Laser ablation-ICP-MS compositional profiling of chamber walls in planktonic Foraminifera; implications for Mg/Ca thermometry

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We have profiled compositional variation through the chamber walls of individual Foraminifera using a new, high resolution, laser ablation ICPMS technique. Mg/Ca ratios are able to be measured accurately and precisely in specific shell parts (wall layers and chambers) along with simultaneous analysis of other trace elements (e.g. Mn, Zn, Sr, Ba, Cd, U) and their isotopes with detection limits to low ng/g levels in <60 seconds. The mass of material consumed by each analysis is ~20-30ng (cf. typical test mass of ~10-30µg) and replicate analyses can be made on individual chambers. The technique readily distinguishes outer crust and inner primary wall layer compositions, as well as the presence of an outermost zone characterised by Mg, Mn, Ba and Zn concentrations increasing strongly towards the surface. Exploratory studies on planktonic Foraminifera (Globigerina and Neogloboquadrina sp.) define the capabilities of our technique, highlight the inherent limitations of conventional bulk analysis methods, and provide new insights into fundamental biomineralisation processes. Mg/Ca ratios can be reproducibly measured within particular chamber wall layers to ±2-5% and more uniformly distributed Sr/Ca ratios to ±1%. Inner primary wall layers of different chambers in the same test are commonly found to have distinct Mg/Ca compositions, whereas the inner portions of the outer crust on all chambers have similar and lower Mg/Ca. The strong enrichment in Mg, Mn, Ba, and Zn toward the outermost crust surface in both modern and fossil shells, suggests a significant vital effect change during the biomineralisation process. The ability to measure Mg/Ca in shell parts grown under specific seawater conditions, rather than bulk compositions integrated over the life-cycles of entire shells, may enable calibration of more accurate and precise Mg/Ca thermometers than is currently possible. The tiny amount of sample consumed also allows for subsequent $\delta^{18}O$ microanalysis of the same shell material, and the simultaneous acquisition of other trace elements presents an opportunity to further develop their potential as proxies for seawater temperature, composition, and nutrient levels.

The structure of hematite (0001) surfaces in water: STM and resonant tunneling calculations of coexisting O and Fe terminations

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The structure of hematite (0001) surfaces is not fully understood; questions remain about the existence of Fe- and O- terminations of (0001) terraces. The presence or lack of Fe atoms at the (0001) surface that can be partially coordinated by adsorbed molecules is important for understanding a wide range of adsorption phenomena. We have imaged hematite (0001) surfaces in air and aqueous solution using STM and electrochemical STM (EC-STM), and interpreted images with the aid of a resonant tunneling model (RTM) parameterized using ab-initio calculations.

Our STM and RTM results are consistent with mixed O- and Fe-terminated (0001) surfaces (Figure 1). For surfaces that had been acid etched and extensively annealed, a periodic (period = 2.2 ± 0.2 nm) arrangement of O- and Fe-terminated domains was observed. Two different borders between domains should occur, one in which the Fe-termination is high relative to the O-termination and vice versa. These borders have significantly different heights, allowing us to conclude that the Fe-termination is topographically high on most terraces. Surface domains appear to be quite stable, with little evidence for dissolution at pH 1.

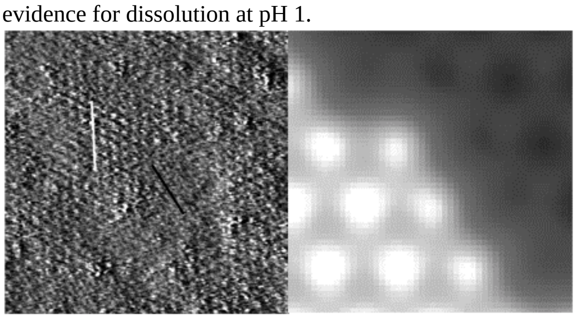

Figure 1: Two different domains in a 20x20 nm STM image of hematite (0001)(+500 mV; left) compared to an RTM calculation (2x2 nm) for +500 mV, Fe termination high.

Consistently, nonperiodic material is imaged at higher negative sample biases, and the characteristics of this material are consistent with resonant tunneling through "adsorbed" Fe atoms at the surface.