



# Atmospheric carbon dioxide mineralisation in anthropogenically-derived carbonate deposits

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**Abstract** | Removing carbon dioxide from the atmosphere is important in minimising the impact of anthropogenically-induced climate change. Anthropogenic geomaterials, such as slag and cement, can be utilised in an engineered context for mineralising CO<sub>2</sub>. However, such anthropogenic geomaterials, typically waste products, were usually deposited on the land surface and left to passively mineralise CO<sub>2</sub>, resulting in the formation of anthropogenic carbonates. In this study, we document anthropogenic carbonates from a suite of locations across Scotland and Northern England, and use stable carbon and oxygen isotopes to show that they are formed from atmospheric CO<sub>2</sub>. Carbonates which formed in subaqueous settings recorded  $\delta^{13}\text{C}$  values of -25 to -28 ‰ and  $\delta^{18}\text{O}$  values of -15 to -20 ‰, which indicate rapid precipitation from atmospheric CO<sub>2</sub>. Subaerially-formed samples recorded slightly higher delta values, indicating partial re-equilibration of the dissolved atmospheric CO<sub>2</sub> towards expected equilibrium values with ambient conditions before precipitation. The broad suite of samples from multiple locations across Scotland and Northern England show anthropogenic carbonates are more common than previously realised, which demonstrates their effectiveness in passive drawdown of atmospheric CO<sub>2</sub>.

**Lay summary** | Rocks which incorporate carbon form naturally by a range of processes and can take in the carbon from different sources, such as organic carbon from plant material or carbon dioxide from the atmosphere. Here we show that rocks (referred to here as ‘anthropogenic carbonates’) can form from atmospheric carbon dioxide reacting with human-created materials, such as by-products from making steel. We conducted chemical analysis to show that the carbon dioxide came from the atmosphere. This has implications for carbon dioxide removals and the fight against human-induced climate change.

**Keywords:** Anthropogenic carbonates; Carbon and oxygen isotopes; Mineralisation; Carbon dioxide removal

## 1. Introduction

Mechanisms for the removal of carbon dioxide from the Earth's atmosphere are needed to achieve Net Zero and minimise the impact of anthropogenically-driven climate change (e.g., IPCC, 2018). One form of this carbon dioxide removal (CDR) involves CO<sub>2</sub> mineralisation, where carbonate minerals precipitate using dissolved inorganic carbon provided by atmospheric CO<sub>2</sub>. The process of silicate weathering – where atmospheric CO<sub>2</sub> reacts with silicate rocks and sediments at the Earth's surface – occurs widely and naturally but over long periods in geological time (Berner, 1990). In rock types with high concentrations

of divalent metal cations, particularly Ca and Mg (Lackner et al., 1995), however, rapid reaction rates result in CO<sub>2</sub> mineralisation. This is typically observed in areas where ultramafic rocks have been brought to the Earth's surface, e.g., in ophiolites (Kelemen et al., 2018; Paukert et al., 2012). In the ophiolitic rocks of Oman, for example, CO<sub>2</sub> mineralisation occurs in springs and stream waters, which dissolve Mg and Ca from silicate minerals in the ultramafic rocks. This causes an increase in alkalinity and subsequently results in ingassing of atmospheric CO<sub>2</sub> which reacts with the dissolved cations to precipitate carbonate minerals (Clark et al., 1992; Falk et al., 2016; Mervine et al., 2014; Olsson, Stipp, & Gislason, 2014). This CO<sub>2</sub>

mineralisation occurs naturally without human activity, but natural rocks rich in Ca and Mg can also be used to engineer CO<sub>2</sub> mineralisation. At the Carbfix project in Iceland, CO<sub>2</sub>-rich waters are injected into basaltic rocks in the sub-surface. This results in Ca and Mg being leached from rock surrounding the fractures, which then reacts with the CO<sub>2</sub> to precipitate carbonate minerals (e.g., Matter et al., 2011; Snæbjörnsdóttir et al., 2020).

