Experimental study of analytical methods for marine osmium isotopes in pelagic clay using HCl leaching

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Pelagic clay is widely attracting attention as a recorder of geochemical cycle in the Earth’ s surficial system. It sometimes concentrates specific elements such as rare-earth elements and, thus, can be a potential resource for the industrially critical elements [1,2], as well as a paleoenvironmental archive [3]. To reconstruct the (pale)oceanographic information from pelagic clay, determination of the depositional ages is crucial. However, poor preservations of age-diagnostic microfossils and paleomagnetic records have hampered precise dating of pelagic clay. Recently, a dating method using the marine osmium isotope stratigraphy was successfully applied to pelagic clay [3]. The osmium isotope ratio in seawater fluctuated through the Earth’ s history and it has been recorded in sediments as the hydrogenous component. In the osmium isotope analysis for this purpose, inverse aqua regia digestion method has been widely used to extract the hydrogenous osmium from the sediments. More recently, a chemical leaching using 1 M HCl was proposed as a new effective method to extract hydrogenous osmium from pelagic clay [4]. However, the phases extracted by these two methods, and whether their osmium isotope ratios are equivalent to the seawater value, have not been quantitatively evaluated.
In this study, we attempted to extract hydrogenous osmium from the uppermost pelagic clay sample, which is expected to have osmium isotope ratio of the present-day seawater, by using the inverse aqua regia digestion method and 1 M HCl leaching method. We implemented extraction experiments with the two methods and compared the results. The concentration and isotope ratios of osmium and rhenium were measured using multiple collector-inductively coupled plasma-mass spectrometer (MC-ICP-MS), and the chemical compositions of residues and extracted solutions were analyzed using ICP-QMS. Our results suggest that the chemical leaching method using 1 M HCl could effectively extract marine osmium from pelagic clay selectively.

[1] Kato et al. (2011) *Nature Geoscience* **4**, 535-539. [2] Iijima et al. (2016) *Geochemical Journal* **50**, 557-573. [3] Ohta et al. (2020) *Scientific Reports* **10**, 9896. [4] Dunlea et al. (2021) *Chemical Geology* **575**, 120201.

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