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Early diagenetic silica precipitation, in relation to redox boundaries and bacterial metabolism, in late Cretaceous chalk of the Maastrichtian type locality

Comment

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Introduction

Zijlstra's (1987) interpretation of the occurrence and formation of silica concretions can be considered as a synthesis of various current theories and observations put forward in an extensive body of geological and chemical research papers and monographs (see Iler, 1979). As a new element he introduced the redox boundary and suggested that at that boundary both microbiological activity and physico-chemical conditions constitute a micro-environment favourable for silica precipitation. Because the mechanisms of the formation of silica concretions in carbonate sediments are still not completely understood, each new idea on this topic should be welcome. While appreciating Zijlstra's contribution to the ongoing debate on this topic, we dispute various aspects of his rationale from a geochemical point of view.

Polymerization

Zijlstra's (1987) description of silica solubility in terms of monomer concentration is correct. However, we have problems with some parts of his discussion of polymer formation. Oligomers and polymers form not only at pH > 9 but also at lower pH values. Not just negatively charged complexes, but also uncharged species combine in a condensation reaction. This reaction can, for instance, be formulated for the case of dimerization:

$$2\ Si(OH)_4 = Si_2O(OH)_6 + H_2O \qquad (1)$$

Applin (1987) has shown that at pH ≃ 5.5 dimeric species are already present at a total Si concentration in solution ($\sum$Si) as low as 0.1 mM. In the range pH 7–8. which is typical for marine pore waters, dimeric species may already make up some tenths of $\sum$Si. Iler (1979) and Crerar et al. (1981) referred to experiments in which polymerization had indeed been shown to be pH-dependent, but the maximum polymerization rate was at pH 6–8, and thus well below Zijlstra's pH 9 boundary.

In general, oligomeric and polymeric species become increasingly important at increasing $\sum$Si. Although, in comparison with the solubility of the stable quartz phase, the degree of supersaturation caused by the dissolution of biogenic silica is only of the order of 10–20 times, polymerization may still occur in marine pore waters. Crerar et al. (1981) demonstrated that cations, especially the divalent earth alkali ions, catalyze polymerization at pH 7. Siever (1962) even stated that in solutions high in divalent cations (as are marine pore waters) polymerization is high, regardless of pH.

It is beyond the scope of this letter to review the extensive literature on Si polymerization. It is, however, important to note that polymerization in supersaturated marine pore waters can occur in the normal range pH 7–8 and that there is no need to have recourse to more alkaline pore waters to explain the polymerization of dissolved Si and the precipitation of silica. Moreover, although poly-

merization may be viewed as a first step to precipitation, this does not imply that silicate will precipitate out of any solution containing polymers of silicic acid. Stable solutions of monomeric and polymeric species do exist.

Role of pH

On the basis of the assumption that polymerization and precipitation only occur at pH >9, Zijlstra (1987) attempted to locate such environments in marine pore waters. As he correctly mentioned, pore waters in marine sediments generally have pH <8. In order to reconcile factual and supposedly required pH regimes, he had recourse to micro-environments within the pore fluids, where such high pH could be induced by bacterial activity.

An increase of pH does indeed raise the solubility (in terms of $\sum$Si) of amorphous silica and does not bring about precipitation of less soluble silica polymorphs. The driving force for precipitation is not the pH as such, but the difference in the solubility of silica polymorphs at any pH. For pore waters in apparent equilibrium with opal, an increase in pH will generally increase $\sum$Si, a decrease of pH, on the other hand, will cause a decrease of $\sum$Si due to precipitation. This means that the role of pH as a controlling factor for silica precipitation is probably the reverse of what Zijlstra proposed. The diagenetic reactions that he considered in fact decrease rather than increase the pH of pore waters. Although micro-environments do sometimes play a role in diagenesis, it is questionable whether the pH in such environments can really be raised drastically. The intimate contact between solid carbonates and organic matter, even within the chambers of dead planktonic or benthic species, strongly and relatively rapidly buffers the pH of the pore waters. It should also be taken into account that marine pore waters are open rather than closed systems. This means that the buffering capacity of the system is actually larger than that of the restricted layers or micro-environments where specific diagenetic reactions occur.

