Determination of multi-element/Ca ratios in coral and foraminiferal samples using paired cold- and hot-plasma techniques on ICP-SF-MS

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Abstract

Coral and foraminifer are two of the most important carbonate archives to reconstruct paleo-environmental conditions, such as sea surface temperature (Sr/Ca and U/Ca in coral, and Mg/Ca in foraminifer), nutrient (Cd/Ca in coral and foraminifer), and river runoff (Ba/Ca in coral and foraminifer). Here we present a newly-developed assemblage on an inductively coupled plasma sector-field mass spectrometer (ICP-SF-MS), Thermo Electron ELEMENT II, combined with cold- and hot-plasma techniques, to measure ppm-to-ppb metals in the carbonates. Cold and hot plasma conditions of 800-W and 1200-W radio frequency- (RF-) power levels were employed for requirements of (1) permil-level precision measurement of Mg/Ca, Sr/Ca, and Ba/Ca, and diminishment of spectral interference at low-mass domain, less than m/z = 80 amu, and (2) of wide mass range scanning from Mg to U with high signal/background ratio, respectively. A wet introduction system with a Scott-type double-pass spray chamber and an ESI-50 micro-nebulizer with a sample uptake rate of 50 μl/min were used, which offers low blank and high ion beam stability. Nitric acid was carefully calibrated to 5.00 (+- 0.02) % and Ca content adjusted to 3.0 ppm in coral and 6.0 ppm in foraminiferal solutions to effectively diminish matrix effect.

At cold-plasma condition, intensities of ion beams were detected in pulse-counting mode. Element/Ca ratios were determined directly from intensity ratios using external, matrix-matched standard to correct for mass discrimination and low-frequency ratio drift. The sensitivity of Sr/Ca values on Mg/Ca determination is 0.18% per mmol/mol, which causes only 0.1% or less on Mg/Ca ratio in both coral and foraminiferal samples. Replicate measurements show that this cold-plasma technique can give an internal precision of 0.1-0.2% (2RSD) and reproducibility of 0.45% for Mg/Ca and 0.35% for Sr/Ca. The corresponding uncertainty is 0.05 ^{o}C for foraminiferal Mg thermometer and 0.5^{o}C for coral Sr thermometer.

For precise measurements of the ultra-trace metals, the RF-power level was increased to 1200 W to provide a 1.7-to 3.0-fold enhancement in sensitivity for Mg to

U. At the hot plasma condition, ^{24}Mg, ^{43}Ca, and ^{86}Sr were detected in analog mode, ^{27}Al, ^{55}Mn, ^{112}Cd, ^{138}Ba, ^{208}Pb, and ^{238}U in pulse-counting mode, and ^{57}Fe and ^{64}Zn in both modes. This technique give the analytical performance of 0.6% for Mg/Ca, 0.5% for Sr/Ca, 13% for Al/Ca, 10% for Mn/Ca, 6.4% for Fe/Ca, 5.0% for Zn/Ca, 2.5% for Ba/Ca, 2.0% for Pb/Ca, and 1.0% for U/Ca. Advantages of this assemblage include (1) short measurement time of 3-5 minutes and (2) only 2-μg carbonate consumed for each sample, and (3) throughput of 10 samples per hour.