Modeling of Plagioclase Weathering Rates in the Sordo River Basin (North of Portugal)

Modelação de Taxas de Alteração da Plagioclase na Bacia Hidrográfica do Rio Sordo (Norte de Portugal)

Pacheco, F.A.L.[1]; Van der Weijden, C.H.[2]

[1] Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal
[2] Universidade de Utrecht, Utrecht, Holanda

Abstract

Plagioclase weathering rates have been estimated in the Sordo river basin using spring water data. Relative to previous work, two improvements have been accomplished: the incorporation of travel time in the formula used to calculate the rates; the use of variable hydraulic conductivities and drainable porosities (one for each spring site) for the calculation of reacting surfaces, instead the use of average values assumed representative for the entire basin. As a consequence of such improvements, estimates of plagioclase weathering rates have been decreased by a factor of 8.7, from an average of $W_{Pl} = 18.65 \times 10^{-14}$ mol·m^{-2}·s^{-1} (Pacheco and Alencoão, 2006) to an average of $W_{Pl} = 2.15 \times 10^{-14}$ mol·m^{-2}·s^{-1} (this study). Incorporating the effect of time resulted in a decrease of the rates by a factor 3.2 while considering variable hydraulic conductivities and drainable porosities resulted in a decrease by a factor 2.6.

The calculated weathering rates are in good agreement with experimentally measured weathering rates.

Keywords: weathering rates, hydrologic travel times, reacting surface area, hydraulic conductivity, drainable porosity

Resumo

Taxas de alteração da plagioclase foram estimadas na bacia hidrográfica do rio Sordo usando dados de nascentes. Relativamente a trabalho anterior, dois melhoramentos foram alcançados: a incorporação do tempo de percurso na fórmula usada para calcular as taxas; a utilização de condutividades hidráulicas e porosidades efectivas variáveis (um valor para cada nascente), em vez do uso de valores médios considerados representativos da totalidade da bacia. Em consequência desses melhoramentos as estimativas das taxas de alteração da plagioclase decresceram segundo um factor 8.7, de um valor médio de $W_{Pl} = 18.65 \times 10^{-14}$ mol·m^{-2}·s^{-1} (Pacheco e Alencoão, 2006) para um valor médio de $W_{Pl} = 2.15 \times 10^{-14}$ mol·m^{-2}·s^{-1} (este estudo). A incorporação do efeito tempo resultou num decréscimo das taxas de alteração segundo um factor 3.2 enquanto que a utilização de condutividades hidráulicas e porosidades efectivas variáveis resultou num decréscimo segundo um factor 2.6.

As taxas de alteração calculadas neste estudo estão de acordo com taxas calculadas em laboratório.

Palavras-chave: taxas de alteração, tempos hidrológicos de percurso, superfície de reacção, condutividade hidráulica, porosidade efectiva.

Introduction

Field assessment of plagioclase weathering rates (W_{Pl}, mol·m^{-2}·s^{-1}) using spring water data involves determination of travel times of fluid parcels (t,yr), their plagioclase concentrations at spring sites ([Pl], mol·L^{-1}), the volumes of groundwater with steady-state concentration [Pl] that discharge at the spring sites in unit time (V_d, L), and the surface areas of plagioclase reacting with aquifer water in unit time (A_{Pl}, m^2). Determination of some of these variables (e.g. t, A_{Pl}) requires prior estimation of aquifer characteristics (hydraulic conductivity – K, m·s^{-1} – and drainable porosity – n_e, dimensionless) within the springs' catchment areas.

Pacheco and Alencoão (2006) estimated plagioclase weathering rates from spring water data within the Sordo river basin, but did not include the effect of time in the analysis because most springs are seasonal and therefore the authors assumed a constant travel time of one year for all springs. On the other hand, average K and n_e values estimated for a small area at the South of the basin were assigned to the catchment areas of all springs, i.e. the spatial variations in the aquifer characteristics were not fully accounted.

In this study, plagioclase weathering rates associated with the Sordo basin springs are recalculated, now incorporating the effects of travel time and of spatial variation in K and n_e, and the results compared with those obtained by Pacheco and Alencoão (2006). As a secondary objective, plagioclase weathering rates are checked against a theoretical model validated in laboratory experiments (Burch et al., 1993). A good agreement between the field-based and the experimentally-derived rates implies that the old-standing disagreement between field and laboratory results may after all be reconciled.

