

DETERIORATION OF CONCRETE: APPLICATION OF STABLE ISOTOPES

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Abstract

Multiproxy approaches provide advanced understanding of concrete deterioration processes such as sulfate attack. We introduce here isotopic signatures supplementary to hydrochemistry, elemental compositions, mineralogy, and microstructure of solids. The carbonate origin for thaumasite can be deciphered on the basis of the $\delta^{13}\text{C}_{\text{VPDB}}$ values, which indicate the dissolved inorganic carbon from groundwater. In contrast, CaCO_3 sinter in drainages can be referred to CO_2 absorption. The $\delta^{34}\text{S}_{\text{VCDT}}$ values are used for identifying the source of sulfate. It shows that thaumasite formation is related to the sulfate from local infiltrating groundwater. Interstitial solutions from concrete that has suffered sulfate attack were squeezed by a hydraulic press. The extracted solutions contain up to 65 g/L total dissolved solids. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values (VSMOW) display a strong enrichment of the heavy isotopes versus the local infiltrating solutions. This trend is in accordance with an enrichment of conservative (trace) elements (e.g., Rb^+ and Li^+). Consequently, highly enriched and deleterious sulfate solutions are related to evaporation.

Keywords: sulfate attack, concrete, thaumasite, stable isotopes

1 INTRODUCTION

Under the most common environmental conditions, concrete has high durability. However, various degradation processes of concrete structures such as the thaumasite form of sulfate attack (TSA), alkali-aggregate reactions (AARs), and drainage clogging can be induced by external water–rock interaction. As a result, the appearance of any of these damaging mechanisms leads to a reduced service life and additional costs for remediation and maintenance. Therefore, processes causing concrete damage are of great economic and scientific interest, leading to numerous field and laboratory studies [1–9]. Despite the large number of studies available, a detailed understanding of the interaction between the actual environmental conditions and all the substances used in concrete is still lacking.

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By introducing multiproxy approaches for the water–cement aggregate system, new fundamental insights can be gained. This includes trace element measurements such as Sr^{2+} , Rb^+ , Li^+ , and stable isotope ratios of $^{34}\text{S}/^{32}\text{S}$, $^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$, and $^2\text{H}/\text{H}$ supplementary to the main elemental composition of solids and liquids, as well as the mineralogy and microstructure of solids. In this study, we demonstrate their potential in the field of concrete degradation by selected case studies where thaumasite formation appears.

In earlier scientific studies, the application of stable isotopes has successfully been introduced to inorganic binder research to gain a better understanding of processes such as cement and mortar setting, carbonation of concrete, or sinter formation in drainage systems by groundwater–concrete interaction [10–16]. Nevertheless, for studies implicating thaumasite formation in concrete, these techniques have been used rarely. Early investigations of concrete with thaumasite and carbonation unveiled that there are significant isotopic variations at the microscale, representing both primary and secondary signatures [17]. The origin of aggressive ions for mineral formation (CO_3^{2-} , SO_4^{2-} , and OH) is still debated [18–21].

2 MATERIALS AND METHODS

2.1 General

In several case studies in Austrian tunnels, solid materials and aqueous solutions were sampled. The solids included deteriorated and nonaltered concrete as well as calcium carbonate sinters (Figure 1). Unconsolidated mushy material could be shoveled into plastic bags, while concrete with stable appearance was sampled by taking 10-cm drilling cores. Solutions comprised drainage solutions and local groundwater. In addition, interstitial solutions were separated from the sampled damaged concrete materials by a specially adapted hydraulic press [22]. Solutions were pressed out a few hours after sampling at room temperature at pressures up to 1300 kN. Depending on the amount of used material, volumes of 35–200 ml solution were acquired corresponding to about 5–20 wt% of water.

