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The Ge/Si ratio as a tool to recognize biogenic silica in chert

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ABSTRACT

Germanium and silicon, dissolved in seawater, are considered to be incorporated into biogenic opal with no or little fractionation, which permitted to use diatoms as reliable recorders of seawater Ge/Si. Does some fractionation occur during diagenesis, preventing the use of Ge/Si in ancient sediments? We examined the Ge/Si ratio of fossil sponges and flint nodules of the Cretaceous Chalk Formation of northern France. Though disputed, silica in this formation is considered to originate from sponges. No fractionation is observed between sponges and diagenetic flints, which allows us to observe whether Ge/Si bears a biogenic or detrital signature. We may thus confirm that sponges were the main silica supplier during the chalk deposition. The Ge/Si ratio may be used to identify a biogenic signature in cherts where the origin of silica is dubious.

1. Introduction

Germanium (Ge) and silicon (Si) have similar properties in the marine environment (similar ionic and covalent radii, same typical tetravalent coordination when present as dissolved species, i.e., germanic and silicic acids, respectively); consequently, the marine cycles of inorganic Ge and Si are coupled and substitution of Ge for Si in mineral phases forming in seawater is common (e.g., Bernstein, 1985; Pokrovski and Schott, 1998; Siebert et al., 2006). The two main sources of Ge and Si to the ocean are mineral weathering and hydrothermal fluids (Hammond et al., 2000; King et al., 2000; McManus et al., 2003; Mortlock et al., 1993; Wheat and McManus, 2005). The main sink for Si and Ge removal from the ocean is the transfer to sediments via incorporation into biogenic opal (main opal-secreting organisms are diatoms, radiolarians and sponges) followed by burial, but Ge has an additional sink, namely, loss via non-opal phases during sediment early diagenesis. Germanium may be associated with U and Mo in bacterially-mediated, authigenic iron phases, notably Fe-rich clay minerals (King et al., 2000; Hammond et al., 2000; McManus et al., 2003; Tribovillard et al., 2011). The authigenic capture of Ge takes place in organic matter-rich sediments deposited under reducing conditions (see details in Rouxel et al., 2006; Tribovillard et al., 2011). The differences in the relative importance of the source terms for Ge and Si, combined with the fact that siliceous microfossils may record the Ge/Si ratio of the water column, has led to the proposal that the Ge/Si ratio recorded in diatoms could serve to monitor the variations of the relative importance of the following geologic phenomena: continental weathering and hydrothermalism, both releasing major- and trace-elements to the ocean (e.g., Froelich and Andreae, 1981; Froelich et al., 1985a,b, 1989; Mortlock and Froelich, 1987; Mortlock et al., 1993; Shemesh et al., 1989), as well as the influence of redox conditions, since reducing benthic environments may promote Ge capture through the formation of authigenic clay minerals. Using diatom Ge/Si as a tracer of ocean chemistry is only possible if discrimination between Si and Ge is not occurring during frustule construction, relative to the seawater Ge/Si ratio. Azam et al. (1973), Azam (1974), Azam and Chisholm (1976) concluded to the absence of such discrimination, nevertheless, recent works demonstrated the possibility for some biologic fractionation (Bareille et al., 1998; Ellwood and Maher, 2003; Ellwood

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et al., 2006; Sutton et al., 2010), but concluded that its impact is not significant. Preliminary results by Tribovillard et al. (2011) suggest that what is said about diatoms also applies to radiolarians but further testing is needed. However, biogenic silica undergoes extensive dissolution during early diagenesis and most often, in ancient sediments, biosiliceous hard parts are massively dissolved and recrystallized in the form of flint nodules, chert beds and diffuse impregnations. Such diagenetic accumulations are usual in diatomites and radiolarites, and frequent in sedimentary rocks deposited under conditions of high productivity by silica-secreting organisms. For instance, such concretions are much common in (hemi-)pelagic Cretaceous formations straddling the Cenomanian-Turonian boundary, such as the Tarfaya sections of Morocco, the La Luna Formation of Venezuela or the Italian sections of the Marche-Umbria Basin.

