# CHEMICAL CONTROLS ON THE OPAL-A TO OPAL-CT TRANSFORMATION

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Since early Paleozoic the major mechanisms of silica precipitation at ordinary temperatures and pressures is biochemical. Other mechanisms are: adsorption, organo-silicon complexing, evaporation or cooling of silica-rich waters (with subsequent precipitation), and neutralization of strongly alkaline solutions.

Evidence from deep-sea sediments supports the following diagenetic sequence Opal-A (siliceous oozes) → Opal-CT (porcelanite) → chalcedony or cryptocrystalline quartz (chert) → mega-quartz (chert). A solution and precipitation mechanism is involved in the above first two transformations. Exceptions to the overall maturation sequence are numerous, suggesting that temperature (burial depth) and time are not the only important factors that control the transformation of Opal-A to Opal-CT. The kinetics of the above transformations are strongly affected by the composition of the host sediments; in clayey sediments Opal-CT (porcelanite) predominates while in carbonate sediments quartz (chert) predominates. There is no simple way to relate either the crystalline state of silica or the texture of porcelanite and chert horizons to the age of surrounding sediments.

Experiments at 25°C and 150°C over a period of one to six months, using both chemical and mineralogical analyses, suggest that the transformation rate of Opal-A to Opal-CT is greatly enhanced in carbonate versus clayey pelagic sediments. The role of carbonate can be explained as follows: Opal-CT lepispheres co-precipitate with a hydrous magnesium complex. In carbonate sediments the continuous dissolution of carbonate provides the necessary alkalinity, and sea water provides the magnesium for the magnesium hydroxide complex. In contrast in clayey sediments, in particular, those rich in expandable clays, the clay minerals compete with Opal-CT formation for the available alkalinity. As a result, the expandable clays transform to a magnesium-rich mixed layered clay and/or to chlorite and the rate of Opal-CT formation is highly reduced.

## DISCLAIMER

Table 1. Solution chemistry of hydrothermal experiments in sea water, at 150°C.

| Experiment Number | Starting Materials | Time Months | $Si(OH)_4$ µM/l | Mg mM/l | Alkalinity meq/l |
|---|---|---|---|---|---|
| 1 | Eocene Radiolarians | 1 | 2550 | 50.6 | 0.2 |
| 2 | Eocene Radiolarians | 6 | >10,000 | 50.4 | 0.1 |
| 3 | Eocene Radiolarians + Foraminifera | 1 | 1980 | 19.2 | 3.8 |
| 4 | Eocene Radiolarians + Foraminifera | 6 | 7850 | 7.3 | 2.7 |
| 5 | Eocene Radiolarians + Montmorillonite | 1 | 2400 | 51.1 | 0.2 |
| 6 | Eocene Radiolarians + Foraminifera + Montmorillonite | 1 | 2060 | 18.5 | 3.7 |
| 7 | Quaternary Diatoms | 1 | 6000 | 46.9 | 0.1 |
| 8 | Quaternary Diatoms | 6 | >10,000 | 50.1 | 0.1 |
| 9 | Quaternary Diatoms + Foraminifera | 1 | 2050 | 3.2 | 2.1 |
| 10 | Quaternary Diatoms + Foraminifera | 6 | 7350 | 5.0 | 1.4 |
| 11 | Quaternary Diatoms + Montmorillonite | 1 | 8000 | 46.6 | 0.1 |
| 12 | Quaternary Diatoms + Foraminifera + Montmorillonite | 1 | 1950 | 26.6 | 0.7 |
| Average Surface Sea Water | | | 2-3 | 53.0 | 2.5 |

Table 2. Solution chemistry of room temperature experiments.

| Experiment Number | Starting Materials | $Si(OH)_4$ μM/l | | |
|---|---|---|---|---|
| | | 1 week | 2 weeks | 3 weeks |
| a | Eocene Radiolarians + distilled $H_2O$ | n.d. | 22 | 42 |
| b | Eocene Radiolarians + sea water | 47 | 125 | 142 |
| c | Eocene Radiolarians + Foraminifera + sea water | <40 | 105 | 120 |
| d | Quaternary Radiolarians + distilled $H_2O$ | 1300 | 1430 | 1610 |
| e | Quaternary Diatoms + distilled $H_2O$ | 105 | 143 | 195 |
| f | Quaternary Diatoms + sea water | 920 | 1030 | 1020 |
| g | Quaternary Diatoms + Foraminifera + sea water | 840 | 935 | |
| h | Quaternary Diatoms + Reagent grade $CaCO_3$ powder + sea water | 120 | 125 | 125 |
| i | Quaternary Diatoms + Iceland Spar 150-250μ + sea water | 910 | | |
| j | Quaternary Diatoms + Iceland spar 63-105μ + sea water | 860 | | |
| k | Quaternary Diatoms + Iceland spar <44μ + sea water | 840 | | |
| l | Cultured Diatom, Navicula pelliculosa + sea water | 480 | 950 | 1110 |
| m | Cultured Diatom, Nitzschia thermalis + sea water | 350 | 960 | 1120 |

n.d. = not detected

Table 3. The effects of Mg, Ca, Na, K, and alkalinity on the rate of opal-A to Opal-CT transformation; solution chemistry of hydrothermal experiments at pH 8, 150°C.

