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Alkaline-extractable silicon from land to ocean: A challenge for biogenic silicon determination

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Abstract

The biogeochemical cycling of silicon (Si) along the land-to-ocean continuum is studied by a variety of research fields and for a variety of scientific reasons. However, there is an increasing need to refine the methodology and the underlying assumptions used to determine biogenic silica (BSi) concentrations. Recent evidence suggests that contributions of nonbiogenic sources of Si dissolving during alkaline extractions, not corrected by standard silicate mineral dissolution correction protocols, can be substantial. The ratio between dissolved Si and aluminum (Al) monitored continuously during the alkaline extraction can be used to infer the origin of the Si fractions present. In this study, we applied both a continuous analysis method (0.5 M NaOH) and a traditional 0.1 M Na_2CO_3 extraction to a wide array of samples: (1) terrestrial vegetation, (2) soils from forest, cropland and pasture, (3) lake sediments, (4) suspended particulate matter and sediments from rivers, (5) sediments from estuaries and salt marshes and (6) ocean sediments. Our results indicate that the 0.1 M Na_2CO_3 extraction protocol can overestimate the BSi content, by simultaneously dissolving Si fractions of nonbiogenic origin that may represent up to 100% of the Si traditionally considered as biogenic, hampering interpretation especially in some deeper soil horizons, rivers and coastal oceanic sediments. Moreover, although the term amorphous Si was coined to reflect a growing awareness of nonbiogenic phases we show it is actually inappropriate in samples where silicate minerals may account for a large part of the extracted Si even after linear mineral correction.

During the last decades the analysis of biogenic silica (BSi) has become important to a variety of scientific fields including biogeochemistry, aquatic sciences, paleoecology, and agricultural science (Ragueneau et al. 2000; Conley and Schelske 2001; Ma and Yamaji 2006; Tréguer and De La Rocha 2013). The principal source of all Si on Earth is the chemical weathering of silicate minerals. There is an important connection between Si-weathering and atmospheric CO_2 concentrations (Berner et al. 1983), where recent studies emphasize that even on centennial timescales weathering processes affect atmospheric CO_2 (Beaulieu et al. 2012). A substantial part of the weathered Si cycles through terrestrial vegetation and soils, where it is stored in the biogenic form of phytoliths. This ecosystem Si cycle has been called the "ecosystem Si filter" (Conley 2002; Carey and Fulweiler 2012; Struyf and Conley 2012), as it influences the delivery of dissolved silica (DSi) from terrestrial systems to aquatic systems (Derry et al. 2005). DSi exported from land is important for the development of diatom communities in adjacent waters and influences the eutrophication response of coastal waters to enhanced N & P inputs (Cloern 2001). The riverine systems linking terrestrial, estuarine and oceanic Si cycles (Struyf et al. 2006; Dürr et al. 2011; Müller et al. 2013), also play their biological role in Si transport. In addition, diatoms, which represent a significant portion of the ocean primary production (Tréguer and De La Rocha 2013) and are responsible for 40% of CO_2 oceanic sequestration (Tréguer et al. 1995), are also abundant in river, estuary and lake ecosystems. Quantification of BSi contained in diatoms in lacustrine and marine sediments is used as a proxy for the reconstruction of past environmental conditions and diatom productivity (Ragueneau et al. 2000; Verschuren et al. 2002). The correct determination of BSi in soils, sediments and suspended matter is therefore essential to a wide variety of researchers.

The most widely used methods for BSi determination, are wet chemical, sequential alkaline extractions, where the sediment is mixed with an alkaline solvent (typically but not exclusively Na_2CO_3, with a range of molarities applied) at

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75–85 °C in a water bath for five hours (DeMaster 1981; Mortlock and Froelich 1989; Conley 1998). A correction for minerals co-dissolving is applied based on the assumption that after the first two hours, all BSi has completely dissolved (nonlinearly) and only minerals contribute to the subsequent (linear) increase in DSi concentrations in the solvent. The same approach has later been applied to soils (e.g., Saccone et al. 2007; Clymans et al. 2011; White et al. 2012). However, dissolution of nonbiogenic, pedogenic Si phases in soils contributes to the nonlinear DSi increase during the first part of the extraction, demonstrating that even the corrected Si extracted is not all of biogenic origin (Saccone et al. 2007; Meunier et al. 2014). DSi in soil solution can also, under certain conditions, precipitate as pedogenic opal A, or into short order range minerals, or become adsorbed/occluded on Al and Fe oxyhydroxides (Sommer et al. 2006; Cornelis et al. 2011; Ronchi et al. 2013). Methodological approaches including the use of Al have been proposed to correct for the nonbiogenic contribution extracted. For example, Kamatani and Oku (2000) proposed the use of Si: Al ratios to identify the presence of BSi remains. In suspended particulate matter from rivers where the influence of nonbiogenic silicate-phases can be significant, Si: Al fractions were also used to separate biogenic from nonbiogenic fractions (Ragueneau et al. 2005). The most sophisticated approach was proposed by Koning et al. (2002), who continuously monitored Si and Al concentrations during extraction in 0.5 M NaOH. Results showed that non-BSi contamination could impact the measurements in marine sediments, especially when the mineral load was dominant.

However, the potential for using Si: Al ratios to quantify BSi has received little attention in studies determining BSi in aquatic or terrestrial systems. We hypothesized that such an analysis would demonstrate systematic variations across the land-ocean continuum in the type and magnitude of the contribution of nonbiogenic phases, if compared with the conventional Na_2CO_3 methodology for determining biogenic Si. In this study, we applied an approach based on continuous monitoring of Si and Al during a 0.5 M NaOH extraction [after Koning et al. (2002) and Barão et al (2014)] to a range of samples taken along the land-ocean continuum and compared the results with the ones obtained when 0.1 M Na_2CO_3 extraction was applied followed by a mineral correction.

Material and Procedures

Samples

A variety of samples were analyzed including (1) vegetation and phytoliths, (2) forest, grassland and cropland soils, (3) lake sediments, (4) riverine suspended matter and sediments, (5) estuarine and salt marsh sediments and (6) ocean sediments, with the majority of samples from temperate regions in the northern hemisphere. Samples in the Southern hemisphere and the tropics are limited to ocean sediments and river suspended matter (Fig. 1). The sample range was selected to represent currently investigated ecosystems regarding BSi accumulation and concentration.

Phytoliths were separated by heavy liquid floatation according to Piperno (2006) from the humic A horizon of a Luvisol in the south of Belgium and in a forest soil from southern Sweden (*Cambisol*). Fresh biomass for grass (*Lolium species*), beech (*Fagus sylvatica*) and oak (*Quercus robur*) was collected at the end of the growing season at one grassland and one forest (Luvisol) in the Belgian Loam Belt. Archived soil samples previously collected from undisturbed profiles in the Hubbard Brook Experimental Forest, grasslands from the Great Plains (U.S.A.) (Saccone et al. 2007) and a land use gradient from a south-Swedish Cambisol (Clymans et al. 2011) were used. Two lake sediments were collected from Yellowstone Lake and Lewis Lake (Conley 1998). Suspended particulate matter samples were collected from the Mississipi, Fly, Kikori, and Pukaki rivers and riverine sediments were collected from the Elorn river in northern France (Raimonet et al. 2013). Estuarine sediments were collected from the Chesapeake Bay estuary (Conley 1998) and the salt marsh sediments were collected in the Wadden Sea (Germany) (Müller et al. 2013). Finally, ocean surface sediment samples were collected in the Atlantic (Ragueneau et al. 2001), Antarctic (Gallinari et al. 2008), Equatorial Pacific (McManus et al. 1995), and the Congo fan (Raimonet et al. 2015). These last samples remain as a particular challenge for BSi determination due to high Al content.

Some samples have been previously analysed for BSi using the Na_2CO_3 extraction (see references above). A detailed description of all samples, referring to origin and previous determined BSi content, is provided in Table 1.

