An X-ray analysis of solid-phase bromine in Gulf of Alaska marine sediments: Proxy development and paleoceanographic applications

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In marine environments, bromine (Br) predominantly exists in two pools: dissolved in seawater as an inorganic bromide (Br^-), and as a variety of organic Br-containing biological compounds. We use a diverse set of X-ray-based analytical techniques (WD-XRF, core scanner ED-XRF, synchrotron-based μ-XRF and μ-XANES spectroscopy) to examine the distribution and speciation of Br within Gulf of Alaska marine sediments as a proxy for marine-derived total organic matter (m-TOC). Sediment geochemistry analyses from four types of marine depocenters (suboxic temperate fjord; anoxic fjord; glacier-influenced nearshore shelf; offshore continental shelf) show that, while there are significant correlations between total Br and chlorine in freeze-dried marine sediments ($R^2 = 0.71$), there is also a strong correlation between total Br and m-TOC ($R^2 = 0.56$). Rinsing a subset of samples to remove inorganic Br hosted in porewater improved the correlation between Br and m-TOC drastically ($R^2 = 0.89$). Br speciation was also examined in the anoxic fjord sediments using μ-XANES spectroscopy, and results show that Br is unequivocally hosted in organic phases. These observations all support the viability of using Br as a proxy for m-TOC when corrected for porewater Br. We use these new results to generate a Br-based record of past phytoplankton dynamics for the last 7,500 years that exhibits decadal-scale variability, consistent with modern models of North Pacific climate dynamics.