Improved in situ measurements of lead isotopes in silicate glasses by LA-MC-ICPMS using multiple ion counters

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A new technique that improves the spatial resolution and detection limits of the measurement of lead isotope ratios in silicate glasses with < 15 ppm total Pb by laser ablation-multicollector magnetic sector-inductively coupled plasma mass spectrometry (LA-MC-ICPMS) is presented. The method allows for the concurrent, static measurement of ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb, along with ^{202}Hg and ^{235}U, in six Multi-Ion Counters (MICs) fitted on a Finnigan NEPTUNE MC-ICPMS. Use of a collector array consisting only of MICs eliminates the need for cross calibration between Faraday cups and ion counters, as employed in previous methods reporting ^{204}Pb values by LA-MC-ICPMS. Standard-sample-standard bracketing using BCR-2G as the calibrant is used to correct for instrumental mass bias. Accuracy and precision of the method was evaluated by replicate analyses of various MPI-DING reference glasses, with low Pb concentrations (1.38 to 11.6 ppm total Pb) and well-determined isotopic ratios. Typical spot sizes for in situ analyses ranged from 40-69 microns, providing better spatial resolution than previous LA-MC-ICPMS reporting ^{204}Pb. Ablations for all analyses were carried out using a 193 nm ArF GeoLas laser at a repetition rate of 10 Hz and a pulse energy of 5 J/cm^2. Mercury derived from argon gas is a chronic problem for ICPMS measurements of the minor ^{204}Pb isotope because of the isobaric inteference by ^{204}Hg. Due to the high sensitivity of the MICs, the Hg-correction of the measured 204-mass was significant, especially for samples with < 5 ppm total Pb. Two different methods were used to correct for Hg on the 204-mass with the results agreeing within error for each method on all lead isotope ratios. Measured lead isotope ratios for the MPI-DING reference glasses T1G (11.6 ppm Pb) and ATHO (5.67 ppm Pb) agree within 0.10% and 0.16% respectively of the accpeted values. For MPI-DING KL2G (2.07 ppm Pb) and ML3B (1.38 ppm Pb), measured Pb ratios involving ^{204}Pb agree within 1% of the accepted values with typical precisions of < 2.9 % RSD (2 sigma). Measured ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb ratios for KL2G and ML3B are within 0.40% of the accepted values and typical precisions are < 0.75% RSD (2 sigma). The results for KL2G and ML3B demonstrate improvement over previous LA-MC-ICP-MS data in terms of both detection limits and spatial resolution, while retaining similar levels of accuracy and precision. The new method provides the capability of making quantitative in situ lead isotope measurements on tiny objects of geologic interest such as mineral growth bands, melt inclusions, and accessory minerals, even where they are lead poor.

Mineral phase identification of coral skeletal microstructure

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Mineral phase identification of the coral skeletal microstructure is important for reconstructing the paleo-climate. Especially, *Porites sp.* is widely used a paleo-climatic proxy. To reconstructing the paleo-environment, those chemical compositions have been studied as coral thermometry. For example, Sr/Ca ratio in coral skeletons is sensitive to the paleo-environment variant so that Sr/Ca ratio has the possibility as the accuracy archive. However, there are one assumption is that trace elements in coral aragonite originate from solid solution. Greegor *et al.* (1997) reported that the as much as 40% of strontium (Sr) in coral aragonite existed as a strontianite which was not the solid solution by using X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). On the other hand, Finch *et al.* (2003a, 2003) and Allison *et al.* (2005) showed no evidence of the presence of strontianite or it's intermediate state in coral aragonite. They attempted to seek out the strontianite in coral samples using EXAFS. However, XANES and EXAFS could not identify the mineral phase directly. In addition, few studies have referred to mineral phase in coral skeletons with micro scale. X-ray diffraction analysis (XRD) with synchrotron radiation plays a role in detecting the mineral phase identification of coral skeletal microstructure for their strong energy, which enables phase identification with small range of X-ray spots: X-ray spot sizes of this study are 15μm and 40μm.

We performed XRD analysis with synchrotron radiation for coral, *Porites sp.*, living/fossil microstructure. The experiment conducted with imaging plate (IP) on BL-18c at Photon factory, KEK (HIGH ENERGY ACCELERATOR RESEARCH ORGANIZATION), Tsukuba, Japan. A monochromatic incident X-ray beam with a wavelength of 0.616Å was used and was collimated to a diameter of 15μm or 40μm. The two-dimensional IP data were integrated and conducted to one dimensional intensity data.

The size of the centre of calcification (COC) is approximately 30μm in diameter in the samples of this study. That size correspondents to the X-ray spot sizes of this study in 15 or 40μm in diameter, so we got the different mineral structural information between the COC and fibres. All diffraction peaks of COC and fibres can be explained as aragonite, and no significant difference of cell parameters can be observed. This indicates that COC and fibres consist of aragonite: this study could not detect calcite phase.

Reference

Greegor R. B., Pingitore N. E. Jr., and Lytle F. W., (1997). *Science.* **275**, 1452–1454.