Analysis

Chemical extraction

Samples of variable weight (15–100 mg) were mixed for 30–50 min in a stainless steel vessel with an initial 180 mL of 0.5 M NaOH at 85 °C (Koning et al. 2002; Barão et al. 2014). The closed vessel (to avoid evaporation) is directly connected to a continuous analyser (Skalar®, The Netherlands) and a rotating motor continuously homogenizes the sample in the extraction liquid, maintaining a constant solid/solution ratio. DSi concentration is determined according to the molybdate—blue method (Grasshoff et al. 1983), while dissolved Al is determined according to the fluorimetric method of Hydes and Liss (1976). Standard samples of 1 mg L^{-1}, 2 mg L^{-1}, 4 mg L^{-1}, 6 mg L^{-1}, 10 mg L^{-1}, 20 mg L^{-1}, and 40 mg L^{-1} were used for calibration of Si and Al and only regressions with correlation coefficients ≥ 0.999 were accepted. Two independent reference samples were tested before and after the extractions to guarantee an error below 10%. Replicas were not measured because studies using this methodology in the past showed good reproducibility (Koning et al. 2002; Saccone et al. 2007). Additionally,

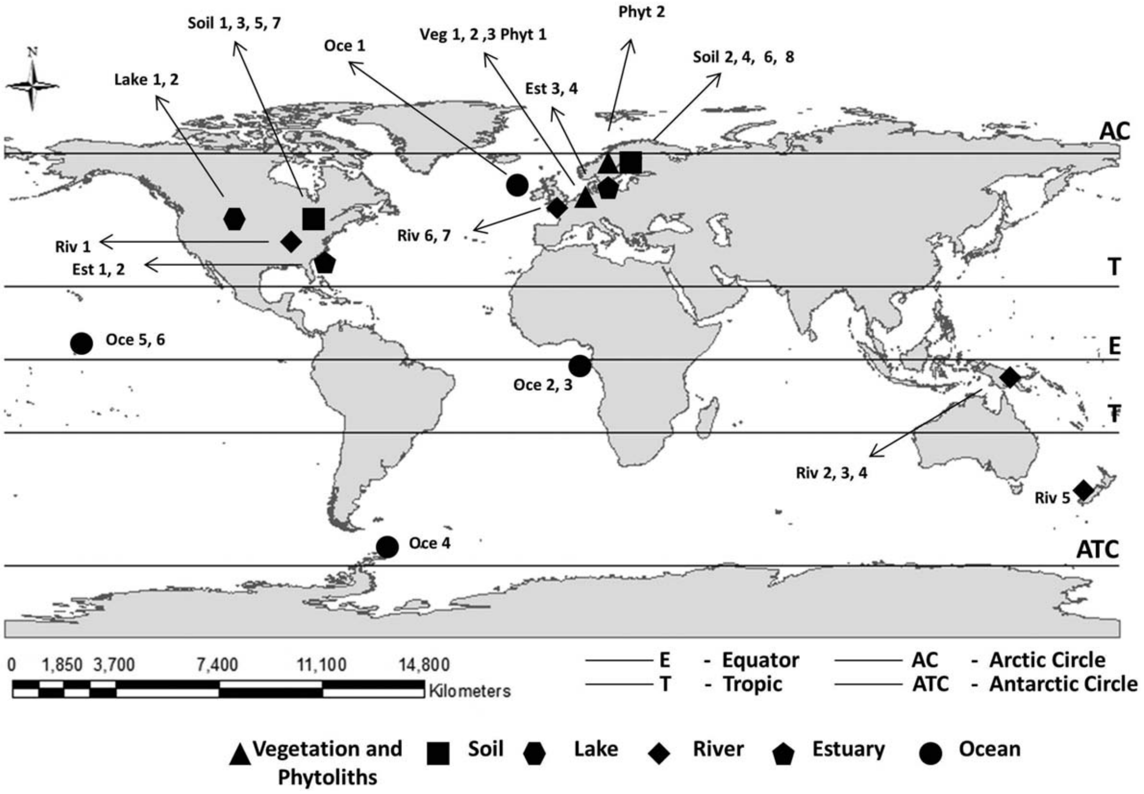

Fig. 1. Location of samples.

the relatively large amount of sediment used (100 mg in the majority of the samples) ensures the subsample is representative.

The samples analyzed prior to this study were digested (30 mg) in a 0.1 M Na_2CO_3 extraction at 85 °C for five hours according to the method of DeMaster (1981). Subsamples of one milliliter were taken after three, four, and five hours to perform the mineral dissolution correction and the DSi was determined by the molybdate-blue method (Grasshoff et al. 1983).

Analytical procedures

Each extraction in the continuous analysis procedure provides dissolution data for Si and Al through time at a 15 s resolution (Fig. 2). Determination of the biogenic component follows a procedure that assumes the presence of two discrete phases: a linear and a nonlinear phase. The linear phase represents mineral dissolution with a constant Si: Al ratio and corresponds with the assumption inherent in the sequential analysis method, i.e., that mineral solubility is lower, and therefore dissolution rates are slower than BSi such that silicates will dissolve at an apparently linear rate on the time scale of the experiment in weakly alkaline solutions (DeMaster 1981). The nonlinear phase—defined as alkaline-extractable Si in NaOH ($\mathrm{AlkExSi_{NaOH}}$)—dissolves faster than the minerals in the alkaline medium (0.5 M NaOH) and is modelled as a first order reaction as assumed for diatoms (Barker et al. 1994; Rickert et al. 2002). $\mathrm{AlkExSi_{NaOH}}$ comprises all fractions (biogenic or nonbiogenic) dissolving nonlinearly, as described before. Equation 1 is used to model both Si and Al curves assuming the presence of both phases. The numerical solutions are reached minimizing the quadratic error between the data and the estimations for Si and Al simultaneously using the Solver program (Excel).

The $\mathrm{AlkExSi_{NaOH}}$ phase is composed of several fractions, each one characterized by its reactivity (k) and Si: Al ratio. The number of $\mathrm{AlkExSi_{NaOH}}$ fractions is determined by consecutively fitting Eq. 1 with $i + 1$ fractions and using an F test that determines when the extra fraction no longer significantly benefits the model. Importantly, the k reactivity parameter is assumed to be independent of the initial concentration of Si present and invariant during the experiment.

$$\begin{aligned}\mathrm{Si}_t &= \left(\sum_{i=1}^{n}\mathrm{AlkExSi}_i\times\left(1-\mathrm{e}^{-\mathrm{k}_i\times t}\right)\right)+b\times t\\ \mathrm{Al}_t &= \left(\sum_{i=1}^{n}\frac{\mathrm{AlkExSi}_i}{\mathrm{Si:Al}_i}\times\left(1-e^{-k_i\times t}\right)\right)+\frac{b\times t}{\mathrm{Si:Al_{min}}}\end{aligned}\tag{1}$$

Si_t is the Si dissolved at time t, $\mathrm{AlkExSi}_i$ is the alkaline extractable Si of fraction i (μmol Si L^{-1}), k_i is the reactivity of fraction i (min^{-1}), b is the mineral dissolution slope

Table 1. Sample description. The AlkExSi$_{Na2CO3}$ concentration (mgSi g$-^{1}$) analyzed previously using 0.1 M Na_2CO_3 is listed when available from previous research, as well as the content of organic matter (%) and the oxalate-extractable Al and Fe (mg g$-^{1}$)

