THE ORDOVICIAN: A WINDOW TOWARD UNDERSTANDING ABUNDANCE
AND MIGRATION PATTERNS OF BIOGENIC CHERT AND IMPLICATIONS FOR
PALEOCLIMATE

A thesis presented to
the faculty of
the College of Arts and Sciences of Ohio University

In partial fulfillment
of the requirements for the degree
Master of Science

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August 2004
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This thesis entitled

THE ORDOVICIAN: A WINDOW TOWARD UNDERSTANDING ABUNDANCE AND MIGRATION PATTERNS OF BIOGENIC CHERT AND IMPLICATIONS FOR PALEOClimate

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The comprehensive global survey of Ordovician chert deposits undertaken in this study reveals that most of them are biogenic, and documents significant paleoceanographic relationships. Peritidal/lagoonal and shelf cherts hosted mainly by carbonate facies are nodular, and formed predominantly by lithistid demosponges. Slope/basinal cherts are bedded, hosted by siliciclastic sediments, and bear radiolarians. Lower Ordovician cherts are abundant in all settings. The Middle Ordovician shows a decrease in cherts characterized by a strong decline in silica burial within peritidal/lagoonal and shelf environments. The distribution of silica secreting biotas suggests an Arenigian- Llanvirnian onshore-offshore migration whereby siliceous sponges migrate from peritidal/lagoonal to shelf-basinal environments, and radiolarians move to basinal settings. The Caradocian marks the highest peak in the abundance of Ordovician cherts, in both shelf and slope/basinal environments, that appears to correlate with a warming interval. A decline of cherts takes place in the Ashgillian, when glaciation was in effect.

Approved:

David L. Kidder
Professor of Geological Sciences
Acknowledgments

My sincere thanks go to Dr. David Kidder, my mentor. He introduced me to the silica system and all its biotic and abiotic components. During our long discussions he kindly guided me through the maze of the Ordovician Earth system and Paleozoic silica-secreting organisms. I am very grateful for having had the chance to work with him.

I would also like to thank Drs. Thomas Worsley and Gregory Nadon. Dr. Worsley opened the world of Earth system evolution to me. His broad-picture integrative models were a constant source of inspiration, and his feedback greatly encouraged me in my scholarly pursuits. Dr. Nadon was always available for discussions and interactions with him sharpened my critical thinking.
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Chapter 1

THE SIGNIFICANCE OF THE STUDY

The present study represents a unique comprehensive systematic survey of the worldwide Ordovician early diagenetic _in situ_ chert deposits, addressing not only bedded cherts, but also less conspicuous cherty facies such as nodular cherts and associated silicified oolites. The distinction of the chert deposit types (nodular cherts _vs._ bedded cherts _vs._ silicified oolites), the depositional environment in which cherts formed (peritidal/lagoonal _vs._ shelf _vs._ slope/basin), and a systematic analysis of the content in siliceous skeletal remains (radiolarians and siliceous sponges) preserved in the compiled chert deposits, were among the main targets in surveying the data. The compilation was realized with a high temporal resolution at the epoch level, and where possible, even at the stage level (e.g., the Caradocian).

This study is the first qualitative and quantitative test of two common assumptions: 1) the biogenic origin hypothesis for most of the Ordovician cherts and a biologically controlled marine silica cycle and burial and, 2) the relationship between the chert deposit types (nodular _vs._ bedded chert) and the hosting facies (carbonate _vs._ siliciclastic environments). This research also evaluates: 1) the relationship between the chert deposit types (nodular _vs._ bedded) and the depositional environment in which they formed (peritidal/lagoonal/shelf _vs._ slope/basinal); and 2) the relationship between the chert deposit types (nodular _vs._ bedded) and the content in biogenic siliceous remains.
(radiolarians vs. siliceous sponges). The results demonstrate that the Ordovician onshore-offshore organism migration, a mechanism suggested to date only for the benthic invertebrate calcareous macrofauna, included planktonic radiolarians and siliceous sponges as well.

The study goals were: 1) to identify and interpret Ordovician temporal and spatial patterns in the locus of marine silica accumulation in fluctuations of the marine biogenic chert abundance, in possible migrations of the silica secreting organisms, 2) to correlate these patterns with paleoclimate, paleoceanography, paleogeography, nutrient level inputs, and the behavior of silica secreting organisms, and 3) to translate these interconnections in terms of causal relationship. Through this, the study represents a multi-approach analysis of the Ordovician Earth system, whose main goal is to explore the connections between the biotic and abiotic worlds.
Chapter 2

THE HYPOTHESES OF THE STUDY

Based on previous work (discussed in Chapter 4) the following hypotheses have been proposed to be tested:

I. Did the Early Paleozoic radiolarians and siliceous sponges behave similarly to diatoms regarding their response to abrupt changes in oceanic circulation and climate parameters?

Assessing the worldwide abundance and distribution of Early Paleozoic cherts in relation to paleoclimatic events will help clarify whether radiolarians and siliceous sponges were as responsive to oceanographic changes as are diatoms. This behavior was tested for the Ordovician, a geological period characterized by a succession of antagonistic climates: Lower and Middle Ordovician warm greenhouse periods, as opposed to the late Upper Ordovician, an icehouse interval. A chert peak is expected to be associated with an upwelling environment driven by the late Ordovician glaciation. In contrast, a gap in chert abundance in the Early Silurian may reflect sluggish ocean circulation and possible climate warming similar to the Middle Cretaceous and Early Triassic, both of which are marked by lows in chert abundance.

The accumulation and formation of cherts depends on different factors – upwelling is very important in offshore environments, while in nearshore facies other
factors are important, such as the amount of dissolved silica supplied to seawater by riverine input and by the siliceous organisms that inhabit these areas (e.g., siliceous sponges). Consequently, during glacial periods bedded chert accumulation should be common in offshore settings, driven by an enhanced upwelling. On the contrary, in nearshore facies the amount of siliceous deposits could decrease as a consequence of changes in the ecological distribution of siliceous organisms due to sea level fluctuations. Changes in chert distribution could be driven by a drop in sea level appreciated to have amounted to at least 50m for the Late Ordovician glaciation. On the other hand, a drop in sea level would increase the volume of terrestrial silicates available to weathering, and possibly the dissolved silica input into the basinal facies, while the shelf would witness decreased deposition being more or less emergent. The amount of dissolved silica that enters the oceans via rivers (the exogenous silica input) is directly connected to the continental weathering rates, whose intensity is a result of the interplay between the rock volume exposed to weathering, atmospheric conditions (temperature, precipitations), and the average paleolatitudinal distribution of the world landmasses. If the interaction between the three parameters drives a higher weathering rate, the exogenous, dissolved silica input in coastal seawaters will be higher resulting in more chert accumulation in areas of low detrital influx.
**II. The timing of the Late Ordovician glaciation - Did a brief glaciation result in a short cherty interval? Did cherts respond quickly enough to reflect the duration of the glaciation?**

The Late Ordovician is characterized by a glaciation the timing of which is open to controversy. Brenchley et al. (1994) suggest that the late Ordovician glaciation may have lasted less than 1 m.y. during an otherwise long greenhouse interval. Conversely, Pope and Steffen (2001) suggest that extensive chert in the Montoya Group represents a glacial-related upwelling system that persisted for up to 15 m.y.

If the Paleozoic siliceous organisms can be demonstrated to be sensitive to climatic and oceanographic variations, then we need to know the degree of this sensitivity. A short-lived chert pulse, coeval with the glaciation, would support the short glaciation hypothesis, and would argue that Ordovician biogenic cherts are very sensitive to abrupt changes in ocean circulation. A longer interval of chert deposition would be consistent with a glaciation of longer duration or in the case of a short glaciation, might mean that siliceous sponges and radiolarian cherts were not as responsive to oceanographic changes as are diatom cherts. If glaciation was short, an alternative explanation for abundant, pre-glacial chert in the Late Ordovician is required.

**III. The Early Paleozoic dominant locus of silica deposition migrated from shallow water to deeper water environments within the Ordovician period.**

Analysis of the Ordovician spatial and temporal distribution of chert sedimentary facies, such as bedded, nodular, and silicified oolite deposits, can be used to: 1) estimate
the dominant locus of silica deposition, onshore vs. offshore; 2) infer onshore-offshore migration patterns of silica secreting organisms perceived through changes in the depositional environment of biogenic siliceous facies; 3) analyze the timing, the rate and the nature of this retreat of chert to deeper water settings; and 4) identify and interpret marine chert abundance fluctuations and patterns.
Chapter 3

THE ASSUMPTIONS OF THE STUDY

The theory according to which seawater was undersaturated with respect to amorphous silica not only during the Cenozoic and Mesozoic, but also during the Paleozoic, is widely accepted today (Siever, 1957; Grunau 1965; Hein and Parrish, 1987; Maliva et al., 1989). Paleozoic marine burial of silica has been controlled for most of the time by thePaleozoic silica secreting organisms represented by radiolarians and siliceous sponges. In a marine silica cycle in which silica burial is dominated by the biogenic component, the dissolution of the siliceous skeletons, which takes place during the living stage of the organisms (Spencer, 1983; De la Rocha et al., 1997) as well as within the water column while dead organisms are sinking and continues during burial (DeMaster, 1981), represents the main mechanism for remobilizing and recycling dissolved silica in the sea water (Tréguer et al., 1995). The silica secreting biotas, due to their biochemical efficiency of silica uptake, are responsible for keeping the seawater undersaturated with respect to amorphous silica, and thus preventing the precipitation of silica and the formation of extensive inorganic cherts.

The Ordovician chert deposits are considered in this study to be mainly biogenic in origin, induced either organically (based on biological silica recycling), or inorganically (based on inorganic silica and other nutrient inputs that drive biological blooms of the silica secreting organisms). Deposits demonstrated to be inorganically
generated (e.g., chert units associated with tephra layers or bentonites, and possibly the bedded cherts formed in peritidal/lagoonal environments characterized by restrictive circulation) are exceptions. Biogenic chert deposits are considered those for which the bulk silica input originates in the opal skeletons of silica secreting biotas, representing a net output of Si from the biochemical cycle.

Taking into account that skeletons of the siliceous organisms are the main supplier of reactive silica to sediments, the abundance of nodular and bedded cherts would reflect environments rich in such organisms, in either deep or shallow waters. In other words, “in situ” early diagenetic chert deposits are assumed to reflect the presence of silica-secreting organisms in their proximal environment, and temporal changes in the depositional environment of silica burial perceived through the rock record reflect biological variations of the silica-secreting organisms.
Chapter 4

PREVIOUS WORK

Previous chert compilation-based studies surveyed worldwide records of bedded chert deposits only, with the aim to identify and interpret Phanerozoic chert abundance patterns (Grunau, 1965; Dietz and Holden, 1966; Ramsay, 1973; Ronov, 1982; Hein and Parrish, 1987; Kidder and Erwin, 2001). Grunau’s (1965) work led to the suggestion that past chert abundance (such as radiolarites) may have been related to ophiolite genesis. This theory was based on his finding that ophiolite thickness appears to correlate with the thickness of approximately coeval chert deposits. This direct relationship between ophiolite and chert formation, combined with the “eugeosynclinal” position of many of these radiolarites (Grunau, 1965) implied a volcanic source of silica. Racki and Cordey (2000) suggest that volcanic sources of silica may have been more significant in the Paleozoic than in younger rocks. Given the relative lack of orogenic activity in the Cambrian and early to middle Ordovician, it is reasonable to suspect a greater relative role for mid ocean ridge silica sources. Silicate weathering associated with Late Ordovician orogenic activity (e.g., Kump et al., 1999) probably increased the terrestrial input of silica. The bedded chert compilations of Ramsay (1973) and Ronov (1982) attempted to compare the volume of chert abundance through time along with volumes for other sedimentary rocks. Hein and Parrish (1987) expanded the work of Grunau (1965) and Ramsay (1973), and constructed a paleo-upwelling model of bedded chert
distribution (fig. 4.1). All these chert data were assembled into period-level groupings. The high sensitivity of radiolarians to water temperature and chemistry has rendered radiolarians an excellent paleoceanographic and paleoclimatologic marker, mainly for the Cenozoic era. Distribution patterns and abundance of distinct modern radiolarian assemblages are tightly linked to the amount of nutrients dissolved in the seawater and to water depth (Kruglikova, 1993; Abelmann and Gowing, 1997). Based on an actualistic scenario, the abundance of radiolarian-bearing strata has been used as an indicator of paleo-upwelling and high productivity areas for the Phanerozoic (Hein and Parrish, 1987). Also, radiolarian-bearing chert deposits preserved since the Ordovician have been used successfully as an indicator of deep-water settings (distal basinal or oceanic environments associated with orogenic belts), but have been also associated with cratonic seas of moderate depths as well (Aubouin, 1965; Ormiston, 1993). Vishnevskaya (1997) has shown that evolutionary changes undergone by radiolarians throughout the Phanerozoic could be linked to sea level changes, paleoceanographic regime, and plate tectonics events. Numerous Lower Paleozoic radiolarian assemblages are incorporated into the accretionary prisms associated with ancient subduction zones (Aitchinson, 1998). Because numerous Paleozoic radiolarian-bearing chert deposits are associated with ophiolitic complexes, many authors emphasize the use of radiolarians as a biostratigraphic tool in dating lower Paleozoic orogenic belts devoid of other biostratigraphic markers and consequently lacking a good age control, (Grunau, 1965; Aitchinson et al., 1998; Blome et al., 1995b; Nazarov and Ormiston 1993).
Figure 4.1: Ordovician paleogeography, chert distribution (after Hein and Parrish, 1987), and oceanic circulation (after Berry et al., 1995).
Kidder and Erwin (2001) analyzed the Phanerozoic distribution of bedded chert in order to determine the effects of extinctions and climate changes on siliceous facies. They refined the Hein and Parrish (1987) data to the epoch level and distinguished basinal from shelf cherts based on facies associations. The raw abundance data at system-level shows a marked decrease in both basinal and shelf chert during the Silurian period but the Ordovician period displays no peak or decrease in the number of chert occurrences (fig. 4.2.). On the other hand, the chert data normalized to outcrop area/time (after Raup, 1976) suggests a small Ordovician chert peak (fig. 4.3.). The distribution of chert data compiled at the epoch level produces an Upper Ordovician chert peak (fig. 4.4.) that might be associated with the Late Ordovician glaciation through enhanced oceanic circulation that would favor stronger upwelling and implicitly higher organic productivity and chert formation rate. The difficulty with the Kidder and Erwin (2001) compilation is that the number of bedded cherts per epoch is commonly less than ten. This low sample size provides only weak support for high versus low oceanic productivity. Those results are sufficient however, to stimulate testable hypotheses.

Maliva at al. (1989), Kidder and Erwin (2001), and Kidder and Mumma (2003) analyzed the dominant locus of biogenic silica burial and its migration patterns throughout the Phanerzoic. The work of Maliva at al. (1989), based on the depositional distribution of chert facies, showed that the Cambrian-Ordovician interval represents a transitional period in the dominant style of silica burial from peritidal-dominated environments of early diagenetic chert facies, to a pattern of bedded chert-dominated basinal and nodular chert-dominated shelf/slope environments, that they suggest to have
Figure 4.2: Phanerozoic distribution of bedded cherts compiled at the system level (after Kidder and Erwin, 2001). Raw abundance data. Arrows highlight Ordovician chert.

Figure 4.3: Phanerozoic distribution of bedded cherts compiled at the system level (after Kidder and Erwin, 2001). Raw chert data presented in figure 4.2 is normalized to outcrop area. Arrows highlight Ordovician chert.
Figure 4.4: Phanerozoic distribution of bedded cherts compiled at the series (epoch) level (after Kidder and Erwin, 2001).
persisted from the Silurian through the Cretaceous (fig. 4.5). During the Cenozoic the main locus of silica burial is confined to bedded chert-dominated deep-sea settings (Maliva et al., 1989).

The worldwide compilation of the Phanerozoic in situ silica-replaced oolites silicified during early diagenesis (Kidder and Mumma, 2003), and the depositional environment analysis of shelf bedded cherts vs. basinal bedded cherts (Kidder and Erwin, 2001), suggest that the Early Paleozoic migration of cherty facies from shallow-water to deeper environments may have occurred within the Ordovician (fig. 4.6). Again, however, low sample size restricts this interpretation to the status of a testable hypothesis.

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<td>Nodular cherts &amp; Bedded cherts</td>
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<td></td>
<td>Platform, shelf, basinal slope</td>
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<tr>
<td>CAMBRIAN-ORDOVICIAN</td>
<td>Transitional</td>
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<tr>
<td>NEOPROTEROZOIC</td>
<td>Peritidal facies (stromatolites, ooids, laminated dolomites)</td>
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**Figure 4.5:** Sedimentary silica through time (after Maliva et al., 1989).
Figure 4.6: (A) Temporal distribution of silicified oolites and bedded cherts at the series level. Numbers at right are the percentages of shelf chert occurrences from total chert occurrences in each series. (B) Onshore-offshore migration patterns of the three faunas after Cowen’s (2000) reinterpretation of Sepkoski and Miller’s (1985) data (after Kidder and Mumma, 2003).
Chapter 5

BEDDED CHERTS versus NODULAR CHERTS

5.1. What is chert?

5.1.1. Definition and terminology

After siliceous organisms die, their opaline skeletons either accumulate on the sea bottom (in the case of the planktonic siliceous fauna), or dissolve and reprecipitate (in the case of the benthic siliceous organisms) and are subsequently transformed into chert through complex diagenetic processes. Chert refers to any siliceous sedimentary rock whose origin can be inorganic (volcanic and/or hydrothermal) and organic (biochemical or biogenic). “Siliceous sedimentary rocks are fine grained, dense, very hard rocks composed mainly of the SiO₂ minerals such as quartz, chalcedony, and opal, with minor impurities such as siliciclastic grains and diagenetic minerals” (Boggs, 1987, p.239). In a strict sense, the term chert designates a dense microcrystalline or cryptocrystalline sedimentary rock, consisting of quartz crystals less than about 30 µm in diameter (Calvert, 1974). Other names of chert are: flint, designating a dark gray or black variety of chert; jasper, a red variety of chert containing disseminated hematite; novaculite, defined as a very dense, fine-grained, even-textured chert that occurs mainly in mid-Paleozoic rocks of the Arkansas, Oklahoma, and Texas region of the south-central United States; porcellanite, representing a fine-grained impure siliceous rock characterized by a texture and fracture close to unglazed porcelain and composed mainly of cristobalite and
subordinately clay minerals; silex, representing early diagenetic siliceous nodules in limestones of biochemical origin, with a large variety of colors, fine grained and very hard, composed mainly of chalcedony and cryptocrystalline quartz.

5.1.2. Mineralogy, texture and chemical composition

The main minerals that constitute the chert deposits are: amorphous silica (opal-A), cristobalite (opal-CT and opal-C), tridymite, chalcedonic quartz, microquartz and various combinations of these phases. Cristobalite and tridymite are polymorph varieties of quartz. According to Lancelot (1973b), the mineralogy of chert is influenced by the lithology of the host rock. His hypothesis claims that chert in clay-rich sediments (zeolitic clays, clayey radiolarian oozes, marls and marly limestones) is porcelanite (rock composed mainly of disordered cristobalite – opal-CT), whereas in calcareous oozes chert mineralogy is exclusively represented by quartz. Based on clay mineralogy of the bed, Lancelot suggests that chert is more prone to form within a silicic environment relatively rich in K-felspars, and palygorskite (a chain-lattice clay mineral with good bleaching and adsorbent properties).

Opal-A or amorphous silica, with up to 10% water, represents the constituent material of the skeleton in siliceous organisms. Von Rad and Rösch (1974) define opal-A as highly disordered, nearly amorphous natural hydrous silica. It is metastable and therefore it becomes less frequent back through time, being absent from Paleozoic cherts (Tucker, 2001).

Opal-CT represents an intermediate phase of the opaline silica transformation into chert (quartz). The 3-layered mineralogical structure is represented by disordered
stacking of a low temperature cristobalite layer and two low-temperature trydimite layers (Wise and Weaver, 1974; Boggs, 1987). Opal-CT may occur as microcrystalline aggregates 5-15 µm in diameter called lepispheres, in turn composed of fine blade-shaped crystals 300-500 Å thick (Calvert 1974). Cristobalite represents an important constituent of many deep-sea cherts. In the chert literature, low temperature cristobalite can be found under various names such as: cristobalite, α-cristobalite, disordered cristobalite, lussatite, opal-CT, opal-cristobalite, unidimensionally disordered cristobalite (Wise and Weaver, 1974). It is considered to be an early diagenetic product of low temperatures.

**Quartz** in chert is a late diagenetic product and based on grain size is divided into megaquartz (> 20 µm) and microquartz (< 20 µm). Microquartz can be of two types: microcrystalline (1-4 µm), and chalcedonic quartz with a fibrous habit (Carson, 1991). According to von Rad and Rösch (1974), a quartz-chert lacks fossils and porosity.

**Chalcedonic quartz** is fibrous quartz of three types, depending on the optical orientation of the fibers: two length-slow types (quartzine and lutecite), and one length-fast type of chalcedony (chalcedonite). The latter is considered a late diagenetic product (Heath, 1974).

From a chemical point of view, in addition to silica (SiO₂), cherts contain minor amounts of Al, Fe, Mn, Ca, Na, K, Mg, plus some impurities such as authigenic hematite and pyrite, siliciclastic minerals, or pyroclastic particles. Aluminum represents commonly the second most abundant element in cherts, followed by Fe, Mg, or K, Ca, and K. The amount of silica in chert ranges from 99% for a pure chert (such as the Arkansas Novaculite), to less than 65% in some chert nodules (Boggs, 1987).
5.2. Chert formation

Boggs (1987, p.92) maintained that chert formation is a dual process: 1) a sedimentary process reflecting the accumulation and concentration of biogenic opaline tests by burial and, 2) a diagenetic process reflecting crystallization and recrystallization of the amorphous silica after burial.

The amount of dissolved silica in the pore water of marine sediments is higher than that of adjacent bottom waters (Tréguer et al., 1995). Within the sediment, silica is a mobile component: a part is recycled into the overlying water by dissolution, another part is involved in the formation of aluminosilicate mineral phases, and the rest crystallizes and is preserved as chert. From the total biogenic silica production, 97.5% is recycled and only 2.5% is preserved in the sediment as chert (Tréguer et al., 1995). According to Heath (1974), 4% of the dissolved silica is buried, out of which only 2% will be left after the post-depositional dissolution, and preserved as chert. Within the sediment high dissolved silica concentrations correlate with biogenic silica-rich sediments. Dissolved silica increases rapidly in concentration in the uppermost layers of the sediment, and reaches a constant value some tens of centimeters below the surface of the sediment (Calvert, 1983).

Von Rad and Rösch (1974) contend that the first steps in chertification are the remobilization of dissolved biogenous opal-A and precipitation of lussatite blades (low temperature cristobalite), with formation of microspherules (an early diagenetic process), followed by the conversion of the lussatite into chalcedony and/or micro- (>1 µm) to cryptocrystalline (< 1 µm) quartz (a late diagenetic processes).
Rapid siliceous test accumulation results in a high opal concentration per surface unit area. Burial and continuous dissolution of the opaline skeletal material increasingly enriches the pore waters in silica favoring a slow precipitation of chert. The most widely accepted diagenetic progression is the maturation theory (Kastner et al., 1977) in which opal-A passes into opal-CT (disordered cristobalite) that in turn converts with time into quartz. However, opal-A can pass directly into quartz (Kastner, 1981). According to Calvert (1974), the transformation of opal-CT into quartz is a solid-solid inversion whose rate depends solely on temperature.

The rate of this chert diagenetic evolution depends on different factors: *in situ* temperature (Li, 1995; Carson, 1991; Calvert, 1974; Kastner et al., 1977), pore fluid chemistry, pH, time, host rock mineralogy, organic matter abundance, clay minerals, burial depth, host bed porosity and permeability, specific surface area (Williams et al., 1985; Tribble et al., 1995). Von Rad and Rösch (1974) state, “under normal deep-sea conditions, time appears to be the single most important parameter” (p. 344). The ideal diagenetic sequence derived from the solubility-specific surface area graph of Williams et al. (1985) would be represented by a sedimentary column in which opal-A overlies opal-CT, that in turn overlies quartz, with transitional zones of mixed phases. Kastner et al. (1977) demonstrated experimentally the strong influence of the host rock and the solution composition, along with time and temperature, over the transformation rate of opal-A to opal-CT. Their conclusion was that the transformation rate is greatly enhanced within a carbonate host rock, as compared to clay-rich host sediments, by highly alkaline solutions rich in magnesium. The idea is that magnesium (provided by the seawater) and hydroxide
(OH\(^{-}\), provided by calcite dissolution) act as magnesium hydroxide sites of opal-CT nucleation and subsequent growth of opal-CT lepispheres. The affinity between carbonate and chertification is explained in terms of alkalinity – by calcite dissolution the pore water solutions become alkaline favoring the transformation of opal-A into opal-CT at a higher rate. According to the experiments by Kastner et al. (1977), active clay minerals, such as smectites, retard the opal-A to opal-CT transformation, by competing with opal-CT for the available alkalinity in seawater, which results in an enrichment of the clay minerals in Mg.

### 5.3. Chert deposit types: characteristics and genesis theories

Chert deposits in the geological record are preserved mainly as bedded and nodular cherts. They can form in shallow and deep waters, but many shallow water siliceous deposits do not become cherts because they are masked by a high terrigenous input. Numerous Mesozoic and Cenozoic bedded chert deposits occur in orogenic belts and within ocean floor deposits.

The difference between bedded and nodular chert deposits is regarded as either a morphological difference (Boggs, 1987) or as a genetic difference. Bedded cherts are considered primary accumulations of siliceous tests of planktonic silica-secreting organisms, such as radiolarians for the Paleozoic (radiolarites), and radiolarians and diatoms (diatomites) for the Mesozoic and Cenozoic (Grunau, 1965; Aubouin, 1965; Ramsay, 1973; Hein and Parrish, 1987; Maliva and Siever, 1989), whereas nodular cherts are regarded as diagenetic products resulting from silica remobilization and mineral
precipitation within a limestone host rock (Maliva and Siever, 1989; Maliva et al., 1989). Some authors differentiate between the two types based on the host rock – the chert deposits occurring in carbonate host rock being considered nodular cherts, and the chert deposits occurring in siliceous sequences termed bedded cherts (Wise and Weaver, 1974).

5.3.1. Bedded Cherts

*General characteristics*

Bedded cherts, regarded as primary chert accumulations of either diatom or radiolarian tests, can form in both deep and shallow water. Presently silica is concentrated in deep oceans, below the CCD, forming siliceous oozees composed entirely of biogenic silica of radiolarian tests and diatom frustules. Bedded cherts can form also beneath shallower waters on the shelf, if surface waters are fertile, there is a paucity of calcareous plankton, and there is a very low terrigeneous sediment input. Therefore, the formation of bedded cherts depends directly on the organic productivity of the planktonic siliceous organisms (diatoms and radiolarians), that in turn depends on oceanic circulation and nutrient supply, on the sediment input, the presence of calcareous plankton, and water depth. Aubouin (1965), discussing radiolarites, defined them from two points of view: 1) petrographically and stratigraphically. The former form through test accumulation, occurring in all sedimentary environments of an epicontinental domain, and considered of local significance. The latter are composed of a massive, homogenous sequence of siliceous facies “uniquely characteristic of geosynclinal chains, and
particularly of the eugeosynclinal furrows” (p. 115). These can be associated with pelagic limestones, limestone microbreccias, pelites, sandstones, and ophiolites.

**Origin and genesis theories**

The abiogenic *versus* biogenic origin of chert has long been debated. The main factors supporting the inorganic origin theory are the association of cherts with volcanic complexes in many cases, on the presence in certain bedded cherts of some minerals regarded as volcanic alteration products, such as montmorillonite, palygorskite, sepiolite, and clinoptilolite (Wise and Weaver, 1974), and on the lack of siliceous skeletal remains. Bedded cherts associated with bentonites and devoid of any siliceous skeletal remains are widely considered to be inorganic in origin.

