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Tracing carbon: natural mineral carbonation and the incorporation of atmospheric vs. recycled CO₂

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Abstract

Mineral carbonation is a process whereby CO₂ reacts with ultramafic rocks to form carbonate minerals such as calcite (CaCO₃) and magnesite (MgCO₃). This process can be induced artificially at high pressures and temperatures and therefore has potential to be adapted as a carbon capture and storage (CCS) technology.

Large-scale surface and subsurface carbonate deposits of probable Quaternary age are associated with major faulting across the Oman-UAE ophiolite. Here, fractured rock forms a natural fluid pathway and increases the surface area available for carbonation. Modern springs along these faults typically discharge hyperalkaline (pH ~11), Ca(OH)₂-rich waters that precipitate carbonates on reaction with atmospheric CO₂.

Carbonates formed by absorption of atmospheric CO₂ into Ca(OH)₂ waters tend to display low δ¹³C (<<-20‰ PDB) as a result of kinetic fractionation. However, ancient travertines show a large range in δ¹³C of -10.5 to -21.8‰ PDB, produced by the mixing of the low δ¹³C end member with other carbon sources such as limestones or organic-derived soil bicarbonate.

Strontium isotope ratios of samples indicate fluids that formed calcite and magnesite veins may have interacted with limestones around and beneath the ophiolite. These are a carbon source which can easily be reworked and incorporated into carbonate deposits elsewhere. Carbonate deposits may not be created solely from atmospheric CO₂, but instead represent a mixture of carbon sources.

Failure to account for multiple carbon sources or recycled carbon may result in poor estimates of the rates and volumes of carbon that natural systems sequester. Further investigation is therefore necessary to determine how much of the carbon held within carbonate deposits has been incorporated from reworked sources.

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1. Introduction

Carbon capture and storage is generally considered to be essential for the mitigation of anthropogenic CO₂ emissions [1]. Of particular importance is the development of technologies which safely store CO₂ over acceptable timescales. Whilst long-term geological storage in depleted hydrocarbon reservoirs and saline aquifers is gaining increasing attention within the energy industry, alternative methods are also being developed. A wide portfolio of technologies is necessary to fulfil targets to reduce industry emissions [2]. Of the technologies mentioned in this portfolio, mineral carbonation is of interest due to its production of a chemically stable product that may provide permanent carbon storage.

Mineral carbonation is a process that occurs as part of the natural weathering of ultramafic rock. These rocks are particularly reactive with CO₂ and naturally produce carbonates such as calcite (CaCO₃) and magnesite (MgCO₃) in a range of settings [3].

Proponents of mineral carbonation point to a huge excess of suitable rock available at the Earth's surface; plus the formation of a solid, stable, naturally occurring product would gain public acceptability [4]. However, a major criticism of mineral carbonation is that it may not proceed rapidly enough to mitigate emissions. Our study questions whether measurements and estimates of natural mineral carbonation take into account the recycling of older carbon. Failure to account for recycled carbon will lead to underestimation of the rate of sequestration, and overestimation of the total amount of contemporary carbon sequestered.

Our study focuses on the Oman-UAE ophiolite, which contains ~16,000 km³ of ultramafic rock. Here large-scale, ancient, surface and subsurface carbonate deposits are found, along with actively forming deposits [5–8]. These have formed through a complex system of interactions between surface fluids, mantle peridotites and CO₂. Much of the CO₂ sequestered in these carbonates is believed to be of atmospheric origin, making them a natural carbon sink [7]. These carbonates are thus natural analogues of possible industrial processes [6].

2. Carbonate Facies

Ultramafic rocks such as peridotites react with meteoric waters under open system conditions to form Ca and Mg-bicarbonate type fluids [9–10]. Under conditions closed to CO₂, MgCO₃ and CaCO₃ are precipitated in subsurface vein systems, removing bicarbonate and causing evolution to a Ca(OH)₂ fluid chemistry. These fluids have extremely low pCO₂ and, upon reaching the surface, will interact with atmospheric CO₂ to deposit carbonate minerals [10–11]. This process implies that all CO₂ incorporated into surface deposits is of atmospheric origin. Previous studies have shown that this drawdown of atmospheric CO₂ is reflected in stable C and O isotope values for surface carbonates [5, 12–14].

