



**Mineralogical Trends of Plagioclase Weathering
Along Fault-Zone Pathways**
***Tendências Mineralógicas de Alteração da Plagioclase
ao Longo de Zonas de Fractura***

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Abstract

Ground waters flowing through granite and metasediment fault zone aquifers were sampled at boreholes in the region of Vila Pouca de Aguiar (North of Portugal). In these geological environments, especially in the granites, weathering of plagioclase plays a dominant role as source of solutes to ground water, namely of bicarbonate and silica. The bicarbonate to silica ratios (B/Si) of the sampled waters span a wide range of values in both environments (1.10 ± 0.87 in the granites and 1.67 ± 1.21 in the metasediments) which is indication that weathering of plagioclase results in precipitation of a multiplicity of secondary products including gibbsite, halloysite and smectite. Reactions producing these clay minerals are believed to operate at different places along the flow path: gibbsite is the prevailing product when groundwater is flowing along the saprolite horizon towards the fault zone, whereas halloysite and smectite precipitate along gravity and capillary flow sectors of the fault zone, respectively.

Keywords: plagioclase weathering, fault zone pathways, advection, diffusion

Resumo

Águas subterrâneas circulantes em zonas de falha de granitos ou metassedimentos foram amostradas em furos na região de Vila Pouca de Aguiar (Norte de Portugal). Nestes ambientes geológicos, especialmente nos granitos, a alteração da plagioclase assume um papel dominante como fonte de solutos para a água subterrânea, nomeadamente de bicarbonato e sílica. A razão bicarbonato/sílica (B/Si) das águas amostradas cobre um intervalo de valores muito alargado (1.10 ± 0.87 nos granitos e 1.67 ± 1.21 nos metassedimentos) dando indicação de que a alteração da plagioclase resulta na precipitação de uma multiplicidade de produtos de alteração incluindo a gibsite a haloisite e a esmectite. Acredita-se que as reacções que produzem estes minerais argilosos operam em locais diferentes ao longo do trajecto da água: a gibsite é o produto dominante quando a água atravessa o horizonte saprolítico em direcção à zona de falha, ao passo que a haloisite e a esmectite precipitam em sectores da zona de falha onde predominam fluxos hídricos gravíticos e por capilaridade, respectivamente.

Palavras chave: alteração da plagioclase, trajectos de fluxo em zonas de falha, advecção, difusão

Introduction

Weathering of plagioclase is the major natural source of solutes dissolved in ground water in granite and carbonate-free metasediments. Reactions of plagioclase release sodium, calcium and, most importantly, bicarbonate and silica to solution. The bicarbonate to silica ratio (B/Si) in ground water is a key parameter in distinguishing between different reactions (Garrels, 1967; Pacheco and Van der Weijden, 1996). Low B/Si ratios are usually related to reactions of plagioclase producing gibbsite, medium ratios to reactions producing halloysite and high ratios to reactions producing smectite, although the ratios also depend on the anorthite content of plagioclase. When this content is higher than 5% reactions producing smectite consume silica and therefore the B/Si ratios are even higher.

The purpose of this study is: 1) to describe the evolution of B/Si ratios in ground water along saprolite and fault zone pathways of the Vila Pouca de Aguiar granites and metasediments; 2) relate that evolution with flow environments and trends of plagioclase weathering.

Study Area

The region of Vila Pouca de Aguiar is located in the North of Portugal and occupies an area of approximately 437 km². The geology of the area is characterized by Hercynian (syn- to post-tectonic) granites that intruded Palaeozoic (Cambrian to Devonian) metasediments and were covered by Quaternary alluvial and terrace deposits along a large-scale tectonic structure known as the Vila Real fault. The Vila Pouca de Aguiar granites are composed of quartz (31.5%), plagioclase (35.3), K-feldspar (26.7), biotite (4.4) and muscovite (1.4), with minor amounts of apatite and ilmenite. The plagioclase composition ranges from albite-An₈ to andesine-An₃₇ (Pacheco et al., 1999). The metasediments, which include greywackes, phyllites, quartzites and graphitic slates, contain quartz, muscovite and smaller amounts of biotite, K-feldspar and albite-oligoclase (Pacheco, 1995). Climate in the area is temperate with wet-cold and dry-warm alternating seasons. The annual precipitations range from 900 mm·yr⁻¹ in the Northeast to 1900 mm·yr⁻¹ in the Southwest of the region (Figure 1).

