2+}$) = 99 pm; $r$(Sr$^{2+}$) = 113 pm; $r$(Ba$^{2+}$) = 135 pm).\textsuperscript{83}

The fraction of the hydrogen carbonate signal is significantly higher for samples with low mole fractions of calcium carbonate. To obtain more information about the distances between the protons and the carbonate group in the different samples, 2D HETCOR NMR spectra were recorded.

Figure 6 shows prototypical $^1$H-$^{13}$C HETCOR spectra of aCCP 0.5 recorded with contact times of 50 and 2000 μs. The spectra of aSCP and aBCP are displayed in Figure S9 and S10 (Supporting Information). The HETCOR spectrum recorded with a contact time of 50 μs (short range contacts) reveals correlations between the proton signal at 12.2 ppm (bicarbonate) and the signal at 162 ppm (Figure 6c). Long range contacts due to the heteronuclear dipole-dipole couplings are displayed in the HETCOR experiment recorded with 2000 μs contact time. Correlation between the $^{13}$C resonances and protons with a shift in the range of the entrapped solvents (especially cyclohexane) appear additionally in the spectrum (4 ppm).

The spectra with short contact times allow different proton environments around the $^{13}$C nuclei and thus the carbonate ions to be resolved. The signal of the amorphous carbonate species at 168 ppm correlates strongly with a proton signal of 15.6 ppm (Figure 6b). This signal can be assigned to protons of hydrogen phosphates. In contrast, the signal of the hydrogen carbonate species at 162 ppm correlates weaker with the hydrogen phosphate signal. Furthermore, an additional proton signal at 12.4 ppm appears, which can be assigned to the hydrogen carbonate species. This is an indication that unreacted hydrogen phosphates enclose carbonate ions and hydrogen carbonate ions are surrounded by orthophosphate ions. This assumption becomes even more evident in the HETCOR spectra of aSCP and aBCP due to the higher hydrogen carbonate content (see Supporting Information).

The spectra with long contact times additionally reveal $^1$H signals in the range of the entrapped solvents (especially cyclohexane). Therefore, the heteronuclear dipole-dipole coupling reaches to $^1$H atoms of entrapped solvents in the grain boundaries.
Figure 6. $^1$H-$^{13}$C HETCOR spectra of aCCP ($x_{\text{Carbonate}} = 0.5$) recorded with contact times of 50 and 2000 $\mu$s and respective projections, in particular (a) $^1$H SPE spectra, (b) projection at 168 ppm with contact times of 50 $\mu$s, (c) projection at 162 ppm with contact times of 50 $\mu$s, (d) projection at 168 ppm with contact times of 2 ms, (e) projection at 162 ppm with contact times of 2 ms.

Chemical Transformations during Ball-Milling: FTIR Spectroscopy

FTIR spectroscopy provides complementary information to solid state NMR spectroscopy on the chemical transformations of MCO$_3$/CaHPO$_4$ (M = Ca, Sr, Ba) during ball-milling. $^{13}$C enriched samples of aMCP (M = Ca, Sr, Ba) were used to facilitate the assignment of the carbonate or phosphate bands in the FTIR spectra. The higher mass of the $^{13}$C isotope shifts the carbonate bands to lower wavenumbers.$^{84}$ The difference between samples containing carbon in natural abundance and enriched with $^{13}$C is displayed for aCCP for milling time of 480 min in Figure 7. The difference spectrum shows the bands assigned to (or affected by) the carbonate vibration modes. Particularly relevant are the bands at $\sim$1640 and 850 cm$^{-1}$. The first is related to the (HO)CO$_2$ stretch.$^{85,86}$ Since the $v_2$ (out of plane) mode of the carbonate ion is not degenerate, the associated band splits in two sub-bands. One of them at 862.7 cm$^{-1}$ can be assigned to the amorphous calcium carbonate environment, the one at 828.2 cm$^{-1}$ is associated with calcium
hydrogen carbonate. Fitting the FTIR spectra for aCCP 0.5 revealed a ratio of 7:1 for the amorphous and hydrogen carbonate species (see Figure S11, Supporting Information) which perfectly matches the results from ssNMR. Unfortunately, a similar comparison was not possible for aCCP (x_{Carbonate} = 0.2) due to the overlap with the ν₄ P-O(H) stretch at 884.2 cm⁻¹.

![Figure 7](image)

**Figure 7.** Difference spectra of aCCP (a) with x_{Carbonate} = 0.2 and (b) with x_{Carbonate} = 0.5 enriched with $^{13}$C and with C in natural abundance for aCCP. The spectra show the essential bands at ~1640 and 850 cm⁻¹ assigned to (or influenced by) the carbonate vibrations. The visualized ν₄ vibration mode shows that the carbon atom has only a small influence on the position of these bands.

The FTIR spectra confirm a proton transfer reaction associated with the formation of a chemical bond (HCO₃⁻) during ball-milling according to:

$$\text{CaCO}_3 + \text{CaHPO}_4 \rightarrow (\text{HCO}_3)^- + (\text{CaPO}_4)^- + \text{Ca}^{2+}.$$  

Replacement monetite by tricalcium phosphate did not lead to complete amorphization (Supporting Information S2b). Thus, *proton transfer is crucial for the amorphization*. Remarkably, alkaline earth hydrogen carbonates in solid-state have not been reported so far although they are quite common in solution. Pyrophosphates were detected for aCCP (x_{Carbonate} = 0.2) based on the band at 750 cm⁻¹. This band disappears for higher carbonate contents, in agreement with the NMR results (*vide supra*). Finally, the ν₄ band at 683 and 727 cm⁻¹ in aCCP (x_{Carbonate} = 0.5) shows no $^{13}$C-related shift, although it can be clearly assigned to the carbonate ion. An explanation is that the ν₄ mode is associated with displacements of the oxygen atoms. Therefore it is nearly independent from the mass of the carbon atom.$^{64}$
**Structure: $^{31}$P - static spin echo experiments**

