

Isotope analyses of extremely small amounts of Pb using ^{205}Pb - ^{204}Pb and ^{207}Pb - ^{204}Pb two double spikes

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Introduction

By application of the double spike technique, precise and accurate lead isotope analyses are now routinely made for relatively large Pb samples (> 10 ng of Pb). On the other hand, routine determination of isotopic compositions for small amounts of Pb (< ~3 ng) have not yet been possible, due mainly to the large uncertainty for the measurements of ion beam intensity of minor ^{204}Pb (" ^{204}Pb error"). In this study, we present a simple practical method for the isotope analyses of extremely small amounts of Pb by utilizing two different types of double spikes: those consisting of ^{205}Pb and ^{204}Pb and those enriched in ^{207}Pb and ^{204}Pb .

Experiments and Results

In two runs of the normal double spike technique (i.e., spiked and unspiked runs), the unspiked run ($^{208}\text{Pb}/^{204}\text{Pb}$: ~38) is susceptible to ^{204}Pb error, whereas the spiked run ($^{208}\text{Pb}/^{204}\text{Pb}$: ~1) is much less so. The "two double spikes" method presented in this study enable reduction of the ^{204}Pb error by addition of the ^{205}Pb - ^{204}Pb double spike to the "unspiked sample" of the normal method.

The methods for mass spectrometry are essentially similar to those described in Kuritani and Nakamura (2002). The ^{205}Pb - ^{204}Pb double spike with the $^{205}\text{Pb}/^{204}\text{Pb}$ ratio of ~5 has been newly calibrated using the compositions of NBS982 (Kuritani and Nakamura, submitted), after the optimization of the spike composition. A ^{204}Pb - ^{207}Pb spike with the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio of ~1 (Kuritani and Namamura, submitted) was used in this study.

Using this technique, replicate analyses for 1.5 ng Pb of NBS981 were performed, yielding highly precise compositions as follows: $^{208}\text{Pb}/^{206}\text{Pb} = 2.1677 \pm 2$, $^{207}\text{Pb}/^{206}\text{Pb} = 0.91487 \pm 4$, $^{204}\text{Pb}/^{206}\text{Pb} = 0.05903 \pm 1$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.723 \pm 7$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.499 \pm 3$ (2sd, n = 6). These compositions are on the theoretical mass fractionation line for NBS981 proposed by Doucelance and Manhès (2001), suggesting that accuracy of the method is satisfactory (free from " ^{207}Pb problem"). Compared with the results for 1.5 ng of Pb by the normal double spike method (Kuritani and Nakamura, submitted), the external precision of the isotopic ratios involving ^{204}Pb are reduced to about 60 %, simply by addition of the ^{205}Pb - ^{204}Pb double spike.

References

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High-resolution isotopic record of total organic carbon in Cretaceous black shales

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We determined isotopic ratios of total organic carbon ($\delta^{13}\text{C}_{\text{org}}$) for samples collected throughout "Livello Bonarelli", Cretaceous black shales enriched in organic carbon (up to 25%). About 500 samples were measured in a 1 m sequence of Bonarelli to reconstruct high resolution $\delta^{13}\text{C}_{\text{org}}$ record in the black shales. The $\delta^{13}\text{C}_{\text{org}}$ record shows an upward increasing trend throughout the horizon with the maximum values of -22.0‰ in the upper part of the horizon. The trend probably reflects a widely recognized positive excursion of carbon isotopic ratio around Cenomanian/Turonian boundary due to the enhanced burial rate of organic matter associated with Oceanic Anoxic Event 2 (OAE2; Arthur et al., 1988). In addition to this trend, we found some fine-scale isotopic fluctuations. The $\delta^{13}\text{C}_{\text{org}}$ values of light laminae are generally 0.5-2.0 ‰ lighter than those of adjacent dark layers. The difference may be attributed to either different carbon isotopic ratios of major primary producers or different source organisms constituting the organic matter between depositions of dark and light laminae.

The most striking result is that certain, narrow intervals show remarkably ^{13}C -depleted values down to -36‰. The value is substantially lighter than those previously reported both from the Livello Bonarelli and other Cretaceous black shales. The large and rapid negative spikes of $\delta^{13}\text{C}_{\text{org}}$ could not simply be ascribed to variability of isotopic fractionations by source organisms of the black shales. Instead, it would reflect quite different biological community metabolizing isotopically light carbon like methane. We suppose that methane oxidizing bacteria might partially contribute to the organic matter of the black shales. The ^{13}C -depleted intervals precisely correspond to lithological boundaries where alternative patterns of light/dark layers remarkably varied. If the lithological boundaries are interpreted as boundaries of oceanic change, the negative $\delta^{13}\text{C}_{\text{org}}$ spikes occurring at the lithological boundaries suggest that methane emissions to the environments sporadically occurred during the black shale formation induced substantial changes in oceanic environments during OAE2. In the presentation we will report carbon isotopic compositions of lipid biomarkers in the ^{13}C -depleted intervals to further understand the short-term events we found.

References

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