At the beginning of the twentieth century Davis (1918, in Wise & Weaver, 1974), studying some radiolarian bedded cherts of the Franciscan mélange in California, proposed another theory known as the “gel theory”. This theory explains bedded cherts as being formed by the solidification of layers of silica gel entrapping radiolarian tests as the gel was solidifying. The main mechanism that induces a high accumulation rate of siliceous tests of the planktonic silica-secreting organisms, and ultimately the transformations into bedded cherts, has been debated for centuries: submarine volcanism-induced plankton blooms (the so-called volcanic-sedimentary hypothesis of Aubouin, 1965) based on the spatial association between many bedded cherts and igneous rocks in eugeoclinal settings (Grunau, 1965; Aubouin 1965); abyssal accumulations below the calcite compensation depth, unrelated to igneous activity (Aubouin 1965; Garrison, 1974;
Heath, 1974); and upwelling-induced high planktonic productivity (Calvert 1966; Ramsay, 1973; Hein and Parrish, 1987).

The concept of maturation of siliceous oozes from an initial biogenic silica ooze through porcelanite to chert, was introduced by Bramlette (1946, in Kastner et al., 1977). In concordance with this theory, the transformation of biogenic opal-A is regarded and interpreted as a process dependent on depth and temperature and ultimately is viewed as a time-dependent process (Wise and Weaver, 1974; von Rad and Rösch, 1974).

5.3.2. Chert nodules

General characteristics

Chert nodules are highly variable in size and shape, ranging from spherical to irregular. They may coalesce to form more continuous layers resembling bedded cherts. Their internal structure can be laminated or not, and they may contain silicified fossils. Chert nodules, regarded as diagenetic products, occur predominantly in carbonate rocks such as shelf limestones, pelagic carbonates and chalks, in environments ranging from tidal flats to deep ocean basins (Maliva and Siever, 1989). According to Maliva and Siever (1989; p.425), “there is no intrinsic depositional environmental restriction on nodular chert formation”. Nodular cherts form in hypersaline, marine, and mixed marine-meteoric pore waters. Also, nodular cherts can form in mudrocks, evaporites, burrow fills, but to a much smaller extent, and can nucleate around fossils. In general, chert nodule distribution is a non-random stratigraphic event tending to occur parallel with the bedding planes. The great affinity between carbonate rocks and silica precipitation was in part explained experimentally by Kastner et al. (1977).
Origin and genesis theories

Based on mineralogical transformation, Wise and Weaver (1974) discuss 2 basic theories of nodular chert formation: 1) the maturation theory, and 2) the quartz precipitation theory. According to the maturation theory proposed by Heath and Moberly (1971, in Wise and Weander, 1974), chert nodule formation begins with precipitation of disordered cristobalite that in time converts to chalcedonic quartz from the nodule center toward the periphery.

The quartz precipitation theory was suggested by Lancelot (1973a). To this theory the driving mechanism of chert nodule formation is primary quartz precipitation, with disordered cristobalite representing a by-product of the process. The theory is applicable only for carbonate ooze sequences in which the chert mineralogy is exclusively represented by quartz. The steps are: precipitation of quartz, growth of the quartz grains along a quartzification front assuming a high permeability of the sediment, and precipitation of cristobalite at the periphery of the quartz nodule.

Analyzing the two theories concomitantly with their own analyses of the Kerguelen chert through scanning electron microscopy, Wise and Weaver (1974) concluded that chert nodule formation occurs as follows: 1) diffusion of supersaturated fluid with respect to silica; 2) precipitation of cristobalite lepispheres; 3) development of a dense nodule nucleus with concomitant dissolution and expulsion of host rock carbonate; 4) growth of nodule; 5) inversion of the cristobalite to quartz from the center toward the periphery; 6) pore space filling by fibrous chalcedony and cryptocrystalline quartz; and 7) growth until the depletion of dissolved silica.
Maliva and Siever (1989) describe three earlier models proposed for the origin of nodular chert, and propose themselves a fourth chert nodule genesis model: 1) the organic-matter oxidation model, 2) the hydrogen-sulfide oxidation model, 3) the mixing zone model, and their own model 4) force of crystallization-controlled replacement model.

**The organic-matter oxidation model** claims that the decomposition of organic matter may induce early diagenetic nodule formation. When organic matter is oxidized, the pore water CO₂ partial pressure increases driving an increase in the solubility of carbonate minerals. On the other hand the solubility of amorphous silica decreases with decreasing pressure. This model is applicable only for early diagenetic chert nodules, occurring as long as there is organic matter available for oxidation (Siever, 1962).

**The hydrogen-sulfide oxidation model** was proposed by Clayton (1986, in Maliva and Siever, 1989) to explain the flint nodule formation in the Upper Cretaceous Chalk of Western Europe. According to Clayton, the flint nodules formed at the oxic-anoxic boundaries within the sediment. Below the anoxic-oxic boundaries anaerobic bacterial sulfate reactions produce hydrogen sulfide (H₂S). If the sediment is clay-rich, the H₂S will combine with iron derived mainly from the clay minerals and will form iron sulfide. But if the sediment is clay-poor, the excess of H₂S will migrate toward the oxic-anoxic interface where it will combine with free molecules of oxygen according to the following reaction:

\[
H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+
\]
The released hydrogen ions will react energetically with the calcite rock resulting in intense calcite dissolution. At the site of this boundary the pH registers a significant decrease allowing the nucleation of opal-CT and formation of flint nodules.

**The mixing model** was proposed by Knauth (1979) who suggested that many nodular cherts in limestones have formed in mixed meteoric-marine coastal systems. According to this model, the mixing zone is characterized by diagenetic solutions that are undersaturated with respect to calcite and aragonite, and supersaturated with respect to silica. This geochemical environment is one where carbonate can be replaced by silica under equilibrium conditions. The assumptions of the model are: the meteoric water passes through a carbonate stack rich in debris of biogenic silica (“proportional to the amount of offshore silica production”, p. 274), a relatively high permeability of this zone, and the system is closed with respect to CO₂.

Assessing the three previous models, Maliva and Siever (1989) conclude that none of them are consistent with their observations obtained by studying six limestone sequences of different ages (Paleozoic, Mesozoic, and Cenozoic), nor with the different carbonate diagenetic histories. Their model is that calcite dissolution during chertification is restricted to areas of replacement and that the rate of silica precipitation has to be equal to the calcite dissolution rate. None of the previous three models explains these two necessary conditions in the formation of chert nodules and therefore they proposed the **force of crystallization-controlled replacement model**. This model is an expression of the force of crystallization combined with intergranular pressure solution. According to the model, the undersaturation with respect to calcite occurs only at silica-calcite contacts.
and therefore calcite dissolution is restricted to sites of silicification. The rate of silica precipitation is then equal to the rate of calcite dissolution. This model explains the formation of chert nodules in all environments and suggests that the only necessary condition for chert nodule formation is the presence of pore water supersaturated with respect to opal-CT or quartz. Maliva and Siever (1989) listed three properties of the host sediment as possible controls of chert nodule nucleation and the inter- and intra-bed distribution of chert nodules: 1) organic matter content, 2) porosity and permeability influencing the silica transport and molecular diffusion, and 3) biogenic-opal concentration.

The force of crystallization-controlled replacement model of Maliva and Siever (1989) explains only how individual crystal grains of quartz or opal-CT can replace carbonate grains. The formation of a chert nodule consists of silica nucleation and growth. Nucleation is not enough to generate nodule formation but has to be accompanied by nodule growth. Any crystal formation includes two steps: 1) the formation of crystal embryo by nucleation, and 2) the crystal growth. It is known that opal-CT nucleation during chertification is principally a heterogeneous nucleation on pre-existing opal-CT crystals (isomineralic heterogeneous nucleation; Maliva and Siever, 1989). If a nucleus forms in contact with some surface, commonly another solid, the nucleation process is called heterogenous nucleation in contrast with the homogenous nucleation in which nucleus form in the bulk of the solution (Drever, 1997). However, chert nodule formation is a combined process of heterogenous and homogenous nucleation of opal-CT lepispheres, followed by crystal growth (Maliva and Siever, 1989).
The growth of the silica phase generates a pressure at the silica-carbonate grain contact, driving an increase in the Gibbs free energy and therefore in the solubility of the calcite.

5.4. Time and temperature of chertification and the depth of formation

According to von Rad and Rösch (1974), a period of 70-90 My is necessary for an initial biogenic silica sediment to become a mature quartz chert. Kastner et al. (1977) suggested that siliceous oozes can transform into cherts in 25-50 My. If the in situ temperature is increased by different mechanisms, for example by burial, the period necessary for the completion of the opal-A to quartz transition decreases. For a temperature close to 30ºC, less than 30 My are necessary to form quartz (Heath, 1973, in von Rad and Röch, 1974). However, these estimates are valid only if the silica diagenetic history includes the whole maturation process: opal-A passes into cristobalite, that then passes into quartz. If quartz precipitates directly form solution during early diagenesis as suggested by Lancelot (1973a,b), the age estimates does not apply.

Chert nodules can represent early or late diagenetic events occurring at moderate to deep burial depth (Maliva and Siever, 1989). According to Maliva and Siever, the depth of chert nodule formation can be estimated by the presence of ghosts of intergranular pressure solution contacts and deformed grains. However, they assert that the minimum depth of burial and the time of chertification are uncertain. Studies have showed that opal-CT forms before significant burial at temperatures close to the temperature of the overlying bottom water, while granular microcrystalline quartz forms during deeper burial at higher temperatures (Wise and Weaver, 1974).
Data from the Miocene Monterey Formation of California suggest an even lower temperature for chert formation (Matheney and Knauth, 1993). Oxygen isotopic analysis of opal-CT and quartz suggest that silica diagenesis can occur at temperatures as low as 17° - 21°C, instead of 35° - 50°C as previously supposed to be for opal-CT, and 44° – 77°C for quartz, while $\delta^{18}O_{\text{pore water}} = 0\%$ (Murata et al., 1977; Pisciotto 1981). Based on the difference in formation temperatures of the opal-CT and quartz chert samples studied (differences of 40° - 50°C), Matheney and Knauth (1993) concluded that quartz chert formed from opal-CT at approximately 900 – 1000 m beneath the opal-CT transition zone, and that opal-CT formed from biogenic siliceous deposits at approximately 330 m beneath the sea floor. The assumptions of the model are: a geothermal gradient of 45.2°C/Km, a sea-floor temperature of 5°C, and the precipitation temperature of opal-CT of 20°C.
Chapter 6

METHODOLOGY

6.1. Data acquisition

Compilation of the worldwide Ordovician early diagenetic *in situ* chert deposits, such as bedded cherts, nodular cherts, and associated silicified oolites yielded a high resolution record at the epoch/series level and, in some cases, at the stage/age level. The compilation is based on several sources: a) online databases - GeoRef, Science Citation Index Expanded, geology journals, General Science Full Text, and Journal Storage, the scholarly journal archive (JSTOR), b) electronic journal archives such as the American Association of Petroleum Geologists Bulletin since 1917, and the CD-ROM archive of the Journal of Sedimentary Research between 1931 and 1997 and, c) printed articles. All the electronic sources (GeoRef to a lesser extent) present a predilection toward the North American literature, therefore a chert database built solely based on them would have presented a strong bias toward the North American continent (Tomescu and Kidder 2002). The bias was highly diminished toward an equitable balance between the North American continent and the rest of the world, by running Georef literature searches, and especially by analyzing numerous printed reports. The electronic search, using “chert” and “Ordovician” as keywords, yielded around 1900 articles, but only around 400 of those articles were relevant to this study. Approximately 100 articles obtained in addition to those found using electronic search engines produced useful results.
6.2. Data management

The chert database was designed, built and managed using FileMaker Pro software. The wide range of information collected is shown in Figure 6.1. The chert occurrences were plotted on Ordovician paleogeographic maps at the epoch level, using the Paleogeographic Information System/Mac™ program, version 5.0, designed by Ross (1997) based on the data of C.R. Scotese.

6.3. Data structure

Each chert occurrence included in the FileMaker database is characterized by four main types of information: 1) bibliographic references, 2) geographic localization, 3) geologic information and 4) comments (fig. 6.1). The bibliographic references section contains all the useful works analyzed and used in extracting any valuable data pertaining to the chert deposit considered. The geographic localization section includes the name of the area where the outcrop was described (country, region, town) and the geographic coordinates (the latitude and the longitude). The geologic information section comprises information about: a) the type of the chert deposit (nodular versus bedded versus oolitic chert) and its fossil content in siliceous organic remains, if such data was available; b) the name of the rock formation and, if applicable, that of higher rank stratigraphic units; c) the geologic age at the epoch level (Lower/Early, Middle and Upper/Late Ordovician), and even at higher resolution if data was available (e.g., Caradocian, Ashgillian); d) the associated lithologies and the stratigraphic position of the chert unit within the
**Figure 6.1:** FileMaker database entry sample.
sedimentary sequence; e) the depositional environment in which the chert deposit was formed, with the aim to differentiate lagoonal/peritidal from shelf and from slope/basin settings; f) tectonic and paleogeographic settings; and g) diagenetic features of the chert deposit. The workable database built for the present study and that has been used in quantifying the Ordovician chert distribution, includes only those Ordovician chert deposits of well defined age at the epoch level, or as strata bearing siliceous organisms but not defined as chert deposits.

All these various types of data linked to a chert deposit represent important information in assessing the determining factors that could lead to the accumulation and preservation of a certain type of chert deposit, in differentiating late from early diagenetic cherts, in evaluating the origin of a chert deposit, and etc. For example, closed, semi-open, epeiric, and foreland basins should be regarded differently from the point of view of chert formation because they are characterized by differences in specific features such as tectonic activity, volcanism, local sources of dissolved silica, and local oceanic circulation patterns.

6.4. Data manipulation

The main goals followed in assessing each chert deposit were: a) to establish the age at the epoch/series level (Lower versus Middle versus Upper Ordovician) and, where data were available data, at higher resolution, respectively at the stage/age level, especially for the Upper Ordovician (Caradocian versus Ashgillian); b) to identify the type of the chert deposit (nodular versus bedded cherts and subsequently silicified
oolites); c) to determine if a chert unit contains siliceous organic remains (siliceous sponge spicules and/or radiolarians); d) to recognize the depositional environment in which the chert deposit formed (peritidal/lagoonal versus shelf versus slope/basinal settings); and e) to infer the genesis of the chert units.

Some of the recorded chert occurrences were obtained from general descriptive sedimentologic and stratigraphic studies of particular areas and sedimentary sequences of interest. Many of these cases bore useful and reliable information pertaining to the cherts (age, origin, fossil content, and depositional environment). The remaining occurrences were collected from different geological studies focusing on problems other than the cherty formations. Most of these merely mentioned the chert occurrences and in these cases, various interpretations related to the goals of the study were made insofar as the available data allowed.

6.4.1. Interpreting the type of a chert deposit – nodular chert versus bedded chert

The types of in situ chert deposits considered and quantified herein are: nodular cherts, bedded cherts, deposits with both nodular and bedded cherts, and “type undetermined”. A priori, while compiling the data, the difference between bedded and nodular chert deposits was regarded mainly as a morphological difference, and only subordinately as a genetic difference. Laminated and stringer chert units have been considered bedded chert deposits, even though a layer/bed of rock usually refers to a thickness from a few inches to a few feet. The reason for this decision is that they still represent a layered sedimentary structure that occurs continuously on a certain surface. In
contrast, nodular morphology is a spatially-restricted chert occurrence within a host rock. Many terms are used in the literature to designate a chert deposit. These include: chert, flint, jasper, ooze, ribbon chert, radiolarian chert, spiculitic chert, chert with radiolarians and sponges, solid chert, chert in shales, chert lime, chert facies, cherty limestone, cherty dolomite, cherty carbonate, silicified limestone or dolomite, cherty argillite, cherty or chert shale, cherty mudstone, siliceous shales, siliceous bed, siliceous argillites, siliceous mudstones, and siliceous slate-like shale. The term “siliceous” is ambiguous and inconsistently used in the literature. For example, theoretically, siliceous shales refer to shales with very high silica content, as much as 85%, compared to the average shale that has around 58% silica (Pettijohn, 1975). By extrapolating the definition of the siliceous shales to any siliceous deposit type we should expect to have a sedimentary rock very rich in silica (much above 50%). On the other hand, Shepard (1973) and Duxbury et al. (2002), in analyzing the deep-sea sediments, define a siliceous ooze as a pelagic sediment that contains more than 30% biogenous material. Usually, the term “siliceous” is used as a descriptive word for any rock containing noticeable chert components. Hence, in some cases it was hard to discern a compact and well-individualized chert-bearing unit from a siliceous deposit that could bear siliceous particles disseminated within a host rock. Still, “siliceous” deposits containing siliceous skeletal remains could give valuable information about the silica secreting organisms living in the proximity of that depositional environment. Therefore, if a chert deposit was mentioned as a “siliceous” deposit with no further information regarding any siliceous faunal remains or the chert itself, the deposit was not taken into account as a “true” chert unit, but was still recorded as a putative chert
Many “siliceous” deposits are mentioned in the literature as radiolarian-bearing strata devoid of further details regarding the type of the chert deposit, depositional settings, and associated lithologies. Even though they are presumably bedded cherts, these chert facies were not classified as well-individualized chert deposits such as nodular and bedded cherts, but as an undetermined type, in order to prevent a supra-representation of one type of chert deposits over the others.

6.4.2. Interpreting the depositional environment of a chert deposit

Environmental interpretations of the chert occurrences belong to the original authors, and rely on paleogeography, lithologic associations, sedimentary structures and other paleobathymetric and environmental reconstruction criteria. Based on this information chert-forming environments were classified into three categories: 1) lagoonal/peritidal 2) shelf and, 3) slope/basin. Difficulty in determining the environment of some deposits is an ongoing problem (Murray, 1994), leaving some of the analyzed cherts in an undecided category (see Appendix).

The general paleogeography of the area in which sedimentation occurred provided useful information with respect to the depositional environment of the chert deposits. Within this context, clastic and carbonate platforms point to shallow water – shelf environments in miogeoclinal settings. Tectonically active settings in which volcanism is associated with clastic sediments and located away from the craton, suggest deeper water settings.
Lithologic associations, sedimentary structures and other depositional environment indicators have represented some of the best tools in evaluating the depositional setting. A peritidal/lagoonal depositional setting was inferred based on the presence of paleobathymetric indices represented in many cases by silicified oolites and/or, to a lesser extent, stromatolite associations. *Cruiziana* ichnofacies and hummocky cross-stratification indicate a shelf depositional setting (Pemberton et al., 1992; Pratt et al., 1992). Graptolite-rich shales, turbidite facies, flysch sequences, ophiolitic, pillow-basalt and volcaniclastic chert associations are ascribed to basin/slope environments (Aubouin, 1965; Grunau, 1965; Murchey et al., 1983). Bentonites, the chemical alteration product of volcanic ash, might represent significant silica sources due to their high content of clay minerals, covering vast areas. Consequently, some bedded chert deposits have been discovered associated in the geologic record with volcanic ash layers. Owing to the fact that bentonites do not reflect local environmental conditions, bedded cherts associated with them were not interpreted in terms of depositional environment in which they have been found.

**6.4.3. Biases in designating a chert deposit type and the corresponding depositional environment in which it formed**

It is tempting to classify any radiolarian-bearing chert as bedded and any siliceous sponge-bearing chert as nodular, but it has been demonstrated (Coniglio, 1987, for the Cow Head Group) that both types of siliceous skeletal remains can occur in both bedded chert and nodular chert deposits. Therefore no such assumptions were made in the absence of other pertinent information.
Using the type of the host rock as an indicator for the depositional environment in which cherts occur, introduces another strong bias. In the case of limestone host rocks, chert deposits tend to be classified as nodular, shallow water, or shelf deposits. At the other end of the spectrum, if the host rock is shale, especially black shale with graptolitic fauna, the tendency is to designate the chert deposit as bedded, deep water, or basinal (e.g., the geosynclinal cherts of Pettijohn, 1975). Biogenic components and pelagic clays dominate many deep-sea sediments (Kennett, 1982). However, even though these associations between host rocks and depositional environments are in most of the cases consistent, some exceptions to the rule are inevitable.

Pettijohn (1975) described bedded cherts, termed cratonic cherts, from shallow water limestone sequences, which he considered stable shelf associations (p. 401). Also, a siliceous argillite deposit can accumulate in various settings extending from shallow water shelves to deep-water environments (Murray 1994; Girty et al., 1996). Murray (1994) asserts, “general criteria by which depositional environments of cherts can be determined are not yet available” (p. 213). Coniglio (1987) in describing the chert units of the Cow Head Group of western Newfoundland, pointed to the presence of chert nodules in shale sequences. Berry and Wilde (1978) in analyzing lower Paleozoic black shales concluded that they can form on shelves, slopes and in deep-sea settings. Their differentiation is possible by integrating paleotectonic and associated lithologic information. For example, a eugeoclinal tectonic setting correlated with volcanic rocks indicates deep-sea environments. This tectonic setting could also be a back-arc basin (e.g. the Sea of Japan) which is of shelf depth. I am not aware of any chert in back-arc basins,
perhaps because of siliciclastic dilution. In the absence of other types of evidence, no depositional environment or chert deposit type was assigned.

**6.4.4. The fossil content analysis**

No assumptions were made regarding the content of siliceous organic remains. Therefore, only explicit information from the analyzed works has been taken into consideration in assessing the siliceous fossil content of the rocks.

**6.4.5. The geologic age adjustment**

A crucial requirement for compiling worldwide chert occurrences with epoch-level resolution is the integration of different Ordovician stratigraphic scales – British, Scandinavian, Russian, North American, Chinese, Australian (fig. 6.2.). In order to compare and interpret worldwide chert deposits within a consistent temporal framework at the epoch/series level, and even at a higher temporal resolution, a unifying correlative Ordovician stratigraphic scale was built and used (based on Nikitin et al., 1986; Harland et al., 1990; Webby, 1995; Harris et al., 1995; Palmer and Geissman, 1999; Veevers, 2000; Ferguson and Fanning, 2002). The Ordovician time scale used herein as a template is the “1999 Geologic Time Scale” of the Geological Society of America (Palmer and Geissman, 1999) that in turn relies on the British stratigraphic nomenclature.

Potential for confusion arises at the stage level in the Upper Ordovician. This epoch includes the Caradocian and Ashgillian stages. Unfortunately, the epoch placement of the Caradocian stage has not been consistent through time. Presently it is widely
Figure 6.2: Ordovician correlation chart used in this study (compiled from Nikitin et al., 1986, 1991; Harland et al., 1990; Harris et al., 1995; Webby, 1995; Palmer and Geissman, 1999; Veevers, 2000; Ferguson and Fanning, 2002).
accepted that the Caradocian represents the basal stage of the Upper Ordovician epoch. However, until less than one decade ago, the American geological literature considered the Caradocian stage as the uppermost stage of the Middle Ordovician. Even some of the most recent works that deal with the Ordovician use this stratigraphic system. One of the main problems encountered during this study in terms of age, was facing published Ordovician reports that did not define the stratigraphic system used. Hence, a late Middle Ordovician chert deposit in the old stratigraphic system is an early Upper Ordovician deposit according to the new stratigraphic system. In concordance with the newest geochronological scale for the Ordovician period (Palmer and Geissman, 1999), the duration of the Caradocian stage was 9 My (458 Ma – 449 Ma). Including these 9 million years into the Middle or the Upper Ordovician changes significantly the duration of the two epochs. Furthermore, analysis and interpretation of the abundance of the same rock type at a worldwide scale for periods of time with coincident names but different age ranges can yield considerable errors.

6.4.6. The chert occurrence quantification guidelines – over-representation versus under-representation of the Ordovician chert abundance at the epoch level

The basic geological stratigraphic unit, that is, the formation, represents the quantifying unit used in this study: one chert-bearing formation is counted as one chert occurrence. At the epoch level, the same one chert-bearing formation spanning over two Ordovician epochs or even the whole Ordovician, can result theoretically in two and respectively three chert occurrences. Considering any deposit of suspicious age as a
deposit that spans multiple epochs, and counting it as such, could eliminate the errors, but at the same time it would generate a over-representation of chert. The risk of such a chert over-representation is even greater if we consider that one of the most problematic Ordovician age limits at epoch level is that between the Middle and the Upper Ordovician, a time demonstrated herein as a transition from a period poor in chert formation to a very rich chert deposition period. In view of these facts, the chert deposits of uncertain or widely spread age were eliminated, and only those with well defined epoch or stage ages were considered in the quantitative results, even though this decision results in an under-estimation of the worldwide Ordovician chert abundance.

Each formation was considered as only one chert occurrence, even for formations with more than one chert members. If a group had more than one chert formation, as many chert occurrences as defined formations were taken into account. Additionally, the same formation can correspond to two different adjacent depositional environments (lagoonal/peritidal and shelf or shelf and slope/basinal settings), in which case it resulted in two chert occurrences, each corresponding to one of the two depositional settings. The chert deposits associated with bentonites were not counted in the quantification phase of the depositional environment analysis, and are not included in chert abundance plots. They were nevertheless recorded as bedded chert deposits.

6.5. Pitfalls/Problems of a study compiling data from published reports:

In any compilation of data from multiple sources, inconsistencies arise. Some of the problems encountered in this study are listed below.
1) Older rocks are less represented in the rock record and therefore an extrapolation of the Ordovician chert deposits with the aim to compare their abundance with those of other geological periods could generate errors. Normalization to outcrop area can lessen the impact of this problem at the system level, but to date outcrop area has not been calculated at the epoch and stage level for the Ordovician.

2) Some chert deposits are less well documented than others, resulting in sparse information regarding the age, stratigraphy, sedimentology, faunal content, depositional environments, and etc.

3) The lack of information of the published data relative to the definition of certain geological notions whose connotations may largely vary, with strong implications on interpretation (e.g., the Ordovician time scale used considering that it has been changed through time, the common shallow- vs. deep-water setting ambiguity with respect to the basin morphology and implicitly the basin type).

4) Some stratigraphic intervals are easier to date than others depending mainly on the type of faunal content.

5) Some paleoenvironmental settings are characterized by particular factors (e.g., starved, closed basins) and therefore certain inter-basinal correlations are pointless. Moreover, the formation of chert deposits within such localized-conditions may not follow a general chert genesis mechanism, but they are useful because they evidence endemic conditions and the amplitude (at the basin and even global level) of a peculiar mechanism responsible for their formation.
6) Stratigraphic inconsistencies regarding definitions of formations and groups lead to some artificial variations in chert abundance. For example, an over-estimation of the chert occurrences is possible when a sedimentary unit with multiple chert horizons was considered a group and not a formation (e.g., the Plattin Group with three chert formations resulting in three chert occurrences; before it was considered a formation and not a group, and would have been recorded as only one chert occurrence).

7) The paleogeographic position of some micro-continents is still debated and thus the data interpretation with respect to the paleolatitudinal distribution of the occurrences encounters errors. An eloquent example is that represented by the Argentine Precordillera which is considered either as part a of Gondwana that collided with Laurentia during the Ordovician (Dalla Salda et al., 1992), or as a microcontinent that rifted from the Ouachita embayment of North American Laurentia during the Cambrian and collided with Gondwana during the Ordovician (Thomas and Astini, 1996).

8) The worldwide rock sequences are unequally studied due to objective impediments (relief, scientific potential, political regimes, and etc.), and thus the absence of a geological character of certain geographical areas might reflect a lack of knowledge and not a physical absence. A prime and very strong bias of a worldwide compilation study is represented by the geographic component.

9) The published information easily accessible is strongly biased toward the North American continent, and thus geological studies achieved in regions with a weak international communication system are highly underrepresented in databases (e.g., South America, Western Europe, Asia, Eastern Europe, and etc.). This bias is even larger if we
consider that these modern regions were representing different paleocontinents, paleolatitudes, and very likely different physical and biologic ecosystems.

6.6. The usefulness of a study compiling data from published reports:

1) This study integrates the biotic component with the abiotic physico-chemical factors as interconnected parts of the same Earth system.

2) Lithologic compilations offer a general image of the worldwide Ordovician early diagenetic chert occurrences such as bedded, nodular cherts, and silicified oolites.

3) Paleogeographic chert distribution can be used to infer paleo-upwelling areas and/or high endogenous and exogenous dissolved silica and other nutrient inputs that could lead to the organic, inorganic or organic but induced inorganically chert formation. The study can also offer a good image of the Ordovician shelf areas suggesting the spatial position of the paleo-shorelines.

4) Based on depositional settings, siliceous organism migration patterns, as well as potential factors responsible for the formation, accumulation, and preservation of chert units can be inferred.

5) Local and general oceanic circulation patterns can be distinguished pointing toward local and global events.

6) Possible source rocks and hydrocarbon reservoirs could be identified.