$^{31}$P - static spin echo experiments were performed for different compositions $x$ of calcium hydrogen phosphate and alkaline earth carbonates. The Hahn spin echo intensity was measured as a function of evolution time to deduce the homonuclear dipole-dipole interaction. At short evolution times ($2\tau$) the normalized intensities ($\frac{I}{I_0}$) were fitted with a Gaussian function to obtain the second moment $M_{P-P}$ (Figure S12, Supporting Information):\(^{87-89}\)

$$\frac{I(2\tau)}{I_0} = \exp \left[ - \left( \frac{M_{P-P}}{2} \right) (2\tau)^2 \right]$$  (1)

The NMR second moment reflects the strength of the nuclear magnetic dipole–dipole interaction in solids. The second moment is inversely proportional to the sum of all distances between the nuclei of the same kind and can be calculated on the basis of Van Vleck formula:\(^{90}\)

$$M_{P-P} = P \left( \frac{\mu_0}{4\pi} \right)^2 \gamma^4 S(S+1)\hbar^2 \sum_j \frac{1}{r_{ij}^6}$$  (2)

![Figure 8](image-url). Second moment of aMCP (M = Ca, Sr, Ba) as a function of composition ($x_{\text{Carbonate}}$). (CaHPO$_4$, $x_{\text{Carbonate}} = 0$) has the highest second moment because it is not completely amorphous in the absence of CaCO$_3$. The second moment of crystalline monetite is (for comparison) $4.6 \times 10^6$ rad$^2$s$^{-2}$. The addition small amounts of alkaline earth carbonates lead to a significant decrease of the second moment. The curve is discontinuous, with two steps for calcium and strontium carbonates. This may be rationalized by a chemical reaction (rather than by a physical mixture of the components) for compositions of $x_{\text{Carbonate}} < 0.3$. The curve suggests four different processes to occur: (i) Dilution of the phosphates, (ii) condensation reaction to pyrophosphates, (iii) protonation of carbonate and formation of orthophosphates and (iv) increase of the disorder.

Here, $\gamma$ is the gyromagnetic ratio of the nuclei studied, $S$ the nuclear spin, $r_{ij}$ the internuclear distance, $\mu_0$ the Bohr magneton, and $\hbar$ the Planck constant divided by $2\pi$. Due to the $r^6$ dependence, 90-95% of the first two coordination spheres contribute to the second moment.\(^{91}\)
In systems containing abundant magnetically active nuclei of different kind both homo- as well as heteronuclear dipole-dipole couplings are present. Both interactions have an influence on the Hahn echo intensity, however, esp. for amorphous systems containing solvent molecules (in this case water and cyclohexane) these contributions are difficult to evaluate. Thus, our aim is to follow the trend in the Hahn echo signal intensity and relate it with the composition of the mixture of CaHPO$_4$ and earth-alkali carbonates rather than investigating in detail the coupling contributions. Figure 8 illustrates the dependence of the second moment on the composition of the amorphous alkaline earth carbonate hydrogen phosphate. Monetite shows the highest value of the second moment after mechanochemical treatment because it is not completely amorphous. The second moment of crystalline monetite is (for comparison) with $4.6 \cdot 10^6$ rad$^2$s$^{-2}$ only slightly higher. The addition of only 5 mmol of alkaline earth carbonate lead to a significant decrease of the second moment, i.e. to a higher average phosphorus-phosphorus distance. The curve has a discontinuous shape with two steps for calcium and strontium carbonates, which can only be explained by a chemical reaction (and not merely by a physical mixture of the components) for compositions up to $x_{\text{Carbonate}} = 0.3$. For compositions with $x_{\text{Carbonate}} > 0.3$ the behavior is linear, compatible with a solid solution. The shape of the curve suggests four different processes to occur: (i) Dilution of the phosphates, (ii) condensation reaction to pyrophosphates, (iii) protonation of carbonate and formation of orthophosphates and finally (iv) increase of disorder. The curves in Figure 8 are in good agreement with the results of the $^{31}$P MAS and $^1$H-$^{31}$P TEDOR NMR experiments. We assume that due to the reaction of hydrogen phosphate to pyro- and orthophosphates the amorphization becomes more favorable.

X-ray total-scattering experiments were performed to probe the local structure of the amorphous products. GudrunX4 was used to calculate the pair distribution function (PDF) from this data. Figure 9a shows the PDFs of aCCP 0.5, aSCP 0.5 and aBCP 0.5 with seven significant peaks. The first can be assigned mainly to the phosphorus-oxygen (phosphate ion) distance at 1.52 Å (Figure 9b: Peak 1). We assume that carbon-oxygen (carbonate ion) distances contribute to this peak as well. This can be explained by the shift of the peak to lower distance values depending on the amount of the starting material calcite and thus a higher ratio of carbonate (aCCP 0.1: 1.54 Å, aCCP 0.2: 1.54 Å, aCCP 0.5: 1.52 Å, aCCP 0.6: 1.50 Å). Further, the decrease of the height of the peak with increasing carbonate amount can be explained by the higher amount of the carbonate due to its less neighbor atoms compared to phosphate. However, the effective shift is small as the peak is a superposition of both, the P-O as well as the C-O distances, the latter contributing far less (in comparison to synthetic hydrous ACC: 1.25 Å, Figure S13, Supporting Information) because of the small atomic form factor of both carbon and oxygen which
keep the contribution of the C-O pair small. Hoeher et al.\textsuperscript{92} reported a C-O distance of 1.3 Å which could also be an explanation for the merged peak. The peak height is not only a measure of the coordination number, but also the total number and product of the atomic form factors.

The most pronounced peak at 2.42 Å for aCCP 0.5 is assigned to the metal-oxygen bonds of the phosphate and carbonate ions. As expected, this peak shifts to higher distances with the larger strontium and barium ions (aSCP 0.5: 2.56 Å and aBCP: 2.78 Å) (Figure 9a: Peak 2). Note, that this peak, again, is a superposition. The contribution of the molecular O-O pairs of the phosphate ions is low (as above). Further, only for the PDF of aBCP the peaks split due to the Ba-O and Ca-O pairs (due to the mixture of BaCO\textsubscript{3} and CaHPO\textsubscript{4}).