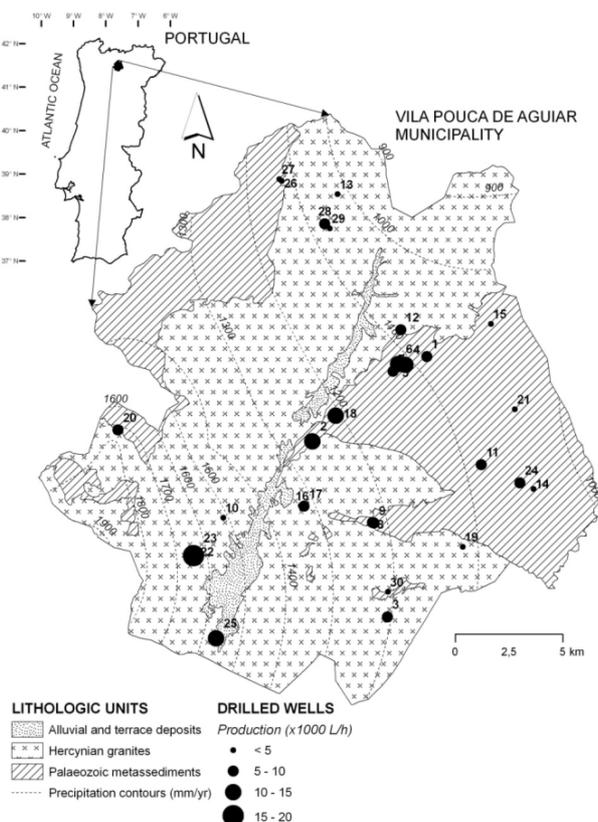


Fig. 1 – Location and simplified geologic map of the Vila Pouca de Aguiar region. Distribution of the annual precipitation (contours) and production of drilled wells used for public supply of water (graduated filled circles). The labels close to the circles are in agreement with the Id numbers in Table 1.

Boreholes

In the past three decades, about 50–60 boreholes were drilled in the region of Vila Pouca de Aguiar to be used as sources of water for public supply. The yields evaluated for 30 of these boreholes are illustrated in Figure 1 and result from a combination of factors encompassing the annual precipitation, the abundance of quartzites within the metasediments, and the proximity of the borehole to the Vila Real fault or to the contact between the granites and the metamorphic rocks. During the drillings, several conductive fractures were intersected by the boreholes releasing variable amounts of water. The depths to the productive sectors (D_{med} , m) are listed in Table 1 for the above mentioned 30 boreholes, being on average 51 ± 21 m.

Table 1 – Identification (Id code) and associated rock type (A – Hercynian granites; B – Palaeozoic metasediments) of 30 boreholes drilled in the region of Vila Pouca de Aguiar; depth of the productive sectors (D_{med}); bicarbonate ($[HCO_3^-]$) and silica ($[H_4SiO_4^0]$) concentrations of the borehole waters; results of the weathering modelling: concentration of silica derived from plagioclase reactions ($[H_4SiO_4^0]_{Gibb}$), ($[H_4SiO_4^0]_{Hal}$) and ($[H_4SiO_4^0]_{Sm}$). The subscripts mean: Gibb – gibbsite, Hal – halloysite, Sm smectite.