7) The study offers the possibility of not only intra-basinal correlations, but also of inter-basinal stratigraphic correlations.
Chapter 7

RESULTS

The comprehensive compilation of Ordovician cherts yielded 191 deposits covering 5 continents: North America, South America, Europe, Asia, and Australia. The appendix includes all chert formations that have been found, regardless of the degree of certainty of their age. However, the analysis of chert abundance includes only the 161 chert deposits with ages well defined at the epoch level or higher resolution. The descriptive information included in the appendix represents a concise statement of the information in the FileMaker database that is available upon request.

7.1. Epoch - level temporal trend in the chert abundance

Figure 7.1A illustrates the epoch-level chert distribution expressed as both raw data (counts) and time-normalized data (Table 7.1). Both representations show the same pattern throughout the three Ordovician epochs: abundance peaks for the Lower and Upper Ordovician, contrasting with a sharp decline during the Middle Ordovician. More than half of the Upper Ordovician chert deposits (approximately 51%) are Caradocian, 14 deposits are attested as Ashgillian (19%), and the rest of 22 deposits (30%), have undifferentiated Upper Ordovician age (fig. 7.1B). Time normalized data (Table 7.1) shows that the Caradocian chert peak stands as the highest Ordovician chert abundance.
Table 7.1: Temporal distribution of the chert deposits at epoch and age/stage level. Raw and time-normalized data.

<table>
<thead>
<tr>
<th>Epoch</th>
<th>No.</th>
<th>Normalized data to time N/Ma</th>
<th>Duration Ma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ashgillian</td>
<td>14</td>
<td>2.3</td>
<td>6</td>
</tr>
<tr>
<td>Caradocian</td>
<td>38</td>
<td>4.9</td>
<td>9</td>
</tr>
<tr>
<td>Middle</td>
<td>24</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>Lower</td>
<td>63</td>
<td>3.2</td>
<td>20</td>
</tr>
</tbody>
</table>

Total = 161

* the number represents 14 (Ashillian) + 38 (Caradocian) + 22 (undifferentiated Upper Ordovician)

Figure 7.1: Ordovician distribution of chert deposits. Numbers next to dots represent number of cherts per million years. (A) Epoch level distribution: raw (N) and time-normalized data (N/Ma). (B) Stage level distribution expressed as percentages from a total of 74 chert deposits.
interval, with 4.2 chert deposits per 1 million years. If all of the undifferentiated Upper Ordovician cherts would prove to be Ashgillian, then the maximum chert abundance would shift toward the Ashgillian. However, this is not likely, because stratigraphic information on these cherts suggests that some of them may have extended over both the Caradocian and Ashgillian.

In concordance with the Late Ordovician short duration glaciation theory (Brenchley et al., 1994), the two stages of the Upper Ordovician represent geological periods of contrasting climates: the Caradocian corresponds to an ice free world whereas the Ashgillian was an icehouse world. Hence, the differentiation of the Upper Ordovician cherts at the stage level proves is significant.

7.2. Epoch-level temporal trend in chert types

The chert-bearing formations were differentiated into: i) nodular cherts, ii) bedded cherts, and iii) formations with both nodular and bedded cherts (Table 7.2). Figure 7.2A illustrates the epoch-level distribution in both raw and time-normalized absolute counts for the three types of chert deposits, and shows a trend similar to that of the chert abundance at the epoch-level: Lower and Upper Ordovician peaks – the latter steeper than the former – separated by a Middle Ordovician drop. Nodular cherts decline in relative abundance from the Lower to the Upper Ordovician while the number of bedded cherts increases (fig. 7.2B), revealing a significant facies change in chert type through the Ordovician.
Table 7.2: Temporal distribution of the chert deposit types at epoch (A) and stage (B) level. Raw, time-normalized, and relative abundance data. 17* = 3 + 10 + 4 (undifferentiated Upper Ordovician); 28* = 2 + 5 + 11 (undifferentiated Upper Ordovician); 16* = 6 + 7 + 3 (undifferentiated Upper Ordovician).

<table>
<thead>
<tr>
<th>Epoch</th>
<th>Nodular cherts</th>
<th>Bedded cherts</th>
<th>Nodular &amp; bedded cherts</th>
<th>Undetermined</th>
<th>Total N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>%</td>
<td>N/Ma</td>
<td>N</td>
<td>%</td>
</tr>
<tr>
<td>Upper</td>
<td>17</td>
<td>23</td>
<td>1.1</td>
<td>28</td>
<td>37.8</td>
</tr>
<tr>
<td></td>
<td>74</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Middle</td>
<td>4</td>
<td>16.7</td>
<td>0.3</td>
<td>9</td>
<td>37.5</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower</td>
<td>21</td>
<td>33.3</td>
<td>1.1</td>
<td>20</td>
<td>31.7</td>
</tr>
<tr>
<td></td>
<td>63</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Epoch</th>
<th>Stage</th>
<th>Nodular cherts</th>
<th>Bedded cherts</th>
<th>Nodular &amp; bedded</th>
<th>Undetermined</th>
<th>Total N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>N</td>
<td>N/Ma</td>
<td>N</td>
<td>N/Ma</td>
<td>N</td>
</tr>
<tr>
<td>Upper</td>
<td>Ashgillian</td>
<td>3</td>
<td>0.5</td>
<td>17*</td>
<td>1.1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Caradocian</td>
<td>10</td>
<td>1.1</td>
<td>15</td>
<td>1.6</td>
<td>7</td>
</tr>
<tr>
<td>Middle</td>
<td>2</td>
<td>0.2</td>
<td>5</td>
<td>0.4</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>Lower</td>
<td>21</td>
<td>1.1</td>
<td>21</td>
<td>1.1</td>
<td>17</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>161</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Figure 7.2A:** Temporal distribution of chert deposit types at the epoch level. Raw (N) and time-normalized (N/Ma) data. Numbers next to dots represent number of cherts per million years.

**Figure 7.2B:** Temporal variation of the relative abundance of chert deposit types at the epoch level (light gray - nodular cherts; medium gray - bedded cherts; dark gray - deposits with nodular and bedded cherts; white - undefined chert deposits).
7.3. The spatio-temporal distribution of chert occurrences

Table 7.3 and Figure 7.3 display the variation in time, space and depositional environment of both raw and normalized count data through the Ordovician. The variation of the normalized data parallels that of the raw data. The main Ordovician chert deposition sites are plotted on paleogeographic maps (fig. 7.4, 7.5, and 7.6). The epoch-level distribution of these sites along with their depositional environments reveal temporal, spatial, and evolutionary patterns in silica accumulation throughout the Ordovician.

7.3.1. Lower Ordovician

Chert depositional environments during the Lower Ordovician are dominantly shallow water carbonate settings in which most silica burial occurred as peritidal silicified oolites, and as nodular and bedded cherts that are evenly dispersed between peritidal/lagoonal and shelf environments. All peritidal/lagoonal chert occurrences are silicified oolite-bearing formations. On the other hand, the slope/basin chert-bearing sequences (a quarter of the Lower Ordovician total) indicate that deep-water silica deposition represented a quite significant component of silica burial during this time as well. The deep water chert facies are dominated by bedded cherts supplemented by nodular cherts (Table 7.4, fig. 7.7A).

The paleolatitudinal range of the Lower Ordovician cherts (fig. 7.4) extends from the equator up to 45 – 50° north and south. The deep-water cherts, confined principally to lower paleolatitudes (0 - 30°), cluster on the southeastern margin of Laurentia (in modern Canada and Great Britain), plus a few on the Kazakhstan block and Gondwana.
Table 7.3: Temporal (A epoch level; B stage level) and spatial (Onshore – Offshore) distribution of the chert deposits. Raw and time-normalized data. $33^* = 17 + 9 + 7$ (undifferentiated Upper Ordovician); $38^* = 19 + 4 + 15$ (undifferentiated Upper Ordovician); * the total 171 is different from the total 161 (Tab. 7.1) because a couple of chert deposits have been assigned to multiple depositional environments. Raw, relative abundance, and time-normalized data.

<table>
<thead>
<tr>
<th>A</th>
<th>Epoch</th>
<th>Peritidal/Lagoonal</th>
<th>Shelf</th>
<th>Slope/Basin</th>
<th>Undecided</th>
<th>Total N*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>%</td>
<td>N/Ma</td>
<td>N</td>
<td>%</td>
<td>N/Ma</td>
</tr>
<tr>
<td>---</td>
<td>-------</td>
<td>-------</td>
<td>------</td>
<td>----</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>Upper</td>
<td>3</td>
<td>3.8</td>
<td>0.2</td>
<td>33</td>
<td>42.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Middle</td>
<td>2</td>
<td>7.7</td>
<td>0.2</td>
<td>5</td>
<td>19.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Lower</td>
<td>21</td>
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<td>21</td>
<td>31.3</td>
<td>1.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B</th>
<th>Epoch</th>
<th>Peritidal/Lagoonal</th>
<th>Shelf</th>
<th>Slope/Basin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>N/Ma</td>
<td>N</td>
<td>N/Ma</td>
</tr>
<tr>
<td>---</td>
<td>------------</td>
<td>-------------------</td>
<td>-------</td>
<td>-------------</td>
</tr>
<tr>
<td>Upper Ashgillian</td>
<td>0</td>
<td>0</td>
<td>9</td>
<td>33*</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.2</td>
<td>17</td>
<td>1.9</td>
</tr>
<tr>
<td>Caradocian</td>
<td>2</td>
<td>0.2</td>
<td>5</td>
<td>0.4</td>
</tr>
<tr>
<td>Middle</td>
<td>21</td>
<td>1.1</td>
<td>21</td>
<td>1.1</td>
</tr>
<tr>
<td>Lower</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 7.3: Ordovician spatio-temporal distribution of chert occurrences (percentages and time-normalized data). The dots represent number of cherts per million years.
Figure 7.4: Paleogeographic distribution of Lower Ordovician cherts
Figure 7.4.: Paleogeographic distribution of Lower Ordovician cherts. Red bullets represent peritidal/lagoonal cherts; black bullets represent shelf cherts; stars represent slope/basinal cherts; dotted bullets are cherts bearing siliceous sponge spicules from Argentina, not included in the Appendix; diamonds represent cherts whose depositional environment is unknown. Solid arrows represent cold currents and dashed arrows represent warm currents (after Berry et al., 1995). The paleogeography was obtained using the PGIS/Mac™ software, version 5.0 (Ross, 1997)
Figure 7.5: Paleogeographic distribution of Middle Ordovician cherts
**Figure 7.5.:** Paleogeographic distribution of Middle Ordovician cherts. Red bullets represent peritidal/lagoonal cherts; black bullets represent shelf cherts; stars represent slope/basinal cherts; diamonds represent cherts whose depositional environment is unknown. Solid arrows represent cold currents and dashed arrows represent warm currents (after Berry et al., 1995). The paleo-gography was obtained using the PGIS/Mac™ software, version 5.0 (Ross, 1997).
Figure 7.6: Paleogeographic distribution of Upper Ordovician cherts
**Figure 7.6.** Paleogeographic distribution of Upper Ordovician cherts. Red bullets represent peritidal/lagoonal cherts; black bullets represent shelf cherts; stars represent slope/basinal cherts; diamonds represent cherts whose depositional environment is unknown. Solid arrows represent cold currents and dashed arrows represent warm currents (after Berry et al., 1995). The paleogeography was obtained using the PGIS/Mac™ software, version 5.0 (Ross, 1997).
Table 7.4: Distribution of the chert deposit types by epoch and depositional environment (TL – TM – TU = total Lower – total Middle – total Upper; e.g. 21 - 2 - 3). Raw data.

<table>
<thead>
<tr>
<th>Epoch</th>
<th>Peritidal / Lagoonal</th>
<th>Shelf</th>
<th>Slope/Basin</th>
<th>Undefined</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>16</td>
</tr>
<tr>
<td>Middle</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Lower</td>
<td>13</td>
<td>0</td>
<td>7</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>21-2-3</td>
<td>21-5-33</td>
<td>17-12-38</td>
<td>8-7-4</td>
<td>171</td>
</tr>
</tbody>
</table>
Figure 7.7: Relationships between chert types and depositional environments over time. Relative abundance data. (A) Lower; (B) Middle; (C) Upper Ordovician.
supercontinent (in Australia and New Zealand). Only one slope/basin chert deposit occurs beyond 30° south on Gondwana (Bolivia). The mid-latitudinal cherts (30° - 50°), which are represented mainly by shelf deposits, are located north of the equator on Gondwana (China and Korea). All the peritidal/lagoonal cherts are restricted to Laurentia (the south-southwestern margin) at low paleolatitudes, all occur in the USA, except for one in Great Britain.

Overall, the trend of the silica burial during the Lower Ordovician is dominated by low paleolatitudinal cherts (90.5%), followed by mid-latitudinal cherts (9.5%; Table 7.5). Geographically, approximately 75% of the total Lower Ordovician cherts occur on Laurentia, averaging 2.4 deposits per My (Table 7.6).

7.3.2. Middle Ordovician

During the Middle Ordovician, a pronounced decline in silica burial occurred, coeval with a significant migration of chert deposits from shallow settings, peritidal/lagoonal and respectively shelf, toward slope/basin sites (fig. 7.3). Middle Ordovician deep-water environments represent the dominant locus in silica accumulation, mainly as bedded cherts (fig. 7.7B, Table 7.4). The formation of silicified oolites almost ceases (Table 7.7), and that of the shelf cherts strongly diminishes. A slight decrease is recorded in the abundance of mid-latitudinal cherts concomitant with an increase of the low-latitudinal ones (Table 7.5). Paleogeographically, the Laurentia data reveal a decrease in the chert abundance by approximately 20%, or by more than a half considering the time-normalized data (Table 7.6), most of the occurrences again on the southern margin (fig. 7.5). Only the Kazakhstan block registers a slight increase in the
Table 7.5: Temporal trends in the paleolatitudinal distribution of Ordovician silica burial. Raw and relative abundance data.

<table>
<thead>
<tr>
<th>Epoch</th>
<th>0 - 30°</th>
<th>30 - 60°</th>
<th>&gt; 60°</th>
<th>Total N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>%</td>
<td>N</td>
<td>%</td>
</tr>
<tr>
<td>Upper</td>
<td>71</td>
<td>96</td>
<td>1</td>
<td>1.3</td>
</tr>
<tr>
<td>Middle</td>
<td>22</td>
<td>91.7</td>
<td>2</td>
<td>8.3</td>
</tr>
<tr>
<td>Lower</td>
<td>57</td>
<td>90.5</td>
<td>6</td>
<td>9.5</td>
</tr>
</tbody>
</table>

161

chert abundance. The geographic distribution of deep-water cherts follows the same patterns as that characteristic for the Lower Ordovician ones, that is, the southeastern margin of Laurentia, the Kazakhstan microcontinent, and Australia.

7.3.3. Upper Ordovician

The Upper Ordovician silica burial as recorded by numbers of chert deposits surpasses by far the two older Ordovician epochs (fig. 7.3). Both shelf and slope/basinal deposits record a significant increase compared to both previous epochs, Lower and Middle Ordovician. A balance between shelf and deep-water cherts, that was tipped heavily toward deep-water cherts in the mid-Ordovician, is restored. The few peritidal/lagoonal chert facies hosting silicified oolites all occur in the Caradocian (Table 7.6). The first high latitude and north margin Laurentian cherts appeared in this time
Table 7.6: The temporal and geographical distribution of the chert deposits. Raw, relative abundance, and time-normalized data.

<table>
<thead>
<tr>
<th>Epoch</th>
<th>Laurentia</th>
<th>Gondwana &amp; close blocks</th>
<th>Kazakhstan block</th>
<th>Others</th>
<th>Total</th>
<th>Duration Ma</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>N/Ma</td>
<td>%</td>
<td>N</td>
<td>N/Ma</td>
<td>%</td>
</tr>
<tr>
<td>Upper*</td>
<td>9</td>
<td>1.5</td>
<td>64.3</td>
<td>3</td>
<td>0.2</td>
<td>21.4</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>3.1</td>
<td>73.7</td>
<td>9</td>
<td>1</td>
<td>23.7</td>
</tr>
<tr>
<td>Middle</td>
<td>13</td>
<td>1.1</td>
<td>54.2</td>
<td>5</td>
<td>0.4</td>
<td>20.8</td>
</tr>
<tr>
<td>Lower</td>
<td>47</td>
<td>2.4</td>
<td>74.6</td>
<td>13</td>
<td>0.7</td>
<td>20.6</td>
</tr>
</tbody>
</table>

* The Upper Ordovician cherts do not include the deposits whose age is either undifferentiated Upper Ordovician (12 deposits) or span the whole Upper Ordovician (10 deposits). The numbers were obtained from Appendix.

Table 7.7: Temporal distribution of Ordovician silicified oolites. Raw and time-normalized data.

<table>
<thead>
<tr>
<th>Epoch</th>
<th>Stage</th>
<th>N</th>
<th>N/Ma</th>
<th>Ma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper</td>
<td>Ashgillian</td>
<td>0</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Caradocian</td>
<td>3</td>
<td>0.3</td>
<td>9</td>
</tr>
<tr>
<td>Middle</td>
<td>2</td>
<td>0.16</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Lower</td>
<td>12</td>
<td>0.6</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>
interval (fig. 7.6; Table 7.5). The low latitude deposits continued to dominate the system. Deep-basin deposits center around Laurentia and numerous Gondwanan deep chert facies are identified in Australia. Most of the shelf deposits are limited to the southern and western margins of Laurasia. The examination of the spatial distribution of the cherts by continents shows that Caradocian cherts increased by almost a factor of three in Laurentia, and doubled in Gondwana and the proximal microcontinents (Table 7.6).

7.4. Chert type - depositional environment relationship over time

Figure 7.7 illustrates the relationship between the chert deposit types and the depositional environment in which they formed (Table 7.4). Nodular cherts dominate the peritidal/lagoonal and shelf settings, in contrast to the bedded cherts that dominate deep-water habitats. This relationship between chert type and depositional environment persists throughout the Ordovician: shelf settings are characterized by evenly dispersed nodular and bedded cherts within a carbonate environment, whereas deep-water settings are clearly dominated by bedded cherts within a siliciclastic environment. Nodular cherts can nonetheless occur in slope/basinal settings, and bedded cherts in shelf and even shallower environments. By the Middle Ordovician the silicified oolites almost disappear from the chert system.
7.5. The temporal and spatial distribution of the Ordovician silica secreting organisms present in chert deposits

More than a third of the chert occurrences (37.2%) contain siliceous skeletal remains (Table 7.8). The majority host radiolarians, others siliceous sponge fragments, and a few contain both types (fig. 7.8).

A look at the depositional environments of cherts bearing siliceous organisms reveals that during the Early Ordovician both radiolarians and siliceous sponges inhabited deep as well as shallow water niches (Table 7.9Ab). During the Lower Ordovician most of the radiolarian remains are hosted by slope/basin bedded cherts. The siliceous sponge remains have been found only in nodular and bedded chert type. Most sponge-bearing cherts are found in shallow-water sedimentary sequences (peritidal/lagoonal and shelf), and only two, or possibly three, slope/basin cherts associated with ophiolitic successions preserve siliceous sponges (e.g., the Burubaital Formation in Kazakhstan, the lower part of the Cow Head Group of Newfoundland, and possibly the Durness Limestone of Scotland). Overall, siliceous sponges are associated with carbonate rocks, and radiolarians with clastic sediments such as shales, graptolitic black shales, and ophiolitic complexes.

During the Middle Ordovician, more than half of the chert occurrences contain siliceous skeletal remains (Table 7.8), the majority represented by radiolarians. Radiolarian-bearing formations are exclusively bedded chert from deep-water sequences (Table 7.9 Ba and Bb). The few siliceous sponge-bearing formations are both shallow and deep water cherts of bedded and nodular types.
Table 7.8: Epoch level distribution of chert deposits with siliceous skeletal remains. *SSR = siliceous skeletal remains. Raw and relative abundance data.

<table>
<thead>
<tr>
<th>Epoch</th>
<th>Radiolarians</th>
<th>Sponges</th>
<th>Radiolarians &amp; Sponges</th>
<th>Total fm. with SSR*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>%</td>
<td>N</td>
<td>%</td>
</tr>
<tr>
<td>Upper</td>
<td>19</td>
<td>25.7</td>
<td>5</td>
<td>6.8</td>
</tr>
<tr>
<td>Middle</td>
<td>10</td>
<td>41.7</td>
<td>2</td>
<td>8.3</td>
</tr>
<tr>
<td>Lower</td>
<td>8</td>
<td>12.7</td>
<td>6</td>
<td>9.5</td>
</tr>
<tr>
<td>Total</td>
<td>37</td>
<td>23</td>
<td>13</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 7.8: Epoch-level variation of the relative abundance of chert formations that bear siliceous skeletal remains (deposits with radiolarians, deposits with siliceous sponges, and deposits with both radiolarians and siliceous sponges).
Table 7.9: Relationships between chert deposit types and types of siliceous skeletal remains for the Lower (Aa), Middle (Ba), and Upper Ordovician (Ca). Relationships between depositional environments and types of siliceous skeletal remain for the Lower (Ab), Middle (Bb), and Upper Ordovician (Cb). Absolute counts.

**Lower Ordovician**

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>B</th>
<th>N&amp;B</th>
<th>U</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiolarians</td>
<td>6</td>
<td>2</td>
<td></td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Sponges</td>
<td>2</td>
<td></td>
<td>2</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Both</td>
<td>1</td>
<td>2</td>
<td></td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

**Middle Ordovician**

<table>
<thead>
<tr>
<th></th>
<th>P/L</th>
<th>Shelf</th>
<th>S/B</th>
<th>U</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiolarians</td>
<td>2</td>
<td>7</td>
<td></td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Sponges</td>
<td>3</td>
<td>3</td>
<td></td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Both</td>
<td>1</td>
<td>2</td>
<td></td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

**Table 7.9 (continued)**

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>B</th>
<th>N&amp;B</th>
<th>U</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiolarians</td>
<td>6</td>
<td>1</td>
<td>3</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Sponges</td>
<td>2</td>
<td></td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Both</td>
<td>1</td>
<td>1</td>
<td></td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

**Middle Ordovician**

<table>
<thead>
<tr>
<th></th>
<th>P/L</th>
<th>Shelf</th>
<th>S/B</th>
<th>U</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiolarians</td>
<td>8</td>
<td>2</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Sponges</td>
<td>1/2</td>
<td>1</td>
<td>1/2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Both</td>
<td>2</td>
<td></td>
<td></td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>
Siliceous skeletal remains (SSR), mostly radiolarians, occur in 28 Upper Ordovician chert facies. Here too, radiolarians characterize deep-water sedimentary successions, whereas siliceous sponges are found in nodular and bedded cherts in either shelf or slope/basin settings.

The Ordovician formations with siliceous skeletal remains reveals a clear affinity between radiolarians and deep-water bedded cherts, in contrast to the siliceous sponge remains that can occur in any type of chert deposit (bedded or nodular) and depositional environment (deep or shallow water) (Table 7.9). From the Lower to the Upper Ordovician, formations bearing siliceous organisms change from mainly
peritidal/lagoonal settings to shelf/basin settings, so that by the Upper Ordovician there is
no evidence of peritidal/lagoonal chert formations bearing siliceous sponge skeletal
remains. Radiolarian-bearing formations also exhibit trend from shelf to slope/basin
settings by the Middle Ordovician, so that in the Middle and Upper Ordovician
radiolarians are almost exclusively preserved in deep-water sedimentary sequences.

Most nodular cherts are hosted by carbonate rocks such as limestones and
dolomites, and most bedded cherts by shales. This finding supports the view according to
which some authors make a difference between the two types based solely on the host
rock – the chert deposits occurring in carbonate host rocks being considered nodular
cherts, and the chert deposits occurring in shale sequences being considered bedded
cherts (Wise and Weaver, 1974).

7.6. Testing the significance of associations between the type of siliceous
skeletal remains, chert deposit styles, and depositional environments

The chi-square test is a statistic used for testing the significance of certain
distributions (the distribution between the columns and the rows of a table) or in other
words for comparing observed data with data expected to be obtained according to a
specific hypothesis. The null hypothesis (Ho) states that there is no significant difference
between the expected and observed data. If any expected value of any category is less
than 5, a correction has to be applied. In this respect, Yates’ correction represents an
arbitrary adjustment to the chi-square test when applied to tables with one or more cells
with frequencies less than 5 (e.g., the expected values of the R-P/L and SS-P cells in fig. 7.10). However it can be applied only to 2x2 tables.

The Chi-square test was applied to the following distributions: 1) chert deposit type (nodular vs. bedded cherts) and silica secreting organisms (radiolarians vs. siliceous sponges) (fig. 7.9); 2) the silica secreting organisms (radiolarians vs. siliceous sponges) and the depositional environment (shallow represented by peritidal/lagoonal together with shelf vs. slope/basinal) (fig. 7.11); and 3) the chert deposit type (nodular vs. bedded cherts) and the depositional environment (peritidal/lagoonal vs. shelf vs. slope/basinal) (fig. 7.10). All of the distributions proved to characterize statistically significant associations between the tested pairs of variables.

7.7. Evaluation of the efficiency of the method

The global compilation of Ordovician chert occurrences undertaken in this study has several characteristics that single it out among other such attempts, both in its approach, and the results generated. The approach which targeted only one geological period, the Ordovician, allowed extensive data gathering and detailed processing of these data with respect to multiple aspects: the chert deposit type, depositional environment, fossil content with respect to silica secreting organisms, and age. The results thus obtain offer a solid empirical base for tackling several questions related to chert formation and preservation, and allow outlining and discussion of patterns in the spatial and temporal biogenic chert distribution.
Figure 7.9: Chi square test of the relationship between the type of siliceous organisms (R = radiolarians; SS = siliceous sponges) and the chert deposit style (B = bedded cherts; N = nodular cherts).

<table>
<thead>
<tr>
<th></th>
<th>R</th>
<th>SS</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>34</td>
<td>15</td>
<td>49</td>
</tr>
<tr>
<td>N</td>
<td>6</td>
<td>16</td>
<td>22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>R - B</th>
<th>R - N</th>
<th>SS - B</th>
<th>SS - N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper</td>
<td>16</td>
<td>2</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Middle</td>
<td>9</td>
<td>2</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Lower</td>
<td>9</td>
<td>2</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>E</th>
<th>O - E</th>
<th>(O - E)^2</th>
<th>(O - E)^2/E</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-B</td>
<td>34</td>
<td>27.61</td>
<td>6.39</td>
<td>40.89</td>
<td>1.48</td>
</tr>
<tr>
<td>R-N</td>
<td>6</td>
<td>12.39</td>
<td>-6.39</td>
<td>40.89</td>
<td>3.30</td>
</tr>
<tr>
<td>SS-B</td>
<td>15</td>
<td>21.39</td>
<td>-6.39</td>
<td>40.89</td>
<td>1.91</td>
</tr>
<tr>
<td>SS-N</td>
<td>16</td>
<td>9.61</td>
<td>6.39</td>
<td>40.89</td>
<td>4.26</td>
</tr>
</tbody>
</table>

χ²_{calc} = 10.94; χ²_{0.05,1} = 3.84

H₀: there is no relationship between the chert deposit type and the organisms
H₁: there is a relationship between the chert deposit type and the organisms
calculated χ > theoretic χ → the null hypothesis is rejected
**Figure 7.10:** Chi square test of the relationship between the siliceous organisms (R = radiolarians; SS = siliceous sponges) and the depositional environment (P/L = peritidal/lagoonal; Sh = shelf; S/B = slope/basinal).