Consequently, to use the Ge/Si ratio for ancient sediments where biogenic silica has been dissolved and secondarily concentrated (with possible migration between the sites where dissolution took place and those where reprecipitation occurred), one must be sure that no Si–Ge fractionation occurred during the diagenetic course. To address this question, we compared the Ge/Si ratio values of fossil sponges of the Chalk Formation of Boulonnais (North France) to those of flint concretions of the same formation and originating from the diagenetic recrystallization of silica released predominantly through sponge dissolution. With regards to the Chalk flint nodules, the most common opinion is that silica comes from the dissolution of opal-made hard parts of sponges, diatoms or radiolarians (e.g., Lindgreen et al., 2011; Robaszynski and Amédro, 2003; Wray and Gale, 2006) but some authors point to sponges as the main suppliers of silica (Jakobsen et al., 2000; Shepherd, 1972). In addition, some authors also indicate that volcanic products (bentonites) could have contributed some silica to flint growth (Godet et al., 2003; see also Lindgreen et al., 2011). Finally, a participation of seawater-dissolved silica to the growth of early diagenetic nodules is envisioned (e.g., Zijlstra, 1995). To sum up, the consensus is that the silica inventory of the Chalk derived from sponge dissolution, with possible minor contribution of other opal-secreting planktonic forms (diatoms and radiolarians) and adjunction of silica released by dissolution of volcanic ashes.

The rationale of the present paper is that we must study situations where the initial biologic state of silica is known (here, sponges as the main supplier) and where the corresponding final, post-depositional state is identified – here flint nodules. In the present case, we admit that the silica of the nodule exclusively or dominantly originates from sponges that underwent dissolution, as explained above. Apart from the Chalk, we do not identify other marine situations where we can observe both the initial and final end-members of the diagenetic process. With modern, biosilica-rich sediments, the present initial end-member is observed, but the post-diagenesis one is not observable; with ancient sediments only the final post-diagenesis end-member is observed because the initial, non-recrystallized organisms are no longer present. However, the Miocene Monterey Formation could be suitable for such a study, because both end-members are present as diatomites including opal CT-chert nodules (K. Föllmi, personal communication).

One limitation of our approach is that the fossil sponges are probably not made up today with their initial stock of biosilica and they may have undergone (at least) partial dissolution-reprecipitation with possible exchange with the silica inventory mentioned above. However, fossil sponges must be the closest possible to the initial biosilica composition, compared to flint nodules that do not contain initial biosilica.