Diagenetic reactions

The following reactions apply to early diagenesis in marine (carbonate) sediments, where Zijlstra's $CMH_2O = (CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$ (Redfield et al., 1963):

Oxic conditions

$$CMH_2O + 138\ O_2 \rightarrow 106\ CO_2 + 16\ NO_3^- + HPO_4^{2-} + 18\ H^+ + 122\ H_2O \quad (2)$$

Suboxic conditions

$$CMH_2O + 94.4\ NO_3^- \rightarrow 13.6\ CO_2 + 92.4\ HCO_3^- + 55.2\ N_2 + 84.8\ H_2O + HPO_4^{2-} \quad (3)$$

$$CMH_2O + 236\ MnO_2 + 364\ CO_2 + 104\ H_2O \rightarrow 470\ HCO_3^- + 8\ N_2 + 236\ Mn^{2+} + HPO_4^{2-} \quad (4)$$

$$CMH_2O + 424\ FeOOH + 756\ CO_2 \rightarrow 862\ HCO_3^- + 16\ NH_4^+ + HPO_4^{2-} + 424\ Fe^{2+} + 120\ H_2O \quad (5)$$

Anoxic conditions

$$CMH_2O + 53\ SO_4^{2-} \rightarrow 39\ CO_2 + 67\ HCO_3^- + 16\ NH_4^+ + HPO_4^{2-} + 53\ HS^- + 39\ H_2O \quad (6)$$

Except for reactions 4 and 5, these processes tend to decrease the pH. In the case of decreasing pH the presence of $CaCO_3$ in the sediments constitutes a quickly reacting buffer reservoir, according to the reaction:

$$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca^{2+} + 2\ HCO_3^- \quad (7)$$

Among the secondary reactions that can act as pH buffers, the precipitation of iron sulphides is the most conspicuous one:

$$Fe^{2+} + HS^- \leftrightarrow FeS + H^+ \quad (8a)$$

$$2\ FeOOH + 3\ H^+ + 3\ HS^- \rightarrow FeS + FeS_2 + 4\ H_2O \quad (8b)$$

As was shown by Emerson et al. (1982) for reactions 2 and 3 in combination with reaction 7, the pH does not change or it decreases in the presence of $CaCO_3$. For the combination of reactions 6 and 7 it also can be shown that the pH is rather effectively buffered, with a slight decrease of not more than 0.5 pH-unit. Only in the case of suboxic diagenesis involving reactions of Mn and Fe oxides (reactions 4 and 5 in combination with 7) can one calculate (assuming a closed system) that the pH buffering is insufficient at an organic degradation beyond roughly 1 μmole organic matter per dm^3 pore water and that for such a system the pH will rise. But in a more realistic open system the pH would only reach values >9 when much more organic matter is degraded. It should be borne in mind, however, that such high pH values have not been reported in the suboxic zone of marine pore waters! Zijlstra (1987) assumed that 'hydrogen' ($= H^+$) is removed from pore waters in the zone of reduction by the formation of gaseous species (H_2S, NH_3, CH_4). He supposes that these gases subsequently diffuse upwards and become oxidized again in the zone of oxidation.

Firstly it should be emphasized that Zijlstra does not properly define a 'zone of reduction or oxidation'. By zone of oxidation he probably means the zone in which oxygen is present, but in fact organic matter is also oxidized by nitrate, Mn and Fe oxides, and sulphate in consecutive zones (cf. Froelich et al., 1979).