| Experiment Number | Starting Materials | Time Months | $Si(OH)_4$ μM/l | Mg mM/l | Alkalinity meq/l |
|---|---|---|---|---|---|
| 1 | Eocene Radiolarians + sea water | 1 | 2550 | 50.6 | 0.2 |
| 3 | Eocene Radiolarians + Foraminifera + sea water | 1 | 1980 | 19.2 | 3.8 |
| 13 | Eocene Radiolarians + artificial sea water without Mg* | 1 | 2160 | -- | n.a. |
| 14 | Eocene Radiolarians + Foraminifera + artificial sea water without Mg* | 1 | 2130 | -- | n.a. |
| 15 | Eocene Radiolarians + 0.5M NaCl, 0.03M $MgCl_2$ sol. (I = 0.68) | 1 | 6820 | 29.0 | 0.1 |
| 16 | Eocene Radiolarians + Foraminifera + 0.5M NaCl, 0.03M $MgCl_2$ sol. (I = 0.68) | 1 | 2550 | 2.2 | 2.8 |
| 17 | Eocene Radiolarians + 0.027M $MgCl_2$, 0.028M $NaHCO_3$ sol. (I = 0.12) | 1 day | 4920 | 13.4 | 2.2 |
| 18 | Eocene Radiolarians + 0.03M $MgCl_2$, 0.03M $NaHCO_3$ sol. (I = 0.12) | 1 | 6550 | 16.6 | 1.1 |
| 19 | Eocene Radiolarians + 0.03M $MgCl_2$, 0.03M $NaHCO_3$ sol. (I = 0.12) | 3 | 9750 | 14.4 | 0.8 |
| 20 | Eocene Radiolarians + 0.03M $MgCl_2$, 0.006M $NaHCO_3$, 0.024M NaCl sol. (I = 0.12)** | 1 | 9100 | 27.2 | 0.4 |
| 21 | Eocene Radiolarians + 0.03M $NaHCO_3$, 0.1M NaCl. sol. (I = 0.13) | 1 | 3400 | -- | 30.4 |
| 22 | Eocene Radiolarians + Montmorillonite + 0.03M $MgCl_2$, 0.03M $NaHCO_3$ sol. (I = 0.12) | 1 | 7400 | 15.1 | 1.6 |
| 23 | Montmorillonite + 0.03M $MgCl_2$, 0.03M $NaHCO_3$ sol. (I = 0.12) | 1 | 3100 | 15.4 | 3.1 |
| 24 | Eocene Radiolarians + 0.03M $MgCl_2$, 0.03M $KHCO_3$ sol. (I = 0.12) | 1 | 7900 | 16.0 | 1.6 |
| 25 | Eocene Radiolarians + 0.03M $MgCl_2$, 0.015M $Na_2B_4O_7$ $10H_2O$ sol.** | 1 | 7350 | 27.5 | 0.1 |

n.a. = not analyzed

* Artificial sea water according to Lyman and Fleming (1940)

** The pH of the solution was adjusted to pH 8 by acid titration. The alkalinity of the final solutions were 5.6 meq/l.

Table 4. The effect of ionic strength on the rate of opal-A to opal-CT transformation; solution chemistry of hydrothermal experiments at pH 8, 150°C, 1 month.

| Experiment Number | Starting Materials | $Si(OH)_4$ µM/l | Mg mM/l | Alkalinity meq/l |
|---|---|---|---|---|
| 18 | Eocene Radiolarians + 0.03M $MgCl_2$, 0.03M $NaHCO_3$ sol. (I = 0.12) | 6550 | 16.6 | 1.1 |
| 26 | Eocene Radiolarians + 0.03M $MgCl_2$, 0.03M $NaHCO_3$, 0.58M NaCl sol. (I = 0.7) | 6425 | 19.1 | 13.6 |
| 27 | Eocene Radiolarians + 0.03M $MgCl_2$, 0.03M $NaHCO_3$, 0.88M NaCl sol. (I = 1.0) | 6225 | 16.6 | 3.2 |
| 24 | Eocene Radiolarians + 0.03M $MgCl_2$, 0.03M $KHCO_3$ sol. (I = 0.12) | 7900 | 16.0 | 1.6 |
| 28 | Eocene Radiolarians + 0.03M $MgCl_2$, 0.03M $KHCO_3$, 0.58M NaCl sol. (I = 0.7) | 6975 | 17.4 | 2.8 |

Figure 6. Scanning Electron Microscope Photographs of:

(a) A cluster of well formed Opal-CT lepispheres that crystallized in Exp. 18, Table 3.