Study area and previous work

The hydrographic basin of Sordo river is located in Trás-os-Montes and Alto Douro (north of Portugal) and covers an area of approximately 50 km^2 (Fig. 1).

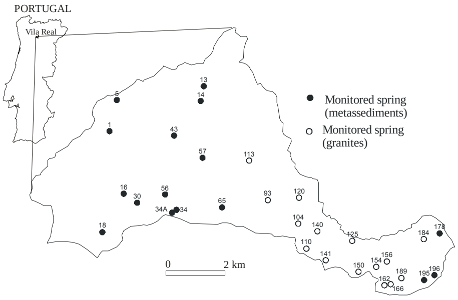

Fig. 1: Location of the study area and of springs within their boundaries monitored for discharge rate (Q) and analyzed for major element composition.

The geology of Sordo river basin is characterized by Paleozoic metasediments (mostly alternating phyllites and greywackes dated from the Cambrian) that were intruded by Hercynian (syn-D3) two-mica medium- to coarse-grained granites and covered in the valleys by alluvial deposits. The rock massifs are fractured intensely by conjugate sets, one striking to NE-SW till NNE-SSW and the other to NW-SE. The metasediments are composed essentially of quartz, albite, chlorite and muscovite, the granites of quartz, K-feldspar, plagioclase (albite-oligoclase), biotite and muscovite. The soils covering the basin are dominantly of the leptosol type, with fluvisols in the stream valleys and minor spots of anthrosols near the villages. The clay fraction of the soils is composed of kaolinite with small amounts of vermiculite (Pacheco and Alencoão, 2006).

The formula used by Pacheco and Alencoão (2006) to calculate plagioclase weathering rates was:

$$W_{Pl}(mol/m^2.s) = \frac{Q_{med}(l/s) \times [Pl](mol/l)}{A_{Pl}(m^2)} \qquad (1)$$

where Q_{med} is the spring's median discharge rate. In order to calculate the rates, Q_{med} values pertaining to 31 springs (Fig. 1) were calculated from discrete discharge rate measurements performed at the spring sites on a monthly basis in the period July 2002-October 2003. The concentrations of dissolved plagioclase ([Pl]) were determined using a mole-balance algorithm (the SiB algorithm of Pacheco and Van der Weijden, 1996), which models sets of weathering reactions by taking into account the chemical composition of spring waters, of rock minerals (e.g. plagioclase, biotite, chlorite), and of soil clays (e.g. kaolinite, vermiculite). The reacting surface areas (A_{Pl}) were estimated by the formula:

$$A_{Pl} = 2\alpha_{Pl} R \times \sqrt{\frac{\rho_w g n_e}{12\mu_w K}} \qquad (2)$$

where α_{Pl} (dimensionless) is the proportion of plagioclase in the rock, R (m^3) the annual recharge, ρ_W (999.1 kg/m^3 for T = 15ºC) and μ_W (1.14 × 10^{-3} kg/(s.m) for T = 15ºC) the specific weight and dynamic viscosity of water, respectively, and *g* (9.81 m/s^2) the acceleration of gravity. The hydrograph method described in Domenico and Schwartz (1990) was used in the calculation of R, while for the estimation of K and n_e a finite-differences method was employed, based on flow and transport equations, using solely dug-well water table and chemical data pertaining to a small area (75 hectares) located at the South of the basin, giving the following results: K = 2.77×10^{-6} m·s^{-1} and n_e = 0.014. The weathering rates calculated by Pacheco and Alencoão (2006) for all 31 springs and the associated Q_{med}, [Pl] and A_{Pl} values are shown in Tab. 1.

Hydrologic travel times and spring-site scale estimates for K and n_e

The effect of time on weathering rates can be incorporated in Eq. 1 if the instant discharge (Q_{med}, L·s^{-1}) is replaced by the volume of water discharged annually (V_d, L) and the result divided by the hydrologic travel time (t,yr):

$$W_{Pl} = \frac{[Pl]}{t} \times \frac{V_d}{A_{Pl}} \times 3.17 \times 10^{-8} \quad (3)$$

where 3.17 × 10^{-8} converts seconds into years.