Sample		Description	AlkExSi$_{Na2CO3}$ (mg g−1)	Organic matter (%)	Al (mg g−1)	Fe (mg g−1)
Vegetation and Phytoliths	Phyt 1	Phytolith extracted from the top layer of a grassland (Luvisol) in the south of Belgium	—	—	—	—
	Phyt 2	Phytolith extracted from the top layer of a forest (Cambisol) in the south of Sweden	—	—	—	—
	Veg 1	Beech leaves from a forest (Luvisol) in the Belgian Loam Belt	—	—	—	—
	Veg 2	Oak leaves from a forest (Luvisol) in the Belgian Loam Belt	—	—	—	—
	Veg 3	Grass vegetation from a grassland (Luvisol) in the Belgian Loam Belt	—	—	—	—
Soil	Soil 1	Soil from the Horizon Oa/A of a Forest (Podzol) in North America*	8.35	—	3.98	6.92
	Soil 2	Soil from the Horizon Oa/A of a Continuous Forest (Cambisol) in South Sweden[†]	6.63	—	0.72	1.12
	Soil 3	Soil from the Horizon A of a Grassland (Chernozem) in North America*	26.93	2.2	1.07	0.40
	Soil 4	Soil from the Horizon A of an Arable Land (Cambisol) in South Sweden[†]	2.99	2.8	1.73	1.85
	Soil 5	Soil from the Mineral Horizon of a Forest (Podzol) in North America*	4.92	—	0.93	3.12
	Soil 6	Soil from the Mineral Horizon of a Forest (Cambisol) in South Sweden[†]	5.18	2	18.49	10.63
	Soil 7	Soil from the Horizon C of a Grassland (Chernozem) in North America*	2.01	0.04	0.14	0.05
	Soil 8	Soil from the Mineral Horizon of a Arable Land (Cambisol) in South Sweden[†]	0.51	0.7	1.38	0.34
Lake	Lake 1	Sediment from Lewis Lake, North America[‡]	207	—	—	—
	Lake 2	Sediment from Yellowstone Lake, North America[‡]	179	—	—	
River	Riv 1	SPM collected from the upper Mississippi in April 2004	—	—	—	—
	Riv 2	SPM collected from the Fly river, Papua New Guinea	—	—	—	—
	Riv 3	SPM collected from the Fly river, Papua New Guinea	—	—	—	—
	Riv 4	SPM from the Kikori river, Papua New Guinea	—	—	—	—
	Riv 5	SPM from the Pukaki river, Papua New Guinea	—	—	—	—
	Riv 6	Sediment from the Elorn River, France[§]	—	—	—	—
	Riv 7	Sediment from the Elorn River, France[§]	—	—	—	—
Estuary	Est 1	Sediment from Still Pond in Chesapeake Bay, North America[‡]	10.5	—	—	—
	Est 2	Sediment from site R-64 in Chesapeake Bay, North America[‡]	24.9	—	—	—
	Est 3	Sediment from the top layer of a Salt Marsh in the Wadden Sea (Germany)[‖]	16.80	—	—	—
	Est 4	Sediment from 40 cm of a Salt Marsh in the Wadden Sea (Germany)[‖]	21.25	—	—	—
Ocean	Oce 1	Sediment from the Porcupine abyssal plain, NE Atlantic[¶]	—	—	—	—
	Oce 2	Sediment from the Congo deep sea fan[#]	—	—	—	—
	Oce 3	Sediment from the Congo deep sea fan[#]	—	—	—	—
	Oce 4	Sediment from collected from the Antarctic Peninsula**	—	—	—	—
	Oce 5	Sediment from the Equatorial Pacific, EqPac cruise, 2°N[††]	—	—	—	—
	Oce 6	Sediment from the Equatorial Pacific, EqPac cruise, 9°N[††]	—	—	—	—

SPM, stands for suspended particulate matter.

*Saccone et al. 2007

[†] Clymans et al. 2011

[‡] Conley 1998

[§] Raimonet et al. 2013

[‖] Müller et al. 2013

[¶] Ragueneau et al. 2001

[#] Raimonet et al. 2015

**Gallinari et al. 2008

[††] McManus et al. 1995

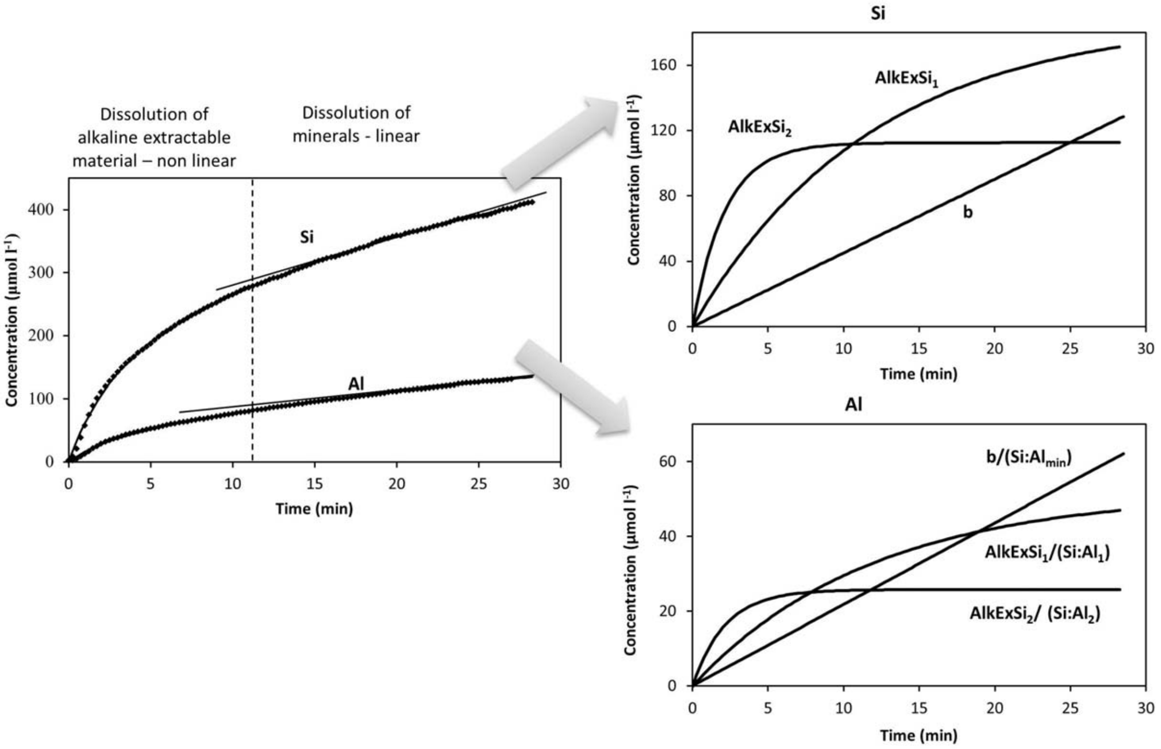

Fig. 2. Representation of the method developed by Koning et al. (2002), showing the dissolution of Si and Al during extraction in 0.5 M NaOH with the linear and nonlinear dissolution phases (left). After fitting the data points into the first order equations (Eq. 1), each fraction identified can be isolated for both silicon (Si) and aluminum (Al) contribution (right). $AlkExSi_1$ and $AlkExSi_2$ are two nonlinearly alkaline extracted Si fractions and b is the Si minerals interfering the analysis. $AlkExSi_1$/(Si: Al_1), $AlkExSi_2$/(Si: Al_2), and *b*/(Si: Al_{min}) are the corresponding Al content of the fractions.

(μmol L^{-1} min^{-1}), Al_t is the Al dissolved at time *t*, Si: Al_i is the Si: Al ratio of fraction *i*, Si: Al_{min} is the Si: Al ratio of the mineral fraction and *n* is the number of fractions. All alkaline extractable fractions mentioned above refer to NaOH as solvent ($AlkExSi_{NaOH}$).

The $AlkExSi_{NaOH}$ content of each sample in mgSi g^{-1} is calculated according to Eq. 2, by summing all the individual $AlkExSi_{NaOH}$ fractions and taking into account the Si molar mass (*M*), the extraction volume of NaOH (*V*) and the mass of the sample (*m*).

$$\mathrm{AlkExSi_{NaOH}}\ \left(\mathrm{mg\ g^{-1}}\right) = \frac{\mathrm{AlkExSi\ _{NaOH}}(\mu\mathrm{mol\ L^{-1}})\cdot M(\mathrm{g\ mol^{-1}})\cdot V(\mathrm{L})}{m\ (\mathrm{g})\cdot 1000} \qquad (2)$$

Based on the Si: Al ratio, each fraction's origin can be evaluated (Barão et al. 2014). Fractions of biogenic origin are highly enriched in Si with low incorporation of Al by diatoms (Ren et al. 2013) or phytoliths (Fraysse et al. 2009), thus Si: Al ratios are high (Si: $Al > 5$). Clay minerals were assumed to have a Si: Al ratio between 1 and 4 (Koning et al. 2002) based on typical clay stoichiometries and assuming congruent dissolution. Fractions with Si: Al lower than 1 are considered the product of pedogenesis since Al levels in these fractions are generally high (Schaetzl and Anderson 2005; Barão et al. 2014). Implications of these assumptions, and potential errors associated with them, are discussed below.

