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# Radiolarian palaeoecology and radiolarites: is the present the key to the past?

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## Abstract

Radiolarian productivity pulses and related radiolarite deposition are phenomena difficult to understand from an exclusively actualistic viewpoint. Evolutionary selection pressure among silica-secreting marine plankton, both radiolarians and diatoms, has led toward more economic usage of rapidly shrinking nutrient resources, including dissolved silica, of the photic zone in the late Cenozoic oceans, and, in particular, a substantial modification of oceanic cycle by the diatom explosive radiation. Even if there is a proved link between biomineralization and dissolved silica loading among the phytoplankton only, the relative independence of modern siliceous planktic biotas from the available silica pool reflects mainly their progressive physiological specialisation during evolutionary history. Oceanic chemistry and productivity, as well as patterns of circulation/upwelling have changed radically during the Phanerozoic. Radiolarites apparently represent an 'anachronistic' facies, as exemplified by their long-lived and ocean-wide distribution in palaeo-Pacific, and hitherto, highlighted actualistic models of localized intra-oceanic wind-driven upwelling loci are of largely questionable applicability. In addition to plate drift, hypersiliceous domains and intervals are explainable mostly by a large-scale volcano–hydrothermal activity during major plate-boundary reconfigurations, which, in many ways, favoured siliceous biotas acme, and their skeletal remains accumulation and preservation. Factors tied to rapid, voluminous submarine eruptions, such as thermal buoyant megaplumes and basin overturns, offer a viable alternative for traditional climatic/circulation scenarios in case of hypersiliceous high productivity events irrelevant to greenhouse-to-icehouse climatic change. The evolving carbon and silica cycles were coupled through the greenhouse effect and enhanced chemical weathering. Volcano-hydrothermal and tectonic uplift events, related mostly to extensive rifting and/or accelerated oceanic spreading, were the endogenous driving force that created this perturbation of the exogenous system. The present biogeochemical cycle is representative only for the overall silica-depleted post-Eocene oceanic ecosystems, which broadly correlates with a major expansion of diatoms groups extremely efficient in silica removal, and closely linking the silica budget with phosphorus and nitrogen cycles. Thus, an orthodox uniformitarian approach to biosiliceous sedimentation, based on a silica-starved vigorous ocean, is of limited significance when applied to the pre-Neogene settings, especially in the peculiar planktic habitats of epeiric seas, as well as during biotic crises marked by strong geotectonic overprint. The major turnovers in marine siliceous biota composition, in particular after the end-Permian radiolarite gap, may have been coupled with discernible changes in an increasing biological

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control on the long-term oceanic silica cycling ('punctuated equilibrium'). The evolutionary turnovers have induced a stepdown decrease of dissolved silica levels through the Phanerozoic, contemporaneously with the general secular trend of upward scaling of nutrient-related ecological processes and increased effectiveness of resource utilization. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** radiolaria; diatoms; biogenic silica; radiolarites; biogeochemical cycles; uniformitarianism; palaeoceanography; palaeoecology; volcanism; mass extinctions

## 1. Introduction

Siliceous microplankton makes up one of the major marine microfossil groups. Abundant dissolved silica was frequently considered as one of the principal promoting factors for biogenic siliceous deposits, particularly for the widespread Jurassic-Cretaceous radiolarite formations, as reviewed by Conti (1958), Grunau (1965), Steinberg (1981), Hein and Parrish (1987) and Vishnevskaya (1995). This traditional approach to the ancient biosiliceous deposition has recently been questioned by De Wever et al. (1994) and De Wever and Baudin (1996). From an actualistic perspective, it appears that generally, *there is no minimum dissolved silica content in seawater for biogenic blooms and subsequent siliceous ooze accumulation* (for similar earlier views, see Tappan and Loeblich, 1971; Baumgartner, 1987; Hein and Parrish, 1987). This school of thought also holds that the intensity of wind-driven upwelling is the primary factor influencing the bioproductivity and radiolarite deposition, implying a belief that other controls are irrelevant. If these hypotheses are correct, the long-held assumption of a causal link between abundance of radiolarians, radiolarites and volcanogenic silica input (see Fig. 1) is essentially erroneous.

In this paper, the controversy is reviewed in light of recent ecological, palaeoecological and biogeochemical-facies data related with endogenous controls of silica cycling. This review focuses finally on critical discussion of the actualistic paradigm in palaeoecology and sedimentology, as pointed out previously, among others, by Plaziat (1978), Racki (1986), Kauffman (1987), Bottjer et al. (1995), Bottjer (1997) and Harper et al. (1997). The main conclusion is that the apparent relative independence of living radiolarians from the dissolved silica pool

reveals only progressive adaptation to an evolving biogeochemical silica cycling, as addressed by an insight into the Eocene turning point. Furthermore, limited applicability of actualistic models of localized upwelling-mediated zones is emphasized by examples of extended in space and time palaeo-Pacific biosiliceous successions (cf. Jones and Murchey, 1986; Cordey, 1996; Jansa, 1997). Tectono-volcanic trigger is considered herein to be an overlooked issue in the preservation versus production controversy, supplementing wind-driven upwelling during puzzling anoxic oceanic events corresponding to a

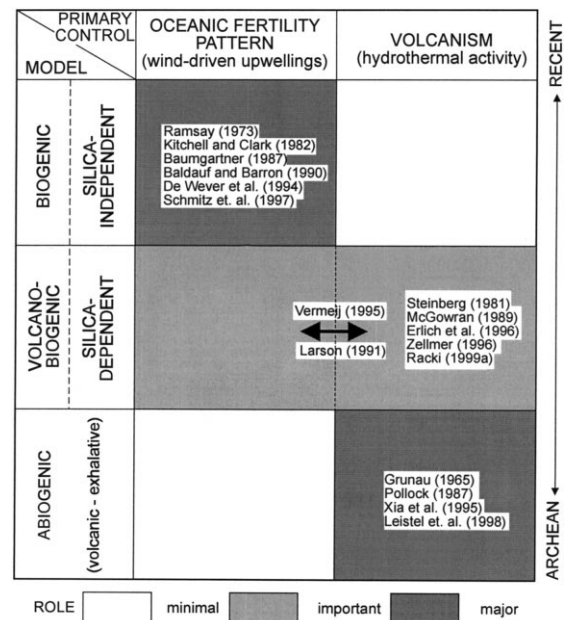


Fig. 1. Scheme of the principal 'controls' of radiolarite deposition, and in general, biosiliceous accumulation (cf. Castellarin and Sartori, 1978; Zellmer, 1996), with selected 'classical' and recent references for particular scenarios (see also Table 1). Secular change of silica cycle is marked (see Fig. 15 for further details).

basin-wide plankton bloom (see Parrish, 1995). The presumed endogenous scenario for the obviously non-actualistic ('anachronistic' sensu Bottjer, 1997) hypersiliceous events is validated in the context of the reference Cretaceous greenhouse epoch of worldwide tectonic re-arrangements, and as indications for major biotic crises (cf. Racki, 1999a).

### *1.1. The record quality and some basic terms*

The fossil record of the siliceous biomineralization is still erratically known. This uncertainty concerns especially diatoms and diatom-like protists (e.g., Martin, 1995; Kemp et al., 1999; Schieber et al., 2000). Because of large-scale taphonomic and diagenetic effects (see review in Hesse, 1989; De Wever et al., 1994), a great loss of information limits all interpretations of secular changes of sedimentary biomineralized silicate. This permits only a crude estimation based on distribution pattern of siliceous deposits (e.g., Distanov, 1974; Steinberg, 1981; Hein and Parrish, 1987; Baldauf and Barron, 1990). A double enhancement in the Phanerozoic stratigraphic record is associated with sedimentary and diagenetic processes, because the precursor biosiliceous signal (i.e., biogenic bloom) is usually considerably magnified via preferential preservation (Nelson et al., 1995), and diagenetic silica redistribution to layers already rich in silica (De Wever et al., 1994; Murray, 1994). Nevertheless, the sources of silica at least for Palaeozoic cherts were varied, and in some sequences, were predominantly inorganic in origin (largely from clays; La Porta, 1998). For the later Mesozoic and Cenozoic, there are far more accurate data on distribution patterns and rates of biogenic silica accumulation from oceanic drilling (Miskell et al., 1985; Owen and Rea, 1985; Ogg et al., 1992; Berger et al., 1998; and many others), particularly the results derived from the geochemical modelling (e.g., Zhou and Kyte, 1992; Kyte et al., 1993).

The term 'radiolarite' is herein used in a broad sense. The review is focused not only on distinctive facies of bedded radiolarian cherts ('ribbon' chert–argillite couplets; Jenkyns and Winterer, 1982; De Wever et al., 1994), because other radiolarian-rich rocks (e.g., black shales and cherty limestones; see Bogdanov and Vishnevskaya, 1992) are also extensively considered. In addition, Cenozoic diatom-

dominated biosiliceous deposits are fragmentarily included to reveal a more full perspective of evolving biotas and biogeochemical cycling. The term 'nutrient' refers to inorganic biolimiting nutrients (especially nitrate and phosphate), and not to organic preformed nutrients, whilst eutrophication refers qualitatively to regimes of high nutrient availability and increased levels of primary productivity (cf. Brasier, 1995a,b).

## **2. Status of silica in recent planktic biota**

Silicon is essential for a variety of biological processes, including DNA synthesis (in diatoms) and intercellular silica deposition within a vesicle bounded by a specialized membrane (see review in Volcani, 1983). Dissolved silicon, utilised by different eukaryotic phyla, occurs as the undissociated monomeric silicic acid  $\text{Si}(\text{OH})_4$ . Radiolarians represent primary opal-biomineralizing holoplanktic protozoans, in addition to silicisponges (sessile passive filter-feeding metazoans), and, since the Cretaceous, diatoms (microscopical unicellular golden-brown algae, mostly planktic). Other planktic protists, silicoflagellates, were also locally rock-forming by the Cenozoic (silicoflagellite; Distanov and Glezer, 1973). Very rapidly reproducing diatoms are the dominant marine prime producers (see Nelson et al., 1995 for a synthesis), whilst radiolarians play a larger role only in peripolar and equatorial belts, and the western sides of continents (Lisitzin, 1985; Casey, 1993). Hence, there are far more detailed data on ecology of the phytoplankton.

### *2.1. Radiolarians in the present-day plankton*

Radiolarians are marine organisms of different trophic types: bacterivores, herbivores, symbiotrophes, detritivores, etc. (Casey, 1993). With increasing size of the species, there is a passage from herbivory to omnivory (Anderson, 1996). The presence of algal plastids determines mixotrophic nutrition, i.e., behavior deriving energy both from ingestion of prey (spanning from bacteria to invertebrates, including copepods, to fish larvae; see Fig. 8 in Anderson, 1996) and from photosynthesis by symbionts.

Baumgartner (1987), De Wever and Baudin (1996) and De Wever et al. (1994) have stressed that actual radiolarian blooms are only typical of high fertility upwelling regions, where the overall phyto- or protozooplankton levels are prolific and where only major nutrient loadings (i.e., phosphates and nitrates) are high in the near-surface zones. Thus, there are no marked differences in the habitats between siliceous and calcareous pelagic organisms (De Wever et al., 1994). Members of both the sarcodine groups are commonly symbiotrophes, thus, partially reducing interspecific trophic competition among species occupying the same water mass (see Anderson, 1996). Nonetheless, as summarized by Brasier (1995a,b) and Takahashi (1997), these microbiotas differ markedly, because calcareous plankton tends to prosper better in the vast areas of central gyres and is less productive in oceanic regions.

Even if diatom-to-radiolarian ratio usually increases toward the most fertile parts of upwelling areas (see Brasier, 1995a), close ecological links between silica-secreting phyto- and protozooplankton production and similar biosiliceous particle flux are indeed established (e.g., Abelmann and Gersonde, 1991; Sanfilippo, 1995; Takahashi, 1997; Abrantes, 2000). Whilst diatoms and silicoflagellates are more variable and tightly coupled with ambient near-surface changes, radiolarian water-column communities smooth out extreme environmental conditions (Boltovskoy et al., 1993; Takahashi, 1997); notably, radiolarians are at least one trophic level removed from basic agents, such as primary productivity and nitrogen dynamics (Gowing, 1993).

Gradients of temperature, but also silica and other macronutrient concentrations probably influence the latitudinal abundance patterns of living radiolarians (Abelmann and Gowing, 1996). In fact, different productivity levels, rather than surface temperatures, play the dominant role in structuring many radiolarian biotas (Boltovskoy et al., 1996; Takahashi, 1997). On the other hand, some radiolarian species are capable of competing very effectively for silica in ambient seawater concentrations of approximately 1.0  $\mu\text{M}$ . Changes in seawater silicate may not have a dramatic effect on longevity, skeletal size, or weight of the radiolarians (Sugiyama and Anderson, 1997); the authors concluded that such environmental variables as temperature, salinity and available micronu-

trients may impress a relatively more conspicuous signal in today's microfossil record. As a whole, the radiolarian distribution and abundances certainly control several agents, many of which we cannot define with certainty (see Sanfilippo, 1995).

## 2.2. Silica regulation of phytoplankton production

Links between diatom dynamics and the silicic acid cycle are strongly supported, and half-saturating levels for silica-limited growth ranged from 0.04 to 1  $\mu\text{M}$  (see Nelson and Dortch, 1996; Rahm et al., 1996). Thus, widely fluctuating minimum loading is partly related with interactions with other agents, such as other nutrients, temperature, light, fungal infections (see summary in Willén, 1991). As shown by Grover (1989), for instance, chlorophytes dominate at low Si/P supply ratios (20:1), diatoms are most abundant at intermediate Si/P ratios (80:1), and the siliceous chrysophyte *Mallomonas* is most frequent at high Si input rates (160:1). The silica control is thus apparent in the transition towards non-diatom communities, with green algae, cyanobacteria and flagellates, wherever dissolved silica becomes a limiting resource due to progressive eutrophication (e.g., Nelson and Dortch, 1996; Rahm et al., 1996; Turner et al., 1998), and/or restricted nutrient flows coinciding with onset of stratification (McMinn et al., 1995). This concerns also a shift from diatom to coccolith abundances (Harrison, 2000).

The response of diatom species to silica starvation varies broadly and local population maxima of major species never coincide (Willén, 1991; Nelson and Dortch, 1996; Interlandi et al., 1999; among others). Extreme nutrient depletion results in shifts to prevalence of small lightly-silicified species whose competitive advantages are enhanced by considerable morphological plasticity to minimize silica requirements, and prolonged vegetative survival (e.g., Støermer, 1993; Dell'agnese and Clark, 1994; McMinn et al., 1995; Turner et al., 1998). Silica pumping from the euphotic zone to deep water drives even diatom-dominated open-ocean upwelling ecosystems toward silica starvation; the model of 'low-silicate, high-nitrate, low-chlorophyll' conditions, where production is in balance for upwelled Si supply, was recently developed (Dugdale and Wilkerson, 1998; see discussion in Brezinski et al., 1997 and Dunne et

al., 1999). In addition, Fe (and other transition metal ions; see Butler, 1998) is potentially wind-blown terrigenously derived limiting micronutrient, especially in equatorial Pacific areas and Southern Ocean (Watson, 1997; Falkowski et al., 1998; Dunne et al., 1999).