The peak at 3.12 Å for aCCP 0.5 can be assigned most probably to the metal-phosphorus distance (Figure 9a: Peak 3). Since the peak shifts depending on metal cations, a metal is involved in these pairs (aSCP 0.5: 3.26 Å aBCP 0.5: 3.50 Å). In the next peak at 3.66 Å for aCCP 0.5, phosphorus-metal, phosphorus-phosphorus and metal-metal distances are expected to have a large contribution (in comparison to crystalline monetite, Figure 9a: Peak 4).\textsuperscript{78} The shift to lower P-P distances compared to crystalline monetite (3.91 Å) indicates changes in the phosphorous coordination sphere and most probably a stressed and distorted system. Furthermore, a variety of different interatomic distances contribute to the higher peaks (4.3 Å, 6.3 Å and 9.42 Å, Figure 9a: Peak 5,6,7), mainly metal-metal distances. The PDF fade out early and become
virtually flat at ~10 Å indicating a total lack of translational coherence. The PDF of aSCP and aBCP are in Figure S14 (supporting information).

**Dynamics of the Amorphous Alkaline Earth Carbonate Hydrogen Phosphates: X-ray photon correlation spectroscopy**

X-ray photon correlation spectroscopy (XPCS) is a powerful tool to probe the dynamics of disordered systems, giving information about the rate of structural rearrangements per unit of time (see Supporting Information for further details about data analysis). XPCS experiments yield relaxation curves from which structural relaxation times and shape factors related to the nature of the dynamics (Figure 10) can be extracted. XPCS confirms the extraordinarily low dynamics in this system, i.e. the rate of rearrangements per unit of time is very slow. Values for the structural relaxation time are one to two orders of magnitude higher than those of synthetic hydrous ACC precipitated from solution (see Table 1). Furthermore, and similar to synthetic hydrous ACC, the shape factor $\beta$ shows extremely high values. In comparison, Brownian molecular motion has a value of one. This is a strong indication for a dynamically highly strained system.

**Table 1.** Fitted parameters ($\tau$, $\beta$) obtained from the intensity auto-correlation functions measured at the start of the experiment, i.e., minimizing the effect of vacuum and related water loss. Relaxation times for the aCCP 0.2 sample cannot be determined precisely, only lower boundary can be established.

| Sample  | $\tau$ (s)  | $\beta$         |
|---------|-------------|----------------|
| aCCP 0.2| >7000       | -              |
| aCCP 0.5| 756 ± 27    | 1.69 ± 0.067   |
| aSCP 0.5| 1707 ± 133  | 1.91 ± 0.096   |
| ACC     | 572 ± 11    | 1.64 ± 0.041   |

As discussed by Koishi *et al.*, ACC shows physical aging, i.e. $\tau$ evolves over time. The same behavior was observed for ball-milled ACC (Figure 10). This can be explained for ACC by the loss of small amounts (few weight %) of water during the measurement due to an active vacuum. These minor changes in the mass of water cannot be detected by the static structure factor $S(q)$, but they can have a large impact on the dynamics. DTA/TG measurements (Figure S15, Supporting Information) showed that ball-milled ACC is almost anhydrous, with water mass losses (temperature range from RT to ~200°C) of <1 % (as opposed to 15-20 % in synthetic hydrous ACC). *Ex situ* measurements for aCCP ($x_{\text{Carbonate}} = 0.2$) and aCCP ($x_{\text{Carbonate}} = 0.5$) with and without these vacuum conditions showed a decrease in the mass loss after exposing the samples to vacuum, confirming the hypothesis for the observed aging of the dynamics under...
active vacuum (Figure S16, Supporting Information). The relatively broad band at about 3000 cm$^{-1}$ in the FTIR spectra can be assigned to the O–H stretch of the hydrogen carbonates and hydrogen phosphates ions (with the exception of $\text{CH}_3$-$\text{CH}_2$ stretching bands between 3000-2800 cm$^{-1}$). The FTIR spectra of the same samples before and after exposure to vacuum show a lower stability to vacuum of the sample aCCP ($x_{\text{Carbonate}} = 0.2$), the spectra of the aCCP ($x_{\text{Carbonate}} = 0.5$) remaining unchanged (Figure S17, Supporting Information). These complementary observations confirm the observed aging response of each of the samples, with a more pronounced aging for the aCCP ($x_{\text{Carbonate}} = 0.2$) sample (Figure 10).

Figure 10. (a) Intensity auto-correlation functions at initial experimental time for synthetic ACC prepared from solution (red triangles), aCCP for $x_{\text{Carbonate}} = 0.2$ and 0.5 and for aSCP for $x_{\text{Carbonate}} = 0.5$ at $q = 0.012$ Å$^{-1}$ (d = 50 nm). (b) Evolution of the relaxation times $\tau$ as a function of the experimental time for aCCP for $x_{\text{Carbonate}} = 0.2$ and 0.5 and for aSCP for $x_{\text{Carbonate}} = 0.5$.

DISCUSSION
Reactions and Mechanisms
The $^1\text{H}$-$^{31}\text{P}$ TEDOR spectrum (see Figure 4a) reveals that only the environment of one phosphorous atom in pure CaHPO$_4$ is significantly affected (loss of the $^{31}\text{P}$ resonance at -1.6 ppm) during the ball milling process, whereas the other resonance signal is only broadened. As a result of a condensation reaction, a signal at -5.5 ppm (typical for pyrophosphates) appears in the $^1\text{H}$-$^{31}\text{P}$ TEDOR spectrum. Based on the structural and spectroscopy data the following scenario may be derived for the sequence of events in the ball-milling reaction between CaHPO$_4$ and MCO$_3$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) for different ratios $x_{\text{Carbonate}}$ (Figure 11).

