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Oxygen Isotopic Composition of Mediterranean Deepwater Since the Last Glacial Maximum: Constraints from Pore Water Analyses

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Interstitial waters recovered from Ocean Drilling Program, Leg 161 in the western Mediterranean Sea are used in conjunction with a numerical model to constrain the $\delta^{18}O$ of seawater since the Last Glacial Maximum, including the last sapropel event. This method of investigating paleo-oceanic deepwater provides an alternative to reconstructions of seawater oxygen isotopic composition based on benthic foraminiferal calcite, which reflect a combination of temperature at the time of precipitation and changes in seawater $\delta^{18}O$. In order to differentiate between these two factors, it is necessary to independently determine the contributions of seawater temperature and $\delta^{18}O$ change (resulting from changes in the extent of continental ice sheets and marine salinity). The oxygen isotopic composition of sediment pore fluids provides an attenuated $\delta^{18}O$ record of the overlying bottom water that diffuses down from the seafloor through time; thus, a profile of seawater $\delta^{18}O$ variability that is unaffected by glacial-interglacial variations in marine temperature. This approach is also particularly useful in the Mediterranean where only sparse benthic foraminiferal data exist making the isotopic composition of paleo-bottom waters difficult to constrain. Site 976 (approximately 1108 m water depth) located in the Alboran Sea was dedicated to high-resolution pore water sampling (approximately every 3 m in the upper 30 m) to reconstruct the oxygen isotope geochemistry of the original deepwater in the basin. The isotopic measurements of sediment pore fluids from Site 976 display a distinct negative anomaly at around 15 m followed by a clear positive trend with maximum $\delta^{18}O$ values occurring between 30 and 40 m depth. These two peaks in the profile are considered to represent Sapropel Event 1 (around 8 ka) and the Last Glacial Maximum (around 20 ka), respectively. We then use an approach similar to that of Schrag and DePaolo (1993) to model the diffusive transport of oxygen in the sediment column and to asses changes in seawater $\delta^{18}O$, specifically over the last 20,000 years. Theoretical profiles of fluid oxygen isotopic composition are calculated using a forward modeling approach and then compared to the observed pore-water vs. depth profile from Site 976.

To constrain the oxygen isotopic composition of the deep Mediterranean, we have developed a numerical model that couples fluid diffusion with advective transport. This model uses an implicit solver and a finite-difference scheme (Peacock, 1989) for implementing the advection and diffusion terms and calculating the isotopic evolution through time. As Site 976 has a relatively high sedimentation rate (approximately 200-250 cm/ky) through the Pleistocene and Holocene, sedimentation is simulated by successively adding layers of carbonate sediment. The sediment itself is treated as a porous medium and porosity and thermal gradient are modeled to reproduce measured profiles. The model simulates one million years of geologic time at a resolution of 1000 years. Isotopic input derived from benthic foraminifera from ODP Site 659 (eastern tropical Atlantic) (Tiedemann et al., 1994) is used to simulate seawater $\delta^{18}O$ and drive the model from 500 ka to 20 ka. From 20 ka to 0 ka (present), isotopic input is based on the model of sea level change (Fairbanks, 1989). To include a simulation of the last sapropel event, estimates of seawater $\delta^{18}O$ were taken from a model of Mediterranean seawater isotopic composition (Rohling, 1999).

Initial model runs done without the inclusion of a negative sapropel excursion in $\delta^{18}O$, suggest that the glacial to interglacial change in oxygen isotopic composition of Mediterranean bottom waters was less than 0.7‰. Thus, less than the 1.0‰ glacial-interglacial change determined by Schrag and DePaolo (1993) and considerably less than the previously accepted change in the seawater ratio of 1.3‰(Fairbanks, 1989). Including a pulse of isotopically light $\delta^{18}O$ at the sediment-water interface around 10 ka produces results which more closely fit the observed pore-water isotopic profile from Site 976 and suggest a glacial-interglacial change in seawater $\delta^{18}O$ of around 0.8‰. Model results also indicate the existence of isotopically light water circulating down to bottom water depths in the western Mediterranean coincident with the formation of the most recent sapropel. In addition, results suggest that the size of the deepwater $\delta^{18}O$ excursion at Sapropel Event 1 was smaller than that affecting the surface water isotopic ratios.

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