I. The depositional environment is divided in three different depth-related settings

<table>
<thead>
<tr>
<th></th>
<th>R</th>
<th>SS</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/L</td>
<td>1</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Sh</td>
<td>3</td>
<td>11</td>
<td>14</td>
</tr>
<tr>
<td>S/B</td>
<td>38</td>
<td>8</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>24</td>
<td>66</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>R-P/L</th>
<th>R-Sh</th>
<th>R-S/B</th>
<th>SS-P/L</th>
<th>SS-Sh</th>
<th>SS-S/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper</td>
<td>0</td>
<td>1</td>
<td>19</td>
<td>0</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Middle</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Lower</td>
<td>1</td>
<td>2</td>
<td>9</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3</td>
<td>38</td>
<td>5</td>
<td>11</td>
<td>8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>O</th>
<th>E</th>
<th>O-E</th>
<th>(O-E)²</th>
<th>(O-E)²/E</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-P/L</td>
<td>1</td>
<td>3.82</td>
<td>-2.82</td>
<td>7.94</td>
</tr>
<tr>
<td>R-Sh</td>
<td>3</td>
<td>8.91</td>
<td>-5.91</td>
<td>34.92</td>
</tr>
<tr>
<td>R-S/B</td>
<td>38</td>
<td>29.27</td>
<td>8.73</td>
<td>76.17</td>
</tr>
<tr>
<td>SS-P</td>
<td>5</td>
<td>2.18</td>
<td>2.82</td>
<td>7.94</td>
</tr>
<tr>
<td>SS-Sh</td>
<td>11</td>
<td>5.09</td>
<td>5.91</td>
<td>34.92</td>
</tr>
<tr>
<td>SS-S/B</td>
<td>8</td>
<td>16.73</td>
<td>-8.73</td>
<td>76.17</td>
</tr>
</tbody>
</table>

| 23.65 |

Because three cells have values equal or less than five, and because the Yates’s correction can be applied to only 2x2 table, the significance has been tested between the silica secreting organisms and shallow waters represented by peritidal/lagoonal together with shelf environments vs. slope/basinal settings.
II. The depositional environment is divided in two different depth-related settings: shallow (peritidal/lagoonal and shelf) vs. deep (slope/basinal)

<table>
<thead>
<tr>
<th></th>
<th>R</th>
<th>SS</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/L &amp; Sh</td>
<td>4</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>S/B</td>
<td>38</td>
<td>8</td>
<td>46</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>E</th>
<th>(O-E)-0.5</th>
<th>(O-E-0.5)^2</th>
<th>(O-E-0.5)^2/E</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/L&amp;Sh-R</td>
<td>4</td>
<td>12.73</td>
<td>-9.23</td>
<td>85.14</td>
<td>6.69</td>
</tr>
<tr>
<td>S/B-R</td>
<td>38</td>
<td>29.27</td>
<td>8.23</td>
<td>67.69</td>
<td>2.31</td>
</tr>
<tr>
<td>P/L&amp;Sh-SS</td>
<td>16</td>
<td>7.27</td>
<td>8.23</td>
<td>67.69</td>
<td>9.31</td>
</tr>
<tr>
<td>S/B-SS</td>
<td>8</td>
<td>16.73</td>
<td>-9.23</td>
<td>85.14</td>
<td>5.09</td>
</tr>
</tbody>
</table>

χ_{calc} = 23.40

χ_{0.05,1} = 3.84

H0: there is no relationship between the depositional environment type and the siliceous organisms

H1: there is a relationship between the chert deposit type and the siliceous organisms calculated χ > theoretic χ → the null hypothesis is rejected
Figure 7.11: Chi square test of the relationship between the depositional environment (shallow waters represented by P/L = peritidal/lagoonal together with Sh = shelf vs. deep waters represented by S/B = slope/basinal) and the chert deposit style (B = bedded; N = nodular).

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>B</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/L&amp;Sh</td>
<td>68</td>
<td>36</td>
<td>104</td>
</tr>
<tr>
<td>S/B</td>
<td>11</td>
<td>53</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>79</td>
<td>89</td>
<td>168</td>
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</tbody>
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<tr>
<th></th>
<th>O</th>
<th>E</th>
<th>O - E</th>
<th>(O - E)^2</th>
<th>(O - E)^2/E</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/L&amp;Sh - N</td>
<td>68</td>
<td>48.90</td>
<td>19.10</td>
<td>364.63</td>
<td>7.46</td>
</tr>
<tr>
<td>P/L&amp;Sh - B</td>
<td>36</td>
<td>55.10</td>
<td>-19.10</td>
<td>364.63</td>
<td>6.62</td>
</tr>
<tr>
<td>S/B - B</td>
<td>53</td>
<td>33.90</td>
<td>19.10</td>
<td>364.63</td>
<td>10.75</td>
</tr>
</tbody>
</table>

$\chi_{calc} = 36.94$

$\chi_{0.05,1} = 3.84$

H0: there is no relationship between the depositional environment and the type of the chert deposit

H1: there is a relationship between the depositional environment and the type of the chert deposit

calculated $\chi >$ theoretical $\chi \rightarrow$ the null hypothesis is rejected
This global compilation resulted in the extensive database of 191 worldwide Ordovician chert occurrences. Another important contribution of the study resides in the fact that, in contrast to previous surveys that have focused only on bedded cherts or silicified oolites, the present study compiles chert occurrences including three types of chert deposits - bedded cherts, nodular cherts, and silicified oolites. This differentiation provides a strong quantitative foundation for reliable inferences that can lead to much deeper, broader, and more detailed insights into various aspects of the silica cycle.

The epoch-level age resolution of this study is the highest achieved for an analysis of chert occurrences. A total of 161 are dated at the epoch level or even higher resolution, at the stage level. Work at this resolution demonstrates that perturbations in the silica cycle exist, they can be perceived at a level of detail higher than the system level, and they can be interpreted in terms of physico-chemical oscillations in the Earth system.

The temporal resolution of the study highlighted problems with stratigraphic nomenclature in previous surveys. Resolution of these problems and compilation of data for the Caradocian and Ashgillian separately was particularly important as these two Upper Ordovician stages were very different climatically. Their separate treatment reveals important changes in chert abundance between the two stages, changes that would have been assigned to the Middle – Upper Ordovician transition otherwise, and particularly linked to the Late Ordovician glaciation. These observations allow detailed insights into the climate fluctuations during the Upper Ordovician, fluctuations that a gross epoch-level treatment would have overlooked because of lack of resolution.
The structure of the dataset provided a comprehensive, and at the same time detailed, framework for systematic surveys undertaken within this compilation on the depositional environment of formation corresponding to each chert occurrence (peritidal/lagoonal vs. shelf vs. slope/basin), and on the type of siliceous skeletal remains (radiolarians vs. siliceous sponges) preserved in each chert deposit. The volume and resolution of data thus developed allow quantitative analyses that demonstrat for the first time, with statistically significant results, relationships between chert deposit types, depositional environments, and silica secreting organisms. These tests support the organic origin interpretation of most Ordovician chert deposits.

The quantitative results of this study show environmental and geographic patterns in chert abundance, as well as temporal and spatial trends in chert distribution. Considered in conjunction with various types of data of different nature developed by previous studies for the Ordovician, the patterns and relationships revealed by this study help to better understand the paleoecology of the Paleozoic silica secreting organisms, their needs in terms silica and nutrients, and affinity for other physical and chemical parameters, as well as their behavior regarding their response to changes in oceanic circulation and climate parameters. They allow documentation and timing of an onshore-offshore migration of silica secreting organisms in response to evolutionary patterns and system perturbations.

The results also shed light onto the various factors that controlled the production, accumulation and preservation of opal, such as organism productivity, sediment influx, water temperature, salinity, host rock, or depositional environment. Interpreted in light of
actualistic and non-actualistic scenarios, the Ordovician data reveal functioning of a chert preservation model associated or not with volcanically-induced high organism productivity, within well aerated or anoxic bottom environments. Within this context, another important result is the documentation of chert accumulations on the shelf, a depositional environment not known to accumulate cherts in modern oceans.
Chapter 8

THE LOWER PALEOZOIC SILICA SECRETING ORGANISMS:
RADIOLARIANS AND SILICEOUS SPONGES

8.1. RADIOLARIANS

8.1.1. Systematics

Radiolarians are single-celled, siliceous-skeletonized planktonic marine protozoa, classified within the Superclass Actinopoda, Subphylum Sarcodina, Phylum Sarcomastigophora, Kingdom Protista (De Wever et al., 2001). As fossil remains, only polycystine radiolarians (Order Polycystina) have been well preserved due to their opaline silica skeleton. Polycystines are represented by spumellar radiolarians (Suborder Spumellaria) exhibiting a spherical symmetry, and nasellar radiolarians (Suborder Nasellaria) characterized by bilateral symmetry.

Radiolaria studies greatly intensified with the initiation of the Deep Sea Drilling Project in the 1960s, and a well-developed radiolarian systematics has emerged. Even though radiolarians have extant representatives, the systematics of the modern assemblages is based on skeleton morphology and not on cell anatomy and morphology as in classic taxonomy, due to the difficulty in growing and studying radiolarians in the laboratory. Radiolarian biozonation became a powerful biostratigraphic tool not only for the Cenozoic and Mezozoic Eras (Aitchinson, 1998), but also for the upper Paleozoic Eon. However, Jones and Murchy (1986) asserted that good taxonomic radiolarian
Descriptions were achieved only for Cenozoic and upper Mesozoic faunas, and that 95% of the Paleozoic radiolarian assemblages were undescribed.

It is worth mentioning that the impossibility of extracting radiolarian skeletal remains from chert samples in view of a taxonomic study has represented a major impediment in the development of radiolarian taxonomy and biostratigraphy. Only after designing of a technique for extracting radiolarians from siliceous rocks, the hydrofluoric acid etching method (Pessagno and Newport, 1972; Dumitrica, 1970), did the biostratigraphy and taxonomy of radiolarian assemblages greatly improve.

8.1.2. Ecology

Modern radiolarians are among the marine zooplanktonic microorganisms that are represented by various species adapted to a wide ecological spectrum, inhabiting all of Earth’s oceans from shallow water settings to deep waters of the abyssal plain. They range from 30 microns to 2 mm in diameter, and have various test shapes with attached spines. Radiolarians are filter feeders, predators, or live as symbionts with unicellular algae such as dinoflagellates (http://www.ucmp.berkeley.edu/protista/radiolaria/rads.html). Radiolarians can be bacterivores, herbivores, symbiotrophes, detritivores, and etc (Casey, 1993). Although most radiolarians are solitary, some species are prone to form thread colonies up to a few meters in length (Casey 1993).

Modern radiolarians are most abundant in eutrophic, nutrient-rich warm surface waters principally of the equatorial zone, but are also present in subtropical and tropical environments. Their spatial distribution is controlled mainly by salinity, temperature, and
nutrient richness among other factors
(http://www.ucmp.berkeley.edu/protista/radiolaria/rads.html). However, as pointed out by Abelman and Gowing (1997; p.4) “the knowledge of the vertical distribution of polycystine radiolarian taxa in the water column is limited” so that the latitudinal and basinal distribution patterns of radiolarians and a consistent relationship between global distribution patterns and physico-chemical parameters of the seawater are lacking (Chang et al., 2003). Most controlled-environmental laboratory studies have analyzed the extent to which the seawater temperature, salinity and light intensity influence the growth, longevity, abundance, and opal productivity of modern radiolarian species (Anderson et al., 1989a,b,c; Anderson et al., 1990; Matsuoko and Anderson, 1992), and a few looked at the effect of dissolved silica levels (Sugiyama and Anderson, 1997). In this respect, studies of two modern radiolarian species demonstrate that polycystine radiolarians can be very effective in silica uptake, occurring abundantly in surface waters that exhibit low concentrations of dissolved silica (ca. 1 µM), and yet mineralizing robust siliceous skeletons (Sugiyama and Anderson, 1997). The four cultures of the study characterized by different dissolved silica level (0 µM, 50 µM, 100 µM, and 150 µM) showed that: 1) increased silica levels do not increase the mean weight of silicate deposited per shell (the skeletal size), 2) nor the longevity, 3) the test morphology is not enhanced with increasing dissolved silica, 4) silica levels as high as 150 µM strongly influence negatively the longevity, growth, and weight gain of the two species of radiolarians, probably having a poisoning effect that inhibits their metabolic activity and kills them. However Sugiyama and Anderson (1997) pointed out that other environmental factors
such as temperature, salinity, and nutrients may represent more significant limiting factors on radiolarian growth and longevity than a low silica concentration level. Anderson et al. (1989c) show that the optimum growth and longevity of *Spongaster tetras tetrass* occurred at moderately warmer temperature and higher salinities (27.5°C and 40‰ salinity); conversely, too high (above 33°C) or too low a temperature (15°C) has strong negative effect on longevity.

### 8.1.3. Evolution

Radiolarians go back in time as far as the Middle Cambrian (Knoll and Lipps, 1993; Won and Below, 1999) and represent the oldest planktonic microorganisms capable of secreting a mineral skeleton (Tolmacheva et al., 2001). Their ancestor is unknown.

The earliest-known reliably identified fossil radiolarians are known from Middle Cambrian phosphorite-rich sediments that have accumulated in relatively shallow water facies of a siliciclastic platform in the Georgina basin, Australia (Won and Below, 1999). Many radiolarian siliceous spicules were extracted from calcareous concretions of three different formations. Many other radiolarian-like fossils have been reported for the early and middle Cambrian times (Nazarov and Ormiston, 1986; Nazarov and Ormiston, 1993; Rozanov and Zhuravlev, 1992; Iams and Stevens, 1988; White, 1986), but they have been regarded with skepticism by some authors (Aitchinson et al. 1998; Lipps, 1992).

The validity of the oldest reports of radiolarian skeletal remains is a debated problem because the siliceous skeletal components most frequently preserved within early Paleozoic facies are spicular skeleton elements, the morphology of which resembles
that of both siliceous sponge and radiolarian spicules. The hollow tube structure that seems to be characteristic only for early Paleozoic radiolarians is a morphological style common to sponge spicules and Silicoflagellata skeletons (Won and Below, 1999). As a consequence, many Early and Middle Cambrian radiolarian-like spicules that have been reported are regarded as hexactinellid or demosponge siliceous spicules.

The depositional environment where radiolarians emerged is a disputed subject too – deep water versus shallow water. A few radiolarian-bearing strata from relatively shallow water sedimentary facies of Middle and Upper Cambrian age, argue for a shallow water radiation (Won and Below, 1999; Xiping et al., 1997). Xiping et al. (1997) in their study of Late Cambrian Radiolaria of the Bitiao Formation (part of the Yangzte platform margin in China), describe radiolarian species classified in the family Entactiniidae, Suborder Spumellaria. The polycystine remains were found in shallow-water facies, supporting the shallow water origin of the radiolarians. However, the depositional environment of the oldest radiolarian fauna (Middle Cambrian of the Georgina Basin) described by Won and Below (1999) is puzzling considering that during the Cambrian, certain southern regions of the Georgina basin subsided at a much higher rate than the rest, exhibiting rapid changes in facies (shales, limestones, dolomites and sandstones) and thickness (Brown et al., 1968). Other deep-sea radiolarian-bearing strata often associated with remnants of oceanic crust in accretionary prisms of ancient subduction zones, suggest a deep water (basinal) origin. According to Tolmacheva et al. (2001), the oldest possible deep-sea radiolarian bearing strata could be those occurring in the basalt-siliceous-terrigenous Zasuriya Formation of Upper Cambrian age, in the Altai Mountains.
of central Asia. Aitchinson et al. (1998) describe lower Ordovician radiolarian-rich sediments (spherical – spumellarian, and bi-polar forms) associated with ophiolitic complexes, from the Little Port Complex in western Newfoundland (Tremadocian) and from the Ballantrea Complex in Scotland (middle Arenigian). To date, the oldest well-attested abyssal deep-sea biogenic chert was reported recently from south-central Kazakhstan by Tolmacheva et al. (2001). The ribbon-banded radiolarian chert formation is part of an ophiolitic sequence. The ages based on conodont biozonation showed that the sequence represents 15 m.y. of continuous deep-sea biogenic siliceous sedimentation across the Cambrian-Ordovician boundary. In addition to radiolarians, megasclerites of hexactinellid sponges have been identified in the chert, illustrating the fact that siliceous sponges were already present in deep-sea environments by the Early Ordovician.

Another issue still open to controversy is the style of life that characterized the first radiolarians. The fact that the oldest radiolarian-like fossils have been found associated with and attached to sponge spicules (Bengston, 1986; Won and Below, 1999), along with laboratory cultures that show the ability of radiolarians to attach to surfaces, lend some support to the hypothesis that radiolarians originated from benthic forms (Petrushevskaya, 1977; Rigby and Milsom, 2000). With regard to this, Nazarov and Ormiston (1986) assert that Radiolaria stand for that group of organisms that might reflect the transition from a benthic to a planktic life habit. The fauna including definitive Cambrian radiolarians is represented by specimens of only one family, the Echidninidae, which are supposed to have lived as equatorial plankton (De Wever et al., 2001).
Regardless of the depositional environment in which radiolarians originated in the Middle Cambrian, by the Lower Ordovician radiolarians inhabited shelf (Blome et al., 1995a; Renz, 1990; Kozur et al., 1996), as well as deep-water settings (Aitchinson et al., 1998; Tolmacheva et al., 2001). However, the present study shows that most Lower Ordovician radiolarian remains are predominantly associated with bedded cherts of deep water sedimentary sequences, a style that probably represents a continuation from the Upper Cambrian, and possibly the Middle Cambrian. Twenty million years later, all Middle Ordovician radiolarian-bearing formations are exclusively bedded, chert-dominated deep water facies, suggesting a shelf to slope/basin migration from the Lower to Middle Ordovician. This status is preserved in the Upper Ordovician and apparently in the Silurian too (Tomescu et al., 2003).

During the Ordovician, radiolarians became the dominant component of the microzooplanktonic fauna (Tappan and Loeblich, 1973). Radiolarian diversity increased during the Ordovician when several groups were present, dominated by spherical porous polycystines (Nazarov and Ormiston, 1986; De Wever et al., 1994). The Ordovician radiolarians were diverse and widespread enough to allow interbasinal biostratigraphic correlations between Eurasia and North America (Nazarov and Ormiston 1993), and a radiolarian biozonation (Noble and Aitchinson, 2000). Nonetheless, the Ordovician-Silurian radiolarian biota records a slow evolution of spherical Spumellarians since their emergence, compared with Middle and Late Paleozoic biotas (Nazarov and Ormiston, 1986; Vishnevskaya, 1997). If the Ordovician and Silurian radiolarian assemblages are characteristic at the series level, during the Middle and Upper Paleozoic they developed a
higher diversity, allowing biostratigraphic subdivision at the stage level, and even at a finer scale for Permian assemblages (Nazarov and Ormiston, 1988; Nazarov and Ormiston 1993). Vishnevskaya (1997) studying Paleozoic and Mesozoic radiolarian assemblages of the Northwestern Pacific Rim (including eastern and northeastern Russia), distinguished four Paleozoic megacycles in the development of radiolarian fauna, of which the first, represented by the Ordovician-Silurian interval, is characterized by a low diversity compared to the other Upper Paleozoic megacycles. Vishnevskaya’s worldwide compilation table (Fig. 11.1) based on radiolarian literature published until 1995, points out that world-wide species diversity of radiolarians was much higher during the Ordovician (10 species in the Tremadocian and up to 100 species in the Caradocian) than during the previous and subsequent periods - Cambrian with around 20 species, and Silurian with approximately 30-40 species. According to her data, the Middle Ordovician species diversity is surpassed only by Late Devonian (up to 125 species) and Lower Carboniferous (around 115 species) faunas in the Paleozoic.

Contrary to the view of a low Ordovician diversity, Renz (1990), analyzing the Ordovician radiolarian assemblages from Nevada and Newfoundland at the family level, reported a significant radiolarian diversification as a component part of Ordovician evolutionary changes. His study showed that by the Upper Ordovician, the dominance of spherical polycystines (family Inaniguttidae of Nazarov and Ormiston, 1986) is replaced by a group characterized by bilateral symmetry and similar to family Palaeoscenidiidae, a family considered by Nazarov and Ormiston (1986) and Jones and Murchey (1986) to have emerged in the Middle Silurian. The Upper Ordovician radiolarian assemblages
inhabiting Gondwana (Australia) and Laurentia (Nevada, Newfoundland), but situated in the same paleolatitudinal range (20° from the equator), have distinct characteristics (Renz, 1990), suggesting at least a continental-level endemism.

Whether or not the Late Ordovician glaciation affected radiolarian faunas is controversial. In contrast to the lack of major radiolarian extinction suggested by Noble et al. (1997), Vishnevskaya (1997) remarks a noteworthy radiolarian extinction across the Ordovician-Silurian boundary (Ashgillian – Llandoverian), the first one among the five identified Paleozoic extinctions. Across this boundary the radiolarian diversity drops to 20 species. Following this drop, the rest of the Silurian witnesses a slight increase in diversity upwards of 60 species (Vishnevskaya, 1997; Vishnevskaya Kostyuchenko and 2000).

8.1.4. Geologic importance

Radiolarians exemplify the oldest and the only skeletonized planktonic organisms preserved in sedimentary sequences of all Phanerozoic systems, inhabiting the oceanic realm since at least the middle Cambrian and until Recent times. Polycystine radiolarians also represent the only skeletonized protists that have been found in Cambrian rocks, albeit in low abundance (Horodyski et al., 1992). Numerous Lower Paleozoic radiolarian assemblages are incorporated into the accretionary prisms associated with subduction zones (Aitchinson, 1998). Because Paleozoic radiolarian-bearing chert deposits are commonly associated with ophiolitic complexes, many authors emphasize the use of radiolarians as a biostratigraphic tool in dating lower Paleozoic orogenic belts devoid of other biostratigraphic potential and consequently lacking a good age control (Grunau,
According to Noble and Aitchinson (2000), early Paleozoic radiolarian faunas include several test morphotypes. A Lower Paleozoic radiolarian biostratigraphy and biozonation was set up by Nazarov and Ormiston (1993) for Eurasia, and extended subsequently toward the North American continent, most recently by Noble and Aitchinson (2000).

The high sensitivity of radiolarians to water temperature and chemistry has rendered them an excellent paleoceanographic and paleoclimatologic marker, mainly for the Cenozoic era. Distribution patterns and abundance of distinct modern radiolarian assemblages are tightly linked to the amount of nutrients dissolved in the seawater and to water depth (Abelmann and Gowing, 1997; Kruglikova, 1993; Chang et al., 2003), in addition to warm temperature (around 27°C) and salinity (35-40‰) (Anderson et al., 1989a,b,c; 1990; Matsuoko and Anderson, 1992; Sugiyama and Anderson, 1997). Based on an actualistic scenario, the abundance of radiolarian-bearing strata has been used as an indicator of paleo-upwelling and high productivity areas for the Phanerozoic (Hein and Parrish, 1987). Also, radiolarian-bearing chert deposits preserved since the Ordovician have been used successfully as an indicator of deep-water settings (distal basinal or oceanic environments associated with orogenic belts), as well as of cratonic seas of moderate depths (Aubouin, 1965; Ormiston, 1993). Vishnevskaya (1997) has shown that evolutionary changes undergone by radiolarians throughout the Phanerozoic can be linked to sea level changes, paleoceanographic regime, and plate tectonics events.

Modern Spumellarian species inhabit mainly shallow waters, as opposed to Nasellarian species that inhabit deep waters. This ecological separation has been used to
deduce nearshore versus offshore environments and to propose sea level fluctuations by calculating the Spumellarian/Nasellarian ratio (Casey, 1993). However, this is possible only for sediments younger than the Jurassic because the oldest unquestioned Nasselarians date from the Middle Jurassic (Vishnevskaya, 1997).

8.2. SILICEOUS SPONGES

8.2.1. Systematics

Sponges, the simplest metazoan organisms (Wainright et al. 1993; Conway, 1994), feature specialized cells, but these are not grouped into distinct tissues. Sponges are grouped into Phylum Porifera, Kingdom Animalia. The sponge classification system is based, as in the case of radiolarians, mainly on skeleton morphology. Presently, phylum Porifera comprises 4 classes: Demospongea, Hexactinellida, Calcarea, and Sclerospongea (Rigby 1983). Fossil siliceous sponges have siliceous spicules as structural skeletal elements and are represented by Class Hexactinellidae or Hyalospongea (glass sponges), and Class Demospongea.

8.2.2. Ecology

Sponges are sessile, benthic filter-feeding metazoans. Presently, Demosponges represent approximately 95% of all sponges (Rigby 1983), with over 600 living genera that inhabit almost any aquatic environment from shallow to deep settings (Prothero, 2004). In the past, including the Ordovician and the Silurian, Demosponges were important reef-building organisms or major components of the reef communities (Finks, 1970; Rigby, 1983). Even though most of the modern species of sponges prefer clear, shallow marine
waters, siliceous sponges prefer deep quiet waters up to 5000 m deep (Prothero, 2004). If we consider the hexactinellids versus lithistid demosponges, there is a differentiation in their most favorable living habitat. Most living Demosponges prefer relatively warm, shallow, tropical seas. However, they are known to inhabit environmental settings as deep as 1500 m (Rigby, 1983; van Soest, 1994), and some modern Demospongea species (e.g., *Halichondria panicea*) live in shallow-waters of high latitude environments (55° N) as cold as 10°C, such as those offered by the Baltic Sea (Reincke and Barthel, 1997). This siliceous sponge genus with a cosmopolitan distribution (van Soest, 1994) represents an important epifaunal component of the red algae zone at depths ranging from 4 to 11 m. As such, it could compete with diatoms for the available dissolved silica in the seawater, but this is a topic still open to controversy. On the other hand, Hexactinellids inhabit mainly the upper bathyal zone (between 200 and 2000 m in depth, Noble, 1997; Tabachnick, 1994), and are found also toward the deepest habitats such as abyssal and hadal niches (below 6000 m) (Hartman 1983; Tabachnick, 1994).

The differentiation between Demosponges and Hexactinellids in terms of their most favorable living habitat is seen as a result of their different requirements for dissolved silica levels in the seawater: hexactinellid sponges need higher Si(OH)_4 levels than demosponges. Consequently, the deep water habitats of modern hexactinellids are known to be the silica-rich environments (Tréguer et al., 1995; Nelson et al., 1995), or shallow water settings that are rich in dissolved silica, such as those of higher latitudes, or microhabitats with enhanced Si supply via rivers (Maldonado et al., 1999; Boury-Esnalut and Vacelet, 1994).
Siliceous sponges generally need higher dissolved silica levels than the diatoms and radiolarians and consequently the silica limitation characteristic for neritic environments could explain the Cenozoic migration of most siliceous sponges toward deeper silica-rich settings (Maldonado et al., 1999). Under very low silica concentration environments, as low as $0.741 \pm 0.133 \mu M$ (the mean $\pm$ s.e. of a silica concentration range from 0.03 to 4.5 $\mu M$), siliceous sponges are capable of secreting only very small and thin needle-like spicules (Maldonado et al., 1999). Experiments demonstrated that there is an asymptotic relationship between the silica uptake rates in Demospongea and the amount of dissolved silica in the seawater (Reincke and Barthel, 1997; Frøhlich and Barthel, 1997; Maldonado et al., 1999) – the silica uptake rate increases asymptotically with increasing silica concentration. The higher the available dissolved silica level, the more complex and varied the spicules that are secreted by siliceous sponges (Maldonado et al., 1999). In contrast to diatoms, the saturation level of the Demosponge genus *Halichondria panicea* is much higher (above 150 $\mu M$ Si-concentration) and silica uptake rates are much lower (17 $\mu mol \ h^{-1} g^{-1}$ ash-free dry weight) (Frøhlich and Barthel, 1997). By comparison, the saturation point of some diatom species is reached at 10$\mu M$, with an uptake rate of 0.001 $\mu mol \ Si \ h^{-1} cell^{-1}$.

Is silica or nutrient limitation of greater importance? This a question raised by many authors trying to explain the growth and evolution of siliceous sponges. However, modern studies still argue about which parameter dominates. The silicon limitation growth theory is supported experimentally by the work of Reincke and Barthel (1997) and Maldonado et al. (1999). However, Maldonado et al. (1999) studying cultures of
Crambe crambe, a demosponge species characteristic of relatively low latitude coastal waters in tropical/subtropical environments (e.g., the Mediterranean Sea, between approximately 30° and 45° north), notice that overly high seawater silica concentrations (100 µM) may inhibit silica uptake. This observation does not fit the results obtained by Reincke and Barthel (1997) in their experiments, probably because they used a different demosponge taxon also characteristic for shallow waters, but populating much higher geographical latitudes, respectively around 55° north.

The nutrition limitation growth theory is supported by experiments of Frøhlich and Barthel (1997). They showed experimentally that silica uptake is an energy-consuming process and therefore in a nutrient-starved environment the biogenic secretion of dissolved silica decreased by 15%. However, their experiment does not show what happens to siliceous sponges if the low nutrient level goes below a certain threshold (do siliceous sponges cease silica uptake and die?).

