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Isotope chemistry to trace carbon mineralization in construction materials

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Abstract

This contribution presents an overview of the current literature and application potential of carbon isotope analysis in cementitious systems. Stable carbon isotope ratios ($^{13}C/^{12}C$) offer powerful insights for tracking carbonation processes, especially in the context of carbonation hardening and the characterization of recycled concrete fines. Isotope methods can help determine the extent of carbonation and to distinguish between naturally formed carbonates and those resulting from enhanced carbonation by fossil CO_2. This approach offers a valuable tool in circular construction strategies.
Alongside published studies, we highlight recent experimental work that further demonstrates potential applications of this method. However, to fully exploit carbon isotopes as a diagnostic tool, several questions remain open. In particular, isotope fractionation during carbonation is not yet fully understood. Key factors of influence include temperature, pH, relative humidity, porosity of the carbonated material and the isotope composition of the CO_2 source. Moreover, differences between aqueous and gaseous carbonation must be evaluated, as they may result in different isotope fractionation. Understanding these fractionation mechanisms is essential to establish robust interpretation frameworks for isotope-based approaches in cement and concrete research and applications.

Keywords: Isotopes, Carbon mineralization, Recarbonation, Construction materials, CO_2 tracing.

1 Introduction

Permanent carbon storage and carbon dioxide removal (CDR) strategies are important levers to reach global carbon neutrality [1]. CDR is considered critical in off-setting residual carbon emissions, e.g., from hard-to-abate industrial sources such as cement, lime, steel or chemicals production. Among CDR strategies, carbon mineralization or mineral carbonation offers the advantage of storing CO_2 as calcium and magnesium carbonates. These have a long-term stability up to hundreds of millions of years under a wide range of environmental conditions [2]. Moreover, in contrast to most other CDR methods such as afforestation, soil management or biochemical production, mineral carbonation is not intrinsically limited by land surface availability or CO_2 release by (hydro)carbon oxidation [3].

Carbon mineralization occurs in natural systems where CO_2 reacts with Ca-Mg bearing rocks in aqueous environments [4]. The process is inorganic, yet it is often mediated and exploited for structural and functional support as skeletons by a wide range of organisms (e.g., plankton, bivalves, corals) [5]. Humans have also benefitted from carbonate-rich limestone for shelter. From caves to cathedrals, from lime to cement, limestone has played a primordial role in construction. The use of mineral carbonation in construction can be dated back to prehistoric times when lime was burned and slaked for use as binder in mortars and renders. Here, hardening occurs by carbonation of slaked lime ($Ca(OH)_2$) with CO_2 from the air [6]. Today, mineral carbonation technologies exist as efficient means to produce building materials while permanently storing CO_2 that can be captured from emission point sources, i.e., directly at the carbon emitter industries or from atmospheric air, a process referred to as direct air capture (DAC). Over the last decade, a wide range of common construction materials such as aggregates and supplementary cementitious materials as well as building products such as

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pre-cast concrete elements (blocks, bricks, pavers) have been developed based on enhanced or accelerated mineral carbonation [7, 8, 9]

While the use of carbonation in production processes is accelerated by applying higher CO_2 concentrations, pressures and/or temperatures, natural carbonation of concrete and other cementitious materials is a slow process. Also referred to as "recarbonation", natural carbonation of concrete takes place over years to decades during and after service life and partially resorbs the CO_2 that was emitted by calcination of limestone during cement production [10]. The rate and extent of recarbonation of various cementitious products depends on many factors, ranging from concrete formulation and use over exposure conditions to recycling practices. This renders estimations of total recarbonation fraught with uncertainty [11]. Nonetheless, the large amount of cement used in products to date, arguably renders recarbonation a sizeable global CO_2 sink which is not yet fully accounted for in climate models and mitigation plans [12 – 16].

Resonating with the global challenge of climate change mitigation, mineral carbonation and recarbonation of cementitious materials receive considerable attention from academic and industrial research. This is reflected within the RILEM community by the present activity of two technical committees (TC). These are known as TC 309-MCP "Mineral Carbonation Products" and TC CUC "CO_2 Uptake by Concrete during and after service life". A common challenge identified by both TCs relates to the measurement of CO_2 uptake of carbonated materials during defined life cycle stages (e.g., raw materials, production, service life, end-of-life). The work of these committees serves to address knowledge gaps and to better understand mineral carbonation processes. This knowledge gain also translates into economic value as part of carbon emission allowance trading and carbon credit schemes. As CO_2 pricing depends strongly on the CO_2 source and the fixation process, distinguishing between CO_2 uptake from industrial emissions or from direct air capture (DAC) is of particular interest for carbon market credibility and regulation [17].