2. Material and methods

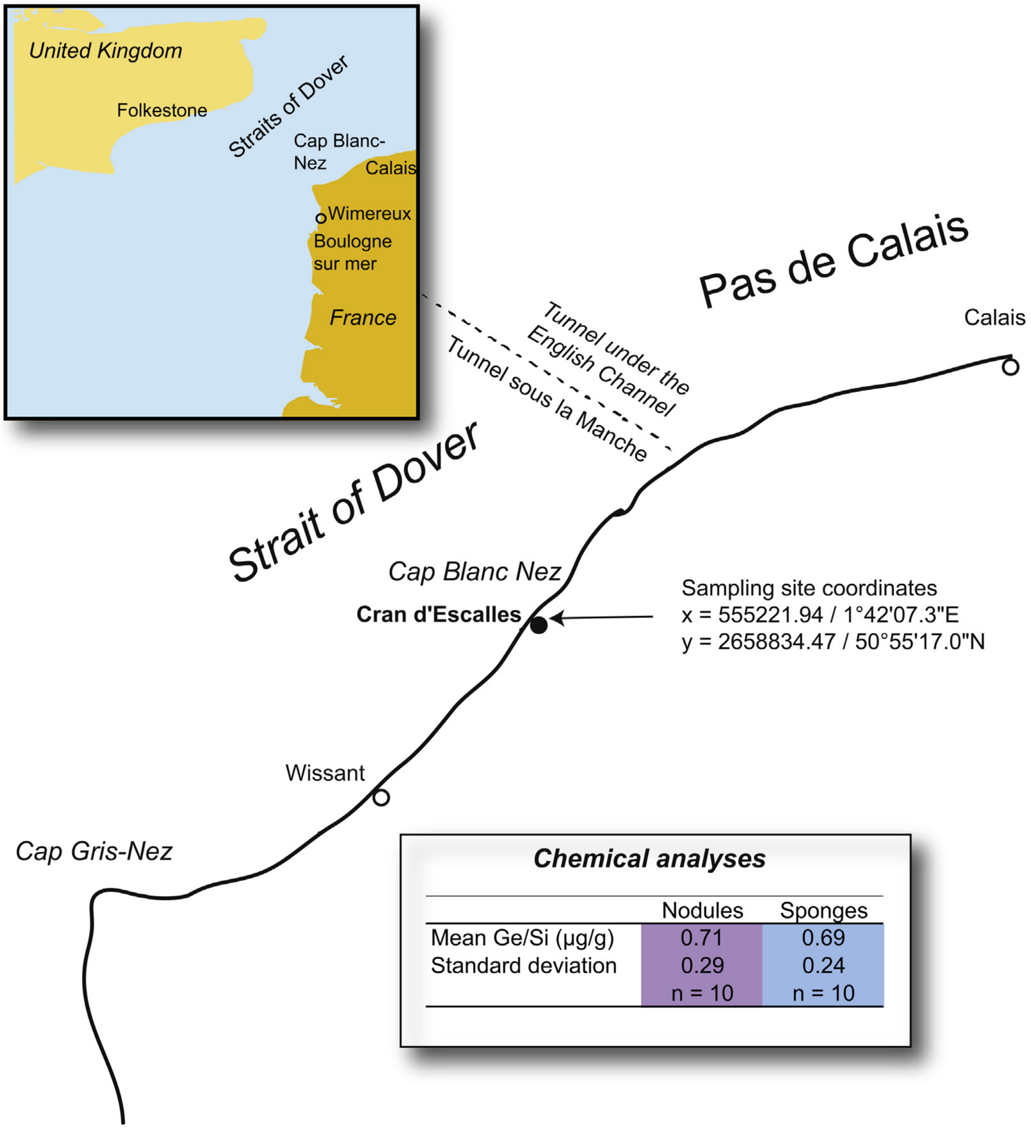
The Cretaceous Chalk is well exposed along the cliffs of the Cap Blanc Nez (Blanc Nez Cape) of Boulonnais, facing the English Channel (Fig. 1). This much-studied formation is extensively described and commented in numerous papers (e.g., Amédro and Robaszynski, 2000, 2001 and references therein). At Cap Blanc Nez, the chalk is rich in fossil sponges, the Siphonia-type being quite common. For the present study, we analyzed ten siphonia-type fossil sponges and ten flint nodules of the same size as that of the sponges; all these objects were picked at the foot of the cliff at the Cran d'Escalles access to the beach (Fig. 1). One of the nodules is a silicified echinoid. According to Robaszynski and Amédro (2003), the objects studied here correspond to three degrees in diagenetic precipitation of biosilica: the fossil sponges represent the earliest stage of diagenesis with the lowest intensity of modification of the initial stock of silica; the silicified echinoid derives from the filling of the skeleton, which represents a step further in the diagenetic course; the other nodules, that are generally present along discrete stratigraphic levels, must have formed somewhat later during diagenesis. The chemical analyses were performed by ICP-AES (major and minor elements) and ICP-MS (trace-elements) at the spectrochemical laboratory (SARM) of the Centre de recherches en pétrographie et géochimie, Vandœuvre-les-Nancy, France (French Centre national de la recherche scientifique). The samples were prepared by fusion with $LiBO_2$, followed by HNO_3 dissolution. Precision and accuracy were both better than 1% (mean 0.5%) for major-minor elements and 5% for trace metals, as checked by international standards and analysis of replicate samples (Carignan et al., 2001).

3. Results

The twenty objects studied here show homogeneous Si/Ge ratio values (Table in Fig. 1). Mean Ge/Si of the sponges is 0.69×10^6 (with standard deviation of 0.24; $n = 10$); for nodules, the mean ratio is 0.71×10^6 (with standard deviation of 0.29; $n = 10$). The whole dataset yields values closely corresponding to those measured on modern sponges (Fig. 2; Ellwood et al., 2006).