### 2.3. Discussion

Although Si to P ratios and rates of recycling may vary over a large range in upwelling areas (Brezinski et al., 1997; Berger and Lange, 1998), a general relationship between the concentration of C, N, P and Si is established in the contemporary ocean (Lisitzin, 1985), as well as in the sedimentary record (Si–P–C association; Parrish, 1995). Silicate levels in most parts of the world oceans are remarkably low, typically 1–2  $\mu\text{M}$ , locally 0.6  $\mu\text{M}$  and less in the Atlantic (Nelson and Dortch, 1996). The unusually large standing crop of diatoms and some radiolarians occurs in silica-rich waters upwelled at the polar divergence (e.g., Casey, 1993, p. 265; Falkowski et al., 1998), and the larger and most thick-walled shells occur in cold-water habitats (see Empson-Morin, 1984; Conley et al., 1994; Cortese and Bjorklund, 1997). The maximal silica production rates are attributed to an *inefficient silica pump*: on average, 72% of the biogenic silica produced in the upwelling plume was retained in the surface waters of the California system, resulting in silicic acid concentrations mostly above 8  $\mu\text{M}$  (Brzezinski et al., 1997). Bacteria-mediated Si regeneration may critically control this productivity (Bidle and Azam, 1999). Dissolved silica concentrations are thus at least regionally correlated with the overall abundance of biogenic opal in surface waters (e.g., Johnson, 1976; Ragueneau et al., 1996), as well as with silica contents in sea-floor sediments (see Lisitzin, 1985). Consequently, upwelling intensity is not the only factor promoting opal deposition, and both P and Si enrichments ('quality') of the upwelled water are equally important as a control of new production (Berger et al., 1998; Berger and Lange, 1998).

Radiolarian ecology is probably no more dependent on dissolved silica than on a wealth of other environmental factors (D. Boltovskoy, personal communication), but, by analogy to diatoms, interspecific variation of silica demands possibly occurs.

In contrast, there is a well-proved connection between silica production rates and dissolved silica loading in phytoplankton. Indeed, all silica-secreting groups seem to be ecologically tied, including plankton and benthos (e.g., Maliva et al., 1989). The concentration of silicic acid in seawater is insufficient today for sponges to secrete desmas and, thus, modulates the phenotypic expression of the various spicule types genetically available in a sponge species, as established experimentally by Maldonado et al. (1999).

As stressed by Ragueneau et al. (1996), silicic acid is often unreasonably neglected as a potential limiting nutrient in pelagic ecosystems. Most recent research already accepts that Si, in addition to P, N and Fe, belongs to the major elements needed for the primary production and plankton growth (see summary in Herbert et al., 1989; Brasier, 1995a; Falkowski et al., 1998). Siliceous microplankton fluxes, diversity indices and characteristic assemblages are thus used as indicators of pelagic biological productivity and marine silicon cycling. For example, some key nassellarian species (e.g., *Ceratospyrus borealis*), and total radiolarian diversity (anticorrelated with nassellarian fluxes) are successfully applied to these purposes (Takahashi, 1997), as well as the thermocline versus near-surface population ratio (Jacot Des Combes et al., 1999). Nevertheless, the output of silica is not related to primary production in a straightforward fashion (see Section 3). Opal-derived palaeoproductivity estimates may be strongly biased by the winnowing of sediments and dissolution (e.g., Kyte et al., 1993; Kemp et al., 1999; Harrison, 2000) and/or terrigenous admixture (Jacot Des Combes et al., 1999).

Balancing present pelagic budgets and nutrient–limitation interactions are poorly known (cf. Falkowski et al., 1998). Only multiproxy approaches, intergrating many geochemical tracers of export production and nutrient utilization (organic C,  $\text{SiO}_2$  excess, barium,  $\text{P}_2\text{O}_5$ , Cd/Ca, as well as isotopic data, including Si), supplemented by independent sedimentary and palaeoecological records, may provide better understanding of biogeochemical cycling (Ragueneau et al., 1996). This holistic approach to past ocean fertility has been progressively developed (Brasier, 1995a; Parrish, 1995), as exemplified by several interdisciplinary studies (Kyte et al., 1993;

Föllmi et al., 1994; Schmitz et al., 1997; Weissert et al., 1998; Jacot Des Combes et al., 1999; Salamy and Zachos, 1999; Abrantes, 2000). Notably, Bartolini et al. (1996, 1999) regarded the percentage of visible chert in outcrops to be indicative of the evolution of silica/carbonate ratios in sediments; in addition, Spumellaria/Nassellaria ratios and the fluctuations of relative abundance of selected genera (e.g., *Transsuum*, *Parahsuum*) tend to correlate with  $\delta^{13}\text{C}$  and chert abundance values, and seem, indeed, to be related to the degree of nutrient mobilisation and/or anoxia (see also Premoli Silva et al., 1999).

### 3. Silica balance in the present-day ocean

On a time scale of 10 ka or less, the mean concentration of silicic acid,  $70.6 \mu\text{M}$ , is assumed to be constant, and determined by balance between geological and biological cycles (Tréguer et al., 1995; see also Gnanadesikan, 1999). The oceanic surface reservoir receives silica inputs from the lithosphere via chemical continental weathering of silicates by  $\text{CO}_2$ -charged waters, and through aeolian transport (*exogenous silica* of Lisitzin, 1985). The deep-sea reservoir is affected by sea-floor weathering, both

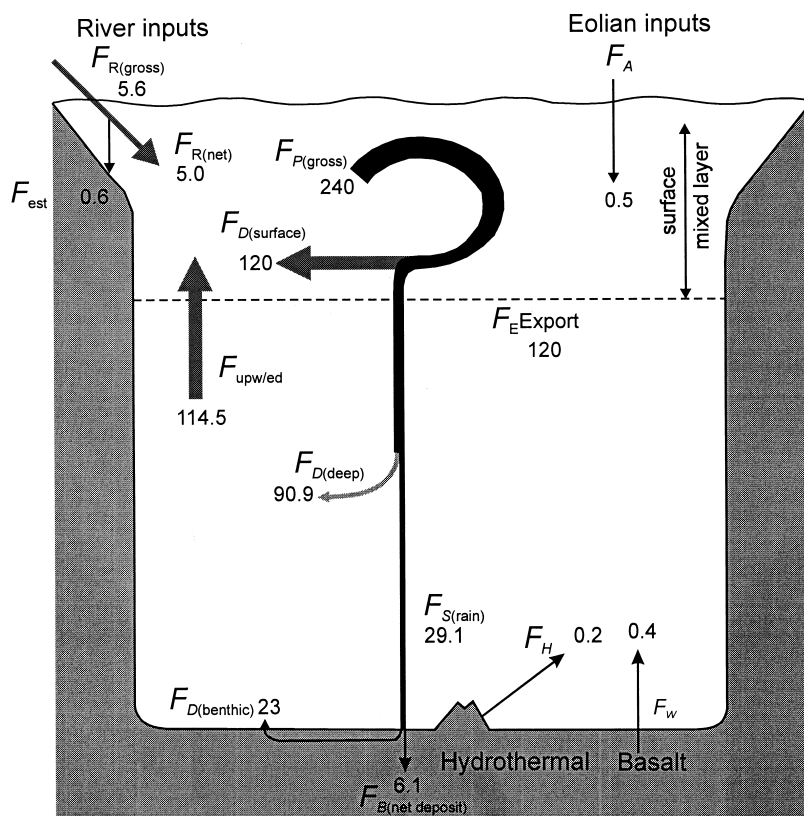


Fig. 2. Biogeochemical silica cycling (in teramoles of Si per year) of the Recent ocean at steady state. Gray arrows correspond to fluxes of dissolved silica (silicic acid), and black arrows to fluxes of particulate biogenic silica. Abbreviations: river fluxes,  $F_R$  (gross and net inputs); aeolian inputs,  $F_A$ ; sea-floor weathering inputs,  $F_w$ ; hydrothermal inputs,  $F_H$ ; net deposit of biosilica in estuaries,  $F_{est}$ , and coastal and abyssal sediments,  $F_B$ ; biosilica gross production,  $F_{P(gross)}$ ; flux of silicic acid recycled in the surface reservoir,  $F_{D(surface)}$ ; flux of biosilica exported toward the deep reservoir,  $F_E$ ; flux of silicic acid recycled in the deep reservoir,  $F_{D(deep)}$ ; and at the sediment–water interface,  $F_{D(benthic)}$ ; flux of biosilica that reaches the sediment–water interface,  $F_{S(rain)}$ ; flux of silicic acid transferred from the deep reservoir to the surface mixed layer,  $F_{upw/ed}$ . Reprinted with permission from Tréguer et al., (1995, fig. 1). Copyright© 1995 by the American Association for the Advancement of Science.

high- and low-temperature, and input in solution by hydrothermal-volcanic systems (*endogenous silica*). The major contribution, about 80%, comes from river runoff (Fig. 2), which is very climate dependant, and 75% of the river supply is derived from the humid equatorial zone (Lisitzin, 1985).

The effective transfer of silica from the hydrosphere to biosphere initiates the biological cycle. As much as 80–85% of siliceous remains are masked by terrigenous input in productive nearshore settings (Heath, 1974). The biological activity of diatoms caused undersaturation of seawater with respect to silica, resulting in tremendous dissolution (Siever, 1991), primarily linked with bacterial colonization and hydrolytic attack (Bidle and Azam, 1999). The global burial/production ratio is merely ca. 3%, but actually, this average reflects contrasting situations with preservation as high as 24% in the Southern Ocean (Nelson et al., 1995). Biogenic sediments are at present deposited in three accumulation belts, and above half of the total silica sink occurs in the Southern Ocean (Tréguer et al., 1995). Opal deposition results from several poorly known interacting factors that lead to regionally enhanced burial of biosilica. Essentially, the depth of the undersaturated water column (carbonate compensation depth; CCD) controls the sedimentary processes (e.g., Hesse, 1989), but the preservation of the biosiliceous ‘snow’ is also augmented by lower temperatures and trace-element chemistry of the surface layer, especially high Al/Si ratios, and several biological factors (mass flocculation and rapid self-sedimentation of diatom cells, selective grazing and faecal-pellet production, more heavily silicified frustules and tests; see Nelson et al., 1995 for the review). However, occasional blooms in non-steady conditions of intense nutrient upwelling, and subsequent flux events are critical to support formation of siliceous oozes (Nelson et al., 1995; Dunne et al., 1999), as spectacularly recorded in self-deposited diatom-silicoflagellate mats (Grimm et al., 1997).

#### 4. Evolutionary palaeoecology of siliceous plankton

There are numerous examples of changing ecological requirements within the same group of organisms through geological time. The palaeoecological

extrapolation of environmental significance from living biota is full of uncertainties, particularly for (1) ancestors of extant groups exhibiting a non-marine or marginal marine preference (e.g., charophyte algae and phyllo pods), and for (2) living survivors of groups with a long evolutionary history (e.g., articulate brachiopods and crinoids; see Plaziat, 1978; Racki, 1986; Bottjer, 1997 for other examples and references). The ecological shifts are elements of larger palaeoecological trends, especially tiering and guild occupation, and onshore-offshore patterns (e.g., Bottjer et al., 1995; Martin, 1995, 1998).

##### 4.1. Radiolarian anachronistic habits and lost habitats

Radiolarians, which have existed throughout the Phanerozoic, clearly belong to the groups with eventful evolutionary history (Fig. 3). As early as in the Cambrian, they were one of the first groups to change from benthic and epipelagic to a free-floating pelagic life (Nazarov and Ormiston, 1986; Knoll and Lipps, 1993). Some species probably continued a sedentary habit in shallow Palaeozoic seas. The ancestral forms of later nassellarians possibly retained a morphological adaptation to a benthic life even during the early Mesozoic (Bogdanov and Vishnevskaya, 1992; Vishnevskaya, 1997), but this hypothesis remains controversial (Zhamoïda, 1995).

From the Cretaceous, radiolarians have had to share their nannoherbivore and symbiotic niches with radiating planktic foraminifera (Casey et al., 1983; Anderson, 1996). In fact, the pre-Cretaceous plankton food chain was dominated by radiolarians, feeding on a variety of non-skeletal organisms (Baumgartner, 1987). Assuming overall low phytoplankton densities in mostly oligotrophic conditions during the Cambro-Devonian, radiolarians may have lived either in highly productive shallow waters, in oceanic gyres with symbiotic algae (such as the green alga *Tasmanites*; Vishnevskaya et al., 1993), or in deeper-oceanic subphotic zones as detritivores and bacterivores (Casey, 1993; Martin, 1995). In trophic terms, the protozoans are separated from primary productivity, and because their overall robust tests are much slower to dissolve, silica would have been linked less directly to nutrient recycling and upwelling zones (Siever, 1991).



