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Calcites from Ocean Crust Basalts: Reliable Proxy Archives?

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Calcite cements in ocean crust basalts of the deep sea form from mixtures of cold seawater and warm hydrothermal fluids (about 0-70°C). These low temperature alteration (LTA) calcites have recently gained new interest as proxy recorders of seawater composition (Refs. 1-5). Recent LTA calcite reconstructions of the Sr/Ca and Mg/Ca evolution in ocean waters point to considerably lower Sr/Ca and Mg/Ca ratios during the Cretaceous and Paleogene than in the modern ocean. However, diagenetic alteration in contact with the basalt host rock may change the composition of the LTA calcites. For testing the reliability of LTA calcite records of seawater composition multi-proxy approaches are applied: oxygen isotopes indicate precipitation temperatures, strontium isotopes (87Sr/86Sr) and trace elements indicate influences from hydrothermal fluids. Additional information about the influence of basement rocks on LTA calcite composition can be derived from analyses of stable calcium and strontium isotopes ([U+F064]44/40Ca, [U+F064]88/86Sr).
We find low [U+F064]44/40Ca values for DSDP and ODP sites where the 87Sr/86Sr ratios of LTA calcites indicate basement influence. On the other hand, for some sites the 87Sr/86Sr values inidicate precipitation from pristine seawater, while low [U+F064]44/40Ca values indicate basement influence. All of these sites are either older than 50 Myr or show calcite precipitation temperatures >50°C. Sites that are younger than 25 Myr and had formation temperatures <10°C show high [U+F064]44/40Ca values indicating no basement influence, in agreement with the 87Sr/86Sr ratios. Average [U+F064]44/40Ca values of the latter sites are in good agreement with the Neogene seawater [U+F064]44/40Ca evolution (Ref. 6). Stable strontium isotopes show little variability at most sites ([U+F064]88/86Sr= 0.30 to 0.35‰. Only at temperatures >50°C significantly higher [U+F064]88/86Sr values were observed.
The calcium isotope results indicate basement influence on LTA calcite composition at temperatures >10°C. Radiogenic strontium isotopes, in contrast, can be used as unequivocal basement influence indicators only at temperatures above 30°C. Below about 20°C 87Sr/86Sr ratios are no reliable indicators of basement influence.
All LTA calcites of sites older than 50 Myr formed (or recrystallized) at temperatures >15°C. Low [U+F064]44/40Ca values indicate that the fluids from which these calcites formed were isotopically altered, not pristine seawater. The ∼0.3‰ lowered [U+F064]44/40Ca of Cretaceous LTA calcites indicates that about one third of the calcium in the LTA fluids was derived from leaching of basement rocks. From the difference in 87Sr/86Sr between Cretaceous seawater and the LTA calcites we estimate that between 20 and 40% of the Sr in the LTA fluid were leached from the basement. Therefore, Sr/Ca ratios in the Cretaceous LTA fluids were probably only slightly altered compared to seawater. Sr/Ca ratios of LTA calcites can consequently provide useful estimates about the seawater composition of the Cenozoic and Mesozoic oceans.

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