

## Rare Earth Elements in biogenic silica of giant diatoms *Ethmodiscus rex*

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Biogenic silica plays an important role in rare earth element cycle in the ocean. Trivalent REE distribution in ocean water is very similar to that of dissolved silica. REE content in the biogenic silica currently remains unknown. The earlier data on the REE composition [1] for diatoms *Ethmodiscus rex* from the Indian Ocean sediments were obtained without chemical pretreatment. Thus the purpose of the present work is to consider REE concentrations in the frustules of diatoms. Diatom oozes (Sta. 1537, 19°05.5'S, 24°02.9' W, depth 5000 m) were disaggregated in distilled water to remove sea salts. Fragments of diatom (size fraction >100  $\mu\text{m}$ ) were isolated from slurry of oozes by sieving and washing through the polyamide net.

Chemical cleaning of the diatom shells included 4 stages.

1. Dissolving in solution 0.6M  $\text{NH}_2\text{OH}\times\text{HCl}$  + 1M HCl to remove coatings and micronodules.
2. Filtration through filter Millipore 0.45  $\mu\text{m}$ , washing with 1M HCl and Milli-Q water.
3. Treatment with 6.3M HCl, then solution was diluted with deionized water and after heating was agitated in an ultrasonic bath.
4. Filtering is similar to stage 2. Then samples were dried to a constant weight.

REE were determined by ICP-MS in 2%  $\text{HNO}_3$  solution with internal standards In and Re after digestion of biogenic silica in a mixture of HF and  $\text{HNO}_3$  (ultrapure grade Fluka) in PTFE beakers. The ratio of background/signal was less than 2% for Sm, Eu, Gd and Tb, for the other REE it was less than 1%.

REE pattern in diatom shells is similar to the composition of the dissolved REE in the ocean water. The surprise is the absence of the anomalous behavior of cerium. REE content in diatom shells is lower an order of magnitude than in the carbonate lattice of foraminifera [2]. The absence of cerium anomaly may be the result of the shell formation in oxygen minimum zone in the ocean water during diatom bloom in the glacial period.

[1] Elderfield *et al.* (1981) GCA 45, 513-528. [2] Palmer (1985) EPSL 73, 285-298.

## Effect of anharmonic lattice vibrations on the reaction rates in minerals

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Chemical reaction rates in minerals are shown to be accelerated by large amplitude lattice vibrations (a.k.a. intrinsic localized modes (ILM's) or discrete breathers (DB's)) that can appear in crystals with sufficient anharmonicity. As a result, Arrhenius law is violated, and the reaction rate averaged over large macroscopic volumes and times including many DB's is increased by a factor that depends on the DB statistics. The breather statistics in thermal equilibrium is considered, and the corresponding reaction rate amplification factor is derived.

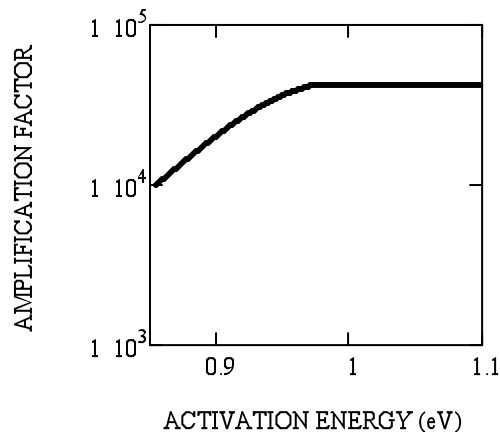


Figure 1. Amplification factor dependence on the reaction activation energy.

The model is shown to explain anomalous low-temperature reconstructive transformations in layered silicates [1] and the brittle to ductile fracture transition in  $\alpha$ -uranium at elevated temperatures [2].

[1] J. F. R. Archilla, J. Cuevas, M. D. Alba, M. Naranjo, J. M. Trillo, J. Phys. Chem. (2006) **B110** 24112-24120. [2] M.E. Manley, Acta Materialia (2010) **58**, 2926-2935.