Secondly it appears from reactions 2–6 that in the pore water environment H_2S and NH_3 are not the dominant products. The pK values are: 9.2 ($NH_4^+ \leftrightarrow NH^3 + H^+$) and 7 ($H_2S \leftrightarrow HS^- + H^+$). The stability fields for both N and S species in marine pore waters with pH 7.5–8 are such that NH_3 and H_2S make up only $4 \pm 2\%$ and $20 \pm 10\%$ respectively of the total concentrations. Moreover NH_3 and H_2S have a fairly high solubility in pore waters. Transport in a gas phase is highly unlikely. Diffusion along dissolved concentration gradients occurs for all species, but acid – base equilibrium is maintained throughout. Methane production is not very likely in the sediments under consideration, because dissolved sulphate constitutes a large reservoir for organic matter breakdown through sulphate reduction. However, if methane diffuses upward (again most likely in the dissolved state), it forms a suitable carbon source for sulphate reducers (Reeburgh, 1980). The reaction is written as

$$SO_4^{2-} + CH_4 = HCO_3^- + HS^- + H_2O \qquad (9)$$

and produces carbonate and sulphide alkalinity, without a drastic effect on the pH.

From the foregoing discussion, the contents of which are supported by numerous pH measurements in marine pore waters, it will be evident that the change of pH in connection with the diagenetic reactions considered by Zijlstra (1987) is the reverse of what he expects. The two suboxic diagenetic reactions that he did not take into account might have the effect on the pH that he needed for his rationale, but only in the unrealistic case of a closed pore water system.

If not this model, which one?

As was discussed above, more acid rather than more alkaline conditions can be expected to prevail at redox boundaries. But large pH gradients are not observed in pH profiles of marine sediments. Therefore, other processes incorporating most of the ingredients of Zijlstra's (1987) model must be considered. The majority of such processes have been earlier discussed in literature by a number of authors and we draw attention to some of them.

All models are based on diagenetic dissolution/precipitation reactions with biogenic silica (opal-A) as the original Si source. Supersaturation with respect to more stable silica (opal-CT, quartz) is driving force. The solubility of these phases is thermodynamically defined by the equilibrium activity of monomeric silicic acid (H_4SiO_4) in solution, according to the dissolution reaction

$$SiO_2 + 2\ H_2O \leftrightarrow H_4SiO_4 \qquad (10)$$

but the actual solubility ($\sum Si$) depends on the solution chemistry (pH, ionic strength, complexing by cations, etc.), and on the kind of polymorph, its surface area per unit of volume of solution and the

purity of its surface (absence or presence of organic or inorganic coatings; see e.g. Morris & Fletcher, 1987). Also, the concentration of dissolved $\sum$Si is influenced by the presence of other solid phases which can act as adsorbing substrates. Adsorption on reactive solid particle sites is often considered to be the most likely process initiating precipitation. Such sites can be present in sedimentary organic matter (Siever, 1962; Chanda et al., 1976). Degradation of organic matter and concomitant production of CO_2 acidity would dissolve proximate $CaCO_3$. In summary the role of organic matter results in the replacement of solid $CaCO_3$ by silica.

Other sites possibly relevant for incipient silica adsorption/precipitation are surface hydroxyl groups of solid $Mg(OH)_2$ (Williams & Crerar, 1985). As was demonstrated by Kastner et al. (1977), the transformation of opal-A to opal-CT is also greatly enhanced by solution high in Mg^{2+} and in alkalinity, in the absence of clay minerals. In carbonate sediments the formation of nuclei with Mg and OH and subsequently of opal-CT lepispheres would reduce the alkalinity and thus promote the dissolution of $CaCO_3$, which enables the reaction to continue. The presence of minor amounts of palygorskite or dolomite in the vicinity of the concretions would be an indication of this catalysis, because the trapped Mg is liberated upon the transformation of opal-CT into quartz.

Something that has not been taken into account in relation to chert formation, but is worth considering is the precipitation of ferrous silicate (De Lange & Rispens, 1986) as a precursor phase. When oxidation of this phase occurs at some stage after its formation, ferrous silicate will be transformed into iron(III) oxide and Si will become partially adsorbed (Winters & Buckley, 1986; Loder et al., 1978) or precipitated, in both cases forming reactive sites for further silica growth.

Homogeneous precipitation of silica from solution requires a high level of supersaturation. We doubt whether such conditions, although implicitly assumed in Zijlstra's model, are present under prevailing diagenetic conditions in marine pore waters.