The first - and fast - reaction is a proton transfer resulting in a local charge disorder. This forces the system to reorganize. The carbonate anions act in this step as proton acceptors (bases), the hydrogen phosphates act as proton donors (acids). The formation of hydrogen carbonates and orthophosphates ($i.e.$ higher Coulomb energy, the tetrahedral unit can fill space more efficiently) appears to be the driving force of the reaction.
This rearrangement quickly reaches mechanochemical equilibrium. There are two possible reasons for the observed incomplete reaction to hydrogen carbonate. (a) Only the disordered protons statistically distributed between the two positions of the phosphate unit are involved in the reaction, whereas those protons bound covalently to one phosphate group do not react (activation barrier too high). (b) The newly formed structures may be stabilized by strong hydrogen bonds. The proton transfer reaction leads to local charge disbalances which can be compensated by cation motion. The strong hydrogen-bonded network hinders cation motion (the energy of the ball mill is not sufficient to induce cation “jumps”). The result is a highly strained system. Additionally, a second -and slow - condensation reaction to pyrophosphates occurs, which competes with proton transfer. Although the energy balance of pyrophosphate formation from two equivalents of hydrogen phosphate (\(2\text{HPO}_4^{2-} \rightarrow \text{P}_2\text{O}_7^{4-} + \text{H}_2\text{O}\)) may not be strongly disfavored, the kinetics is slow.\(^{94}\)

It has been suggested that crystalline monetite has an ordered low temperature phase (space group \(P1\)) and a disordered high temperature phase (space group \(P\overline{1}\)).\(^{78}\) A second order phase transition (order/disorder transformation) occurs between 273 and 287 K, where only H positions are significantly affected. Therefore, the disordered phase is present at room temperature with small amounts of the ordered phase. We speculate that in aCCP (\(x_{\text{Carbonate}} = 0.2\)) H atoms undergo an order/disorder transformation under vacuum conditions. Since this phase transition
only affects protons, no difference can be detected in the structure factor. Furthermore, the proportion of monetite in the aCCP \((x_{\text{carbonate}} = 0.2)\) sample is significantly higher.

No pyrophosphates are formed at higher carbonate contents \((x(\text{carbonate}) > 0.2)\). Possible reasons are: (i) At higher dilution the mean distance between two \(\text{HPO}_4^{2-}\) groups (and therefore contact probability and time) decreases. Therefore, it is much less likely that two hydrogen phosphate ions will be able to stay in contact long enough and react. (ii) The formation of orthophosphates \((\text{PO}_4^{3-})\) in the acid-base reaction between \(\text{CO}_3^{2-}\) and \(\text{HPO}_4^{2-}\) preceding pyrophosphate condensation leads to an even stronger dilution effect. (iii) The highly-strained system leads to such a large energy barrier that any reaction is suppressed.

Conclusions

In conclusion, we have explored the formation of amorphous anhydrous alkaline earth carbonates in a planetary ball mill. The phosphate anions do not simply substitute the carbonate anions, they undergo a mechanochemical acid/base and condensation reaction. The metastable amorphous \(\text{Ca(HCO}_3\text{)}_2/\text{ACC}\) product is stabilized through the formation of a highly strained calcium phosphate network that hinders recrystallization kinetically. The minimum concentration of phosphate “impurities” (50%) for the successful amorphization of calcite was determined by PXRD, \(^{31}\text{P}\) and \(^1\text{H}\) MAS-NMR and electron microscopy. Since diffraction is not suited for studying amorphous solids, the intermediates of the ball-milling reaction were studied by local probes using vibrational spectroscopy, double resonance \(^1\text{H}\)\(^{31}\text{P}\) TEDOR and \(^1\text{H}\)\(^{13}\text{C}\) HETCOR spectroscopy, which are highly sensitive to symmetry changes of the local environment. Mechanistically, \(\text{CO}_3^{2-}\) anions are protonated \textit{via} an acid-base process by hydrogen phosphate groups in the first - and fast - reaction step of the ball-milling reaction. The concomitant formation of unprecedented hydrogen carbonate \((\text{HCO}_3^-)\) anions and orthophosphate groups are the driving force of the reaction, because the phosphate group has a higher Coulomb energy and the tetrahedral \(\text{PO}_4^{3-}\) unit can fill space more efficiently. In a competing second - and slow - reaction step, pyrophosphate anions are formed in a condensation reaction. No pyrophosphates are formed at higher carbonate contents. The structure and dynamics of the amorphous ball-milled products were studied by vibrational spectroscopy, \(^{31}\text{P}\) - static spin echo experiments, pair distribution analysis and X-ray photon correlation spectroscopy, which show the evolution of the phosphorus environment and the strength of the hydrogen bonded network.

Our findings aid not only in the understanding of the mechanochemical amorphization of calcium carbonate and the effect of impurities for the stabilization of the amorphous phase. They shed light on elementary reaction steps during ball-milling reactions which are ubiquitous
in pharmaceutical or chemical industry, although a mechanistic understanding required for their development is still lacking. The ball-milling process allowed the synthesis of a new ACC defect variant containing the unique hydrogen carbonate anion that may be stable enough to act as an ion buffer for bone regeneration, but still have sufficient reactivity in aqueous conditions for the transformation to hydroxyapatite (HA).

**METHODS**

**Materials.** Calcite (98%, Socal 31, Solvay), monetite (CaHPO₄) (>98.5%, anhydrous, Sigma-Aldrich), SrCO₃ (99+%, chempur), BaCO₃ (99+, Sigma-Aldrich), β-Tricalcium phosphate (96+, Sigma-Aldrich), Strontium chloride (anhydrous, 99.5%, Alfa Aesar), Calcium carbonate¹³C (99 atom % ¹³C, isotec), Sodium carbonate (¹³C 99%, deutero), Barium carbonate (¹³C 98%, deutero), cyclohexane (Analytical reagent grade, Fisher Chemicals), ethanol (absolute 99.8+, Fisher Chemicals) and milliQ deionized water.

*Synthesis of Calcium Pyrophosphate.* Loaded in a corundum jar, monetite (7.35 mmol) was heated to 800 °C in a horizontal tube furnace oven for 8 h (5 °C/min). Afterward, the resulting product was grinded.

