

Systematic thallium isotope variation in Fe-Mn crusts: A proxy for changes in ocean chemistry?

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We have measured the thallium (Tl) isotope composition of samples from the Pacific Fe-Mn crust CD29-2, which have recently been dated using Os isotope stratigraphy [1]. The samples have a spatial resolution of about 1mm which equates to about 0.5 Ma. Thus far we have investigated the time interval spanning 60 to 30 Ma and large systematic Tl isotope variations ranging between $\epsilon^{205}\text{Tl} = +6.8$ and $\epsilon^{205}\text{Tl} = +11.4$ are apparent (where $\epsilon^{205}\text{Tl} = 10^4 \times ((^{205}\text{Tl}/^{203}\text{Tl})_{\text{sample}} - (^{205}\text{Tl}/^{203}\text{Tl})_{\text{NIST 997}}) / (^{205}\text{Tl}/^{203}\text{Tl})_{\text{NIST 997}}$). The most striking feature is a systematic increase from $\epsilon^{205}\text{Tl} = +6.5$ to $+10.5$ occurring in the time interval 58 to 50 Ma. A small number of previous analyses at various depths in CD29-2 [2] are fully consistent with our more detailed investigation.

Rehkämper *et al* [2] argued that these variations most likely reflected a change in the Tl isotope composition of seawater and this remains a firm possibility. However, recent theoretical calculations of the mechanism controlling Tl isotope fractionation have shown that there is a large equilibrium isotope fractionation between Tl^{1+} and Tl^{3+} [3]. Published Tl isotope compositions of modern Fe-Mn crusts [4] and altered mid ocean ridge basalts [5] are consistent with these two reservoirs exclusively incorporating Tl^{3+} and Tl^{1+} , respectively. Hence, changes in the speciation of Tl in seawater may also be responsible for the observed Tl isotope variation recorded in Fe-Mn crusts. This proposition appears to be in agreement with the fact that the timing of Tl isotope change in CD29-2 coincides exactly with the massive change in atmospheric CO_2 inferred from boron isotope compositions of planktic foraminifera [6].

We are currently performing thermodynamic calculations aimed at determining the speciation of Tl in seawater in order to investigate the potential for Tl isotopes to be used as a proxy for changes in the chemical and physical conditions of seawater.

References

- [1] Klemm *et al*, *EPSL*, 2005
- [2] Rehkämper *et al* *EPSL*, 2004
- [3] Schauble, *GCA*, 2007
- [4] Rehkämper *et al*, *EPSL*, 2002
- [5] Nielsen *et al*, *EPSL*, 2006
- [6] Pearson and Palmer, *Nature*, 2000

Geochemical analysis of obsidian and the pattern recognition of sites spatial distribution in the chalcolithic of the Eastern Lake Urmia, Northwestern, Iran

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Results presented here are the chemical analysis of significant numbers of obsidians from several Chalcolithic sites in the eastern shores of Lake Urmia, Northwestern Iran, as part of a large and most comprehensive study of obsidian sources in this region. In this study, XRF is used to generate trace element data for some elements. A number of analytical methods such as Bivariate plots of the incompatible trace elements were used to separate the obsidian sources in study area and source separation was confirmed by using linear Discriminant analysis. The existence of multiple sites containing obsidian artifacts in the area of Urmia and on some of the other nearby regions, however, has enabled the study of specific spatial patterns of source exploitation and the trade mechanisms which resulted in the distribution of obsidian hundreds of kilometers away during the Chalcolithic period (ca. 5000-3000 BC).