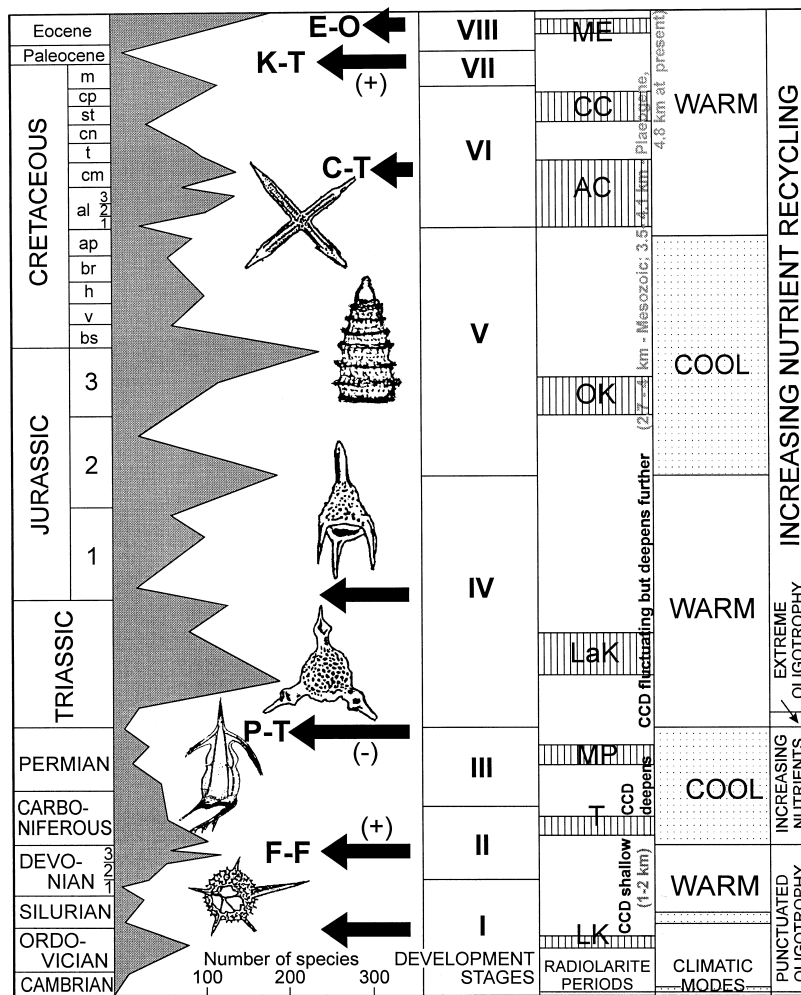


Fig. 3. Species diversity of Radiolaria (after Vishnevskaya, 1997, fig. 3; see also Vishnevskaya and Kostyuchenko, 2000, fig. 1), major global bioevents (indicated by arrows; + and - mean the biosiliceous acme or decline, respectively; Racki, 1999a), the main developmental stages in radiolarian evolutionary history (Roman numerals), against the principal hypersiliceous periods (compiled from Distanov, 1974; Steinberg, 1981, fig. 1; Hein and Parrish, 1987; Murchey and Jones, 1992), climatic modes and marine productivity evolution (after Martin, 1995; figs. 1–3). Radiolarian evolutionary faunas according to Nazarov and Ormiston (1985, 1986) for Palaeozoic, and Vishnevskaya (1997) for Mesozoic and Palaeogene. Succession of typical radiolarian groups mostly after Jones and Murchey (1986, Fig. 2). Main hypersiliceous periods: LK — Llandeilan–Caradacian, T — Tournaisian, MP — mid-Permian, LaK — Ladinian–Carnian, OK — Oxfordian–Kimmeridgian, AC — Albian–Cenomanian, CC — Coniacian–Campanian, ME — mid-Eocene.

Although the pelagic ocean is usually considered as the main scene of radiolarian activity, Bogdanov and Vishnevskaya (1992) proposed an overall shift of radiolarian habitats from mostly epeiric, carbonate shelves in the Palaeozoic to exclusively oceanic today. This might be an element of an overall displacement across the shelf in the main locus of the silica

sink (Schubert et al., 1997), even if radiolarian biota still influenced platform-type sedimentation through Cretaceous (Fig. 4; Ellis and Baumgartner, 1995). As noted above with reference to actualistic data, biogenic silica deposits are a priori viewed as tracers of eutrophic water masses. Nevertheless, even this principle must be applied with caution because some

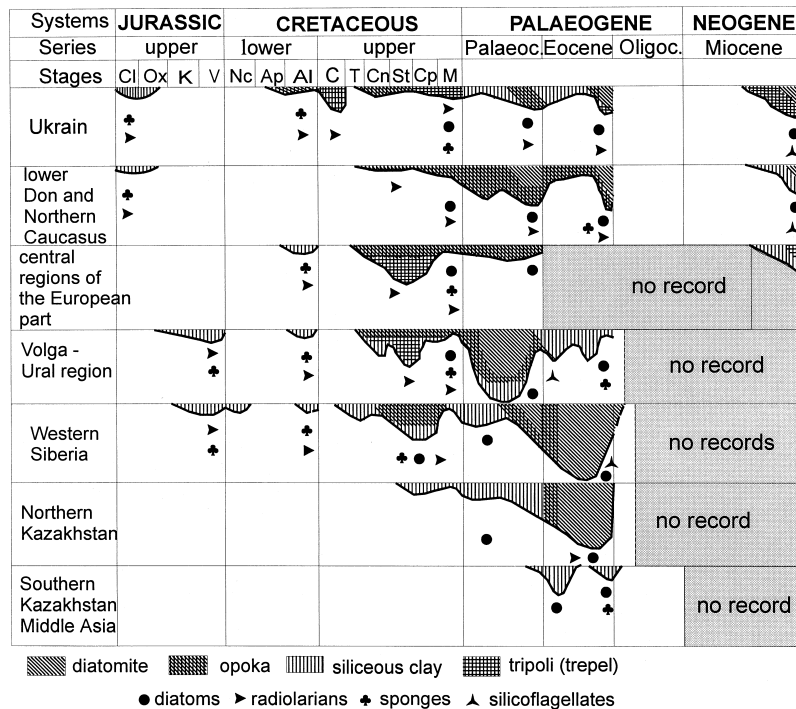


Fig. 4. Stratigraphic pattern of siliceous sedimentation over the Mesozoic to Miocene shelves of Eurasia (after fig. 1 in Distanov, 1974, modified, and V.S. Vishnevskaya, personal communication). Note an increasing participation of modern-type diatom-silicoflagellate floras that started in latest Cretaceous (see Maliva et al., 1989), as well as the Eocene biosiliceous acme. Radiolarites are limited to partings in Mesozoic clays, but the pattern is partly obscured by phosphatisation (Ilyin, 1998). No distinctive record of the end-Cretaceous biotic crisis is recognizable. Opokas represent carbonate-siliceous rocks with glauconites and detrital quartz; tripolis (trepels) correspond to weakly-cemented opaline siliceous rock, with globular fabrics as rule, derived from dissolved diatomaceous ooze. Cl — Callovian, Ox — Oxfordian, K — Kimmeridgian, V — Volgian, Nc — Neocomian, Ap — Aptian, Al — Albian, C — Cenomanian, T — Turonian, Cn — Coniacian, St — Santonian, Cp — Campanian, M — Maastrichtian.

siliceous microfaunas may have thrived in moderately fertile regimes, e.g., linked with Jurassic reefs (Kiessling, 1996).

No modern analogues to bedded cherts are known, but Jenkyns and Winterer (1982) and Hein and Parrish (1987) argued that diatoms provide clues to the radiolarian habitats. Thus, upwelling-influenced narrow ocean basins (arc-related or transform-dominated), such as the Gulf of California, are a traditional actualistic model that views radiolarite basins as ancient analogues of modern-day diatomite basins. Ancient radiolarite basins were compared by De Wever et al. (1994) with the Recent Owen and Somalia basins, all places of active moonsonal upwellings, but only partially influenced by fully open-marine conditions.

However, there is no reason to assume that all radiolarites must have formed in small ocean settings only. From palaeogeographic analysis of Tethyan biosiliceous and organic-rich rocks, De Wever and Baudin (1996) concluded that, in contrast to present and Jurassic upwelling systems, the biosiliceous and bituminous deposits were often spatially associated in Cretaceous basins. Baumgartner (1987) implied that broad equatorial convergence zones were a likely setting for many Tethyan and circum-Pacific Mesozoic radiolarites (the effect of equatorial 'silica bulge'; Ogg et al., 1992, Fig. 11 therein). In combination with scarcity of calcareous oozes, this differentiation was responsible for a shallow, irregular and sharply defined CCD. Abrupt changes in tropical upwelling and periodically enhanced radiolarian pro-

duction, in response to Milankovitch climatic fluctuations, are indicated for ribbon-type radiolarite deposition (Ogg et al., 1992).

Major differences are seen by Jones and Murchey (1986) in their comparison of Palaeozoic and Mesozoic radiolarian cherts with Cenozoic diatomaceous deposits. The best pre-Cenozoic analogues of today's biosilicates are sponge spicule-dominated deposits (see Gammon et al., 2000). It is not very easy to find radiolarian cherts that duplicate precisely two main modern upwelling settings, i.e., along continental margins or in cold polar seas (Jones and Murchey, 1986). In particular, many thick radiolarite sequences are included within ophiolite complexes of spreading zones of Cretaceous and older ages. The peculiar co-occurrence of ultrasiliceous biogenic sediments in an intermediate position between ultrabasic igneous rocks and pelagic carbonates and clays (the 'Steinmann trinity') is even seen as a proof of minimal significance of exhalative volcanism and dominating upwelling processes (Hesse, 1989). This could be explained by a general CCD deepening trend through the Phanerozoic (Fig. 3). However, from about 140 Ma, the radiolarian productivity and, consequently, radiolarian oozes, are subordinate along oceanic ridge areas (Herbert et al., 1989). Certainly not all ophiolites formed in regions of upwelling, either along continental margins or near the equator, as shown below for the palaeo-Pacific domains (see Section 7).

#### 4.2. *Competitive pressure for dissolved silica*

Silica gel precipitated on a large scale in Precambrian sedimentary environments when the silica cycle was controlled by inorganic reactions among dissolved silica, clay and zeolite minerals, organic matter, and possibly bacterial activity (Siever, 1992; Knauth, 1994; Fig. 1). Conversely, no unequivocal record of common inorganic precipitation exists for the post-Ordovician times (Maliva et al., 1989). Thus, it was often expected that no compelling evidence exists for very radical silica excursions in the post-Ordovician interval (e.g., Heath, 1974; Berner and Berner, 1987, p. 373; Knauth, 1994).

The significantly increasing utilization of amorphous silica by Eukaryota existed probably since the Ordovician, paralleled with evolving radiolarian-silicisponge biotas (Maliva et al., 1989). Appearance

of both groups, however, as well as silica-secreting inarticulates (Williams et al., 1998), is already conspicuous in the Cambrian (Xiping et al., 1997; Mazumdar and Banerjee, 1998). This primitive (i.e., pre-diatom) biogenic precipitation helped control the Si output of the oceans. The silicate levels at this time were depressed, possibly a little higher than the most disordered opal-CT saturation levels (see also Fig. 15), inasmuch as the high concentrations were needed to cause diffusion to an opal-CT precipitating nodule during chertification (Siever, 1991, 1992). In fact, the radiolarian productivity in the Si-saturated greenhouse habitats were probably controlled by severe nitrate and iron limitation (cf. Berger, 1991; Berger et al., 1989). The intermittent expansion of diatoms finally drastically depressed the concentration of dissolved silica to its present low level (Maliva et al., 1989). Today, the vast bulk of deep and surface waters is at least one order of magnitude undersaturated with respect to quartz, and close to two orders of magnitude undersaturated with respect to biogenic opal (Siever, 1991).

A substantial evolutionary-biogeochemical turnover occurred in marine siliceous plankton during early Oligocene, marked by the demise of many thickly silicified Palaeogene planktic species (see Conley et al., 1994; Khokhlova, 2000). This directionality in the Cenozoic radiolarian record could not be a preservational artifact (Moore, 1969): the average Eocene radiolarian test weighs four times as much as the average Quaternary specimen (Fig. 5). The evolutionary trend is viewed as a record of competitive pressure for dissolved silica, especially heightened during this cooler part of the Cenozoic Era, that was brought about by the diatom and silicoflagellate explosive radiation (Harper and Knoll, 1975). Thus, in silica-depleted, exclusively warm-water pelagic habitats, radiolarian species showed a progressive decrease in the amount of silica incorporated in their skeletons (Casey et al., 1983). Many living tropical surface-dwelling zooplanktic species, including radiolarians, contain photosymbionts, and appear perfectly adapted to nutrient-poor ocean biotopes (Anderson, 1996; D'Hondt and Zachos, 1998).

A similar phylogenetic shift toward less silicified shells was established also among Palaeozoic radiolarians, but is interpreted by Nazarov and Ormiston

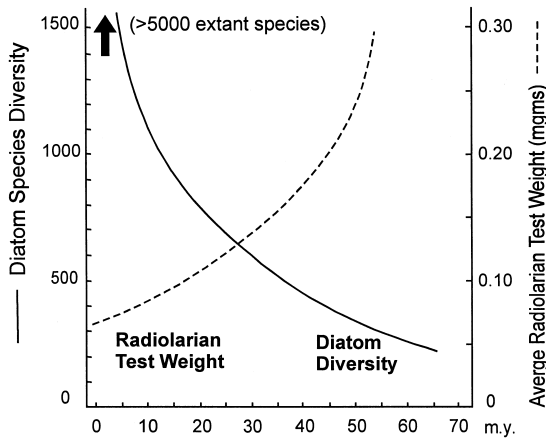


Fig. 5. Secular changes of radiolarian test weight versus diatom species diversity (and approximately, also diatom abundance) during the Cenozoic (simplified from the composite fig. 1 in Harper and Knoll, 1975, and references therein).

(1986) as a more economical arrangement of material, coupled with an appropriate adaptation toward planktic habit. Likewise, during the Cenozoic, skeletons became twisted networks instead of perforate shells, which is apparently paired with increasing porosity and reduction of specific gravity (Petrushevskaya, 1974; Hurd et al., 1979). Nonetheless, such an evolutionary selection for lighter tests entirely to enhance buoyancy is dubious, because this improved flotation is regulated by highly vacuolated protoplasm, paired with contained gases of the symbiotic algae and oil droplets (Harper and Knoll, 1975; Vishnevskaya et al., 1993). Modern-day spumellarine radiolarians, which prevail in the warm-water subsurface sphere, possess thinner shell walls than the deeper-living nassellarians, but the faunal composition with depths has shown distinct variation since the Cretaceous (Empson-Morin, 1984). This may also be an evolutionary response to intensified competition for silica in the photic zone, and, in fact, an inverted bathymetric distribution of the shell wall thickness of Mesozoic radiolarians is noted (Erbacher and Thurow, 1997).

Marine planktic diatoms, contrary to benthic forms, during the early Oligocene have also evolved into lightly silicified species that are suitable to modern-type silica-stressed habitats (Conley et al., 1994; Barron and Baldauf, 1995). Many of the deli-

cate and elongated late Cenozoic species form long colonial chains (e.g., *Chaetoceros*), and an additional adaptation aimed at limiting sinking rates cannot be excluded (cf. Willén, 1991).

Consequently, the documented selective pressure pattern among phyto- and zooplankton is clearly explainable as a physiological response to the decrease of relative silica availability (Knoll and Lipps, 1993; Conley et al., 1994; Barron and Baldauf, 1995). Furthermore, silica limitation may have forced neritic sponges with desmas to either lighten their skeletons or move to deeper, silica-rich environments (Maliva et al., 1989; Maldonado et al., 1999; see also Gammon et al., 2000). The relative silica-independence of present-day biota is thus clearly understandable in the context of their *progressive trophic specialisation*. The increased ability to concentrate silica from the undersaturated seawater (maybe even decomposing aluminosilicates by diatoms; see Tappan and Loeblich, 1971), quartz dissolution by sponges (Bavestrello et al., 1995), and, on the other hand, detrimental effects of silica overload on radiolarians (Sugiyama and Anderson, 1997) indicate the farthest adaptations.

