Ionization constants and thermal decomposition kinetics of uracil and adenine under hydrothermal conditions by UV-visible spectroscopy

E. BALODIS, L. N. TREVANI AND PETER R. TREMAINE*

[1]Department of Chemistry, University of Guelph, Guelph, ON, Canada N1G 2W1
(*correspondence: tremaine@uoguelph.ca)
(ltrevani@uoguelph.ca)

Biomolecules Under Hydrothermal Conditions

The chemistry of amino acids, nucleic acid bases, and other biomolecule precursors under hydrothermal conditions is of increasing importance in formulating mechanisms that may have led to the creation of life on earth. Attempts to model the thermochemical and kinetic stability of biomolecule precursors have been limited by a lack of quantitatuve experimental data [1]. In this work we report ionization constants of uracil and adenine and rate constants for their thermal decomposition as a function of pH at temperatures as high as 250 °C at 40 MPa.

UV-Visible Flow Measurements

UV-visible spectra were obtained in the high-pressure flow cell with sapphire windows developed by Trevani *et al*. [2]. Ionization constants were determined from pH-dependant spectra of uracil and adenine in buffer solutions NH_3/NH_4Cl, $NaHCO_3/Na_2CO_3$, HCOOH/NaHCOO and NaH_2PO_4/Na_2HPO_4. Rates of thermal decompostion were determined by operating the flow system as a stopped-flow reactor.

Results and Discussion

Acid ionization constants (K_a for uracil, K_{a1} and K_{a2} for adenine) were determined up to 200 °C to a precision of 0.1 log units. Rate constants at 200 and 250 °C were determined by factor analysis methods, similar to those of Cox and Seward [3], although our data are less extensive. Uracil and adenine decomposition occurred by one-step and two-step processes, respectively. Kinetic results are in quantitative agreement with the less-extensive pioneering study by White [4].

[1] LaRowe & Helgeson (2006) *GCA* **70**, 4680-4724. [2] Trevani *et al.* (2001) *J. Sol. Chem.* **30**, 585-622. [3] Cox & Seward (2007) *GCA* **71**, 797-820. [4] White (1984) *Nature* **310**, 430-432.

Zn stable isotope variability up the Kruger Park trophic chain

V. BALTER[1], F. MOYNIER[2], S. PICHAT[3], M.L. PONS[3], F. THACKERAY[4] AND F. ALBARÈDE[3]

[1]Université Lyon 1, Villeurbanne, France (Vincent.Balter@univ-lyon1.fr)
[2]Washington University, St Louis, USA
[3]Ecole Normale Supérieure, Lyon, France
[4]Transvaal Museum, Pretoria, South Africa

Zinc is an essential metal for life and its concentration in organisms is regulated by a set of complex metabolic mechanisms. MC-ICP-MS data on Zn stable isotope compositions show variations in plants [1] and in animal and human organs [2]. Here, we focus on how Zn isotope variations change up the land trophic chains. The National Kruger Park ecosystem (South Africa) is particularly suite for its high level of mammal biodiversity and the reduced of anthropogenic Zn.

Zn in mammal bone and plants samples was purified by anion-exchange chromatography using a procedure adapted from Moynier *et al.* [3]. Zn isotopic compositions were measured by MC-ICP-MS (VG Plasma 54 or Nu Plasma HR), equipped with a desolvating nebulizer.

The results confirm that Zn fractionation in biological material is mass dependent. Isotope compositions vary by about 0.5‰ per amu for plants and 0.8‰ per amu for mammals. δ^{66}Zn values (vs JMC) for plants and bones range from -0.1‰ and 0.4‰, and from 0.9‰ and 1.6‰, respectively. Such fractionation corresponds to a 1‰ trophic fractionation factor between herbivores and plants. Surprisingly, no enrichment is not observed between herbivores and carnivores (hyenas), which suggests that the Zn uptake by predators is essentially quantitative. The range of Zn isotope values up the Kruger Park trophic chains exceeds the bulk terrestrial variability.

[1] Weiss, D. *et al.* (2005) *New Phytologist* **165**, 703-710. [2] Stenberg, A. *et al.* (2004) *Anal. Chem.* **76**, 3971-3978. [3] Moynier, F. *et al.*, 2006. *Geochim. Cosmochim. Acta*, **70**, 6103-6117.