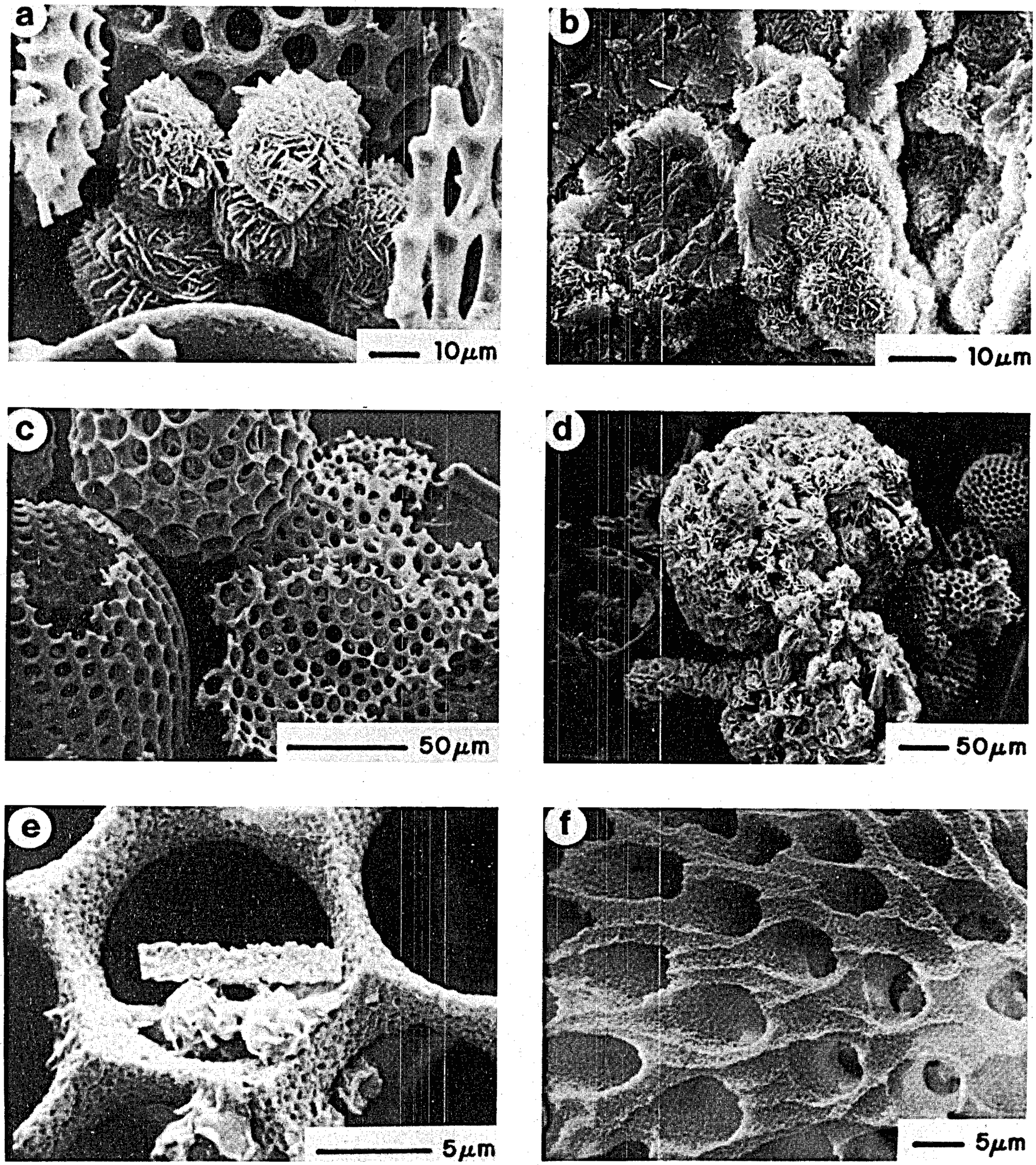
(b) Opal-CT lepispheres from a deep-sea porcelanite of Early Cretaceous age. The lepispheres line the inside of a radiolarian mold and texturally are very similar to the lepispheres of Fig. 6 (a).

(c) Several severely corroded radiolarian fragments and two less corroded robust species. Exp. 18, Table 3.

(d) Pseudomorphs of Opal-CT after robust radiolarians. Exp. 19, Table 3.

(e) Small embryonic Opal-CT lepispheres are attached to the surface of a radiolarian test and cement a radiolarian fragment to the test. Exp. 20, Table 3.

(f) Severe corrosion of a robust radiolarian test. Exp. 21, Table 3.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