Id	Rock Type	D_{med}	$[HCO_3^-]$	$[H_4SiO_4^0]$	$[H_4SiO_4^0]_{Gibb}$	$[H_4SiO_4^0]_{Hal}$	$[H_4SiO_4^0]_{Sm}$	B/Si
		m						
1	B	96.3	520	437	92	392	-47	1.19
2	B	62.0	207	328	130	198	-1	0.63
3	A	41.3	264	513	404	111	-2	0.51
4	B	38.9	766	602	504	199	-100	1.27
5	B	35.9	761	595	509	186	-101	1.28
6	B	43.3	787	571	454	224	-106	1.38
7	B	48.5	1141	560	421	320	-180	2.04
8	B	47.7	628	707	570	196	-59	0.89
9	B	74.0	823	662	412	346	-97	1.24
10	A	69.8	113	342	110	209	nd	0.33
11	B	75.0	287	584	331	244	nd	0.49
12	A	88.4	1513	584	272	556	-245	2.59
13	A	44.3	395	405	283	160	-38	0.98
14	B	50.7	239	215	66	170	-21	1.11
15	B	33.3	469	93	18	160	-85	5.06
16	A	84.3	195	532	239	267	nd	0.37
17	A	43.1	290	432	315	131	-14	0.67
18	B	18.4	361	326	315	56	-46	1.11
19	A	34.4	151	193	114	88	-9	0.78
20	B	22.6	316	77	49	86	-58	4.11
21	B	66.8	266	269	50	235	-17	0.99
22	A	32.2	220	299	230	84	-15	0.73
23	A	31.4	764	286	219	197	-131	2.67
24	B	80.9	830	279		409	-131	2.98
25	A	77.5	348	820	556	246	nd	0.42
26	B	51.3	466	538	386	191	-39	0.87
27	B	40.8	361	137	31	163	-56	2.63
28	A	26.7	1107	447	401	236	-189	2.47
29	A	17.5	251	351	345	27	-21	0.71
30	B	38.2	225	270	174	112	-16	0.83

Borehole Chemistry

Samples of granite and metasediment borehole water were collected within the limits of the Vila Pouca de Aguiar municipality in a campaign that started in January 2006 and finished in April 2006. The sampling sites are shown in Figure 1. At the sampling site, a water sample was collected and filtered through a 0.4 μm membrane filter. The filtered water was split into 2 portions: one was stored for analysis in the home laboratory, acidified to pH 2, the other was stored for analysis of alkalinity in the field laboratory, within 24 hours using the Gran plot method. In the home laboratory, ICP-OES was used for analysis of Si. The analytical results are shown in Table 1.

Groundwater Flow Paths and Dissolved Silica Concentrations

The fate of rainwater infiltrating a fractured massif in a region of temperate climate comprises the recharge of the massif during the transition between winter and spring and the lateral flow of shallow ground water within the saprolite horizon and towards fault zones for the duration of the recharge as well as the spring–summer interflow episodes. Figure 2 illustrates lateral flow of shallow ground water along a saprolite horizon succeeded by its infiltration into a couple of fault zones. Fault zones are complex fracture environments composed of gravity flow systems (wide open fractures) in hydraulic connection with adjacent networks of capillary flow systems made of micro fractures, joints, solution pores, etc. Infiltration replenishes every year the gravity as well as the capillary flow systems with precipitation water, but flow takes place mainly along the larger pathways. The whole system is frequently called a double porosity system (Barenblatt et al., 1960).