CO<sub>2</sub> can also be mineralised with anthropogenic geomaterials. Anthropogenic geomaterials are mineral-based solid materials that share many properties with natural rocks, but are created by anthropogenic activities, (e.g., furnace slags, cement, ceramics, ashes). CO<sub>2</sub> mineralisation with anthropogenic geomaterials has been explored widely through laboratory experimental testing (e.g., Huijgen et al., 2005), but can also occur passively. In this scenario, the CO<sub>2</sub> from the atmosphere is mineralised naturally (as in the ophiolite rocks, for example) but the provider of the divalent cations is anthropogenic in nature (e.g., Dietzel et al., 1992; MacDonald, Khudhur, et al., 2023; MacDonald et al., 2025; Mayes et al., 2018). The mechanism for carbonate precipitation in these settings involves reaction of the anthropogenic geomaterial with water, resulting in dissolution of Ca and/or Mg, plus other reactive species such as OH<sup>-</sup> from portlandite or brucite, which increases the water pH. This promotes ingassing of atmospheric CO<sub>2</sub> which is hydroxylated and reacts with the Ca and/or Mg to precipitate carbonate minerals (e.g., Dietzel et al., 1992; Mayes et al., 2018; Renforth et al., 2009; Washbourne et al., 2015). The precipitated carbonate can be formed in-situ, i.e., on the anthropogenic geomaterial itself (e.g., MacDonald, Khudhur, et al., 2023), or ex-situ, i.e., carbonate precipitation occurs downstream from the anthropogenic geomaterial, in leachates draining the deposits of anthropogenic geomaterials (e.g., Mayes et al., 2008; Riley & Mayes, 2015; Roadcap et al., 2005). We use the term ‘anthropogenic carbonates’ and define them as carbonate deposits which are associated with anthropogenic geomaterials, either in-situ or ex-situ.

Individual anthropogenic carbonate deposits have been shown to have mineralised atmospheric CO<sub>2</sub>, for example the slag-derived tufa at Consett in Northeast England (Holdsworth et al., 2022; Knapp et al., 2023; Mayes et al., 2018; Renforth et al., 2009). It is not known whether this formation mechanism applies more widely in anthropogenic carbonates. Therefore, this study uses carbon and oxygen stable isotope analysis to show that a range of forms of anthropogenically-derived carbonate deposits, which precipitate due to a range of anthropogenic processes/materials, draw down and mineralise atmospheric CO<sub>2</sub>.

## 2. Sample characterisation

Twelve samples of anthropogenic carbonates were collected from eight locations in Central Scotland and Northern England (Table 1). Nine of the anthropogenic carbonates

