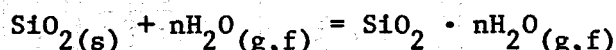


HYDROTHERMAL TRANSPORT AND DEPOSITION OF SILICA

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The strong Si-O-bond under dry conditions and in absence of impurities needs high activation energy for mobilization. Chemical activation with water based on the reaction:



lowers the energy barriers remarkably. Under normal conditions the equilibrium is extremely shifted to the left, however at increased temperatures and water-pressures (hydrothermal conditions) the reaction may cause strong chemical transport. The efficiency (rate) of transport depends on the physico-chemical and physical parameters (temperature, pressure, viscosity e.g.) as well as on the mechanism of flow.

The phase composition and micro-structure of the silica-deposit formed by the reverse process, strongly depends on rate of transport and deposition and on temperature of the substrate.

Experiments designed to study this were run in hydrothermal bombs with a cooling finger acting as substrate. The transport was achieved by convection due to density-differences in a temperature gradient. The experiments were carried out under mobilization-temperatures between 900 and 400°C and deposition-temperatures between 750 and 150°C with low to high rates of deposition.

The rate of deposition-temperature of substrate-field roughly may be divided into four domains:

1. high rate of deposition and high substrate temperature: prevailing deposition of cristobalite and cristobalite-tridymite disordered stacking polytypes with minor amounts of idiomorphic quartz and tridymite
2. low rate and high substrate temperature: prevailing deposition of idiomorphic quartz or chalcedony with minor amounts of quartz whiskers and idiomorphic tridymite
3. high rate of deposition and low substrate temperature: deposition of hyalite and minor amounts of opal-CT
4. low rate and low substrate temperature: deposition of opal-CT and some idiomorphic quartz.

The crystallographic properties of these deposits and the role of water-bonded as $(\text{H}_2\text{O})_{\text{mol}}$ or $(\text{H}_2\text{O})_{\text{SiOH}}$ in the silica-phases are discussed.

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Transformation kinetics of pure (<0.02%) and impure (>0.02%) silica in absence of liquid; influence of time neglected

① SiO ₂ pure normal pressure		② SiO ₂ impure normal pressure		③ SiO ₂ pure with H ₂ O 300 bar			
start material	QUARTZ NON-CRYSTALLINE	QUARTZ NON-CRYSTALLINE		QUARTZ CRISTOBALITE NON-CRYSTALLINE		TRIDYMITE	
[°C]							
700							
800							
900							
1000							
1100							
1200							
1300							
1400							
1500							
1600							

① SiO₂ pure, normal pressure:

- QUARTZ → CRISTOBALITE disordered (dashed arrow, ~1000°C)
- NON-CRYSTALLINE → CRISTOBALITE disordered (dashed arrow, ~1000°C)
- QUARTZ → CRISTOBALITE ordered (dotted arrow, ~1500°C)
- CRISTOBALITE disordered → CRISTOBALITE ordered (dashed arrow, ~1200-1400°C)

② SiO₂ impure, normal pressure:

- QUARTZ → Nuclei of disordered-ordered CRISTOBALITE and TRIDYMITE disordered (~900°C)
- NON-CRYSTALLINE → Nuclei of disordered-ordered CRISTOBALITE and TRIDYMITE disordered (~800°C)
- TRIDYMITE disordered → TRIDYMITE ordered (~1200-1300°C)
- TRIDYMITE ordered → CRISTOBALITE ordered (~1400-1500°C)

transformation products, temperatures and rates strongly depending on kind and amount of impurity.

③ SiO₂ pure with H₂O, 300 bar:

- QUARTZ → QUARTZ and TRIDYMITE (~900°C)
- CRISTOBALITE → QUARTZ and TRIDYMITE (~800°C)
- NON-CRYSTALLINE → TRIDYMITE (~700°C)
- TRIDYMITE → TRIDYMITE (~700°C)

transformation products, temperatures and rates are strongly modified by impurities; e.g.: Na-contents >0.03% cause complete transformation of tridymite into quartz between 700 and 950°C.