2.2 Solid analyses

Solid materials were carefully dried at 40°C and powdered for X-ray diffraction (XRD) analyses. The XRD patterns for mineralogical compositions were recorded with a cobalt tube operating at 45 kV and 40 mA. High-resolution surface imaging was performed using scanning electron microscopy (SEM) with the secondary electron imaging (SEI) mode and AuPd sputtered samples. In situ chemical analyses and back-scattered electron (BSE) imaging were carried out on polished and carbon-coated thin sections by electron microprobe (EPMA). The operation settings were 10 kV and 6 nA for quantitative analyses and 15 kV and 10 nA for BSE imaging. Stable isotope ratios of carbon and oxygen ($^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$) of solid carbonate were obtained by isotope ratio mass spectroscopy (IRMS) applying the phosphoric acid method. The results are given as $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ in ‰. For sulfur isotope measurements, the samples were pretreated by dissolution in diluted HCl. In the filtrated solution, the dissolved sulfate ions were quantitatively precipitated as BaSO_4 by the addition of BaCl_2 in excess. Sulfur isotope ratios ($^{34}\text{S}/^{32}\text{S}$) were analyzed by mass spectrometry and the results are given as $\delta^{34}\text{S}_{\text{VCDT}}$ values in ‰. Stable isotope measurements on thaumasite were performed on prepurified material similar as described in [5]. Sieved out material (<500 μm) was placed in either ethanol or MQ water and treated with ultrasound. Subsequently, the thaumasite-containing suspension was decanted to separate particles with higher specific weight (aggregates, secondary calcite) compared to thaumasite. After repeating this procedure several times, the XRD analysis of the remaining suspended material indicated up to about 98 wt% thaumasite.

2.3 Aqueous solution analyses

During sampling in the field, the pH, electrical conductivity (EC), and temperature of the drainage solutions and groundwater were measured. The alkalinity was measured by titration with 0.05 M HCl in 0.45- μm -filtered solutions. The concentrations of major and trace elements were determined by ion chromatography (IC) and inductively coupled plasma mass spectroscopy (ICP-MS). The $\delta^{13}\text{C}$ values of dissolved inorganic carbon (DIC) were acquired by adding phosphoric acid and using IRMS. For sulfur isotope ratios ($^{34}\text{S}/^{32}\text{S}$) measurements, the solutions were acidified and aqueous SO_4^{2-} was precipitated as BaSO_4 by BaCl_2 as described above for solids. The $^{18}\text{O}/^{16}\text{O}$ ratios of H_2O molecules were analyzed by the classical $\text{CO}_2\text{-H}_2\text{O}$ equilibrium technique. The isotopes of hydrogen $^2\text{H}/\text{H}$ were measured using a mass spectrometer coupled to a high-temperature oven by chromium reduction. Results are given as $\delta^{18}\text{O}_{\text{VSMOW}}$ and $\delta^2\text{H}_{\text{VSMOW}}$ in ‰.

3 RESULTS AND DISCUSSION

A typical XRD pattern and an SEI for a heavily damaged concrete sample are displayed in Figures 2 and 3. While the SEI shows pure thaumasite needles for this specific area, the XRD pattern reveals thaumasite, gypsum, bassanite, dolomite, calcite, aragonite, and quartz. From the investigations of nondeteriorated material, it is known that dolomite, calcite, and small amounts of quartz were used as aggregates. Furthermore, portlandite ($\text{Ca}(\text{OH})_2$) and poorly crystalline CSH phases are found by XRD. Subsequently, thaumasite, gypsum, secondary calcite, and aragonite are newly formed during the sulfate attack. Bassanite is interpreted as a product of sample drying. Figure 4 shows a BSE image of a damaged concrete sample. Apparently, the dissolution of dolomitic aggregates is a by-product of the sulfate attack. As dolomite is incongruently dissolving, the reaction products are calcite and brucite. This assumption is verified as newly formed calcites are highly enriched in Sr^{2+} . The elevated Sr^{2+} content is from local Sr^{2+} -rich groundwater (Table 1). EPMA measurements of newly formed calcite rise up to 0.202 ± 0.011 wt% of Sr.