4. Interpretations

Our results indicate that no fractionation between Ge and Si is observed between the fossil sponges and the nodules, including the silicified echinoid. In other words,



	Nodules	Sponges
Mean Ge/Si (μg/g)	0.71	0.69
Standard deviation	0.29	0.24
	n = 10	n = 10

Fig. 1. Location of the sampling site and average values of the Ge/Si ratio of fossil sponges and diagenetic flint nodules.

the Ge/Si ratio is the same for objects representing various degrees in the diagenetic process. We cannot be sure that the ratio of the spicules had been the same when the sponges were alive, but the ratio of the spicules, once dissolved and reprecipitated with possible adjunction of other sources of silica as evoked above, is the same for any object for which the transport of silica between loci of opal-dissolution and loci of flint formation was more or less long in time and space, ranking from the fossil sponges themselves to the silicified echinoid, and to the nodules. These preliminary results apply to the sponge-originating biosilica of the Chalk formation but we see no compelling reason why they should not also apply to other sponges and other biosilica-secreting organisms (radiolarians and diatoms): opal-dissolution – (migration) – recrystallization is an abiotic process that at first sight, should be the same with any biosilica, whatever the secreting organisms. Thus basing upon our results, we observe that no differential alteration of the Ge/Si ratio can be evidenced for various objects deriving, at various steps of the diagenetic course, from the same initial inventory of dissolved silica. The Ge/Si signature seems to be robust through diagenesis. The Ge/Si signature observed in the Chalk is close to the value of modern sponges, and clearly lower than that of seawater. Modern sponges show Ge/Si values lower than that of seawater and a specific Ge-isotope composition [see discussion in Reincke and Barthel (1997), De La Rocha (2003) and Rouxel et al. (2006)]. Thus, the Ge/Si signature observed in the Chalk suggests that the silica present as flints and silicified fossils in the Chalk Formation has a dominant biogenic origin and only a minor part (if any) originating from silica dissolved in seawater or volcanic sources of silica (such as bentonites).

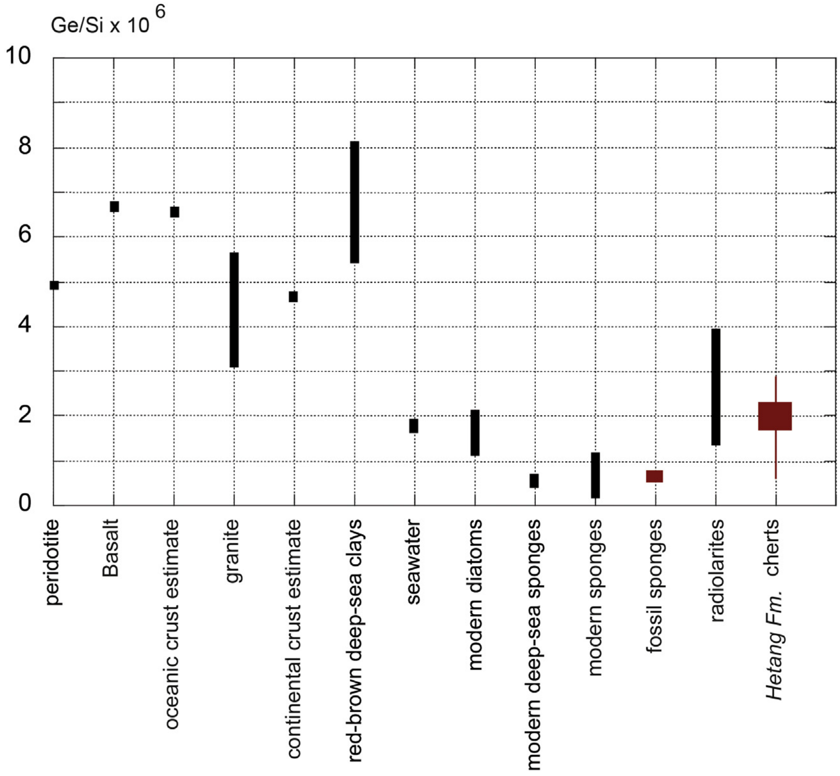


Fig. 2. Values of the Ge/Si ratio allowing one to compare the ratio of various forms of biosilica to that of various lithologies. Data from Rouxel et al., 2006 and Tribovillard et al., 2011.