NON CRYSTALLINE: condensed aerosol, gel, glass

———— = enantiotropic transformation

----- = monotropic " "

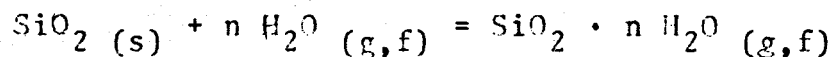
..... = only minor amounts

>>>> = increasing structural order

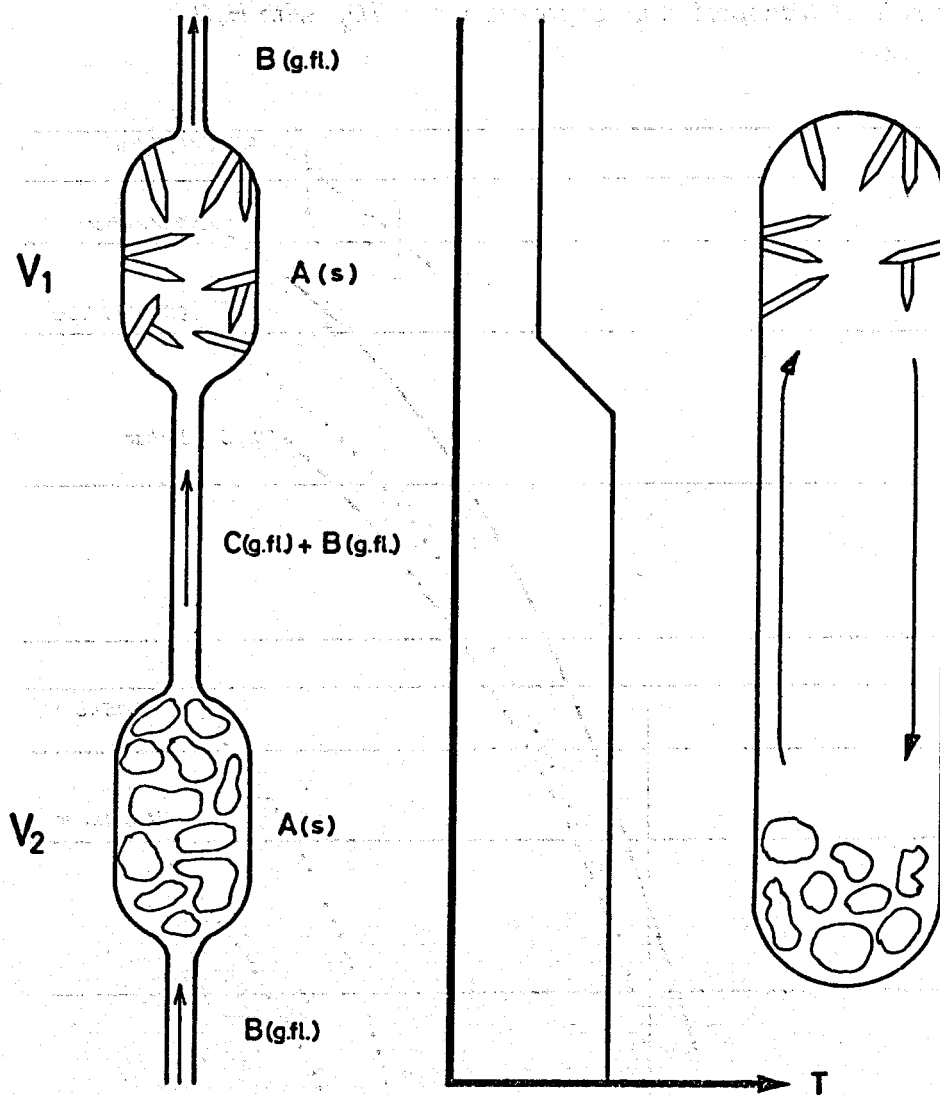
- - - - - = recrystallization without or before monotropic transformation

