

High-precision MC-ICP-MS lead isotope analysis using Tl-normalization: Calibration and applications to lead isotope study of ore deposits

I.V. CHERNYSHEV, A.V. CHUGAEV AND K.N. SHATAGIN
IGEM RAS, Moscow, Russia (cher@igem.ru)

The demands for radical improvement (compared to conventional TIMS method) of lead isotope ratios measurements precision exist in isotope geochemistry for last 30 years. It becomes practicable owing to multicollector-ICP-mass-spectrometry which makes possible to correct lead isotopes mass-discrimination with $^{205}\text{Tl}/^{203}\text{Tl}$ ratio. This method was elaborated and adapted to different MC-ICP-MS instruments in wide number of works (for example, [1-5]).

Developing this method [5] we use 9-collector-ICP-MS NEPTUNE. The $^{205}\text{Tl}/^{203}\text{Tl}$ value in TlNO_3 reference sample which we use for normalization, being important for accuracy of final results was determined through certificated values of $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratio in two NIST standard samples SRM 982 and 981. Results obtained for two mixtures Tl+Pb (SRM 982) and Tl+ Pb (SRM 981) in 10 parallel analyses for each one respectively are: 2.38898 ± 12 and 2.38883 ± 20 . Analyses of both mixtures yield $^{205}\text{Tl}/^{203}\text{Tl}$ ratio in excellent agreement between them, when a total mean value 2.3889 ± 1 coincides in error limits with recent data 2.3887 ± 7 [3] and 2.3889 [4].

Isobar interference of $^{204}\text{Hg}^+$ contribution to total peak 204 m/e intensity was controlled and corrected by $^{202}\text{Hg}^+$. Its contribution didn't exceed $4 \times 10^{-17}\text{A}$ or $<0.001\%$ in terms of $^{204}\text{Pb}^+$ peak. Background signals in analyses were less than $1.5 \times 10^{-15}\text{A}$, whereas $^{208}\text{Pb}^+$ peak intensity during analyses ranges from 2.5×10^{-11} to $8 \times 10^{-11}\text{A}$.

Precision of the method involved has been evaluated from long-term (1.5 years) reproducibility of 90 parallel analyses of common lead standard SRM 981 and galena samples ($\pm 2\text{SD}$): $^{206}\text{Pb}/^{204}\text{Pb} - \pm 0.016\%$; $^{207}\text{Pb}/^{204}\text{Pb} - \pm 0.016\%$; $^{208}\text{Pb}/^{204}\text{Pb} - \pm 0.018\%$; $^{207}\text{Pb}/^{206}\text{Pb} - \pm 0.005\%$; $^{208}\text{Pb}/^{206}\text{Pb} - \pm 0.009\%$.

The method described was applied to detailed lead isotope study of same well known ore deposits. Systematic study of 12 massive sulphide and base metal deposits of Ural, Russia was performed. Another object was Banska Stiavnica Au-Ag deposit (West Carpathian, Slovakia), which demonstrated perfect homogeneity of lead isotope composition.

References

1. Rehkämper M., Mezger K. (2000). *JAAS* **15**, 1451-1460.
2. White M.W. *et al.* (2002). *Chem. Geol.* **167**, 257-270.
3. Collerson K.D. *et al.* (2002). *Chem. Geol.* **188**, 65-83.
4. Thirlwall M.F. (2002). *Chem. Geol.* **184**, 255-279.
5. Chernyshev I.V. *et al.* (2004). *XVII Symp. Geochem. Iso. Abstr. Vol.*, 274-275.

Stable nitrogen isotopic composition of amino acids: Implications for aquatic food web studies

Y. CHIKARAISHI, Y. KASHIYAMA, N.O. OGAWA,
H. KITAZATO AND N. OHKOUCHI

Japan Agency for Marine-Earth Science and Technology
(ychikaraishi@jamstec.go.jp)

Compound-specific stable nitrogen isotope analysis of amino acids is a potential tool for elucidating trophic position of organisms in the food web (McClelland and Montoya, 2002). Large ^{15}N -enrichment ($\sim 7\%$) in glutamic acid along the trophic level provides a greater scope for defining trophic position than the small change ($\sim 3\%$) in bulk material, and little change in $\delta^{15}\text{N}$ of phenylalanine along the trophic level provides information of nitrogen sources at the base of the food web. However, it is still uncertain whether or not the $\delta^{15}\text{N}$ relationship observed in McClelland and Montoya (2002) is generally applicable to other sets of ecosystems.

We investigated the nitrogen isotopic composition of individual amino acids from macroalgae and gastropods in a natural marine coastal environment, to further evaluate them as a tool for ecological studies and to understand the factor(s) controlling the isotopic compositions in terms of biosynthetic and metabolic processes (Chikaraishi *et al.*, 2007). The isotopic compositions of 12 amino acids range from -3.3 to $+12.9\%$ for marine algae, and from -0.6 to $+16.6\%$ for gastropods (Fig. 1). The isotopic distribution between algae and gastropods are consistent with those in the previous report, suggesting them to be quite useful for studying the food web structure. The nitrogen isotopic variation between amino acids would strongly reflects their biosynthetic and metabolic processes. We suggest that the metabolic fate is an important factor to produce the distinct trophic relationship in the nitrogen isotopic compositions between amino acids.

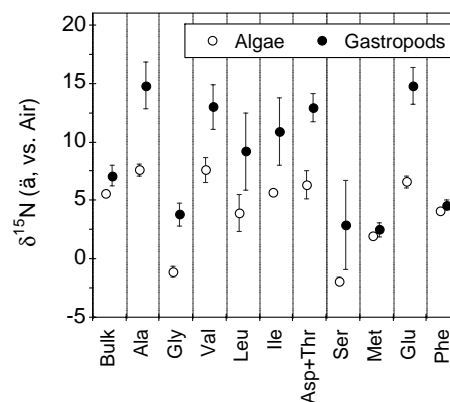


Figure 1: Nitrogen isotopic composition of individual amino acids in marine macroalgae and gastropods.

References

- Chikaraishi Y, Kashiya Y, Ogawa NO, Kitazato H, Ohkouchi N (2007) *Marine Ecology Progress Series*, in press.
- McClelland JW, Montoya JP (2002) *Ecology* **83**: 2173-2180.