Tab. 1: Weathering rates and associated variables (Q_{med}, [Pl], A_{Pl}; Eq. 1), as calculated by Pacheco and Alencoão (2006).

Nº	$W_{Pl} \times 10^{-14}$ (mol.m^{-2}.s^{-1})	Q_{med} L.s^{-1}	[Pl] µmol.L^{-1}	$A_{pl} \times 10^{8}$ (m^2)
1	16.47	0.49	82.7	2.46
5	13.73	0.43	72.4	2.27
13	13.54	0.05	34.6	0.13
14	18.65	0.84	42.2	1.9
16	23.73	0.38	45.3	0.73
18	45	1.54	48.9	1.67
30	36.79	0.98	53.6	1.42
34	21.15	0.16	59.3	0.44
34A	86.38	0.14	65.7	0.1
43	18.43	0.06	67.6	0.22
56	53.54	0.35	57.7	0.37
57	19.14	0.48	76.9	1.91
65	61.08	0.95	77	1.2
93	6.41	0.15	61.6	1.44
104	7.18	1.13	76.8	12.09
110	9.5	0.93	90.7	8.88
113	12.02	3.6	52.7	15.79
120	11.81	0.44	70.9	2.64
125	12.9	0.15	80	0.93
140	11.35	0.14	72.5	0.89
141	16.34	0.17	73.7	0.74
150	20.26	0.18	162	1.44
154	0	0.11	0	0
156	0	0.1	0	0
162	56.25	0.02	261.7	0.07
166	0	0.03	0	0
178	26.4	0.66	263.8	6.6
184	33.92	0.16	294.5	1.39
189	48.35	0.08	244.3	0.41
195	45.19	0.12	216.3	0.57
196	39.5	0.06	229	0.81

The V_d values can be estimated by the hydrograph method in the same manner as the R values were determined by Pacheco and Alencoão (2006). Travel times can be estimated by a numerical (finite differences) method assuming the system to be at steady-state and the transport of solutes to be advective, as follows (Pacheco and Van der Weijden, 2007):

$$t = \frac{[Pl] \times n_e}{\nabla[Pl] \times K} \quad (4)$$

where ∇[Pl] is the gradient of [Pl], calculated by:

$$\nabla[Pl] = \sqrt{\left(\frac{[Pl]_E - [Pl]_W}{2\Delta x}\right)^2 + \left(\frac{[Pl]_N - [Pl]_S}{2\Delta y}\right)^2} \quad (5)$$

where $[Pl]_{N\ (S,\ E,\ W)}$ are the concentrations of dissolved plagioclase at distances Δy to the north and south, and Δx to the east and west, of the sampling site.

Usually, calculation of ∇[Pl] requires the use of spatial analysis software packages that in a first step calculate the values of [Pl] within a grid of regularly spaced nodes (separated Δx and Δy from each other), from an array of irregularly distributed points (spring sites), using interpolation methods (e.g. kriging), and then implement Eq. 5 using that information. For the Sordo river basin, the spatial distribution of [Pl] and ∇[Pl] is shown in Figs. 2a and 2b, respectively.

To complete the calculation of travel times it is required that values for K and n_e are known in advance. In this study, these values are calculated for each spring site using a hydrological approach developed by Brutsaert and co-workers (e.g. Brutsaert and Lopez, 1998). The individual values of K and n_e will also replace the average values ($K = 2.77\times10^{-6}$ m·s^{-1} and $n_e = 0.014$) used by Pacheco and Alencoão (2006) to calculate A_{Pl} (Eq. 2), providing more accurate estimates of this parameter.

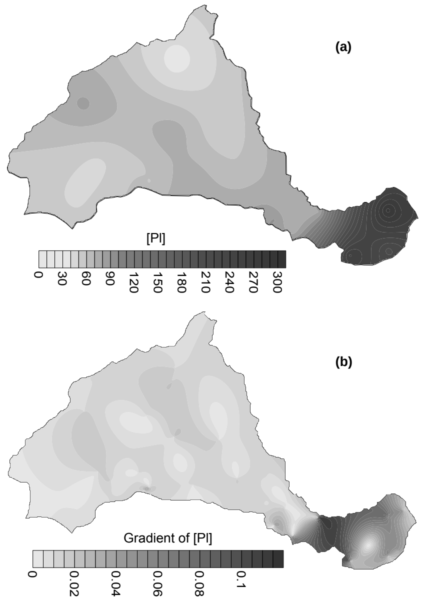

Fig.2: Spatial distribution of [Pl] (a) and of ∇[Pl] (b).