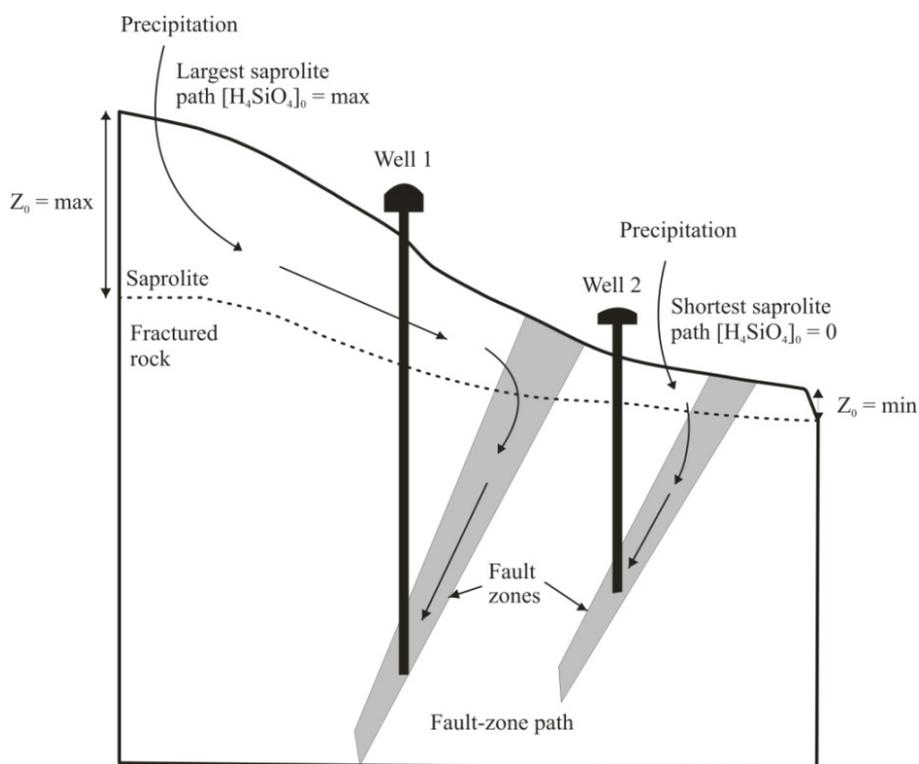


Fig. 2 – Flow paths of shallow ground water towards two fault zones.

During the saprolite and fault zone pathways, reaction of water with rock forming minerals releases solutes and precipitates clay minerals, oxyhydroxides, etc. One of the reaction-derived solutes is silica (H_4SiO_4^0) and for the studied borehole waters the concentrations of H_4SiO_4^0 ($[\text{H}_4\text{SiO}_4^0]$, $\text{mol}\cdot\text{L}^{-1}$) increase with depth (Figure 3).

The sympathy between $[\text{H}_4\text{SiO}_4^0]$ and depth (D_{med}) in Figure 3 is unquestionable despite the scatter marked by the departure between the two dashed lines. The scatter can be ascribed to the contribution of saprolite weathering to $[\text{H}_4\text{SiO}_4^0]$, i.e. to weathering occurring before the

entrance of shallow ground water into the fault zones intersected by the drilled wells. The saprolite contribution to weathering is referred to as $[H_4SiO_4]_0$ and represented by the dotted line. If the path followed by ground water during the stage of saprolite weathering is the largest (e.g. flow towards Well 1 in Figure 2) then $[H_4SiO_4]_0$ is also the largest and represented by the intersection between the upper dashed line and the dotted line in Figure 3. If this path is the shortest (flow towards Well 2) then $[H_4SiO_4]_0$ will approach zero and be represented by the intersection between the lower dashed line and the dotted line.

In general (values in Table 1),

$$[H_4SiO_4]_0 = [H_4SiO_4] - 0.0043(D_{med} - z_0) \quad (1)$$

where 0.0043 is the slope of the dashed lines and z_0 the thickness of the saprolite layer (mean value), represented by the intersection between the lower dashed line and the X-axis of Figure 3 ($z_0 = 16$ m).