In and around the Oman-UAE ophiolite, carbonates occur in a diverse range of settings, with each locality often displaying numerous phases of carbonate development with highly diverse forms and textures [5, 6, 9, 15–18]. This variation implies spatial and temporal differences in the carbonate formation processes. Building on these previous studies, we sampled carbonates from the ophiolite and, incorporating published data, distinguished major facies. These carbonates are dominantly calcite, with magnesite, dolomite and aragonite present in some facies. Previous authors have also identified the presence of portlandite and huntite [7, 15].

The major carbonate facies have been classified as follows:

- i). Magnesite veins in host peridotite; (± dolomite, calcite, antigorite, amorphous silica).
- ii). Calcite veins in host peridotites; (± serpentine).
- iii). Dolomite cemented Miocene conglomerates; [18].
- iv). Calcite cemented Quaternary conglomerates;
- v). Sedimentary breccias;
- vi). Ancient travertine;

- vii). Soil zone travertine, containing calcite replaced vegetation;
- The following facies are found forming at the present day:
- viii). Carbonate efflorescence;
- ix). Modern carbonate precipitates;
- x). Modern carbonate crusts;

Inactive, ancient surface carbonates display a common, non-cyclical stratigraphy across the region, suggesting common processes of formation. Here, we are focussing on two major sites of carbonate production, Wadi Madaq in the UAE and Nizwa, Oman. Wadi Madaq is located to the NW end of the Wadi Ham fault zone, a major lineament running NW-SE through the mantle sequence [19].

3. Results

3.1. Stable isotopes

Stable isotope data has been collected from various facies at two sites: Nizwa, Oman and Wadi Madaq, UAE. These samples include modern carbonates, soil zone travertines, ancient travertines, conglomerates and veins (Figure 1).

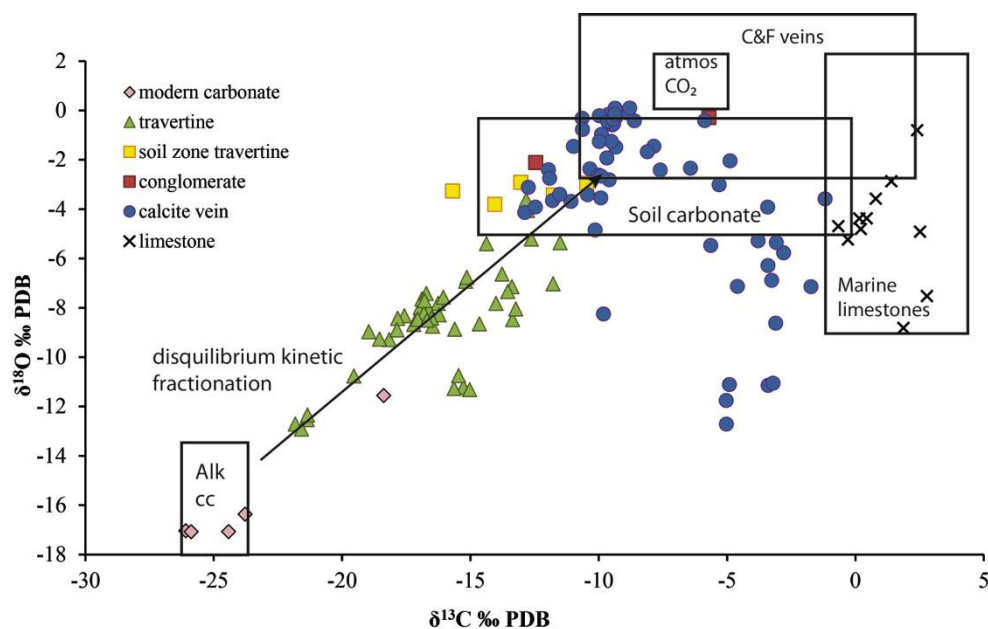


Figure 1. Our $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from different carbonate facies occurring across the ophiolite. Fields for Alk cc, Soil carbonate and C&F veins are from Clark and Fontes [5]. Marine limestones field includes Tertiary and Cretaceous age data from Veizer et. al.[21]. Alk cc = carbonate crusts formed from kinetic fractionation of atmospheric CO_2 , C&F veins = analyses of calcite veins.