For the sake of completeness the model of Knauth (1979) for the replacement of $CaCO_3$ by silica in carbonate sediments should be mentioned. Knauth proposed that $CaCO_3$ is dissolved by the mixing of meteoric water and marine pore water and that this mixing provides favourable conditions for both dissolution of $CaCO_3$ and precipitation of silica. We have no evidence, for instance from data on oxygen isotopes in Maastrichtian nodular silica, that would support this model.

Conclusions

We have shown that Zijlstra's (1987) interesting model for the formation of chert in late Cretaceous chalk of the Maastrichtian type locality cannot be reconciled with the basic (geo)chemistry governing the behaviour of Si in marine sediments. We do not agree with Zijlstra's interpretation of the roles of polymerization and of pH, and with his view on the effect of diagenetic reactions on the pH. Nevertheless we appreciate Zijlstra's attempt to shed new light on the genesis of such silica concretions. We are convinced that process can only be made if there is close cooperation between sedimentologists, with their good field observations and interpretations, and geochemists who develop the right chemical framework into which such models for silica precipitation can be fitted.

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Reply

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It was suggested (Zijlstra, 1987), that the distribution of flint in the chalk of the Maastrichtian type locality, reflects the former presence of a redox zone. This zone was situated close to the marine sediment/water interface and it favoured precipitation of silica during early diagenesis. The precipitation of silica resulted from the dissolution of opal, oversaturation due to increase of the pH, and subsequent polymerization of a less soluble silica polymorph. The flint nodules grew, during late diagenesis, due to the diffusion of silica towards the sites with an elevated concentration of early diagenetic silica precipitates.

Van der Weijden et al. object against the proposed model and argue as follows:

1. regardless of the pH of the fluid, silica polymerization and precipitation may occur;
2. the porefluid in sediment is open to seawater and the pH of the porefluid is buffered;
3. the decomposition of organic matter yields reactions, that do not lead to a higher pH and even if they did, than only to a negligible small amount;
4. according to other models, silica may precipitate around nuclei that are not the result of pH dependent silica precipitation during early diagenesis.

With respect to points 1 and 4: Indeed, it may be that pH dependent silica precipitation is not the only possible mechanism to create nucleation sites for silica concretion growth. However, Van der Weijden et al. hardly specify the nature of these mechanisms, nor demonstrate their validity in the sediments under discussion. Their arguments do not demonstrate the invalidity of the proposed model.

With respect to points 2 and 3: In the restricted marine environment, in the presence of metabolizing organisms, buffering of pH can be rather poor. For instance, it was observed that removal of CO_2 by means of photosynthesis of marine plants, may cause the pH to rise as high as 10.2 (Alderman, 1965).

In the anoxic carbonate sediment CO_2 and hydrogen ions are removed by methane producing bacteria ('Methane bubbles formed ....', Reeburgh, 1980), according to the reactions:

$$2CH_2O + 2H_2O \leftrightarrow 2CO_2 + 8(H)$$
$$8(H) + 8H^+ + 2CO_2 \leftrightarrow 2CH_4 + 4H_2O \qquad (1)[1]$$

The decrease of the hydrogen ion concentration, will lead to an increase of the pH, because of insufficient buffering by means of the reactions:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$
$$H_2CO_3 \leftrightarrow CO_3^{--} + 2H^+$$
$$M^{++} + CO_3^{--} \leftrightarrow MCO_3 \qquad (2)$$

In the presence of soluble silica, however, the increase of the pH due to reaction (1) is buffered by means of the reaction:

$$H_4SiO_4 \leftrightarrow H_3SiO_4^- + H^+ \qquad (3)$$

This results in an increased concentration of negative silica complexes in solution, and if hydrogen ion consuming reactions (1) slow down again and pH decreases, then silica precipitates from a supersaturated fluid.

Unfortunately, a mere sequence of equations of chemical reactions is a primitive and inadequate way to express the complex chemistry of marine sediments. Discussion seems useless if we can not consider a.o. diffusion, adsorption, changing surface properties, reaction rates, and the effects of microbial metabolism.

