# Supplementary Information

**Detection and Localization of Eu on Biosilica by Analytical Scanning Electron Microscopy**

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## SI 1: On the Spatial **Resolution of EDX and** CL Measurements

As stated by Eggert (Eggert, 2005), the local resolution in EDX (energy dispersive X-ray) elemental analysis can be expressed by the depth *Z* at which the characteristic X‑ray line is generated in the sample with the highest probability. This depth is given by . Here, is the mass density of the material in g/cm³, is the kinetic energy of the electrons in the electron beam (with the unit charge *e* and the acceleration voltage *V*), and is the critical energy for the generation of a characteristic X‑ray photon, with both energies in keV.

According to Everhart and Hoff (Everhart & Hoff, 1971), the penetration depth *R* of the electrons in SiO2 can be roughly estimated by the equation with *E*B in keV. The equation is applicable for an electron energy range between 5 keV and 25 keV and for atomic numbers between 5 and 15. The resulting value of *R* is in agreement with the Monte Carlo simulations described in SI 2. For a stationary electron beam, the quantity *R* is likewise a measure of the size of the sample region in which the CL (cathodoluminescence) radiation is generated (Yacobi & Holt, 1990).

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Figure S1. Temperature dependency of the thermal conductivity of spectrosil (Heraeus, 2019) with supporting points for the temperature simulation.

## SI 2: Modeling of the Local Temperature Distribution

The local temperature increase within the diatom biosilica under electron beam irradiation (as shown in Figure 4) was modeled by solving a nonlinear inhomogeneous heat conduction equation (Equation S1). These calculations were performed with the Comsol Multiphysics ® Software Version 5.6 using the Heat Transfer Module (Comsol AB, 2020). In order to take into account the scattering processes of the primary electrons in the diatom material, Monte Carlo simulations were performed by the Casino Software Version 2.4.8.1 (cf. Figure S2b), providing the absorbed heat power density function (see Figures S2a and S2c) (Drouin et al., 2007; Demers et al., 2011).

Equation S1.

with

|  |  |
| --- | --- |
|  | inside the frustule structure, *p*A = 0 otherwise. |

Meaning of the symbols:

specific heat capacity

temperature

mass density of the material

position vector from the spot center of the stationary electron beam (incident parallel to the *z*‑direction) on the diatom frustule structure in an *xyz* coordinate system as shown in Figure 4

time

Nabla operator

coefficient of thermal conductivity

absorbed heat power density function

backscatter coefficient (*η* = 0.167 according to Monte Carlo simulations)

acceleration voltage

electron beam current

standard deviation of Gaussian approximation for the extent of the interaction volume of primary electrons in the *xy*‑plane in bulk diatom material, estimated from Monte Carlo simulations (*σ* = 236 nm, cf. Figure S2a)

*f*A(*z*) normalized function (in units 1/m) for the *z*-dependence of the absorbed heat power density, determined from Monte Carlo simulations by integration of in the corresponding *xy*‑planes (see Figure S2c)



(b)

(c)

(a)

Figure S2. Results of the Monte Carlo simulation for the absorbed heat power density *p*A resulting from inelastic scattering processes of an idle focused electron beam, which is incident perpendicularly to the *xy*-surface plane on bulk diatom material; (a) Gaussian approximation of the radial latitude of *p*A in the *xy*-planes, (b) absorbed heat power density in the *xz*-plane for *y* = 0 with color coding, (c) normalized function *f*A(*z*) for the *z*‑dependence of the absorbed heat power density, determined by integration of in the corresponding *xy*‑planes.

## SI 3: Imaging, EDX, and CL in the SEM

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Figure S3. SEM image of a diatom valve after Eu loading, indicating object 1 (area scan), object 2, and object 3 as well as the position of an EDX line scan (top) and the result of the elemental line scan for Eu over the whole diatom valve through object 3 (bottom).

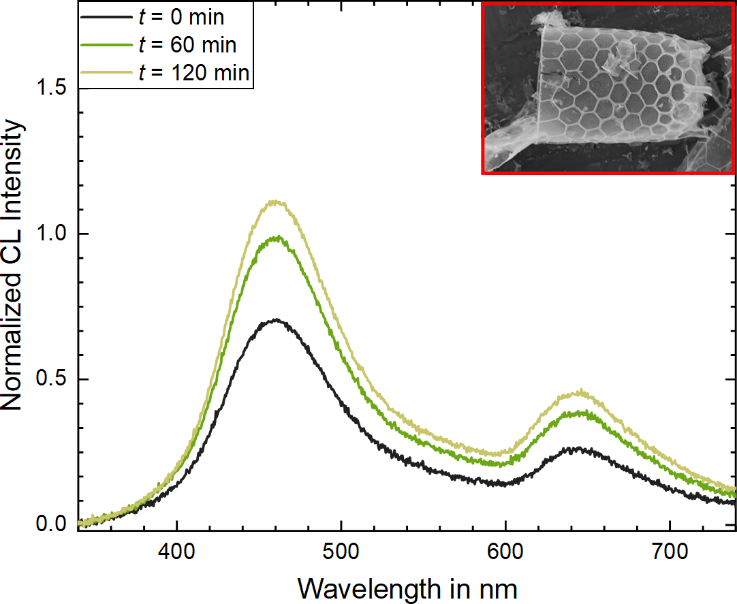


Figure S4. Exposure time dependency of the CL spectra from a scan on the entire diatom valve without Eu loading for comparison with Figure 8. The intensity was normalized by the same value as in Figure 8.

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(b)

(a)

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(c)

Figure S5. Irradiation time dependent CL spectra of a diatom valve after Eu sorption (cf. Figure S3), excited by different modes; (a) beam scan on the entire area of the diatom valve (object 1), (b) point excitation on the valve (object 2), (c) point excitation on an Eu-containing precipitate (object 3). In contrast to the other spectra, the CL intensity is not normalized in order to visualize the differences in signal intensity over time.

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