Small amounts of modern carbonate can be observed forming at the present day in the ophiolite at hyperalkaline ($\text{pH} > 11$), $\text{Ca}(\text{OH})_2$ springs [10], these include surface crusts and layered deposits in channels. Modern carbonate crusts are part of this group, forming on the surface of stagnant hyperalkaline waters. These form a small field with highly depleted $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values ($\sim -26\text{‰ PDB}$, -16‰ PDB respectively). Similarly, layered deposits from shallow irrigation channels have very low $\delta^{13}\text{C} \sim -25\text{‰}$.

In comparison, our analyses of ancient travertine deposits show a large range in $\delta^{13}\text{C}$ of -10.5 to -20% . Soil zone travertines and conglomerates cluster towards the upper end of this range, within the field of formation in equilibrium with soil bicarbonate. Compared to surface deposits, magnesite and calcite veins have relatively high $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of -12 to -2% PDB and -6 to $+1\%$ PDB respectively.

3.2. Strontium Isotopes

Given their similar hydrogeochemical behaviours, strontium can be used as a proxy for calcium, and can provide insight into Ca sources in carbonate minerals. Its wide range of isotope variation makes it easier to distinguish individual source reservoirs (Table 1). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations have been used to trace the source of Ca incorporated into carbonate deposits.

Table 1: Average measured Sr analyses. Tertiary and Cretaceous limestone values from [21]; Harzburgite values from [22–23]. Meteoric and modern seawater values from [24].

Rock Type	Samples (n)	$^{87}\text{Sr}/^{86}\text{Sr}$ ratio (range)	$^{87}\text{Sr}/^{86}\text{Sr}$ ratio (average)	Sr ppm (range)	Sr ppm (average)
Potential source water samples					
Meteoric water		0.7092	0.7092	7.9	7.9
Modern seawater		0.7092	0.7092	8.0	8.0
Tertiary limestone		0.70766 – 0.70914	0.70867	No data	No data
Cretaceous limestone		0.70722 – 0.70796	0.70755	945 – 1208	1055
Potential source rock samples					
Harzburgite	3	0.70588 – 0.70767	0.70677	0.6 – 2.3	1.3
Gabbro	1	0.70540	0.70540	287	287
Local Cretaceous limestone	3	0.70837 – 0.70886	0.70865	76 – 520	315
Local Tertiary limestone	3	0.70807 – 0.70820	0.70816	203 – 344	274
Carbonate samples					
Magnesite veins	5	0.70837 – 0.70868	0.70851	14 – 14330	3553
Calcite veins	6	0.70831 – 0.70882	0.70862	133 – 5532	1709
Ancient Travertine	12	0.70775 – 0.70834	0.70802	114 – 394	218
Modern Carbonate	2	0.70807 – 0.70821	0.70814	164 – 277	221

Surface deposits (modern carbonates and ancient travertines) have a small range in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations, 0.70775 – 0.70834 and 114 – 394 ppm respectively (Table 1). These overlap values for Tertiary limestones and have similar Sr concentrations to Cretaceous limestones (Figure 3). Subsurface veins display an extensive range in Sr concentrations (14 – 14,330 ppm), which is much greater than any other carbonate facies. However, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have a similar range to Cretaceous limestones.

4. Discussion

Measurements and estimates of natural mineral carbonation show relatively rapid rates. Using the average age of carbonate in the ophiolite, together with an estimate of total volume of carbonate, Kelemen et al. [11] calculate that carbonate is formed at a rate of $\sim 5 \times 10^4$ t/year. Our study questions whether these estimates take into account recycling of older carbon within natural systems. Failure to account for recycled carbon will lead to underestimation of the rate of sequestration, and overestimation of the total amount of carbon sequestered.