This letter aims to scope the role of isotope chemistry in advancing research on mineral carbonation. It also underscores potential applications in carbon tracing and certification. First, some fundamentals of carbonate isotope chemistry are introduced. Based on these, we explore key opportunities for carbonate isotope chemistry as well as unresolved knowledge gaps within three major application areas related to mineral carbonation and recarbonation, i.e., mineral carbonation research and technology development, differentiation of fossil versus recent carbonates in products, and distinguishing carbonates from different CO_2 sources.

2 Background

Isotopes of an element differ in the number of neutrons in their nucleus and therefore possess different atomic masses even though they are otherwise chemically identical. Some isotopes are stable, while others decay over time and are radioactive. Due to the isotopic mass difference, physicochemical and biological processes commonly result in fractionation, i.e., isotopes are distributed differently by their mass across gaseous, liquid, and solid phases.

The use of isotope ratios for tracing environmental processes is well established. Carbonate isotope (geo)chemistry makes use of variations in isotopic abundance, expressed as ratios of carbon and oxygen isotopes in carbonate minerals such as calcite, aragonite or dolomite. Typical applications include studies of past climates, global carbon cycling or carbonate reservoir characterisation [18, 19].

Common stable carbon isotopes are ^{12}C with a global abundance of 98.93% and ^{13}C with an abundance of 1.07%. Stable isotope ratios are usually expressed by a delta notation (δ). The δ-value represents the deviation of the isotope ratio in a sample relative to a standard material:

$$\delta = \frac{R_{Sample}}{R_{Standard}} - 1 \quad (1)$$

where δ is the isotope value ($\delta^{13}C$ or $\delta^{18}O$) in per mille (‰) and R represents the ratio of the heavy to the light isotope ($^{13}C/^{12}C$ or $^{18}O/^{16}O$). For carbonates the standard material is Vienna Peedee Belemnite (V-PDB) [20, 21].

The isotope values of dissolved carbonate species in aqueous environments e.g., water, rapidly equilibrate with soil or atmospheric CO_2 as a function of pH and temperature. Processes such as dissolution of gaseous CO_2 in water or precipitation of solid phase carbonate from a solution causes a re-distribution of the $^{13}C/^{12}C$ isotope ratios. This shift or change of δ-values between phase transitions is referred to as "fractionation" in isotope terminology. Fractionation is quantitatively described by the temperature dependend "fractionation factor" for which different definitions exist in the literature with the exact usage and expression often being discipline dependend [22]. Carbonates precipitating under equilibrium conditions will have isotope values that are controlled by well understood physicochemical reactions and fractionation factors have been experimentally derived for a wide range of conditions, temperatures, and materials. This is referred to as "equilibrium fractionation". In many cases, δ-values of phases can be calculated and predicted using established fractionation factors from the literature. This, however requires that the system and the reaction of interest follows the rules of equilibrium fractionation. In nature, this is for example in use in paleo temperature reconstructions using the carbon and oxygen isotope ratios of marine calcite fossils, speleothems or cellulose extracted from tree rings.

Fractionation is further controlled by kinetic (i.e. nonequilibrium) differences of the different isotopes. In general, light isotopes (e.g., ^{12}C) usually react faster than heavy isotopes (^{13}C) in kinetic reactions. This is for example of importance in biologically controlled reactions such as CO_2 uptake by photosynthesis or degradation of contaminants by microbes. This is referred to as "kinetic fractionation" and cannot always be predicted from well-established fractionation factors, temperature and pH as mentioned above for equilibrium reactions. In some cases, the two processes are also shifting isotope values in the opposite direction. In addition to the two aforementioned fractionation types, isotope values can also be changed by

"non-mass dependend" (NMD) fractionation, something that is for example important in atmospheric sciences [23].

Carbon isotope ratios of organic matter are generally depleted in ^{13}C due to preferential uptake of ^{12}C during photosynthesis. Consequently, fossil fuels and their derived CO_2 exhibit strongly $\delta^{13}C$ depleted values, with values ranging from -24‰ to -30‰ for coal and petroleum and from -35‰ down to -85‰ for methane. These values contrast with the $\delta^{13}C$ value of atmospheric CO_2 of around between -8.5 and 9‰ [24 – 26]. This large difference in $\delta^{13}C$ values between carbon sources can be exploited for CO_2 source tracing and quantification, provided that fractionation during carbonate formation is either negligible or well understood so it can be corrected for. Building on this background, the next section explores how isotope principles can be applied to mineral carbonation products.