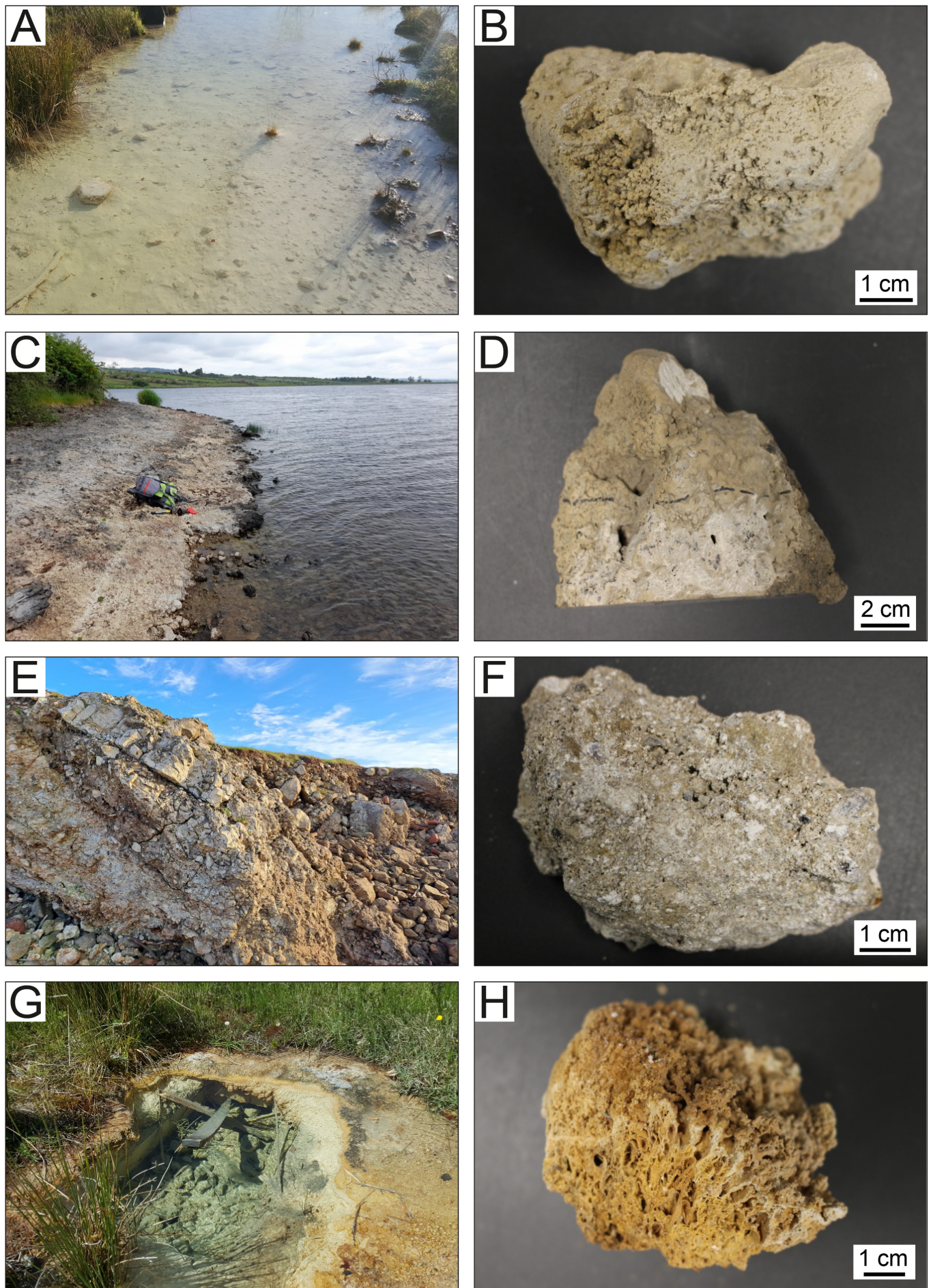
were found as hard scaling coatings on other materials. The samples from Ravenscraig (Figure 1A) were coatings on ferrous slags collected from within a small pond. There was abundant evidence of carbonate precipitation in this pond with micritic powder settling on the pond floor. Pebble- to cobble-sized pieces of slag had harder carbonate deposits with more defined crystal forms precipitated on them (Figure 1B; Figure S1A-C). The sample from Glengarnock (JK3) was similar and found on the shores of a lake (Figure 1C) where lake level fluctuates, meaning that the sample (Figure 1D) will have experienced a mix of subaerial and subaqueous conditions (MacDonald, Brolly, et al., 2023). The samples from Barrow (BW; Figure S1D-E), Clydesdale (CD2; Figure S1F-G) and Stevenston (STV; Figure 1E-F) were also carbonate scaling on ferrous slags, but from subaerial exposures, away from any water bodies. The sample from Darnrigg (DN; Figure S1H-I) is a flaky carbonate scaling on a substrate of grey brittle flaky waste fragments and natural gravel. This sample is also from an area of fluctuating water level and so may have experienced both subaerial and subaqueous conditions. The anthropogenic carbonate sample from Plains (AH; Figure 1G-H) is a tufa-like deposit, forming on and around a concrete-block-lined flooded shaft. The main deposit around the shaft where the sample was obtained is hard with a semi-bulbous morphology. The thickness of the deposit was noticeably greater around the water-air interface at the time of sampling, compared to below the water surface or above it. Two samples with different morphologies were collected from Cults (CfL and COO), both associated with lime waste (Figure S1J). Sample CfL had a flaky texture, forming tufa-like masses on the deposit surface (Figure S1K). Sample COO had a moist, cohesive clay-like texture and occurred as chunks or as matrix in among other material (Figure S1L).

## 3. Methods

### 3.1. Study area and sampling methodology

Stable isotope ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) measurements of the anthropogenic carbonate samples were made by continuous flow isotope ratio mass spectrometry at the School of Geographical and Earth Sciences at the University of Glasgow, following a standard methodology previously outlined in MacDonald, Khudhur, et al., (2023). Aliquots of 200  $\mu\text{g}$  of powdered sample were acidified with phosphoric acid ( $\geq 1.90$  SG) and heated for 1 hr at 60 °C on an Elementar GasBench and analysed on an Isoprime 100 mass spectrometer. Samples were run in triplicate and averages reported as the result with 1 standard deviation. Analyses were run over three analytical sessions and values were calibrated to V-PDB using NBS-18 and IAEA-603 reference standards in each session (Table S1). A secondary standard, IA-RO22 (Iso-Analytical Ltd.), was used to validate the calibration linearity for more depleted values of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  than the reference standards have. Analytical uncertainties of  $< 0.36\%$  on  $\delta^{13}\text{C}$  and  $< 0.75\%$





**Figure 1** | Field and sample photographs of example samples from different settings. A) The pond at Ravenscraig (foreground field of view = 2 m) showing subaqueous setting where sample ES (B) was taken from. C) The lake shore at Glengarnock (50 cm long rucksack for scale), where fluctuating water levels mean sample JK3 (D) experienced subaqueous and subaerial conditions. E) Slag deposit at Stevenston (foreground field of view = 4 m) above the high water mark, where sample STV (F) experienced subaerial conditions. G) The flooded mine shaft at Plains (foreground field of view = 3 m) with tufa-type anthropogenic carbonate sample AH (H).



on  $\delta^{18}\text{O}$  were obtained on measurements of IAEA-603 ( $n = 50$ ) across the three analytical sessions (Table S1).

