Computational determination of thermochemical values for biomass synthesis using model biopolymers

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Geochemical reactions can support life (1) if the habitat sustains exergonic reactions, (2) if organisms can mediate the conversion of chemical into biochemical energy and (3) if the energy gain is sufficient to support growth. The first criterion is fulfilled by the chemical composition of the environment and its oxidation potential. The second criterion requires that organisms have metabolic pathways to assimilate the necessary nutrients and the third that they can couple energy conversion to the formation of biomacromolecules and grow.

We use principles of thermodynamics to address criterion (3), developing model monomer compounds based on the elemental composition of microbial biomass and the most common bond types in biopolymers. We then calculate thermochemical values (Hf°, Gf°) for these monomers, employing semi-empirical and ab-initio additive calculation methods (G3MP2) with the software GAMESS-US (Table).

Thermochemical values for biomass monomers

Synthesis model monomers for	Model structure	Hf° (1) [kJ/mol]	Gf° (1) [kJ/mol]
carbohydrates	$C_4H_8O_4$	-790.51	-611.9
proteins	$C_6H_8O_3N_2$	-1147.8	-989.39
lipids	$C_8H_{16}O$	-316.84	-76.45
P-compounds	CH_5O_5P	-1401.25	-1318.58
S-compounds	$C_2H_4O_2S$	-158.7	-91.81

(1) values for STP, solvatation correction included

Using model structures, we designed condensation reactions for biopolymers and assembled them into biomass of an average stoichiometric C:H:O:N:P:S ratio of 123:172:44:19:1:0.7. The average oxidation state of the C is -0.25. Lipid-rich and carbohydrate-rich biomass show elemental ratios of 132:187:36:19:1:0.7 (C_{av}-0.46) and (118:158:48:19:1:0.7, C_{av} -0.07), respectively.

Chemical thermodynamics applied to model biomass synthesis in an aqueous matrix enables a quantitative evaluation of the ability of any organism to energetically couple oxidation reactions with ATP-synthesis and biomass formation. The approach is used to predict microbially mediated geochemical activities in subsurface environments – also to their possibility on other planets – as well as to the analysis of the habitability of ecosystems with extreme conditions.

High precision U-Pb dating analyses with the CAMECA IMS 1280

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SIMS is a powerful microanalytical technique that provides direct *in situ* measurement of elemental and isotopic composition in selected µm-size areas of the sample. The CAMECA IMS 1280 is a ultra high sensitivity ion microprobe that delivers unequalled analytical performance for a wide range of SIMS applications (isotope ratio measurements [1,2], analyses of trace elements [3,4], ...).

In particular, this tool has been extensively used for geochronology applications (U-Pb dating in Zircon) [5, 6] as it provides isotope measurements at high sensitivity. The instrumental design has been optimized for this application [7]: high transmission at high mass resolution mass spectrometer, high density O^-/O_2^- primary beam spots, combined with oxygen flooding technique for improved sensitivity and highly reproducible analytical conditions.

For achieving high precision results, it is also mandatory to guarantee excellent stability over long time analyses. In recent years, the high level of automation of the CAMECA IMS 1280, in particular the introduction of automated routines for a precise control of all relevant parameters before each analysis, has led to a dramatic improvement in external reproducibility for isotope ratio measurements [1,2,7].

A campaign of U-Pb analyses was carried on during 98hours (>4 days) for a total of 334 spots both on unknown and standard 91500 Zircon grains (259 and 75 analyses, respectively). The duration of each analysis was ~14minutes. Measurements were performed during five analysis sessions, each one consisting of an automated, unattended sequence of analysis on user-selected positions. All data obtained on the standard grains fit into a unique calibration curve (Pb/U vs. UO_2/U using power law parameters). A Concordia age of 1067.4 ±3.7 Ma (95% confidence, decay-const. errs included) was obtained for the total of 75 standard analyses.

[1] F.Z. Page *et al.*, *Ame. Min.* **92** (2007) 1772. [2] A.A. Nemchin *et al.*, *Nature* **454** (2008) 92. [3] G. Srinivasan *et al.*, *Science* **317** (2007) 345. [4] E.B. Watson *et al.*, *Science* **308** (2005) 841. [5] E. Deloule *et al*., *Geochim. Cosmochim. Acta* **65** (2001), 1833. [6] J. P. Platt *et al.*, *EPSL* **71** (1999) 571. [7] M. Schuhmacher *et al., Proceedings of the Fourteenth International Conference SIMS XIV* (2003) 878-882