#### 4.3. Global weathering and exogenous silica fluxes

In a broad sense, the global silica output seems to correlate best with sea-level fluctuations: although less continent was exposed to chemical weathering during eustatic highstands, the change to more humid climate led to higher release of nutrients to the ocean (Miskell et al., 1985). If so, late Cenozoic low sea-levels could result in progressive decline in the rates of Si supply, especially when combined with decreasing volcanism, reduced tectonic uplift, and the great evolutionary success of silica-consuming grasses envisioned by Harper and Knoll (1975), and also, by Conley et al. (1994).

However, the question of which factors primarily control the weathering cycle is extremely complex (see Gibbs et al., 1999 for the summary). Especially, the supposed influence of plants on exogenous processes still remains uncertain (Siever, 1991). The worldwide deposition of diatomites in the mid-Miocene is alternatively seen as resulted from elevated rates of plant-mediated denudation due to the global spread of grasslands (Johansson, 1995; cf.

also Martin, 1995). On the other side, recent results of Meunier et al. (1999) demonstrate that the storage of biogenic silica in soils may be significant and may indeed retard the output of silica to rivers and ocean.

The susceptibility of continental silicates to weathering is frequently interpreted in connection with active tectonism (François et al., 1993), with a maximal rate enhanced by a factor of 2–3 during the early Palaeozoic relative to present-day; the Quaternary chemical weathering and, thus, riverine supply is inferred to be rather high in comparison with late Permian to Early Cenozoic times (Fig. 6). Most recent modelling by Gibbs et al. (1999) highlights a weaker-than-predicted CO<sub>2</sub>-climate weathering feedback, overshadowed by palaeogeographic changes. Silicate weathering rates are generally similar to supply rates of volcanic and metamorphic CO<sub>2</sub>, and times of supercontinental stasis (e.g., Pangean) represent low outgassing but also high aridity due to extreme continentality and, thus, decreased chemical erosion fluxes. Weathering effects of continental collision and orogeny were markedly controlled by the water supply to the uplifted areas.

#### 4.4. Unique features of present-day silica cycle

The evolving silica budget through the Phanerozoic may be accepted as a combination of two trends: (1) increasing biogenic removal of dissolved silica (Maliva et al., 1989), and (2) fluctuating, but generally diminishing flux of exogenous silica (Fig. 6). The modern biogeochemical cycle is representative obviously only for silica-depleted post-Eocene oceanic ecosystems (see Section 6). The Eocene turning point broadly correlates with a major expansion of diatoms groups extremely efficient in silica removal, and closely link the silica budget with phosphorus and nitrogen cycles (Siever, 1991). On the other hand, 16% of the gross riverine load is presently delivered as diatomaceous silica (Conley, 1997), which is another biogeochemical novelty after the Neogene expansion of the freshwater silica-secreting algae (Barron, 1987).

The opal deposition has remained overall balanced during Quaternary glacial cycles (see Lisitzin, 1985). Although promoted changes in terrestrial weathering and related silica riverine fluxes are un-

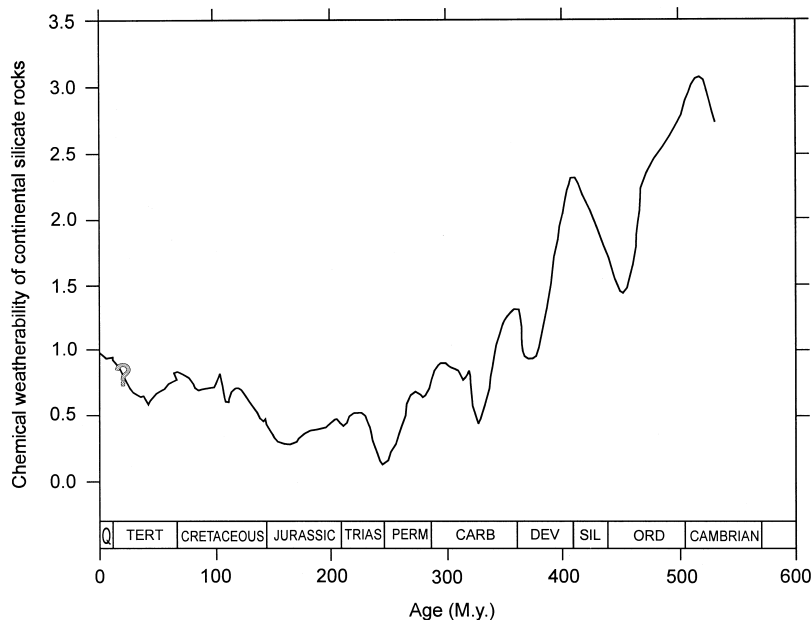


Fig. 6. The evolution of continental silicate weathering during the Phanerozoic time (after fig. 6 in François et al., 1993; simplified with permission), as the best available approximation of exogenous silica fluxes, is guided by modelling of strontium cycling. The inferred strong increase of weathering flux throughout the Cenozoic, consistent with the progressively higher rates of continental uplift and mountain (Himalayan) building events, has been questioned recently (Gibbs et al., 1999; L.M. François, personal communication).

certain (see discussion in Gibbs and Kemp, 1994), atmospheric transport of Si as mineral aerosols may be at icehouse times dominant source of dissolved silica to the oceans (Harrison, 2000). Significantly, the late Cenozoic timespan corresponds to minimum mantle outgassing and decreasing hydrothermal input (e.g., François et al., 1993; Kadko et al., 1995; Gibbs et al., 1999; see also Fig. 10). Thus, tectonic/magmatic phenomena, as manifestation of the endogenous driving force, are assumed herein to be an additional key to the biogeochemical puzzle recorded in pulses of widespread siliceous deposition simultaneously in oceanic and shelf settings (see Fig. 3).

### 5. Plate tectonics, volcanism and radiolarian productivity

A cold-water/upwelling model is commonly applied to ancient biosiliceous productivity bursts (Herman, 1972; Ramsay, 1973; Kitchell and Clark, 1982; Hein and Parrish, 1987; Baldauf and Barron, 1990; Murchey and Jones, 1992; Dell'agnese and Clark, 1994; and many others; but see Kidder et al., 1998). A similar approach is invoked, for example, for the initiation of the Late Devonian–Early Carboniferous siliceous deposition related to cold deep-water current circulation coming from a glacial North-Gondwanian area (e.g., Raymond and Lethiers, 1990). However, coeval cherts of the Iberian Pyrite Belt record prolonged low-temperature submarine siliceous-sulphide hydrothermal activity (Leistel et al., 1998). Volcano-hydrothermal factors should be taken into consideration in any interpretation of biosiliceous facies for this timespan (cf. Racki, 1999a), as well exemplified by the tectonically controlled distribution pattern of biosiliceous deposition on the East European Platform (Fig. 7). The data confirm a dubious validity of the upwelling paradigm in the Palaeozoic greenhouse settings (Ormiston and Oglesby, 1995).

The principal challenge in studying the past oceanic record is to establish whether “shifts in the distribution of sedimentary facies signal changes in the global input and output of silica and/or other nutrients, or whether they merely reflect shifting loci of deposition because of changes in ocean circulation” (Herbert et al., 1989, p. 414). As already

remarked by Miskell et al. (1985), a global productivity acme caused by an increase in circulation rate cannot, in itself, result in increased opal burial over several million years. This is due to the short residence time of dissolved silica and other major nutrients ( $< 10^5$  years; e.g., Tréguer et al., 1995). The resources would be rapidly depleted and, thus, the long-term bursts of extreme biosiliceous production imply an inefficient silicate pump driven by very intensified flux of nutrients from an outside source, as exemplified by the 5.5 Ma biosiliceous interval at the Miocene–Pliocene transition (Dickens and Owen, 1999). Based on this scenario (cf. Steinberg, 1981; Föllmi et al., 1993, 1994; Bartolini et al., 1996; Berger et al., 1998; Dickens and Owen, 1999), unusual fertile conditions and widespread siliceous plankton blooms are causally tied to large-scale change in global nutrient cycling involving (1) addition of biolimiting elements to the ocean, and/or (2) effective redistribution of the nutrients within the ocean.

Baumgartner (1987) considered radiolarites as the normal sediment for the pre-late Cretaceous pelagic settings, if a number of inhibiting factors (e.g., terrigenous or calcareous dilutions, low surface fertility, current activity) were not effective. For instance, highstand oceanic settings result in a reduced supply of carbonate for pelagic calcareous communities via carbonate storage in widespread reef and platform complexes (Sheridan, 1987); the shelf sediment trap influences also silica basin/shelf partitioning (Baldauf and Barron, 1990). Both surface and vertical oceanic circulation have been impacted by the movement of crustal plates, particularly the opening and closing of gateways, and changes in the size of ocean basins, as well as in the volume of water masses (Casey et al., 1983; Baldauf and Barron, 1990). The varied oceanographic phenomena may be placed in the framework of long-term assembly and dispersal of supercontinents (e.g., Worsley et al., 1986; Siever, 1992). In terms of the recently developed mantle convection eruption models, the episodic perturbations punctuate the relatively steady-state crustal production at spreading centres. The ‘mantle overturns’ (Stein and Hofman, 1994) potentially account for changes in plate drift patterns, crustal thinning and breakup, (super)plume-related pulses of magmatic activity, epeirogeny and orogenic episodes (e.g.,

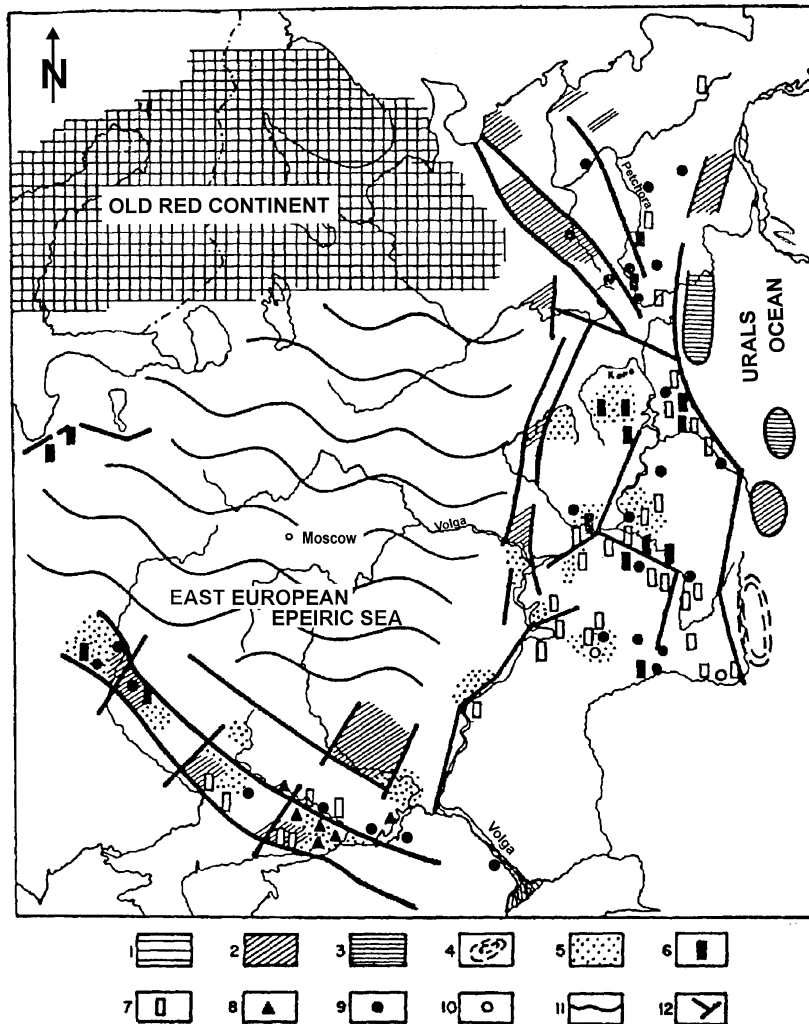


Fig. 7. Palaeogeographic distribution of biosiliceous deposits in the Late Devonian and Early Carboniferous of the eastern part of the East European Platform and Urals (modified after Maksimova, 1978, fig. 1, and V.S. Vishnevskaya, personal communication). Note a strict linkage between tectonic fractures and biosiliceous sedimentation. (1) land; (2–4) extrusives and tuffs in Late Devonian (2), Late Devonian through Early Carboniferous (3) and Early Carboniferous (4); (5) tuffs and ash admixture in sediments; (6) spongolites in Late Devonian; (7) spongolites in Early Carboniferous; (8) spongolites and spiculitic limestones in Late Carboniferous; (9–10) radiolarites and siliceous radiolarian-rich limestones in Late Devonian (9) and Early Carboniferous (10); (11) areas without biogenic siliceous deposits; (12) deep-seated faults.

Sheridan, 1987; Larson, 1991; Coffin and Eldholm, 1994; White and McKenzie, 1995; Loper, 1997; Carpenter and Lohmann, 1999; Kharin, 1999). Numerical simulations indicate that plate motions can be impacted by the lubricating effects of plume heads even to the point of inducing a drift reversal (Ratcliff et al., 1998). Rapid subaerial or shallow-water emplacement of oceanic plateaus and synrift uplift

markedly change basin geometry and water mass circulation by creating intrabasin gatekeepers (Coffin and Eldholm, 1994). The role of tectonism, associated with plate divergence and transform faulting, that generated a series of closed basins shielded from terrigenous input, is likewise suggested for modern diatomaceous basins (e.g., Heath, 1974; Barron, 1987). The entire key changes in the palaeo-

ceanographic settings of biosiliceous production, such as surface and vertical circulation, as well as the CCD history (see Fig. 18 in Bralower et al., 1994), can be assessed within this conceptual framework.

### 5.1. *Volcanic/hydrothermal processes and living siliceous biota*

Cause and effect relationships between siliceous organisms and volcano–hydrothermal processes are rarely reported from Recent and even Quaternary seas (e.g., Buljan, 1972; Huang et al., 1974; and references therein). Such a link is supposed, among others, for the radiolarian clays of the Tyrrhenian Sea (Castellarin and Sartori, 1978; Poluzzi, 1982). Direct correlation between atmospherically transported volcanic dust and the enhancement of planktic activity, with a selective radiolarian proliferation, has also been shown (Huang et al., 1974). Increased zooplankton biomass (including radiolarians), paired with considerable infiltration of shallow fauna into the deep oceanic layers, has been described over the main vent field at Endeavour Ridge (northeast Pacific), extending 10–15 km off-axis (Burd and Thomson, 1995). Visual observations above Broken-Spur Vent Field, Mid-Atlantic Ridge, show two aggregations, one within the main pycnocline and the other near borders of the hydrothermal plume, and gelatinous animals and radiolarians dominate in both aggregations by biomass (Vereshchaka and Vinogradov, 1999). Deep-water radiolarians may even be locally integrated in a trophic chain, via chemosynthetic bacteria, triggered by hydrothermal emanations (Poluzzi, 1982). Also flourishing of demosponges is probably stimulated by volcanic Si-bearing solutions, e.g., in the periphery of vent fields of Rabaul Caldera (Papua New Guinea; Tarasov et al., 1999).

