Unveiling method-derived element fractionation in determining seawater REEs using chelating resin and ICP-MS: Enhanced accuracy for finer-scale water mixing

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Abstract	Dissolved Rare Earth Elements (REEs) concentrations have been widely used in geochemical studies due to their systematic changes in the environment, acting as tracers in various natural processes. In addition to the usefulness of naturally controlled chemical REE fractionations used in the ocean, the extraction and measurement procedures of seawater REEs using chelating resin and ICP-MS may also be subject to method-derived analytical fractionations, leading to potential misinterpretations. The bracketing standard and the Lu methods were compared to verify any fractionation or deviation associated with the analytical processes. Four preconcentration times and four ICP-MS runs, with a total of more than 110 samples, were carried out in this study. This study first reported that despite having relatively identical normalized intensities (corrected with In-internal standardization and sample volume) between the two methods, deviations from the Lu method are more than 5 % for LREEs and less than 5 % for HREEs, suggesting a method-derived fractionation. This study further evaluated the accuracy of both methods by analyzing three natural Reference Materials (RMs), namely NASS-7, SLEW-3, and NMIJ7204 A, demonstrating good agreement with the reported values. It was also emphasized that short-term time series observation of HREEs quantified by both methods is comparable and reliable and, thus, could clarify finer-scale variabilities, particularly useful for nearshore or coastal studies with complex water circulation. More finer-scale spatial and temporal ocean observation is expected to improve our understanding of global marine biogeochemical cycles.
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