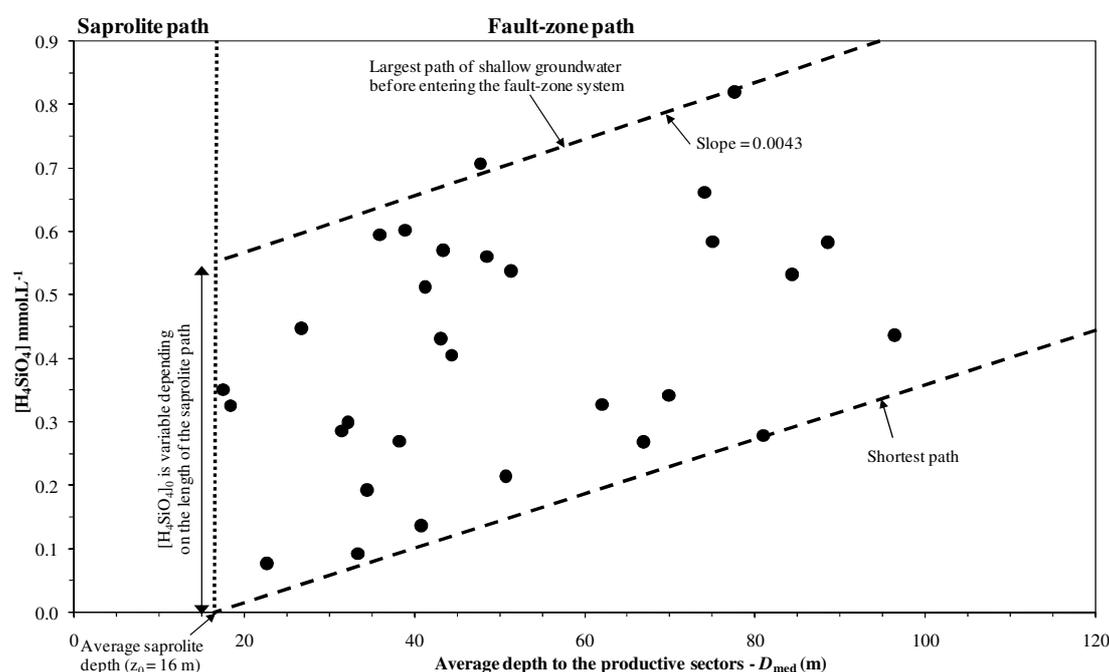


Fig. 3 – Relation between the concentrations of dissolved silica ($[H_4SiO_4]$) and the depth to the productive sectors of the drilled wells (D_{med}).

Trends of Plagioclase Weathering

In granite and metasediment environments, dissolved silica typically results from weathering of plagioclase, biotite (granites) and chlorite (metasediments), but plagioclase plays the dominant role. Pacheco and Van der Weijden (1996), working in the Fundão plutonite (central Portugal), estimated for several granitoid units that the contribution of plagioclase weathering varies from 96.9% to 100% relative to the contribution of biotite weathering. Contributions around or greater than 90% were also estimated for plagioclase in other granite and metasediment areas in Portugal by Pacheco et al. (1999), Pacheco and Alenção (2006) and Van der Weijden and Pacheco (2006). The secondary products formed by alteration of plagioclase depend on the local climatic and hydrologic conditions. For example, alteration under precipitations greater than $1000 \text{ mm}\cdot\text{yr}^{-1}$ in a medium characterized by gravity flows (e.g. saprolites, wide open fractures) usually results in formation of gibbsite, whereas for precipitations lower than $1000 \text{ mm}\cdot\text{yr}^{-1}$ the most common product is kaolinite or halloysite (Martins et al., 1995; Van der Weijden and Pacheco, 2006). However, if the flow of percolating water gets sluggish, as it occurs with capillary flow in micro fractures, concentration of solutes will go up and smectites will tend to precipitate (Meunier et al., 2007).

Reactions of plagioclase producing gibbsite, halloysite, or smectite are listed in Table 2. A key parameter in distinguishing between different reactions is the bicarbonate to silica ratio, r

(Garrels, 1967; Pacheco and Van der Weijden, 1996). For the reactions listed in Table 2 the r ratios are:

$$r_{Gibb} = \frac{1+x}{2-x} \quad (2a)$$

$$r_{Hal} = \frac{1}{2} \left(\frac{1+x}{1-x} \right) \quad (2b)$$

$$r_{Sm} = \frac{0.9(1+x)}{0.95 - 5.65x} \quad (2c)$$

where x is the anorthite content of plagioclase ($0 \leq x \leq 1$). In the Vila Pouca de Aguiar region plagioclase is faithfully represented by an oligoclase An_{20} ($x = 0.2$), which means that $r_{Gibb} = 0.43$, $r_{Hal} = 0.75$, and $r_{Sm} = -4$. The negative value of r_{Sm} means that production of smectite consumes silica and consequently that the bicarbonate to silica ratio in ground water (B/Si) will be high if this reaction prevails.

The B/Si ratios of the borehole water samples are depicted in Table 1 (last column). They vary from a minimum of 0.33 to a maximum of 5.06, being on average equal to 1.44 ± 1.12 . They are also higher in the metasediments (1.67 ± 1.21) than in the granites (1.10 ± 0.87). Comparison of these ratios with the ones resulting from R_{Gibb} , R_{Hal} and R_{Sm} (Table 2) suggests that, with few exceptions, borehole water compositions might be influenced by all these reactions, however acting at different points along the flow path. Weathering of plagioclase along the saprolite path is likely to form gibbsite because the annual precipitation in the vicinity of the drilled wells is invariably greater than 1000 mm (Figure 1). Halloysite and smectite will form along major fractures and adjacent micro fractures of the fault zone path, respectively, in keeping with the prevailing conditions of flow (gravity, capillary). The exceptions are boreholes nr. 10, 11, 16 and 25 because their B/Si ratios (0.33 – 0.49) are lower than (or very close to) the lowest r (r_{Gibb}) and therefore no reaction is adequate to describe their composition.