A further implication of our results is that the Ge/Si ratio may be used to identify the source of silica in flint or chert or any other form of diagenetically concentrated silica where the origin of opal/quartz concretions or beds is dubious (silica released through silicate-mineral transformation or biogenic silica). This is the case for Early Cambrian rocks, deposited at times when opal-secreting organisms may have not existed yet. For instance, the Lower Cambrian Hetang Formation in South China is a black shale sequence that accumulated under prevailing anoxic – possibly euxinic conditions, but with recurrent episodes of bottom ventilation permitting the presence of sponges (Zhang et al., 2012; Zhou and Jiang, 2009). The presence of radiolarians in this formation is discussed by several authors (Braun et al., 2007; Zhang et al., 2012), and Zhou and Jiang (2009) report on the identification of sponge spicules in the chert levels. Ten chert samples of this formation were analyzed for chemical composition at the SARM facility (see Section 2) and the results were published by Zhang et al. (2012). The Ge/Si range value is 0.5–2.7 $\times$ 10^6, with mean ratio equal to 1.5 $\times$ 10^6. These values fall within the range corresponding to the opal-secreting organisms and plot far from the value attributed to the average clastic supply (Fig. 2; Tribovillard et al., 2011). The most straightforward interpretation of these results is that the chert beds originate from biosilica, implying (hence confirming) that opal-secreting organisms did exist by these ancient times (either sponges or radiolarians, or both). However, an additional factor may have intervened. Clay minerals are known to concentrate Ge relative to Si during silicate weathering. The retention of Ge by clay minerals is reputed to be the main factor fractionating Ge/Si ratios in the weathering environments (Kurtz et al., 2002). In addition, secondary clay minerals in the marine environment (e.g., glauconite) are also known to incorporate preferentially Ge (Rouxel et al., 2006). If, during (early) diagenesis, the (secondary) clay minerals of the Hetang Formation black shale's had been solubilized and thus could have released Ge-rich fluids fuelling chert formation the cherts would be expected to yield high Ge/Si ration values, in sharp contrast to what is actually observed for the Hetang Formation. However, these black shales were deposited under largely reducing conditions, possibly favoring the diagenetic formation of minerals prone to Ge preferential incorporation. In such circumstances, the parent fluids feeding chert formation would have lost a part of their dissolved Ge inventory, and thence would have induced the precipitation of chert or flint yielding low Ge/Si, which would mimic a biogenic signature. This multi-step scenario is relatively hypothesis-demanding, compared to the straightforward interpretation involving biosilica as the main source of both Ge and Si. This more complex scenario would imply a very high fractionation of Ge/Si, taking into consideration the markedly-contrasted Ge/Si values opposing the alumino-silicate signature to the signature of the cherts of the Hetang Formation. Consequently, this complex scenario will not be retained in the present case but it must be kept in mind when one intends to decipher the silica sources of chert/flint.

5. Conclusion

This short, preliminary study leads to two conclusions. The Ge/Si ratio may be used to study the ocean paleogeochemistry when measured not only on the hard parts of the opal-secreting organisms as usually conducted, but also on the diagenetic objects issuing from the dissolution-recrystallization of the fragile biosiliceous organisms. This result is important because, owing to their propensity to dissolution, biosiliceous organism hard parts are only encountered in recent sediments. However, if their recrystallized silica may be considered with confidence, paleocean geochemistry reconstruction is not restricted to recent sediments any longer.

The second conclusion is that, if Ge/Si is considered to be a reliable proxy even when measured on diagenetic objects, the ratio may be used to identify a possible biogenic origin for chert or flints, the silica of which is of dubious origin. In the present study, we confirm that sponges were the major source of silica for flint growth in the Chalk formation at Cap Blanc Nez. We also suggest that the Ge/Si ratio may be used to identify the presence of biosilica in diagenetical opal/quartz concentrations. Lastly, we propose the Ge/Si ratio as a tool for tracking the first occurrences of siliceous biomineralization during the Lower Cambrian (Latest Proterozoic?) times.

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