Assessment

$AlkExSi_{NaOH}$ and $AlkExSi_{Na2CO3}$ concentrations

In general, total $AlkExSi_{NaOH}$ concentrations are higher than $AlkExSi_{Na2CO3}$ concentrations for each sample, indicating that 0.5 M NaOH extracts more Si than 0.1 M Na_2CO_3. The magnitude of the difference between methods is highly variable depending on sample origin (Table 2; Fig. 3A). Vegetation, topsoils, some deep soils, lakes and two estuarine (Est 1, Est 2), river (Riv 3, Riv 4), and oceanic samples (Oce 4, Oce 5) extracted with both AlkExSi reagents (NaOH and Na_2CO_3) are similar in concentration (i.e., 1–32% difference). On the contrary, in some deeper soil horizons, the majority of river, salt marsh (Est 3 and Est4) and oceanic samples (Oce 1, Oce 2, and Oce 6) the difference between the results of the two methods is consistently higher and up to 74% of the AlkExSi extracted. Results from a set of soil samples from the study of Saccone et al. (2007) who applied both methods are in close agreement with our study (Fig. 3B).

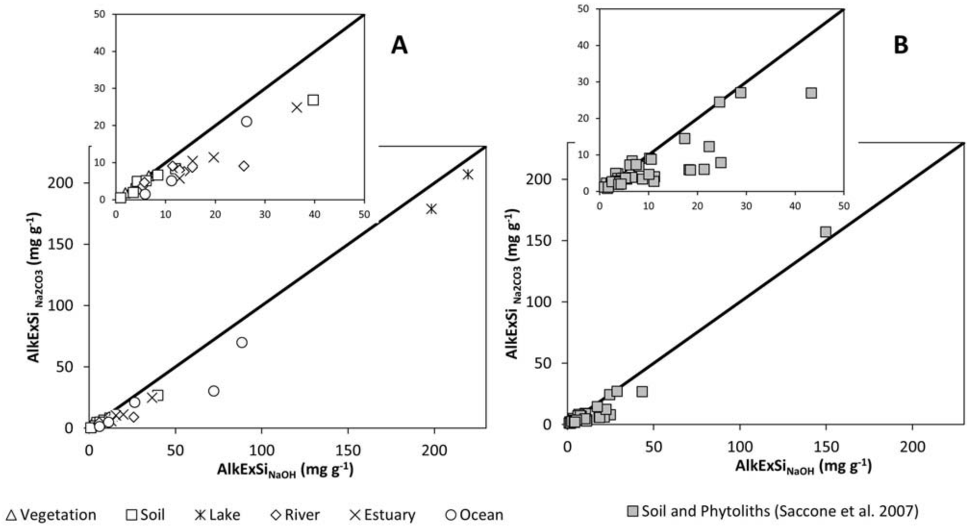

Fig. 3. (A) Correlation between nonlinearly dissolved Si (mgSi g^{-1}) in 0.1 M Na_2CO_3 (AlkExSi$_{Na2CO3}$) and 0.5 M NaOH (AlkExSi$_{NaOH}$) in this study. Triangles represent vegetation and phytolith samples, squares represent soil samples, stars represent lake samples, diamonds represent river samples, crosses represent estuarine samples and circles represent ocean samples; (B) correlation between nonlinearly dissolved Si (mgSi g^{-1}) in 0.1M Na_2CO_3 (AlkExSi$_{Na2CO3}$) and 0.5 M NaOH (AlkExSi$_{NaOH}$) from Saccone et al. (2007). Grey squares represent soil and phytolith samples. The bold line represents a 1-1 relation in both graphics. In both plots the inset panel displays an enlarged region near the origin.

Separation of AlkExSi$_{NaOH}$ fractions

Phytoliths, vegetation and soil

Isolated soil phytoliths and vegetation samples could be modelled with one nonlinear phase with high Si: Al (> 5), indicating a clear biogenic origin (Fig. 4). The linear phase corresponding to the mineral dissolution was absent as expected, except for Phytolith 2 (Table 2). The latter suggests that this sample was not successfully cleaned beforehand. A large variability in the reactivity parameter (k) was observed during the extraction, ranging from 0.23 min^{-1} in the grass to 1.03 min^{-1} in the oak leaves (Fig. 5). Total AlkExSi$_{NaOH}$ concentrations ranged between 4 ± 2 mgSi g^{-1} in vegetation to 211–279 mgSi g^{-1} for separated soil phytoliths. For all samples extracted aluminium levels were negligible compared to Si release.

Soil samples are more complex as indicated by (1) the presence of a linear phase in the majority of the samples ($b \sim 0.03 \pm 0.02$ mgSi g^{-1} min^{-1}) and (2) the detection of higher Al quantities in some samples (Fig. 4). The relative Al contribution and source appears to differ between soil horizons. Organic horizons have dominantly (± 100%) high Si: Al (> 5) with low reactivity (0.23–0.42 min^{-1}). Conversely, some of the mineral horizons contain large amounts of fractions with low Si: Al (< 1) (44–100% of the total AlkExSi$_{NaOH}$) (Table 2). Average AlkExSi$_{NaOH}$ concentrations in the soil were 12 ± 18 mgSi g^{-1}, with high variability due to the range of soil horizons and different ecosystems sampled (Fig. 5).

Lakes and rivers

Si and Al curves for lake sediments indicated negligible Al contribution and high Si release, similar to that observed in phytoliths (Fig. 4). The samples were modelled as a single nonlinear fraction with Si: Al ratio (> 5) with a low reactivity k (< 0.3 min^{-1}), indicating a BSi origin (Table 2). Total AlkExSi$_{NaOH}$ concentrations ranged between 198 and 219 mgSi g^{-1}.

Riverine samples appear to have more complex composition with at least two nonlinear and a substantial linear source for Si and Al. The linear dissolution rates of the mineral fraction are the highest observed in this study, on average $\sim 0.18 \pm 0.15$ mgSi g^{-1} min^{-1}, indicating the presence of an important mineral pool in the sediment transported by the rivers (Fig. 5). Nonlinear phases exhibit Si: Al ratios between 1 and 4 and k-values between 0.04 min^{-1} and 0.78 min^{-1} corresponding to our initial assumptions with the dissolution of clay minerals. There appears to be no trace of BSi. Total AlkExSi$_{NaOH}$ concentrations averaged 16 ± 17 mgSi g^{-1} in the riverine samples, and are comparable in concentration to soil samples.

Estuaries and ocean

Estuarine sediment samples all present two nonlinear fractions with an apparent biogenic origin (Si: Al > 5) (Fig. 4). While the first fraction detected was consistently more reactive ($k = 0.5$–0.8 min^{-1}), the second fraction, contributing up to 40–80% of the AlkExSi concentration showed much lower reactivity (0.05–0.07 min^{-1}) (Table 2). Mineral contributions are limited (Fig. 5). AlkExSi$_{NaOH}$ concentrations measured were on average 21 ± 10 mgSi g^{-1}.

Higher AlkExSi$_{NaOH}$ concentrations were observed in the ocean sediment samples (47 ± 41 mg g^{-1}) (Fig. 5). Further, the Si arising from mineral dissolution increased in the

Table 2. Parameters from the Si and Al continuous dissolution with 0.5 M NaOH. AlkExSi$_i$ (mgSi g^{-1}) is the total concentration of each fraction dissolving non linearly, k_i (min^{-1}) is their respective reactivity and Si: Al$_i$ ratio. Parameter *b* refers to the slope of the fraction dissolving linearly. Total content of AlkExSi (mgSi g^{-1}) is listed extracted with 0.5 M NaOH and 0.1 M Na$_2$CO$_3$ (AlkExSi$_{NaOH}$ and AlkExSi$_{Na2CO3}$).

