

Biogenic and inorganic cherts

P. Buurman

ABSTRACT

Association of cherts with authigenic minerals at the continental margins, and the diminishing quantity of chert formed since the Eocene, suggest a link of chert genesis with terrestrial weathering and tectonic rest. Sedimentation of hydroxide-bound silica in periods of tectonic rest might lead to quartzous cherts in chalk rocks, while cristobalitic cherts (porcelanites) are biogenic and occur in silica oozes and in detritic sediments.

Introduction

Results of the Deep Sea Drilling Project (DSDP) have led to an enormous increase in our knowledge of oceanic chert formation (1, 7, 8, 24, 26). Before the DSDP, cherts were almost exclusively studied on the terrestrial parts of the continents, and many of the older papers on chert formation suggest inorganic genesis for quartzous cherts, while organic genesis was excluded in many theories.

The results of the DSDP, that are mainly based on the study of biogenic cherts (porcelanites) turned the scales the other way, and many authors now defend an exclusively organic genesis for most cherts. Some authors (43) even allow themselves fulminations against those investigators who still believe in the possibility of inorganic chert formation. The denial of the possibility of inorganic chert formation is mainly due to the fact that till now no reasonable mechanism was proposed. The present paper intends to point out that, although cherts are indeed frequently of organic origin, inorganic formation should not be ruled out beforehand.

Chert in the marine environment and in the geological record
There are several features that should be explained by any theory on chert formation. It was observed that chert and chert-like substances (porcelanite) abound in sediments of Cretaceous till Eocene age, while they are much rarer in younger sediments, where chert is almost invariably restricted to the equatorial zone.

Cherts are frequently associated with deposits with a relatively high amount of silica-rich authigenic minerals (clinoptilolite, palygorskite, K-feldspar) (29). It was observed that in deposits of authigenic minerals, that occur at the continental margins, high silica minerals (clinoptilolite) were dominant in pre-Oligocene sediments, while authigenic minerals with lower silica contents (philipsite) are more frequent in younger deposits (3). In the Atlantic Ocean, pre-Oligocene deposits with palygorskite and sepiolite are overlain by younger layers in which detritic minerals such as kaolinite and chlorite are common. Another aspect is, that quartzous cherts, which are frequently of nodular habit, are generally found in nannofossil chalk, while bedded cherts (porcelanites) are generally linked with biogenic silica sediments and detritic sediments (15).

A theory on the genesis of cherts should therefore explain: 1. the occurrence of cherts in the stratigraphic record, 2. the structural differences and mineralogical differences between quartz- and porcelanite (lussatite) cherts, and their occurrence in different environments and 3. the association of cherts with authigenic minerals. To develop a hypothesis, we will have to regard the three most important aspects in the genesis of cherts: a) the source of the silica, b) the sedimentation process and c) the post-sedimentary recrystallization and accretion.

The source of silica

Several authors have published balances of the silica budget in the oceans. These budgets are calculated for actual circumstances and not for fossil environments. A compilation of four silica budgets is given in table 1. It appears that there are several major and minor sources of dissolved silica in the oceanic waters:

Table 1 Balances of oceanic silica

INPUT				
Ref. →	1	2	3	4
Source ↓				
Continental drainage	4.3	4.3	4.3	4.3
submarine weathering + redissolution	0.03	1.0	0.03	0.8
				3.8-7.6
submarine volcanism	≪ 0.01	-	7.0	≪ 0.05
antarctic weathering	-	≪ 7.0	-	-
SEDIMENTATION				
Ref. →	1	2	3	4
Source ↓				
Antarctic oozes	3.0	< 1.9	12	8.5-12
other oozes	0.6			
estuarine removal	-	0.9	-	0.4

All amounts in 10^{14} gram SiO_2 /year

Refs:

1. Calvert, 1968; 2. Burton & Liss, 1973;
3. Leclaire, 1974; 4. Heath, 1974.

- silica resulting from superficial weathering of terrestrial rocks, that is transported by rivers (32).
- submarine weathering of sedimentary aluminosilicates, and redissolution of sedimented siliceous tests. These sources are sometimes taken together as the contribution of diffusion processes from the interstitial waters of sea bottom sediments (11,22,25,39).
- alteration of fresh volcanic material at the ocean floor (at sites of sea floor spreading) (16, 23).
- antarctic weathering (the dissolution of 'rock flour' set free by melting glaciers) (4, 30).
- redissolution of siliceous tests of organisms before sedimentation (this is not a real source, since the silica was not removed from the oceanic budget. It is left out in the balance).