Table 2 –Reactions of plagioclase ($Na_{1-x}Ca_xAl_{1+x}Si_{3-x}O_8$, where x is the anorthite content) producing smectite ($(Mg_{0.35}Al_{1.65})Si_4O_{10}(OH)_2 \cdot 5H_2O \cdot Ca^{2+}_{0.175}$), halloysite ($Al_2Si_2O_5(OH)_4$) and gibbsite ($Al(OH)_3$). Structural formula of smectite adopted from Van der Weijden and Pacheco (2006).

Id	Clay	Reaction
R_{Gibb}	gibbsite	$\frac{2}{1+x} Pl + 2CO_2 \xrightarrow{nH_2O} Gb + 2\frac{1-x}{1+x} Na^+ + 2\frac{x}{1+x} Ca^{2+} + 2HCO_3^- + 2\frac{3-x}{1+x} H_4SiO_4^0$
R_{Hal}	halloysite	$\frac{2}{1+x} Pl + 2CO_2 \xrightarrow{nH_2O} Kl + 2\frac{1-x}{1+x} Na^+ + 2\frac{x}{1+x} Ca^{2+} + 2HCO_3^- + 4\frac{1-x}{1+x} H_4SiO_4^0$
R_{Sm}	smectite	$\frac{1.65}{1+x} Pl + 0.35Mg^{2+} + 0.6CO_2 \xrightarrow{nH_2O}$ $Sm + 1.65\frac{1-x}{1+x} Na^+ + \frac{1.475x - 0.175}{1+x} Ca^{2+} + 0.6HCO_3^- + \frac{0.95 - 5.65x}{1+x} H_4SiO_4^0$

By solving a set of mole balance equations based on the stoichiometries of the plagioclase reactions (Table 2), namely on the bicarbonate to silica ratio, it is possible to estimate the concentrations of silica derived from each other. The mole balance equations are:

$$[HCO_3^-] = r_{Gibb} [H_4SiO_4^0]_{Gibb} + r_{Hal} [H_4SiO_4^0]_{Hal} + r_{Sm} [H_4SiO_4^0]_{Sm} \quad (3a)$$

$$[H_4SiO_4^0] = [H_4SiO_4^0]_{Gibb} + [H_4SiO_4^0]_{Hal} + [H_4SiO_4^0]_{Sm} \quad (3b)$$

The unknowns of the system are the partial concentrations of dissolved silica, but $[H_4SiO_4^0]_{Gibb}$ can be equated to $[H_4SiO_4^0]_0$ (Equation 1). Under these settings the system is determined, i.e. has a single solution for $[H_4SiO_4^0]_{Hal}$ and $[H_4SiO_4^0]_{Sm}$. The concentrations of silica derived from R_{Gibb} , R_{Hal} and R_{Sm} are depicted in Table 1 and plotted as a function of D_{med} in Figure 4.

No correlation exists between $[H_4SiO_4^0]_{Gibb}$ and D_{med} , but even wasn't expected as production of gibbsite is ascribed to the saprolite path, not to the fault zone path. A correlation between the remainder of silica ($[H_4SiO_4^0]_{Hal} + [H_4SiO_4^0]_{Sm}$) and D_{med} was already mentioned (Figure 3) but Figure 4 shows that only $[H_4SiO_4^0]_{Hal}$ is correlated with it. This is a remarkable result because confirms that production of halloysite is associated with plagioclase weathering along the mean direction of flow, and that the same does not holds for production of smectite. In keeping with these results, it may be concluded that production of halloysite do occurs along the walls of gravity flow fractures, a medium where solute transport is advective and therefore concentrations must increase with increasing flow path lengths (D_{med}), justifying the observed correlation, whereas production of smectite occurs at micro fractures adjacent to the gravity flow fractures, where solute transport is diffusive, mediated by local gradients of chemical potential and by the length of diffusion trajectories between the capillary and gravity flow fractures, and hence not necessarily dependent on the flow path lengths.

