

## Spring residence times: Role in weathering rates

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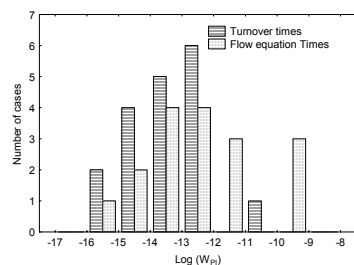
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Estimation of plagioclase (Pl) weathering rates ( $W_{Pl} = ([Pl]/t) \times (Q/A_{Pl})$ ) at the watershed scale of springs requires the prior evaluation of a number of parameters which include the mole fractions of Pl ([Pl]) and their fracture surface areas ( $A_{Pl}$ ), the residence times of springs ( $t$ ) and their annual discharge ( $Q$ ). An attempt to relate the weathering of plagioclase to mixtures rich in halloysite and to quantify the  $W_{Pl}$  for a number of very small spring watersheds from the Vila Pouca de Aguiar region (VPA, North of Portugal) is documented in [1]. In this paper we take a step further by focusing our attention on adjusting the previously used advective flow equation and introducing hydraulic turnovers for the assessment of  $t$ . Now, the advective flow equation ( $t = (n_e/K)(F^2/D_h)$ ) replaces the average watershed depth ( $D$ ) by the average depth of the saturated aquifer ( $D_h$ ), whereas hydraulic turnovers assign  $t = V_h n_e / Q$ .  $V_h$  is the saturated volume of the aquifer characterized by an effective porosity  $n_e$  and a hydraulic conductivity  $K$ , and  $F$  is the average lateral path from the recharge area to the spring site.

The evaluation of  $n_e$ ,  $K$ ,  $F$  and  $Q$  has been addressed by [1]. The  $D_h$  of the VPA springs could be related to their isotopic composition ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) and to annual precipitation ( $P$ ):  $D_h = [ (^{87}\text{Sr}/^{86}\text{Sr})_{\text{spring}} - (^{87}\text{Sr}/^{86}\text{Sr})_{\text{rain}} ] / (5.62 \times 10^{-7} P - 4.66 \times 10^{-4})$ . The corresponding  $V_h$ 's were determined from the total watershed volumes ( $V$ ) as calculated by a terrain modeling software:  $V_h = V \times (D_h/D)$ .

The plagioclase log rates (Figure 1) are:  $-12.4 \pm 1.8$  (adjusted flow equation) and  $-13.5 \pm 1.1$  (turnover times). Relative to the former results, there is a decrease in the average log rates, by 0.2 in the first case and 1.4 in the second case.



**Figure 1:** Log rates of plagioclase.

[1] Pacheco F.A.L., Van der Weijden C.H. (2008). *Geochimica et Cosmochimica Acta*, v. 72, no. 17, Page A715.

## Methane oxidation rates by AMS

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In the marine environment methane ( $\text{CH}_4$ ) oxidation consumes up to 84% of the  $\text{CH}_4$  produced and mitigates the release of  $\text{CH}_4$ , a potent green house gas, to the atmosphere [1]. The microbially mediated process is an important sink in the global  $\text{CH}_4$  budget, yet it remains poorly quantified because only a small number of direct oxidation rate measurements are available.

Traditional oxidation rate measurements use regulated levels of radiotracers ( $^{14}\text{C}$ - and  $^3\text{H}$ - $\text{CH}_4$ ) in conjunction with scintillation counting and come with certain limitations: safety and contamination factors restrict the measurements to isotope vans, and radioisotope use may not be permitted in foreign venues and may complicate shipping.

We have developed a rate measurement that utilizes non-regulated levels of  $^{14}\text{C}$ - $\text{CH}_4$  tracer (<50nCi/g) [2] in conjunction with accelerator mass spectrometry (AMS). The high sensitivity of AMS allows for a  $10^3$  reduction in tracer activity which relaxes complications with tracer shipping, handling and waste disposal. Together with ease of performance, this method could provide a larger sample throughput and therefore a better quantification of the marine  $\text{CH}_4$  oxidation sink. Further, it allows for easy quantification of the fraction of  $\text{CH}_4$  taken up in microbial biomass as well as the fraction oxidized, thereby providing important information about the activity of methanotrophs in the ocean.

Our rate measurements compared to  $^3\text{H}$ - $\text{CH}_4$  rate measurements on water from the same Niskin bottles are generally consistent. The two measurements are similar when ambient rates are high, but diverge when rates are low.

[1] Reeburgh (2007) *Chem. Rev.* **107**, 486-513. [2] Vogel (2000) *Nucl. Instrum. Methods Phys. Res. B* **172**, 885-891.