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Construction of Secular Seawater Sr Isotope Curves: Comparison of $^{87}Sr/^{86}Sr$ Analysis by Laser Ablation MC-ICPMS and TIMS

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A study undertaken to evaluate the potential for constructing secular seawater Sr isotope curves by laser ablation multicollector (MC)-ICP-MS compares $^{87}Sr/^{86}Sr$ data obtained by TIMS and by solution and laser ablation MC-ICP-MS for Cambrian marine cements and Mississippian brachiopods and marine cements. The laser ablation $^{87}Sr/^{86}Sr$ ratios define a Cambrian secular Sr isotope curve that is in good agreement with that delineated by TIMS data. Mississippian samples define a linear rise in $^{87}Sr/^{86}Sr$ ratios that overlap the recently established European Carboniferous Sr isotope curve, and are in accord with independent biostratigraphic constraints. Analysis of cements and brachiopods was carried out on thick (100 to 150μm) sections using straight line scans and a beam size between 60 and 95μm and 80 to 100% laser output. Typical acquisition time is 1-2 minutes, depending on the length of lines and the preset scan speed. The ablated carbonate material is typically on the order of a few micrograms, leading to a few nanograms of analyzed Sr. Average internal precision is better than 50ppm. Accuracy of measured $^{87}Sr/^{86}Sr$ ratios was verified by measuring the NIST Sr standard and a suite of in-house carbonate standards, and further augmented by TIMS analyses of microdrilled samples adjacent to laser ablation spots. Observed heterogeneity in marine cement $^{87}Sr/^{86}Sr$ ratios typically covaries with submm-scale variations in cathodoluminescence suggesting that the spatial resolution afforded by laser ablation identifies diagenetic heterogeneity that cannot be resolved through microsampling and solution analysis. Heterogeneity at the resolution of the laser ablation in carbonate marine cements and biogenic grains would lead to artificial homogenization of $^{87}Sr/^{86}Sr$ ratios obtained by TIMS. Overall, the results of this comparison study indicate that laser ablation MC-ICP-MS has the potential for

high quality, rapid construction of seawater Sr isotope curves through analysis of least altered marine cements and biogenic calcites. Laser ablation MC-ICP-MS derived Sr isotope records may deviate from previously defined secular Sr isotope curves with implications for paleoweathering fluxes and rates, tectonic history, and paleoenvironmental and paleoclimatic conditions inferred from TIMS based records.