*Synthesis of ¹³C Enriched SrCO₃.* SrCl₂ (2.1 mmol) was dissolved in 50 mL of deionized water. The solution was degassed with an argon stream for 30 minutes. Under argon atmosphere and vigorous stirring ¹³C enriched Na₂CO₃ (2 mmol) was added to the solution. The reaction solution was stirred for one hour. Afterward, the precipitate was separated by centrifugation and washed with water and ethanol. The product was dried in vacuo.

*Synthesis of Amorphous Earth Alkaline Metal Carbonate Hydrogenphosphates.* Monetite (0.136 g, 1 mmol) was treated with different amounts of earth alkali metal carbonates (e.g. aCCP 0.5: 0.100 g, 1 mmol) in a planetary ball mill (Pulverisette 7 Classic, Fritsch). The starting materials and 10 mL of cyclohexane were transferred together with 3.65 grams of grinding balls (about 1100 balls, 1 mm diameter, ZrO₂) into ZrO₂ grinding jars. The mixture was milled for certain times at 720 rpm. To avoid overheating, alternate 10 minutes of grinding and then a 10 minute rest phase was used. Therefore, 480 min of ball milling results in 950 minutes of reaction time. Afterward, the cyclohexane was removed with a pipette. The product was dispersed in ethanol and separated from the grinding balls by decanting. The product was isolated by centrifugation and dried in vacuo.
Characterization

X-ray Powder Diffraction. X-ray diffractograms were recorded with a STOE Stadi P equipped with a Mythen 1k detector using Mo Ka1 radiation (λ=0.7093 Å). The dry samples were prepared between polyvinyl acetate foils in perfluoroether (Fomblin Y, Aldrich). The measurements were performed in the 2θ range from 2° to 45° with a step size of 0.015° (continuous scan, 150 s/deg). Crystalline phases were identified according to the PDF-2 database using Bruker AXS.

ATR-FTIR Spectroscopy. The attenuated total reflection (ATR) FTIR spectra were recorded on a Nicolet iS10 spectrometer (Thermo scientific) using a frequency range from 650 to 4000 cm^-1 with a resolution of 1.4 cm^-1 per data point.

Solid-State NMR Spectroscopy. All solid state NMR spectra were recorded on a Bruker Advance 400 DSX NMR spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany operated by Topspin 1.3, 2007, patchlevel 8) at a 1H frequency of 399.87 MHz, 13C frequency of 100.55 MHz and 31P frequency of 161.87 MHz. A commercial 3 channel 4 mm Bruker probe head at 10 kHz magic angle spinning (MAS) was used for all experiments. The 1H NMR spectra and 1H background corrected spectra were recorded averaging 32 transients with 8 s recycle delay. For all solid-state 13C cross-polarization (CP) magic angle spinning (MAS) NMR experiments, an initial 90° pulse with 4.0 µs length and 5 s recycle delay were used. A ramped CP pulse (from 64 to 100%) with duration of 20 µs, 50 µs, 100 µs, 200 µs, 500 µs, 1 ms, 2 ms, 3 ms, 5 ms and 7 ms was used for recording the CP build-up curves. Two pulse phase modulation (TPPM) 1H decoupling scheme was used while acquiring the 13C signal. 512 transients were averaged for the CP experiments. The spectra were baseline-corrected and a broadening of 30 Hz was applied. Quantitative 13C single pulse excitation experiments allowing full relaxation have been recorded averaging 16 transients with a recycle delay of 2200 s and TPPM heteronuclear decoupling. The spectrum was background corrected and a broadening of 30 Hz was applied. The 1H-13C heteronuclear correlation (HETCOR) 2D NMR spectra were acquired using 1H-13C magnetization transfer with contact times of 50 and 2000 µs and 256 transients/t1. The data points recorded were 1 k (t1) and 96 or 128 (t2) and zero-filled to 4 k (t1) and 256 (t2) before the 2D Fourier transformation. The other parameters were identical to those for the 1D CP NMR experiments. Single pulse excitation 31P experiments were recorded using 60 s recycle delay averaging 16 scans under TPPM heteronuclear decoupling while acquiring the NMR signal. For all 31P cross-polarization (CP) magic angle spinning (MAS) NMR experiments, an initial 90° pulse with 4.0 µs length and 5 s recycle delay were used. A ramped CP pulse (from 64 to 100%) with duration of 20 µs, 50 µs, 100 µs, 250 µs, 500 µs, 1 ms, 2 ms, 3 ms, 4 ms and
5 ms was used for recording the CP build-up curves. Two pulse phase modulation (TPPM) $^1$H decoupling scheme was used while acquiring the $^{31}$P signal. Transients of 64 were averaged for the CP experiments. The spectra were baseline-corrected and a broadening of 30 Hz was applied. The $^1$H-$^{31}$P heteronuclear correlation (HETCOR) 2D NMR spectra were acquired using $^1$H-$^{31}$P magnetization transfer with contact times of 20 and 2000 μs and 64 transients/t1. The data points recorded were 2 k (t1) and 128 (t2) and zero-filled to 4 k (t1) and 256 (t2) before the 2D Fourier transformation. The other experimental parameters were identical to those for the 1D CP NMR experiments. All $^1$H-$^{31}$P transferred echo double resonance (TEDOR) experiments were recorded averaging 512 scans using TPPM heteronuclear decoupling while acquiring the NMR signal. 1, 2, 4, 6, 8 and 10 full rotor periods ($\tau_R$) were used for recoupling the heteronuclear dipolar couplings corresponding resp. to 40 μs, 80 μs, 160 μs, 240 μs, 320 μs and 400 μs recoupling time. A broadening of 30 Hz and background correction were applied. All static $^{31}$P Hahn echo experiments were recorded with echo delays of 30, 40, 50, 60, 70, 80, 90 and 100 μs. A broadening of 150 Hz and background correction were applied. The spectra were referenced to external adamantane at 1.63 ppm ($^1$H) and 38.5 ppm ($^{13}$C) and to external NH$_4$HPO$_3$ at 0.9 ppm ($^{31}$P). Spectral deconvolution and fitting the intensity decrease in the spin-echo experiments were performed using self-written MatLab scripts (version 2017b).

