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

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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 δ^{18}O 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 δ^{18}O results is NO_2. We propose that it is the product from the thermal decomposition of nitric acid molecule which favored at high temperature:

$$NO_3^- + H^+ \rightarrow HNO_3$$

$$4HNO_3 \rightarrow 4NO_2 + O_2 + 2H_2O$$

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 δ^{13}C and δ^{18}O values are indistinguishable from normal results. This approach can be applied to some nitrate-rich speleothems, evaporites and other samples with nitrate contamination.