Code	AlkExSi$_1$ (mgSi g^{-1})	AlkExSi$_2$ (mgSi g^{-1})	AlkExSi$_3$ (mgSi g^{-1})	k_1 (min^{-1})	k_2 (min^{-1})	k_3 (min^{-1})	Si: Al$_1$	Si: Al$_2$	Si: Al$_3$	*b* (mgSi g^{-1} min^{-1})	Si: Al$_{min}$	AlkExSi$_{NaOH}$ (mgSi g^{-1})	AlkExSi$_{Na2CO3}$ (mgSi g^{-1})
Phyt 1	211.33			0.37			64.67					211.33	—
Phyt 2	278.85			0.24			861.32			0.140	0.48	278.85	—
Veg 1	4.49			0.35			5173.03					4.49	4.05
Veg 2	1.90			1.03			217999					1.90	1.86
Veg 3	0.004	6.57		1.18	0.23		41.22	341.72				6.57	6.53
Soil 1	0.00001	11.97		0.95	0.26		0.000004	54.84		0.009	2.47	11.97	8.35
Soil 2	2.08	6.34		0.05	0.42		265.16	6.85		0.010	0.87	8.42	6.63
Soil 3	8.86	30.85		0.35	0.09		6.60	10.50		0.290	3.69	39.71	26.93
Soil 4	4.04	0.01		0.23	0.79		10.40	0.003		0.034	2.59	4.05	2.99
Soil 5	0.00003	4.32		2.04	0.31		0.00008	840.21		0.046	3.48	4.32	4.92
Soil 6	6.07			0.72			0.27			0.055	1.46	6.07	5.18
Soil 7	2.88	0.59		0.04	0.89		5.43	5.26		0.018	4.21	3.47	2.01
Soil 8	0.43	0.53		1.08	0.07		0.31	6.64		0.004	11.30	0.95	0.51
Lake 1	219.42			0.26			26.42					219	207
Lake 2	198.32			0.27			23.17					198	179
Riv 1	6.73	19.00		0.41	0.04		4.88	3.12		0.032	0.78	25.72	9.1
Riv 2	2.76	2.62		0.07	0.41		1.94	1.21		0.192	0.95	5.38	3.73
Riv 3	2.99	2.75		0.21	0.51		1.54	1.63		0.242	1.52	5.74	4.67
Riv 4	10.10	1.25		0.53	0.22		2.39	0.40		0.374	1.76	11.35	9.1
Riv 5	5.87	9.46		0.57	0.14		1.45	1.33		0.333	1.44	15.33	8.77
Riv 6	9.33	4.42		0.20	0.37		3.64	3.39		0.187	4.37	13.74	7.6
Riv 7	5.38	0.46	6.96	0.78	0.04	0.07	3.47	0.77	4.75	0.061	16.15	12.80	8
Est 1	6.81	8.60		0.79	0.07		4.59	6.99		0.031	0.32	15.42	10.5
Est 2	20.25	16.15		0.53	0.10		11.41	9.52		0.068	1.00	36.40	24.9
Est 3	3.88	15.79		0.68	0.11		2754	9.97		0.098	2.33	19.67	11.46
Est 4	3.68	9.12		0.53	0.06		10.13	10.22		0.049	2.47	12.80	5.81
Ocean 1	4.35	1.23	0.29	0.05	0.72	0.10	2.72	3.44	12.83	0.058	3.32	5.87	1.5
Ocean 2	5.33	0.98	4.86	0.17	0.88	0.70	2.33	6.93	3.32	0.193	1.16	11.17	5.1
Ocean 3	16.01	12.03		0.63	0.09		7.57	5.51		0.173	1.18	28.04	—
Ocean 4	88.37			0.28			38.19			0.182	3.22	88.37	69.9
Ocean 5	26.25			0.57			10.18			0.372	9.45	26.25	21.1
Ocean 6	53.07	7.64	11.35	0.61	0.06	0.08	9.15	3.26	1.59	0.298	34.93	72.06	30.5

ocean sediments (0.2 ± 0.2 mgSi g^{-1} min^{-1}) (Table 2). AlkExSi$_{NaOH}$ present in the ocean sediment samples has a dominant BSi signature (Si: Al ratio > 5) with the exception of two samples (Ocean 1 and Ocean 2). Here, a fraction with lower Si: Al ratio (1–4), interpreted as clay minerals, contributes up to 91–95% of the alkaline-extractable Si (Fig. 5).

Discussion

Application of alkaline extractions using sequential Si extraction and continuous analysis of Si and Al

Differences between AlkExSi concentrations in NaOH and Na_2CO_3 have been reported in the past (Kamatani and Oku 2000; Koning et al. 2002; Saccone et al. 2007). It is generally accepted that NaOH extracts higher AlkExSi quantities when compared to Na_2CO_3, since it is a stronger solvent and "less soluble" fractions are prone to dissolution. A stronger solvent could potentially dissolve a less soluble BSi fraction [e.g., older phytoliths in deeper soil profiles (Meunier et al. 2014), sponges or more resistant diatoms (Kamatani and Oku 2000)] and therefore more accurately estimate the biological pool. Conversely, it may inadvertently dissolve more clay minerals, decreasing accuracy. This is the primary reason why most scientists perform the 0.1 M Na_2CO_3 extraction instead of NaOH when assessing the biogenic Si content of samples. Our results show that vegetation, top soils and lakes (where fresh BSi is dominant, i.e., Al content is very low to absent) show smaller differences between AlkExSi$_{NaOH}$ and AlkExSi$_{Na2CO3}$, when compared to rivers, some deeper soil horizons and some of the ocean sediments, where the content of Al is much higher (Fig. 6). Saccone et al. (2007) also found significant differences between both methods when analyzing mineral horizons lower in soil profiles, attributing it to the simultaneous dissolution of other amorphous but nonbiogenic fractions. However, a closer look at our results demonstrates that other samples comprised entirely of BSi (Si: Al > 5) also differ significantly between the methods (Est 3, Est 4, Oce 6), complicating the hypothesis suggesting that differences are explained by contributions of non-BSi sources. A potential explanation is the level of accuracy obtained when using the continuous analysis to calculate AlkExSi concentrations. The AlkExSi$_{NaOH}$ method allows for a more accurate estimate of the mineral contribution during the linear phase of the extraction: higher resolution of Si measurements is achieved avoiding the assumption of a starting point for the linear phase (e.g., after three hours as in the 0.1 M Na_2CO_3 extraction). Moreover, the application of first order models with increasing number of fractions allows the detection of AlkExSi fractions with very low reactivity that may otherwise appear linear to "simpler models." This resolution, together with (1) the higher extractability of nonbiogenic Si pools (Si: Al < 5) and (2) a more accurate linear correction obtained with the continuous method provides explanations for the differences between the 0.1 M Na_2CO_3 extraction and the 0.5 M NaOH continuous extraction results. These are expressed in two groups of analysed samples: (1) samples where the difference between both methods is high and can be explained by the higher contribution of fractions with low reactivity ($k < 0.1$ min^{-1}) that are only detected in the continuous analysis; and (2) samples where the difference between both used methods is high but the contribution from low-reactive fractions is minor; in this case, it concerns river and ocean samples where the contribution of non-BSi pools is significant. The majority of samples from vegetation, top soil and lakes, mainly comprised of BSi, have small differences between the two methods (Fig. 6). Two samples (i.e., Soil 2 and Ocean 6 samples) show distinct results from these two patterns. At this point it is not entirely clear what the reason for this difference is.

Koning et al. (2002) also observed fractions with lower reactivity in samples from aged sediments and attributed them to chemically altered diatoms. If AlkExSi$_{NaOH}$ concentrations are calculated excluding the fractions with very low reactivity ($k < 0.1$ min^{-1}), the results are closer to the ones achieved with the 0.1 M Na_2CO_3 extraction (Table 3).