Normally, at higher temperatures higher silica uptake rates should occur. With increasing temperature the silica cycling is increased by higher dissolution rates of the skeletons that generate higher dissolved silica levels, and therefore trigger higher silica uptake rates. However, it was shown that an increase from 10°C to 15°C, did not produce a measurable increase in silica uptake rate for modern demosponges (Frøhlich and Barthel, 1997). This could be explained by differences in the magnitude of the effects of temperature changes on the rates of silica dissolution and silica uptake. A higher increase in temperature would perhaps trigger perceivably higher silica uptake rates.
The role of the siliceous sponges in the modern silica cycle is viewed as insignificant because of the silica cycle domination by diatoms. Maliva et al. (1989) claim that siliceous sponges once exerted the main control on the Si cycle in neritic environments, and that throughout the Phanerozoic siliceous sponges have undergone changes in their environment.

8.2.3. Evolution

Phylogenetic theories propose that metazoans evolved from a protist by acquiring specialized multicellularity (Cowen, 2000), but their phylogeny is still an issue open to controversy. Molecular work based on comparisons of small subunit ribosomal RNA (rRNA) sequences (Wainright et al. 1993) shows that within the Metazoa sponges were the first to radiate. Different molecular studies of sponge phylogeny since the late 1980s support this interpretation and suggest that sponges have paraphyletic rather than monophyletic origins (Borchiellini et al., 2000; Borchiellini et al., 2001).

All the major classes of sponges (Calcarea, Hexactinellida and Demospongea) are known from at least the Cambrian. Porifera has been considered a conservative group of organisms because sponge taxa display long geologic ranges (Carrera and Rigby, 1999). Siliceous sponges occur as far back as the Neoproterozoic, as a part of the Ediacaran or Vendian faunas. According to Wood et al. (2002), calcareous sponges could be as old as 549 Ma (Neoproterozoic). They describe a calcite-biomineralized large, modular metazoan from a shallow marine carbonate - siliciclastic sequence (the Nama Group) in southern Namibia. The fossil, dated at 548.8 ± 8 Ma B.P. (Grotzinger et al. 1995), presents some morphological structures of both poriferan and cnidarian affinity.
The oldest well-preserved siliceous axial spicules discovered to date were identified as monaxonid Demosponges, and dated at approximately 580 Ma (Li et al. 1998), a time of expansion of the Ediacaran fauna. They are preserved within the Vendian Doushantuo phosphatic sequence in south China, central Guizhou. The shape of the siliceous spicules is mostly globular, but a few of them are tubular. The identification of the oldest well-documented siliceous sponge spicules as Demosponges suggests that a demosponge was the ancestor of the sponges.

Younger Vendian spicules that are unequivocally from sponges, classified as hexactinellids and not as demosponges, have been described by Brasier et al. (1997). These spicules exhibit various morphologies demonstrating that skeletal diversity had been achieved by Hexactinellids by the latest Precambrian. They were discovered in Mongolia within the upper part of the Tsagaan Formation in a limestone unit overlying a phosphorite-ocher-black shale succession. The unit was dated as late Ediacaran age, 543–549 Ma (Grotzinger et al., 1995). This finding refuted the earlier theory according to which hexactinellids appeared during the early Cambrian (Finks, 1970; Finks, 1983) or Middle Cambrian (Webby, 1984a). Ediacaran-age siliceous sponge spicules attributed to Hexactinellids, have also been reported from South Australia, in the Pound Subgroup (Gehling and Rigby, 1996), but their origin is disputed (Li et al., 1998).

The issue of the ancestry of either Demospongea or Hexactinellida within Porifera is still debated. However, the emergence of siliceous biomineralization preceding the calcareous biomineralization in sponges is widely accepted (Li et al., 1998; Brasier et al., 1997).
Based on associated lithologies, it was shown that the Late Proterozoic siliceous sponges inhabited eutrophic environments within shallow seas, in contrast to early Cambrian calcareous sponges that inhabited “more interior” oligotrophic settings (Li et al., 1998; Brasier, 1992). Speculations are made on a eutrophic outer shelf origin of the Neoproterozoic mineral skeleton faunas, closely related to high Si, P and Ca concentrations in the water column, and on a shoreward migration of these faunas during the Cambrian transgression (Brasier, 1992; Brasier et al., 1997). The shallow water radiation of sponges is supported by the widely accepted theory of the shallow water origin of life (Crimes, 1992). In contrast, Webby (1984a) proposes that sponges emerged in deeper slope environments during Late Precambrian – early Cambrian times, and migrated and dispersed subsequently onto carbonate platform habitats “after the demise of archaeocyaths”. Since the Neoproterozoic sponge faunas have been characterized by high tiering levels (Yuan et al. 2002), demonstrating their evolved ability in extracting nutrients from the water column. By the Neoproterozoic, shallow waters were dominated by calcareous sponge associations and subordinate siliceous sponges, in contrast to deep waters characterized by basin siliceous assemblages (Finks, 1960).

In the Early Cambrian, both monaxonic Demosponges and Hexactinellids already represented a relatively diversified component of the benthic fauna (Finks, 1970), inhabiting both shallow and deep-water settings. Numerous siliceous sponge fossils have been discovered in China (early Cambrian Hexactinellids and Lithistids; Zhang and Pratt, 1994), South Australia (early Late Cambrian hexactinellid type spicules; Bengston, 1986), and the Siberian platform (Early Cambrian Hexactinellids and Demosponges;

During the Ordovician the siliceous sponge faunas, mainly Lithistid demosponges (Finks, 1970; Rigby 1983), became even more complex, diversified, and widespread being represented not only by endemic but also by cosmopolitan genera. According to Finks (1970), by the Middle Ordovician lithistids reached a relatively high diversity (17 genera), representing an important reef-building component. Overall, Ordovician sponge records point to a higher diversity of demosponges compared to hexactinellids (Carrera and Rigby, 1999). By the end of the Ordovician, several orders of sponges with multiple
suborders had already evolved, demonstrating a high degree of diversification. According to Carrera and Rigby (1999), the most abundant Ordovician endemic sponge fauna occurs in Australia, especially in the New South Wales area, with endemism levels being lower in the Laurentian Appalachians and China. Calcareous sponges, especially sphinctozoan sponges, almost equaled the siliceous sponge diversity in the Middle and Upper Ordovician.

The paleogeographic distribution patterns of Ordovician sponges illustrates a change in sponge faunas during the Ordovician period (Carrera and Rigby, 1999). Early Ordovician sponge faunas have relatively low diversity and are dominated by demosponges. Middle Ordovician faunas, also dominated by demosponges, display a higher diversity characterized by two main associations – Appalachian faunas (including South China and the Argentine Precordillera), and Great Basin faunas. The Late Ordovician exhibits pronounced increases in diversity of both siliceous and calcareous sponges and provincialism with two biogeographic associations: the Pacific association (western North America and New South Wales of Australia), and the Atlantic association (Midcontinent Laurentia and Baltica).

Rigby and Webby (1988) analyzed Late Ordovician sponge associations from the Malongulli Formation of Central New South Wales, Australia, and described 34 genera divided into 44 species of siliceous sponges (both demosponges and hexactinellids, with the lithistid type dominating) and calcareous sponges. According to the authors, this sponge assemblage exemplifies a unique record of deeper-water carbonate environments bordered by an island-arc shelf sequence. This Late Ordovician New South Wales sponge
association also suggests a clear-cut differentiation between calcareous sponges that
dominated shallow waters, and siliceous sponges (both demosponges and hexactinellids)
that dominated slope-basin environments (Rigby and Webby, 1988).

Within a shallowing interval of the lower Hanson Creek Formation (late Upper
Ordovician) Finney et al. (1999) recognized a faunal turnover in siliceous sponges. The
change from deep water, hexactinellid-dominated assemblages, to shallow, subtidal
lithistid-dominated assemblages provides an example of the association between sponge
types and depositional environment and illustrates the responsiveness of sponges to
environmental changes.
Chapter 9

DISCUSSION: THE ORIGIN OF THE ORDOVICIAN CHERTS - ORGANIC VS. INORGANIC GENESIS

9.1. Previous theories on chert origin

The inorganic formation of chert through direct precipitation from seawater supersaturated with respect to silica seems the most appropriate mechanism to explain the formation of Precambrian cherts. Conversely, the genesis of most chert deposits from the mid-Paleozoic on is viewed and widely accepted as a biologically induced process with the common inference on association of bedded cherts with radiolarians (Grunau, 1965; Ramsay, 1973; Hein and Parrish, 1987), and nodular cherts with siliceous sponges (Maliva and Siever, 1989; Maliva et al., 1989) are genetic associations. However, controversy still exists regarding the dominant mechanism responsible for the formation of chert deposits during the Early Paleozoic, principally the Cambrian and to a lesser extent the Ordovician.

The Proterozoic cherts are unanimously thought to be inorganically generated through the precipitation of silica from a silica supersaturated sea, based on dearth of skeletal structures within cherts owing to the absence of major silica secreting biotas that could balance the excess of silicic acid in the seawater (Siever, 1957). Several workers have proposed that the silica cycle has changed through time, from an ocean supersaturated with respect to silica during the Precambrian, toward a silica-undersaturated ocean during
the Phanerozoic, as siliceous organisms evolved (Siever, 1957, 1962; 1992; Maliva et al., 1989).

The organic theory proposed as the main mechanism responsible for the formation of most chert deposits, principally of bedded cherts, from the mid-Paleozoic on, is widely accepted because the Paleozoic silica secreting organisms had reached an evolutionary level that could explain their ability to keep the silica concentrations undersaturated at all times. This conclusion is based on the high biological diversity (Nazarov and Ormiston, 1986; Vishnevskaya, 1997), the abundance of skeletal remains preserved in cherts during the Late Silurian, Devonian, Carboniferous and Permian, and the inference that dissolved silica concentrations might have been highest where sediments contained more biogenic silica. The latter is based on a modern scenario (Calvert, 1983). The lack of any consistent inorganic process of sufficiently high magnitude to account for the genesis of areally extensive cherts and the lack of any coherent association patterns between sedimentary sequences supposed to be responsible for high silica inputs and chert deposits further support a biogenic origin of Mid- to Late Paleozoic chert.

The inorganic genesis as a dominant mechanism responsible for the formation of Early Paleozoic cherts is supported mainly by a higher magnitude of the volcanic activity (Ronov et al., 1980) and of silicate rock weathering (François et al., 1993). This theory is consistent with the presence in certain bedded cherts of minerals regarded as volcanic alteration products, such as montmorillonite, palygorskite, sepiolite, and clinoptilolite (Wise and Weaver, 1974) and the hypothesis that there is a direct relationship between
the abundance of clay minerals in sediments and silica concentrations (Lancelot, 1973a,b; La Porta, 1998a). The association of certain siliceous deposits such as the bedded cherts with volcanogenic massive sulfide (VMS), (Grenne and Slack, 2003) and the dearth or low preservation of skeletal remains in many cherts (Von Rad and Rösch, 1974), principally for the Cambrian, also suggests an inorganic mechanism for chert formation. This is consistent with the calculation that seawater concentration with respect to dissolved silica was high enough to allow the precipitation of opal-CT as chert nodules (Siever, 1991). The Early Paleozoic oceans had high endogenous and exogenous silica input levels driven by high continental weathering rates during the Cambrian (as inferred from the isotopic strontium curve; Qing et al., 1998) and energetic marine volcanic activity mainly during the Ordovician. The general assumption is that silica-secreting organisms during the Cambrian and to a lesser extent during the Ordovician, were at the beginning of their development, and had not reached the level of evolution and abundance beyond which they could regulate the marine silica cycle and control the biogenic burial of silica.

Siliceous sponges originated in the Neoproterozoic but were probably not able to influence the marine silica cycle by lowering the silica concentration under the precipitation level and produce biogenic cherts at a global scale until at least the Middle Cambrian, when another group of organisms capable of extracting silica from the seawater, the radiolarians, originated (Won and Below, 1999). The Cambrian is moderately rich in bedded chert deposits, most of them formed in shelf environments (Hein and Parrish, 1987; Kidder and Erwin, 2001). There is no survey regarding the
faunal content of these cherts and the question remains: Did radiolarians and siliceous sponges induce their formation?

The earliest reliably identified fossil occurrence of radiolarians is known from the Middle Cambrian (Won and Below, 1999), but hypotheses were put forward for their emergence earlier, in the Early Cambrian (Ormiston, 1993). Regarding the depositional environment where radiolarians originated, evidence of Middle Cambrian radiolarian-bearing sedimentary sequences argues for a shallow water radiation (Won and Below, 1999), a hypothesis supported by Late Cambrian radiolarian-bearing facies (Xiping et al., 1997), and also in harmony with the shallow water origination of most major groups of organisms (Webby, 1984a; Sepkoski and Miller, 1985). On the other hand, the deep-sea origination hypothesis is supported by a Late Cambrian basalt-siliceous-terrigenous formation bearing well identified radiolarians (Tolmacheva et al., 2001), the skepticism regarding the identification of the earlier radiolarian-like fossils for the Early and Middle Cambrian times (Aitchinson et al., 1998), and the consideration that during the Cambrian certain southern regions of the Georgina basin, which is the area of the earliest-known reliably identified radiolarians (Won and Below, 1999), subsided at a much higher rate than the rest of the basin, exhibiting rapid changes in facies (shales, limestones, dolomites and sandstones) and thickness (Brown et al., 1968), and thus casting doubt over the hypothesized shallow environment.

The shallow water origination of radiolarians during the Cambrian would be consistent with the more abundant shelf bedded cherts during the same period (Kidder and Mumma, 2003), only if the association of bedded cherts and radiolarians was an
interconnected genetic process as thought by many authors, and demonstrated herein at least from the Ordovician on. It could also be that siliceous sponges were chiefly responsible for chert formation in both the Early and Middle Cambrian, and that some radiolarians accumulated in sponge cherts. No taxonomic evidence of radiolarian fossils exists for the Lower Cambrian, when bedded cherts were forming as well (Hein and Parrish, 1987). Yet, by the Early Cambrian, both monaxonic Demosponges and Hexactinellids already represented a relatively diversified component of the benthic fauna, inhabiting both shallow and deep-water environments (Finks, 1970). Thus it is possible that by the Early Cambrian the siliceous sponge fauna might had came to the point where it could reduce silica concentrations under the saturation levels, driving the formation of the first biogenic cherts of both types – bedded and nodular. It is very likely that the Cambrian witnessed a shift from a dominantly inorganic silica precipitation to a globally biogenic induced chert formation, and from a siliceous sponge dominated silica burial to a radiolarian-sponge dominated silica deposition, so that during the Ordovician the silica burial was mainly biogenically controlled. The Early-Middle Cambrian shift from a dominated inorganic silica precipitation to a biologically induced process is supported by the deleterious effect of high silica concentration levels on the behavior of siliceous sponges and radiolarians, finding discovered through experiments on modern faunas (Sugiyama and Anderson, 1997; Maldonado et al., 1999). Some Cambrian nodular chert bearing formations have been suggested of inorganic origin based on lithological associations such as the presence of clay-rich seams at chert contacts and of clay
inclusions within the silica matrix (La Porta, 1998a,b), but these deposits are not well studied.

**9.2. Evidence from this study**

The data that support the organic origin of Paleozoic chert deposits, and the association patterns between the type of skeletal remains (radiolarians vs. siliceous sponges), the chert style (bedded vs. nodular), and the depositional environment in which they form (peritidal/lagoonal vs. shelf vs. slope/basin) is mainly quantitative. The few compilations of worldwide Phanerozoic bedded cherts (Grunau, 1965; Ramsay, 1973, Hein and Parrish, 1987) show the affinity and a possibly genetic relationship between radiolarians and bedded cherts. As regards the possible association between nodular cherts and siliceous sponges, to date there is no systematic survey, for any geological period, of the nodular cherts and their corresponding content in biogenic siliceous remains. The present study brings the first quantitative evidence in support of the biogenic origin of cherts and genetically-dependent association patterns.

The organic origin of most Ordovician cherts are organic in origin is supported by two aspects of this study. First, approximately 38% of the Ordovician chert formations contain siliceous skeletal remains, mainly radiolarians and subsequently siliceous sponges. Second, the onshore-offshore migration of the silica secreting organisms perceived through the rock record of the siliceous organism bearing chert formations, is accompanied by an onshore-offshore change in the locus of silica burial, perceived in the stratigraphic record of cherts that lack preserved siliceous skeletal remains. The
systematic analysis of chert content in terms of biogenic remains demonstrates that Early Paleozoic silica secreting organisms have been underestimated with respect to their role within the marine silica cycle and silica burial. It is worth mentioning that the impossibility of extracting radiolarian and sponge skeletal remains from chert samples has undoubtedly represented an impediment in the development of radiolarian and siliceous sponge taxonomy and biostratigraphy, and hence in discovering which cherts bear fragments of silica secreting organisms, until the 1970s. Many of the Ordovician chert deposits were identified and described prior to the discovery of a technique capable of extracting siliceous organisms from siliceous rocks, the hydrofluoric acid etching method (Pessagno and Newport, 1972; Dumitrica, 1970). Based on this, it seems probable that the number of Ordovician cherts bearing siliceous skeletal remains might actually be higher than found by this study.

The various relationships examined in this study (Chapter 7) reveals four statistically significant associations: first, a strong affinity between radiolarians and deep-water (slope/basinal) bedded cherts; second, siliceous sponge spicules can be found in either bedded or nodular cherts formed preferentially in shallow environments of peritidal/lagoonal and shelf settings; third, bedded cherts form preferentially in slope/basinal environments, and subordinately in shallower settings; and fourth, nodular cherts form preferentially in shallow waters of shelf and peritidal/lagoonal environments.

Even though this study reveals no single example of bedded chert deposits containing only sponge spicules, the statistical analysis reveals an equal tendency of siliceous sponges occurring in either type of chert deposit but mainly with shallow water
deposits (peritidal/lagoonal and shelf). This finding supports the common conception that bedded cherts formed principally in slope/basinal environments within a siliciclastic regime represent primary accumulations of siliceous tests of silica secreting planktonic organisms (Grunau, 1965; Aubouin, 1965; Hein and Parrish, 1987), and that nodular cherts represent diagenetic products whose silica source is represented principally by siliceous sponges (Siever, 1962; Maliva and Siever, 1989). It also emphasizes that the formation of some shelf bedded cherts might by formed by siliceous sponges. None of the chert occurrences from this study identified as bedded cherts that formed on the shelf are associated with any volcanic elements or other potentially high silica generating factors that could explain their inorganic formation. However, for a couple of Lower Ordovician bedded cherts associated with peritidal/lagoonal environments, the biogenic origin seems less probable (Pettijohn, 1975).

The present study shows that chert nodule formation occurred in the shallow water settings of the shelf and peritidal/lagoonal environments, and not in slope/basinal environments. This suggests there was a genetic relationship between siliceous sponges and nodular cherts. The question is: why is the formation of nodular cherts mainly confined to these shallow settings largely populated by siliceous sponges, when the required inorganic precipitation level of opal-CT, which is much lower than that of biogenic opal (40-60 mg/L SiO2 at 25°C) and which was achieved during the Ordovician (Siever, 1991), indicates that the deeper, much richer silica environments would be more suited for their inorganic chert formation regardless of the presence of benthic silica secreting organisms? Moreover, the fact that many shallow water cherts have been found
containing siliceous sponge spicules, in contrast with the scarcity of sponge spicules in
deep chert deposits, indicates an intrinsic relationship between the formation of nodular
cherts and siliceous sponges inhabiting the proximal shallow environments.

The transition from the Lower to the Middle Ordovician witnesses a migration of
the formations bearing biogenic siliceous remains toward deeper environments,
concomitant with a sharp decline in the peritidal/lagoonal and shelf cherty facies. Why
would the general pattern of the marine silica burial follow the migration of the silica
secreting organisms? The conjunction of the two events suggests that there is a direct
relationship between chert formation and the silica secreting organisms inhabiting the
most proximal environments. One could argue that during the early Middle Ordovician
the sharp sea level drop (Finney, 1997) exposed the shelf area, so that the change in the
locus of silica burial could be an artifact of a sea level lowering, and not a consequence of
the migration of the silica secreting organisms from the peritidal/lagoonal and shelf
environments. An argument against this view would be given by the total retreat of
radiolarians from shelf to basinal settings (indicated by the absence of Middle Ordovician
shelf radiolarian-bearing cherts) and the sharp drop in the abundance of the silicified
oolites (Table 7.7) characteristic of peritidal/lagoonal settings. The exposure of an
important part of the shelf area, as the one that has occurred at the Lower-Middle
Ordovician boundary, would diminish the area extent of the optimal environment for the
formation of oolites, and consequently fewer silicified oolites would be generated. Did
this surface reduction generate the drop in silicified oolites, while siliceous sponges were
still populating such very shallow environments? An answer to this question is provided
by the depositional distribution of the chert facies in the Caradocian. During the Caradocian, when the Ordovician sea level was at its highest (Ross and Ross, 1992), the locus of silica burial is mainly confined to shelf and basinal settings, whereas the peritidal/lagoonal environments are characterized by just two silicified oolite deposits.

It is true that the presence of skeletal remains does not guarantee the organic genesis of a deposit, but neither does the lack of such remains demonstrate inorganic precipitation of silica. While the preservation of biogenic siliceous fragments in a chert can introduce a bias toward the idea that the chert might be of biogenic origin, the lack of any skeletal structures gives equal chances to both organic and inorganic origins, as valid mechanisms. Multiple types of evidence are needed in order to decide between these two origins, and here I present the lines of evidence in support of biogenic origin for most chert deposits:

1) The siliceous skeletal remains are found associated with cherty rocks only.

2) The onshore-offshore silica secreting organism migration is accompanied by a corresponding change in the locus of silica burial, or in other words the depositional patterns in which cherts occur are in concert with evolutionary events, such as onshore-offshore faunal migrations.

3) The Early Paleozoic, silica-secreting organisms represented by radiolarians and siliceous sponges were relatively well diversified, abundant, and globally dispersed with efficient capabilities of silica uptake (as demonstrated by modern studies), with a high ability to balance globally the excess of silicic acid in seawater. Additionally, studies of modern species of radiolarians and siliceous sponges show that while they have the
capacity to extract dissolved silica from the seawater at very low concentrations (ca. 1µM), high dissolved silica levels in the seawater (100 - 150 µM) might be toxic (Sugiyama and Anderson, 1997; Maldonado et al., 1999) (Chapter 8). Under these circumstances, it is improbable that the dissolved silica concentration reached saturated or supersaturated levels at the basin level, favoring in this way the inorganic formation of areally extensive cherts. Even though radiolarians and siliceous sponges are not as efficient as diatoms in processing silica uptake, they still secrete silica and serve as an effective “micro site” of silica bio-precipitation. Through the aggregation of their skeletal parts silica-rich sites develop that, in turn, act as a silica source much higher than the amount of the dissolved silica from the seawater. Moreover, thermodynamically it is easier to export enough silica to generate the formation of a chert deposit via siliceous organisms that are so efficient in silica uptake at the very low concentrations, than to raise the dissolved silica level in the seawater at concentrations so high that a direct precipitation of a chert deposit could occur.

4) Limestone is a very common rock in the Phanerozoic record. However only some of them contain cherts even though, there is a great affinity between carbonate rocks and certification (Kastner et al., 1977) (Chapter 5). The selective occurrence of chert in only some limestones supports the biogenic origin as does the loss of chert nodules from most Cenozoic limestones when sponges moved to deeper waters.

5) The spatial distribution of chert deposits does not not correlate with volcanic sites or other high silica input sites. Instead it matches the distribution of the silica-secreting organisms.
6) The weathering of continental silicate rocks is a continuous process maintaining a permanent flux of oscillating magnitudes of silica into the basins, and thus a pervasive formation of early diagenetic in situ silicified oolites should occur throughout the Phanerozoic where calcareous oolites formed. However, few of the calcareous oolites became silicified (Tomescu et al., 2003), and Phanerozoic onshore-offshore patterns of cherts, as well as the decline of silicified oolites, seems to correlate with distribution patterns of the silica secreting organisms (Kidder and Mumma, 2003). None of the arguments alone proves the biogenic origin, but integration of all of them is consistent with it.

9.3. Silica burial: a balance between silica dissolution and preservation rates

The geological record of chert deposits is an issue of the preservation rate of biogenic opal that might not correlate with either high biosiliceous productivity areas and high silica-nutrient inputs, or with eutrophic water masses. The net silica output into chert expresses the balance between biogenic silica production, dissolution, dilution by host sediment, and the degree of preservation. A change in the amount of chert burial could be the result of variations in the above factors, and reflect an end product of the conjugated action of the parameters that play a role in the silica cycle and burial as chert. An analysis of the factors that influence the marine biogenic silica production, dissolution and burial is required in order to understand chert abundance patterns through time and their underlying mechanisms. Some key factors include: 1) the productivity of the silica-secreting organisms, 2) the magnitude of the terrigenous sediment input, 3) surface water
temperature, 4) water column depth, 5) opal rain rate, 6) the presence of trace metals (Al, Fe, Ga, Gd, Y), and especially of Al, 7) the presence of organic matter, 8) test aggregation through organism blooms due to high silica-nutrient influxes, 9) the specific surface area of the siliceous skeleton, and burying sediment composition (Nelson et al., 1995; Maliva and Siever, 1989; Bidle et al., 2002).

The evidence that most modern biogenic silica accumulates in areas with cold surface waters (DeMaster, 1981), suggests that the surface water temperature is a dominant factor for the opal preservation, due to the strong dependence of silica dissolution on temperature (Kamatami, 1982). Based on an actualistic upwelling scenario, biogenic silica accumulations discovered in the stratigraphic record are viewed as tracers of eutrophic water masses induced by the upwelling of cold nutrient-rich deep waters (Ramsey, 1973; Miskell et al., 1985; Hein and Parrish, 1987; Barron and Baldauf, 1995; Murray et al., 1994; Kidder and Erwin, 2001). However, studies showed that the accumulation and burial of modern biogenic silica is governed by different mechanisms in coastal settings and deep-abyssal environments (Nelson et al.1995; DeMaster, 1981; Tréguer et al., 1995).

• **Preservation of silica in the deep-sea: the temperature-dependent preservation model**

The deep-sea domain is generally characterized by low terrigenous influx, so that, the sediment input will play a minimal role in the dilution of silica accumulation. Deep-sea sediments are dominated by biogenic components and pelagic clays (Kennett, 1982). Sediment thickness in the ocean basins depends on the biological productivity, proximity of the basin to areas characterized by high river discharge (hence the amount of sediment
influx), rates of dissolution versus rates of preservation of the skeletons, the age of the ocean floor, and the distribution of bottom currents (Kennett, 1982; Duxbury et al., 2002).

Silica dissolution is strongly temperature dependent, so that the specific dissolution rate (dissolution rate per unit mass of biogenic silica) increases by approximately an order of magnitude with each 15°C increase in temperature (Kamatani, 1982). Silica dissolution also increases with increasing pressure. Heath (1974) found that a temperature decrease of 1/2°C per kilometer cancels out the solubility increase due to rising pressure, which accounts for the high silica concentrations are found in deep waters where temperature is low and pressure is high.

In the deep sea, modern biogenic silica accumulations occur in high latitude regions, representing the largest present-day opal accumulation sites (Tréguer et al., 1995; DeMaster, 1981). The assessment of the abyssal siliceous sediments points out that “the largest and most important area of modern opal accumulation in the ocean is one where annual rates of opal accumulation in surface waters are not particularly high nor is the annual carbon-based primary productivity” (Nelson et al., 1995; p.366). According to this model, the dominant mechanism for enhancing deep-sea (abyssal) opal preservation is the low dissolution rate of biogenic opal at low surface water temperature (the upper 100 m), irrespective of high or low surface productivity (Nelson and Gordon, 1982 in Nelson et al., 1995; DeMaster, 1981). By contrast, the oligotrophic areas where the production of biogenic silica in surface waters represents about 75-90% of the global
production, is characterized by very little preservation; the dissolution of silica within the water column and at the sediment/water interface is almost total (Nelson et al., 1995).

• *Preservation of biogenic silica in coastal margins: the high productivity model*

Although the preservation of biogenic opal in abyssal areas is strongly influenced by surface water temperature and latitude, in the shallower waters of continental margins, it is tightly linked to upwelling (Nelson et al., 1995). The upwelling of nutrient-rich deep waters to the photic zone favors high organism productivity that increases the opal rain, decreases the test dissolution rate through test aggregation, and leads to enhanced burial rates. The formation of ice caps at the poles triggers low and middle latitudinal deep water upwelling, a mechanical motion that introduces into the nutrient cycling system important quantities of nutrients buried upon deep sedimentation. As Nelson et al. (1995) remark, opal sediment formation in coastal areas is associated with high primary productivity regardless of the latitude.