In addition to the stable isotopes ^{12}C and ^{13}C, carbon also has radiogenic isotopes, i.e., isotopes that decay over time with specific half-life time. The radioisotope ^{14}C is well known with a half-life of 5730 years. It is widely used in various disciplines for dating purposes by the 'radiocarbon' method [27 – 29]. The rare ^{14}C isotope occurs with a global abundance of only 10^{-10} % and thus needs expensive instrumentation for precise analyses. In the context of building materials and concretes, this method has been applied for example to historical mortars [30, 31].

3 Application of isotope chemistry to mineral carbonation products

Isotope chemistry can be a valuable tool in studying carbonation processes as well as for identifying carbon sources in carbonates. Recently, stable isotope analysis ($^{13}C/^{12}C$ fractionation) demonstrated that newly formed carbonates in oil well cements originated directly from the injected gaseous CO_2, confirming the source and mechanism of mineralization. This approach nicely shows the potential to distinguish carbonates and their formation pathways [32]. Both $\delta^{13}C$ and $\delta^{14}C$ have been proposed as tracers for CO_2 origin in carbonated construction materials [33, 34]. A key advantage of $\delta^{13}C$-based methods lies in the significantly lower analytical cost and broader accessibility of the required instrumentation: laser-based benchtop devices are nowadays commercially available and affordable. In contrast, due to the low abundance of ^{14}C, $\delta^{14}C$ analyses require advanced accelerator mass spectrometry (AMS), which entails investment costs in the million-Euro range, alongside with large floor space and specialized laboratory facilities to avoid contamination. Moreover, if $\delta^{14}C$ is applied as an indicator independent of isotope fractionation effects, $\delta^{13}C$ measurements are typically required as well for normalization purposes.

The following sections focus on $\delta^{13}C$ isotope analyses by discussing its potential applications and by outlining the knowledge base that must still be developed to support its broader use in characterizing carbonated construction materials.

3.1 Analytical techniques for mineral carbonation research

The growing interest in mineral carbonation strategies within the field of construction materials opens pathways for rapid research and development of new processes and products, but equally raises fundamental questions regarding the accuracy of analytical methods used to quantify CO_2 in solid matrices. The RILEM Committee TC 309-MCP is actively engaged in this area, striving to identify and evaluate robust methodologies that can reliably determine CO_2 uptake in building materials. The scope includes established solid characterization techniques such as TGA (thermogravimetric analysis), combustion analysis, solid-state NMR (Nuclear Magnetic Resonance), FT-IR (Fourier-Transform Infrared Spectroscopy) or Raman spectroscopy, X-ray diffraction, and wet-chemical methods.

These methods currently represent the state of the art in characterizing solid-phase transformations and can yield relevant results when applied with the necessary analytical expertise. However, several limitations must be acknowledged. Many of these techniques require labourintensive sample preparation steps, such as precise grinding and sieving, which can influence reproducibility and data quality. Moreover, the reliability and interpretive power of techniques like X-ray diffraction (particularly Rietveld refinement) or solid-state NMR depend on technical proficiency and experience of users. Some of the most informative methods — especially NMR — also involve substantial instrumentation and operational costs, which can limit accessibility. From a process-analytical perspective, it remains technically challenging to interrupt carbonation reactions at defined stages to recover representative solidphase samples without inducing further transformation. Most importantly, these methods focus on quantifying total CO_2 uptake, however they generally do not allow for the identification of the origin of the CO_2 source. This fact complicates possible later attribution of CO_2 uptake to specific sources, processes or life cycle stages.

Carbon isotope analyses hold promise to overcome these challenges. As demonstrated in Figure 1, enhanced aqueous carbonation of C_2S (Ca_2SiO_4, belite) undergoes a distinct fractionation of carbon isotopes. Under experimental conditions involving a 100% CO_2 gas phase, the heavier ^{13}C isotopes are preferentially incorporated into the solid phase. This selective incorporation in turn results in a depletion of ^{13}C in the gas phase. This observation matches with reported literature data that show enrichment of ^{13}C in the solid phase during carbonation under high CO_2 concentrations [35 – 38]. Compared to other methods, isotope fractionation in enforced carbonation shows high sensitivity to formation of carbonates. Recent work demonstrated detectable changes corresponding to less than one percent by weight of newly formed carbonates in oil well cements [30].

With a thorough understanding of the carbonation mechanism and the associated isotope fractionation, the degree of carbonation can be directly assessed via the C isotope ratio development of the solid material. Alternatively,

in closed systems, carbonation can also be followed indirectly via fractionation dynamics in the gas phase (Figure 2). Such indirect determination from the gas-phase offers several advantages. First, unlike solid-phase sampling, it is inherently representative, because gases are naturally homogeneous. Second, gas-phase sampling requires only minimal sample volumes and can be conducted in situ during carbonation. As long as sufficient gas volume can be sampled this avoids destructive sampling of the material.