➤ approximate temperature of starting of transformation

Mobilization of SiO_2 with H_2O



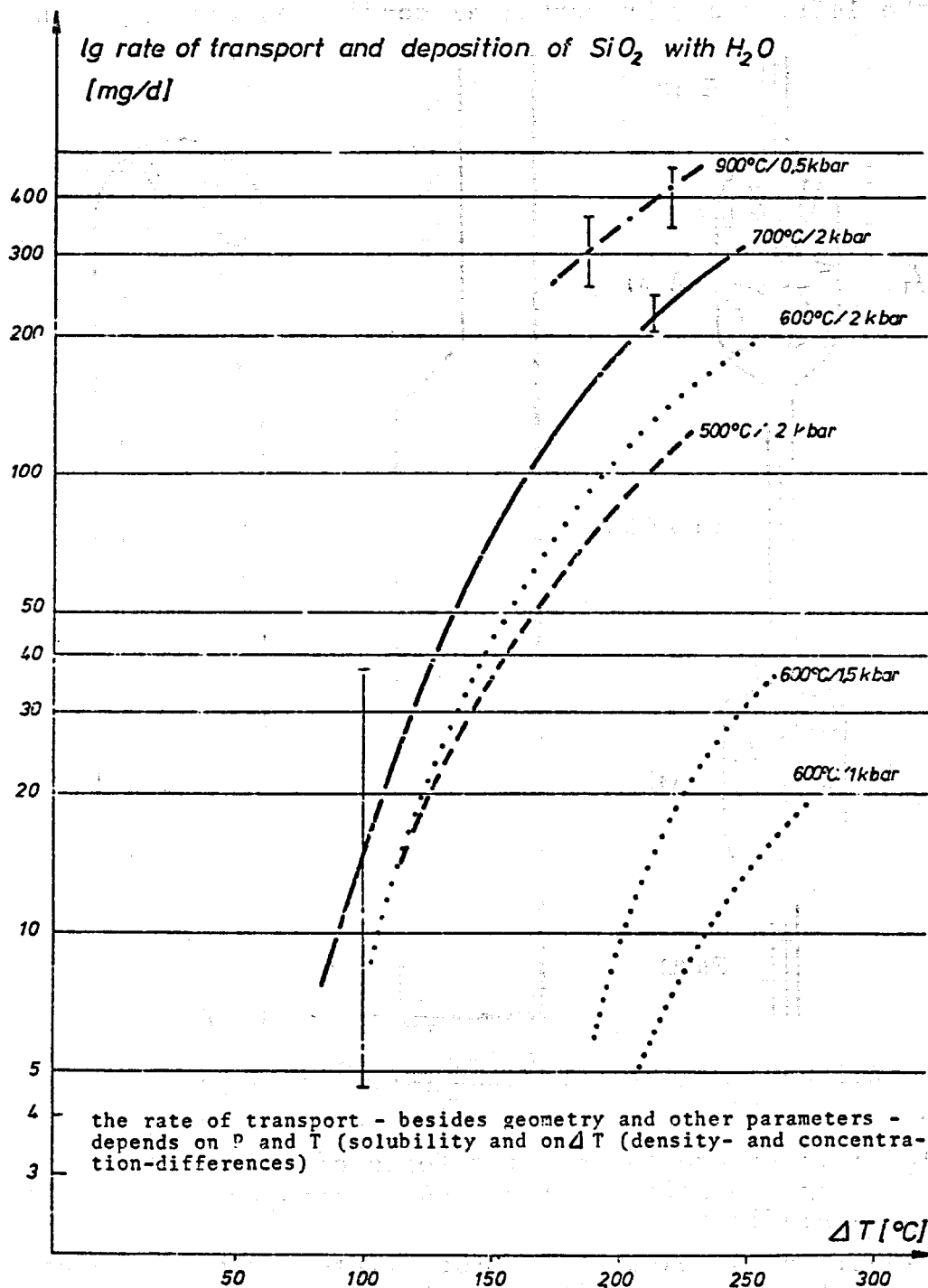
at normal conditions the equilibrium is extremely shifted to the left, under hydrothermal conditions the reaction