**Thermal Analysis.** Coupled thermogravimetry-differential thermal analysis (TG-DTA) was carried out at a Netzsch STA 449 F3 Jupiter device. About 10 mg of the sample was heated in an alumina cup in argon atmosphere from 50 to 900 °C at a heating rate of 10 K/min.

**Transmission Electron Microscopy (TEM).** Samples were prepared by drop-casting 20 μL of the respective sample dispersion on 400 mesh carbon copper grids (Plano GmbH, Wetzlar, Germany) and measured with a Technai Spirit G2 at 120 kV acceleration voltage, equipped with a standard 4K CCD camera.

**Total Scattering.** Total scattering measurements of amorphous earth alkali metal carbonate hydrogen phosphates were performed at beamline P02.1 at Petra III, DESY, Germany using an X-ray energy of 60 keV ($\lambda = 0.20724$ Å). All samples were prepared in a 0.5 mm borosilicate capillary and measured in transmission mode with a 2D Perkin Elmer area detector with 2048 x 2048 pixels. The exposure time for each sample was 15 min. The resulted 2D images were integrated by using the program DAWNscience. The analysis of the atomic pair distribution function (PDF) was performed utilizing the Gudrun X software using an empty capillary (0.5 mm) for background subtraction with $Q_{max} = 24$ Å$^{-1}$.

**X-ray Photon Correlation Spectroscopy.** XPCS experiments were performed at the beam line P10 of PETRA III at DESY synchrotron radiation source at Hamburg (Germany), using an...
incident energy of Xrays of 15 keV. Samples were prepared by loading the powders into 1 mm diameter holes drilled in ~100 µm thickness Al foils. The hydrated, plastic texture of the sample results in a homogeneous filling of all the space. The ~100 µm thickness ensure a transmission of ~9% at 15 keV. Measurements were performed under active vacuum (of ∼10⁻³ mbar), covering a 0.007-0.013 Å⁻¹ q range (small-angle configuration) and with a beam size of 15×15 µm. Series of speckles patterns were collected in transmission geometry by a CCD detector (Andor, 13 µm pixel size). In order to avoid radiation damage of the sample, a delay time (waiting time between two consecutive frames) of 1.9 s was set after each 0.1 s acquisition. Series of acquisitions were taken for at least 2000 frames, covering relaxation times of several hours. These series of measurements were taken by moving the sample by at least twice the beamsize to avoid exposing the same spot for long time, preventing radiation damage and beam induced dynamics. All measurements were carried out at T = 25°C. Details about the XPCS data analysis are given in the Supporting Information.

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Author contributions
N. K. carried out the experiments, L. N. initiated the study, L. N., M. D. and W. T. conceived the experiments, I. L., C. L., M. P. A., A. F.-M., A. D., B. B. and S. L. contributed to methods, N. K. wrote the manuscript with contributions of L.N., F. N., M. P. A., A. F.-M., A. D., and W. T.

Additional Information
The data that support the plots within this paper and other findings of this study are available from the corresponding authors on request.
Table S1, quantification of the ball-milled precursors; Table 2, shifts of the carbonate vibration bands; Table S3, chemical shifts of TEDOR signals; Figure S1, TEM images of aSCP and aBCP 0.5; Figure S2, XRPD patterns of reference samples; Figure S3, Best Fits of SPE NMR and FTIR spectra, Figure S4, results of thermogravimetric (DTA and TGA) studies, Figure S5, ex situ TGA plots; Figure S6, ex situ FTIR plots

Competing Interests

The authors declare no competing financial interest.

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Monitoring a Mechanochemical Reaction Reveals the Formation of Stable Alkaline Earth (Ca, Sr, Ba) Hydrogen Carbonates Encapsulated by an Amorphous Phase

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Table S1. Quantification of ball-milled precursors by FTIR
Table S2. Positions of CO$_3^{2-}$ bands in amorphous calcium carbonate/calcium hydrogen phosphate (aCCP), amorphous strontium carbonate/calcium hydrogen phosphate (aSCP) and amorphous barium carbonate/calcium hydrogen phosphate (aBCP).
Figure S1. $^1$H NMR spectra of aCCP 0.2 with and without drying in an vacuum oven at 40°C for 8 h.
Figure S2. Powder diffractograms of the ball-milled starting materials (a, left) and a mixture of CaCO$_3$ (calcite) and tricalcium phosphate (b, right).
Figure S3. TEM images and associated diffraction patterns for (a) aSCP (0.5) and (b) aBCP (0.5).
Figure S4. $^{31}$P-MAS-ssNMR spectra of aCCP 0.5 as a function of milling time.
Figure S5. $^{31}$P-MAS-ssNMR spectra of (a) SrCO$_3$ 0.2, (b) SrCO$_3$ 0.5, (c) BaCO$_3$ 0.2 and (d) BaCO$_3$ 0.5 as a function of milling time.
Figure S6. $^{31}$P signals of ball-milled amorphous strontium (a) and barium (b) carbonate phosphates. Signal maxima of ball-milled amorphous strontium (b) and barium (d) carbonate phosphates as a function of the carbonate mole fraction $x_{\text{Carbonate}}$. 
Figure S7. TEDOR spectra of (a) amorphous aSCP ($x_{\text{Carbonate}} = 0.2$) and (b) amorphous aSCP ($x_{\text{Carbonate}} = 0.5$) as a function of the rotor period recorded at 1, 2, 4, and 6 rotor periods (40, 80, 160 and 240 μs recoupling time respectively), with the respective $^{31}$P single pulse excitation (SPE) spectra.

Figure S8. TEDOR spectra of (a) amorphous aBCP ($x_{\text{Carbonate}} = 0.2$) and (b) amorphous aBCP ($x_{\text{Carbonate}} = 0.5$) as a function of the rotor period recorded at 1, 2, 4, and 6 rotor periods (40, 80, 160 and 240 μs recoupling time respectively), with the respective $^{31}$P single pulse excitation (SPE) spectra.