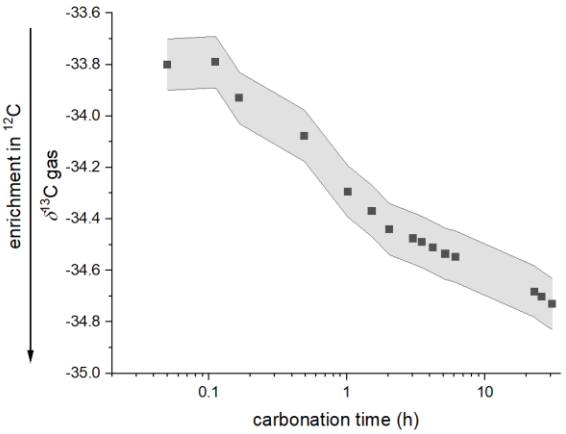

Figure 1. Evolution of the $\delta^{13}C$ isotope ratio in the gaseous phase during enhanced aqueous carbonation of C_2S in 100% CO_2 exposure and room temperature [38].

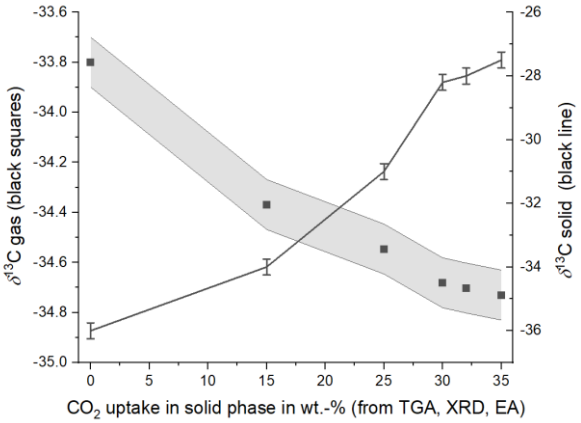

Figure 2: Correlation between carbon uptake in solid materials and its isotope trend together with the mirrored trend of the CO_2 carbonation gas (enhanced aqueous carbonation of C_2S in 100% CO_2 exposure) [38]. TGA–Thermogravimetric Analysis, XRD–X-ray diffraction, EA–Elemental Analyzer

The example shown above demonstrates that isotope analyses can be a versatile alternative to traditional solidstate analytical techniques. Particularly isotope analyses of gases provide deeper insights into carbonation dynamics and can be used for real-time process monitoring.

3.2 Differentiating fossil limestone from CO_2 mineralization products

A key challenge for future applications will be to distinguish between (i) CO_2 removed from the atmosphere e.g., via direct air capture (DAC) or natural carbonation, (ii) process CO_2 from industrial processes used for mineral carbonation applications and (iii) fossil carbonates present as limestone filler or aggregates in the same product. Note that conventional analytical methods to determine carbonate content are unable to differentiate between these different types of CO_2.

For instance, one conventional method measures increases in solid carbonate contents over a process or exposure step of interest. Differences to a defined starting point can help to determine the amount of newly formed carbonates. However, such differential determinations are only accurate under well-controlled conditions. Corrections must be applied to account for concurrent mass changes in the material. For instance, the mass gain from CO_2 uptake during carbonation must be balanced against the mass loss due to release of H_2O and other volatiles [39]. Figure 3 shows that only with complex corrections it is possible to differentiate the carbonate content present as a filler before carbonation from the one that was newly formed as a result of carbonation treatment. It must be noted that not only the determination of the carbonate content is subject to uncertainties, but also mass determinations contribute to measurement errors, and should be properly accounted for.

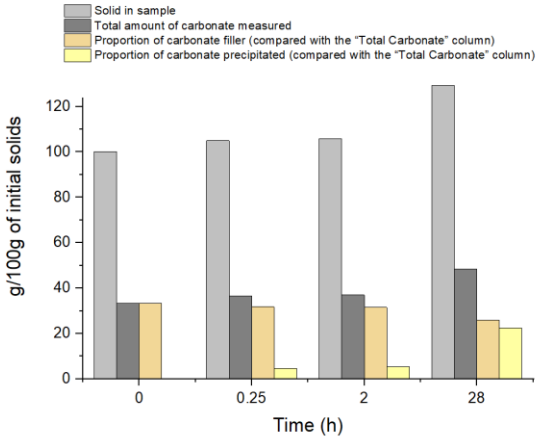

Figure 3: Recalculation of the evolution of phase composition of during carbonation curing of C_2S in a mixture with calcite filler. The amount of precipitated carbonate was calculated through mass balance (enhanced aqueous carbonation of C_2S in 100% CO_2 exposure) [38].