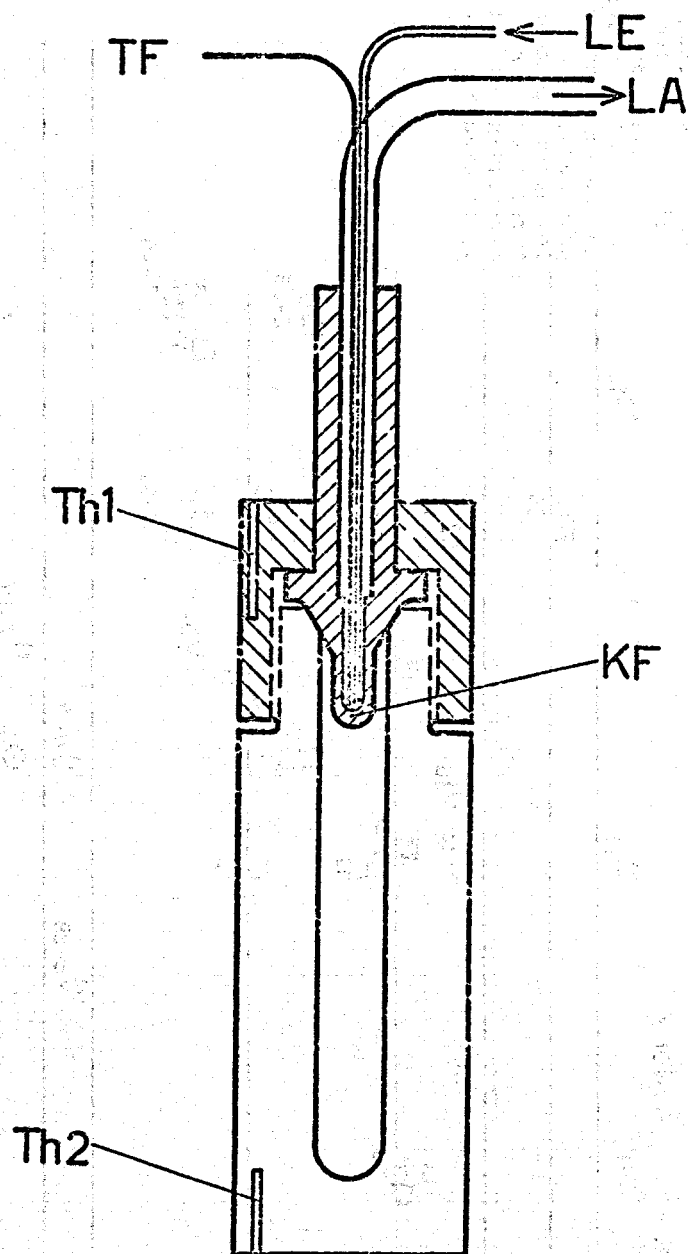


gets more and more balanced and chemical transport may take place.