Although the balances are highly contradictory with respect to the importance of the various processes (riverine input excepted), we will make a few speculations on the importance of these sources of silica in the past. These speculations are made in order to check the possibility that silica levels in pre-Oligocene Oceans would have been higher.

- The composition of interstitial waters, and their attribution to the oceanic budget will vary with the amount of amorphous silica in the sediment, unless equilibrium with amorphous silica exists. This attribution will have been

higher in times when siliceous sediments were more widespread than they are now, but it cannot be the cause of high silica concentrations in the oceans, it is the result of it.

- Antarctic weathering will hardly have contributed to the oceanic silica in the oceans during pre-Oligocene times, because there were no glaciers at that time. Moreover, Antarctic weathering is said not to contribute now (25).

- The alteration of suboceanic basalts as a source of dissolved silica depends on the rate of sea floor spreading, which has varied (23). Recent increases in the rate of sea floor spreading, however, are not associated with an increase in chert formation, while periods of slower spreading, that occurred in the past, did not result in sediments without chert (30).

- The last major source, the supply of silica by rivers may have varied considerably. The amount of silica in rivers depends on the type of weathering in the source area. In regions with lateritic (ferrallitic) weathering, silica discharges of rivers can be very high, while they are lower in regions with other types of soil formation. Ferrallitic weathering (hydrolysis of silicates) is nowadays restricted to a more or less equatorial zone (about 10-15%) of the terrestrial surface) while, from Jurassic till Oligocene times the tropical zone extended over $\frac{3}{4}$ of this surface. Moreover, the regions that are now subject to lateritic weathering, are already considerably weathered and hardly supply any silica at all. During the beginning of laterization, however, silica discharges of tropical rivers must have been much higher.

Nowadays, the two largest tropical rivers, the Amazon and the Congo River, account for 30% of the yearly supply of silica in the oceans. This large amount is mainly due to the very high water discharges and not to their silica concentrations.

In tropical areas there is a considerably higher circulation of atmospheric water, and therefore, total water discharges will have been higher when the tropical climate was more widespread, in pre-Oligocene times. So there are two factors that suggest higher discharges of dissolved silica of pre-Oligocene rivers: a) a wider extension of the tropical zone and b) the onset of laterization. The onset of climatic zonation resulted in a smaller zone of tropical weathering and therefore in smaller silica discharges.

A second very important factor is that the amount of terrigenous debris, deposited in the oceans, that was low in Late Cretaceous and Early Tertiary times, increased considerably with the onset of tectonic activity in the Late Tertiary.

Terrestrial weathering as a main source for silica in the oceans of the past corroborates well with the occurrence of silica-rich authigenic minerals at the continental margins. Furthermore, if terrestrial silica is the main source of silica for chert and authigenic minerals, their abundance in pre-Oligocene sediments is explained.

The deposition of silica

The organic deposition of silica, by way of siliceous tests of micro-organisms is very well known. Such organic silica sediments seem to occur at sites where upwelling deep-ocean waters provide sufficient food for a plentiful growth of these organisms. Organic removal of silica from the seawater is virtually unaffected by the silica concentrations. Till now, it was thought, that inorganic deposition of silica, and inorganic chert formation, should be linked with supersaturated seawater. Recently, it was pointed out, that such precipitation is very unlikely (25).

However, a mechanism that removes silica inorganically from undersaturated silica, does exist.

Experiments on the removal of silica from natural waters by means of amorphous hydroxides of ferric iron, manganese and aluminum have shown that silica is nearly quantitatively removed by freshly prepared amorphous hydroxide (17, 19, 20, 34). Silica concentrations in such adsorbing hydroxide flakes may be as high as 80%. Adsorption

on wellcrystalline hydroxides is lower, but still important. Adsorption was found to increase with pH, between pH 5 and 9, and it is higher at lower temperatures.

It is to be expected, that most of the silica, in natural river waters will be bound to hydroxides in the sediment load. Adsorption of silica on the hydroxides will increase upon mixing of riverwater with sea water, (pH rises).

Recently, many scientists have concentrated on the inorganic removal of silica during estuarine mixing, but there is still some discussion on the amount of removal (4, 5, 11, 31, 44, 2). It should be noted, that tropical rivers were not investigated, and that the most remarkable results were found in rivers where the sediment load is fairly rich in iron oxides (4).

