

How to improve the accuracy of cosmogenic ^3He determinations?

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^3He is a powerful cosmogenic isotope for quantifying a large variety of Earth surface processes. However, accurate and precise applications of cosmogenic ^3He require a proper determination of the non cosmogenic ^3He components. Many studies based on the analysis of cosmogenic ^3He have used the two step routine (1st crushing, 2nd melting) proposed by Kurz, (1986) [1] to correct for the magmatic ^3He component. However, the initial crushing step may induce an undesirable release of cosmogenic ^3He , leading to underestimate the cosmogenic ^3He concentration. Moreover, the standard correction proposed by [1] is valid only if the ^4He extracted by melting the samples is entirely magmatic. This assumption is however not satisfied in many cases because significant amounts of radiogenic ^4He may be present in the analyzed phenocrysts. Neglecting this radiogenic production may induce significant overestimate of the magmatic ^4He correction and, hence, underestimate of the actual cosmogenic ^3He concentration.

In the present study are presented and discussed several techniques that may be useful to overcome these different issues and to improve the accuracy of cosmogenic ^3He measurements:

(i) 'Cosmogenic ^3He isochrons' can be built by analyzing several phenocrysts replicates. The main advantage of this alternative method is to avoid the preliminary crushing step, and thus to avoid any bias due to possible crushing release of cosmogenic ^3He [2].

(ii) To account for the influence of radiogenic ^4He , the appropriate approach depends on the erosion history of the sample, which determines the helium closure age to exposure age ratio [3]. In any case it is however important to properly estimate the radiogenic ^4He production rate, by measuring the U and Th concentrations of both phenocryst and host, and the phenocryst size. To illustrate the importance of this radiogenic correction, the present work revisits several previous studies in which the radiogenic ^4He was not recognized.

[1] Kurz (1986) *Nature* **320**, 435-439. [2] Blard & Pik (2008) *Chem. Geol.* **251**, 20-32. [3] Blard & Farley (2008) *EPSL* **276**, 20-29.

The dire consequences of being away from the interface: What peat bogs tell us about limits to anaerobic organic matter decomposition

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Thermodynamic disequilibrium at redox interfaces drives biogeochemical transformations in soils and sediments. While overall disequilibrium persists, key processes in anaerobic organic matter decomposition may approach partial thermodynamic equilibria, which can result in their slowdown. We hypothesized that in diffusion dominated systems, for which thick peat deposits provide a model, thermodynamic constraints can pose a limit to methanogenic decomposition of organic matter and ultimately to closing the carbon cycle. To test this hypothesis we (I) conducted controlled column experiments with homogenized peat over an 18 month period, (II) investigated transport, *in situ* respiration pathways, rates and thermodynamic conditions in a northern peatland, and (III) modelled depth profiles of CO_2 and CH_4 in the deposits.

Vertical transport in the peatland was dominated by diffusion leading to the buildup of DIC and CH_4 with depth (5500 $\mu\text{mol L}^{-1}$ DIC, 500 $\mu\text{mol L}^{-1}$ CH_4). Highest DIC and CH_4 production rates occurred close to the water table (decomposition constant $k_d \sim 10^{-3}$ to 10^{-4} a^{-1}) and decreased to about $k_d = 10^{-7} \text{ a}^{-1}$. The accumulation of metabolic end-products diminished *in situ* energy yields of acetoclastic methanogenesis to the threshold for microbially mediated processes (-20 to $-25 \text{ kJ mol}^{-1} \text{ CH}_4$). The methanogenic precursor acetate also accumulated (150 $\mu\text{mol L}^{-1}$). In line with these findings, CH_4 was formed by hydrogenotrophic methanogenesis at Gibbs free energies of -35 to $-40 \text{ kJ mol}^{-1} \text{ CH}_4$. This was indicated by an isotopic fractionation $\alpha_{\text{CO}_2\text{-CH}_4}$ of 1.069 to 1.079. Fermentative degradation of acetate, propionate and butyrate attained Gibbs free energies close to 0 kJ mol^{-1} substrate. In peat columns with homogenous peat-sand mixtures of 50 %, 15% and 5% dry weight, steady state CO_2 production also decreased from about 10 to 0 $\text{nmol cm}^{-3} \text{ d}^{-1}$ and of CH_4 from 1 to 0 $\text{nmol cm}^{-3} \text{ d}^{-1}$ with depth. Very similar depth profiles of concentrations and volumetric rates developed near endproduct thresholds of 600 $\mu\text{mol CH}_4$ and 10 $\text{mmol L}^{-1} \text{ CO}_2$, despite the differences in organic matter content. The modeling exercise showed that a consistent development of CH_4 concentration profiles over time in the columns could only be accomplished with rates of acetoclastic methanogenesis decreasing to 0 near a critical Gibbs free energy of about -27 kJ mol^{-1} . The results thus suggest that even in absence of inorganic electron acceptors, respiration rates are likely higher near the redox interface to the atmosphere due to lower respiration endproduct concentrations. Similar effects ensue when rates of transport are elevated or pools of CO_2 and CH_4 are eliminated.