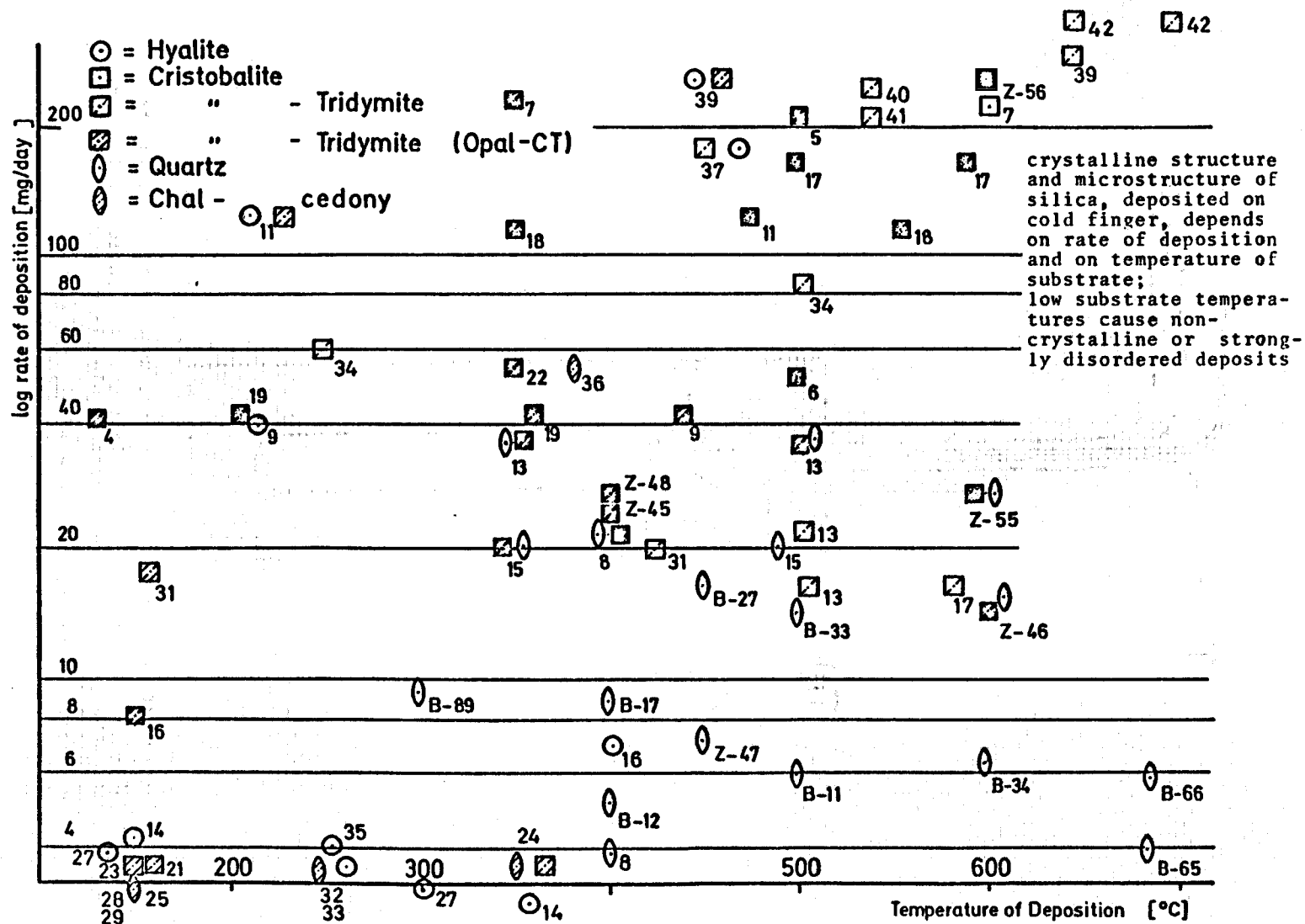
at left: in nature the driving force of transport is an expansion current with pressure- and temperature-gradients

