Impact of nitrate contamination on the analysis of carbon and oxygen isotopes in carbonate

BIN Hu1,2, JIANFEI GAO1, CHANGFU FAN1, YANHE LI1, YAN QIN1, YIYONG TIAN2

1Ministry of Natural Resources Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing, China
2Email address: hubin@cags.ac.cn
3Thermo Fisher Scientific, Beijing, China

High-temperature phosphoric acid digestion combined with continuous-flow isotope ratio mass spectrometry (CF-IRMS) is one of the standard methods for the determination of carbon and oxygen isotopes in carbonate. However, the routine sample gas preparation protocol has not been tested by samples with nitrate contamination. We tested the standard high-temperature (72 °C) phosphoric acid digestion method combined with CF-IRMS for the measurement of natural carbonate samples with ~1% nitrate content and nitrate-doped carbonate standards. The δ18O values of doped standards show much poorer precision (1SD = ±0.7‰ on average) than routine measurements (1SD = ±0.1‰), and are systematically higher than the predicted values by ~1.7‰. An abnormal increase in m/z 46 background by > 20 mV was observed after 2 h of measurement for nitrate-doped carbonate standards, indicating a gas contaminant with m/z 46. The elevated baseline may further affect the subsequent samples, even if they are nitrate-free. From the Raman spectra of gases extracted from the nitrate-doped carbonate standards, we identified that the gas species that affect the δ18O results is NO. We propose that it is the product from the thermal decomposition of nitric acid molecule which favored at high temperature:

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\text{NO}_3^- + \text{H}^+ \rightarrow \text{HNO}_3
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4\text{HNO}_3 \rightarrow 4\text{NO}_2 + \text{O}_2 + 2\text{H}_2\text{O}
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Water cleaning and Cu reduction at 250 °C can be used to remove the nitrate contamination. However, these methods either will cause loss in soluble carbonates or is not easy to be integrated to a continuous-flow system. We suggest a low temperature (25 °C) digestion method which requires no pretreatment nor modification on the instrument. For measurements of doped standards reacted at 25°C, the accuracy and precision of the δ13C and δ18O values are indistinguishable from normal results. This approach can be applied to some nitrate-rich speleothems, evaporites and other samples with nitrate contamination.