Figure S9. $^1$H-$^1^3$C HETCOR spectra of aSCP ($x_{\text{Carbonate}} = 0.5$) recorded with contact times of 50 and 2000 μs and respective projections, in particular (a) $^1$H SPE spectrum, (b) projection at 168 ppm with contact times of 50 μs, (c) projection at 162 ppm with contact times of 50 μs, (d) projection at 168 ppm with contact times of 2 ms, (e) projection at 162 ppm with contact times of 2 ms.

Figure S10. $^1$H-$^1^3$C HETCOR spectra of aBCP ($x_{\text{Carbonate}} = 0.5$) recorded with contact times of 50 and 2000 μs and respective projections, in particular (a) $^1$H SPE spectrum, (b) projection at 168 ppm with contact times of 50 μs, (c) projection at 162 ppm with contact times of 50 μs, (d) projection at 168 ppm with contact times of 2 ms, (e) projection at 162 ppm with contact times of 2 ms.

Figure S11. Comparison of the best fits (blue line) of the FTIR (left) and $^{13}$C SPE (right) spectra. The ratio of the areas of the bimodal pseudo Voigt fits correspond to the carbonate to hydrogen carbonate ratio (top: aCCP, middle: aSCP, bottom: aBCP).

Figure S12. $^{31}$P spin echo decay of aCCP 0.5 (left) with the corresponding static Hahn echo delay spectra (right). The solid line shows the best fit using the Gaussian function (equation 1).

Figure S13. Pair distribution function of hydrous ACC (from previous study).

Figure S14. Pair distribution function of aSCP 0.2 (red) and aBCP 0.2 (blue). The PDFs show clear broad peaks beyond 10 Å. This proves a higher crystallinity in comparison to the aCCP samples.

Thermal analysis and Figure S15. DTA and TGA traces for aXCP (top: X = Ca, middle; X = Sr, bottom: X = Ba. $x_{\text{CaCO}_3} = 0.2$ (left side). $x_{\text{CaCO}_3} = 0.2$ (right side).

Figure S16. TGA traces under vacuum (blue line) and normal pressure (black line) for aCCP (0.2) (a, left) and aCCP 0.5 (b, right). The mass loss for aCCP 0.2 occurs at lower temperature ($\Delta T = 9^\circ$C) under vacuum conditions.

Figure S17. Vibrational region of the generalized VDOS for water at 300 K in aCCP for (left) $x_{\text{Carbonate}} = 0.2$ and (right) $x_{\text{Carbonate}} = 0.5$. The intensity is normalized to the unity within the 2500–3500 cm$^{-1}$ range. Black lines represent data for aCCP in air, blue lines for aCCP under vacuum conditions.
Table S3. Quantification of ball-milled precursors by FTIR.

| Sample          | Fraction of crystalline phase |
|-----------------|-------------------------------|
| BM-calcite      | 29.1 %                        |
| BM-monetite     | 19.8 %                        |

The quantification is based on the FTIR data. For ball-milled calcite the band of the $\nu_2$ vibration mode was fitted using a bimodal pseudo Voigt function. The area ratio of the function is shown in Table S1 for the amorphous and crystalline phase. To quantify portion of ball-milled monetite the band of the $\nu_{\text{P-O}}$ vibration mode at $\approx 1000$ cm$^{-1}$ was fitted for the crystalline, ball-milled and amorphous phases. The full width at half maximum (FWHM) of the crystalline phase was set to “100% crystalline” and the FWHM of the amorphous phase to 0%. The ratios are in good agreement with the XRPD patterns (Figure S8).
Table S4. Positions of CO$_3^{2-}$ bands in amorphous calcium carbonate/calcium hydrogen phosphate (aCCP), amorphous strontium carbonate/calcium hydrogen phosphate (aSCP) and amorphous barium carbonate/calcium hydrogen phosphate (aBCP).

| Sample  | $\nu_2$ | $\nu_3$          | $\nu_4$          |
|---------|---------|------------------|------------------|
| aCCP 0.5| 862     | 1410, 1493       | 693, 728         |
| aSCP 0.5| 864     | 1406, 1483       | 689, 724         |
| aBCP 0.5| 865     | 1397, 1470       | 683, 717         |

For the $\nu_2$ vibration mode, the band are shifted to higher wave numbers for increasing cation mass. Soft Pearson acids lead to weaker interactions with the oxygen atoms of the carbonate ion. Therefore, the carbon atom polarizes a higher electron density on the oxygen atoms, and the out-of-plane vibration appears at higher frequency. The $\nu_3$ and $\nu_4$ vibration modes are shifted to lower wave numbers with increasing cation mass. Sr$^{2+}$ and Ba$^{2+}$ ions polarize the electron density around the carbonate oxygen atoms less strongly. As a result, the stretching modes are shifted to lower frequencies.

Figure S1. $^1$H NMR spectra of aCCP 0.2 with and without drying in an vacuum oven at 40°C for 8 h.
Figure S2. Powder diffractograms of the ball-milled starting materials (a, left) and a mixture of CaCO$_3$ (calcite) and tricalcium phosphate (b, right).

Figure S3. TEM images and associated diffraction patterns for (a) aSCP (0.5) and (b) aBCP (0.5).
Figure S4. $^{31}$P-MAS-ssNMR spectra of aCCP 0.5 as a function of milling time.
Figure S5. $^{31}$P-MAS-ssNMR spectra of (a) SrCO$_3$ 0.2, (b) SrCO$_3$ 0.5, (c) BaCO$_3$ 0.2 and (d) BaCO$_3$ 0.5 as a function of milling time.
**Figure S6.** $^{31}$P signals of ball-milled amorphous strontium (a) and barium (b) carbonate phosphates. Signal maxima of ball-milled amorphous strontium (b) and barium (d) carbonate phosphates as a function of the carbonate mole fraction $x_{\text{Carbonate}}$. 
Figure S7. TEDOR spectra of (a) amorphous aSCP ($x_{\text{Carbonate}} = 0.2$) and (b) amorphous aSCP ($x_{\text{Carbonate}} = 0.5$) as a function of the rotor period recorded at 1, 2, 4, and 6 rotor periods (40, 80, 160 and 240 $\mu$s recoupling time respectively), with the respective $^{31}\text{P}$ single pulse excitation (SPE) spectra.