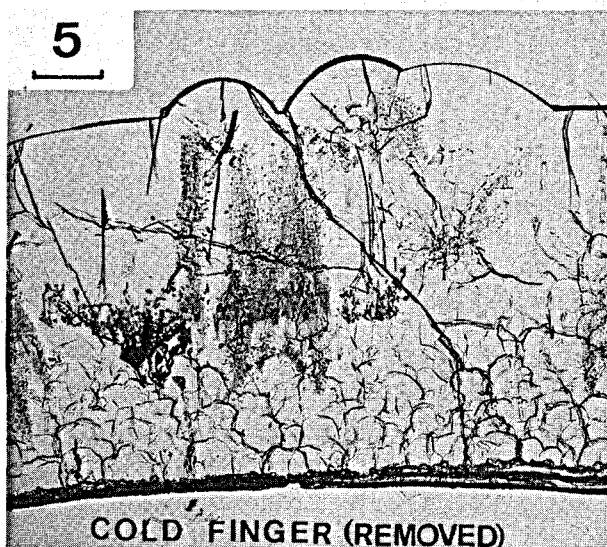
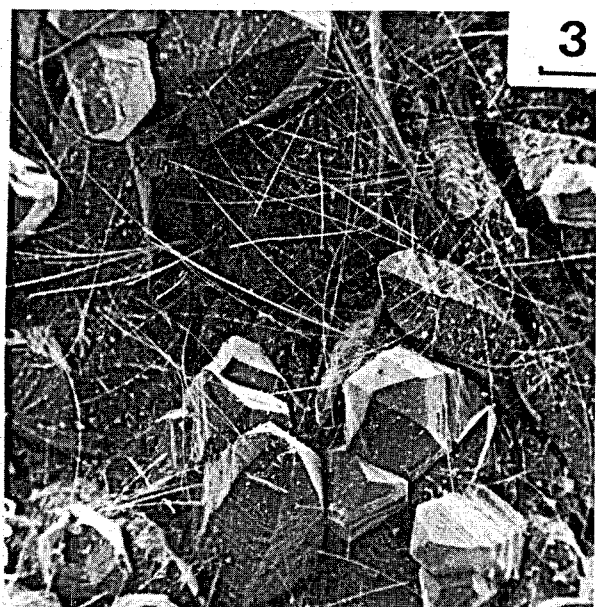
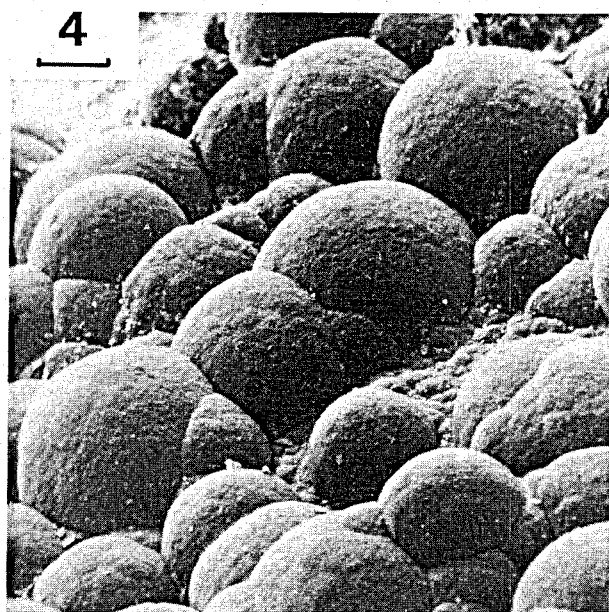
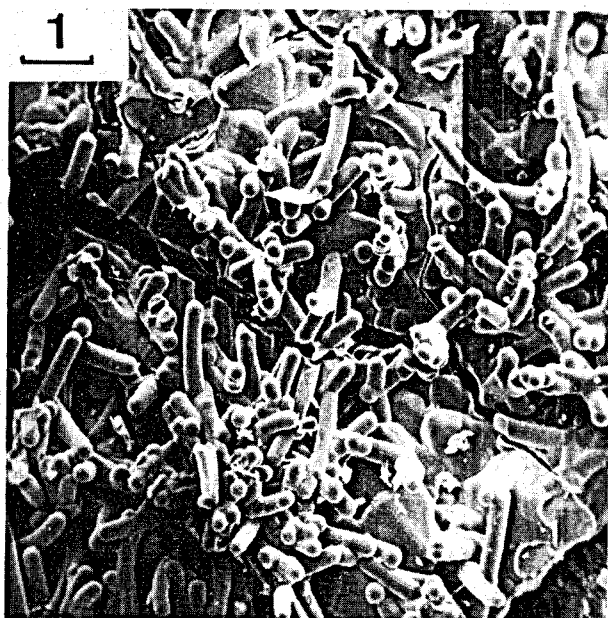
at right: in the experiments the driving force was a convection current with density- and temperature-gradients





hydrothermal bomb with cold finger, used in the experiments
 KF = cold finger; LE = air inlet; LA = air outlet; Th1 = bore
 for upper, Th2 for lower thermocouple; TF = thermocouple in
 cold finger;
 diameter of reaction volume = 12 mm, length = 120 mm





SEM-photographs:

- | | | |
|----|-----------------------------|------------|
| 1. | T(dep) low, rate (dep) high | 33 μ m |
| 2. | " high " " high | 33 |
| 3. | " high " " low | 100 |
| 4. | " low " " low | 100 |
1. hyalite (hydrous silica glass);
2. cristobalite; 3. quartz and quartz-whiskers; 4. opal-CT.

Micro-photograph:

5. thin section of deposit on cold finger; lower part T (dep) and rate (dep) high - well ordered cristobalite; upper part T(dep) and rate(dep) low - opal-CT (— 100 μ m).