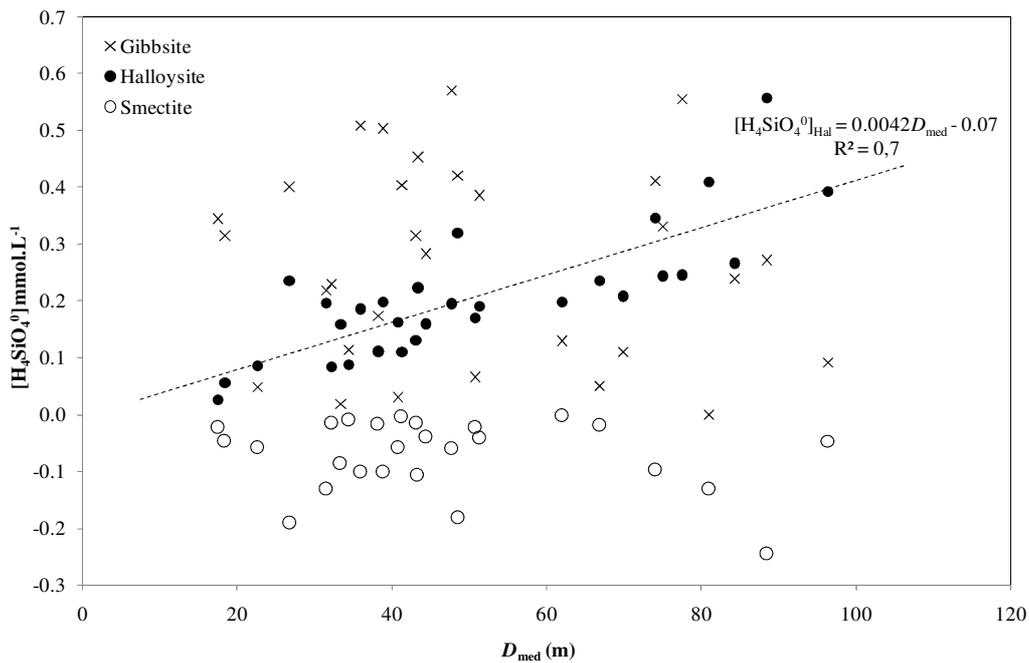


Fig. 4 – Plot of $[H_4SiO_4^0]_{Gibb}$, $[H_4SiO_4^0]_{Hal}$ and $[H_4SiO_4^0]_{Sm}$ as a function of D_{med} .

Evolution of the B/Si Ratio

As mentioned above, in case R_{Sm} consumes silica the reaction proceeds only if there's some silica available in the solution, for example transported along the flow path from places where weathering of plagioclase has released this solute, e.g. from places where R_{Gibb} or R_{Hal} were the prevailing reactions. The bicarbonate to silica ratio in cases where smectite starts precipitating and consuming silica released by R_{Gibb} and R_{Hal} is given by (r'_{Sm}):

$$r'_{Sm} = \frac{[H_4SiO_4^0]_{Gibb} (r_{Gibb} + r_{Sm}) + [H_4SiO_4^0]_{Hal} (r_{Hal} + r_{Sm})}{[H_4SiO_4^0]} - r_{Sm} \quad (4)$$

The plot of Equations 2a, 2b and 4 in case $x = 0.2$ is illustrated in Figure 5 (dotted lines) for increasing values of $[H_4SiO_4^0]$ and fixed values of $[H_4SiO_4^0]_{Gibb}$ and $[H_4SiO_4^0]_{Hal}$ (the minimum and maximum values as given in Table 1). The borehole water samples fall within the theoretical lines, being represented by the filled circles.

Evolution of the B/Si ratio of a given water sample in the course of weathering is determined by the contributions to ground water composition of reactions R_{Gibb} , R_{Hal} and R_{Sm} . The points along the flow path where contribution of R_{Sm} is significant are particularly difficult to identify because the extension and geometry of the capillary flow systems are determined locally and

hence specific from each fault zone. For an academic scenario where plagioclase weathering in the capillary flow systems contributes to groundwater chemistry solely at the end of the fault zone path, the evolution of the average B/Si ratio would be represented by the arrowed line and described as follows: 1) During the stage of saprolite weathering shallow ground water has an average $[\text{H}_4\text{SiO}_4] = 276 \mu\text{mol}\cdot\text{L}^{-1}$ ($[\text{H}_4\text{SiO}_4]_{\text{Gibb}}$) and a concomitant B/Si = 0.43 ($\equiv r_{\text{Gibb}}$); 2) after entering the fault zone velocity of ground water slows down, the leaching of solutes is less intense, and conditions are created for precipitation of halloysite which raises the B/Si ratio towards r_{Hal} (0.75). The maximum ratio achieved is B/Si = 0.57 for an average $[\text{H}_4\text{SiO}_4] = 483 \mu\text{mol}\cdot\text{L}^{-1}$ ($[\text{H}_4\text{SiO}_4]_{\text{Gibb}} + [\text{H}_4\text{SiO}_4]_{\text{Hal}}$); 3) When weathering in the micro fractures starts contributing to ground water composition production of smectite becomes the prevailing reaction. This consumes silica reducing its concentration to an average $[\text{H}_4\text{SiO}_4] = 415 \mu\text{mol}\cdot\text{L}^{-1}$ and raising the concomitant bicarbonate to silica ratio to B/Si = 1.31.