Figure S8. TEDOR spectra of (a) amorphous aBCP ($x_{\text{Carbonate}} = 0.2$) and (b) amorphous aBCP ($x_{\text{Carbonate}} = 0.5$) as a function of the rotor period recorded at 1, 2, 4, and 6 rotor periods (40, 80, 160 and 240 $\mu$s recoupling time respectively), with the respective $^{31}\text{P}$ single pulse excitation (SPE) spectra.
Figure S9. $^1$H-$^{13}$C HETCOR spectra of aSCP ($x_{\text{Carbonate}} = 0.5$) recorded with contact times of 50 and 2000 μs and respective projections, in particular (a) $^1$H SPE spectrum, (b) projection at 168 ppm with contact times of 50 μs, (c) projection at 162 ppm with contact times of 50 μs, (d) projection at 168 ppm with contact times of 2 ms, (e) projection at 162 ppm with contact times of 2 ms.
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Figure S3. Comparison of the best fits (blue line) of the FTIR (left) and $^{13}$C SPE (right) spectra. The ratio of the areas of the bimodal pseudo Voigt fits correspond to the carbonate to hydrogen carbonate ratio (top: aCCP, middle: aSCP, bottom: aBCP).
**Figure S4.** $^{31}$P spin echo decay of aCCP 0.5 (left) with the corresponding static Hahn echo delay spectra (right). The solid line shows the best fit using the Gaussian function (equation 1).
Figure S5. Pair distribution function of hydrous ACC (from previous study).

Figure S64. Pair distribution function of aSCP 0.2 (red) and aBCP 0.2 (blue). The PDFs show clear broad peaks beyond 10 Å. This proves a higher crystallinity in comparison to the aCCP samples.
**Thermogravimetric and differential thermal analysis**

DTA and TGA measurements were performed on samples of aXCP 0.2 and 0.5. The first endothermic effect at $\approx 91^\circ$C is caused by surface-bound solvents, e.g. cyclohexane, ethanol and water. This is supported by the observed mass changes ($<1\%$). The second endothermic effect at about 220 °C (depending on the cation) shows the evaporation of entrapped solvent (specifically cyclohexane), and it is followed with a significant weight loss. We assume that the solvents are encapsulated in cavities between grain boundaries of the amorphous phase. The thermal energy increases the diffusion. This can lead to cracking of grain boundaries and a rapid release of the gaseous solvent. In samples with a mol fraction $x = 0.2$ this occurs at higher temperatures for the heavier alkaline earth cations. As shown by Zhang et al., hydrogen bonded hydroxyl groups have a large impact on the thermal stability of phases. Therefore, we assume that due to the higher hydrogen carbonate content (aCCP<aSCP<aBCP, Figure S10) more hydrogen bonded hydroxyl groups are present, which leads to the observed higher thermal stability. A small endothermic effect occurs at $\sim 500^\circ$C. Thermally induced crystallization to calcite, tricalcium phosphate and several polyphosphates occurs at $\sim 600^\circ$C. The mass loss at higher temperature is due to decarboxylation of calcium carbonate.
Figure S15. DTA and TGA traces for aXCP (top: X = Ca, middle: X = Sr, bottom: X = Ba. $\chi_{\text{CaCO}_3} = 0.2$ (left side), $\chi_{\text{CaCO}_3} = 0.2$ (right side).
Thermogravimetric analysis of samples subject to vacuum

*Ex situ* TGA measurements were performed to investigate the vacuum stability of the samples (Figure S14). In accordance with the XPCS data, the aCCP (0.2) sample shows a significant change under vacuum. This is another indication that hydroxyl groups (with hydrogen bonds) are either broken or reorganized. In contrast, the water loss of sample aCCP (0.5) is less affected by the vacuum treatment. This is consistent with the less extent of sample aging observed in XPCS experiments.

**Figure S76.** TGA traces under vacuum (blue line) and normal pressure (black line) for aCCP (0.2) (a, left) and aCCP 0.5 (b, right). The mass loss for aCCP 0.2 occurs at lower temperature ($\Delta T = 9^\circ$C) under vacuum conditions.
Figure S87. Vibrational region of the generalized VDOS for water at 300 K in aCCP for (left) $x_{\text{Carbonate}} = 0.2$ and (right) $x_{\text{Carbonate}} = 0.5$. The intensity is normalized to the unity within the 2500–3500 cm$^{-1}$ range. Black lines represent data for aCCP in air, blue lines for aCCP under vacuum conditions.
X-ray Photon Correlation Spectroscopy.

A high-flux coherent X-ray beam is used to detect time-dependent intensity fluctuations of the “speckle pattern”, which directly relates to local dynamics, e.g. rearrangement of particles and density fluctuations in the probed volume.\(^2\) The spatial size of the dynamics depends on the experimental \(q\) value, the scattering vector. The \(q\)-dependent intensity fluctuations are evaluated with the following autocorrelation function, which is a measure of the similarity of the intensity with itself after a lag time \(\Delta t\).

\[
g^{(2)}(\Delta t, q) = \frac{\langle I(t,q)I(t+\Delta t,q)\rangle}{\langle I(t,q)\rangle^2} \tag{3}
\]

In order to obtain information about the dynamics of the system, the autocorrelation curve is fitted with the Kohlrausch-Williams-Watts model.

\[
g^{(2)}(t) = 1 + c \cdot \exp\left(-2\left(\frac{t}{\tau}\right)^\beta\right) \tag{4}
\]

The parameter \(c\) is the setup-dependent contrast, \(\tau\) is the structural relaxation time and \(\beta\) is the shape factor of the curve.

References

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