Tracing BSi from land to ocean

The samples of separated phytoliths and vegetation do not contain aluminium in significant amounts, and can thus be logically considered as biogenic. The observed biogenic source of Si in estuarine and marine sediments is also expected: diatoms exert strong biological control on Si concentrations in coastal and marine waters (*see* Tréguer and De La Rocha 2013). In the last decade tidal marshes have been highlighted as important bioaccumulators of Si in estuaries (Struyf et al. 2006; Carey and Fulweiler 2013). Previous studies assessing the uptake of silica and deposition as phytoliths in plants separating phytoliths from the soil matrix by heavy-liquid separation (Alexandre et al. 1997; Piperno 2006), and its subsequent accumulation in the top soil from litter input (Blinnikov et al. 2002; Farmer et al. 2005) are also consistent with our results.

In the lower soil horizons the presence of other fractions with no biogenic origin are calculated from our AlkExSi$_{NaOH}$ measurements. Some AlkExSi$_{NaOH}$ fractions from deep soil layers, and to a lesser extent of sediments from rivers, had Si: Al ratios below 1 (Fig. 5) suggesting the presence of weathered products such as short-range order minerals (Koji 1989; Cornelis et al. 2011), Al hydroxides (Sommer et al. 2006) which have the ability to adsorb silica (McKeague and Cline 1963) and amorphous silica-aluminium precipitates (Veerhoff and Brümmer 1993). The presence of this Si pool in the deeper soils can be explained by pedogenic processes (Barão et al. 2014), dependent on the weathering level of the soil (Cornelis et al. 2011) and the original parent material. The presence of the same fraction in the riverine sediments suggests their direct export from land to aquatic continuum

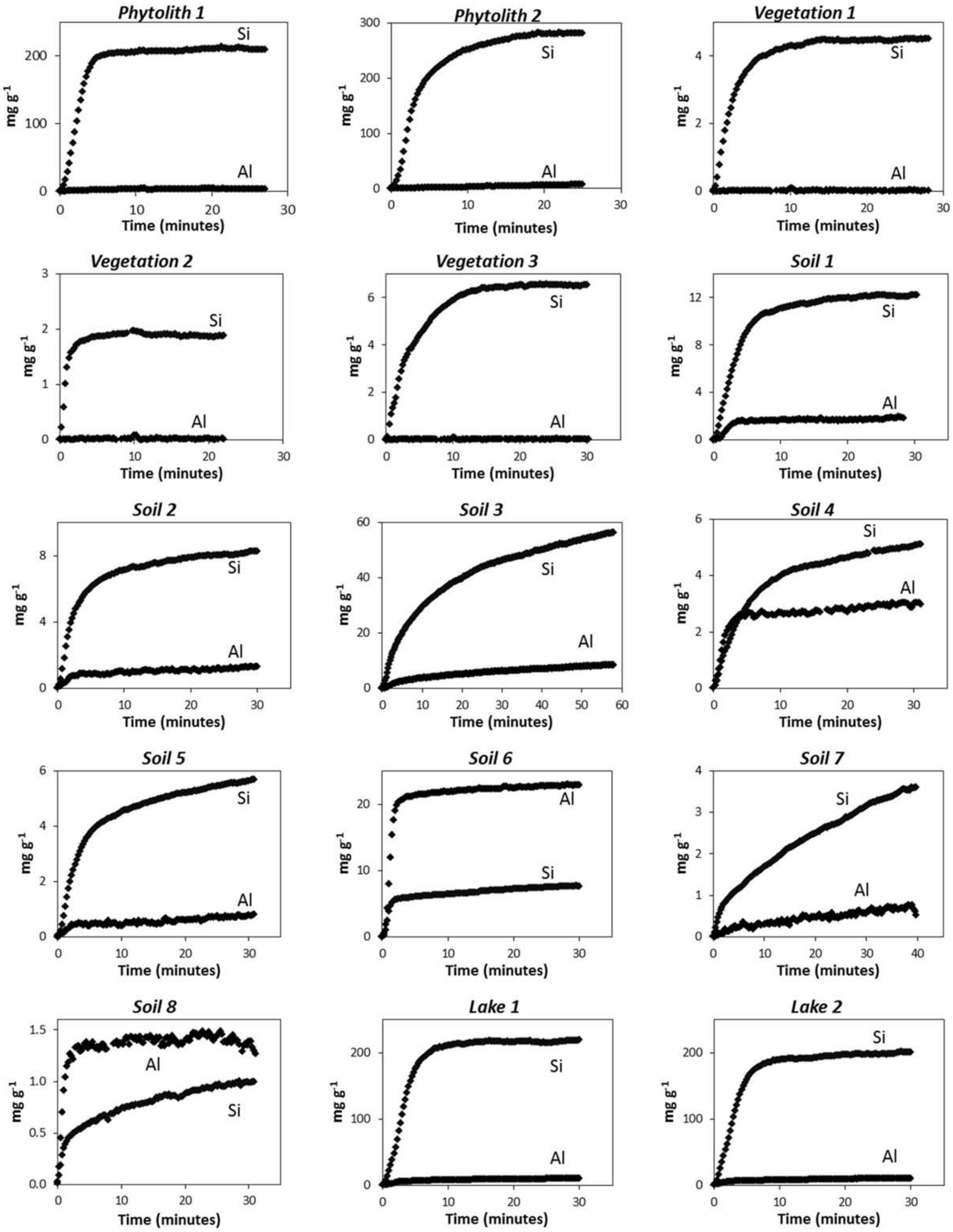

Fig. 4. Extracted silicon and aluminum curves (mg g^{-1}) obtained with the continuous analysis in 0.5 M NaOH for phytolith, vegetation, soil, river, estuarine, and ocean samples.

through erosion, or alternatively Al and Si precipitation taking place in situ (Stoffyn-Egli 1982; Siipola et al. 2012). The lake samples analysed are dominated by biogenic Si, suggesting mainly diatoms and/or phytoliths have contributed to the reactive Si pool isolated from the sediment during the alkaline extraction. While lakes are well known ecosystems