In case of sufficiently different δ-values of the respective endmembers, e.g., limestone filler and newly formed carbonates, isotope analyses can overcome these challenges while avoiding mass change corrections. The isotope approach yields two results: the total amount of carbon, which can be converted into the equivalent amount of $CaCO_3$, and changes in the carbon isotope composition. The latter helps to determine the fraction of newly formed carbonates. Assuming the isotope composition of both the filler (determined from the raw materials analysis or from literature) and the newly-formed carbonate phase (e.g., from comparable experiments without filler or literature) are known, their proportions within the final product can be determined in a straightforward manner using an isotope mass balance:

$$\delta_{total} = \frac{\sum_{i=1}^{n} m_i \times \delta_i}{\sum_{i=1}^{n} m_i} \quad (2)$$

where m represents the molar quantities of the element of interest (in our case C), i identifies the carbon-containing component in the mixture and δ is the isotope ratio.

Figure 4 shows an example of such a mass balance where C_2S was carbonated in water under a 100% CO_2 atmosphere with an added calcite filler. Assuming equilibrium fractionation, the isotope composition of the precipitated carbonate can be calculated based on previous literature [35, 36, 40].

Starting from our CO_2 gas, which has an isotope value of –34‰, these studies predict an expected $\delta^{13}C$ value for carbonate precipitated via aqueous calcite formation at 23°C and pH 6.5 (as is the case in our system [38]) in the range of –24.0‰ (according [36]) to –25.3‰ (according to [35]).

The calcite filler added to the system prior to the experiment had an isotope value of 6‰. Based on this, Figure 4 illustrates the expected isotope mixing relationship between the calcite filler and the newly formed calcite.

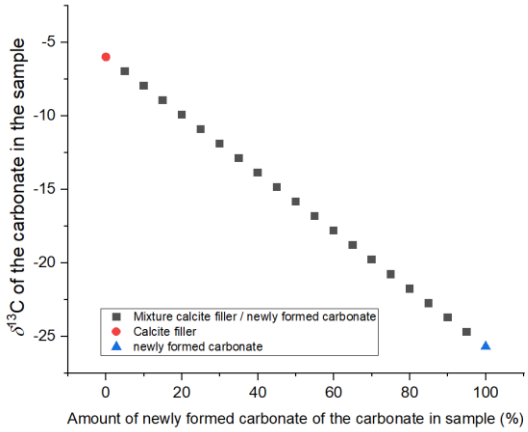

Figure 4: Linear isotope mixing relationship between the calcite filler and newly formed calcite (enhanced aqueous carbonation of C_2S in 100% CO_2 exposure; 23 °C; pH = 6.5) [38].

Once the endmember $\delta^{13}C$ isotope ratios are determined, the proportion of newly precipitated calcite can be calculated in a straightforward manner. The results in Figure 5 show excellent agreement between isotope quantification and independent methods such as TGA and mass balance calculations. This highlights that isotope analyses can serve as a robust and informative tool to quantify carbonation processes. Moreover, the approach offers a direct indication of the overall degree of carbonation in the sample. It must be emphasized that a sound understanding of the carbonation reaction and the associated isotope fractionation is a prerequisite for using mass balance approaches in such quantifications. In our experiment, the fractionation follows the precipitation of calcite from aqueous solution, during which ^{13}C becomes preferentially incorporated into the solid phase, and equilibration fractionation is prevalent. Thermodynamic models describing this equilibrium fractionation are well established and can be applied with reasonable confidence. However, kinetic fractionations and the evolution of pH during the reaction likely also to influence the isotope values of carbonates [36]. This is reflected by the slight deviation between the modelled isotope value of the newly formed calcite (–25.3‰) and the final measured value after the experiment (–27‰ [38]).

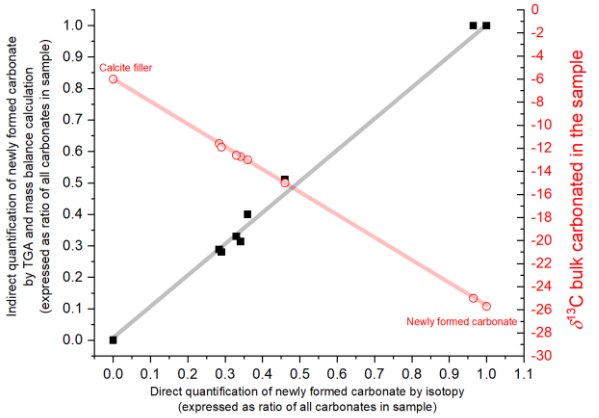

Figure 5: Comparison of the quantification of newly formed carbonate in carbonated samples containing C_2S and calcite filler. Quantification was performed using thermogravimetric analysis (TGA) with mass balance calculations, and direct determination via isotope measurements. (enhanced aqueous carbonation of C_2S in 100% CO_2 exposure as done in [38] but with addition of different amounts of calcite filler).