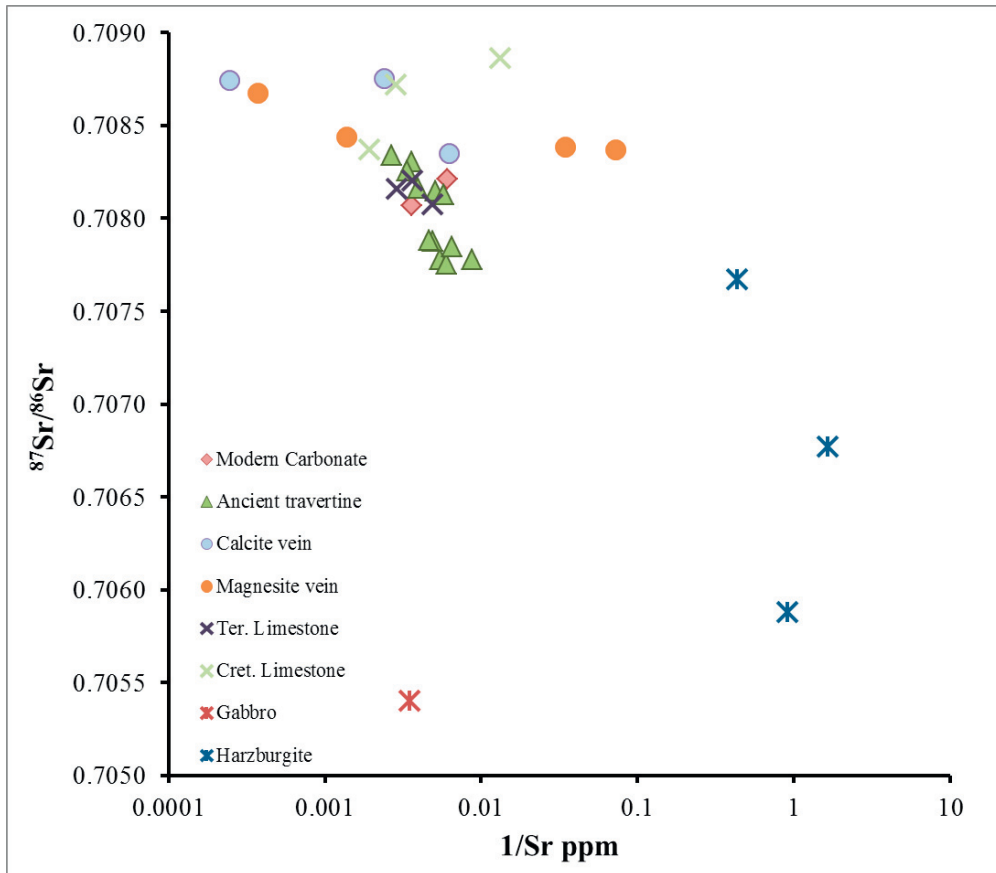


Figure 3: $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1/\text{Sr}$ for analysed carbonates and background rocks.

Previous studies of modern and ancient carbonates show that very negative $\delta^{13}\text{C}$ PDB values occur during the interaction of atmospheric CO_2 and $\text{Ca}(\text{OH})_2$ waters [14, 20]. This depletion has been attributed to kinetic isotope fractionation during the uptake of CO_2 by the hyperalkaline waters [14 and references therein]. On reaching the surface, the reaction of $^{12}\text{CO}_2(\text{atmos}) + \text{OH}^-$ is favoured over that of $^{13}\text{CO}_2(\text{atmos}) + \text{OH}^-$, caused by the lower activation energy of the $^{12}\text{C}-\text{O}$ bonds. This causes preferential incorporation of the $^{12}\text{CO}_3^{2-}$ ion into carbonate minerals, which thus develop a very low $\delta^{13}\text{C}$ signature [20]. Our modern carbonate crusts that were observed forming from atmospheric CO_2 have isotopic values ($\delta^{13}\text{C} \sim -26\%$ PDB) consistent with this process.

In comparison, analyses of ancient travertine deposits show a large range in $\delta^{13}\text{C}$, of -10.5 to -21.8% PDB. None of the samples from ancient travertines have $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ as depleted as the modern crusts. Travertines instead lie on a trajectory from the composition of modern crusts towards the field for bicarbonate fluids in equilibrium with soil CO_2 . Previous studies suggest ancient travertines to have formed by the same process as the minor modern carbonates [5] with the trend to higher $\delta^{13}\text{C}$ interpreted as due to secondary alteration of deposits that initially had values similar to modern carbonates [7, 14]. We interpret this trend as being produced by the mixing of different carbon sources, either at the time of formation or during later alteration. The low end member is most likely atmospheric CO_2 kinetically fractionated into hyperalkaline $\text{Ca}(\text{OH})_2$ waters; other CO_2 sources such as limestone or soil bicarbonate

[3] can provide the higher $\delta^{13}\text{C}$ end-member. Limestones from the surrounding area have $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of -0.3 to $+2.8\text{‰}$ and -8.7 to -0.3‰ respectively, making them plausible candidates for a higher $\delta^{13}\text{C}$ carbon source.