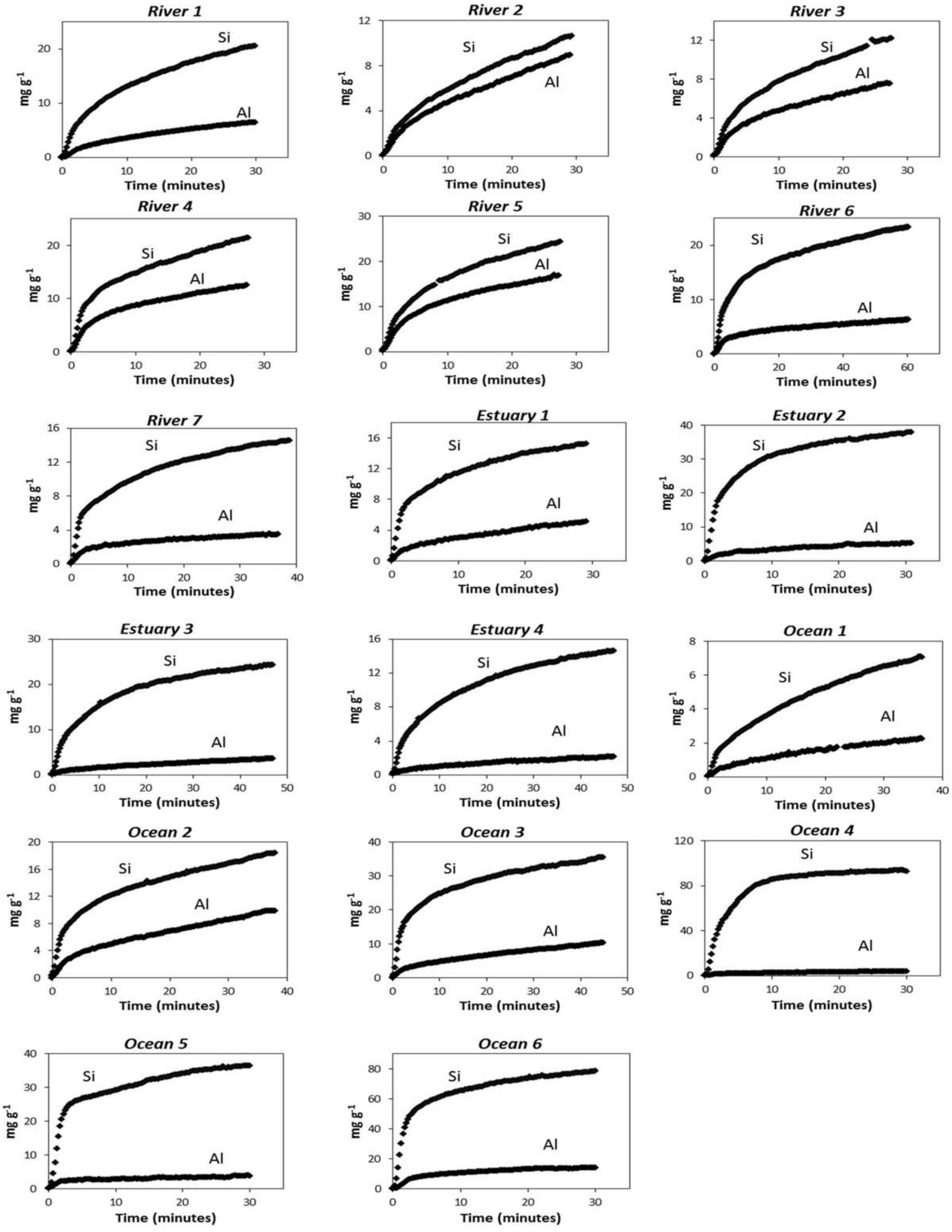

Fig. 4. continued

where BSi is quite dominant and plays an important ecological role (Conley and Schelske 2001; Frings et al. 2014b) it can also be expected that worldwide lakes impacted by erosion or volcanic environments show higher levels of non-BSi fractions that are reactive in alkaline environments (Street-Perrott et al. 2008). As such, the presence of non-BSi measured in our analysis could be more common if we analyzed a wider variety of samples.

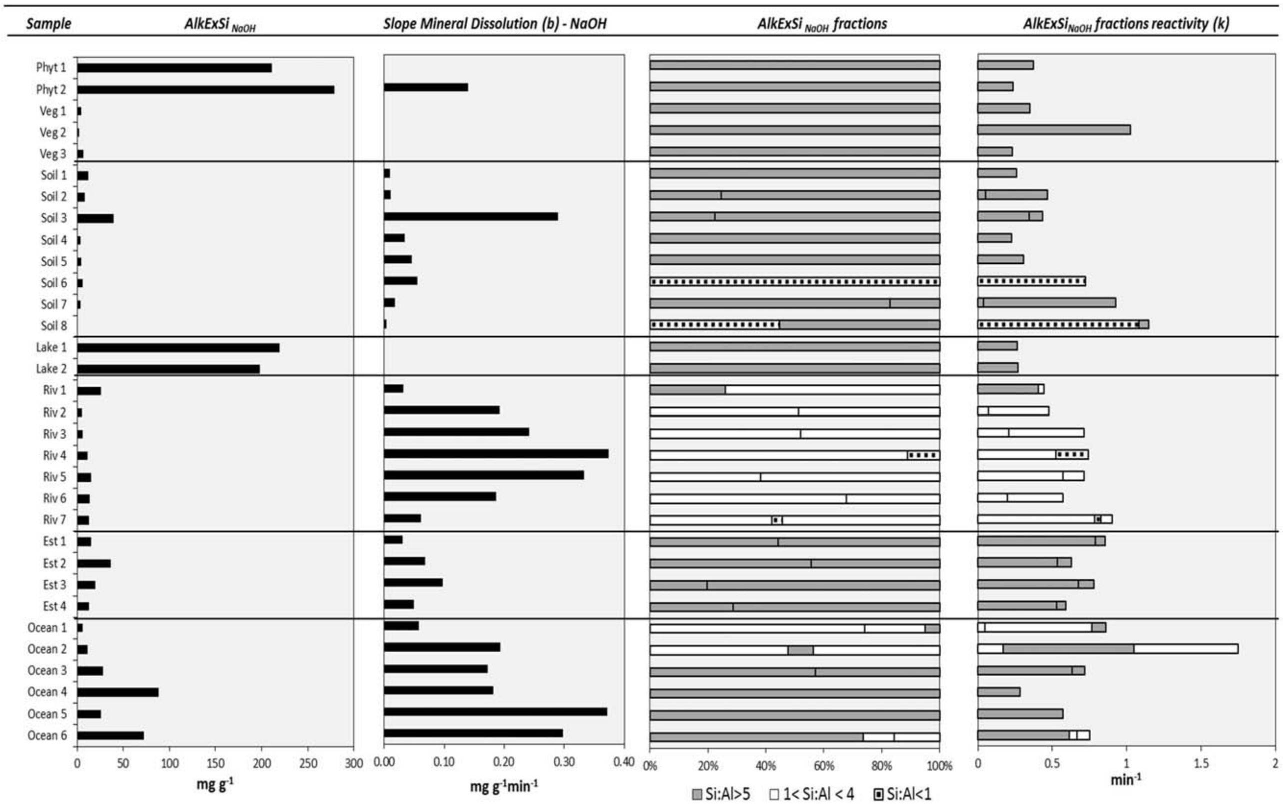

Fig. 5. $\text{AlkExSi}_{\text{NaOH}}$ (mgSi g^{-1}) extracted in 0.5 M NaOH for each sample; slope of the mineral dissolution—*b* (mg g^{-1} min^{-1}); relative importance of the different nonlinearly dissolving fractions, according to their Si: Al ratio and their respective reactivity (*k*) in min^{-1}.

A substantial part of the total $\text{AlkExSi}_{\text{NaOH}}$ in samples collected from rivers and some of the ocean sediments has Si: Al ratios consistent with clay minerals (Fig. 5). Difficulties during measurement of BSi in rivers and coastal waters have been previously reported (Ragueneau and Tréguer 1994; Ragueneau et al. 2005), especially when streams carry large loads of primary or secondary silicate minerals (Griffin et al. 1968) or due to the presence of reverse weathering—precipitation of authigenic clays—from diatom shells (Michalopoulos and Aller 1995). In oceans the presence of reactive minerals (clays) is conventionally linked to terrestrial input via rivers and coastal zones (Griffin et al. 1968), which is reflected in our results from ocean sediment samples. Sediments collected near the coast such as in the North Atlantic (ocean 1) and the Congo deep sea fan (ocean 2), are more vulnerable to accumulate sediments with reactive minerals fractions. Raimonet et al. (2015), in a similar study in the Congo deep sea fan, highlighted the influence of Congo River creating an Al enriched environment affecting the extracted biogenic Si concentrations. Conversely, sediment samples collected in the open ocean (ocean 4, 5, and 6) have biogenic Si as the dominant component of total $\text{AlkExSi}_{\text{NaOH}}$ (Fig. 5).

The dominant presence of non-BSi fractions in the $\text{AlkExSi}_{\text{NaOH}}$ in our river samples, from some deeper soil horizons and ocean sediments highlights the importance of using a method that is able to discriminate between fractions based on their origin. It should be noted that previous work using the Na_2CO_3 protocol demonstrated that diatoms were abundant in river samples (Conley 1997). Our results demonstrate that whichever alkaline solvent is used (NaOH or Na_2CO_3) that a contribution from non-BSi sources can occur depending upon the composition of the sample.

