δ^{44}Ca in *N. pachy* (left): a new SST-proxy in polar regions

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Planktonic foraminifera have long been used to monitor paleoclimatic changes in surface oceans. While different SST-proxies like e.g. δ^{18}O, Mg/Ca, foraminiferal transfer function and alkenones are well established in tropical regions, information on paleotemperatures of polar surface water masses are scarce. In contrast to other SST-proxies used so far, Ca isotopes are insensitive to changes in global ice volume, evaporation or freshwater input. Here, measurements of the Ca-isotopic composition on calcite shells of *Neogloboquadrina pachyderma* (left coiling; *N. pachy* left) are presented. These results demonstrate that δ^{44}Ca has the potential to become a new sea surface temperature (SST) proxy in polar oceans. In this study the genotype of individuals of *N. pachy* left, taken from polar North and South Atlantic surface waters, was determined at the University of Edinburgh. Subsequently the respective calcite shells were analysed for δ^{44}Ca at the University of Bern. Simultaneously, δ^{44}Ca of core-top samples were measured at GEOMAR as fossil equivalents.

The most complete data set of *N. pachy* left so far is from the polar North Atlantic. All samples are from the same genotype and span a temperature range from 1.9°C to 6.5°C. It was found that temperature correlates well with δ^{44}Ca. The total δ^{44}Ca-variation of ca. 1.2‰ results in a δ^{44}Ca-change of 0.24‰ per 1°C defined by a linear regression (R= 0.95). Remarkably, the slope of this temperature dependence (although not the absolute values) is identical to the one previously defined for tropical *G. sacculifer* (Nägler et al., 2000). Thus, even though biological Ca isotope fractionation is known to be species-dependent, the increase of 0.24‰ δ^{44}Ca per 1°C seems to reflect a particular mode of biocalcification. In order to test whether the correlation is influenced by salinity or genotype differences a second set of a Southern Atlantic genotype of *N. pachy* left is investigated. Preliminary observations point to temperature as the main factor controlling δ^{44}Ca variations. Further a similar trend is indicated by initial results on core-top samples. While more calibration work is needed to establish this proxy, it appears that temperature changes of polar surface waters will be quantitatively resolvable.

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Chemically Assisted-Laser Ablation-ICP-Mass Spectrometry

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Elemental Fractionation

A laser ablation-ICP-mass spectrometry (LA-ICPMS) is widely used for in-situ chemical and isotopic analysis of solid geological samples. However, elemental fractionation became serious when a smaller ablation crater (<20 µm) was used. In the case of U-Pb dating, prolonged measurements of the Pb/U ratio using laser ablation techniques show a serious fractionation effect because of nonconstant focusing of the laser beam. Although the Pb/U fractionation can be minimised by an active focus technique (Hirata and Nesbitt, 1995) or soft ablation technique (Hirata, 1997) or by applying an ArF excimer laser system (Horn et al., 2000), there still remains a Pb/U fractionation effect. In this paper, a new technique for the reduction of Pb/U fractionation, referred to as a chemically assisted-laser ablation (CLA) technique, is described.

CLA-ICPMS Technique

Since Pb is more volatile than U, laser heating due to prolonged ablation results in an increase in the Pb signal relative to U and a consequent increase in the Pb/U ratio. This indicates that Pb/U fractionation can be minimised if the volatility of U was increased. In this study, a freon gas (Freon 134a: CH_2FCF_3) was mixed into He carrier gas, aiming at formation of volatile uranium fluoride. The time profile of the Pb/U ratio for Nancy 91500 zircon standard is shown in Fig. 1. The time profile of the Pb/U ratio without freon gas is also shown in this figure, demonstrating that the Pb/U fractionation could be minimised by the addition of freon gas. The details of analytical technique will be presented in this paper.

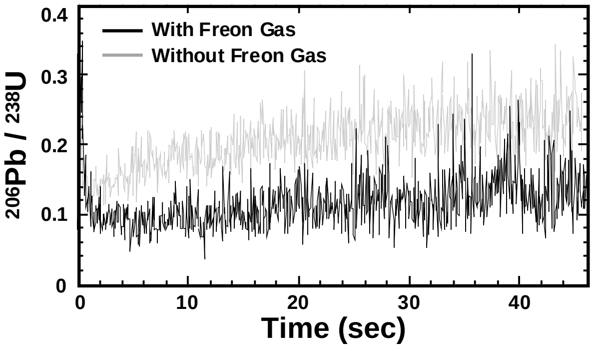

Figure 1: Time profile of the Pb/U ratio for zircon.

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