The combined contribution of hydrothermal efflux and weathering of submarine basalt to the present-day oceanic silica budget (Fig. 2) is conservatively estimated at 10% only by Tréguer et al. (1995). Nevertheless, this poor record is not surprising in light of the above-cited evolutionary shift toward limiting silica uptake and oligotrophy. Otherwise, this causal connection is stressed by Watson (1997) for the eruption of Mount Pinatubo in June 1991, but seen exclusively as the diatom response in distant high-nutrient, low-chlorophyll regions to Fe fertilization

due to atmospheric supply. Cycles of plankton productivity recorded in eastern equatorial Pacific sediments are similarly attributed to pulsed Fe enrichments induced by volcanic, erosional and seismic activity in the island-arc region of Papua New Guinea that lasted up to 3 Ma (Wells et al., 1999).

Taken together, the above observations suggest significant addition of major nutrients and biolimiting trace metals, at least on a regional scale, due to a diversity of volcanic and tectonic processes. Especially, hydrothermal injections could have a major impact on the chemistry of seawater (e.g., via ‘upwelling megaplumes’ during cataclysmic diking-eruptive events; Vogt, 1989; Delaney et al., 1998, and references therein). The silica content of hydrothermal fluids is always much higher than the ambient seawater value (three orders of magnitude; see Table 14 in Elderfield and Schultz, 1996), and even large-scale silica concentration anomalies are caused by hydrothermal discharge, particularly within semi-enclosed basins (e.g., Campbell and Gieskes, 1984; Vishnevskaya, 1984, pp. 77–78; Cember, 1996; Tarasov et al., 1999). Furthermore, increased phosphate levels (by 360%) are attributed to continuous gasohydrothermal exhalation, and to massive expulsions of fluid as a result of seismic activity in the oligotrophic Aegean Sea (Dando et al., 1995; see also Benitez-Nelson, 2000). The global phosphorus budget is markedly affected by scavenging processes within the effluent plumes (Kadko et al., 1995), unless it is balanced in part by off-axis venting (Elderfield and Schultz, 1996, Tables 16 and 17). The net contribution of volcanism to the escogenic P cycle is poorly quantified (Benitez-Nelson, 2000).

### 5.2. *Endogenous aspects of ancient silica cycling*

Prime causes for multiple disturbances in a global silica balance were usually related to peaks of magmatism, hydrothermal influx and greater weathering rates in uplifted areas (e.g., Steinberg, 1981; Siever, 1992; François et al., 1993; Hardie, 1996). Low-temperature siliceous hydrothermal activity may have a distinctive palaeodynamic significance as a marker of overall volcanic quiescence (Leistel et al., 1998), and/or an indicator of the reactivation of deep-seated faults during crustal extension episodes (Fig. 7; Maksimova, 1978; Tsekhovskiy et al., 1996). This is well exemplified by still active low-temperature (20–





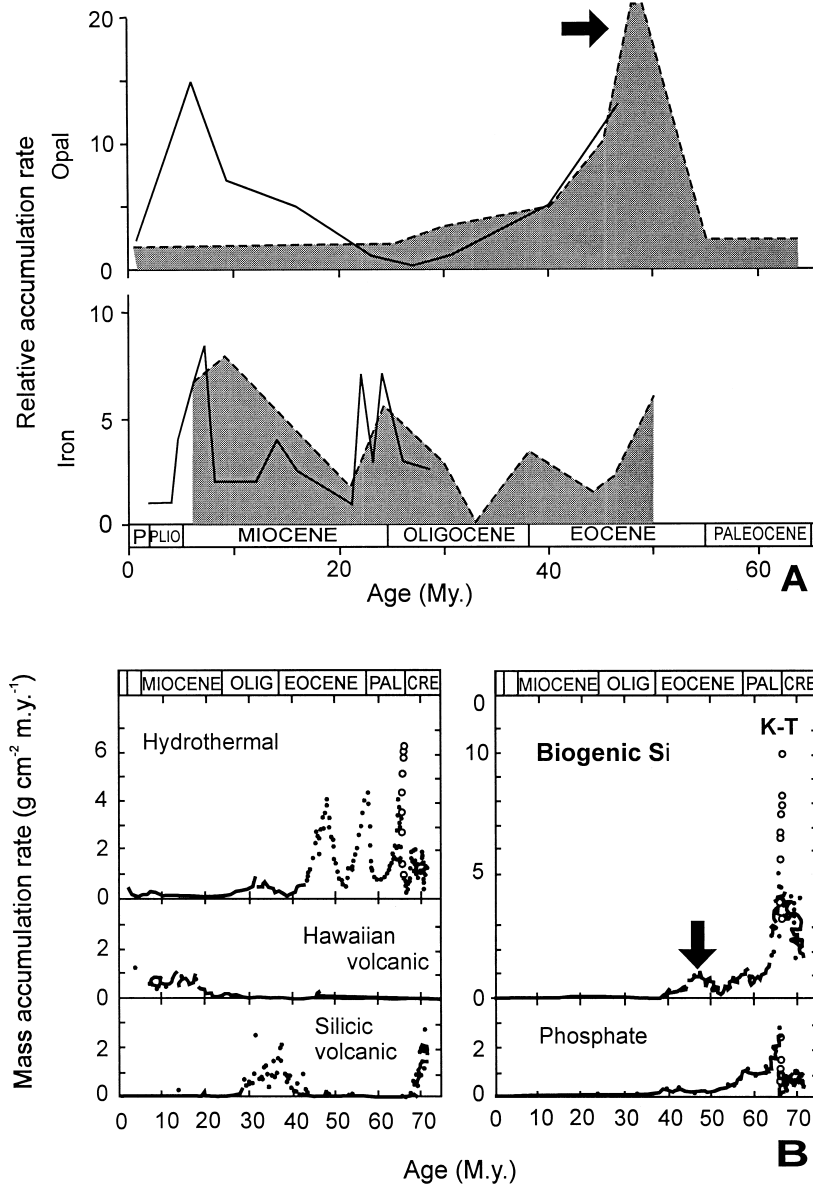


Fig. 9. Sedimentation histories of different oceanic realms, as inferred from geochemical indicators, with emphasis on biosiliceous record and the Eocene hypersiliceous event (arrowed, see also Fig. 11). (A) Relative accumulation rates of iron and opal for North Atlantic (shaded) and Central Pacific (blank) regions over the Cenozoic (modified after Owen and Rea, 1985, fig. 1, and references therein; used with permission, Copyright© 1985 by the American Association for the Advancement of Science). Note that increases in both accumulation rates (as well as a decrease in Sr/Ca ratio) occurred in the early–middle Eocene, ca. 50–55 Ma ago, viewed as a direct record of accelerated sea-floor hydrothermal activity. (B) Mass accumulation rates of opal and other major sedimentary components in the central North Pacific since the late Cretaceous to the present, with ages derived from the hypothesised constant hydrogenous-cobalt input (after Kyte et al., 1993, fig. 11, modified). Note anomalous sedimentary effects through the K–T transition, more significant for siliceous productivity than the Eocene hydrothermal stimulation (arrowed).

crease of hydrothermal venting and geothermal heat inflow is reasonably assumed (Dickens and Owen, 1993; Liu and Schmitt, 1996), maybe even as much as a factor of 20 during the Cenozoic (Lyle et al., 1987; see Fig. 9). When paired with reinforced halmyrolysis of oceanic basalts (see Kharin, 1999), the total endogenous opaline addition to the oceanic cycling likely multiplied as well (Steinberg, 1981), with significant promoting effects on bioproductivity, as demonstrated for hydrothermal Fe (Sinton and Duncan, 1997). Moreover, aeolian oversupply of silica and key metals, related to eruptive and/or terrestrial volcanic activity, is well documented for some biosiliceous deposits (e.g., Huang et al., 1974; Pollock, 1987; Scasso et al., 1991; Stamatakis et al., 1991; Erlich et al., 1996). Biogenic cherts often laterally grade into tuffaceous–biosiliceous deposits (Vishnevskaya, 1995). High-CO<sub>2</sub> and -SO<sub>2</sub> pulses in the disturbed oceanic ecosystem might have created slightly more acidic surface waters additionally favouring siliceous plankton (see e.g., Ogg et al., 1992; Kerr, 1998). Even under optimal light and macronutrient conditions, diatom growth rate can in fact be limited by the supply of CO<sub>2</sub> (Riebesell et al., 1993).

The question is addressed how long any tectonic and/or volcano–hydrothermal enhancement of productivity would last, because the different-scale stimuli have possibly occurred on a variety of timescales (see Table 2 in Lowell et al., 1995). Significantly, however, a low temperature off-axis hydrothermalism is known to persist over vast areas for oceanic lithospheric ages spanning up to 70 Ma (Schultz and Elderfield, 1997, p. 395). As a result, the ubiquitous cooler diffuse fluxes may indeed play a main role in the ocean's chemistry, and possibly exceed the high-temperature black smoker component by an order of magnitude (de Villiers and Nelson, 1999). According to Elderfield and Schultz (1996, Tables 14 and 16), silica fluxes at ridge flanks ( $1.3\text{--}1.8 \times 10^{12}$  mol/year) in modern oceans are ca. three times larger than axial high-temperature fluxes and correspond to at least 20% river input. If so, the above-predicted considerably heightened silica fluxes during geotectonic events could be episodically comparable to the riverine supply.

(3) *Circulation changes.* As noted above, some tectonic settings of radiolarite deposition themselves

favoured local upwelling conditions in areas that are neither along a continental margin nor near the equator (Jones and Murchey, 1986). Rapid regional fluctuations in vertical advection may indeed be associated with intervals of ridge jumps, fracturing the ocean crust, and arc- and mid-plate volcanism (Lyle et al., 1987). Certainly, reduced thermal gradients due to magmatic heating are significant for thermohaline circulation (cf. Cooper, 1965; Buljan, 1972), as known in the Panama Basin (see Kadko et al., 1995, p. 456). By using numerical models, Vogt (1989) demonstrated that rapid large-scale basalt eruptions comparable to the largest historically known (ca.  $10^2\text{--}10^4$  m<sup>3</sup>/s) were sufficiently energetic in terms of heat release ( $10^{12}\text{--}10^{14}$  J/s) to pump nutrient-rich bottom waters as buoyant mega-upwellings to the ocean surface (see also more conservative results of 'hyperplume' modelling by Speer, 1997).

Moreover, geothermal sources can modify sea surface temperature, and phenomena ranging from El-Niño-southern oscillations to large storms are at least partly controlled by such anomalies (see Speer, 1997). Numerical simulations reveal that catastrophic runaway hurricanes can develop when seawater is locally heated by shallow-sea volcanism, or by overturning of superheated brine pools formed by underwater volcanic activity (Emanuel et al., 1995). From the actualistic viewpoint, tsunamis generated by great earthquakes result in sudden overturning of oceanic water masses, and the heat transfer between surface and deep zones induces cooling episodes (Taira, 1982). Volcanic winter may in itself lead to catastrophic upwelling within weakly stratified seas (Genin et al., 1995). These oceanic–atmospheric circulation feedbacks are extremely complex, and physics of the volcanism–induces interactions is unclear in many principal points (Speer, 1997).

### 5.3. *Spreading rate changes versus plate reorganization events*

As discussed by Von Damm (1995, p. 244), resolution of the flux problem over geological timescale is dependent upon poorly known characteristics of hydrothermal systems change as they age, probably with episodic activity recurring at intervals of up to thousand years (see also Elderfield and

Schultz, 1996; Delaney et al., 1998). This could potentially provide a link to the spreading rate because faster ocean crust production should require more frequent outbursts, or on average, larger magma inputs (cf. a model by Baker and Urabe, 1996). It is indeed a common assumption, that the intensity of volcanic/hydrothermal activity and the promoted fluid fluxes varied directly with spreading/subduction rate (e.g., Steinberg, 1981; Rich et al., 1986; François et al., 1993; Hardie, 1996; Gibbs et al., 1999). Thus, coupled changes in the mineralogies of marine nonskeletal limestones and potash evaporites are viewed by Stanley and Hardie (1998) as the result of secular variation in seawater chemistry (i.e., Mg/Ca ratio), controlled primarily by fluctuations in the mid-ocean ridge brine input, which in turn has been driven by the changing rate of ocean-crust production (Fig. 10).

From an earlier study of manganese accumulation rates, Lyle et al. (1987) found a poor time correlation between hydrothermal anomalies and changes of spreading rate that varied by an order of magnitude less during the last 30 Ma than inferred the hydrothermal activity. The exhalative pulses appear to be more closely associated with the tectonic rearrangements and arc and mid-plate volcanic events. Ridge jumps and reorientations apparently strongly affect fracture depth and spacing, resulting in increased access of seawater to deep heat sources (Lowell et al., 1995). The influence of tidal loading

and deformations is indicated as well (Schultz and Elderfield, 1997).

In fact, new observations in the slowest-spreading southwest Indian ridge suggest a higher frequency of hydrothermal plumes and greater chemical discharge than expected (German et al., 1998). Above 20 years after the discovery of sea-floor hot springs, vast fragments of the global spreading centers remain unexplored. Consequently, the understanding of the interplay of magmatic and tectonic controls is still conjectural, and we are a long way from properly quantifying mantle fluxes (Kadko et al., 1995; Lowell et al., 1995; Von Damm, 1995).

#### 5.4. Final remarks

Grunau (1965) thought that the magmatic silica supply theory can be applied only to near-bottom oceanic siliceous biota, but observational data (e.g., Campbell and Gieskes, 1984; Vereshchaka and Vinogradov, 1999), as well as numerical models (Speer, 1997), suggest it is also control of at least intermediate-depth plankton, especially effective in weakly stratified habitats (Vogt, 1989). For instance, the hydrochemical changes are significant in the mesopelagic realm (at 500–600 m depth) in the southern Red Sea, a region of active sea-floor spreading (Cember, 1996). The opaline conservation seems to be rather an additional factor (Fig. 8), also true for the silica-saturated regimes in greenhouse-

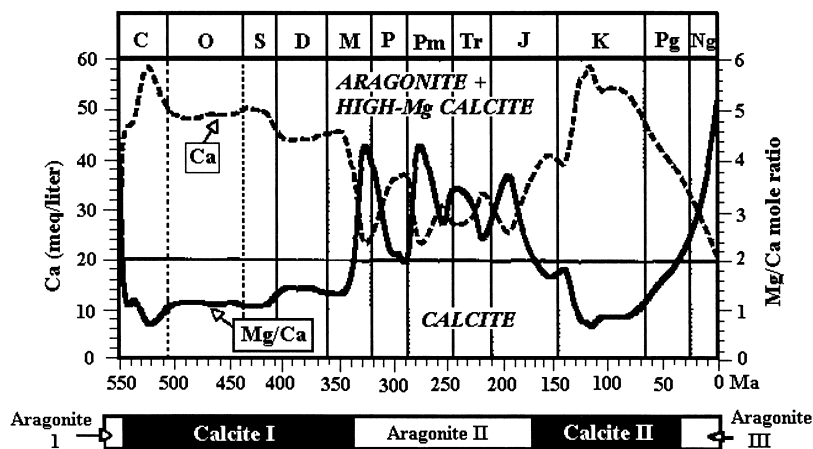


Fig. 10. Secular variation in mineralogy of marine carbonates during the Phanerozoic, attributed to the net effect of changes in middle-ocean ridge Ca-rich brine flux recorded in Mg/Ca ratio (modified from Stanley and Hardie, 1998, fig. 2).

type stratified oceans (e.g., Berger et al., 1989), particularly when coupled with pre-Eocene thick-walled siliceous frustules and tests (Barron and Baldauf, 1995).

