Absolute isotope amount ratio measurements on gases: A basic measurement model

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A basic measurement model [1, 2] and corresponding measurement function for measuring isotope amount ratios on various gases is described and discussed. Performed on similar types of 'hardware' (a gas isotope ratio mass spectrometer) Isotope Amount Ratio Measurements ('IARM') are not intended to replace the traditional (delta) isotope measurements but to complement them: providing "absolute" isotope amount ratio values when there is a need for it.

The measurement functions used in performing 'IARM' describe a transparent and traceable relationship between an isotope amount ratio of an element to its measured ion current ratio (the quantity subject to measurement), based on the gas flow dynamics in the gas inlet system of the mass spectrometer including full consideration of isotope fractionation effects. Through the application of gas kinetic concepts governing isotope fractionation of a gas (consisting of several isotopes) in the spectrometer, and subsequently by a 'calibration' via synthetic isotope mixtures (Primary Measurement Standards), it could be demonstrated that SI-traceable values in terms of the derived measurement unit mol/mol can be obtained. The entire theoretical treatment which is the keystone of this type of measurement is based on pure physical principles in which only a few assumptions must be evaluated and corrected for.

[1] M. Varlam, S. Valkiers, M. Berglund, P. Taylor, R. Gonfiantini & P. De Biévre (2008) *Int. Journ. Mass Spectrom*. **269** (1), 71-77. [2] S. Valkiers, M. Varlam, M. Berglund, P. Taylor, R. Gonfiantini & P. De Biévre (2008) *Int. Journ. Mass Spectrom*. **269** (1), 78-84.

Accurate stable isotope analysis by ion microprobe

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Continuing development of instrumentation and technique have dramatically improved the precision of *in situ* stable isotope analyses by ion microprobe (SIMS). For $\delta^{18}O$ and 10μm diameter pits in silicates, a spot-to-spot precision of 0.3‰ (2SD) is now routine with an IMS-1280 at WiscSIMS. Sub-micron spots are possible at ±2‰ [1]. However, precision does not guarantee accuracy and non-instrumental, potentially confounding, factors include: standardization, X-Y effects, and crystal orientation. (1) SIMS analysis yields a bias that must be corrected by comparison to standards. Sample analyses should be bracketed by analyses of appropriate standards, which are homogeneous, independently calibrated, and have the same crystal structure and chemical composition as samples. For instance, instrument bias for $\delta^{18}O$ at WiscSIMS varies by 8‰ for pyrope vs. andradite and by 14‰ for calcite vs. magnesite. The bias is not necessarily linear with cation composition; multiple standards are desirable. (2) At present, accuracy and precision are degraded if samples and standards are not mounted and polished together within 5mm of the center of a 25mm sample mount that is smooth and flat. Changes in design may enlarge the analysis area. Polishing relief of 30μm, not uncommon for 200-500μm grains in epoxy, can degrade precision from ±0.3 to ±3.0‰ and cause inaccuracy of 4‰ in $\delta^{18}O$ [2]. Depth profiling also affects bias and should be evaluated by analysis of homogeneous material. Relief is easily monitored at sub-micron scale by profilometer. (3) Channelling of the primary ion beam along preferred planes in the crystal lattice has long been proposed to influence instrument bias. For many minerals, analysis of standard grains in random orientation proves that the magnitude of this effect is less than spot-to-spot precision. However, for some minerals, the best known standard yields disappointing results; this is generally attributed to standard heterogeneity, and orientation effects are not evaluated. For magnetite, improvement of $\delta^{18}O$ precision has been stalled at ±2‰ since 1991 even though 15 different materials were evaluated as standards. Recently, EBSD shows that instrument bias varies ~4‰ with crystal orientation. The smallest bias is obtained when the incident Cs beam is parallel to <*hk*0> planes in magnetite, suggesting a possible correction procedure [3].

[1] Page *et al.* (2007) *Am. Min.* [2] Kita *et al.* (2009) *Chem Geol* [3] Huberty *et al.* (2009) this volume.