

## MPI-DING reference glasses for in-situ microanalytical techniques: New trace element and isotope data

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### MPI-DING glasses

The lack of well-known calibration materials is one of the most serious problems for in-situ microanalytical techniques. Therefore, large amounts of eight glasses were prepared from natural geological samples ranging from ultramafic to highly siliceous compositions.

### New results

The reference values for 60 – 65 elements of the MPI-DING glasses (Jochum et al., 2000) were updated because of new results. Especially the data for some poorly investigated trace elements, such as B, Cl and H<sub>2</sub>O, are now more reliable.

Determination of the isotopic composition is also in progress. The results were obtained from high-precision techniques using large amounts of sample powders. <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>143</sup>Nd/<sup>144</sup>Nd were analyzed by TIMS with a precision better than ±0.00001. Measurement of the Pb isotope compositions were done by TIMS using the highly precise triple spike method (Galer, 1999). The hydrogen isotope compositions were measured according to the method of Vennemann and O'Neil (1993). Oxygen isotopes were measured using a method similar to that described by Rumble and Hoering (1994). <sup>δ</sup><sup>11</sup>B values of two reference glasses were determined at the GeoForschungszentrum Potsdam.

### Availability

Because our sample set may be valuable for geochemical microanalytical work, we are willing to distribute small amounts of the MPI-DING reference glasses to the scientific community on request.

### References

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## Controls over the Chemistry of Cocolith Calcite

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Nonequilibrium or "vital effects" on isotopic or elemental partitioning in biogenic carbonates have recently evolved from enemies to allies in a number of paleoceanographic applications. This transition has been especially pronounced in the chemistry of coccoliths, tiny calcite plates produced intracellularly by marine coccolithophorid algae. Recent culture experiments with a number of species have assessed the extent to which their chemistry is controlled by chemical kinetic versus biological factors.

Sr/Ca ratios of coccoliths show strong kinetic effects with coccolithophorid growth and calcification rates [1,2]. These trends are observed for different growth rates of a single species as well as among different species. A similar kinetic effect of Sr partitioning on crystal growth rates has been observed in abiogenic calcites and is hypothesized to reflect surface enrichment effects [3]. Models of crystal growth in coccoliths suggest that surface enrichment effects can explain some of the Sr/Ca variation observed in culture. Higher amplitude Sr/Ca variations observed in surface sediments require an additional mechanism, likely related to the kinetics of ion transport into and within the cell.

Stable isotope fractionation in coccoliths varies widely among different species.  $\epsilon^{18}\text{O}$  is highly correlated to the different maximum growth rates of different species under light saturated and nutrient replete conditions [4]. Unlike the case for Sr/Ca,  $\epsilon^{18}\text{O}$  is nearly constant over a range of growth rates for a single species and  $\epsilon^{18}\text{O}$  is not correlated with different rates of calcite precipitation in different species. Consequently, similar mechanisms related to the kinetics of calcite precipitation cannot be applied for both elemental and isotopic effects.  $\epsilon^{18}\text{O}$  covaries with  $\epsilon^{13}\text{C}$ , with a break point to constant  $\epsilon^{13}\text{C}$  but variable  $\epsilon^{18}\text{O}$  at the lowest ratios. These patterns of covariation are tantalizingly similar to those observed in deep sea corals [5]. However, the mechanism of calcification rate-dependent supply of CO<sub>2</sub> vs "leak" of seawater HCO<sub>3</sub><sup>-</sup> into the calcifying region proposed for corals [5] cannot be applied to intracellular calcification of coccolithophorids. The mechanism of stable isotopic effects in coccoliths remains a mystery, albeit a more clearly delineated one.

### References

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