

In situ determination of carbon isotopes in carbonates by femtosecond laser ablation multi-collector ICP-MS

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We here present a method for *in situ* determination of stable carbon ($\delta^{13}\text{C}$ ‰) isotope compositions for calcite, dolomite, magnesite and siderite by femtosecond laser ablation multi-collector inductively coupled plasma mass spectrometry (fs-LA-MC-ICP-MS). Spectral interferences of doubly charged ions ($^{24}\text{Mg}^{2+}$ for $^{12}\text{C}^+$, $^{26}\text{Mg}^{2+}$ for $^{13}\text{C}^+$) and polyatomic species ($^{12}\text{CH}^+$ for $^{13}\text{C}^+$) were evaluated. The associated internal precision of *in situ* C isotope analysis correlates with intensities, and is better than 0.20‰ (2SE) when the measured ^{12}C ion signal is >12.5 volts. Carbonate samples DOL-8, MGS-1 and SD-5 show relatively uniform bulk and *in situ* carbon isotope compositions with precisions better than 0.24‰ and 0.45‰ (2SD), and are adopted as in-house standards. Laser ablation analyses of various calcite, dolomite, magnesite and siderite with $\delta^{13}\text{C}$ in the range of -6.28‰ to 0.32‰ agree excellently with IRMS determined values using the standard-sample bracketing (SSB) calibration, with precision of 0.37-0.68‰ (2SD). Matrix effects have been investigated and determined to be insignificant for the same carbonate matrix with variable chemical compositions when adopting the femtosecond laser. Instrumental carbon isotope fractionation observed among different carbonate matrices is non-negligible (*e.g.*, up to 4.29‰ between calcite and magnesite) using fs-LA-MC-ICP-MS, and an external multi-reference calibration can be applied for non-matrix matched analyses.