According to the Brutsaert method, in a graphical plot ln(□Q/□t) vs ln(Q), the lower envelope to the scatter points is represented by two straight lines, one of slope b=3 and the other of slope b = 1, with intercept-y values – a – given by:

$$a_{(b=3)} = \frac{1.13}{K n_e D^3 L^2} \quad (6a)$$

$$a_{(b=1)} = \frac{0.35\pi^2 K D L^2}{n_e A^2} \quad (6b)$$

where A (m2) is the area of a watershed surrounding the spring, L (m) is the length of water channels within that area, and D (m) the aquifer thickness. Values for K and ne can be obtained by combining equations 6a and 6b, providing that values for A, L and D are also available. Fig. 3a shows the plot ln(□Q/□t) vs ln(Q) drawn for spring nr. 1, using the Q data published in Pacheco and Alencoão (2006). According to this plot, a(b= 3) = 0.0055 and a(b=1) = 3.39×10–8. The evaluation of quantities A, L and D has been accomplished by analysis of topographic maps, as exemplified for spring nr. 1 (Fig. 3b): (a) A is the area of the smallest watershed surrounding the spring (32.6 hectares), usually a first-order (without tributaries) streamlet; (b) L is the length of the water channels within that watershed (914 m); (c) D is 1/2 the average height of the hills above the streamlet, measured along a central cross-section of the watershed (12.5 m).

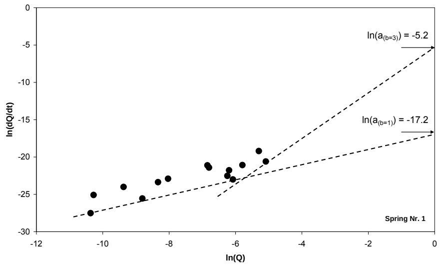

Fig. 3a – Plot ln(dQ/dt) vs. ln(Q) for spring nr. 1 and assessment of the associated intercept-y values. Discharge rate data (Q) available in Pacheco and Alencoão (2006)

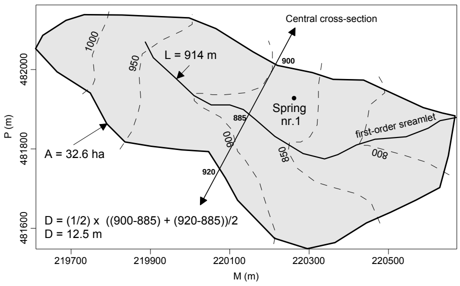

Fig. 3b – Evaluation of A, L and D for spring nr. 1.

Using the methodologies described above, travel times of spring waters were calculated (Eqs. 4 and 5), reactive surface areas were recalculated (Eq. 2) using spring-site scale estimates of K and n_e (Eqs. 6a and 6b), and weathering rates incorporated the effects of travel time and of spatially variable aquifer characteristics. All these results are shown in Tab. 2.

Tab. 2 – Weathering rates and associated parameters, as calculated in this study.