Soil zone travertine containing calcified vegetation has compositions consistent with formation in isotopic equilibrium with either soil or atmospheric CO_2 . Clark & Fontes [5] interpret mixing of the spring waters and shallow groundwater bicarbonate for this facies. Using ^{14}C dating, Clark and Fontes [5] suggested several periods of formation of this facies: 6–8 ka, c. 11 ka, 19–23 ka, 33 ka and >45 ka, interspersed with travertine formation– the last being considerably older than their non-soil zone (vegetation-free) travertine. However, at the same locality, we observed only one cycle of formation, and no evidence of the soil zone travertine interspersed with the vegetation-free travertines [8]. We believe these ‘ages’ are instead the result of mixing with old “dead” carbonate.

Vein carbonates are viewed by most workers as being formed during the formation of ocean crust, emplacement of the ophiolite, and Eocene extension – 30–90 Ma [15, 17]. Geological relations indicate that calcite veins cross-cut magnesite, indicating later formation. Our data show that magnesite and calcite are not in isotopic (C and O) equilibrium with each other, further indicating different times and conditions of formation.

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from our vein samples form a different trajectory from those of Clark et al. [14] indicating that our samples may be earlier veins formed deeper in the ophiolite. Magnesite and calcite veins have relatively high $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values compared to surface deposits. Values are in the range -12 to -2‰ PDB and -6 to $+1\text{‰}$ PDB respectively – significantly closer to those of regional limestones ($\delta^{13}\text{C}$ -0.3 to $+2.8\text{‰}$ PDB and $\delta^{18}\text{O}$ -8.8 to -0.3‰ PDB). It is likely that sub-surface veins incorporate carbon and oxygen that has been partially derived from limestones.

Carbonate samples from the ophiolite have similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations to Cretaceous and Tertiary limestones from the local area. This indicates that carbonate-forming fluids may have interacted with limestones around the ophiolite. These are a natural source of carbon which can easily be reworked and reincorporated into carbonate deposits elsewhere. Therefore, the carbonate deposits may not be created solely from atmospheric CO_2 but instead represent a mixture of carbon sources.

Kelemen et. al. [7] consider Sr, Ca and carbon to all have the same source. The authors indicate that carbonates with $^{87}\text{Sr}/^{86}\text{Sr}$ signatures similar to limestones have “distinctly different” $\delta^{13}\text{C}$ values. Analysis of regional limestones gives $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of -0.3 to $+2.8\text{‰}$ PDB and -8.8 to -0.3‰ PDB respectively, compared to carbonates which have $\delta^{13}\text{C}$ values $\geq -33\text{‰}$, and $\delta^{18}\text{O}$ -17 to 0‰ . They argue that these differences are sufficient to rule out limestones and clastic sediments as source reservoirs. However, our analysis of carbonate veins and ancient travertines, alongside previously published data [7] give $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are identical to those of Mesozoic limestones. The difference in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values between limestones and ophiolite-hosted peridotites is due to the mixing of carbon and oxygen from multiple sources. Dismissing limestones as a potential source for CO_2 is contrary to this evidence for a mixed carbonate source.

4. Conclusion

Geological and isotopic evidence indicates that mixing of contemporary atmospheric carbon and recycled older carbon take place during the ongoing carbonation of the Oman-UAE ophiolite sequence. Cretaceous-Jurassic limestones surrounding the ophiolite provide a potential source of carbon. Isotopic values support this, as they form a mixing trend between contemporary atmospheric carbon drawn down by hyperalkaline waters and marine limestones. Therefore samples appear to reflect input from both atmospheric and recycled sources.

Further investigation is necessary to determine how much of the total carbon held within carbonate deposits has been incorporated from older, recycled sources, and thus an accurate estimate of the rates and volumes of carbon sequestration in the ophiolite.

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