## Re-evaluating acid digestion for the analysis of organic carbon and nitrogen contents and stable isotope ratios in geological reference materials

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The accurate and precise determination of the total nitrogen (TN) and organic carbon (TOC) abundances and its isotopic compositions ( $\delta^{15}N_{TN}$  and  $\delta^{13}C_{org}$ ) in sedimentary rocks have been considered as important proxies for our interpretation of paleoenvironmental and paleoclimate processes. For the carbon and nitrogen analyses, the following acid digestion techniques have conventionally been employed: (1) acidification followed by sequentially rinsing with deionized water (rinse method), (2) acidification by exposure to an acid vapor (fumigation method), and (3) acidification in silver capsules (capsule method). Among these methods, acidification by the rinse method using hydrochloric acid has been widely used and is the standard treatment method for the elemental and isotopic analyses of both nitrogen and carbon in sedimentary rocks. However, some researchers have reported that the acid strength and heating during the decalcification in the rinse method could lead to a change in the TN and TOC contents and its isotopic compositions. Additionally, previous works showed that the TN and  $\delta^{15}N_{TN}$ values of HCl acidified samples had changed compared with that of untreated samples. In this study, we systematically compared the effect of acidified and non-acidified samples (in rinse method) on the reliability of TN and TOC abundances and  $\delta^{15}N_{TN}$  and  $\delta^{13}C_{org}$  values by using geological reference materials (GRMs) issued by the GSJ and USGS: marine sediments (JMs-1, JMs-2, and SBC-1), stream sediments (JSd-3 and JSd-4), and lake sediment (JLk-1).

The TN and TOC concentrations and  $\delta^{15}N_{TN}$  and  $\delta^{13}C_{org}$  values were measured with a Flash EA1112 elemental analyzer coupled to a Thermo-Finnigan DELTA plus advantage isotope ratio mass spectrometer interfaced with a ConFlo IV at JAMSTEC. Acidified and untreated samples were prepared in three batches to ensure accuracy and precision in the analytical data and evaluate the procedural error. Approximately 200–500 mg of powdered samples was weighted in a 15mL glass tube and acidified in 8 mL 2M or 6M HCl at room temperature or at 70 °C in a thermostatic bath for 24 hours, respectively. Subsequent to acidification, the residue was sequentially rinsed three times with Milli-Q water, and dried at 80 °C for 48 hours in a closed oven with a light Al foil cover. Aliquots of the acid-treated and untreated samples were weighted into a tin capsule (9 ×10 mm, Lüdi) for the carbon and nitrogen analyses. The analytical reproducibility of the TN and TOC concentrations was evaluated by repeated analyses of reference materials (USGS40 and USGS41); the reproducibilities were better than ±1.8 % and ±1.0 %, respectively. The  $\delta^{15}N_{TN}$  and  $\delta^{13}C_{org}$  values are represented in ‰relative to atmospheric N<sub>2</sub> and the Vienna Peedee Belemnite (V-PDB) standard, respectively. The uncertainties in the  $\delta^{15}N_{TN}$  and  $\delta^{13}C_{org}$  values were within ±0.13‰ and ±0.09‰, respectively, as determined by the repeated analyses of reference materials.

Our results show that the average values of TN contents in the rinse method of all GMR samples are lower than that of untreated samples by up to 70 %. Additionally, the  $\delta^{15}N_{TN}$  ratios of acid-treated samples, except for SBC-1, were decreased to 2.1‰ in maximum as compared with untreated samples. The magnitudes of the negative shift of TN and  $\delta^{15}N_{TN}$  values were larger when the samples were acidified in 6M HCl and heated at 70 °C. Loss of <sup>15</sup>N has previously reported during the acidification and was attributed to small losses of acid-soluble proteins and amino acids via the volatilization of oxidized

nitrogenous organic compounds. However, the  $\delta^{15}N_{TN}$  values of SBC-1 are almost stable under the acidified and non-acidified conditions, probably indicating that the organic matter composition in SBC-1 was significantly different from the other GMS samples. On the other hand, as similarly to the nitrogen analysis, the magnitudes of the negative shift of TOC and  $\delta^{13}C_{org}$  values were larger when acidification by 6M HCl and heating at 70 °C of GMR samples. It suggests that the decalcification with 2M HCl was unsatisfied with obtaining accurate results probably because of the poorly-soluble minerals, such as siderite and dolomite that were retained during the acidification. Overall, we propose that the analysis of nitrogen and carbon contents and its isotopic compositions should be separately measured, i.e., non-acidified sample for nitrogen analysis and 6M HCl acidified and heated samples for carbon analysis.