In view of all of these facts, the analysis of the stratigraphic chert abundance record and fluctuation patterns through time proves to be more complicated than the hypothesized relationships for radiolarian and sponge cherts of high chert abundance = high organic productivity = coastal upwelling of cold nutrient-rich waters, regardless of the silica burial site within the basin, the type of the silica secreting organisms, or the various physico-chemical factors which directly influence silica dissolution and burial rates. Examination of two systems – continental margins vs. deep-water abundance – should reveal distinct differences between these two depth-defined systems that function differently with respect to silica accumulation and preservation (Nelson et al., 1995).
However, in the stratigraphic record it is difficult to differentiate between slope and basinal settings. For this reason, the data of the present study have been divided into very shallow (peritidal/lagoonal), shallow (shelf), and deep settings (slope/basinal). If biogenic chert formation in peritidal/lagoonal sites and the shallower parts of the shelf is directly influenced by continental weathering fluctuations *via* river runoff, that of deeper environments (the deepest area on the shelf, slope and basin) is tightly linked to the intrabasinal ambient (water depth, oceanic circulation, surface water temperature, salinity, seawater chemical composition, volcanic, hydrothermal, and spreading activities, sediment composition) and latitude, in addition to variations of the continental inputs of silica and other nutrients, as well as clastic sediment fluxes.
Chapter 10

DISCUSSION: THE ORDOVICIAN SILICA SECRETING BIOTAS - LIVING STYLE, DISTRIBUTION AND ONSHORE-OFFSHORE EVOLUTION PATTERNS

The results of Chapter 7 show that at the beginning of the Ordovician the peritidal/lagoonal and shelf waters were inhabited by both siliceous sponges and radiolarians, with the supremacy held by sponges (fig. 10.1). Conversely, the biosiliceous component of slope/basinal sediments was provided mainly by radiolarians, and subordinately by siliceous sponges. During the Middle Ordovician, radiolarians were confined to waters above slope/basin environments, and siliceous sponges retreated from peritidal/lagoonal to shelf and basinal environments, suggesting an Arenigian-Llanvirnian retreat with a migration time of less than 15 Ma. By the Ashgillian, the chert record suggests that siliceous sponges had retreated completely from peritidal/lagoonal settings, inhabiting mainly shelf environments and subordinately basinal areas which were clearly dominated by radiolarians in terms of biosiliceous accumulation (Fig. 10.1).

10.1. Lower Ordovician

The Lower Ordovician distribution pattern of the dominantly biogenic chert deposits is characterized by shallow water siliceous sponge-dominated cherts contrasting with a predominance of radiolarian chert in slope/basinal settings. This is superimposed
Figure 10.1: The Ordovician dominant locus of silica burial and onshore-offshore migration patterns of the silica secreting organisms and the associated facies. The relative size of the radiolarian and sponge symbols reflects the dominance of the corresponding type of organisms in cherts in a particular environment. The relative abundance of the nodular and bedded chert symbols reflects also the dominance of the chert type in a particular environment. Ovals represent nodular chert and horizontal long lines represent bedded cherts.
on another distribution pattern whereby shallow water nodular-bedded chert dominates within carbonate environments, whereas deep water bedded cherts dominate within fine-grained siliciclastic environments (Fig. 10.1). These patterns may represent carryovers from the Late Cambrian and possibly the Middle Cambrian, considering the Middle-Upper Cambrian bedded chert distribution (Kidder and Mumma, 2003), and the distribution of siliceous sponge and radiolarian faunas (Won and Below, 1999; Tolmacheva et al., 2001).

Siliceous sponges were able to populate depositional environments of varying depths, from shelf to basinal environments, since the beginning of the Cambrian, when both lithistid demosponges and hexactinellids were already representing a relatively diversified component of the benthic fauna (Finks 1970; Yuan et al., 2002; Li et al., 1998; Zhang and Pratt, 1994). The fact that the two silica secreting faunas, radiolarians and siliceous sponges, were prevalent in distinct depositional environments emphasizes their ecological separation, probably based on different needs in terms of dissolved silica and other nutrients, water temperature, chemistry, salinity, and sediment substrate. Considering that siliceous sponges generally need higher dissolved silica levels than the radiolarians (Maldonado et al., 1999), I can hypothesize that during the Lower Ordovician the shallower siliceous sponge-rich environments, i.e., peritidal/lagoonal and shelf carbonate platforms, were characterized by higher silica levels compared to the surface waters of the deeper settings, a status quite possibly preserved since the Cambrian. The strontium estimates for the same geological period indeed reveal a relatively high continental radiogenic $^{87}$Sr/$^{86}$Sr input compared to the ensuing Ordovician
epochs (Shield et al., 2003) (Fig. 11.1B). Additionally, siliceous sponges are filter-feeding organisms and the very stable, nutrient rich environments offered by the widespread Lower Ordovician carbonate platforms would explain their preference for these shallow habitats.

Studies of Lower Ordovician siliceous sponge assemblages show a differentiation within the siliceous sponge biota itself, namely between demosponges and hexactinellids, in their distributional patterns within a given basin: the lithistid demosponge fauna, quite diversified at that time, prefered the shallow, warm environments offered by the carbonate platform factories, while hexactinellid sponges, much less diversified, occupied deeper environments of slope and basinal sequences within siliciclastic environments (Mehl and Lehnert, 1997, in Beresi and Esteban, 2004; Beresi and Rigby, 1993, in Beresi and Esteban, 2004; Carrera and Rigby, 1999; Beresi and Esteban, 2004; Tolmacheva et al., 2001). This environmental segregation of the Early Paleozoic siliceous sponge fauna is supported by modern siliceous sponge assemblages. The deep-water Hexactinellids need higher silica concentrations than the shallower water Demosponges (Maldonado et al., 1999). This evidence seems to contradict the hypothesis that during the Lower Ordovician the shallower marine habitats might have been richer in silica and other nutrients than the deeper areas. However, it suggests that other environmental factors, such as the nature of the sediment substrate and seawater temperature, in conjunction with a high silica level might have been responsible for a dominant species-based distribution and it does not rule out the possibility that there was even more dissolved silica in deeper waters like today. It also suggests that the Early Paleozoic siliceous
sponge fauna may have been represented by species different from the modern ones
and/or that the distribution of the Early Paleozoic siliceous sponge fauna was governed
by different factors not present in the modern ecosystems. Overall, during the Lower
Ordovician the Hexactinellid sponges (the deep water population) were a less important
component of sponge faunas compared to the lithistid demosponges (the shallow water
population) that were predominant in the sponge fauna (Finks, 1970; Rigby, 1983;
Carrera and Rigby, 1999). The dominance of Lithistids may explain the abundance of
shallow-warm-water siliceous sponge assemblages within a carbonate environment,
relative to the deep-water siliceous sponge species within a siliciclastic setting, and a
possible biogenic origin via siliceous sponges of the peritidal-shelf nodular cherts and the
shallow water bedded cherts (Chapter 9).

More recent findings bring new data relative to the Ordovician siliceous sponge
fauna. The shallow-water carbonate sequences found in the Argentine Precordillera show
a clear dominance of lithistid demosponges in the siliceous sponge fauna (Beresi and
Esteban, 2004). That study, representing the broadest South American record of
Ordovician siliceous sponge fauna, supports the affinity of lithistid demosponges to warm
shallow carbonate environments, for a fauna included in the “eastern North American
Laurentian faunas” (Carrera and Rigby, 1999; Beresi and Esteban, 2004).

Is silica or nutrient limitation of greater importance? This is a question raised by
many authors trying to explain the growth and evolution of the siliceous sponges and
radiolarians (Maldonado et al., 1999; Maliva et al., 1989). Modern studies on siliceous
sponges still disagree about which parameter exerts the main control, and consequently
two antagonistic theories have been proposed: the silicon limitation growth theory (Reincke and Barthel, 1997; Maldonado et al., 1999; Racki and Cordey, 2000) and the nutrient limitation growth theory (Frøhlich and Barthel, 1997; Pettijohn, 1975; Siever, 1962) (see Chapter 8).

The silicon limitation growth theory is based on experimental demonstration that the silica uptake rate of siliceous sponges increases asymptotically with increasing silica concentration (Reincke and Barthel, 1997; Maldonado et al., 1999). Insufficient silica concentration weakens the ability of the siliceous sponges to develop complex spicule morphology, and very simplified, small and thin skeletons are secreted instead, but the organisms are still capable to survive. Alternatively, seawater with silica concentrations in excess of 100 µM may inhibit silica uptake (Maldonado et al., 1999). The same relationship was observed in the radiolarians' behavior: while they are very effective in silica uptake, occurring abundantly in surface waters that exhibit low silica concentrations (ca. 1 µM) and yet mineralizing robust siliceous skeletons, silica levels as high as 100-150 µM have a deleterious effect on their longevity, growth, and weight gain, acting as a toxin that inhibits their metabolic activity and kills them (Sugiyama and Anderson, 1997).

Conversely, the nutrition limitation growth theory is based on experimental data showing that silica uptake is an energy-consuming process and therefore in a nutrient-starved environment (as that proposed by Pettijohn, 1975, to explain the inorganic formation of some cherts within a lagoonal setting with restricted circulation and starvation of nutrients other than silica), the biogenic extraction of dissolved silica by
siliceous sponges will decrease by 15% (and presumably ceases?) (Frøhlich and Barthel, 1997). Regarding the modern radiolarian fauna, a direct relationship was observed between their abundance and eutrophic, nutrient-rich, highly saline (40‰) warm (28°C) surface waters principally of the equatorial zone or associated to subtropical and tropical environments (Anderson et al., 1989c). Numerous studies point out that the spatial distribution of radiolarians might be controlled mainly by water salinity and temperature (Anderson et al., 1989a,b,c; Anderson et al., 1990; Matsuoko and Anderson, 1992; Chang et al., 2003), showing a negative correlation with nutrients and primary productivity of the surface water (Chang et al., 2003). However, regardless of which parameter prevails, during the Lower Ordovician the strontium isotopic ratios are consistent with the shallow environments being continuously enriched in silica and other nutrients through riverine runoff, which may account for the high abundance of the more silica-dependent siliceous sponges (Fig. 10.1).

The dominance of radiolarians in deeper-water environments may be explained and interpreted in three ways: first, a vestige from the Middle or Upper Cambrian, and possibly of their deep water origin (Tolmacheva et al., 2001); second, while the deep water environments are always characterized by an adequate nutrient supply for their biological needs, other parameters must have prevailed in stabilizing the dominant basinal distribution of radiolarians; and third, they thrive principally in upwelling settings where silica and other nutrients are readily available.

The paleolatitudinal distribution of Lower Ordovician cherts reveals a low to mid latitudinal increase in silica burial (Fig. 7.4 and Table 7.5) with the radiolarian dominated
deep-water and peritidal/lagoonal deposits confined principally to low paleolatitudes (0° - 30°), and the mid-latitudinal cherts (30° – 60°) occurring mainly in shelf deposits (North China and Korea). However, relative to the Lower Ordovician paleogeography of Korea and North China, more recent paleogeographic studies (Xiaofeng and Xiaohong, 1995) place the benthic faunas at low latitudes and not at mid latitudes as shown in Fig. 4.

The distribution analysis of the chert formations bearing biogenic siliceous remains shows their low latitudinal expansion (0° - 30°) was principally in the southern hemisphere, in Kazakhstan, South China, and the southern margin of Laurentia. The reports from Bolivia, Poland, Korea, and North China do not include any mid-latitudinal cherts that contain sponge or radiolarian fragments, but more recent findings of studies from northern Argentina which was situated at middle paleolatitudes (Fig. 7.4) demonstrate the presence of hexactinellids in siliciclastic sedimentary sequences during the Lower Ordovician (Beresi and Esteban, 2004). However, it is worth mentioning that the paleogeography of the Argentine Precordillera (western Argentina) is a debated problem: some workers consider that it was a part of Gondwana during the Cambrian, and that it collided with Laurentia during the Ordovician (Dalla Salda et al., 1992), while others argue that it was a microcontinent that rafted from the Ouachita embayment of Laurentia during the Cambrian, and collided with Gondwana during the Middle Ordovician (Astini, 1995; Thomas and Astini, 1996). The latter view seems to be supported by more pertinent evidence and is more widely accepted.

Assessing this global distribution pattern and interconnecting multiple factors related to it, a paleolatitudinal based partition is evident: 1) deep-water, radiolarian
dominated cherts are present in low latitudes; 2) lithistid demosponge dominated chert facies dominate peritidal/lagoonal and carbonate shelf; and 3) the mid latitudes are characterized by deep shelf and basinal environments dominated by Hexactinellids.

The confinement of radiolarians to low latitudes offers insights into some ecological aspects of the Early Paleozoic radiolarian fauna. Their apparent preference for warmer waters, was a consequence of since their emergence in the greenhouse Middle Cambrian climate (De Wever et al., 2001). The mid and high latitude Lower Ordovician waters were probably too cool for their survival, suggesting that during that time there was a latitudinal thermal gradient high enough to constrain radiolarian latitudinal distribution. The distribution of Early Paleozoic radiolarians is tightly linked to water temperature, a hypothesis suggested by Sugiyama and Anderson (1997) for modern radiolarian communities, and in agreement with the general line of thought that associates plankton distribution with abiotic factors such as temperature and latitudinal zonation (Lipps, 1970; Tappan and Loeblich, 1973).

Siliceous sponge faunas are able to inhabit environments with a wider latitudinal distribution probably because of: 1) either the specialization of the two different sponge groups, Lithistid Demosponges and Hexactinellids, to life in different environments, shallow warm carbonate settings for the former, and respectively cooler, deeper, siliciclastic habitats for the latter, perhaps an evolutionary ability gained due to their participation in and survival from the Latest Precambrian Icehouse; or 2) they evolved as primitive generalists that could adapt readily to variable environments as long as they have clear waters and sufficient nutrients and dissolved silica.
10.2 Middle Ordovician

The distribution of Middle Ordovician cherts within siliceous skeletal remains reveals that radiolarians are exclusively confined to slope/basinal environments whereas siliceous sponges seem to characterize both shelf and slope/basinal settings (Fig. 10.1). The Middle Ordovician distribution pattern of silica secreting biotas reflects a change in of siliceous sponge faunas from peritidal/lagoonal to shelf-basinal environments, and of radiolarians to basinal settings, suggesting an Arenigian- Llanvirnian onshore-offshore migration of the silica secreting organisms in less than 15 My. This shift of the cherts containing preserved skeletal remains is accompanied by a general onshore-offshore drift in the locus of marine silica deposition, so that during the Middle Ordovician the slope/basinal environments represent the dominant domain of silica burial. The faunal retreat is also coeval with a turnover in the chert style from shallow-water carbonate environments dominated by nodular-bedded cherts characteristic for the Lower Ordovician, toward a slope/basin bedded chert-dominated silica system within siliciclastic environments in the Middle Ordovician (Fig. 10.1).

10.2.1. Migration mechanisms

Speculations can be made about the style of the organism migration. If radiolarians moved offshore because of various causes, if the linkage between radiolarians, a phytoplankton food source, and siliceous sponges, a sessile benthic component of the food web, was as strong as in modern marine communities, and if silica was a limiting factor for the Ordovician siliceous sponge fauna, siliceous sponges may
have followed the offshore migration of radiolarians (Kidder, 2000). Today, radiolarians and sponges are both consumers but at different trophic levels (De Wever et al., 2001). The higher trophic levels characteristic for sponges depend on the lower levels including radiolarians. Within the food web as we know it today, benthic faunas, especially sessile organisms such as sponges, depend on the more flexible planktonic organisms. Siliceous sponges may have followed radiolarians because the marine environments proximal to those inhabited by radiolarians were richer in dissolved silica owing to the fact that radiolarians dissolve at faster rates than siliceous sponges (Scholl et al. 1983).

Potential mechanisms for the shallow to deeper water migration of the silica secreting biotas include: i) onshore-offshore evolutionary patterns, and/or ii) changes in availability of dissolved silica and other nutrients used by siliceous sponges and radiolarians (Tomescu and Kidder, 2002).

i) Onshore-offshore evolutionary patterns of silica secreting organisms

The shift of cherty facies from nearshore settings toward deeper environments might have been driven by onshore-offshore patterns of evolution (Kidder, 2000), an Ordovician mechanism suggested for benthic invertebrate calcareous macrofaunas (Sepkoski and Sheehan, 1983; Jablonski et al., 1983). The Ordovician contains evidence of an onshore-offshore migration of the benthic communities of the three Phanerozoic faunas: the declining Cambrian fauna became restricted more or less to deep water environments moving offshore perhaps by the Paleozoic fauna diversifying across the shelf, and the Modern fauna developing in nearshore environments. The displacement of the Cambrian fauna by the Paleozoic fauna occurred over the Lower and Middle
Ordovician, and the rise of the Modern fauna in nearshore settings occurred in the mid to late Ordovician (Jablonski et al., 1983; Sepkoski and Miller, 1985). However, these analyses of Early Paleozoic marine faunas do not include any planktonic group of organisms, and it is unclear whether they apply to the siliceous sponges. Comparable timing of migration would be consistent with siliceous biotas moving in concert with calcareous ones.

**ii) Changes in availability of dissolved silica and other nutrients**

The onshore-offshore migration of the silica secreting biotas can be explained in terms of a shift in the dominant source of silica and other nutrients (P, N, Fe), from an allochtonous-dominated (exogenous input through riverine runoff) to an autochtonous-dominated (endogenous inputs through volcano-hydrothermal and seafloor weathering activities) system.

In modern oceans, among the four silica sources that replenish the marine silicic acid, river runoff accounts for 82%, volcano-hydrothermal together with seafloor weathering inputs only 10% of the total silica, and the remaining of 8% is attributed to eolian supply (Tréguer et al., 1995). The nutrient load of the rivers is strongly influenced by the silicate weathering rates and the volume of rocks exposed to weathering. Consequently, a change in weathering will affect the river flux, that in turn induces changes in the marine realm. The volume of silicate rocks exposed to weathering, and the weathering rates are directly related to changes in uplift of mountain belts, climate, sea level fluctuations, the interplay between the latitudinal disposition of the landmasses and
the emerged land area, and indirectly related to tectonic rifting and oceanic spreading rates.

The Ordovician was a geological period characterized by energetic mid-oceanic ridge activity (Mackenzie and Piggot, 1981), intensive volcanism (Ronov, 1982; Huff and Kolata, 1990; Huff et al., 1992; Huff et al., 1996) common in submarine islands, coastal and cordilleran sites (Stillman, 1984), numerous volcanogenic massive sulfide deposits compared to the Cambrian and the Silurian (Eastoe and Gustin, 1996), a low area of continental deformation and orogenic activity during the Lower and Middle Ordovician (Richter et al., 1992; Miller and Mao, 1995), and intensive reorganization of the major tectonic plates (Ford and Golonka, 2003; Worsley et al., 1994).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in marine sediments is tightly linked to the balance between continental weathering (radiogenic flux) and oceanic spreading rates (non-radiogenic flux). The minimal change in the ration through the Lower and Middle Ordovician is consistent with a relatively unchanging chemical dissolved runoff from the landmasses.

10.2.3. Considerations regarding the Middle Ordovician sea level fluctuations

The Middle Ordovician is a geological time characterized by a generally much lower sea level compared to the Lower Ordovician and the ensuing Caradocian (Ross and Ross, 1992). The sedimentary sequences of most of the Whiterockian series (the lower part of the second-order Tippecanoe sequence of the North American stratigraphy) reveal a sharp Middle Ordovician sea level drop that exposed almost the entire craton of Laurentia (Finney, 1997; Fortey, 1984). The evidence is based on both deep
and cratonic shelves sedimentary successions (Ross and Ross, 1992; 1995). The Whiterockian – Ibexian boundary in North America coincides approximately with the Lower – Middle Ordovician boundary (late Arenigian, Fig. 6.2). According to Finney (1997), this regression boundary is a second-order eustatic sea level drop that represents a conspicuous horizon recognizable across the North American continent, and which lasted 3 to 5 million years. The Sauk-Tippecanoe sequence boundary, known as a global paleokarst unconformity (Sloss, 1963), has been also recognized in South Korea, North China, the Canadian Appalachians, and the Southern Appalachians (Ryu, 2002), in southern Wales, on the Australian platform, as well as in Sweden (Fortey, 1984), and northern Europe (Webby, 1984a,b).

A sea level drop results in a reduced habitable space on the shelf and thus shallow water communities would be forced to track the drop of their habitat (Fortey, 1984). However, shallow waters would still exist even though these environments would suffer the greatest loss in space, and coastal settings might not change much in areal extent. The degree to which sea level changes and glaciations affect marine life is controversial (e.g., Wilde and Berry, 1984; Fortey, 1984).

Unfortunately the potential mechanisms responsible for the global early Middle Ordovician sea level drop are not well documented. According to Ryu (2002) regional and tectonic events generated local and regional variations of the Sauk-Tippecanoe sequence boundary. Considering that the Sauk-Tippecanoe sea level drop is seen as a major eustatic event, driving mechanisms might be represented by:
1) fluctuations in the rate of sea-floor spreading that would directly disturb significantly the volume of ocean water (Donovan and Jones, 1981; Hays and Pitman, 1973). This mechanism that would be in agreement with a decrease in the rate of seafloor spreading suggested by François et al. (1993, after Gaffin, 1987), and implicitly a decreasing area of continental deformation (Richter et al., 1992; Qing et al., 1998). A decrease in the volume of oceanic ridges would affect directly the basin volume process depending on oceanic spreading rates (see paragraph 1) – but seen as a long-term mechanism, lasting 10-30 m.y. (Donovan and Jones, 1981).

2) changes in mean oceanic temperature, through thermal seawater contraction; these would have an effect of smaller magnitude susceptible to be masked by the effects of other processes (Donovan and Jones, 1981).

3) increase in the volume of ice sheets (Fortey, 1984; Lindström, 1984) based on the geographic position of Gondwana over the South pole. However, no glacial deposits support this hypothesis.

10.3. Upper Ordovician

The Upper Ordovician distribution of cherts illustrates a depositional environment distribution pattern similar to that of the Middle Ordovician and consistent with the proposed onshore-offshore patterns inferred previously. Radiolarian bedded cherts were confined to slope/basinal settings, and shelf deposits are dominated by nodular and bedded cherts with siliceous sponge spicules preserved. The three Caradocian silicified oolites on the southern margin of Laurentia suggest that siliceous sponges might have
still been present sporadically in some peritidal/lagoonal areas characterized by peculiar local conditions. During the Ashgillian, the peritidal/lagoonal cherts disappear completely. If the chert depositional migration occurred within the same range of low and middle paleolatitudes in the Lower and Middle Ordovician, during the Upper Ordovician it expanded to the high paleolatitudinal habitats, (the nodular cherts from Italy and France; Loi and Dabard, 2002).
Chapter 11

INTERPRETING THE CHERT ABUNDANCE PATTERNS: WHY CHERT PEAKS OR LOWS?

11.1. Lower Ordovician: a greenhouse interval

The present study demonstrates that the Lower Ordovician was characterized by high chert abundance principally in shallow, peritidal/lagoonal, and shelf environments and secondarily in slope/basinal settings (fig. 7.1A, 7.3, 10.1, and 11.1A). The Lower Ordovician was a period characterized by: 1) high sea level, including the climax of the Precambrian – Lower Ordovician Sauk transgressive sequence that occurred during the late Ibexian (early Arenigian; fig. 6.2), when the sea level reached one of the highest levels in the entire Phanerozoic (Finney, 1997; Ford and Golonka, 2003); 2) maximum dispersion (disassembly) of continents by the northward drifting of Laurentia and Baltica concomitant with widening of the Iapetus Ocean and Tornquist Sea (Worsley et al., 1994; Ford and Golonka, 2003); 3) intensive volcanic activity since the late Cambrian (Stillman, 1984); 4) widespread carbonate platforms (Overstreet et al., 2003); and 5) organism radiation (fig. 11.1A). The strontium curve (fig. 11.1B), during the early Lower Ordovician, that is the Tremadocian, has higher radiogenic values than during the ensuing Ordovician epochs, suggesting higher continental weathering rates of the silicate rocks exposed by the Pan-African orogeny (Ebneth et al., 2001), but still low
Figure 11.1A: The Ordovician biotic system
Figure 11.1A – The Ordovician biotic system: continued.

a. Chert abundance patterns evidenced by the present study. The data is normalized to time.
b. Chert abundance by depositional environments, as evidenced by the present study. Gray bullets represent peritidal/lagoonal cherts, black bullets represent shelf chert deposits, and stars represent slope/basinal chert formations. The data is normalized to time.
d. Black shale abundance patterns in the British Isles; after Leggett et al., 1981.
e. Euxinification episodes based on black shale abundance; after Leggett et al., 1981.
f. Graptoloid diversity; after Leggett et al., 1981.
g. Brachiopod diversity; after Leggett et al., 1981.
Figure 11.1B: The Ordovician abiotic system
Figure 11.1B – The Ordovician abiotic system: continued.

a. Strontium and oxygen isotope curves based on calcitic brachiopods; after Shields et al. (2003).
b. Extent of continental deformation areas; after Reichter et al. (1992) and Qing et al. (1998).
c. Sea level fluctuations; after Ross and Ross (1992; 1995); Qing et al. (1998); Finney, (1997).
d. Tropical seawater temperature based on oxygen isotope values; after Shields et al. (2003) and Tobin et al. (1996).
e. Tectonic data: orogenies and continental migration patterns; duration of Taconic orogeny and continental migration patterns after Ford and Golonka (2003), Qing et al. (1998). A Ringworld is dominated by tropical continents, while a Capworld is characterized by polar continents (Worsley and Kidder, 1991; Worsley et al., 1994). Question marks for uncertain timing.
f. Average latitude of the world landmass for the “2-10” model (Worsley and Kidder, 1991; Worsley et al., 1994).
g. Volcanogenic massive sulfide deposits (Eastoe and Gustin, 1996).
h. Oolitic ironstone accumulations (Van Houten and Arthur, 1989).
enough to allow the development of widespread carbonate platforms, that were
overwhelming the shelf system, up to relatively high latitudes (50° in Asia; Frakes et al.,
1992). Shelf areas were very extensively developed in North America, Australia, Asia,
and South America, and were centered close to the equator and tropics. The widespread
marine carbonates deposited in shallow epeiric seas (Overstreet et al., 2003), the oxygen
isotopic data (Tobin et al., 1996; Shields et al., 2003), and the relatively abundant oolitic
ironstone deposits (Van Houten and Arthur, 1989) provide support for a warm and
humid greenhouse mode.

11.1.1. Peritidal/lagoonal and shelf environments

The peritidal-lagoonal and shelf environments during the Lower Ordovician were
inhabited mainly by siliceous sponges and subordinately by radiolarians (fig. 10.1),
resulting in abundant nodular and less frequent bedded cherts (fig. 7.3 & 7.7).
Geographically, approximately 75% of the worldwide Lower Ordovician shallow water
cherts have been identified on the south-southwestern margin of Laurentia, such as on
the Appalachian and Cordilleran passive margins, the south Oklahoma aulacogen, and
the Ozark Uplift (Overstreet et al., 2003) (Table 7.6), as well as in the Kazakhstan block,
China, Korea, Australia, and Argentina (fig. 7.4).

- Why abundant chert burial?

The modern silica cycle does not exhibit any shallow biogenic opal accumulation
and burial, and therefore we can only speculate about the driving mechanisms that
generated biogenically-induced chert formation in the past. First of all, both
peritidal/lagoonal and shelf depositional environments were inhabited by silica secreting
organisms, principally siliceous sponges and secondarily radiolarians, which provide the necessary silica for the chert formation. Also, these shallow water settings were characterized by a generally low terrigenous input that could not mask the biogenic silica accumulation, or inhibit the development of large carbonate platform factories, and the expansion of filter feeding siliceous sponges and other benthic organisms. Jones and Desrochers (1992) emphasize that shallow platform carbonates can form in areas isolated from extensive siliciclastic flux. The strontium curve (fig. 11.1B) is consistent with the fact that Lower Ordovician riverine runoff must have been still high enough to account for the needs in terms of dissolved silica and other nutrients required by siliceous sponges and radiolarians. Moreover, the host rock represented by carbonates probably played an important role in the chert formation and burial, based on the affinity between carbonates and chertification (Kastner et al., 1977; Maliva and Siever, 1989). Another factor in chert formation could be the presence of abundant organic matter whose decomposition through oxidation may induce early diagenetic nodule formation (Siever, 1962; Maliva and Siever, 1989). According to the force of crystallization-controlled replacement model of Maliva and Siever (1989), the ideal host sediment has three properties: organic matter content, porosity and permeability, and biogenic-opal concentration.