Si reactivity and biogeochemical availability

In addition to a more accurate quantification of the size of biogenic Si pool in different environments, we would also like to address the question of Si availability as this will be the main factor governing Si recycling rates and Si delivery rates. The interpretation of the dissolution parameters is not restricted to the determination of the Si: Al ratio. The fitting of first order equations to the residual total dissolution curves after removing the linear mineral component provides information about the "curve shape" through the parameter *k*, which here we have interpreted as reactivity, specific to the sample in 0.5 M NaOH (pH of $\sim$ 13). In our analysis, the biogenic Si fraction reactivity range is large. For example vegetation samples reflect an extreme range with a beech leaf reactivity of 0.35 min^{-1} and grass' reactivity 0.23

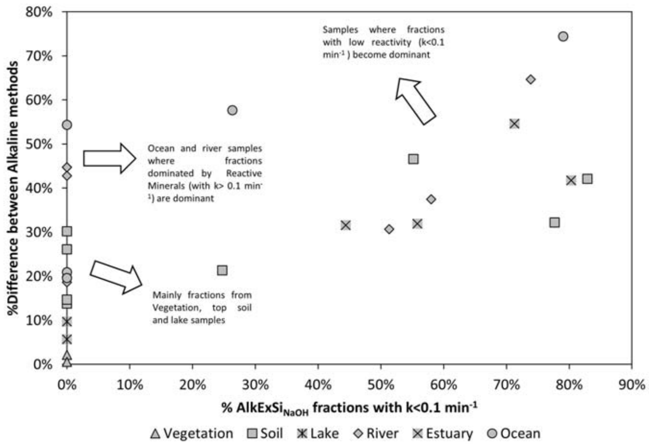

Fig. 6. Percentage difference between AlkExSi$_{NaOH}$ and AlkExSi$_{Na2CO3}$ calculated with the continuous analysis in 0.5 M and the 0.1M Na_2CO_3 extraction respectively, defined as %Difference = (AlkExSi$_{NaOH}$ − AlkExSi$_{Na2CO3}$)/AlkExSi$_{NaOH}$ and plotted with the % of AlkExSi$_{NaOH}$ fractions (for each sample) with reactivity (k) lower than 0.1 min^{-1}.

min^{-1}, while the oak leaf reactivity was much greater at 1.03 min^{-1}. This difference may be related to the phytolith form (Barboni et al. 1999; Ma and Yamaji 2006) and/or preferential deposition: Si may precipitate in the cell wall, the lumen or in the interstices (Piperno 2006). The presence of a protective coating of organic matter or trace elements in the cell wall may also explain the observed range. The parameter k, defined in this study is specific to our experimental conditions and seems to be related to the solubility and relative surface area of the Si fractions. Unfortunately, we cannot immediately conclude that fractions with higher reactivity will be depleted faster in natural conditions. Dissolution rates of diatoms and phytoliths are known to depend on many factors, including ambient conditions such as pH and temperature (Kamatani et al. 1980; Van Cappellen and Qiu 1997; Fraysse et al. 2009).

Another unresolved question is the importance of the non-BSi fractions on the availability of DSi in ecosystems. The non-BSi fractions can significantly bias the measurements of biogenic Si. The ability of different non-BSi fractions to dissolve in the environment may differ from the alkaline extractions used in the laboratory. The dissolution rates of clays decrease with increasing pH (Cama et al. 2002; Amram and Ganor 2005) and adsorption of Si on goethite is greatest at pH 9 but decreases at higher and lower pHs (Hiemstra et al. 2007). Recent studies suggest that the presence in deeper soil horizons of the non-BSi pool may impact Si mobility in soil–plant systems (Barão et al. 2014; Cornelis et al. 2014). Although BSi and non-BSi fractions have variable reactivity values (Table 2) we cannot conclude a priori if those non biogenic Si fractions will be as biogeochemically active as diatoms and phytoliths or if, at natural conditions they will show lower dissolution rates. Such information is crucial, especially for studies addressing DSi availability in natural ecosystems. The current results would imply that other fractions besides BSi are important for short-term DSi availability, with consequences for aquatic ecosystems where the short-term availability of DSi is crucial for diatom productivity. The presence of other sources of DSi in addition to the terrestrial biogenic Si pool suggest that many other factors related to soil processes, soil erosion and transport are also important on short time scales and impact diatom blooms. Correct separation of the different biogenic and nonbiogenic Si fractions remains fundamental to identify BSi pools (phytoliths or diatoms), especially in environments where contribution of non-BSi is high, since as we show those fractions can significantly dissolve when using alkaline extraction.

Comments and recommendations

Future challenges

The continuous analysis of Si and Al used in this study aims to separate biogenic from nonbiogenic Si following first order dissolution kinetics in an alkaline medium. This is an essential step to better constrain biological Si processing and accumulation from land to ocean. However, the

Table 3. Difference (in %) between results of AlkExSi$_{Na2CO3}$ and AlkExSi$_{NaOH}$ when considering all fractions identified in the continuous analysis or only the fractions with k (reactivity) higher than 0.1 min^{-1}.

	Difference AlkExSi$_{NaOH}$ and AlkExSi$_{Na2CO3}$ (%)		**Difference AlkExSi$_{NaOH}$ (only considering fractions with $k > 0.1$ min^{-1}) and AlkExSi$_{Na2CO3}$ (%)**	
	Average	**Range (min-max)**	**Average**	**Range (min-max)**
Vegetation	4%	1–10%	4%	1–10%
Soil	28%	14–47%	23%	3–46%
Lakes	8%	6–10%	8%	6–10%
Rivers	37%	19–65%	25%	9–45%
Estuary	40%	32–65%	23%	13–39%
Ocean	45%	20–74%	26%	5–54%

methodology cannot discriminate between diatoms or phytoliths, or BSi and precipitated pedogenic opal (Cornelis et al. 2011), since all the fractions are chemically indistinguishable. Moreover, the ratio of Si to Al has been critical in distinguishing between the various fractions, but some pedogenic fractions, such as Si adsorbed to iron or titanium hydroxides (e.g., ferrihydrite, hematite; Beckwith and Reeve 1963; Schwertmann and Cornell 2000; Cornelis et al. 2014) may be either not measured by the present alkaline extraction methodology or misinterpreted as biogenic Si due to their lack of aluminium. Future studies using the continuous analysis of Si and Al during extraction of soils should focus on the: (1) analysis of volcanic soils and volcanic products where amorphous volcanic silica is present as well as short-range ordered minerals such as allophane and imogolite (Koji 1989); (2) analysis of soils with different weathering degrees and climates, to assess the influence of variable weathering intensity (Cornelis et al. 2011); (3) analysis of soils rich in iron, where Si may be adsorbed to iron hydroxides in significant quantities (Cornelis et al. 2014) defining new challenges for the continuous analysis that can only separate factions based on Si: Al ratios; (4) lake ecosystems where pedogenic or volcanic Si contamination is expected and (5) the possibility of using the reactivity (*k*) characteristic of each sample to evaluate the age of phytoliths and diatoms, i.e., to separate aged from fresh phytoliths and diatoms, essential for inferring process rates in ecosystems, the construction of corrected paleorecords and quantifying the potential of C sequestration as phytolith occluded C (Song et al. 2012).

Conclusions

The commonly applied sequential alkaline biogenic Si extractions (Conley and Schelske 2001) separates "amorphous Si" with high solubility from primary minerals with typically lower solubility, by assuming linear mineral dissolution and using an extraction for five hours in Na_2CO_3. Here we analyzed a range of samples taken along the land-ocean-continuum with both the conventional method and a method that continuously analyses Si and Al to explore the origin of the amorphous Si based on the Al content (Kamatani and Oku 2000; Koning et al. 2002). This method continuously records the Si and Al concentration in the solvent during the extraction, and these concentrations are later fitted to mathematical models that separate different fractions with different Si: Al ratios.

The results confirm that the most frequently applied Na_2CO_3 extraction technique (Conley and Schelske 2001) also dissolves nonbiogenic fractions, hampering the determination of BSi content in some cases. The continuous method in 0.5 M NaOH provides information on the occurrence of other Si fractions with similar reactivity that can contribute to the apparent BSi. The term amorphous Si, coined to reflect the growing awareness of nonbiogenic phases, is actually incorrect: especially in riverine and ocean sediment samples where we show that Si minerals may constitute a large part of the extracted Si even after linear mineral correction. Samples of river particulate matter and in deeper soil horizons are especially affected, since most of the fractions have high Al contents and were not biogenic, but are the result of pedogenic processes.

The technique applied here has further potential to assess the biogeochemical reactivity of each fraction, although future research should investigate if the differences in the reactivity measured in our laboratory experiments are meaningful in real-world situations. It is clear from our analysis that future work on BSi along the land-ocean continuum cannot neglect the potentially large influence of other $AlkExSi_{NaOH}$ fractions. Broad application of a continuous technique as suggested, as well as its fine-tuning, can shed new light on BSi transport by rivers (Conley 1997; Frings et al. 2014a), BSi accumulation rates in lakes (Stewart et al. 2007) and coastal sediments (Teodoru et al. 2006).

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