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Sequential leaching of carbonate rocks for reconstructing barium systematics in ancient oceans

YU ZHANG[1], YING ZHOU[2], KUN ZHANG[1], XI CHEN[3] AND GRAHAM A. SHIELDS[1]

[1]University College London
[2]Johannes Gutenberg University Mainz
[3]University of Cambridge

The barium concentrations and isotopic compositions of seawater are closely linked with marine biogeochemical processes, especially related to redox conditions, sulphur cycling and primary productivity. Marine sediments and barite have been widely utilised as archives in palaeoceanographic studies but stratiform barite deposition is sporadic, especially during the Precambrian[1] when the deep ocean stayed mainly anoxic. As a much more continuous archive and without known fractionation, carbonates have begun to emerge as a more reliable record to reconstruct palaeoseawater Ba systematics. However, Ba exists in different phases within carbonate rocks, e.g. carbonate, silicates, barite, which could obscure interpretations of a primary seawater Ba signal. Therefore, it is vital to extract Carbonate-Associated Barium (CABa) cleanly. Published studies show that sequential leaching can successfully extract strontium from carbonate[2] and barite[3]. In this study, we combine these two leaching techniques to extract Ba associated with different phases from carbonate rocks using reference limestones and artificial mixtures of barite and limestones, with the aim of extracting CABa from the purest carbonate fraction. The data show that this combined leaching method can successfully differentiate Ba associated with the exchangeable fraction, purest carbonate fraction, remaining carbonate fraction, barite, silicate, and oxide phases. This has been achieved using an ammonium acetate prewash to remove the exchangeable fraction, dilute acetic acid to target the CABa, followed by sodium carbonate to leach Ba from barite, before using nitric acid for the oxide phase. Comparing Ba concentrations of different phases, the exchangeable and oxide phases contain more Ba than the carbonate phase. Additionally, we note that thorough rinsing between leaching steps is crucial, as barium adheres to different phases quite strongly and can only be fully released from the leached phase during repeated rinsing between steps. The newly developed approach refines CABa extraction along with other Ba phases and will be tested using carbonate of Ediacaran age, helping to contribute to more robust and comprehensive interpretations of sedimentary Ba data.

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