Consequently, the question arises whether the dissolution of dolomite contributes to thaumasite formation. This leads to the aspect of the carbonate source for thaumasite formation. It is proposed that the carbonate may be gained from CO_2 absorption, dissolution of aggregates, or infiltration of carbonate-containing solutions [18,21]. Results from a study in a tunnel indicate that DIC of infiltrating carbonate-rich groundwater supplies the carbonate for thaumasite formation. This is based on the $\delta^{13}\text{C}$ values of DIC in local groundwater that interacts with the concrete and of thaumasite from the deteriorated concrete. Both $\delta^{13}\text{C}$ values are close to -7‰ . In contrast, calcite sinters from the same tunnel were found to have $\delta^{13}\text{C}$ values ranging from -40‰ to -25‰ . This $\delta^{13}\text{C}$ range is referred to the absorption of CO_2 gas where $\delta^{13}\text{C}$ values equal to -25‰ are obtained from the earth's atmosphere. The lower values are caused by the impact of CO_2 from combustion of fossil fuels in power engines from traffic or during construction. Carbonate from aggregates, which consist of marine limestone, lies in a completely different range close to $0 \pm 2\text{‰}$. The latter carbonate source is therefore most probably not a valid precursor for both thaumasite and calcite formation (Figure 5).

In the case of potential sulfate phases (thaumasite, gypsum, and ettringite), the sulfate source can be deciphered by $\delta^{34}\text{S}$ values. In a case study performed in a railroad tunnel, $\delta^{34}\text{S}$ of thaumasite, soot from the tunnel wall, and dissolved sulfate from interacting local groundwater that is recharged from areas containing marine evaporates (calcium sulfates) were analyzed. The $\delta^{34}\text{S}$ values of thaumasite and groundwater sulfate are within the same range close to $+20\text{‰}$. Accordingly, the source of sulfate in thaumasite is clearly related to the infiltrating groundwater. Sulfate for intensive thaumasite formation originating from other sources such as the oxidation of soot or pyrite or atmospheric contribution can be ruled out [4,18,20].

Moreover, interstitial solutions of concrete that was deteriorated by TSA were separated by a hydraulic press. The extracted solutions contain a very high content of total dissolved solids (TDS) up to 65 g/L TDS. Both major and trace elements are present at elevated level in the interstitial solutions. A comparison of a local groundwater, a drainage solution, and an interstitial solution is displayed in Table 1. The analyzed $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of H_2O indicate a strong enrichment of ^2H and ^{18}O versus ^1H and ^{16}O isotopes compared to the local infiltrating groundwater, which can be followed by an evaporation trend. This isotopic behavior is in accordance with the respective enrichment of ions such as Rb^+ , K^+ , Li^+ , NO_3^- , Cl^- , and Na^+ in the solution. Obviously, ions that are usually regarded as conservative such as Na^+ and Cl^- do not show constant molar ratios in the interstitial solutions. This may be caused by different rocks in the catchment area of the local groundwater (e.g., rock salt) and various chemical compositions and degrees of interaction with the present concrete (e.g., Na-rich setting accelerators). An extreme Na^+ content can even result in mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) effloresces. Thus dissolved ions that are present in the solution at lower concentration levels seem to be more suitable to follow the evaporation trend (Figure 6). Elevated TDS of extracted interstitial solutions can be directly related to the $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/\text{H}$ isotope fractionation during evaporation. Elemental and isotopic data give clear evidence that highly elevated SO_4^{2-} solutions are caused by the liberation of H_2O from the interstitial solution into the atmosphere. In consequence, evaporation is a process that can lead to TSA even if SO_4^{2-} contents of the infiltrating solutions are comparatively low.

4 CONCLUSIONS

Multiproxy approaches provide promising tools to reconstruct complex dissolution–precipitation reactions in the water–cement aggregate systems.

Stable isotopic signatures are powerful tools to decipher the sources of CO_3^{2-} in calcite as well as CO_3^{2-} and SO_4^{2-} in thaumasite.

Incongruent dissolution of dolomite aggregates is a consequence of intensive sulfate attack. However, there is no evidence that this reaction is providing CO_3^{2-} for thaumasite formation.

Chemical and isotopic compositions of the interstitial solutions give evidence for evaporation as a possible driving force for TSA.

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Figure 1: Concrete completely destroyed by intensive thaumasite formation.