These findings suggest that further investigations into isotope fractionation mechanisms in cementitious systems are needed to improve the method accuracy. It is also not always the case that $\delta^{13}C$ values of carbonates formed during carbonation increase as shown in our experiments [38]. Instead, some studies report that the $\delta^{13}C$ value of the carbonated material decreases if the carbonation occurs in ambient air [33, 34, 41]. This indicates that either the CO_2 concentration, the pH value and/or an adsorption driven carbonation of cementitious materials has a dominant impact on carbon isotope fractionation. Additionally, humidity and porosity of the carbonated material will have to be investigated as well as a gradual change during long-term carbonation. It was demonstrated convincingly that relative humidity strongly influences carbon isotope fractionation during the precipitation of calcite from atmospheric CO_2 [42]. In another article, it was shown that at least three types of carbonates can be distinguished in concrete by isotopy: those derived from the CO_2 gas phase without isotopic equilibrium with water, those originating from dissolved carbon in isotopic equilibrium with water, and “fossil” carbonates resulting either from fillers or from the incomplete decomposition of calcite during cement production [43].

A very promising application of isotope analyses is the evaluation of the carbonation degree of recycled concrete. Isotopes come in particularly useful when limestone was included as an aggregate or filler in the concrete. In this case,

isotope methods allow for a fair and transparent assessment of the carbonation degree of recycled concrete [33, 34].

Note that the fractionation of the ^{13}C isotope differs between natural carbonation in ambient air and accelerated aqueous carbonation under elevated CO_2 concentrations [38]. While accelerated aqueous carbonation at high CO_2 concentrations in closed systems leads to an enrichment of the heavier ^{13}C isotope in the solid phase, during natural carbonation in ambient air and open systems, the heavier ^{13}C isotopes are depleted in the solid phase [33, 34, 41].

To illustrate this, we analysed a recycled concrete fines sample. The recycled fines were collected from a batch of production waste of concrete with a limestone filler. The limestone filler exhibited a $\delta^{13}C$ value of +0.3‰, while the recycled concrete fine fraction had a value of –14‰. A first estimate of the $\delta^{13}C$ value of newly formed carbonates by air exposure can be derived from a recent study where values for $\delta^{13}C$ of –34‰ for calcite formed through natural carbonation were measured [33]. The corresponding mixing trend is shown in Figure 6 (Eq. 2). Based on this relationship, it can be inferred that the recycled concrete contains a remarkably high proportion of carbonate formed through natural carbonation (almost 40% of the calcite in the sample).

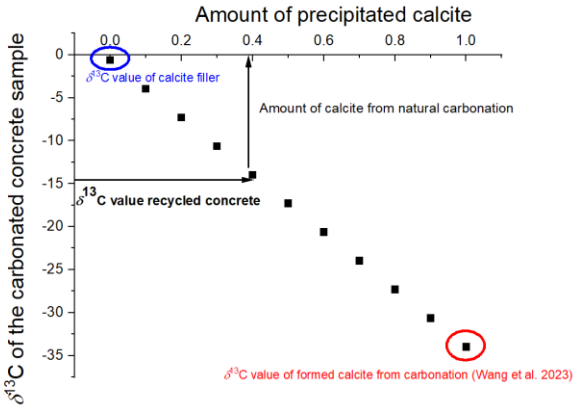

Figure 6: Evaluation of the amount of calcite formed through natural carbonation in a recycled concrete sample (adopted calcite CO_2-negative $\delta^{13}C$ value of –34‰).

To implement tracing of the carbonate source in concrete by isotope methods, new test methods would need to be developed and adopted. First the carbonate content of the recycled concrete should be accurately determined. Next, the limestone aggregate and/or filler isotope value used in the concrete should either be directly measured (e.g. using a microdrill to sample the aggregates) or adopted from literature or database values [44][45]. Field data and predictive models are then combined to provide the expected isotope values of carbonates formed via natural carbonation. By subsequent comparison of the $\delta^{13}C$ value of the carbonates in the concrete with the isotope values of the concrete constituents, the proportion of carbonates formed through natural carbonation can be determined (Figure 7). What is still lacking today are predictive models to describe the kinetic fractionation behaviour as a function of porosity, pH, humidity and other factors. To validate applicability, further robustness studies should also address the effect of other concrete constituents such as carbonated supplementary cementitious materials or even chemical admixtures on isotope values and derived carbonate proportioning.