Higher silicate loadings are therefore reasonably invoked as one of the principal promoting agents for radiolarite deposition. The input of endogenous silica has been inferred from many detailed studies dealing with diverse silica-rich successions of different ages (e.g., Maksimova, 1978; Vishnevskaya, 1984, 1995; Zimmerle, 1985; Scasso et al., 1991; Xia et al., 1995; Erlich et al., 1996; Tsekhovskiy et al., 1996; Zellmer, 1996; Leistel et al., 1998), including radiolarian-rich tidal algal mats (Blendinger, 1985) and diatomaceous swamps (Stamatakis et al., 1991). In particular, Late Cretaceous (Coniacian to Campanian) and Eocene successions are typified by abundant deep-water and platform cherts (see Figs. 3 and 4), probably derived from the polygenic silica resources (Steinberg, 1981; Owen and Rea, 1985), also from local riverine supply (e.g., within estuaries; Distanov, 1974; see also Hein and Parrish, 1987; Ellis and Baumgartner, 1995; Ilyin, 1998).

On the other hand, 'normal' oceanographic factors, especially wind-driven upwelling, can indeed be not very easy to distinguish from tectonic and volcanic effects, assuming that the events were usually only a part of tangled feedbacks (Fig. 8). Even drawing conclusions from elemental distributions (e.g., Amorosi et al., 1995), that may have been diagenetically reset during the chert formation, is suspect (Murray, 1994). In the radiolarite context, for example, a proven direct relationship between ophiolite and chert thicknesses (cf. Grunau, 1965) would be relevant.

## 6. Conclusions from the Eocene opal revolution

The Eocene saw the last major geotectonic, oceanographic and biogeochemical changes, culminating in the biotic turnover at the Eocene–Oligocene transition (Knoll and Lipps, 1993; Khokhlova, 2000). In particular, this was a peculiar time of extraordinarily enhanced silica accumulation in different domains (see Figs. 4 and 9), but revealed particularly by the oceanic cherty Horizon A<sup>c</sup>. The radiolarian-diatom deposits that occur in a broad belt

across the northern Atlantic, equatorial Pacific and in circum-Mediterranean region are correlated with a large hiatus associated with volcanogenic debris. The depositional event has initially been interpreted as the result of vigorous bottom-water circulation and equatorial upwelling caused by opening of the NE Atlantic to the Arctic region, allowing the formation of North Atlantic Deep water, markedly combined with increased volcanic input of silica (Berggren and Hollister, 1977; Baldauf and Barron, 1990). During the early Palaeogene, the intensity of volcanic/hydrothermal activity was indeed much larger than today's rates, perhaps because the overall direction of seafloor spreading changed from predominantly N–S to the E–W regime as seen recently (R. Owen, personal communication). Heightened silica flux of as much as one order of magnitude, compared with the Holocene, has been postulated due to increased hydrothermal input for the Eocene hypersiliceous event (see Fig. 9; also, Liu and Schmitt, 1996; Tsekhovskiy et al., 1996). Interestingly, this is paired with tectonically forced change in seawater Mg/Ca ratio corresponding to the initiation of modern aragonite sea (Fig. 10).

### 6.1. Progress in the Eocene hypersiliceous scenario

The endogenous model for the Eocene hypersiliceous period was established by Owen and Rea (1985): massive submarine volcanism and induced hydrothermal processes, paired with leaching of ash and glass, as well as the diagenetic alternation of clays, account for heightened nutrient input, including silica oversupply. Furthermore, higher atmospheric CO<sub>2</sub> concentrations probably caused CCD shallowing, as well as an increase in weathering, paired with higher rates of riverine silica and organic-matter supply. McGowran (1989) concluded that the links between volcanism and the chert event are more complex; in fact, Miskell et al. (1985) and Zhou and Kyte (1992) have not found a simple correlation between volcanism and opaline accumulation rates during the last 85 Ma. McGowran (1989) stressed that a succession of interrelated events and feedback mechanisms controlled the Eocene silica 'burp' (Fig. 11), including: (1) plate reorganization and new spreading regimes, paired with increased crustal activity and voluminous volcanism, followed

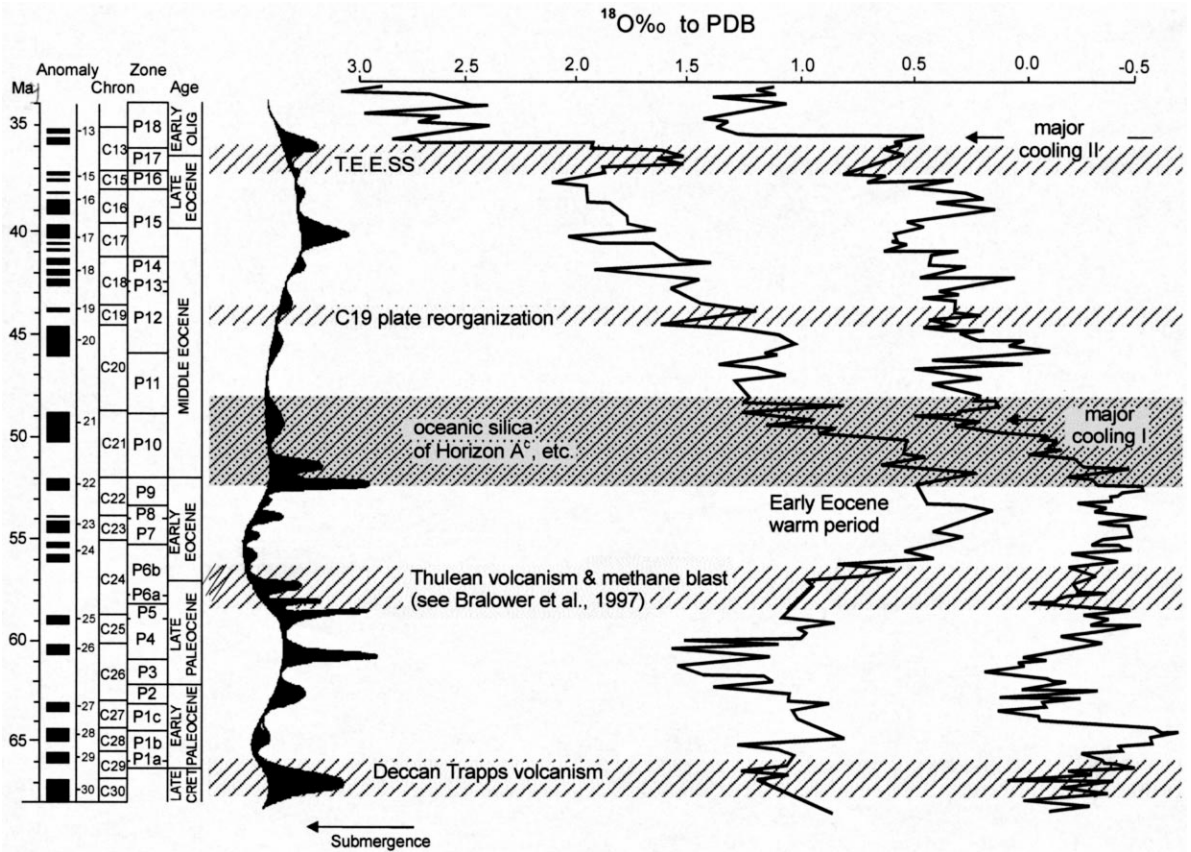


Fig. 11. Succession of early Cenozoic events leading to the Eocene hypersiliceous event (modified from the composite fig. 1 in McGowan, 1989, and references therein). T.E.E. SS, terminal Eocene event, sensu stricto; oxygen isotopic curves for benthic foraminiferal (left) and planktic coccoliths (right) data. For current interpretation of the late Palaeocene thermal maximum as an effect of superimposed volcanic activities, combined with massive dissociation of oceanic methane hydrates caused by deep-water warming, see Bralower et al. (1997).

by (2) a supergreenhouse mode, resulting in deep weathering to high latitudes, and accumulation of released silica in a sluggish ocean, and subsequent (3) sharp global cooling, triggering increasing pole–equator temperature gradients, paired with oceanic upwelling and enhanced fertility in the photic zone. The middle Eocene climatic deterioration may have been a ‘reversed greenhouse effect’, by analogy to the isotopic pattern with the well-known major mid-Miocene cooling step recorded in the Monterey biosiliceous event (see Baldauf and Barron, 1990).

Berger (1991) further refines the causal links between climate change and synchronous sink of opal and organic carbon in his chert–climate hypothesis. The author emphasized that the Eocene ‘opal

revolution’ corresponds to: (1) diminished silica delivery, mostly from vanishing volcanic source, (2) heightened fertility in terms of extended availability of N and Fe (and other terrigenous-derived micronutrients; Salamy and Zachos, 1999), due to vigorous oceanic mixing and progressive oxygenation, supplemented by enhanced aeolian supply (see Harrison, 2000). The oceanographic circumstances were paired with (3) expanding efficiency of the diatom biogenic precipitation in appropriate niches due to intensified upwelling, as well as with (4) effective recirculation of biogenic silica related to rapid dissolution of lightly silicified diatom frustules. The suddenly accelerated ‘biological pump’, due to nutrient extra supply, is recorded in extensive sequestering of or-



feature which is the broad younging of accreted basins away from the cratonic margins associated with protracted interaction of proto-Pacific plates (see references above). This is shown in western Canada where allochthonous chert terranes are progressively younger to the west (Cordey, 1998). A similar distribution is observed in the western conterminous United States. An equivalent feature occurs in Japan broadly from the NE to the SE. Eastern Siberia also comprises long-lived radiolarite successions, which suggest an accretion polarity from NW to SE (Nokleberg et al., 1994).

As outlined by Murchey (1984), an equatorial high productivity zone would be a more stable environment than a restricted marginal basin or trough over a long period of time. Combined palaeomagnetic, biostratigraphic and geochemical evidence for Franciscan cherts suggest their initial deposition on a mid-ocean ridge, intersecting the palaeoequator and subsequently transported towards the American margin (Hagstrum and Murchey, 1993). This is consistent with plate reconstruction models of the Farallon plate moving eastward within the equatorial region during the period of chert deposition. However, well-developed radiolarite successions from east Asia and western America suggest an even broader geographical range for radiolarite sedimentation. Many chert-bearing terranes have a long history of convergence shown by tectonomagmatic and palaeomagnetic studies (Nokleberg et al., 1994), supporting the idea that radiolarite sedimentation occurred within *wide basins* transiting across the palaeo-Pacific ocean, not necessarily tied to high-productivity equatorial depocenters. This is rather consistent with the model integrating radiolarian chert as the 'normal' pelagic sediment in late Palaeozoic and Mesozoic, at times diluted by calcareous or clastic input (Baumgartner, 1987). It also seems substantiated by microfacies observations: sedimentary successions from the circum-Pacific accreted terranes show traces of radiolarian flux whatever time and type of deposition, not only occurring in radiolarian chert but also in siliceous mudstones, pelagic carbonates, fine-grained clastics interbedded with greywacke/breccia or conglomerates, as well as tuffaceous sediments, i.e., in a wide palaeolatitude/palaeolongitude range of depocenters (see Isozaki et al., 1990; Cordey and Schiarizza, 1993; Cordey, 1998). Therefore, actualis-

tic models of restricted radiolarite upwelling-mediated loci seem to be of limited applicability in the context of the late Palaeozoic and Mesozoic palaeo-Pacific oceanic basins.

## 8. Biosiliceous signal and volcano–hydrothermal stimuli: the Cretaceous perspective

The Cretaceous is a particularly well-known period of major geotectonic changes, unusually high sea-level and warm, equable climate (Kauffman and Hart, 1996). Thus, the ocean circulation and chemistry was probably controlled by quite different factors than those acting in Recent seas (Berger et al., 1989), as shown by poleward deep water flow and the ocean and epeiric seas behaved as a single oceanographic unit at least during the Late Cretaceous (Hay, 1995). One manifestation was a widespread organic-rich biosiliceous deposition (oceanic anoxic events; OAEs) in peculiar 'non-actualistic' domains (Parrish, 1995; De Wever and Baudin, 1996), and this corresponds to a peak of the hypersiliceous epochs (Hein and Parrish, 1987). The unsteady tectonically-forced global biogeochemical cycle was resulted in CCD changes and enhanced organic carbon burial (e.g., Bralower et al., 1994; Gibbs et al., 1999).

This was a dramatic time of the biosphere-scale 'Mesozoic Revolution', marked by a series of global bio-events (Kauffman and Hart, 1996; Hallam and Wignall, 1997). This evolutionary escalation, including an expansion of diatoms (see Fig. 4), is explained by Vermeij (1995) as triggered primarily by nutrient and thermal stimuli related to massive submarine volcanism and associated hydrothermalism. In fact, anomalous abundances of hydrothermally enriched trace metals (Co, Mn, Pb, Yb, Cu) are documented for Aptian sediments (Larson and Erba, 1999). The widespread manganese enrichment at the Cenomanian–Turonian (C–T) transition is likewise attributed to the sequestering of hydrothermally-sourced Mn within expanded anoxic zone (Dickens and Owen, 1993; also Orth et al., 1993). Although conjectural in some key aspects (see Loper, 1997; Larson and Erba, 1999), the presumed mid-Cretaceous mantle upwelling in the Pacific, with an acme in the Aptian Ontong-Java and Manihiki Plateaus



eruption, might have driven major plate-boundary rearrangements, orogenic episodes, and transgressive pulses, as well as enhanced CO<sub>2</sub> degassing (Larson, 1991; Garzanti, 1993) and alteration of oceanic basalts (Kharin, 1999).