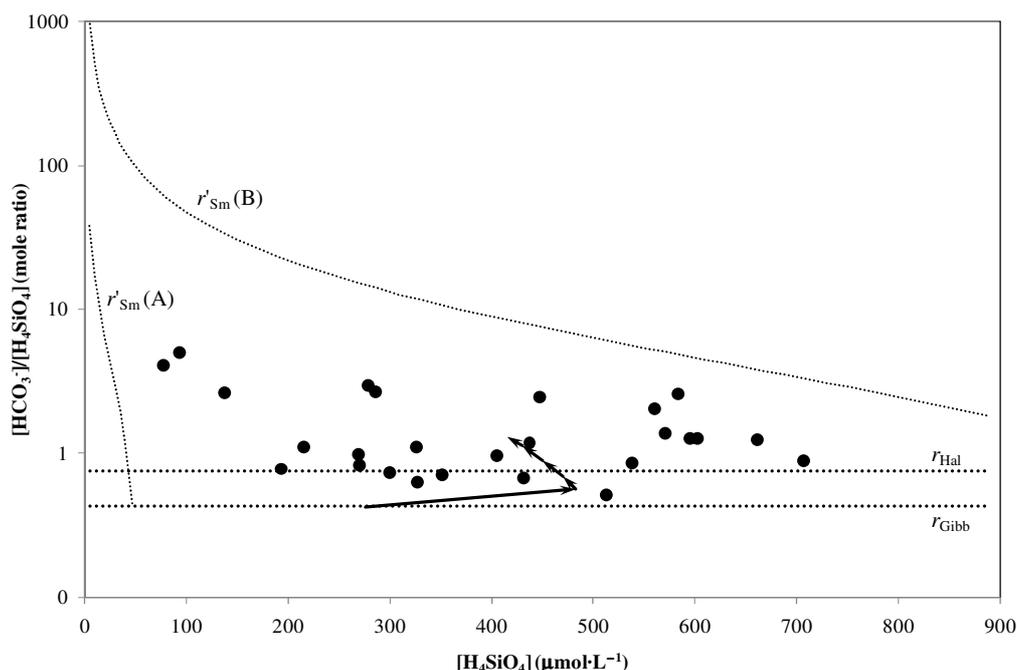


Fig. 5 – Plot of dissolved silica concentrations ($[\text{H}_4\text{SiO}_4]$) versus the bicarbonate to silica ratio ($[\text{HCO}_3^-]/[\text{H}_4\text{SiO}_4]$) of the borehole samples. Comparison with theoretical ratios (dotted lines) resulting from weathering of oligoclase (An_{20}) producing gibbsite (r_{Gibb}), halloysite (r_{Hal}), or smectite after previous precipitation of gibbsite and halloysite ($r'_{\text{Sm}}(\text{A})$ for minimum values of $[\text{H}_4\text{SiO}_4]_{\text{Gibb}}$ plus $[\text{H}_4\text{SiO}_4]_{\text{Hal}}$, as given in Table 1, and $r'_{\text{Sm}}(\text{B})$ for maximum values of those concentrations). A chemical evolution of the average B/Si is represented by the arrowed line and explained in the text.

Conclusions

Weathering of plagioclase modelled on the basis of borehole water compositions collected in the region of Vila Pouca de Aguiar is described as a multi stage process comprising production of gibbsite along a saprolite horizon, of halloysite along the walls of gravity flow fractures and of smectite within a network of capillary flow systems including micro fractures, joints and solution pores. Weathering is mediated by advective transport of solutes, when producing gibbsite and halloysite, and by chemical diffusion when producing smectite.

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