4. Results

Values of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  ranged from  $-14.04 \pm 0.42 \text{ ‰}$  to  $-27.44 \pm 0.24 \text{ ‰}$  and  $-7.87 \pm 0.91 \text{ ‰}$  to  $-21.64 \pm 0.14 \text{ ‰}$  respectively (Table 1, Figure 2). Samples which were subaqueous scaling on ferrous slags (Ravenscraig) clustered towards the lower delta values of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , with  $\delta^{13}\text{C}$  ranging from  $-25.40 \pm 0.07 \text{ ‰}$  to  $-27.44 \pm 0.24 \text{ ‰}$ , and  $\delta^{18}\text{O}$  ranging from  $-17.78 \pm 0.03 \text{ ‰}$  to  $-19.84 \pm 0.15 \text{ ‰}$ . The micritic ooze (Cults) recorded similar values ( $\delta^{13}\text{C}$  of  $-27.44 \pm 0.24 \text{ ‰}$  and  $\delta^{18}\text{O}$  of  $-21.64 \pm 0.14 \text{ ‰}$ ), as did the two samples exposed to both subaqueous and subaerial conditions (from Glengarnock and Darnrigg). The subaerial-only scaling on ferrous slags and one of the tufa samples (Plains) recorded  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values in a trend between the origin and the cluster defined by the subaqueous slag scaling samples, with  $\delta^{13}\text{C}$  of ca.  $-14$  to  $-20 \text{ ‰}$  and  $\delta^{18}\text{O}$  of ca.  $-10$  to  $-15 \text{ ‰}$ . The subaerial slag scaling sample from Barrow-in-Furness recorded a slightly higher  $\delta^{18}\text{O}$  value ( $-7.87 \pm 0.91 \text{ ‰}$ ). The tufa from Cults was something of an outlier from this broad trend: while its  $\delta^{13}\text{C}$  value was similar to the subaerial slag scaling samples ( $-14.93 \pm 0.56 \text{ ‰}$ ), its  $\delta^{18}\text{O}$  value of  $-20.92 \pm 1.11 \text{ ‰}$  was very low.

5. Discussion

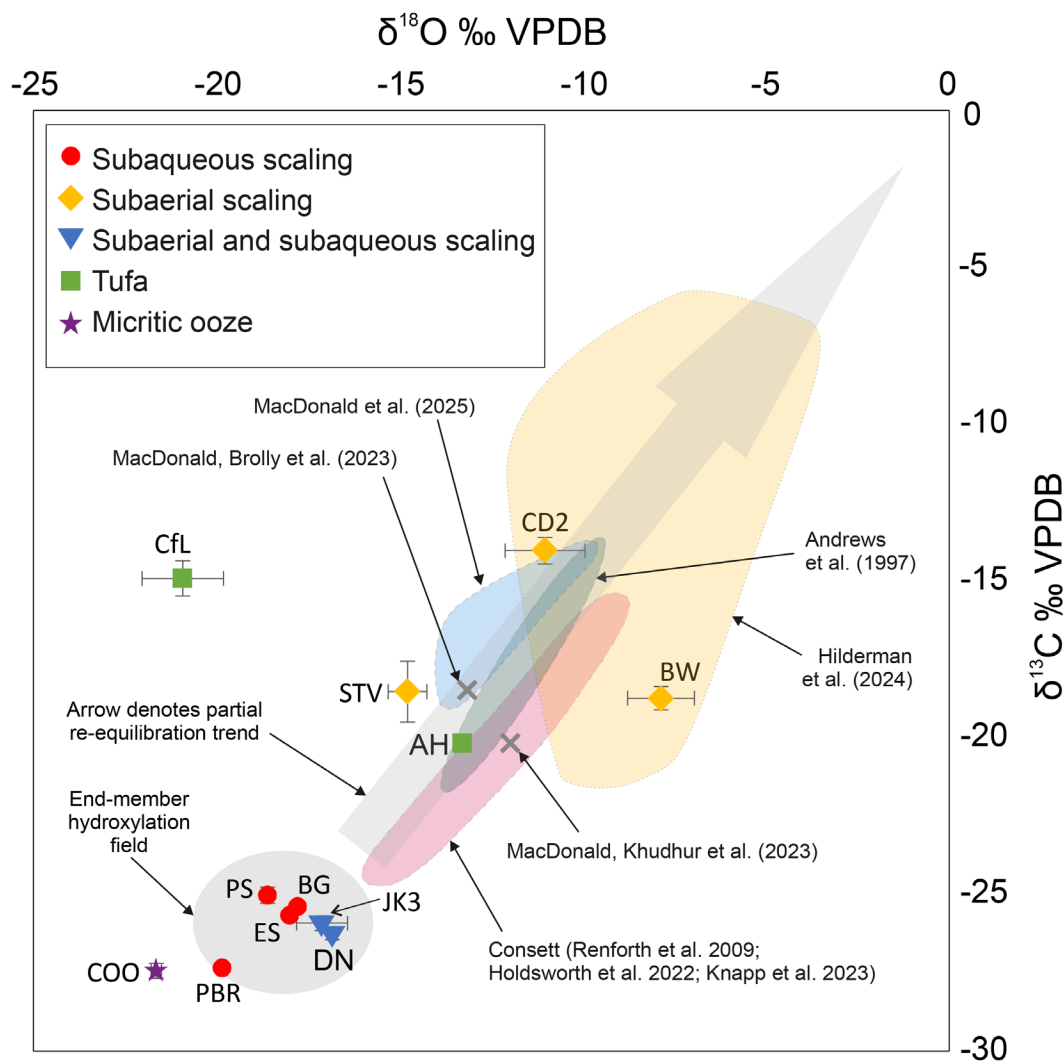
5.1. Comparison with other anthropogenic carbonates