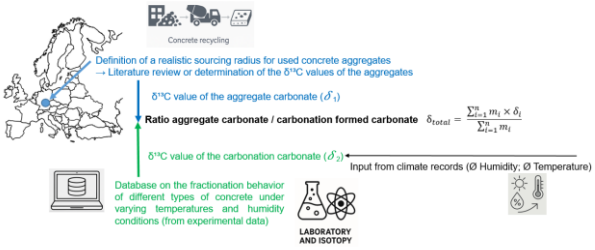

Figure 7: Implementation scheme for isotope-based determination of the content of carbonates formed by natural carbonation of concrete

3.3 Provenancing of CO_2 sources

Negative $\delta^{13}C$ isotope values of fossil-fuel derived CO_2 (-25 to -45‰) versus atmospheric CO_2 (between -8.5 and 9‰) could be exploited for tracing and certification purposes. The premise here is that the isotope value of the gas phase is inherited by the precipitated carbonates. However, as illustrated in the previous sections, the isotope values may not only depend on the gas phase, but also on kinetic isotope fractionation processes that occur during carbonation.

Earlier research has shown that kinetic fractionation, i.e., related to diffusion or differences in rates of chemical reactions, can deplete solid carbonates in ^{13}C. Specifically, kinetic fractionation through aqueous carbonate speciation (deprotonation of CO_2(aq) to HCO_3^- or CO_3^{2-}) can become dominant and result in a $\delta^{13}C$ depletion of -10 to -19‰ for hyper alkaline solutions [46 – 49]. As aqueous carbonate speciation is determined by pH and affected by temperature, carbonation processing conditions also need to be considered, when interpreting isotope values. Further kinetic fractionation by diffusion has been noted to be small for fine powders suspended in solution. However, it can be significant in highly tortuous microporous materials such as concrete. It is relevant to note that gaseous diffusion is a well-known isotope enrichment process. Changes in carbonate isotope values across the depth of a carbonated material thus not only reflect chemical changes, but also the material microstructure and hence may offer an interesting perspective on CO_2 transport properties. On the other hand, thermodynamic equilibrium fractionation, which enriches the solid ^{13}C, was considered subordinate in rapid carbonation of alkaline materials.

As the magnitude of these secondary fractionation processes is not negligible, they may mask the original isotope composition of the source gas. If the CO_2 isotope value is known, or when the compositional change during the carbonation process is separately monitored and declared, claims on CO_2 sourcing can be verified. For instance, if both the isotope value of biogenic CO_2 gas applied during mineralization and the one of biogenic

carbonate formed during service life are known, the isotope method should be able to distinguish enforced biogenic mineralization from passive natural biogenic carbonation. Alternatively, a combination with analysis of other isotope abundance, e.g. ^{14}C [33], or so-called clumped ^{13}C-^{18}O isotope analysis may enable to correct for the ensemble of carbon fractionation processes. Clumped isotopes refer to the measurement of molecules that contain very rare ^{13}C-^{18}O bonds and are expressed as Δ_{47} values [50]. The relative abundance of these bonds in carbonates depends on the formation temperature and is therefore primarily used in paleo-temperature reconstructions. However, questions regarding the fractionation processes are still under investigation [51]. Ultimately, a complete, yet lacking, quantitative understanding of carbon isotope fractionation in typical mineral carbonation conditions should be able to deliver predictive models of broad applicability.

Figure 8 presents $\delta^{13}C$ values for a range of materials of interest. As reference, natural marine limestone fillers and aggregates (Lower Carboniferous, Belgium) are compared to (partially) carbonated materials that are, or can be, used as construction materials. It can be observed that all carbonated materials are significantly more depleted in ^{13}C than natural limestone. This reflects isotope fractionation in alkaline solutions and underpins the differentiation between limestone filler or aggregate, and mineral carbonation products as discussed in section 3.2. The higher abundance of limestone aggregate in recycled concrete fines type B, and in particular in its coarser fraction corroborates this approach. The rather broad ranges of $\delta^{13}C$ in cement pastes, concrete and lime mortars, as well as reported evolutions over time and depth results from a convolution of speciation and diffusion fractionation.

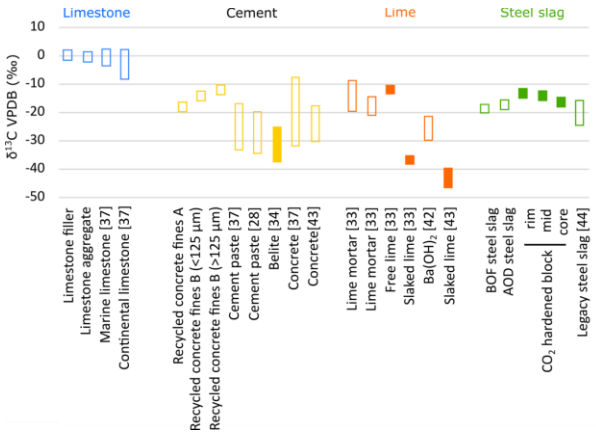

Figure 8: Comparison of $\delta^{13}C$ composition of natural limestone, (partially) carbonated cement and concrete, lime (mortar) specimens, and steel slags. Unfilled bars refer to ranges for carbonation in open systems (air curing), filled bars represent ranges for closed, high CO_2 concentration systems [41][33][38][47][37][46][48].