However, bacterial colonies coated with manganese carbonates, $(Mn_{0.80}Ca_{0.15}Mg_{0.05})CO_3$, and surrounded by a spongy matrix of silica precipitates, occur in anoxic sediments of the Baltic Sea (Fig. 1A, after Suess, 1979). This observation illustrates the role of bacterial metabolism and microenvironments in the precipitation of mineral phases in sediments. Furthermore, the presence of the rather soluble coating of carbonate, suggests that the po-

[1] (modified after Berner, 1980).

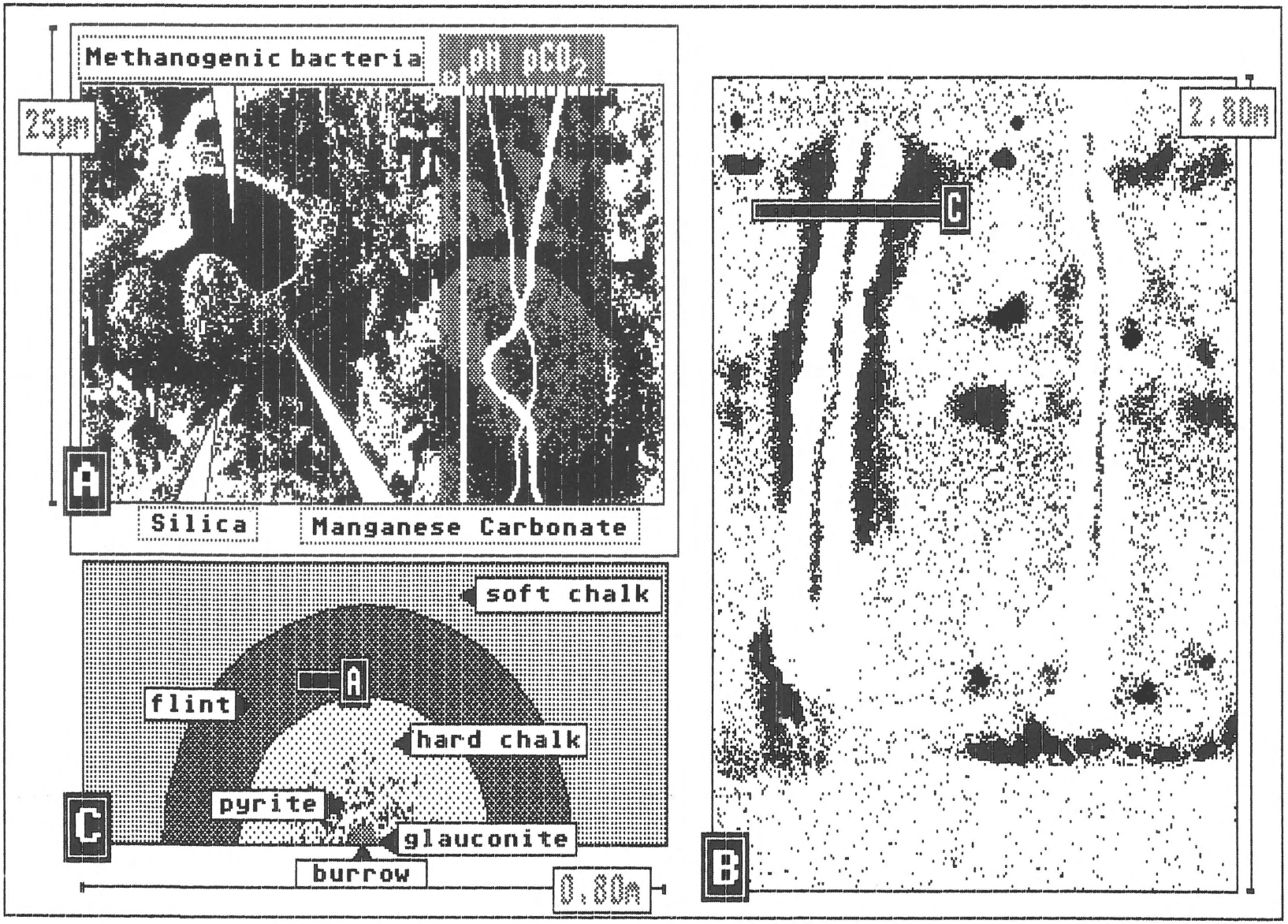

Fig. 1. Methanogenic bacteria and *Bathichnus paramoudrae* (1A, modified after Suess, 1979).

