Carbonate-associated sulfate: A seawater proxy with potential and weaknesses

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It is generally considered that the sulfate ion is incorporated into the carbonate lattice during precipitation, consequently called carbonate-associated sulfate (CAS). Even if the mechanism of incorporation as well as the potential effects that diagenesis might have on the sulfur isotopic composition of CAS are not completely understood, it is regarded as a powerful proxy for reconstructing the primary seawater sulfate sulfur composition. Both, analytical and diagenetic aspects can affect the isotopic composition of CAS and have to be carefully considered when talking about carbonate-associated sulfate in the context of primary seawater composition. Bacterial sulfate reduction, particularly under sulfate limiting conditions in the pore water realm, causes ^{34}S-enrichment in the residual dissolved sulfate. On the other hand, sulfide oxidation results in ^{34}S-depleted sulfate. If incorporated, both would alter $\delta^{34}S_{CAS}$.

When extracting the original CAS signal it is essential that any other sulfates, which could influence this primary information, are removed. Otherwise, a mixed δ^{34}S signal is generated, composed of primary and secondary sulfate sulfur, that does not represent the sulfate sulfur isotopic composition of the paleo-seawater. Various methods of CAS extraction were developd, using different chemicals (e.g., NaCl, NaOCl, H_2O_2) or only deionised water to exclude non-CAS, organic sulfur, and metastable sulfides. These different methods result in variations in $\delta^{34}S_{CAS}$, but, no thorough calibration or comparison between the methods is presently available.

Based on comprehensive leaching procedures and detailed data sets comparing several extraction methods for CAS, we are able to identify the sources of secondary sulfate which has the potential to affect the primary CAS isotopic signal during extraction. Further, we determined the effect of pyrite oxidation on CAS by using δ^{34}S data generated from chromium-reducible sulfur (CRS). The aim of our research is to establish a rigid protocol for CAS extraction that enables the interpretation of sulfur isotope data from carbonate-associated sulfate as a true seawater proxy.

Petrologic significance of high-precision zircon U-Pb dates from the Skaergaard intrusive complex

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The Skaergaard intrusion (East Greenland) has long been regarded as a type example of a layered intrusion that essentially evolved by closed-system fractional crystallization. Late-stage ferrodiorites, however, are depleted with respect to ^{18}O ($\delta^{18}O_{magma}$ ~3-4 ‰), recording incorporation of meteoric water derived oxygen into the magma prior to final solidification [1]. Incorporation of meteoric water into these late-stage differentiates requires either devolatilization of hydrated stoped blocks or remelting after subsolidus hydrothermal alteration. Such processes probably operated on timescales of ~100 ka and are thus potentially resolvable by high-precision ID-TIMS U-Pb geochronology.

We present high-precision zircon U-Pb dates for low-δ^{18}O ferrodiorites from the Sandwich Horizon (SH), a normal-δ^{18}O pegmatite from the lower zone of the layered series and the tholeiitic Basistoppen sill, that was emplaced ~200 m above the SH shortly after solidification of the Skaergaard magma [2]. Weighted mean $^{206}Pb/^{238}U$ zircon dates of statistically equivalent clusters yield precise crystallization ages for the normal-δ^{18}O pegmatite and the Basistoppen sill that overlap within subpermil uncertainty. In contrast, $^{206}Pb/^{238}U$ zircon dates from the SH do not form a statistically equivalent cluster. We interpret the observed scatter to reflect 321 ± 182 ka of crystallization. Notably, the youngest zircon from the SH is 125 ± 84 ka younger than the age of intrusion of the Basistoppen sill. This requires that either the SH was still molten or was remelted after emplacement of the Basistoppen sill. If the latter interpretation is correct, it would support models for the generation of late-stage low-δ^{18}O magmas that involve remelting induced by intrusion of the Basistoppen sill. These results demonstrate the potential of high-precision U-Pb geochronology for resolving complex histories of Cenozoic intrusions.

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