Occasional other examples of anthropogenic carbonates have been documented. Two other samples from the location at Glengarnock have been analysed previously

(one a surface scaling on ferrous slag and the other an intraclast cement), yielding  $\delta^{13}\text{C}$  values of  $-18.50 \pm 0.29 \text{ ‰}$  and  $-20.19 \pm 0.23 \text{ ‰}$ , and  $\delta^{18}\text{O}$  values of  $-13.15 \pm 0.49 \text{ ‰}$  and  $-11.97 \pm 0.71 \text{ ‰}$ , respectively (MacDonald, Brolly, et al., 2023; MacDonald, Khudhur, et al., 2023) (Figure 2). In a similar slag deposit at Warton, England, where the anthropogenic carbonate occurs as a calcite cement between slag clasts, Hilderman et al. (2024) reported  $\delta^{13}\text{C}$  values of ca.  $-6$  to  $-23 \text{ ‰}$  and  $\delta^{18}\text{O}$  values of ca.  $-4$  to  $-11 \text{ ‰}$  (Figure 2). In an alkaline cement-manufacturing waste where anthropogenic carbonate formed as a calcite cement between waste particles, MacDonald et al. (2025) recorded  $\delta^{13}\text{C}$  values of ca.  $-14$  to  $-18 \text{ ‰}$  and  $\delta^{18}\text{O}$  values of ca.  $-10$  to  $-14 \text{ ‰}$  (Figure 2). Other documented anthropogenic tufas which had carbon and oxygen isotope compositions published exhibit tufa morphologies akin to the new samples presented here from Plains (AH) and Darnrigg (DN). At Herbert’s Quarry in Wales, Andrews et al. (1997) recorded  $\delta^{13}\text{C}$  values of ca.  $-20 \text{ ‰}$  and  $\delta^{18}\text{O}$  values of ca.  $-12 \text{ ‰}$  from calcite crusts derived from leaching of limestone quarrying spoil; calcified moss from the same location recorded slightly higher delta values of ca.  $-14 \text{ ‰}$  and ca.  $-10 \text{ ‰}$  for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  respectively (Figure 2). A large tufa has formed in the Howden Burn near Consett in Northeast England, where the burn is the drainage for leachate from a ferrous slag heap associated with the former Consett Iron and Steel Works (Bastianini et al., 2022; Hobson et al., 2018; Holdsworth et al., 2022; Knapp et al., 2023; Mayes et al., 2018; Mayes et al., 2008; Pullin et al., 2019; Renforth et al., 2009; Riley & Mayes, 2015). Carbon and oxygen isotope analysis of carbonates from this anthropogenic carbonate (Figure 2) are broadly similar to other anthropogenic carbonates, with  $\delta^{13}\text{C}$  values of ca.  $-15$  to  $-25 \text{ ‰}$  and

