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Biogenic chert and the Ordovician silica cycle

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ABSTRACT

Analysis of 161 nodular and bedded cherts shows that shallow-water biosiliceous facies, which were common in the Lower Ordovician, had mostly retreated from peritidal–lagoonal facies to deeper settings by the Middle Ordovician. For decades, this retreat was thought to have spanned the Cambrian and Ordovician Periods. Our data suggest that the basinward shift may have taken approximately 2–14 m.y. in the late Lower to early Middle Ordovician. A likely cause for the departure of these often siliceous-sponge cherts from shallow waters was depletion of shallow-water dissolved silica (DSi). Increased use of DSi by radiolarians may have commenced in the Middle Ordovician when radiolarians increased just as a pulse of radiolarite deposition began. Siliceous sponges may have been forced to relocate to deeper waters because radiolarians depleted shallow-water DSi. Apparent low relative sea level in the Middle Ordovician may have hampered the formation and/or preservation of shallow-water cherts by reducing available shelf area to host such deposits. However, the resurgence of shelf chert in the Upper Ordovician while peritidal cherts remained virtually absent suggests that biology was critical to driving the basinward shift of cherty facies.

Formation and preservation of abundant latest Darriwilian through Sandbian cherts may have been favored in deep-water settings during a possible warming interval marked by sea-level rise and extensive anoxia and euxinia that coincided with an ongoing decline in $^{87}Sr/^{86}Sr$ ratios and increased sea-floor volcanic activity that probably enriched the DSi content of deep-ocean waters. Ocean circulation associated with the onset of cooling in the Katian may have optimized chert accumulation by stimulating surface water biosiliceous productivity before DSi-rich chert-preserving anoxic basins were ventilated. As Late Ordovician glaciation intensified, deep-ocean ventilation by thermohaline sinking of oxygen-rich waters probably decreased preservation potential of biosiliceous deposits while increasing oceanic recycling of silica.

1. Introduction

Raymond Siever proposed that the concentration of dissolved silica (DSi) was higher in Precambrian oceans than in Phanerozoic ones (e.g. Siever, 1957, 1992). Ocean DSi levels are expected to have fallen via biogenic opal extraction from ocean waters as critical silica-secreting organisms appeared and expanded their influence on ocean water chemistry. Three influential biotic originations in this regard were the Neoproterozoic rise of the siliceous sponges (Brasier et al., 1997; Li et al., 1998), the Cambrian appearance of radiolarians (Knoll and Lipps, 1993; Won and Below, 1999), and the Jurassic origination of the diatoms (Sims et al., 2006). Maliva et al. (1989) reviewed the importance of the appearance of these silica-secreting skeletons and provide examples of their importance in chert formation through the Phanerozoic. Most Phanerozoic biogenic chert forms via conversion of that skeletal opal to quartz during diagenesis (e.g. Kastner et al., 1977; Williams and Crerar, 1985; Knauth, 1994). Changes in the sedimentary record of chert accumulation may correspond to new biotic innovations as they became potent enough to affect the marine silica cycle, and hence the accumulation of biogenic silica. Factors controlling chert accumulation are complex. The net silica output from ocean waters to siliceous sediment represents the balance between the organic productivity that controls biogenic silica production and other factors such as dissolution before and after deposition, accumulation rates and dilution effects of other sediment and degree of preservation (e.g. Maliva et al., 1989; Nelson et al., 1995; Bidle et al., 2002).

Maliva et al. (1989) used the sedimentary record of chert to propose two seaward shifts in the spatial positioning of biosiliceous chert accumulation as silica secretors evolved. The first of these was an Early Paleozoic retreat of chert from the shallow-water (peritidal) settings in which chert commonly accumulated in the Neoproterozoic. Maliva et al. (1989) suggested that this shift in biosiliceous facies took place over a prolonged Cambro–Ordovician interval, and that by the Silurian, most cherts were confined to shelf and basinal settings from Silurian through most of the Cretaceous. They suggested that radiation of radiolarians drew down the concentration of dissolved silica in shallow waters, forcing siliceous sponges to relocate to more silica-rich waters. Their second proposed shift involved a Late Cretaceous through

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Paleogene transitional retreat of chert from shelf settings that established the pattern of predominantly deep-water accumulation of biosiliceous deposition that persists into the modern world. Maliva et al. (1989) suggested that such modern patterns were well established by the Eocene. The retreat of biosiliceous facies from shelves to deep oceans was most likely driven by increased diatom influence on the silica cycle (Maliva et al., 1989). Rising diatom abundance in late Mesozoic to early Cenozoic oceans may well have reduced the concentration of dissolved silica in shallow waters (e.g. the photic zone) to the point at which other silica-secreting organisms had difficulty forming skeletons. Radiolarians, for example, displayed significant reductions in their volume and mass of opal at this time (Harper and Knoll, 1975). Siliceous sponges responded in two ways. One is the Maliva et al. (1989) point that they abandoned shelf settings and moved to deeper-water settings. Another apparent, but less well-studied response by the siliceous sponges, was their colonization of non-marine waters at about this time (Lowenstam and Weiner, 1989).

Long-term (e.g. Phanerozoic) compilations and syntheses of chert abundance and distribution (e.g. Ramsay, 1973; Steinberg, 1981; Hein and Parrish, 1987; Maliva et al., 1989; Kidder and Erwin, 2001) are instructive with regard to identifying major shifts in the nature of the silica cycle. Shorter-term analyses of the early Cenozoic (Muttoni and Kent, 2007) and the Mesozoic (Baumgartner, 2013) zero in on the interplay among and timing of factors involved in bringing about changes in operation of the silica cycle.

