Grain-scale heterogeneities in the stable carbon and oxygen isotopic compositions of the international standard calcite materials

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The stable carbon and oxygen isotopic compositions of carbonate, especially biological calcite (e.g., foraminifera and coral), are useful as environmental tracers to reconstruct paleoclimate and paleo-oceanic circulations. In recent studies, the stable isotopic analyses for sub-100 micrograms quantities of carbonate are needed to reconstruct high-resolution environmental fluctuations. In this study, we investigated the magnitude of grain-scale (from 6 to 88 micrograms) heterogeneities in carbon and oxygen isotopic compositions of international standard reference calcite materials (NBS 19, NBS 18, IAEA-CO-1, and IAEA-CO-8) in order to determine which standard reference calcite materials are suitable for a microscale, high-resolution, isotopic analysis. In order to serve this purpose, we have upgraded the analytical system reported in Ishimura et al. (2004) and improved both stability and precision during grain-scale isotopic analyses. This continuous-flow isotope ratio mass spectrometry (CF-IRMS) system realizes a simultaneous determination of both the stable carbon and oxygen isotopes with standard deviations (S.D.) of less than 0.05 permil for CO_2 gas.

Based on the S.D. of the stable carbon and oxygen isotopic compositions determined for CO_2 gases evolved from the different grains of the same calcite material, we found that NBS19, IAEA-CO-1, and IEAE-CO-8 were homogeneous for stable carbon isotope (less than 0.10 permil S.D.), and only NBS19 was homogeneous for stable oxygen isotope (less than 0.14 permil S.D.). On the level of single grains, we found that both IAEA-CO-1 and IAEA-CO-8 were heterogeneous for stable oxygen isotope (1.46 permil and 0.76 permil S.D., respectively), and NBS18 was heterogeneous for both the stable carbon and oxygen isotopes (0.34 permil and 0.54 permil S.D., respectively). Closer inspection of NBS18 grains revealed that the highly deviated isotopic compositions were limited to the colored grains. By excluding such colored grains, we could obtain the homogeneous stable carbon and oxygen isotopic values (less than 0.18 permil and less than 0.16 permil S.D., respectively) for NBS18 as well. We conclude that either NBS19, IAEA-CO-1, or pure grains in NBS18 are suitable to be used as the standard reference material for stable carbon isotope, and either NBS19 or pure grains in NBS18 are suitable to be used as that for stable oxygen isotope during the grain-scale isotopic analyses of calcite. By using the standard reference calcite suitable for the grain-scale isotopic studies, we can enhance the resolution of the isotope geochemistry, climatology, and paleoceanography.