Tracing mixing in the upper ocean with the three oxygen isotopes

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We use the relationship between ¹⁷O/¹⁶O and ¹⁸O/¹⁶O ratios of dissolved $O_2({}^{17}\Delta)$ as a unique conservative tracer of mixing below the photic zone. The tracer property of the triple isotopic composition of O_2 is related to relative depletion of $^{17}\mathrm{O}$ that originates in stratospheric photochemistry. O_2 produced by photosynthesis in land and marine plants has identical isotopic composition as the substrate water. Biological uptake fractionates O2 isotopes and results in an increased proportion of ¹⁷O and ¹⁸O over ¹⁶O. This fractionation is mass dependent and the increase in ¹⁷O/¹⁶O with respect to substrate water is about one half of the increase in ¹⁸O/¹⁶O. Photochemical reactions in the stratosphere also affect air O₂ and preferentially remove ¹⁷O and ¹⁸O in comparison to ¹⁶O. However, in contrast to biological uptake, the fractionation in the stratosphere is mass independent, changing ¹⁷O/¹⁶O over ¹⁸O/¹⁶O in equal or large proportion. As a result, atmospheric O_2 becomes relatively depleted in ¹⁷O in comparison to pure biological O₂ (Luz et al, 1999). Consequently, when O_2 is produced from seawater by photosynthesis, it is relatively enriched in ¹⁷O with respect to air O₂ by 249 permeg (Luz and Barkan, 2000). Furthermore, in the absence of biological activity, dissolved O2 in gasexchange equilibrium with air has ${}^{17}\Delta$ of 16 permeg. In dark respiration, O_2 concentration decreases, $\delta^{18}O$ and $\delta^{17}O$ increase, but $^{17}\!\Delta$ behave conservatively and remains constant.

We have monitored seasonal variations of ${}^{17}\Delta$ in dissolved O₂ in the Sargasso Sea near Bermuda. In the mixed layer its typical values are 30-40 permeg and indicate the dominance of air-sea O2 exchange over photosynthesis. In the seasonal thermocline air-sea exchange is attenuated and $^{17}\!\Delta$ reaches high values (100-150 permeg). In the photic zone such high values are indicative of in situ photosynthetic production. However, we have obtained relatively high values ${}^{17}\Delta$ (40-80 permeg) also below the photic zone (150-300m), where incubation experiments show negligible O2 production. These values are considerably greater than 16 permeg (as in equilibrium) and thus they must result from introduction of water from the photic zone. Such introduction may originate from lateral isopycnal mixing. Alternatively, it may indicate intermittent vertical mixing at the onset of the spring bloom when density stratification is weak. Studying these processes is important to the understanding of both biological and physical mechanisms in the upper ocean.

References

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Carbon and boron isotope compositions of Ziyang witherite deposits in southern Qinling, China

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Introduction

As we known, boron isotope compositions of boronbearing minerals can provide insights into the genesis of ore deposits. But up to now, little work has been done on the boron isotope of carbonate deposits. The purpose of this study is to reveal the genesis of witherite deposits based on boron isotope of carbonate minerals, coupled with carbon isotope.

Discussion of the results

The δ^{13} C (PDB) values of witherite and barytocalcite from Ziyang deposit, southern Qinling, vary from -11.6‰ to -22.2‰ (-16.2‰ on average), which are consistent with δ^{13} C (PDB) of organic matter in sedimentary (-11‰~-34‰). It indicates that carbon was from organic matter in sediment during early diagenetic stage. The δ^{11} B values of witherite and barytocalcite vary from -0.4‰ to -18.4‰ averaging -11.0‰, which are inconsistent with $\delta^{11}B$ value of marine carbonate $(22\pm3\%)$ and lower than those of recrystallized calcite (-5.5‰). Thus, the calculated δ^{11} B values of parent solution of -2.4~15.6‰ (5.0‰ on average) and 22.6‰~40.6‰ (30.0‰on average) were obtained according to fractionation factor of 0.984 between calcite and seawater and 0.959 between recrystallized calcite and pore waters. As the above two calculated values are much lower than that of seawater (39.5‰), this paper put forward that witherite and barytocalcite might crystallize from pore waters of sediment during early diagenetic stage. Compared to the $\delta^{11}B$ value of 44.5‰ from the modern sedimental pore waters, such lower calculated values of parent solution (22.6-40.6‰) imply that parent solution had been contaminated by ¹⁰B -rich matter. The correlation of $\delta^{11}B$ with $\delta^{13}C$ (R=0.68) indicates boron in witherite and barytocalcite was mainly released by organic matter. As δ^{11} B values in organic matter range in -4~ -10‰, the lower $\delta^{11}B$ values of parent solution are due to mixing of the boron released from organic matter with boron from pore waters.

Conclusion

From above discussion, we take into account that the witherite and barytocalcite precipitated from the pore waters in sediment during early diagenetic stage, and the carbon and boron were mainly released from organic matter in sediment.