It is quite possible, that the amount of ferric, manganese and alumina-hydroxides, free or as coating on suspended matter, is responsible for the removal of silica during estuarine mixing and for deposition of silica in the open sea.

Again, the process would be most pronounced in tropical regions, and would have been more important in pre-Oligocene times. Hydroxide-bound silica is easily spread homogeneously over large areas (the influence of dissolved silica in the Amazon water is still measurable over distances up to 1000 km from the Brazilian shore (38). In case detritic sedimentation is very slow, and hydroxide-bound silica supply is high, silica might form vast concentrations at the ocean floor.

Next to biogenic oozes and the accumulation of hydroxide-bound silica, the devitrification of submarine volcanic glass, and diagenetic processes such as the chloritization of smectites (28) may be sources of silicifications, but these are of local importance only. They will not be discussed in the following.

Recrystallization and accretion

Now that we have outlined two possible major sources of siliceous sediments: organic and hydroxide-bound precipitation, we shall discuss recrystallization and further accumulation.

Precipitation of silica from highly concentrated solutions, as will occur in siliceous oozes, do not result in quartz (17, 19, 20), but in products as opal-A, opal-C or opal-CT (lussatite) (12, 27). Therefore, 'cristobalitic' cherts or porcelanites can be expected to form from organic silicified sediments. Actually, all biogenous oozes do form porcelanite cherts (9, 10, 15, 40-42).

Cristobalitic cherts will recrystallize to quartz (35, 36, 43). This reaction being of zero order, only requires energy (higher temperature) (9). Actually, a relation exists between amount of recrystallization and the thermal history of the sediment (26). No relation was found between the age of the sediment and the amount of recrystallization. It is believed that about 70 to 90 million years are necessary for complete quartzification of porcelanites (36). Cristobalitic cherts in siliceous oozes are generally platy. Hydroxidebound silica does not crystallize to opaline forms but to quartz, in a matter of days (18, 21, 33).

It was noticed before, that quartzous cherts occur mainly in chalk rocks, irrespective of their age. This might point to hydroxide-bound silica as a source for silica in these rocks. When this holds true, the process of chert genesis in chalk rocks can be described as follows:

- Variations in the accumulation of organic chalk debris and hydroxide-bound silica result in layers with different amounts of silica. Silica in layers with high amounts will tend to crystallize quartz. This creates a concentration gradient, that results in diffusion of silica towards the layers where crystallization takes place. Both siliceous tests and inorganic silica can be dissolved and transported this way.

The diffusion of silica depends on the porosity of the sediment; a high porosity, as may occur around animal burrows, will give a rapid growth, while transport rates are lower at other sites. This accounts for the irregular forms of quartzous cherts in chalk rocks.

Diffusion of silica towards a layer of crystallization results in silicification of the host rock in the zone of accumulation. Because crystallization is rapid, silicification and lithification of cherts will start immediately after deposition. This rapid formation of quartz cherts is more in accordance with observations in the field, because it explains the occurrence of rolled chert pebbles within chalk sediments. This would not have been possible if quartzification were much slower.

Thus, the inorganic accumulation of hydroxide-bound silica explains quite a few things that otherwise remain unexplained:

- the occurrence of quartz cherts without any traces of siliceous organisms, especially in nannofossil chalk
- the association of chert with authigenic minerals at the continental margins (alumina can be readily available in the hydroxides)
- the nodular habit of quartz cherts.
- the rapid quartzification of some cherts
- the abundance of cherts in pre-Oligocene times.

Summarizing, we can say that chert formation is probably not exclusively the result of high silica-levels in the ocean. It may depend on the nature of the silica-supply and on the relative amounts of silica and detritic material in river discharges (dilution effect).

There are probably two genetically different types of chert: 1. cherts that are result of recrystallization of biogenic silica oozes. These cherts show a recrystallization to opals and finally to quartz

2. cherts that are formed by quartz precipitation from hydroxide-adsorbed silica.

The abundance of both types of chert is controlled by the supply of detritic material by rivers. Chert formation is favoured in periods of tectonic rest.

Thus, we may look back 20 years, and cite that quartzous cherts are formed in 'very wide shallow, well aerated seas, bordered by a base-levelled continent from which no sediment was derived' (37).