refluid close to the bacteria had a lowered pCO_2 and a high pH, due to the reduction of CO_2 and the production of methane (1). At some distance of the bacteria, the still high pH of the porefluid caused polymerization and precipitation of the silica.

Considering the silification of the Maastrichtian carbonates under discussion, argument for the early diagenetic precipitation of silica in relation with bacterial metabolism and variations of the pH and the pCO_2 of the porefluid, may be found in *Bathichnus paramoudrae*. Burrows of *Bathichnus paramoudrae* are cm thin shafts, that penetrate the sediment vertically down to depths of 9 m (Bromley et al., 1975). *Bathichnus paramoudrae* (Fig. 1B) is common in the micritic calcisiltites that occur at the boundary between Lixhe and Lanaye chalk of the E.N.C.I. quarry (Maastricht, the Netherlands) (Felder, 1975).

The burrow shaft is surrounded (Fig. 1C) at a distance of several mm, by a thin layer of glauconitic chalk. The chalk around the burrow shaft is lithified. The several dm thick lithified zone contains finely dispersed pyrite in decreasing concentrations, with increasing distance from the shaft. Locally the lithified chalk is surrounded by a cilinder of flint nodules. The chalk just outside the flint cilinders is only weakly lithified and does not differ from the chalk without *Bathichnus paramoudrae.*

Obviously, the presence of the burrow caused diagenesis of the chalk. According to Bromley et al. (1975), the burrower introduced fresh organic matter into sediment and reactivated bacterial metabolism and diagenesis of the chalk. On the other hand, it may be that *Bathichnus paramoudrae* penetrated 'inert' sediment to introduce fresh seawater and reactivate dormant bacterial spores. The introduction of oxygen and sulphate produced redox zones around the burrow, that allowed the development of bacterial colonies, which were subsequently harvested by the burrower.

As oxygen was introduced, an oxygenated zone around the burrow was generated. Glauconite formed, because mobile Fe diffused from more reducing environment towards the burrow shaft where it precipitated as Fe^{3+} hydroxides and subsequently sorbed silica, Fe^{2+}, Al, K, Mg, and B (Harder, 1980).

Pyrite formed in the sub-/anoxic zone around the oxygenated zone, where oxidation of methane and reduction of sulphate occurred (Reeburgh, 1980).

The lithification of the chalk around the burrow shaft, resulted from the reduction of CO_2 and the production of methane (1) outside the zone of sulphate reduction. Silica precipitated in the outermost redox zone that surrounds the central burrow. Subsequent diffusion of silica from the inner redox zones towards the sites of precipitation caused the decrease of the silica concentration in the inner redox zones. The subsequent decrease of buffering (3) allowed the precipitation of carbonate (2) and the lithification of the chalk.

Thus, the deep burrower *Bathichnus paramoudrae* reactivated methanogenic bacteria and caused redistribution and subsequent precipitation of silica in the zone of CO_2 reduction.

The metabolism of methanogenic bacteria generates microenvironments in porefluids of sediment, that are characterized by a low pCO_2, a high pH, and the precipitation of silica.

Because the environment of early diagenetic silica precipitation is marked by a high pH, as well as a low pCO_2, there remains the possibility that precipitation is dependent on pH and/or pCO_2. According to Buurman & Van der Plas (1971), tobermorite ($CaSiO_3$), which is only stable at low pCO_2 and high pH, is the first silicate to precipitate in the chalk under discussion. This uncertainty has no implications for the model proposed (Zijlstra, 1987); if anything, however, it is consistent with it.

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