

A Practical *In-Situ* Approach for Analysis of Lead Isotopes in Biological Carbonate Matrices Using LA-MC-ICP-MS

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Here we demonstrate that LA-MC-ICP-MS is a suitable technique to precisely and accurately determine Pb isotopic composition in bivalve shells, which can be employed to trace the source of Pb pollution in the environment. Moreover, Pb isotope ratios can be continuously profiled along the shells to determine changes on Pb incorporation that occur with sample growth. To demonstrate applicability, we discuss results of bivalve shells from Ilha Grande Bay (Rio de Janeiro, Brazil), data are compared to Pb isotopic composition reported for marine sediments from nearby areas and also to published Pb composition archives that may have an eventual link with the sources that the bivalves have been exposed to.

Analyses were carried out on using an excimer ArF laser ablation system (Photon Machines, 193 nm) coupled to a Neptune Plus (Thermo Scientific) multicollector spectrometer using low resolution mode. Calibration is performed with the synthetic reference material NIST612, using a conventional gas blank correction based on the sample-standard bracket approach. The Pb isotope ratios are measured simultaneously, at a spatial resolution of 110 μm , reproducibility (RSD) is about 5%.

Results reflect signatures of Brazilian galena ores, which suggest that Pb incorporation in shells is related to mining activities associated with the presence of a maritime terminal at the study area. The procedure provides new evidence that it is possible to analyze Pb isotopes in biogenic carbonate matrices using LA-MC-ICP-MS and has been successfully applied for detailed analyses of Pb isotopic composition in bivalve shells. However, a small instrumental drift can potentially occur within a run, therefore, the reduction of elemental fractionation is still a key issue in the determination of accurate and precise isotope ratios. Further investigations should consider to use a femtosecond laser in order to reduce elemental fractionation throughout the analysis to improve data quality and measurement uncertainties.