References

1. Borch, C. C. von der; J. A. Galehouse & W. D. Nesteroff, 1971: Silicified limestone-chert sequences cored during Leg 8 of the Deep Sea Drilling Project: a petrologic study. Initial Repts. DSDP Vol 8: 819-827. U.S. Government Printing Office, Washington.
2. Boyle, E., et al., 1974: On the chemical mass-balance in estuaries. *Geochim. Cosmochim. Acta* 38: 1719-1728
3. Bruty, D.; R. Chester & S. Raston, 1973: Trace elements in ancient atlantic deep sea sediments. *Nature* 245: 73-74
4. Burton, J. D. & P. S. Liss, 1973: Processes of supply and removal of dissolved silicon in the oceans. *Geochim. Cosmochim. Acta* 37: 1961-1973
5. Burton, J. D., P. S. Liss & V. K. Venugopalan, 1970: The behaviour of dissolved silicon during estuarine mixing. I. Investigations in Southampton water. *J. Conseil. Intern. Explor. Mer.* 33: 134-140
6. Calvert, S. E., 1986: Silica balance in the ocean and diagenesis. *Nature* 219: 919-920
7. Calvert, S. E., 1971a: Nature of silica phases in deep sea cherts from the North Atlantic. *Nature* 234: 133-134
8. Calvert, S. E., 1971b: Composition and origin of North Atlantic deep sea cherts. *Contrib. Mineral. Petrol.* 33: 273-288
9. Calvert, S. E., 1974: Deposition and diagenesis of silica in marine sediments. *Spec. Publ. Intern. Ass. Sediment.* 1: 273-300
10. Ernst, W. G. & S. E. Calvert, 1969: An experimental study of the recrystallization of porcelanite and its bearing on the origin of some bedded cherts. *Amer. J. Sci.* 267A: 114-133
11. Fanning, K. A., & M. E. Q. Pilson, 1973: The lack of inorganic removal of dissolved silica during river-ocean mixing. *Geochim. Cosmochim. Acta* 37: 2405-2415
12. Flörke, O. W., 1955: Zur Frage des 'Hoch'-Cristobalits in Opalen, Bentoniten und Gläsern. *Neu. J. Mineral. Mh.* 217-223
13. Froehlich, F., 1974: Nature, importance relative et place dans la diagenèse des phases de silice présentées dans les silicifications de crâtes du Bassin océanique de Madagascar (Océan Indien) et du Bassin de Paris. *Bull. Soc. Géol. France* 16: 498-508
14. Garrels, R. M., 1965: Silica: role in the buffering of natural waters. *Science* 148: 69
15. Greenwood, R., 1973: Cristobalite: its relationship to chert formation in selected samples from the Deep Sea Drilling Project. *J. Sediment Petrol.* 43: 700-708
16. Gregor, B., 1968: Silica balance of the ocean. *Nature*, 219: 360-361
17. Harder, H., 1965: Experimente zur 'Ausfällung' der Kieselsäure. *Geochim. Cosmochim. Acta* 29: 429-442
18. Harder, H., 1967: Ueber das Kalium-Natrium-Verhältnis in Gewässern und die Tonmineralbildung. *Naturwiss.* 54: 613

