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Quantifying carbonate concentration alongside the measurement of isotope ratios in sediment samples via continuous flow IRMS analysis

Rationale: The measurement of $\delta^{18}O$ and $\delta^{13}C$ in carbonate samples has become standard practice for the reconstruction of past climate and oceanographic conditions. Besides the measurement of biogenic carbonates, e.g., foraminifera, brachiopods or corals, bulk sediment containing variable quantities of carbonate is often analysed to understand the evolution of palaeoenvironmental conditions through time. In addition to the isotopic ratios of carbonate in bulk sediments, also the amount of carbonate present in a sample may carry important information about the palaeoenvironment, e.g., as an input into cyclostratigraphic models allowing for precise quantification of age intervals represented by a sedimentary succession.
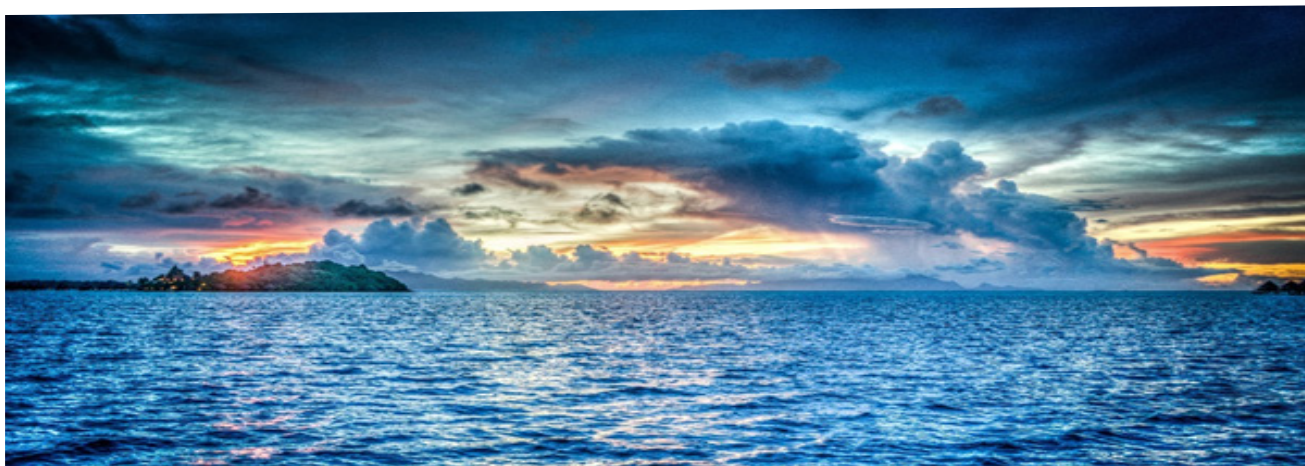
IRMS analysis of carbonate samples is usually only employed to quantify the isotopic ratios of carbon and oxygen. Carbonate concentrations, on the other hand, are not usually quantified. Researchers using EA-IRMS analysis will be familiar with the comparison of the peak areas on simultaneous IRMS and TCD detectors to give elemental composition, with results in good agreement. It is well known that mass spectrometric analysis yields an excellent linear response between signal amplitude and amount of reacted carbonate. It is this linear response that can efficiently be used to derive carbonate concentrations of bulk sediment powders. Carbonate concentrations can thus be quantified simultaneously with $\delta^{18}O$ and $\delta^{13}C$ on small sample aliquots allowing for direct intercomparison of these data, saving sample material and avoiding additional cost and effort for dedicated carbonate concentration measurements.

Analytical Setup: Work was carried out using a continuous flow IRMS system consisting of a heated sample block, Sercon XYZ autosampler and 20-22 IRMS, with manual acid delivery. A measurement routine allowing for the measurement of 80 unknowns alongside 30 aliquots of two in-house standard materials (CAR, NCA) was implemented. This routine allows for two-point calibration of isotopic ratios, as well as constraining (using CAR) and validating (using NCA) a signal yield function that can be used to calculate carbonate concentrations in the unknowns (Fig. 1).
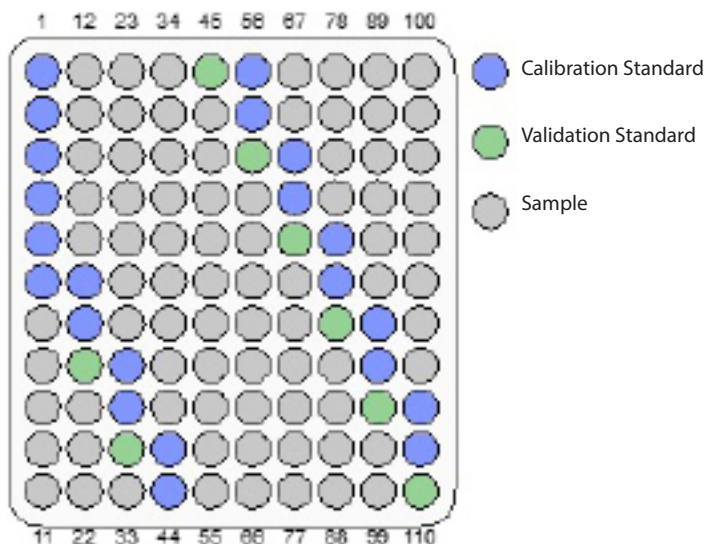

Fig. 1: Arrangement of standards and samples on the autosampler for a routine batch of simultaneous isotope ratio and carbonate concentration measurements. CAR (Carrara Marble, calibration standard) is used to constrain the linear response function of signal yield versus carbonate weight and NCA (Namibian Carbonatite, validation standard) is taken to control the precision of the method.