Sample name	Location (with latitude, longitude)	Carbonate morphology	Source material	$\delta^{13}\text{C} \text{ ‰} (\pm 1\text{SD})$	$\delta^{18}\text{O} \text{ ‰} (\pm 1\text{SD})$
AH	Plains, North Lanarkshire (55.885812, -3.929959)	Tufa	Uncertain (possible concrete-lined shaft)	-20.20 ( $\pm 0.13$ )	-13.28 ( $\pm 0.14$ )
CfL	Cults Hill, Fife (56.264548, -3.061964)	Tufa (flaky)	Limeworks Waste	-14.93 ( $\pm 0.56$ )	-20.92 ( $\pm 1.11$ )
COO	Cults Hill, Fife (56.264548, -3.061964)	Ooze (saturated micrite)	Limeworks Waste	-27.44 ( $\pm 0.24$ )	-21.64 ( $\pm 0.14$ )
BW	Barrow-in-Furness, Cumbria (54.129261, -3.241134)	Subaerial scaling	Ferrous Slag	-18.75 ( $\pm 0.37$ )	-7.87 ( $\pm 0.91$ )
CD2	Clydesdale, North Lanarkshire (55.804720, -3.988045)	Subaerial scaling	Ferrous Slag	-14.04 ( $\pm 0.42$ )	-11.03 ( $\pm 1.09$ )
DN	Darnrigg Moss, Falkirk (55.955283, -3.801710)	Subaerial and subaqueous scaling	Uncertain (possible waste cementitious material?)	-26.26 ( $\pm 0.19$ )	-16.84 ( $\pm 0.11$ )
JK3	Glengarnock, North Ayrshire (55.754049, -4.665579)	Subaerial and subaqueous scaling	Ferrous Slag	-25.92 ( $\pm 0.23$ )	-17.12 ( $\pm 0.69$ )
STV	Stevenston, North Ayrshire (55.625796, -4.749777)	Subaerial scaling	Ferrous Slag	-18.54 ( $\pm 0.98$ )	-14.78 ( $\pm 0.53$ )
ES	Ravenscraig, North Lanarkshire (55.789384, -3.939276)	Subaqueous scaling	Ferrous Slag	-25.68 ( $\pm 0.08$ )	-18.00 ( $\pm 0.03$ )
BG	Ravenscraig, North Lanarkshire (55.789384, -3.939276)	Subaqueous scaling	Ferrous Slag	-25.40 ( $\pm 0.07$ )	-17.78 ( $\pm 0.03$ )
PBR	Ravenscraig, North Lanarkshire (55.789384, -3.939276)	Subaqueous scaling	Ferrous Slag	-27.35 ( $\pm 0.09$ )	-19.84 ( $\pm 0.15$ )
PS	Ravenscraig, North Lanarkshire (55.789384, -3.939276)	Subaqueous scaling	Ferrous Slag	-25.03 ( $\pm 0.26$ )	-18.61 ( $\pm 0.08$ )

Table 1 | List of samples analysed, with location, carbonate morphology, source material and isotopic ratios.



**Figure 2** |  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of anthropogenic carbonate samples, reported against the Vienna Pee Dee Belemnite (VPDB) scale. “End-member hydroxylation field” from Dietzel et al. (1992) and “Partial DIC equilibration trend” from Falk et al. (2016). The colour-shaded fields and two cross-marked datapoints denote  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values from previously reported anthropogenic carbonates (Andrews et al., 1997; Hilderman et al., 2024; Knapp et al., 2023; MacDonald, Brolly, et al., 2023; MacDonald, Khudhur, et al., 2023; MacDonald et al., 2025; Mayes et al., 2018; Renforth et al., 2009). The colour-shaded fields encompass the extent of data points from the respective previous studies.

$\delta^{18}\text{O}$  values of ca. -48 to -17 ‰ (Holdsworth et al., 2022; Knapp et al., 2023; Renforth et al., 2009).

## 5.2. Anthropogenic carbonate formation mechanism

The few anthropogenic carbonates that have been previously documented have typically formed through Ca leached from a source material and  $\text{CO}_2$  ingassed from the atmosphere. In anthropogenic carbonates associated with slag deposits (Bastianini et al., 2022; Hilderman et al., 2024; Hobson et al., 2018; Holdsworth et al., 2022; Knapp et al., 2023; MacDonald, Brolly, et al., 2023; Mayes et al., 2018; Mayes et al., 2008; Pullin et al., 2019; Renforth et al., 2009; Riley & Mayes, 2015), Ca is leached from the slag since iron- and steel-making slags are typically dominated by Ca-rich phases which are relatively unstable at Earth’s surface conditions and are reactive with water (Mayes et al., 2018). The Ca (and OH- from unstable phases like portlandite in fresh slag) leach into porewaters in contact with slag particles, making those porewaters locally hyperalkaline (e.g., MacDonald, Brolly, et al., 2023). Atmospheric