	$W_{Pl} \times 10^{-14}$	$V_d \times 10^{6}$	t	$A_{Pl} \times 10^{8}$	$K \times 10^{-6}$	n_e
Nr	$mol \cdot m^{-2} \cdot s^{-1}$	L	yr	(m^2)	$m \cdot s^{-1}$	
1	4.4	19.5	3.4	3.5	3.5	0.035
5	11.7	18.1	1.4	2.5	8.1	0.050
13	0.1	1.0	14.0	0.5	1.9	0.174
14	4.8	15.2	1.2	3.4	6.5	0.105
16	10.1	7.6	1.2	0.9	13.4	0.103
18	36.0	14.6	0.6	1.1	6.3	0.014
30	15.8	11.5	0.8	1.5	2.1	0.012
34	2.2	4.7	3.7	1.1	1.6	0.046
34A	73.6	1.2	0.4	0.1	4.7	0.016
43	1.3	1.9	6.4	0.5	5.9	0.147
56	0.8	3.2	8.3	0.9	5.8	0.159
57	5.8	16.3	2.9	2.4	0.7	0.005
65	2.1	13.2	6.6	2.4	6.0	0.117
93	0.1	5.1	21.4	6.9	2.3	0.258
104	0.9	41.7	4.6	24.7	1.1	0.022
110	15.4	30.6	0.6	8.8	5.6	0.028
113	0.0	83.4	39.7	92.4	0.0	0.001
120	0.3	9.4	9.9	7.3	3.8	0.143
125	0.6	3.5	5.9	2.6	1.1	0.044
140	0.9	3.1	4.9	1.7	2.8	0.052
141	8.1	3.0	0.7	1.2	1.3	0.017
150	1.2	5.2	3.4	6.6	2.4	0.247
154		2.8		4.1	0.6	0.089
156		3.7		5.1	0.3	0.039
162	7.5	0.3	1.3	0.3	0.3	0.032
166		0.5		0.7	0.6	0.075
178	0.5	31.4	18.9	26.0	4.2	0.328
184	0.4	5.6	20.2	7.3	0.6	0.080
189	1.6	2.3	4.5	2.5	0.2	0.037
195	16.2	4.8	2.6	0.8	0.8	0.008
196	7.7	2.8	3.7	0.7	0.7	0.015

The median travel time of the springs is 3.6 yr, which is slightly higher than the times estimated by Pacheco and Van der Weijden (2007) for Vouga springs (2.2 and 1.4 yr, respectively for metassediment and granite springs). The K ($3.1 \pm 2.9 \times 10^{-6}$ $m \cdot s^{-1}$) and n_e (0.081 ± 0.080) ranges cover the values adopted by Pacheco and Alencoão (2006). As a result of replacing the average K and n_e by spring-site scale values in Eq. 2, the average A_{Pl} increased from 9.86×10^{7} m^2 to 2.39×10^{7} m^2 (factor 2.43).

Comparison of results

Incorporating the effects of travel time and of spatial variation in K and n_e has the consequence of decreasing the estimated plagioclase weathering rates (Tab. 3). The overall decreasing factor is 8.7.

Tab. 3 – Consequences on weathering rates estimates of considering the effects of travel time and spatial variation in K and n_e.

		Average W_{Pl} $\times 10^{-14}$ $(mol \cdot m^{-2} \cdot s^{-1})$	Factor of drecrease relative to Pacheco and Alencoão (2006)
Pacheco and Alencoão (2006)		18.65	1
This study	Specifying spring-site scale K and n_e values	7.23	2.6
	Incorporating the effect of travel time	5.81	3.2
	Overall effect	2.15	8.7

Validation of rates by experimental model

The W_{Pl} values were plotted against the Gibbs energies of plagioclase reactions to kaolinite (Fig. 4). They show a reasonable agreement with the experimental dissolution model of Burch et al. (1993) (R_d, dashed lines). A major conclusion from this study is that field and laboratory rates may after all be reconciled.

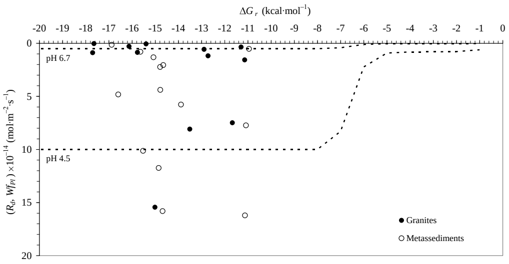

Fig. 4 – Validation of the rates (open and filled circles) by a theoretical model (dashed lines).

References

Brutsaert, W., Lopez, J.P. (1998). Water Resour. Res., 34(2): 233–240.
Burch, T.E., Nagy, K.L., Lasaga, A.C. (1993). Chem. Geol., 105: 137–162.
Domenico, P.A., Schwartz, F.W. (1990). Physical and chemical hydrogeology. John Wiley & Sons Inc., New York, 824pp.
Pacheco, F.A.L., Alencoão, A.M.P. (2006). J. Hydrology, 316: 248–265.
Pacheco, F.A.L., Van der Weijden, C.H. (1996). Water Resour. Res., 32: 3553–3570.
Pacheco, F.A.L., Van der Weijden, C.H. (2007). Hydrologic and kinetic modeling of plagioclase weathering rates in the Vouga basin (Portugal): reconciling field and laboratory rates. Revision in American Journal of Science.