Taking into account that seawater was warm (as shown by oxygen isotopic ratios; fig. 11.1B), the opal dissolution rate is should have been high and thus driving silica recycling and preventing opal accumulation. However, the loss of opal through dissolution would have been counterbalanced and surpassed by: 1) the dominance of
siliceous sponges that dissolve at lower rates than radiolarians (Scholle et al., 1983); 2) the shallow depth of the water column that would reduce the time available for sinking and dissolution of opal radiolarian skeletons; 3) low terrigenous input that could mask silica concentrations; 4) the carbonate composition of the host rock; 5) the presence of abundant organic matter, and 6) a possibly rapid burial of the benthic silicisponges (before their silica can get into ocean water) through a relatively high vertical accumulation of the carbonate production; instead, the dissolution of the opaline skeleton makes chert nodules.

In conclusion, while we can only speculate about a good organism productivity in these shallow settings, due to stable and favorable environmental conditions, the chert abundance could be accounted for in a low sediment dilution - enhanced chert formation model (fig. 11.2).

11.1.2. Slope/Basinal environments

The slope/basinal settings were inhabited principally by the planktonic radiolarians, and subordinately by siliceous sponges. It was demonstrated that at least in certain basinal environments the bottom waters were well aerated (Wilde, 1989) and could sustain the activity of some benthic siliceous sponges (Blome et al., 1995a; Tolmacheva et al., 2001). Also, Leggett et al. (1981) discussed the presence of burrows and primary iron oxide in cherts of the British Isles (Iapetus Ocean) associated with pillow lava, that indicate well oxygenated bottom waters, as well as high silica and other nutrients inputs. The well oxygenated deep water theory is also supported by the presence of deep burrowing trace fossils (up to 79 cm deep), discovered in an early Ordovicia
Figure 11.2: Chert abundance Model. LOWER ORDOVICIAN [490 – 470 Ma]
deep-water flysch sedimentary sequence of Nova Scotia (the Meguma Group; Pickerill and Williams, 1989). That study represents the first evidence of infaunal behavior in deep water environments, in contrast to the previous much shallower estimates that were based on the analysis of shelf settings (Pickerill and Williams, 1989). Also, according to Crimes (1974; 1992) a clear increase in the deep-water Nereites ichnofacies can be seen during the Ordovician.

On the other hand, a warm world with warm surface waters would lead to higher metabolic activity, higher silica dissolution and thus higher silica recycling in the uppermost water layers. This recycling would lead to a decreased potential for biogenic opal preservation. The significant silica accumulation and burial in the deep-sea may account for high preservation rates at the bottom part of the basin. If under these circumstances additional processes generating silica and other nutrients inputs (e.g., volcanic, hydrothermal, and oceanic spreading activities) were active, these could create an environment with a higher potential for blooms of silica secreting organisms, higher opal rain rates, and a higher potential to increase the silica net output through the formation of biogenic chert.

A relatively high radiolarian productivity within a warm water world is consistent with: 1) the ecology of some modern radiolarians shown to be tightly linked to warm, highly saline surface waters (Anderson et al., 1989c); 2) the origin of radiolarians as part of the Cambrian explosion that occurred in a warm climate; 3) the theory that submarine volcanism and hydrothermal activity, coupled with a warm climate, and a sea level rise, provide the right conditions for increased productivity (Vermeij, 1995); and 4) major
tropical continental margins upwelling sites along the equator in western America and
Arctic Islands in Laurentia, North China, New Zealand, and Newfoundland (Wilde,
1989).

In concordance with Vermeij’s theory (1995), a high temperature constitutes the
main stimulus for high productivity through enhanced metabolico-chemical reactions
that are greatly accelerated with increased temperature. The model emphasizes the fact
that increased nutrient supply only is not enough to generate significant high
productivity, and that organisms revolutions are mainly generated by increased energy
(such as temperature) and subordinately by nutrient supply. The survival of radiolarians
during this interval, along with observations showing that for modern taxa high
temperatures above 33° C have deleterious effects on radiolarian longevity (Anderson et
al., 1987c), indicate the presence of favorable marine environments. The presence of
abundant radiolarians appears to rule out the possibility of overly high surface seawater
temperatures at low latitudes, which are suggested by the very negative oxygen values
obtained for this epoch (fig. 11.1B; Shields et al., 2003; p. 2016).

Good preservation rates within a well-aerated deep bottom environment may be
the result of the interplay of multiple factors such as: 1) a fairly high rate of opal rain
induced by a good productivity in the surface waters, 2) the presence of organic matter
that intensifies silica preservation (Spencer, 1983; Siever, 1957); 3) a water column
shorter than that of the modern abyssal sites directly dependent on the basin morphology,
and 4) possibly higher concentrations of cations, such as Al, Fe. These cations that were
shown to combine with diatom silica to decrease dissolution rates (Lewin, 1961). Nelson
et al., (1995) assert the dissolution rate and the equilibrium solubility of diatom silica decreases as the Al/Si ratio increases.

The clustering of Lower Ordovician basinal bedded cherts on the southeastern margin of Laurentia, might be because of least two of the factors that would enhance silica preservation: 1) high cation concentrations of intrabasinal origin, through submarine volcanism driven by the widening of the Iapetus Ocean (Ford and Golonka, 2003) and 2) favorable organic matter concentrations, such as the presence of zooplanktonic graptoloids whose diversity reaches the highest peak for the Ordovician, at least in the Iapetus Ocean (fig. 11.1A; Leggett et al., 1981). Even though black shale studies do not indicate any significant organic-rich sediments formed during this interval, a finding otherwise consistent with well aerated bottom demonstrated for the Iapetus Ocean (fig. 11.1A; Leggett et al., 1981), the levels of organic matter were seemingly high enough to enhance silica burial in concert with other factors. Though it is difficult to prove or test, a preservation model is consistent with abundant chert in a green house model.

However, there is no study showing a relationship between radiolarians and Al intake similar to the one documented for diatoms. Also, the role of organic matter in silica preservation is arguable. It may be enhancing by its adsorption on the silica surface or, on the contrary it may be deleterious by the formation of organic-silica complexes, so that no conclusive relationship has been supported to date (Siever, 1962). Bidle and Azam (1999) and Bidle et al., (2002) showed that bacterial activity is important in silica
dissolution by degrading the organic film that protects the opal diatomaceous frustules from dissolution.

In conclusion, the dominance of bedded cherts in basinal settings (fig. 7.7A) might reflect relatively high biosiliceous productivity, associated with good taphonomic conditions (high preservation rates) induced by the conjunction of various opal enhancing mechanisms, under an oxic regime within the bottom areas (fig. 11.2).

11.2. Middle Ordovician: a greenhouse interval (fig. 11.3)

The general chert abundance is strongly diminished during the Middle Ordovician, exclusively due to a 75% decrease in silica burial in peritidal/lagoonal and shelf environments (Table 7.3 & fig. 7.3). The data show also that the formation of nodular cherts has been intensely affected in comparison with that of the bedded cherts, during this interval (fig. 7.2A). All these facts, along with the genetic relationship that exists between siliceous sponges and peritidal/lagoonal-shelf chert formation (Chapter 7 and 9) suggest that the benthic siliceous sponge biota was more involved in this general chert abundance low. The slope/basinal bedded cherts, during the same interval on the contrary, record a slight augmentation suggesting that radiolarian faunas and implicitly radiolarian-induced chert formation were not responsible for the Middle Ordovician global silica shortage. Geographically, the most affected area by the silica burial low was Laurentia, which suffered a 50% reduction in chert formation (Table 7.6).

The Middle Ordovician shallow water chert low may reflect either an apparent, or a real silica burial slowdown. The apparent curtailment may be due to some common
Figure 11.3: Chert abundance Model. MIDDLE ORDOVICIAN [470 – 458 Ma]
errors and biases inherent to any compilation study, such as sampling issues, afe assignment problems, and/or to the fact that the worldwide sedimentary sequences are unequally studied so that the absence of chert deposits in certain geographical areas might reflect just a lack of knowledge and not a physical absence.

On the other hand, an actual slowdown of silica burial may be linked to changes in the biotic and abiotic Middle Ordovician systems. The Lower-Middle Ordovician onshore-offshore organism migration, especially that of siliceous sponges, that have been demonstrated herein to be responsible for the formation of shallow chert deposits and which proved to be most affected by this chert waning. Physico-chemical changes of the depositional environments (e.g., a sea level transgression) that would have influence the balance between opal dissolution and opal preservation and the balance between shallow (peritidal/lagoonal and shelf) and deep water (slope/basinal) environments.

The Middle Ordovician represents a time of (fig. 11.1): 1) onshore-offshore migration of both benthic and planktonic organisms that try occupy new ecological niches (Sepkoski and Sheehan, 1983; Jablonski et al., 1983); 2) major plate tectonic reorganization as the Iapetus Ocean and Tornquist Sea begin to narrow down, and the Rheic Ocean is forming (Ford and Golonka, 2003); 3) low relative sea level (Ross and Ross, 1995; Finney, 1997); 4) warm surface water temperatures (27°C - 32°C; Shields et al., 2003); 5) decreased emergent land area coeval with lower average latitude of the world landmasses (Worsley et al., 1994); 6) higher radiolarian diversity (Vishnevsksaya, 1997); and 7) more abundant back shale deposits (Leggett et al., 1981). However, the present study reveals a decrease in the mid latitudinal cherts concomitant with an
increase of the low latitudinal deposits (Table 7.5). That suggests either a less warm climate compared with that of the Lower Ordovician or less available shelf area in which chert could form.

11.2.1. Peritidal/lagoonal and shelf environments

The relationship between the formation of shallow water cherts and siliceous sponges (Chapter 9), and the fact that Middle Ordovician proves to be a geological interval of biological adaptation to new, deeper-water ecological niches by a onshore-offshore organism migration (see Chapter 10), suggest that the Middle Ordovician chert low was driven by a decrease in the shallow water silica burial due to unstable conditions in the evolutionary scenario of siliceous sponges and subsequently to a lesser extent of radiolarians.

Another mechanism that could impact the Middle Ordovician chert preservation is represented by a reduction in the shelf area in which cherts could form. In the early Middle Ordovician, the main Lower Ordovician chert bearing continent, Laurentia, was entirely emergent due to a short-lived major regression (Finney, 1997) recognizable worldwide (Ryu, 2002; Fortey, 1984; Webby, 1984a,b; Sloss 1963) (Chapter 10). Thus, it can be argued that the slowdown in chert deposition may be strictly a consequence of the physical displacement of shelf environments by the retreat of the sea level, and not linked at all to the organism migration. Finney (1997) estimated that the regression had a short duration (3-5 Ma), and that the rest of the Middle Ordovician and up to the early Caradocian witnessed a gradual transgression and implicitly a re-expansion of the shelf area. However, at this point in time, the siliceous sponges inhabited deeper sites of the
carbonate shelf environment and radiolarians were populating exclusively the slope/basinal waters, so that siliceous sponges could not compensate for the drop in overall shallow water chert production.

11.2.2. Slope/basinal environments

The planktonic organisms (e.g., radiolarians and graptoloids) that accumulated in deep waters would have greatly benefited from a higher intrabasinal input of silica and other nutrients (P, N, Fe). Such an increased input is consistent with the strontium curve (a change that has occurred before the Lower-Middle Ordovician boundary, sometime in the Ashgillian), and is due to an energetic midocean activity and a higher infaunal activity resulting from the invasion of deeper nutrient-rich areas as a consequence of the onshore-offshore Ashgillian-Llanvirnian organism migration. Innovations in burrowing organisms such as the population of new deeper-water ecological niches would constitute a stimulus for a higher productivity of the planktonic organisms, by making available new amounts of nutrients entrapped into sediments during precedent periods. The release of phosphorous entrapped into the deep-sea sediments triggered by a migration of the benthic organisms was proposed as one mechanism responsible for the Cambrian explosion (Bengston, 1994). The increased deposition of black shales (fig. 11.1A) during this period, coeval with warm surface waters, and a slight increase in the deep basinal silica burial (fig. 7.3), provide support for good organism productivity (Vermeij, 1995) concurrent with enhanced silica preservation mechanisms (i.e., a higher influx of organic matter due to a higher productivity). The intense deep water activity of the benthic faunas
indicates the presence of oxic bottom deep waters at least in some regions (Leggett et al., 1981). However, the higher abundance of organic-rich sediments intercepted through more abundant black shales compared to that of the precedent period (fig. 11.1A), suggests a higher organic productivity and/or somewhat less oxygenated bottom environment than that of the Lower Ordovician. Consequently, the high basinal chert abundance during this interval seems to conform to a high organic productivity and enhanced preservation rates model (fig. 11.3).

11.3. Upper Ordovician: the Caradocian - a warm - cool transitional, ice free mode (?)

During the Caradocian, opal burial reached the highest Ordovician peak in both shelf and slope/basinal environments. A balance between shelf and deep-water cherts that was tipped heavily toward deep-water cherts during the Middle Ordovician is restored. While radiolarians are confined to deep basinal cherts, siliceous sponges populate principally carbonate shelf areas and secondarily deep water niches (fig. 10.1). The three Caradocian silicified oolite occurrences on the southern margin of Laurentia suggest that siliceous sponges may have still been present sporadically in some peritidal/lagoonal settings that were characterized by peculiar local conditions. Geographically, approximately 74% of the worldwide Caradocian cherts have been found around Laurentia, mainly on the southwestern, southern, and southeastern margins. The remaining occurs in Australia and China (23%), and on the Kazakhstan block (3%). Overall, the high chert abundance suggests a biotic-abiotic earth system
highly favorable for chert burial. The changes in the rate of biogenic silica burial may be
due to fluctuations in biogenic silica production, dissolution, and/or preservation rates
that could be linked to physico-chemical modifications of the Earth system.

11.3.1. The abiotic system

The Cardocian epoch witnessed major changes in abiotic components of the Earth
system. Major physical changes that occurred over the Middle – Upper Ordovician
transition and during the Caradocian includ (fig. 11.1B): 1) a volcanic climax (Stillman,
1984); 2) West Gondwana crossed the South Pole (Ford and Golonka, 2003); 3) the
Taconic orogeny (Ford and Golonka, 2003; Qing et al., 1998); 4) a positive shifts in δ¹⁸O
(Shields et al., 2003; Tobin et al., 1996) and δ¹³C (Patzkowsky et al., 1997) values; 5) a
highly non-radiogenic strontium ratio indicating strong mid-oceanic ridge activity (Qing
et al., 1998; Shields et al., 2003) and large ridge volume (Mackenzie and Piggott, 1981); 6)
a minimum in continental deformation (Richter et al., 1992); 7) a peak in global sea
level (Ross and Ross, 1992; Qing et al., 1998); 8) abundant volcanogenic massive sulfide
deposits in the Iapetus Ocean (Eastoe and Gustin, 1996); 9) abundant oolitic ironstone
accumulations (Van Houten and Arthur, 1989); and 10) reduced emergent area coeval
with lower average latitude of the world landmass (Worsley et al., 1994) (fig. 11.1B). All
these activities induced changes in the global climate and oceanic seawater that would
affect the biotic system and the biogenically-controlled silica cycle.

One of the most important changes affecting the Upper Ordovician world is the
initiation of climatic cooling and the development of ice sheets over both the South and
the North Pole (Poussart et al., 1999), but the timing of these processes, Caradocian
versus Ashgillian is still open to controversy (Frakes et al., 1992; Brenchley et al., 1994; Pope and Steffen, 2003). Although the initiation of permanent ice cap sheets in the Caradocian is viewed skeptically, it is accepted that the cooling mode that heralded the late Upper Ordovician glaciation originated in the Caradocian (Patzkowsky and Holland, 1993; Worsley et al., 1994; Tobin et al, 1996; Patzkowsky et al., 1997; Pope and Steffen, 2003; Shields et al., 2003). Recent modeling studies relative to the Late Ordovician glaciation show the necessary conditions for the formation of ice sheets (Herrmann et al., 2004). Based on the relationship between atmospheric $p$CO$_2$ values, sea level, poleward ocean heat transport, and paleogeography, the simulations show that the high sea level and atmospheric $p$CO$_2$ (8 x PAL) during the Caradocian could have induced the formation of small ice sheets if the poleward ocean heat transport was reduced to half of the modern value. However, Caradocian simulations evidence ice volumes that are strongly inferior to those obtained for Ashgillian simulations.

A cooling trend was initiated sometime in the Caradocian based on paleontologic, tectonic and isotopic evidence (Frakes et al., 1992; Patzkowsky and Holland, 1993; Worsley et al., 1994; Tobin et al, 1996; Patzkowsky et al., 1997; Pancost et al., 1999; Ainsaar et al., 1999; Pope and Steffen, 2003; Shields et al., 2003). However, the time of origination of the Caradocian cooling mode is disputed and ranges between the beginning of the Caradocian, based on oxygen isotopic data (e.g., Shields et al., 2003), and middle-late Caradocian, based on high planktonic productivity and carbon isotopic data (Patzkowsky et al., 1997) and an offset feedback induced by the Taconic orogeny that started earlier (Kump et al., 1999).
Oxygen isotopic data and seawater temperature

Numerous studies have looked at the Ordovician seawater oxygen isotopic composition in brachiopod shells and marine cements such as fibrous calcite. The values obtained are controversial but all of them show generally a steady rise of the calcite $\delta^{18}O$ levels throughout the Ordovician (Tobin et al., 1996; Shields et al., 2003), interpreted as a general cooling trend. Upper Ordovician seawater $\delta^{18}O$ values obtained from geographically widespread stratigraphic sequences (Shields et al., 2003) show an oxygen depletion trend, by approximately 3‰ PDB that occurred over a period of less than 10 My around the Middle-Upper Ordovician boundary, (fig. 11.1B; Shields et al., 2003). Two driving mechanisms have been hypothesized with the aim to explain this positive shift in $\delta^{18}O$ (fig. 11.4).

1) The first mechanism is a decrease in minimal tropical seawater temperature from a 27°-32°C to 16°-25° C, within an ice-cap free world, for a $\delta^{18}O$ SMOW (standard mean oceanic water) of -3‰ (Frakes et al., 1992; Tobin et al., 1996; Shields et al., 2003) (fig. 11.1B and 11.4). The estimate for the temperature drop is in agreement with that of Worsley et al. (1994) for equatorial temperatures as low as 25°C, a cooling considered as having occurred prior to the late Ordovician glaciation and within a world that lacked ice sheets.

2) The second mechanism is given by a decrease of the $\delta^{18}O$ SMOW by 2-3‰, along with a decrease of lower magnitude in the tropical sea surface temperature. Although this mechanism is view as a long term process (Gregory, 1991 in Shields et al., 2003) and thus failing to elucidate the short term of the $\delta^{18}O$ SMOW change, more
Figure 11.4: Temperature vs. calcium carbonate shell $\delta^{18}O$ (PDB) for various values of seawater $\delta^{18}O$ (SMOW) assuming an ice-cap free world. Even maximum $\delta^{18}O$ values for the Early Ordovician and early Middle Ordovician (-5.4‰ and -6.3‰, respectively) yield unrealistic minimum seawater temperatures (37°C – 43°C) if $\delta^{18}O$ seawater was -1‰ SMOW, while $\delta^{18}O$ seawater of -3‰ SMOW yields more plausible minimum tropical sea-surface temperatures of 27°C – 32°C (Shields et al., 2003).

Recent modeling studies indicate that such $\delta^{18}O$ SMOW changes can occur over much shorter periods of time (5 to 50 My), particularly during periods of high oceanic spreading rates (Lécuyer and Allemand, 1999). The short-term $\delta^{18}O$ SMOW shift theory is consistent with the inferred high oceanic spreading rates supposed to characterize the Caradocian based on the $^{87}$Sr/$^{86}$Sr isotopic ratio (Qing et al., 1998; Shields et al., 2003). In a world characterized by energetic intra-basinal activities, that would generate not only higher input levels of nutrients (favoring high organism productivity), but also
abundant CO₂, a widespread anoxia event can occur. The more anoxic the bottom waters become, the more the vertical partitioning of the oxygen isotopes takes place, generating positive shifts in the δ¹⁸O. Consequently, a sharp positive shift in the δ¹⁸O documented at the beginning of the Caradocian, could also reflect a strongly stratified water column (Tobin et al., 1996), with the heavier oxygen entrapped in the bottom-most water layers, and not necessarily a climatic cooling. The energetic volcanic activity in the southern margin of Laurentia is also supported by two regionally widespread Middle Caradocian air-fall ash beds, the Deicke and Millbrig k-bentonites (Huff and Kolata, 1990).

11.3.2. The biotic system

Caradocian biotas witnessed high taxonomic diversity for some groups of benthic and planktonic organisms (e.g., radiolarians, graptoloids, brachiopods; fig. 11.1A), and a decreased diversity and extinction for other groups (Sloan, 1988a; 1988b; Patzkowsky and Holland, 1993). High organism productivity is shown by a middle Caradocian positive excursion in the carbon isotopic values (Patzkowsky et al., 1997; Pancost et al., 1999).

Sea level during this epoch was high (Ross and Ross, 1992; Qing et al., 1998), so that the Caradocian chert peak and organism radiation coincide with an important transgression (fig. 11.1B). The Caradocian transgression is believed to be the largest in the Phanerozoic (Ross and Ross, 1992) due to fast oceanic floor spreading resulting in high ridge volume (Qing et al., 1998). Although extinction events have been linked to transgressions through the invasion of the shelf area by anoxic waters (Wilde and Berry, 1984), in this instance there was a proliferation of a variety of benthic and planktonic
groups: radiolarians (Vishnevskaya, 1997), graptolites, brachiopds (Leggett et al., 1981) (fig. 11.1A), and siliceous sponges (Rigby and Webby, 1988). Higher diversities and revolutions in the marine realm have been correlated on one hand with cooling episodes and low nutrient supply (Lipps, 1970), and on the other hand with high submarine volcanism and hydrothermal activity providing a thermal stimulus (Hays and Pittman, 1973; Vermeij, 1995).

The Caradocian radiation was concentrated around regions of active mountain building and volcanisms (e.g., the Iapetus Ocean), which suggests a direct relationship between organism diversity and the proximity of tectonic activity (Vermeij, 1995; Miller and Mao, 1995; Miller, 1997). In addition, many Caradocian deep-sea chert deposits formed in active areas such as the southeastern part of Laurentia characterized by arc-continent collision tectonism, and Kazakhstan, which was a massive island-arc volcanic region (Nikitin et al., 1991), supporting the high diversity - high productivity - high volcanism inter-relationship model.

11.3.3. Considerations on the chert abundance

Slope/basinal environments. Why a chert peak?

The bottom water environment: anoxia?

At the bottom of basins, it appears that anoxic waters develop as a consequence of the converging action of two factors: high CO2 input due to high volcanic – mid-oceanic activity, and high input of organic matter from the surface layers due to an increased productivity volcanically induced (fig. 11.5). Oxygen-depleted bottom water model
would be consistent with the observed abundance of graptolite-rich black shale, (Berry and Wilde, 1978; Leggett et al., 1981), abundant volcanogenic massive sulfide deposits (VMS) identified in the Iapetus Ocean and marginal basins (Eastoe and Gustin, 1996), and abundant oolitic ironstone accumulations (Van Houten and Arthur, 1989) (fig. 11.1A&B). However, whereas the Caradocian age is well documented for the black shale peak (Leggett et al., 1981), the timing of the VMS and oolitic ironstones abundance peaks is less well established.

The analyses of Phanerozoic massive sulfide deposits (Eastoe and Gustin, 1996) and oolitic ironstones (van Houten and Arthur, 1989) and their associated lithologies, emphasized their frequent association with black shales. Sulfide minerals, as well as black shales, may be preserved either in oxygen depleted environments (the preservation model), or due to high organic productivity accompanied by rapid burial under well aerated conditions (the productivity model) (Calvert, 1987; Morris, 1987; Arthur and Sageman, 1994; Eastoe and Gustin, 1996). However, considering that modern VMS deposits that form in oxygenated water on the mid-oceanic ridges are preserved to a small extent, it has been inferred that large accumulations of VMS are tightly linked to anoxic bottom waters (Eastoe and Gustin, 1996).

Based on the common association between massive sulfide deposits, oolitic ironstones, and black shales, along with the Caradocian age of the Ordovician black shale peak (Leggett et al., 1981), it can be speculated that the VMS peak along with that of the oolitic ironstones may be of Caradocian age as well. According to Eastoe and Gustin
Figure 11.5: Chert abundance Model. CARADOCIAN [458 – 449 Ma]
(1996), the abundance of VMS in the Iapetus Ocean and proximal basins during the
Ordovician, is the result of the interplay between anoxic waters and tectonic factors.
Caradocian VMS and oolitic ironstone abundances would be consistent with the
Caradocian climax of the mid-oceanic ridge activity inferred from the strontium isotopic
ratio (Shields et al., 2003) that, in turn, generated a high sea level, conditions that
represent the most favorable ambient for widespread anoxia (Mackenzie and Piggott,
1981). Documenting extensive black shale deposits for the Ordovician and Silurian,
Fischer and Arthur (1977) remarked on their association with transgression phases and
predicted the Caradocian chert peak based on the inference that during a polytaxic
interval (a greenhouse oxygen-depleted state; Fischer and Arthur, 1977), deep water
sediments should be characterized by more widespread cherts than those that form during
oligotaxic times.

The sole presence of black shales, or massive sulfide deposits, does not indicate
anoxic waters, however their coexistence along with oolitic ironstones in a world
characterized by energetic intra-basinal activity, such as high mid-oceanic spreading
rates, marine volcanism and hydrothermal activity, point toward an euxinic environment.
Within such an environment opal accumulation and burial would be greatly enhanced
(e.g., De Wever et al., 1994).

*The surface waters: low or high organism productivity?*

A variety of evidence points toward an anoxic deep water environment during the
Caradocian, but whether or not it was accompanied by a high productivity is unclear. It is
known that radiolarians, graptoloids, and brachiopods record high taxonomic diversities
during the Caradocian (fig. 11.1A). Even though a high diversity and abundance commonly show a reverse correlation (Tappan and Loeblich, 1973), studies of modern radiolarian faunas from the East China Sea show that high productivity and high diversity can co-occur (Chang et al., 2003).

The high productivity and organic carbon burial model proposed for the surface water planktonic organism activity is in agreement with a middle Caradocian (P. tenuis – P. undatus conodont zones) positive excursion in the carbon isotope composition of carbonate (~ 3‰) and of organic carbon (~ 4‰-6‰) (Patzkowsky et al., 1997; Pancost et al., 1999). Huff and Kolata (1990) identified two regionally widespread air-fall ash beds, the Deicke and Millbrig k-bentonites, of the exact same age (P. tenuis – P. undatus interval), which is viewed as chronostratigraphic marker horizons throughout much of the eastern Mid-Continent. The question is did this volcanic pulse induce indirectly the carbon spike by killing organisms? The carbon spike has been also correlated with Caradocian sequences in Estonia (Ainsaar et al., 1999, in Shields et al., 2003), suggesting an event of larger magnitude than one confined to the eastern margin of Laurentia. If this volcanic burst affected marine biotas to such a wide extent as to imprint a strong carbon shift in the rock record, we can ask if it was not also responsible for a short-lived warming driven by the high amount of CO₂ exhaled into the atmosphere. The oxygen data of Shields et al. (2003) show a sharp, short-lived negative shift during the same age interval (fig.11.1B) also coeval with a sea level rise, that could be the result of the same large-scale volcanic event. All these converging phenomena provide evidence in support of the greenhouse hypothesis, at least for the early and middle Caradocian. Further, a
warm Caradocian model implies that the cooling mode did not start until the late Caradocian, which means that the middle Caradocian carbon shift does not reflect a high organism productivity. However, it is possible that the cooling mode could have been triggered by rapid CO₂ drawdown resulting from high biotic productivity. More data are needed in order to test a Caradocian greenhouse mode based on the above evidence.

The Caradocian chert peak is coeval with high oceanic spreading rates, energetic volcanism, and hydrothermal activities that are consistent with a high sea level (Qing et al., 1998). Vigorous intra-basinal volcanic activity would stimulate higher silica and other nutrient fluxes so that the productivity of radiolarians and other planktonic organisms would be boosted inasmuch as the surface water temperatures are still favorable. Energetic intra-basinal activities may initiate energetic vertical water advection, including coastal upwelling (volcanic-induced upwelling of Vogt, 1989). Thus, increased nutrient input has two sources: mid-oceanic activity, and upwelling of rich-nutrient sediments. Numerous studies have stressed the linkage between high biogenic chert abundance, high silica secreting organism productivity, and intensive volcanic/tectonic/magmatic activity (Grunau, 1965; Steinberg, 1981; Aubouin, 1965; Racki, 1999; Racki and Cordey, 2000).