In addition to accelerated exogenous inputs into peculiar oceanic greenhouse regimes, volcanically-derived CO<sub>2</sub> and micronutrients (e.g., Fe) may have stimulated diffusely distributed new organic production (see Ellis and Baumgartner, 1995; Hay, 1995; Sinton and Duncan, 1997; Larson and Erba, 1999). Furthermore, other tectono-volcanic effects include intensified vertical advection, and hypothetical oceanic overturns of nutrient-rich weaker stratified water masses due to a variety of seismic and geothermal factors (Fig. 13; also, Bralower et al., 1994). This kind of trigger is potentially significant in sluggish greenhouse-type oceans, where nutrients (with the exception of silicate) were largely sequestered below the photic zone (Herman, 1972; Berger et al., 1989; Berger, 1991; Martin, 1995, 1998). On the other side, however, anoxic conditions accelerated benthic regeneration of phosphorus (e.g., Hallam and Wignall, 1997, p. 140), and, thus, potentially reduced effect of its hydrothermal scavenging. It is surmised that tectono-volcanic perturbations would have resulted in regionally intensified circulation, episodic oxygenation and punctuated nutrient mobilization (see Figs. 12 and 13), as exemplified by

many productive tropical Pacific areas (see Ogg et al., 1992; Zhou and Kyte, 1992; Kyte et al., 1993).

### 8.1. Regional records of the mid-Cretaceous volcanic / hydrothermal pulse

It is expected that the postulated mid-Cretaceous volcano–hydrothermal stimulus, driven primarily by the anomalous oceanic plateau and ridge eruptions, has been variously recorded, and induced unsteady biosiliceous signals into other marine domains. The weakening of geochemical anomalies is already demonstrated to be a consequence of an increasing distance from a main C–T magmatic centre in the Caribbean-East Pacific region (Orth et al., 1993; Kerr, 1998).

Mid-Cretaceous hypersiliceous-volcanogenic palaeo-Pacific successions, dominated by radiolarian cherts and black shales, are above 600 m in thickness (Mélières et al., 1981; Vishnevskaya, 1995; Erlich et al., 1996). Widespread shallow-water radiolarites on the Australian shelf are the significant correlative depositional anomaly (Ellis and Baumgartner, 1995). On the other hand, only three radiolarian bloom episodes are reported from the deep-water Carpathian basin of the southernmost Poland from the latest Albian, at the C–T transition and in the late Turonian (Bak, 1996). A short-lasting radiolarian-dominated assemblage has been recorded in the epicontinental chalk succession in the C–T anoxic event

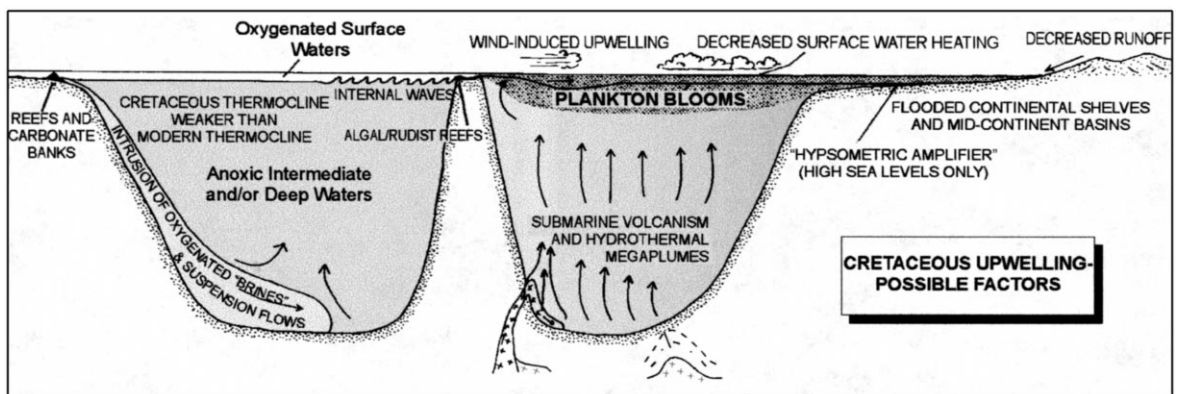


Fig. 13. Scheme of superplume-conditioned middle Cretaceous ocean, where several volcanogenic oceanographic factors/processes, mostly buoyancy driven, and large-scale plankton blooms (cf. Sinton and Duncan, 1997) are depicted (modified from Vogt, 1989, fig. 2A); anoxic water is stippled.

of southern England (Hart, 1996) and southern Germany (Hilbrecht et al., 1996). The latest Cenomanian Bonarelli Level in northern Italy is an exceptional radiolarian-enriched black shale horizon, marked by a large positive carbon isotopic spike and referred to extreme fertility conditions in surface waters (Bellanca et al., 1996; Premoli-Silva et al., 1999; see Fig. 6 and Table 3 in De Wever and Baudin, 1996 for other occurrences). In NE Spain, the C–T interval was characterized by calcisphere limestones with black chert nodules and organic-rich shales, that are interpreted as resulting from anoxic conditions and intense eutrophication affecting catastrophically also adjoining carbonate-producing biotas; the interruption of platform sedimentation and an echinoid bloom recall the impact of artificial eutrophication in present-day coral reefs (Caus et al., 1997), whilst elevated concentrations of Ba, P and biogenic Si, observed in the pelagic facies, are typical of upwelling impact (Drzewiecki and Simo, 1997). In contrast, a calcisphere bloom was probably a sole biotic record of accelerated nutrient supply, established within the C–T marly-limestone sequence of the Danish–Polish Trough (Peryt and Wyrwicka, 1993). The flood of calcispheres, as a possible form of dinoflagellate response to extreme eutrophic conditions in stressed epeiric habitats, was a worldwide C–T phenomenon, fulfilling the criteria for a disaster taxon (Hart, 1996).

Direct links between sea-level changes, productivity levels and extinction/radiation events of Radiolaria in early to mid-Cretaceous pelagic environments, in relation to OAEs, are recently established (Lambert and De Wever, 1996; Erbacher and Thurow, 1997; Bartolini et al., 1999; Larson and Erba, 1999; Premoli-Silva et al., 1999). Higher fertility levels were responsible for a progressive environmental destabilisation in Cretaceous oceans, which favoured phytoplankton-based foodwebs, and black shale (sapropel-type) and biosiliceous sedimentation, at time when growth of calcareous communities became limited (e.g., Weissert et al., 1998; Kemp et al., 1999). This is strikingly exemplified by the superplume-conditioned Aptian nannoconid crisis, when rapid shifts in microplankton structure preceded an abrupt turnover in sedimentation from predominately carbonate to a more reduced, organic-carbon regime, dominated by blooms of opportunistic dinoflagellates (Larson and Erba, 1999).

## 8.2. Indications for other mass extinctions

The distancing from the actualistic paradigm were particularly significant in destabilized ecosystems during biotic crises and recovery intervals (Bottjer, 1997). As reviewed by Racki (1999a), high survival and regional blooms of marine siliceous groups, along with coeval retreat of calcareous organisms, has been evidenced for the Frasnian–Famennian (radiolarians, silicisponges) and the end-Cretaceous (diatoms, radiolarians) mass extinctions. This conclusion concerns primarily overall biovolume patterns (i.e., biosiliceous productivity), whilst diversity data remain more ambiguous (see Fig. 3). The selective effect on skeleton mineralogy is viewed as primarily influenced by major chemical and thermal changes affecting the biomineralisation processes (Harries et al., 1996). Indeed, drastic changes in nutrient availability and productivity accompanied probably major, and perhaps, many minor marine extinctions (Martin, 1998). As shown in most recent studies (Bartolini et al., 1996, 1999; Bellanca et al., 1996; Drzewiecki and Simo, 1997; Schmitz et al., 1997; Weissert et al., 1998; Racki, 1999a; Salamy and Zachos, 1999), high biosiliceous productivity and preservation appear invariably to coincide with the  $\delta^{13}\text{C}$  positive anomalies, mostly when the carbonate periplatform ooze input is drastically reduced. From the mid-Cretaceous perspective, it is evident that the main control was related to fertility levels: biotas adapted to more rich nutrient inventory, such as siliceous plankton, appear to have thrived and even diversified in harsh habitats (see Brasier, 1995b).

The above-reviewed (super)plume-stimulated oceanographic event correlation can be viewed as the key to interpretation of intervals marked by sea-level rise, tectono-volcanic activity, anoxic events and carbonate crisis paired with the rise of biosiliceous sedimentation. Similarities between the Devonian and Cretaceous oceanic ecosystems and bio-events are really noteworthy (Weissert et al., 1998; Racki, 1999b). This biosiliceous signal is explainable by a large-scale rise in volcano–hydrothermal activity during major plate-boundary rearrangements and/or mantle (super)plume activity triggering the global ecosystem perturbances (Racki, 1999a; see also Rich et al., 1986; Carpenter and Lohmann, 1999; MacLeod, in press). Hence, a cumulative stimulus of

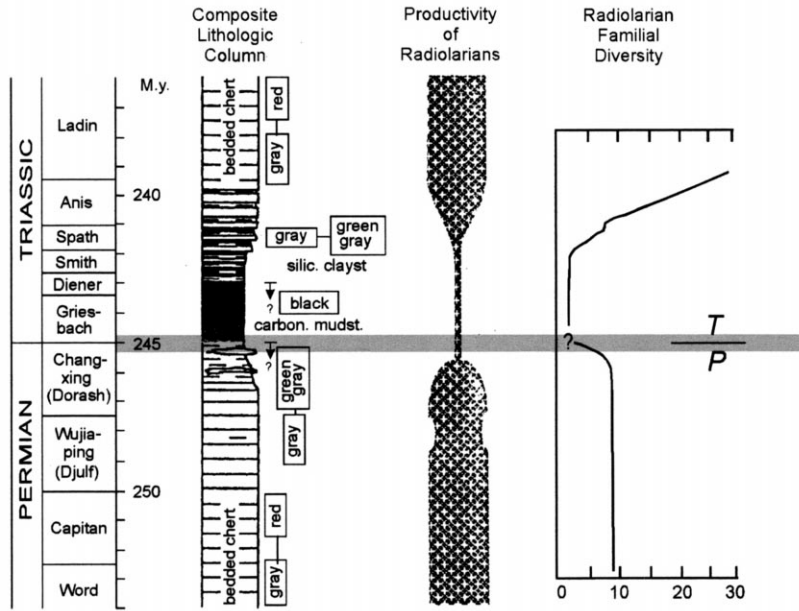


Fig. 14. Synthetic presentation of the chert gap and radiolarian collapse across the Permian-Triassic boundary (combined from Kakuwa, 1996, fig. 11 and Kozur, 1998, fig. 3; see also Isozaki, 1997, fig. 1).

(1) higher rate of silica and other key nutrient input, (2) punctuated greenhouse effect, episodically marked by more vigorous oceanic circulation (cooling interruptions) and a variety of volcanogenic upwellings and overturns, and (3) moderate eutrophication pulses (cf. Bartolini et al., 1999), favoured siliceous versus calcareous biota growth, deposition and preservation (Figs. 8 and 12).

By contrast, radiolarians and silicisponges experienced severe losses during the end-Permian mass extinction (e.g., Vishnevskaya, 1997; Kozur, 1998). The greatest environmental disaster in the Phanerozoic, recorded in a long-lasting radiolarite gap (Fig. 14), was driven by a unique set of killing factors. The destructive impact of the volcanic winter, invoked by Kozur (1998), was probably enhanced by other devastating stimuli, extremely effective in the near-surface productivity zone, such as an expanding superoxia paired with decline of nutrients and productivity collapse (e.g., Hallam and Wignall, 1997; Isozaki, 1997; Martin, 1998). Alternatively, a catastrophic eutrophication episodes ('organic overloading'; Wignall, 1994) may be assumed by analogy to the major Mesozoic radiolarian crises (Bartolini et al., 1999; see also Casey et al., 1983).

The Permian-Triassic timespan was paired with generally decreased seafloor accretion and low continental weathering rates in arid settings populated by gymnosperm forests (Figs. 6 and 10). This probably resulted in lowered silica delivery to apparently greenhouse sluggish oceanic settings. Thus, a selective survival of most efficient radiolarian species (without shell) in overall Si-starved habitats may be hypothesised for the end-Permian evolutionary 're-setting', which, during delayed recovery, evolved into modern-type communities with nassellarians (e.g., Vishnevskaya, 1997; Kozur, 1998; Vishnevskaya and Kostyuchenko, 2000).

## 9. Discussion

Regardless of whether the silica-independence hypothesis of De Wever et al. (1994) is fully valid for Recent plankton, its significance in interpreting of past communities and oceanographic systems seems to be not very great (Fig. 1), as most of the geological history of the oceans cannot be easily anchored in the present. Even the salinity of ancient oceans may have been higher than they are today (up to

53‰ in the Triassic; Hay and Wold, 1997), and seawater chemistry, rather than remaining constant, has oscillated over geologic time (e.g., Kaźmierczak et al., 1985; Falkowski et al., 1998; Stanley and Hardie, 1998; Carpenter and Lohmann, 1999). The Cenozoic accelerated surface and bottom-water circulation, and widespread development of erosion and redeposition are referred even by Berggren and Hollister (1977) as ‘commotion in the ocean’. Wignall (1994, p. 74) concluded that “upwelling zone black shales, for which we have plenty of modern examples, may have been rather rare in past”, which is of substantial importance for this discussion (see Ormiston and Oglesby, 1995; Parrish, 1995; Tsekhovskiy et al., 1996; Kidder et al., 1998). Cretaceous–Palaeogene rhythmic black shales, for instance, were probably not upwelling-conditioned, but might be a taphonomically-biased record of mat-forming diatom blooms due to deep nutrient supply trapped in a halocline under conditions of sustained seasonal stratification (Kemp et al., 1999; see also Schieber et al., 2000).

Biogeochemical turnovers have certainly occurred during the Phanerozoic. One is the enigmatic transition from abiogenic to biogenic chert phases during the Cambrian (Maliva et al., 1989). The rapid onset of silica biomineralization during the ‘biotic explosion’ was probably supported by enhanced fertility and development of new niches created by major Early Cambrian tectonic readjustments, transgression and climate change (Martin, 1995; Mazumdar and Banerjee, 1998). The combined McGowran–Berger volcano–climatic/chert hypothesis is a viable starting point for prediction of some further evolutionary–biogeochemical links, potentially applicable for the mid–Carboniferous radiolarian turnover (Nazarov and Ormiston, 1985, 1986). The latest Devonian–Carboniferous greenhouse-to-icehouse transition was marked by extensive organic carbon and silica sinks in drowned shelf settings (but see Kidder et al., 1998), and this major radiolarian event can be seen as an element of the ‘Palaeozoic Revolution’ of Vermeij (1995). The Permian–Triassic radiolarian crash and a silicisponge crisis was probably followed by a distinctive jump in effective biological extraction of silica and shift of the main locus of opaline sink across the shelf to offshore basins in the Triassic (Schubert et al., 1997). The Mid–Jurassic

turning point in pelagic biotas, corresponding to major plate tectonic reorganization in both Pacific and Atlantic domains (Ogg et al., 1992, p. 576), was stressed by Vishnevskaya (1997). Undoubtedly, the oceanic biogeochemistry and ecosystems changed markedly between the Triassic and Cretaceous. The economic exploitation of the silica reservoir of the photic zone was likely intensified after the subsequent Mesozoic radiolarian turnovers, including Toarcian, Bajocian, Callovian, Valanginian, Aptian and Cenomanian–Turonian bio-events (Lambert and De Wever, 1996; Vishnevskaya, 1997; Bartolini et al. 1999). Notably, the highest radiolarian biodiversity is recorded in the Tithonian (Vishnevskaya and Kostyuchenko, 2000). The escalating competition between radiolarians and silica-precipitating algae, in connection with the calcareous plankton expansion, were the outstanding features of the ‘Mesozoic Revolution’ (Martin, 1995; Vermeij, 1995).

