Mineralization rates of organic carbon in freshwater vs marine environments and implications for carbor burial efficiencies

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The mineralization and burial rates of organic carbon in aquatic sediments influence the global carbon cycle and over geological time scales determine the atmospheric CO_2 and oxygen levels. As organic matter descends through the water and then sediment columns, its reactivity towards mineralization decreases. In marine environments, the decrease in organic carbon reactivity was described as a power-law function of carbon age, sometimes referred to as Middelburg power law. The relationship extends over time scales spanning eight orders of magnitude and is largely independent of temperature, exposure to oxygen, concentration of sulfate, and other factors that have been suggested to affect carbon mineralization rates. In contrast, no relationship of this kind was suggested in freshwater where conditions are typically more variable. Using a compilation of data from large lakes, we show that the reactivity of autochthonous organic carbon in fresh water decreases with time according to a similar power-law. The similarity suggests that mineralization rates of organic carbon are determined primarily by intrinsic factors rather than the characteristics of the enviroment. It also suggests that carbon mineralization by sulfate reduction is not fundamentally faster than by methanogenesis, with a particular implication that carbon mineralization rates in oceanic sediments 0.5Ga ago, when sulfate concentrations were low, were not particularly different from today. Our results indicate that carbon reactivity is higher in presence of oxygen, consistent with the enhanced preservation of carbon in anoxic sediments. Using the obtained relationships for oxic and anoxic mineralization rates, we calculate the theoretical burial efficiencies as a function of oxygen exposure time, which match the previously reported observational trends. In contrast to the effect of oxygen, the effect of temperature on specific (per carbon atom) carbon mineralization rates appears to be minor, suggesting that climate-related warming of lake sediments may not lead to increases in specific rates of carbon mineralization.

Highly sensitive and precise analysis of stable chlorine isotope ratio by continuous-flow isotope ratio mass spectrometry

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Recent advancements in continuous-flow isotope ratio mass spectrometry (CF-IRMS) enable us to determine stable isotope ratios with only subnanomolar quantities. However, the current CF-IRMS methods for stable chlorine isotope ratios ($\delta^{37}Cl$) of CH_3Cl had required more than several hundreds nano-mole CH_3Cl. We thus develope a CF-IRMS system for the $\delta^{37}Cl$ analysis that combines a sample processing procedure largely based on the highly sensitive method for the $\delta^{13}C$ analysis of CH_3Cl with the IRMS setting for the $\delta^{37}Cl$ analysis of CH_3Cl.

The newly developed system successfully reduces sample requirements (>0.6 nmol-CH_3Cl) to less than one hundredth of that required by the previous CF-IRMS systems while maintaining comparable precision in the $\delta^{37}Cl$ determination (±0.1 ‰, 1σ). This system is also able to determine carbon isotope ratio for CH_3Cl with comparable precision (±0.3 ‰, 1σ, >0.3 nmol-CH_3Cl) to the previous study. $\delta^{37}Cl$-SMOC and $\delta^{13}C$-VPDB values of CH_3Cl in commercial tank were determined to be -6.8 ± 0.1 ‰ and -46.9 ± 0.3 ‰, respectively.

The gas emitted from the leaves of *Myrica rubra* was collected near a harbor of Tokyo Bay (35°19.1'N, 139°39.0'E) using the vial method reported previously. On a dry weight basis, *Myrica rubra* was found to emit CH_3Cl with a flux of 3.1–3.9 ng-CH_3Cl/g-leaves/hour, whereas no CH_3Cl was detected in the empty vials. The $\delta^{37}Cl_{SMOC}$ and $\delta^{13}C_{VPDB}$ values of the leaf-emitted CH_3Cl ranged from -4.9‰ to -2.9‰ (n=4) and from -112.7‰ to -108.0‰ (n=4), respectively. The newly developed system is applicable not only to atmospheric CH_3Cl, but also to any chlorine in liquid and solid samples when appropriate treatment such as silver chloride precipitation and its methylation is combined.

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