If we accept the initiation of a climatic cooling at the beginning of the Caradocian, as suggested by the oxygen isotopic ratios, and taking into account that the solubility of silicic acid in water decreases with temperature, in a cooler environment less silica is dissolved in the water column and thus more opal would reach the seafloor to be preserved as chert. A cooling would affect principally the surface waters in contrast to much more stable deep waters. Modern studies show that 50% of the total biogenic silica
production is remobilized in the upper layers of the ocean (the upper 100 m) and therefore a cooling would increase the potential of opal accumulation and burial through an increased opal rain rate. Also, silica dissolution depends directly on water temperature, most of the opal accumulation occurring in areas where the surface water is cold (DeMaster, 1981). Because large temperature variations occur within the surface layers of water (100-200 m) and the deep-sea is confined to a relatively narrow range of low temperatures (Bidle et al., 2002), a very important factor in preservation of opal in basinal settings is ultimately the temperature of surface layers of water (Nelson et al., 1995). However, a decrease in the opal dissolution rate in the surface waters would be triggered by lower water temperature. The magnitude of a potential Caradocian seawater cooling is constrained by the high diversity of radiolarians whose metabolism in modern settings is negatively affected by low temperatures (Anderson et al., 1989c).

In conclusion, higher opal accumulation and burial rates would be generated by:
1) a global productivity acme in coastal and abyssal settings triggered by high endogenous inputs of silica and other nutrients; and
2) excellent taphonomic conditions within an anoxic environment driven by the high fluxes of organic matter, CO₂ and other oxygen-consuming cations. This model suggests that preservation and productivity do not exclude each other as mechanisms that induce the formation of cherts, and that their concurring action only generates a higher chert peak, under the incidence of tectono-volcanically induced taphonomic, oceanographic, and biosiliceous productivity conditions (fig. 11.5). A surface water cooling could add even more to the potential for
opal accumulation due to lower dissolution rates under the circumstances the surface water temperature still represents a favorable environment for radiolarians.

**Shelf settings**

During the Caradocian, widespread carbonate platforms, representing a good environment for the development of siliceous sponge faunas, were again dominating the shelf system. Siliceous sponges that at this point were inhabiting the deeper sites of the shelf area, could have taken advantage of a volcanically-induced coastal upwelling of the nutrient rich waters. Strontium data show strong non-radiogenic values indicating a nutrient input cycle dominated by endogenous fluxes and a possible seawater cooling would not affect too strongly this opportunistic group capable of inhabiting shallow to deep environments since the Early Cambrian (Finks, 1960), and low to high latitudes at least since the Lower Ordovician (Beresi and Esteban, 2004). After a period of ecological adaptation to new ecological niches after their migration from onshore toward more offshore settings during the Middle Ordovician, siliceous sponges would proliferate in a stable, nutrient rich carbonate environment. Chert burial would be increased due to higher silica levels *via* siliceous sponges, and possibly due to a lower opal dissolution rate in cooler seawater.

**11.4 Upper Ordovician: the Ashgillian - an icehouse period**

During the Ashgillian, the chert abundance decreases in all three depositional environments (Table 7.2.B and 7.3.B), but it is still higher than the Middle Ordovician chert low. While the formation of peritidal/lagoonal chert deposits ceases, shelf cherts
dominate by a factor of two over the slope/basinal deposits. The slope/basinal chert deposits exhibit the first drop in abundance for the Ordovician. The shelf cherts that dominate the Ashgillian biosiliceous burial surpass both the Lower and the Middle Ordovician shelf chert occurrences. The distribution of silica-secreting organisms within basins show no changes - planktonic radiolarians are still confined to slope/basinal settings, and siliceous sponges to shallow and deep water environments (shelf and slope/basin). Taking into account the genetic relationship that exists between radiolarians and slope/basinal bedded chert formation (Chapter 7 and 9), it seems that radiolarian fauna played an important part in this general chert abundance decrease. From the point of view of the geographical distribution of cherts, both Laurentia and Gondwana witness significant decreases in silica burial based on the decrease in the number of chert deposits (Table 7.6).

11.4.1. The abiotic system

The Ashgillian was characterized by the presence of ice sheets (over both poles, Poussart et al., 1999), low sea levels, and the ongoing Taconic orogeny. Considerable land area was exposed by the glacially-induced sea level drop whose magnitude has been estimated between 50m and 100m (Brenchley and Newall, 1980; Finney, 1997), and by the ongoing Taconic orogeny, two physical processes that induce the exposure of fresh silicate rocks. However, the strontium data still exhibit strong non-radiogenic values and no differences between the Caradocian and the Asghillian (fig. 11.1B; Shields et al., 2003). These values have been explained by a delay in the continental strontium influx
caused by the time necessary for erosion to remove the emerged widespread carbonate shelves before exposing the more radiogenic basement rocks underneath (Qing et al., 1998). The oceanic circulation underwent an overturn through the formation of ice sheets that cause the sinking of denser oxygenated waters at the poles, thus inducing the formation of active coastal upwelling and an increase in wind, wave and storm action as a consequence of larger thermal gradients between the poles and the tropics (Berry and Wilde., 1978).

Short-lived oxygen (3‰–4‰) and carbon (as much as 7‰) excursions have been used as arguments to confine the timing of the glaciation to the late Ashgillian, the Hirnantian stage, suggesting a short-lived glaciation (Brenchley et al., 1994, 2003; Gibbs et al. 1997). Muehlenbachs (1998) asserts that during glacial periods the seawater $\delta^{18}O$ can increase with up to 2‰ - 3‰ assuming an originally ice-free world. Mechanisms that have been proposed to explain such a short-lived glaciation include high organism productivity (Brenchley et al., 1994) and the Taconic orogeny (Kump et al., 1999), which may have initiated cooling followed by a more dramatic shift into full icehouse conditions. Global biochemical models suggest that the Late Ordovician glaciation has occurred under high $p_{CO2}$, levels between 8 and 16 times higher than today’s level (Berner, 1994; Kump et al., 1999; Yapp and Poths, 1992; Gibbs et al., 1997; Herrman et al., 2003).

**11.4.2. The biotic system**

The Late Ordovician extinction, considered one of the five big Phanerozoic extinctions (Sepkoski, 1995), took place in two phases (two major faunal turnovers)
related to two climatic and environmental changes: first, a cooling period ending with the onset of the glaciation, secondly, a deglaciation and warming event (Brenchley, 1989; Brenchley et al., 2003) the second phase characterized by deglaciation and warming witnessed most part of the late Ordovician animal extinction (Brenchley et al., 2003).

Whether or not the late Ordovician glaciation affected radiolarian faunas is controversial. Noble et al. (1997) reported a lack of major radiolarian extinction while Vishnevskaya (2000) noted a major radiolarian extinction across the Ordovician-Silurian boundary (Ashgillian – Llandoveryan) with radiolarian diversity dropping from 100 to 20 species (fig. 11.1A). Following this drop, the rest of the Silurian witnesses a slight increase in diversity upwards to 60 species (Vishnevskaya, 2000). However, to date there are no known individual rock sequences in which extinction in the siliceous radiolarian fauna is clearly recorded.

Relative to the Ordovician silicisponges, within a shallowing interval of the lower Hanson Creek Formation (late Upper Ordovician) Finney et al. (1999) recognize a faunal turnover in siliceous sponges, defined by a change from deep water, hexactinellid-dominated assemblages, to shallow, subtidal lithistid-dominated assemblages as a consequence of the sea level drop.

11.4.3. Considerations on the chert abundance (fig. 11.6)

During glacial periods abundant chert accumulation should occur at upwelling sites due to a high organism productivity. Within the shallower facies the amount of siliceous deposits could decrease as a consequence of changes in the ecological distribution of siliceous organisms driven by the glacial-eustatic sea level regression.
Figure 11.6: Chert abundance Model. ASHGILLIAN [449 – 443 Ma]
Moreover, a drop in sea level would increase the volume of silicates available to weathering, as well as the dissolved silica input into the basinal facies, while the shelf is more or less emerged. The amount of dissolved silica in seawater could be higher and more offshore chert may occur.

**Shelf environments**

Shelf water environments were populated exclusively by the silicisponges during the Ashgillian. Even though the shelf chert abundance registers a decrease as compared to the Caradocian, the normalized data show that Ashgillian shelf occurrences rank second in abundance even under the circumstances of a severe sea level drop (50-100m) and exposure of shelves. This finding suggests two main possibilities:

1) The siliceous sponge faunas were not affected significantly by seawater cooling induced by the Late Ordovician glaciation. This view is supported by the ecology of modern silicisponges which demonstrates that they tolerate large thermal ranges, paleolatitudinally as well as vertically within the basin (Reincke and Barthel, 1997). The low to mid-paleolatitudinal distribution of silicisponges shown by the present study (Chapter 10), also supports the interpretation that siliceous sponge faunas were not significantly affected by the cooling.

2) The glacial-eustatic sea level drop was of short duration so that the induced loss of living habitats did not affect the opal production and burial to any great extent. The normalized data demonstrates a high shelf chert abundance during the Ashgillian, outnumbered only by the Caradocian silicisponge-induced shelf cherts. Moreover, silicisponges are able to inhabit varied ecological niches, carbonate or not, as long as they
have clear waters and sufficient nutrients. Under these circumstances, the fact that they were populating the shelf environment during the Ashgillian demonstrates low terrigenous inputs, contrary to the high input that we would expect as a consequence of the continental weathering of fresh silicate rocks exposed by the Taconic orogeny. This hypothesis is consistent with the strontium ratio values that still show non-radiogenic characteristics. At the other end of the spectrum, a long-term sea level drop would drastically affect siliceous sponge habitats and implicitly the silica burial. An analysis limited just to Ashgillian siliceous sponge shelf cherts would not offer insight into their opal production potential and the factors that influence it. However, such an analysis is clearly put in perspective when performed in the context of the whole Ordovician.

**Slope/basinal environments**

Because this survey does not differentiate between the slope and deep sea (basinal) environments of chert formation, two oceanographic systems that function differently with respect to opal accumulation and preservation (Nelson et al., 1995), I can only speculate about the implications of the glacially-induced effects on biosiliceous productivity, opal accumulation and burial. The impact of a vigorous oceanic circulation through vertical advection of cold, nutrient-rich, deep waters, might generate volumetrically important chert deposits spatially concentrated at upwelling sites rather than widespread abundant smaller cherts (Kidder, oral communication). In view of this
fact, estimation of chert abundance based on frequency of occurrences becomes futile in interpreting any change in silica burial caused by glacially induced oceanic turnovers.

High chert abundances, on the slope as a result of high organism productivity induced by upwelling, would imply that the silica secreting biota responsible for chert formation behave as well in cooler environments as in warm waters. During the Ashgillian, radiolarians were very likely inhabiting the whole transect of the deep part of a basin, from slope to deep-sea, and thus they were under direct influence of the coastal upwelling. The oxygen isotopic ratios show an important cooling during this interval (11 - 17°C; Shields et al., 2003). To date both modern data (Sugiyama and Anderson, 1997; Anderson et al., 1989, a,b,c) and paleo-ecological results (the present study) show the affinity of radiolarians with warm environments, demonstrating that environmental factors such as temperature and salinity are more significant limiting factors in radiolarian growth and longevity.

The slope/basinal bedded chert drop therefore is interpreted as a negative perturbation of radiolarian productivity due to cold surface seawater. In deep-sea settings, within a scenario of cooler oceanic surface waters, the lower silica dissolution rate would increase the potential for higher preservation and chert formation. However, such a high preservation is not substantiated in the rock record, which supports the hypothesis that the slope/basinal bedded chert drop was a result of productivity slowdown due to low water temperature. Moreover, a general high organism productivity, induced by the oceanic overturn, associated with the whole Ashgillian interval has not been demonstrated either by abundant black shale deposits (Legget et al., 1981), or by positive excursions in $\delta^{13}$C.
The first important Ashgillian change in the amount of organic carbon burial has been documented as occurring in the Hirnantian, the youngest time-defined level of the Ashgillian (Brenchley et al., 1994).

It is worth mentioning that the Ashgillian shelf and slope/basinal cherts surpass and almost equal those of the Lower Ordovician in spite of the sharp decline in silica burial recorded between the Caradocian and the Ashgillian. Silica output into cherts expresses ultimately the balance between biogenic silica production, dissolution, dilution by host sediment, and preservation rates. Therefore two different mechanisms can be considered responsible for triggering the chert formation corresponding to the two antagonistic climatic modes that characterize the Lower Ordovician and the Ashgillian: high biosiliceous productivity, associated with good taphonomic bottom water conditions within a greenhouse mode (Lower Ordovician) vs. low biosiliceous productivity associated with low dissolution rate within an icehouse mode (Ashgillian).
Chapter 12

CONCLUSIONS

A global survey of the spatial and temporal distribution of Ordovician nodular and bedded cherts, and subordinately of silicified oolites, was undertaken to address three questions: 1) Did the Early Paleozoic radiolarians and siliceous sponges behave similarly to diatoms regarding their response to abrupt changes in oceanic circulation and climate parameters? 2) Did cherty facies retreat from peritidal settings during the Ordovician? 3) Can chert deposits be of use in evaluating whether the late Ordovician glaciation spanned most of the Caradocian and Ashgillian (Pope and Steffen, 2003) or was the glaciation more tightly constrained to within the Ashigillian (Brenchley et al., 1994)? Further on, the volume and resolution of the data allowed quantitative and qualitative analyses of the relationships between chert deposit types, depositional environments, and silica secreting organisms.

The results of this study can be summarized as follows:

1) Most Ordovician chert deposits are of biogenic origin due to: a) approximately 38% of the Ordovician chert formations contain siliceous skeletal remain; and b) the onshore-offshore migration of the silica secreting organisms, perceived through the rock record of chert bearing siliceous organisms, is accompanied by an onshore-offshore change in the locus of silica burial, reflected in the stratigraphic record of cherts that lack preserved siliceous skeletal remains.
2) The analysis of chert types and reported skeletal remains within cherts reveals a segregation of chert types due to a genetic relationship between the silica secreting organisms and the types of the chert deposits. Peritidal/lagoonal and shelf cherts are mainly nodular cherts hosted by carbonate facies. These cherts appear to have formed predominantly via silica secretion by lithistid demosponges. Most of these cherts are low latitude occurrences (< 30°N and S). Slope/basinal cherts are predominantly bedded cherts, mainly hosted by fine-grained siliciclastic sediments, and bear radiolarians. Most of these cherts are also confined to low latitudes. At mid latitudes, the skeletal components of these cherts are mainly hyalosponges. Also, the analysis showed that the formation of some shelf bedded cherts might by induced by silicisponges.

3) The Middle Ordovician distribution pattern of silica secreting biotas reflects a migration of siliceous sponge faunas from peritidal/lagoonal to shelf-basinal environments, and of radiolarians to basinal settings, suggesting an Arenigian-Llanvirnian onshore-offshore migration of the silica secreting organisms. This refines the timing of an earlier suggested retreat in the locus of silica burial during this period. It also indicates that Early Paleozoic planktonic faunas accompanied the benthic communities. Whether the timing of the retreat matches the roughly coeval onshore-offshore shift of the benthic Cambrian and Paleozoic faunas (Jablonski et al., 1983) is unclear. The Middle Ordovician minimum of peritidal/lagoonal and shelf cherts may be a result of shelf area reduction during a relatively low sea level. However, the reappearance of shelf cherts in the Caradocian indicates that, although silicisponges did retreat significantly from peritidal/lagoonal settings in the early Middle Ordovician, they still largely populated the
shelf settings. The few Middle Ordovician and Caradocian silicified oolites suggest that silicisponges may have still been present sporadically in some peritidal/lagoonal settings that were characterized by peculiar local conditions.

4) The Ordovician spatial and temporal distribution patterns of siliciponges and radiolarians suggest that silica limitation governed the distribution of silicisponge faunas, and that physical factors such as temperature played a major role in the distribution of radiolarians.

5) Lower Ordovician cherts are abundant and widespread, occurring in equal proportions in peritidal/lagoonal, shelf, and slope/basinal settings. Within a warm world characterized by stable and favorable environmental conditions, high sea level, and widespread carbonate platforms, the chert abundance in peritidal/lagoonal and shelf environments seems to be the result of the interplay between good organism productivity and enhanced chert preservation. The dominance of bedded cherts in slope/basinal settings may reflect relatively high biosiliceous productivity, probably associated with favorable taphonomic conditions under an oxic regime within the bottom waters.

6) A significant decrease in the number of chert deposits occurs in the Middle Ordovician. While the peritidal/lagoonal and shelf environments record a strong decline in silica burial, the slope/basinal bedded cherts record a slight augmentation. This finding suggests that the redistribution of benthic shallow water siliciponges played an important role in this general chert abundance low. The integration of data on biotic and abiotic changes that occurred during the Middle Ordovician indicates that the Middle Ordovician chert low was driven by a shortage in the shallow water silica burial due to redistribution
of silicisponges and their habitat and subsequently to a lesser extent of radiolarians, possibly accentuated by a general Middle Ordovician sea level low. The slightly increased slope/basinal chert abundance during this interval seems to conform to a good organism productivity, enhanced preservation rates and aerated bottom waters model.

7) A resurgence in the number of chert deposits occurs in the Upper Ordovician, more precisely during the Caradocian. This occurs in both shelf and slope/basinal environments, where chert abundance surpasses that of the Lower Ordovician by 50%. However, Upper Ordovician chert abundance in peritidal/lagoonal settings remained at essentially the same low levels as in the Middle Ordovician.

8) The Caradocian marks the highest point in the abundance of Ordovician cherts, that appear to have accumulated during a warming interval. This chert peak is coeval with a transgression, high abundance of black shales, oolitic ironstones, and volcanogenic massive sulfides, as well as the Ordovician peaks in diversity of radiolarians and other organisms, are all consistent with a warm stable world and / or oceanic anoxia. Changes in $\delta^{18}$O values at the Middle-Upper Ordovician boundary are consistent with warming late in the Caradocian. Values of $^{87}$Sr/$^{86}$Sr shift toward non-radiogenic values and the sea level toward transgression. These suggests that continental input of dissolved silica declined instead of rising in the Caradocian, despite the coeval Taconic orogeny. The high chert abundance may have been the result of a global productivity acme triggered by high endogenous inputs of silica and other nutrients, along with excellent taphonomic conditions within an anoxic environment driven by the high fluxes of organic matter, CO$_2$, and other oxygen-consuming cations.
9) The decline of cherts during the Ashgillian, when the glaciation was clearly in effect, was not expected based on assumptions of modern silica accumulation in an icehouse with vigorous ocean circulation. While the slope/basinal cherts record a strong decline, shelf cherts exhibit only a fairly low reduction. This finding suggests that radiolarians played an important role in this relatively low general chert abundance. The decline may reflect: a) a negative perturbation of radiolarian activity due to cold surface seawater; b) accumulation of fewer but volumetrically more important basinal cherts reflecting upwelling settings in the Ashgillian, under the circumstances where radiolarians behave as well as in cold waters as in warm waters; c) depletion of oceanic dissolved silica content via silica burial during glacially induced intensive upwelling again under the circumstances where low temperatures are not a limiting factor for radiolarian growth. The relatively high silicisponge-induced shelf chert abundance within an icehouse world outnumbered only by the Caradocian shelf cherts could be linked to a glacially-induced sea level drop of short duration. An analysis limited just to Ashgillian silica secreting organisms would not offer insight into their behavior and opal production potential and the factors that influence them. However, such an analysis is clearly put in perspective when performed in the context of the whole Ordovician, by epoch. Chert abundance alone probably will not resolve the debate about the duration of the Ordovician glaciation. However, consideration of their abundance patterns in conjunction with other aspects of the Earth system is consistent with Caradocian warming followed by a brief Ashgillian cooling and glaciation, the causes of which remain enigmatic.
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### LOWER ORDOVICIAN

**North America**

<table>
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<tr>
<th>No</th>
<th>Formation</th>
<th>Age</th>
<th>Location Lat/Long</th>
<th>Depositional environment</th>
<th>Chert type</th>
<th>Associated facies</th>
<th>SSR*</th>
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<td>LMS, Dol</td>
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<td>Stonehenge Fm.</td>
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<td>Tribes Hill Fm.</td>
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**Canada**

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**Korea**

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<td>Mungok Fm.</td>
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<td>Yongwol, Taebaeksan basin, 37°11'N/128°28'E</td>
<td>shelf, middle and outer ramp</td>
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**China**

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<td>Hangwula Mountains, Alxa, Nei Monggol, 41°30'N/104°E</td>
<td>shelf</td>
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<td>dark argill, slate</td>
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<td>Zifangzung Fm.</td>
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<td>Shangdong, North China Platf., 36°30'N/117°E</td>
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**Others**

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<td>64</td>
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<td>l, m</td>
<td>Sonora, Mexico; 110°32'W/28°36'N</td>
<td>slope/basin</td>
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<td>Garden City Fm.</td>
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<td>SE Idaho, SW Wyoming, USA, 110°03'/42°31'N</td>
<td>peritidal/lagoonal, shelf</td>
<td>N, B</td>
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<td>66</td>
<td>Heituau Fm.</td>
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<td>Queerqueque area, Tarim block, NW China, 40°54'N/88°20'E</td>
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<td>67</td>
<td>Karmberg Limestone</td>
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<td>Australia, Tasmania, 146°28'E/42°40'S</td>
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**MIDDLE ORDOVICIAN**

### North America

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<td>1</td>
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<td>Mazourka Canyon, California, 36°52'N/117°37'W</td>
<td>middle-out shelf</td>
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<td>Ohio, C Pennsylvania, 40°39'/78°14'W</td>
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<td>SW Texas, 30°24'/103°23'W</td>
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<td>argill LMS</td>
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**UPPER ORDOVICIAN**

**North America**

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<td>46</td>
<td>Hazen Formation</td>
<td>C,Ash</td>
<td>Arctic Canada in northeastern Ellesmere, 79°37'N/81°52'W</td>
<td>slope</td>
<td>B</td>
<td>grpt sh</td>
<td>Rad</td>
<td>Gentzis et al., (1996); Trettin (1970)</td>
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<td>47</td>
<td>Stony Mountain Fm.</td>
<td>Ash</td>
<td>SW Manitoba, Greta, 49°50'N/100°14'W</td>
<td>shelf</td>
<td>N</td>
<td>sh, LMS</td>
<td></td>
<td>Andruchuk (1959); Porter and Fuller (1959)</td>
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<td>48</td>
<td>Ballast beds</td>
<td>u</td>
<td>SC New South Wales, 32°45'N/149°45'E</td>
<td>slope/basin</td>
<td>undet</td>
<td>slts, slates,grpt</td>
<td>Rad</td>
<td>Webby (1981); Iwata et al. (1995)</td>
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<td>50</td>
<td>Bogong Creek beds</td>
<td>C</td>
<td>SC New South Wales, 36°31'S/149°48'E</td>
<td>slope/basin</td>
<td>undet</td>
<td>slts, slates,grpt</td>
<td>Rad</td>
<td>Webby (1981); Lyons and Percival (2002)</td>
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<td>51</td>
<td>Bubalaha Fm.</td>
<td>C</td>
<td>Rockley - Taralga area, 34°30'S/149°40'</td>
<td>slope/basin</td>
<td>undet</td>
<td>grpt black sh</td>
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<td>Webby (1981); Lyons and Percival (2002)</td>
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<td>52</td>
<td>Bumballa Fm.</td>
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<td>SE Australia, Cooma-Mandurama, 36°53'4'S/148°13'4'E</td>
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<td>B</td>
<td>grpt sh</td>
<td>Rad</td>
<td>Dietz and Holden (1966); Fergussan and Fanning (2002)</td>
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<td>Malonguila Fm.</td>
<td>C, Ash</td>
<td>Cliefend caves, 33°50'S/146°25'E</td>
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<td>LMS, tuff, grpt sh</td>
<td>SS, Rad</td>
<td>Rigby and Webby (1988)</td>
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<td>57</td>
<td>Uralba beds</td>
<td>C</td>
<td>Attunga, 30°55'S/150°50'E</td>
<td>slope/basin</td>
<td>undecided</td>
<td>mudst, LMS</td>
<td>Rad</td>
<td>Webby (1981)</td>
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<td>58</td>
<td>Wagonga Fm.</td>
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<td>Narooma, 36°14'S/150°4'E</td>
<td>slope/basin</td>
<td>B</td>
<td>volc, grpt black sh</td>
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<td>Webby (1981)</td>
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<td>59</td>
<td>Warbisco shales, Mallacoota beds</td>
<td>C</td>
<td>SE Australia, E Victoria, -38°04'S/144°43'E</td>
<td>slope/basin</td>
<td>B</td>
<td>grpt sh</td>
<td>Rad</td>
<td>Dietz and Holden (1966); Webby (1981)</td>
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<td>60</td>
<td>- a flysch seq.</td>
<td>C</td>
<td>S Scotland, 57°04'N/4°13'W</td>
<td>slope/basin</td>
<td>B</td>
<td>black sh, mudst</td>
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<td>Grunau (1969); Hubert (1966)</td>
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<td>No</td>
<td>Formation</td>
<td>Age</td>
<td>Location Lat/Long</td>
<td>Depositional environment</td>
<td>Chert type</td>
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<td>61</td>
<td>Currarie Fm.</td>
<td>C</td>
<td>Scotland, 55°N/5°W</td>
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<td>B</td>
<td>basalt, grpt</td>
<td>Rad</td>
<td>Armstrong et al. (1998); Floyd (1996)</td>
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<td>Glenkiln Fm.</td>
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<td>mudos, grpt sh</td>
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<td>Armstrong et al. (1998)</td>
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<td>63</td>
<td>Hartfell Shale Fm.</td>
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<td>Rad</td>
<td>Floyd (1996)</td>
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<td>64</td>
<td>Marchburn Fm.</td>
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<td>Scotland, 55°N/3°W</td>
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<td>B</td>
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<td>Rad</td>
<td>Armstrong et al. (1998); Floyd (1996)</td>
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<td>65</td>
<td>Portixeddu Fm.</td>
<td>u</td>
<td>SW Sardinia, 39°30'N/8°30'E</td>
<td>shelf</td>
<td>N</td>
<td>muds, slts</td>
<td>SS</td>
<td>Loi and Dabard (2002)</td>
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<td>66</td>
<td>Kermeur Fm.</td>
<td>u</td>
<td>Armorican Massif, 48°15'N/4°30'E</td>
<td>inner-outer shelf</td>
<td>N</td>
<td>muds, slts</td>
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<td>Loi and Dabard (2002)</td>
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<td>68</td>
<td>U/P Kuntass Fm.</td>
<td>C,Ash</td>
<td>Chuillik Mountains, 46°53'N/66°18'E</td>
<td>slope/basin</td>
<td>B</td>
<td>LMS</td>
<td>Rad</td>
<td>Blome et al. (1995b); Nazarov and Ormiston (1993)</td>
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<td>69</td>
<td>?Chu-Illik Mt &amp; rocks</td>
<td>Ash</td>
<td>Chu-Illik Mountains, 44°N/75°E</td>
<td>undecided</td>
<td>undet</td>
<td>LMS</td>
<td>Rad</td>
<td>Renz (1990)</td>
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<td>70</td>
<td>Kuvsky Fm.</td>
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<td>Predchingiz, 46°15'N/66°E</td>
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<td>volc, LMS, silts</td>
<td>Rad</td>
<td>Nazarov and Ormiston (1993)</td>
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<td>71</td>
<td>Chengbu Fm.</td>
<td>C</td>
<td>Shaungiakou, 26°49'N/112°07'E</td>
<td>slope/basin</td>
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<td>silic black sh</td>
<td></td>
<td>Yiren and Hanying (1989)</td>
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<td>73</td>
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<td>Yiren and Hanying (1989)</td>
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<td>74</td>
<td>Wufeng Fm.</td>
<td>Ash</td>
<td>Yangze platf, 30°N/107°30'E</td>
<td>slope/basin</td>
<td>undet</td>
<td>silic grpt sh, LMS</td>
<td>Rad</td>
<td>Yu-ting (1991)</td>
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