Recurrent geological and oceanographic circumstances, markedly paired with unidirectional evolutionary changes in biosiliceous biota, led finally to the Eocene opal ‘revolution’ in the greenhouse-to-icehouse transition (Berger, 1991; Siever, 1991; Khokhlova, 2000). An evolutionary selection pressure has ultimately resulted in a more economic exploitation of the rapidly shrinking nutrient resources by planktic and benthic biotas (Maldonado et al., 1999), and diatoms are obvious winners in this competition. Notably, recent synurophyte flagellates are competitively dominant over diatoms at very low silica loadings. Under severe stress, their siliceous scale deposition is completely suppressed, but the depression of silicification is reversible, and the flagellates have no apparent threshold silica requirement (Sandgren et al., 1996). This group may be successful in the future extremely silica-starved oceanic ecosystem, and ensuing changes in silica cycle can be predicted (cf. Siever, 1991).

Accordingly, the apparently relative independence of living siliceous biotas from the dissolved silica pool reveals merely their progressive physiological specialisation toward reduced biomineralization during evolutionary history. Repeated expansion of planktic photosymbiosis is a marked evolutionary character influenced by decreasing nutrient availability (D’Hondt and Zachos, 1998). Among Cenozoic nannoplakton, an evolutionary ‘osteoporosis’ was

similarly manifested as the trend toward reduced biocalcification attributed to a decrease in the absolute concentration of  $\text{Ca}^{2+}$  in seawater (Stanley and Hardie, 1998). Evolutionary response to changing seawater chemistry throughout Phanerozoic time has also been established in hypercalcified reef-builders (Kaźmierczak et al., 1985; Stanley and Hardie, 1998) and bivalves (Harper et al., 1997). The dynamic links between seawater chemistry and the evolution of a particular taxa reveal that “metal ions and mineral nutrients could prime the pump of evolution”, and all aforementioned instances merely represent “(...) the physiological response along and within membranes in terms of regulating structure and composition” (Kaźmierczak et al., 1985, p. 28).

Phanerozoic oceans were marked by a secular increase in productivity, from punctuated oligotrophic conditions during most of the Palaeozoic till the contemporary effective nutrient redistribution (Fig. 3). During post-extinction recovery, marine communities were highly unstable in a disturbed ecosystem exposed mostly to massive eutrophication,

and rediversification of surviving opportunistic species have progressively led to increased effectiveness of resource exploitation (see further discussion in Martin, 1998). In the case of silica cycle, this upward scaling of nutrient-related ecological processes obviously resulted in tremendous evolutionary changes. All major reorganizations in marine siliceous biota composition, especially after the end-Permian near-extinction, may have led to a stepdown decrease of dissolved silica levels. A model of ‘punctuated equilibrium’ is therefore implied for the Phanerozoic budget evolution (Fig. 15), instead of the more steady (‘gradualistic’) trend proposed by Maliva et al. (1989) and Siever (1991). Similar negative biogeochemical feedback is the decreasing soluble ferrous Fe bioavailability through the Phanerozoic as oxygenic photosynthesis led to progressive oxidation the ocean; interestingly, Fe-rich superanoxic conditions, that mark the P-T oceans, might be noticeably involved in the siliceous phytoplankton evolution as recorded in the selective use of Fe by diatoms (Falkowski et al., 1998).

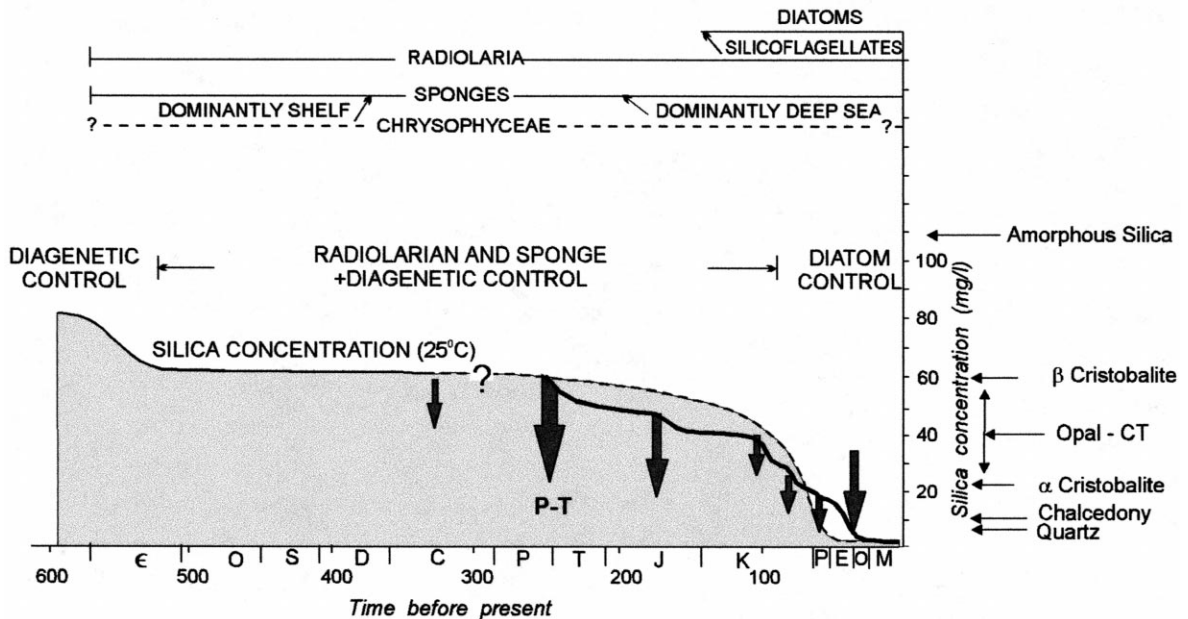


Fig. 15. The evolution of the silica cycle from the latest Precambrian to the present, showing the ranges of silica-secreting biota and hypothesised silica concentrations of the ocean, in terms of saturation values for relevant silica minerals (modified from Siever, 1991, fig. 32.4; see also Maldonado et al., 1999). Instead of a gradual secular trend (broken line), a stepwise decrease of oceanic silica levels (solid line) is proposed as mostly modulated by major radiolarian events (see Fig. 3); compiled from Berger (1991), Schubert et al. (1997) and Vishnevskaya (1997). Pre-Eocene levels may have been less biologically dampened and more changeable over brief-term scales.

## 10. Final remarks and conclusions

Vermeij (1995) implied advancing control by organisms over nutrient and energy supply, which “may explain why observers familiar with evolutionary events of the Proterozoic and early Phanerozoic have tended to emphasize extrinsic factors (...), whereas those whose work on later Phanerozoic history have more often invoked intrinsic factors”. More dynamic palaeoecological models, and truly holistic–vitalistic (geophysiological; Grimm, 1997) approaches to reconstruction of ancient habitats and biotic relationships, are essential for further progress in the understanding of the evolving biosphere (Plaziat, 1978; Bottjer et al., 1995). The ancient taxonomic uniformitarianism (sensu Dodd and Stanton, 1990), paraphrased as: “the past is the key to the past”, is more and more useful palaeoecological approach.

As discussed previously, the past, not the present, is the key to understanding widespread radiolarian blooms and the specific radiolarite deposition (see summary in Table 1). This is proved also for van-

ished normal-marine stromatolites and siliciclastic facies governed by microbial mats (Bottjer, 1997), and for encrinites (Ausich, 1997). The hazard of ‘backtracking of ecology’ for relic groups is again confirmed (Racki, 1986). We still need a better understanding of several key aspects of modern silica cycle, but an orthodox approach to biosiliceous sedimentation is of limited significance, especially for epeiric seas (Bogdanov and Vishnevskaya, 1992; Kiessling, 1996; Kidder et al., 1998), as well as during biotic crises marked by strong geotectonic overprint (Racki, 1999a). In general, pre-Eocene elevated silica levels (by a factor of 50; Fig. 15) and biosiliceous accumulation would have been more influenced by inorganic reactions relative to biological control, and silica cycling may have been far less balanced than today (Siever, 1991, 1992). The ‘anachronistic’ radiolarite deposition records changes, local or global, not solely in wind-driven surface and vertical oceanic circulation and/or preservation patterns, but also an increase in silica and other nutrient supply, perhaps mainly from the endogenous source. Termohaline circulation patterns,

Table 1

Summary of arguments for and against the applicability of the actualistic paradigm for interpreting radiolarian productivity and deposition, given an upwelling-driven production and the virtually total biological control of oceanic silica cycling

Supporting arguments	Contradicting arguments and/or alternative explanations
Relative independence of extant siliceous biotas from the dissolved silica concentration in seawater, and thus, without causal links with increased volcanogenic silica supply (Baumgartner, 1987; De Wever et al., 1994).	Competitive evolutionary specialisation to decreasing silica resources (Fig. 15), recorded in reduced biomineralization by both plankton and benthos (Fig. 5; Harper and Knoll, 1975; Conley et al., 1994; Maldonado et al., 1999).
Biosiliceous deposition restricted to highly-productive localized wind-driven upwelling zones, by analogy to modern-day diatomite basins (Jenkyns and Winterer, 1982; Hein and Parrish, 1987; De Wever et al., 1994).	Examples of long-lived and/or ubiquitous (deep-water and platform), organic-rich biosiliceous sedimentation (palaeo-Pacific; radiolarite ‘events’; Fig. 3; Owen and Rea, 1985; Jones and Murchey, 1986; Parrish, 1995; Cordey, 1996; Jansa, 1997).
No direct temporal correlation between volcanic spasms and opaline accumulation rates (Miskell et al., 1985; Baldauf and Barron, 1990; Zhou and Kyte, 1992).	Complex tectono-volcanic, climatic and oceanographic feedback mechanisms controlled the hypersiliceous depositional events in longer-lasting timespan (Figs. 8, 11 and 12).
Spatially and temporally limited range of volcano–hydrothermal phenomena, and their ‘patchy’ hydrochemical and biotic effects (Baldauf and Barron, 1990; Tréguer et al., 1995), paired with tectonically-controlled distribution of biosiliceous depocentres (Heath, 1974).	— Examples of periods (mid-Cretaceous, early Eocene) marked by far more extensive volcano–hydrothermal and tectonic activity (see Fig. 9; Liu and Schmitt, 1996; Kerr, 1998). — Growing evidence for much larger low-temperature/diffuse off-axial hydrothermal fluxes at present (Schultz and Elderfield, 1997; de Villiers and Nelson, 1999).
Common stratigraphic association of ultrasiliceous biogenic sediments with mafic ophiolitic sequences in cyclic pelagic successions (Hesse, 1989).	Dubious consistent link between upwelling and oceanic ridges (Jones and Murchey, 1986); probably an intense lateral supply from silicic centres (due to advection and diffusion; see Gnanadesikan, 1999).

at least partly controlled by tectono-volcanic factors (see Fig. 13), have led to peculiar biosedimentary processes, exemplified by an intensified but obviously inefficient silica pump from the surface ocean to the deep sea/sediment reservoirs in long-lived palaeo-Pacific settings. This approach, advocated by Zimmerle (1985), Vogt (1989) and Larson (1991), is potentially fruitful for extensively but yet inconclusively debated ocean-wide productivity/anoxic events (Wignall, 1994; Parrish, 1995).

As shown above for the Eocene biosiliceous acme, causal relationships among tectonic/volcanic, climatic and biogeochemical events are complex. The evolving carbon and silica cycles were apparently coupled through the greenhouse effect and enhanced chemical weathering (Figs. 8 and 12). Volcano–hydrothermal and tectonic uplift events, related mostly to extensive rifting and/or accelerated oceanic spreading/subduction, were the endogenous driving force that created this perturbation of the exogenous system (cf. Föllmi et al., 1993, 1994; Vermeij, 1995; Gibbs et al., 1999; MacLeod, in press). The volcanogenic factors are frequently difficult to identify in the sedimentary record (Zimmerle, 1985), although geochemical criteria of chert become more and more refined (Murray, 1994). Likewise, the volcano–hydrothermal influence on marine life may be cryptically recorded and still poorly understood. The study of modern hydrothermal systems is yet in its infancy, and a better understanding of the past ecosystems is impossible before completely understanding the present processes. However, there is no active analogue for large igneous provinces. Anomalous rapid voluminous eruptions ( $10 \text{ km}^3/\text{year}$  or more; White and McKenzie, 1995) must have had a dramatic direct and non-direct impacts on the global oceanic ecosystem (Sinton and Duncan, 1997; Kerr, 1998; Larson and Erba, 1999). This offers a viable alternative for conventional climatic/circulation scenarios to explain hypersiliceous periods evidently unrelated to greenhouse-to-icehouse climatic perturbations (see Fig. 3). Although still speculative in several above outlined lithosphere–hydrosphere–atmosphere and biosphere interactions, the overwhelming tectono-volcanic trigger becomes more plausible causal explanation in the light of above-cited numerical modelling studies.

In a broader perspective, the concept that there is a direct link between mantle convection changes and

Phanerozoic ocean chemistry, related to variable sea-floor hydrothermal fluxes, becomes inescapable. The distinction between ‘convictional’ Wilsonian plate tectonic periods and episodic major mantle overturn and orogenic events (Stein and Hofman, 1994) is particularly significant in the context of non-steady-state geochemical changes. Hydrothermally induced oscillations in seawater chemistry are acceptable as explanation for secular changes in carbonates and evaporites (Stanley and Hardie, 1998), oxygen isotopes (Lécuyer and Allemand, 1999), and the global carbon–oxygen–sulfur system (Carpenter and Lohmann, 1999). Significantly, the oxidation of ferrous iron into ferric iron during submarine hydrothermal processes, and long-term loss of iron from the Earth’s surface in subducted oceanic lithosphere may be seen as important mechanisms for modulating both oceanic primary production and oxygen atmospheric content (Falkowski et al., 1998; Lécuyer and Ricard, 1999). Taken together, there is an intriguing conceptual foundation for further exploration of the endogenous control over mutually linked evolutionary processes, plate tectonics, palaeoceanography and biogeochemical cycles.

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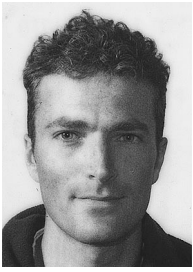
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