Our Ordovician series-level analysis that employs both bedded and nodular cherts expands the range of cherty depositional environments beyond occurrences represented only by bedded chert. It also allows us to refine the timing and examine the nature of the major shift in the silica cycle that took place as radiolarians became an increasingly potent influence on the Ordovician operation of the marine silica and spatial accumulation of chert. By the Lower Ordovician radiolarians inhabited shelf (Blome et al., 1995; Renz, 1990; Kozer et al., 1996), as well as deep-water settings (Aitchison et al., 1998; Tolmacheva et al., 2001). The basinward shift undertaken by siliceous sponges may reflect departure of the sponges from shallow waters that increasing radiolarian populations depleted with respect to DSi. This supports the theory according to which silica is a limiting factor to growth of siliceous sponges (Reincke and Barthel, 1997; Maldonado et al., 1999). The move to deeper waters could have been facilitated by opportunistic behavior by such sponges so as to capitalize on high levels of DSi supplied to deep-water settings by increasing dissolution of expanding Ordovician radiolarian populations and/or increasing submarine volcanic activity in the Ordovician. If radiolarians indeed drew down high levels of DSi in shallow waters (e.g. Maliva et al., 1989), radiolarian biotas may have become more dependent on external inputs of usable silica. Our series-level data allow integration of the chert record with other paleoceanographic records to explore the possibility of a Sandbian–Early Katian climate warmup that precedes later Ordovician cooling. It also leads us to suggest that generation of chert in warm greenhouse climate may be favored more by preservational conditions than those driven by high productivity. Contrastingly, productivity is a stronger influence on chert accumulation in icehouse climates. The cool greenhouse climate suggested by Kidder and Worsley (2012) may allow both preservational and productivity influences to coincide so as to maximize chert accumulation.

2. Methods

Systematic (pre-Google) searching of the geological literature (Tomescu, 2004) yielded considerable data on sedimentary Ordovician cherts. In addition to computer-based searches, we targeted sources for which information revealing the depositional environment could be directly extracted and/or interpreted. Several scientific electronic databases were searched for Ordovician cherts (GEOREF, JSTOR, Science Citation Index, General Science Full Text), as were electronic journal archives (*Journal of Sedimentary Research*, *Bulletin of the American Association of Petroleum Geologists*). Additionally, printed journals (e.g. *Sedimentology*, *Sedimentary Geology*, *Geology*) were consulted. This approach generated a mixture of useful and less informative papers totaling more than 1900 articles. Many of the non-relevant articles were easily deleted. Others were examined with more care to determine which ones bore fruitful information regarding the nature of the chert and the environment in which it accumulated. After this cull, about 500 articles remained. Assembling a profile for each chert-bearing formation often required several sources to establish the most accurate information on location, age, and environment of deposition. The latter was often the most challenging because many sources merely mentioned chert presence as part of a study focused on something other than the chert. Environments of deposition were often obtained by combinations of 1) direct information provided in the primary source and 2) obtaining additional literature describing the depositional of that formation and/or associated facies. In cases in which complete depositional interpretations were not provided in the literature, the chert-hosting strata and associated facies were used to infer a likely depositional environment. Chert-bearing formations were grouped into three categories based on depositional environments: 1) peritidal/lagoonal, 2) shelf, and 3) slope/basinal. For some cherts, insufficient information was found to clearly identify the depositional environment. Those cherts are referred to in tables and figures as U (undefined). In the rare cases in which two distinct depositional environments occurred within a single formation, two separate cherts were tabulated. Also, the chert deposits associated with bentonites were excluded from the depositional environment analysis, and chert abundance plots but were included in bedded chert totals. Many of the data are resolvable only into Lower, Middle, and Upper Ordovician cherts. Cherts that have finer stratigraphic resolution are noted in Table 2 (supplement).

The working unit for our tabulations was the formation. Each chert-bearing formation was counted as one chert. The obvious difficulty with this approach is that it provides no sense of chert volume or mass. Some formations are thick and laterally extensive, bearing a high percentage of chert. Other formations bear much less chert. This approach yields a reconnaissance-level scan of chert abundance that could be refined with better temporal control. A successful endeavor to meet the complex challenge of obtaining reliable chert volume or mass estimates would be another significant step forward. Our first-approximation results appear sufficiently robust to yield valid initial interpretations and hypotheses. Further culling of non-relevant cherts and duplicate reports, coupled with careful scrutiny of the remaining literature, yielded 161 chert-bearing formations that form the basis of our results.

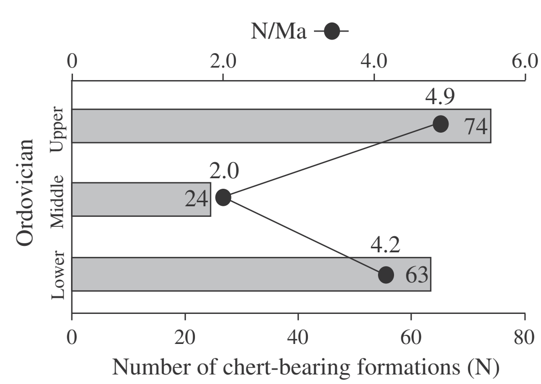

Fig. 1. Chert abundance. Frequency of chert-bearing formations for the Lower, Middle, and Upper Ordovician. Bars represent numbers of chert-bearing formations (N) for each epoch. Numbers to the left of the dots indicate the number of chert-bearing formations per million years. Durations used for all normalizations in this paper are 15 m.y. (Lower and Upper Ordovician), 12 m.y. (Middle Ordovician). Durations are rounded from the time chart (v. 2014/10) posted by the International Commission on Stratigraphy (www.stratigraphy.org).