19. Harder, H., 1971: Quartz and clay mineral formation at surface temperature. *Min. Soc. Japan. Spec. Paper* 1: 106-108
20. Harder, H., & W. Flehmig, 1970: Quarzsynthese bei tiefen Temperaturen. *Geochim. Cosmochim. Acta* 34: 295-305
21. Harder, H., & G. Menschel, 1976: Quarzbildungen am Meeresboden. *Naturwiss.* 54: 561
22. Harriss, R. C., 1966: Biological buffering of oceanic silica. *Nature* 212: 275-276
23. Hart, R. A., 1973: Geochemical and geophysical implications of the reaction between seawater and the oceanic crust. *Nature* 243: 76-78
24. Heath, G. R., 1973: Cherts from the eastern Pacific, Leg. 16, Deep Sea Drilling Project. In: Initial Repts. D.S.D.P. Vol. 16: 609-613. U.S. Government Printing Office, Washington.
25. Heath, G. R., 1974: Dissolved silica and deep sea sediments. in W. W. Hay (ed): *Studies in paleo-oceanography*. Soc. Econ. Paleont. Mineralog. Spec. Publ. 20: 77-93
26. Heath, G. R. & R. Moberly, 1971: Cherts from the western Pacific, Leg 7, Deep Sea Drilling Project. In: Initial Reports of the DSDP, vol 7.2: 991-1007. U.S. Government Printing Office, Washington.
27. Jones, J. B. & E. R. Segnit, 1971: The nature of opal, I. Nomenclature and constituent Phases. *J. geol. Soc. Australia* 18: 57-68
28. Keene, J. B. & M. Kastner, 1974: Clays and the formation of deep-sea chert. *Nature* 249: 754-755
29. Lancelot, Y., 1973: Cherts and silica diagenesis in sediments from the central Pacific. In: Initial Repts. of the DSDP, Vol 17: 377-405. U.S. Government Printing Office, Washington.
30. Leclaire, L., 1974: Hypothèse sur l'Origine des silicifications dans les grands bassins océaniques. Le rôle des climats hydrolisants. *Bull. Soc. Geol. France* 16: 214-224
31. Liss, P. S. & C. P. Spencer, 1970: Abiological processes in the removal of silicate from sea water. *Geochim. Cosmochim. Acta* 34: 1073-1088
32. Livingston, D. A., 1963: Chemical composition of rivers and lakes. U.S. Geol. Survey Prof. Paper 440-G, 64 pp.
33. Mackenzie, F. T., & R. Gees, 1971: Quartz: synthesis at earth surface conditions. *Science* 173: 533-535
34. McPhail, M.; A. L. Page & F. T. Bingham, 1972: Adsorption interactions of monosilicic and boric acids on hydrous oxides of iron and aluminum. *Soil Sci. Soc. Amer. Proc.* 36: 510-514
35. Mizutani, S., 1966: Transformation of silica under hydrothermal conditions. *J. Earth Sci. Nagoya Univ. Japan.* 14: 56-88
36. Rad, U. von, & H. Rösch, 1974: Petrography and diagenesis of deep sea cherts from the central Atlantic. *Spec. Publ. Int. Ass. Sediment.* 1: 327-347
37. Ruten, M. G., 1957: Remarks on the genesis of flints. *Amer. J. Sci.* 255: 432-439
38. Ryther, J. H., D. H. Menzel & N. Corwin, 1967: Influence of the Amazon river outflow on the ecology of the western tropical Atlantic. I. Hydrography and nutrient chemistry. *J. Mar. Res.* 25: 69-83
39. Sillén, L. G., 1961: The Physical chemistry of sea water. In: M. Sears: *Oceanography*. pp 549-581. Amer. Ass. Adv. Sci. Publ. 67
40. Weaver, F. M. & S. W. Wise, 1972: Ultramorphology of deep sea cristobalitic chert. *Nature* 237: 56-57
41. Wise, S. W.; B. F. Buie & F. M. Weaver, 1972: Chemically precipitated sedimentary cristobalite and the origin of chert. *Eclogae geol. Helvet.* 65: 157-163
42. Wise, S. W., & K. R. Kelts, 1972: Inferred diagenetic history of weakly silicified deep sea chalk. *Trans. Gulf Coast Ass. Geol. Soc.* 22: 177-203
43. Wise, S. W., & F. M. Weaver, 1974: Chertification of oceanic sediments. *Spec. Publ. Int. Ass. Sediment.* 1: 301-326
44. Wollast, R., & F. de Broeu, 1971: Study of the behavior of dissolved silica in the estuary of the Scheldt. *Geochim. Cosmochim. Acta* 35: 613-620

Algemene publikaties betreffende de genese van vuursteen zijn de nummers 1, 7-9, 15, 24-26, 29-31, 36, 37 en 41 van de bovenstaande lijst, en voorts nog: L. Cayeux, 1927: La formation des silex dans la craie. *C. R. Somm. Soc. Géol. France* 210-212
G. V. Chilingar, 1956: Distribution and abundance of chert and flint as related to the Ca/mg ratio of limestones. *Bull. Geol. Soc. Amer.* 67: 1559-1562
R. L. Folk & C. E. Weaver, 1952: A study of the texture and composition of chert. *Amer. J. Sci.* 250: 498-510
S. W. Wise & K. R. Kelts, 1972: Inferred diagenetic history of a weakly silicified deep sea chalk. *Trans. Gulf Coast Assoc. Geol. Soc.* 22: 17u-20e.