Diffusion fractionation may also be observed for carbonation hardened steel slag blocks, where a clear ^{13}C depletion from the outer rim to the inner core of the blocks was measured.

As can be inferred from the overlapping isotope ranges of carbonated cementitious and steel slag materials, precursor mineralogy effects on isotope fractionation appear subordinate.

Most of the compiled isotope values were reported for carbonation in open systems, where CO_2 is continuously replenished and isotopically equilibrated by exposure to the atmosphere. In contrast, in closed systems both CO_2 gas partial pressure as well as isotope values of CO_2 evolve upon progressive carbonation [38]. This will in turn shift the isotope value of solid carbonates. Depending on whether mineral carbonation is carried out in batch or continuous (gas flowthrough) processes, the gas and hence the solid material values signatures will evolve differently. Such developments may even materialize in characteristic patterns to enable product fingerprinting.

4 Conclusion and perspectives

The cement and concrete industries face significant challenges in achieving their net zero targets by business-asusual approaches. This includes clinker factor reduction and use of alternative fuels. Carbon Capture and Storage (CCS) will become a necessary driver for CO_2 emission reduction measures. For example, within the Global Cement and Concrete Association (GCCA) roadmap [52], CCS was identified to account for a reduction of 1.37 Gt/y of CO_2 emissions (i.e., 36% of the total projected CO_2 emissions of the global cement industry) by 2050. Despite these ambitious mid-to-long term goals, the sector is already significantly behind targets, mainly due to the combination of high investment costs in CCS infrastructure, regulatory obstacles and lack of public acceptance to enable CCS. It is for example very unlikely that the EU's 2030 carbon storage target of 50 Mt/y CO_2 injection capacity will be reached on time [53].

As an alternative, the exploration of new approaches, particularly the active promotion of local CO_2 utilization measures by mineral carbonation will gain interest. Cementitious materials present a promising path for CO_2 utilization and storage, given their thermodynamically driven tendency to react with CO_2. These materials therefore offer revenue from products sales and can avoid costs and environmental impact related to CCS. To stimulate the required investments for mineral carbonation implementation, a clear financial benefit incentive must materialize. In this respect, a central policy question revolves around how CO_2 utilization versus CCS will be integrated into existing climate policy instruments such as for instance the EU Emission Trading Scheme. The adoption of the EU Carbon Removals and Carbon Farming (CRCF) framework in 2024 [54, 55], established as a voluntary framework for carbon removal certification, may serve as a significant incentive. The prospect of using carbon removal certificates to compensate process CO_2 emissions or to generate revenue in the carbon credits market could leverage further investment in CO_2 utilization by mineral carbonation.

As shown here, isotope systematics emerge as a new tool not only for mineral carbonation research, but also to verify the provenance of CO_2 and solid carbonates. This tool can also

help to identify predominant carbon mineralization processes. Fossil limestone fillers or aggregates can be differentiated from direct air carbonation products (recarbonation) or enforced carbonation processing. Moreover, isotope systematics may enable to retrace or verify the sources of CO_2 by fingerprinting fossil-fuel, biomass or limestone - derived captured and stored CO_2. This capability is very relevant to account for accurate emissions in the future, particularly when considering carbon pricing mechanisms or carbon removal credits [56]. Beyond manufacturing, natural recarbonation, (during which concrete absorbs atmospheric CO_2) represents a potentially significant – but so far hardly quantified --- global carbon sink that may be readily traceable by carbon isotopes. Despite the promising potential of carbon isotopy, several critical knowledge gaps remain to be addressed to support further development and implementation of its practical applications. In particular, secondary isotope fractionation associated with CO_2 diffusion, dissolution and precipitation require further investigation and integration into fractionation models.

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Authorship statement (CRediT)

Daniel Jansen: Conceptualization; Investigation; Visualization; Writing – Original Draft. **Ruben Snellings:** Conceptualization; Investigation; Visualization; Writing – Original Draft. **Thomas Matschei:** Conceptualization; Validation; Writing – Original Draft. **Johannes Barth:** Investigation; Validation; Formal Analysis; Resources; Writing – Review & Editing. **Robert van Geldern:** Investigation; Validation; Formal Analysis; Resources; Writing – Review & Editing.

Data availability

Data will be made available on reasonable request.

Declarations

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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