CAR aliquots of 0.2, 0.4, 0.6, 0.8 and 1.0 mg weight as well as additional 17 CAR aliquots and 8 aliquots of NCA of 0.5 mg weight are weighed into 4.5 ml borosilicate Labco Exetainers® to ±10 % accuracy and 1 µg precision using a Sartorius MSE3.6P-000-DM Cubis® Micro Balance. Unknowns are weighed to 1 µg precision with a target of 500 µg carbonate using estimated carbonate contents from visual inspection. All vials were flushed with He for 80 seconds and then reacted with ca. 100 µL of manually injected, nominally anhydrous phosphoric acid. Measurements followed standard procedures for continuous flow mass spectrometry.

Results: At a trap current of 450 and emission of 1,800 the resulting signal yield on mass 44 was in the range of 360 to 375 nAs/mg. Over three months correlation coefficients of signal intensity versus weight of CAR ranged from $r^2 = 0.9986$ to 0.9999 (n = 12) without any outliers (Fig. 2).
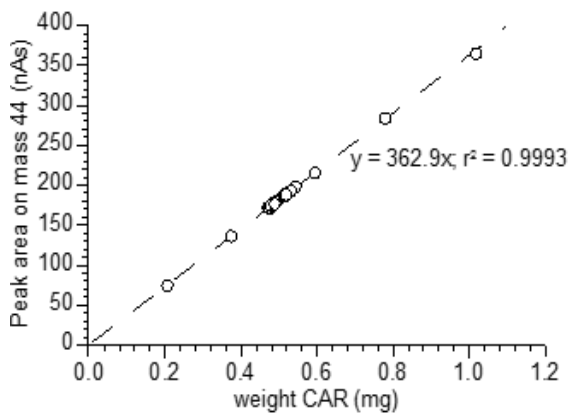
Fig. 2: Correlation of peak intensity and weight of calibration standard CAP for one batch run (May 09th, 2017).

Fig. 3: Reproducibility of calculated carbonate concentrations in validation standard NCA (12 batches, 96 analyses).

Under the assumption that CAR is made of pure $CaCO_3$ and unknowns contain carbonate only in the form of $CaCO_3$, the signal yield for each validation standard and unknown can be translated into a carbonate concentration estimate using the slope of the signal yield function. Over a period of three months, the resulting carbonate concentration estimate for NCA was 96.8 ±0.9 % (2 sd, n = 96) with zero outliers (Fig. 3), evidencing the precision and reliability of the method.

Repeat runs of 64 powdered rock samples with unknown carbonate content confirm the reproducibility of the method (Fig. 4). Correspondence between two repeat measurements of these natural samples is 1.5 % or better in 90 % of the measurements and slightly larger deviations are expected to be related to small scale heterogeneity of the material.
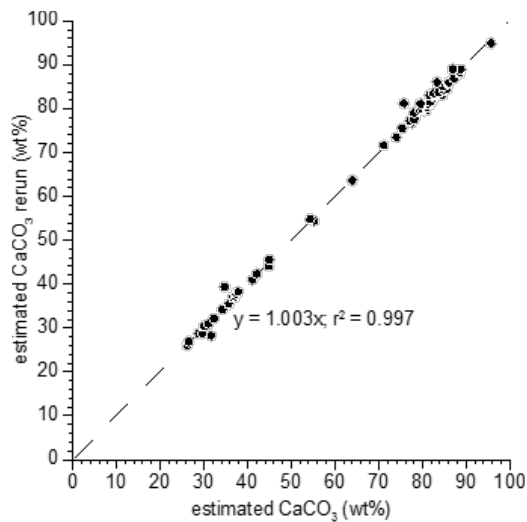

Fig. 4: Repeat measurements of 64 powdered natural samples with unknown carbonate content. The resulting trend line is indicative of 1:1 correspondence. Deviations of > 2 % (up to 5.5 %) between first and second measurement in 5 samples is expected to be related to sample heterogeneity.
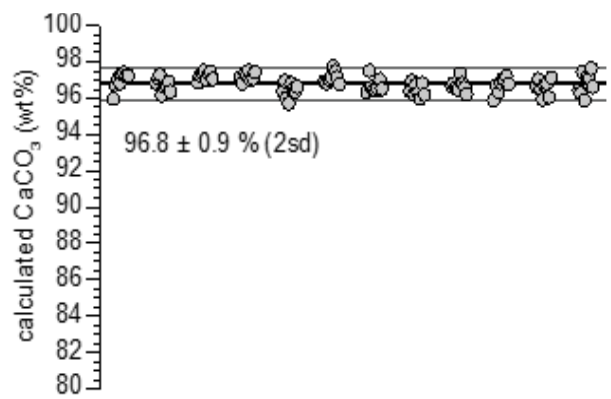
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