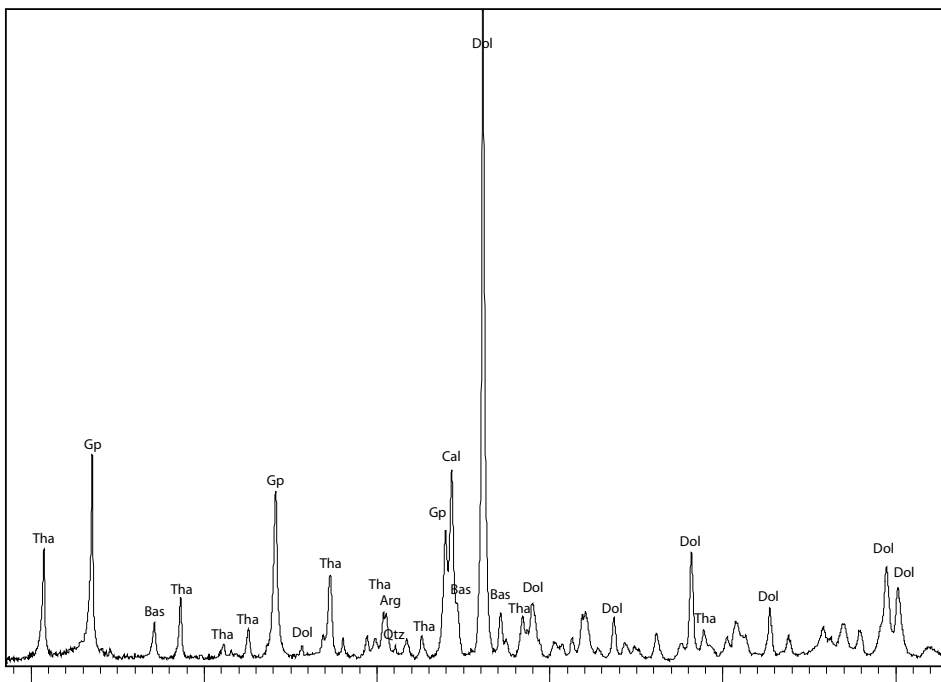


Figure 2: XRD pattern of concrete that has suffered intensive sulfate attack. Gypsum (Gp), bassanite (Bas), dolomite (Dol), calcite (Cal), aragonite (Arg), quartz (Qtz).

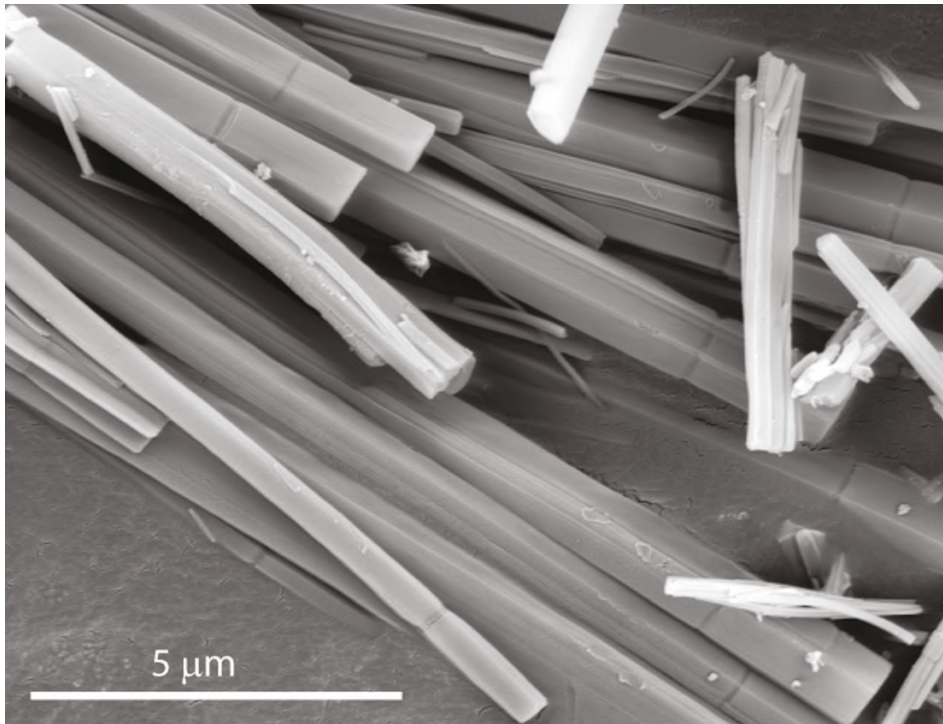


Figure 3: Secondary electron image (SEI) of thaumasite needles found in this region of deteriorated concrete.