$\text{CO}_2$  is then ingassed into this hyperalkaline porewater and hydroxylated, reacting with the dissolved Ca to precipitate calcium carbonate, typically calcite (e.g., Mayes et al., 2018). Many of the source materials for the anthropogenic carbonates documented here are slags. The samples from Cults are not associated with ferrous slag but formed on and around another Ca-rich material – waste deposited from a former lime works. Similarly, the concrete-lined shaft at Plains may contribute Ca to the formation of the tufa sampled there. These are analogous to the carbonated Ca-rich cementitious waste recorded by MacDonald et al. (2025). The sample from Darnrigg did not have a clear association with a Ca-rich source material.

Carbon and oxygen stable isotope analysis is used to determine the source of  $\text{CO}_2$  in anthropogenic carbonates, which has typically been atmospheric. Instantaneous carbonate precipitation of ingassed and hydroxylated atmospheric  $\text{CO}_2$  should result in  $\delta^{13}\text{C}$  values of ca. -27 ‰ and  $\delta^{18}\text{O}$  values of ca. -19 ‰ (Dietzel et al., 1992) (Figure 2). In contrast, lithogenic and biogenic end-members would

have  $\delta^{13}\text{C}$  values of ca. 0 ‰ and ca. -8 ‰, respectively (Cerling, 1984; Renforth et al., 2009). If the rate of carbonate precipitation is not faster than the rate of ingassing and hydroxylation of the  $\text{CO}_2$ , there will be partial re-equilibration of the DIC pool, resulting in a shift of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  towards 0 ‰ (PDB) (e.g., Falk et al., 2016) (Figure 2). The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of anthropogenic carbonates reported in the literature typically fall into this range of partial re-equilibration, as do the samples in this study, which formed in subaerial environments and the tufa from Plains (Figure 2). The samples which formed in subaqueous settings, or were in subaqueous conditions for some of the time due to fluctuating water levels, all plot within the atmospheric  $\text{CO}_2$  end-member field on Figure 2. This suggests rapid carbonate precipitation in shallow water, which agrees with the observed water depth in which the samples formed – a < 20 cm deep pond at Ravenscraig and shallow waters at the edge of a lake at Glengarnock (MacDonald, Brolly, et al., 2023; Figure 1B). Carbonate precipitation in subaerial environments appears to have been less rapid, with more time for partial re-equilibration of the ingassed atmospheric  $\text{CO}_2$  with rainwater  $\text{CO}_2$  or  $\text{CO}_2$  from other sources, resulting in higher  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values.

Measured  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values in anthropogenic carbonates may not solely be determined by atmospheric  $\text{CO}_2$  (Renforth et al., 2009). Higher delta values from the anthropogenic tufa at Consett were attributed to a combination of atmospheric and biogenic  $\text{CO}_2$  (Renforth et al., 2009); there is plenty of scope for input of organic carbon into the tufa at Consett, given its location in draining fields at the base of a wooded valley. In the subaerial slag-scaling samples in this study (Barrow, Clydesdale and Stevenston) with higher delta values than the hydroxylation endmember, forming in largely unvegetated settings, coupled with the fact that the carbonate is restricted to in-situ scaling on slag pieces, suggests that organic carbon input is unlikely, and the higher delta values simply reflect partial re-equilibration of ingassed and hydroxylated atmospheric  $\text{CO}_2$  towards expected equilibrium values for the ambient conditions. The tufa at Plains is generally subaqueous (Figure 1G) but records isotope values more akin to subaerial scaling samples than subaqueous ones. However, given its setting surrounded by vegetation, there is more scope for organic carbon incorporation, which could explain why its isotope values are higher than in similar subaqueous samples.

The micritic ooze sample (COO) associated with the lime works waste at Cults had isotopic values within the range of the atmospheric  $\text{CO}_2$  end member, indicating relatively rapid precipitation of this particular anthropogenic carbonate. The flaky anthropogenic carbonate with tufa morphology from Cults, also associated with the lime works waste, plots some distance in carbon-oxygen isotope space from all other samples and the other anthropogenic carbonates from the literature (Figure 2). The  $\delta^{18}\text{O}$  value of ca. -20 ‰ is in line with an atmospheric  $\text{CO}_2$  end member field, but the  $\delta^{13}\text{C}$  value of ca. -15 ‰ is higher than in

carbonates formed rapidly from hydroxylated atmospheric  $\text{CO}_2$  (Figure 2). This could potentially be due to the incorporation of an organic carbon source with limited oxygen (e.g., coal fragments), which did not affect the hydroxylation end-member signal of the  $\delta^{18}\text{O}$  but brought the  $\delta^{13}\text{C}$  closer to the biogenic carbon end-member (Cerling, 1984).