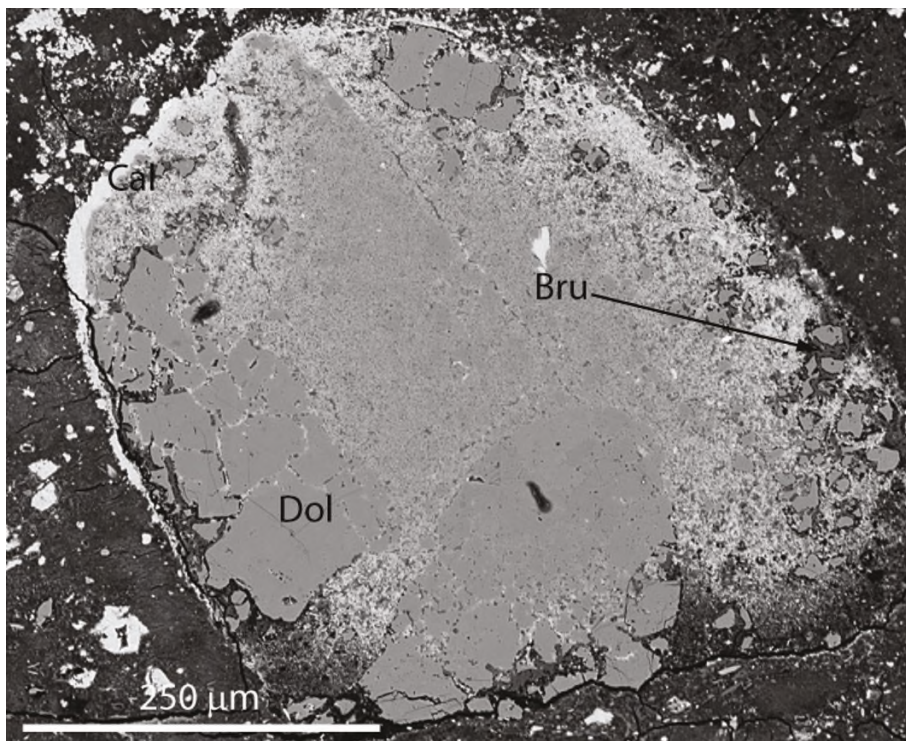


Figure 4: BSE image of a partially dissolved dolomite aggregate (Dol) in a matrix of mainly thaumasite. The reaction products of the incongruent dolomite dissolution are calcite (Cal) and brucite (Bru).