In settings like the anthropogenic tufa at Consett, where there is ample scope for input of non-atmospheric (biogenic, lithogenic) carbon sources, carbon and oxygen stable isotope analyses provide non-unique solutions to determining the percentage contribution of atmospheric  $\text{CO}_2$  to the precipitation of the anthropogenic carbonate (Knapp et al., 2023). At Consett, Knapp et al., (2023) measured radiocarbon activity to determine that ca. 80% of the  $\text{CO}_2$  locked away in the anthropogenic tufa was atmospheric. This approach is valuable in settings like Consett, where carbonate precipitation occurred ex-situ (i.e., downstream from the Ca source), and the resulting  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values are higher than a pure atmospheric end-member signal. Many of the anthropogenic carbonates in this study recorded atmospheric  $\text{CO}_2$  end-member signals (and therefore can be assumed to have formed from ca. 100 % atmospheric  $\text{CO}_2$ ), while most of those with higher delta values precipitated directly on the Ca source (i.e., scaling on ferrous slags), meaning the scope for input of biogenic or lithogenic  $\text{CO}_2$  is limited (Figure 2). The tufa sample from Plains (AH) is surrounded by vegetation (Figure 1G) and could be expected to have a component of biogenic carbon. While radiocarbon analysis of this sample would clarify the percentage of atmospheric  $\text{CO}_2$  in this single sample, this was beyond the scope of this study.

### 5.3. Significance of anthropogenic carbonates

Anthropogenically-derived carbonate deposits have been reported from a relatively small number of locations, but this study shows that they may be more widespread than previously realised. While at present they are not known to be volumetrically significant, the isotopic data presented here shows they are contributing to atmospheric carbon dioxide drawdown and mineralisation. Therefore, they are making a small contribution to Net Zero targets. The isotopic data presented here shows that atmospheric  $\text{CO}_2$  is being mineralised through reaction with a range of materials in a range of settings, from subaqueous ponds to thin moisture films in otherwise subaerial environments. This complements our understanding of  $\text{CO}_2$  mineralisation with a range of feedstocks, particularly in-situ passive mineralisation (Khudhur et al., 2023; MacDonald, Khudhur, et al., 2023) with ferrous slags. Strategies for effective management of such industrial by-products continue to be developed. Findings such as this may be used in economics and life cycle analysis (e.g., Khudhur et al., 2022) to better understand the costs and environmental impacts of  $\text{CO}_2$  removal technologies. Natural carbonate deposits, which formed through the same mechanism as the

anthropogenic carbonates analysed in this study, have been shown to immobilise metals leached from natural source rocks (Olsson, Stipp, & Gislason, 2014; Olsson et al., 2014). Therefore, anthropogenic carbonates have the potential to immobilise metals from anthropogenic waste streams/effluents. Additional investigation into the use of anthropogenic carbonates for the immobilisation of metals would be advantageous.

## 6. Conclusions

This study used carbon and oxygen stable isotope analysis to show that a suite of anthropogenic carbonates draw down and mineralise atmospheric CO<sub>2</sub>. Previously recorded anthropogenically-derived carbonate deposits show similar very low  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values, although often not with a fully end-member atmospheric CO<sub>2</sub> isotopic composition. In our study, samples from subaqueous or partly subaqueous settings typically recorded atmospheric CO<sub>2</sub> end-member  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values (Dietzel et al., 1992), while subaerial samples show evidence of partial re-equilibration with higher  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. This broad suite of samples from multiple locations across Scotland and Northern England show anthropogenic carbonates are more common than previously realised. They demonstrate the effectiveness of passive mineral carbonation in drawing down and mineralising atmospheric CO<sub>2</sub>, providing analogues and the potential to improve understanding of the fundamentals of passive CO<sub>2</sub> mineralisation, which can be utilised in engineered settings to optimise atmospheric CO<sub>2</sub> mineralisation.

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## Author contribution

JM: conceptualisation; data curation; formal analysis; investigation; project administration; visualisation; writing – original draft presentation. CS: formal analysis; investigation; writing – review and editing. AS: investigation; writing – review and editing. MK: investigation; writing – review and editing.

## Data availability

All supporting data is provided in the manuscript and in the Supplementary Material.

## Conflict of interest

The authors declare no known conflict of interest.

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