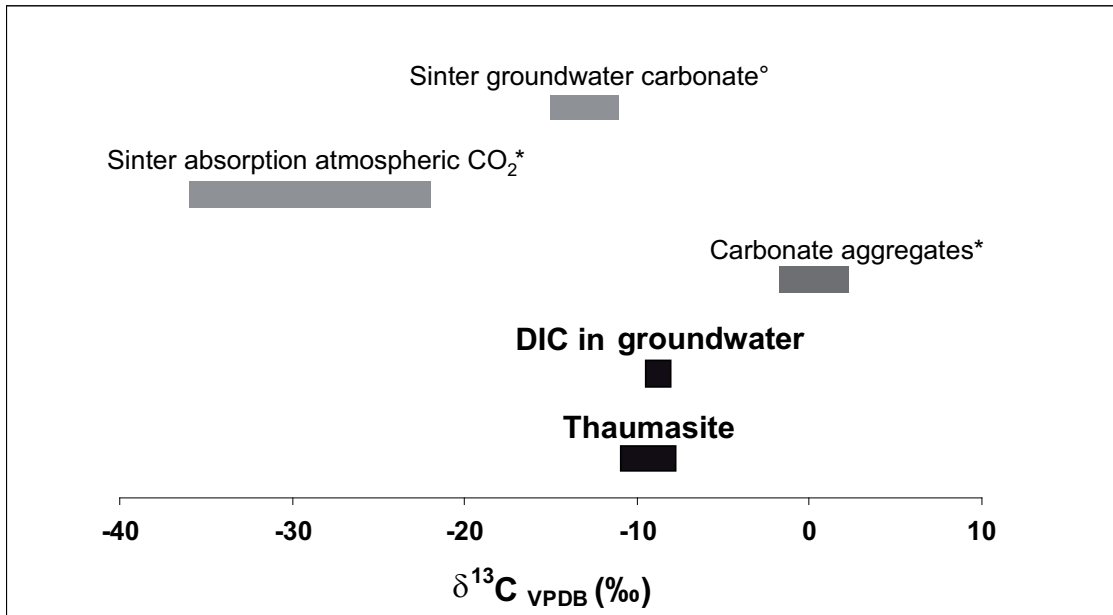


Figure 5: $\delta^{13}\text{C}_{\text{VPDB}}$ values of the thaumasite and local ground water compared with those from the literature (°values from literature, *values this study and literature) [10].

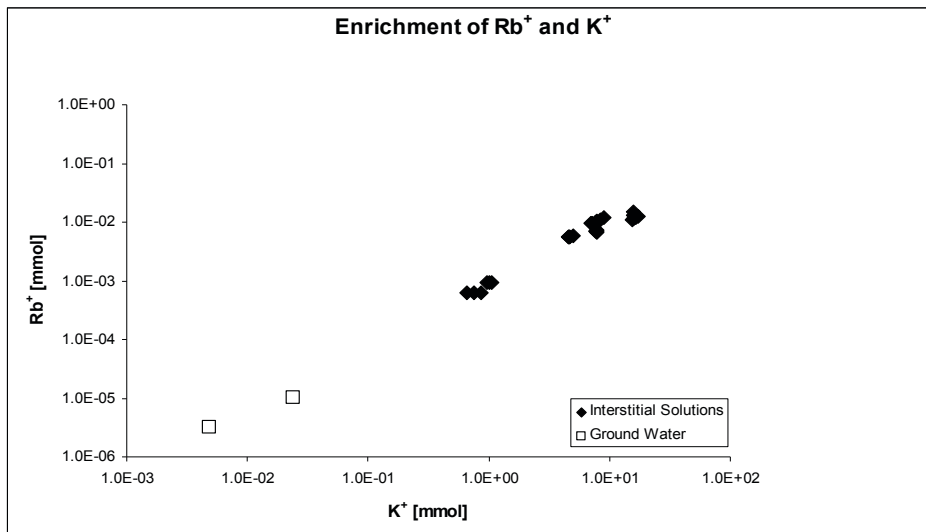


Figure 6: The enrichment of ions with conservative behavior indicating evaporation which leads to high sulfate solutions.

TABLE 1: Typical composition and isotopic signatures of groundwater, drainage water and an interstitial solution by IC, ICPMS, and IRMS.

	Ground water	Drainage water	Interstitial solution
pH	7.54	7.78	8.79
Na ⁺ 0.10	3.5	9.5, 7.78	7239
K ⁺ 0.01	0.9	1.3	307
Ca ²⁺ 0.01	193	206	942
Mg ²⁺ 0.04	31.6	35.4	636
NO ₃ ⁻ 0.01	1.9	1.5	70.0
Cl ⁻ 0.01	3.8	12.9	2930
HCO ₃ ⁻ 0.02	162	167	188
SO ₄ ²⁻ 0.50	464	502	15953
Li ⁺ 0.01	0.0058	0.0050	0.87
Sr ²⁺ 0.01	2.26	3.78	3.76
Rb ⁺ 0.01	0.00087	0.00086	0.62
TDS ¹ 0.01	865	935	28274
δ ¹⁸ O	-12.0	-12.4	-6.6
δ ² H	-82.8	-82.7	-50.0

¹Total dissolved solids.

Concentrations are given in mg/L; δ²H and δ¹⁸O values in ‰ (VSMOW).