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Radiogenic $^{87}Sr/^{86}Sr$ and stable $^{88}Sr/^{86}Sr$ ratios in late Miocene to mid-Pleistocene Mediterranean waters - the role of brackish submarine groundwater discharge

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The temporal changes in the Sr isotopes: the $^{87}Sr/^{86}Sr$ and the $^{88}Sr/^{86}Sr$ are used to evaluate and quantify the sources, sinks, and input fluxes of Sr to the oceans. The input fluxes of Sr from rivers and hydrothermal sources (at the mid-ocean ridges) are not in balance with the output fluxes. Previous studies suggested that this imbalance reflects a delay in the Sr input stemming from the difference in the weathering regime of continental material during glacial and interglacial periods. Here, we deal with this topic by analyzing the Sr-isotopic ratios and chemical compositions of the fossils collected from the sedimentary marine sequences of the late Neogene – Pleistocene Mediterranean (spanning the time interval of ~ 5.3 to 0.8 Ma). These marine sequences are exposed at the banks of the Stirone and Arda Rivers that currently flow from the Apennines to the Po Valley. Sr isotope and chemical data were used to construct a simple box model that helped to evaluate the question of the Sr balance in the oceans. The marine sedimentary sequence contains various fossils: brachiopods, mollusks and foraminifers that were identified and analyzed chemically and isotopically. The isotope analyses indicate that between ~5.3 to 0.8 Ma the $^{87}Sr/^{86}Sr$ ratios follow the global array with a significant excursion to lower ratios around ~5 Ma that is attributed to the contribution of continental groundwater in the early Pliocene. We think that the contribution of continental brackish groundwaters to the sea, a generally neglected pathway, is an important component in the global budget of marine Sr. The importance of this water source is reflected by the calculated $\delta^{88/86}Sr$ ratios and the measured modern ratios, which are largely constant. This means that the amount of Sr that was deposited in the oceans versus the amount that was removed remained roughly the same during the past 5 Ma. We conclude that the Sr budget cannot have been balanced only during the ice ages. Modeling of all known inputs to the marine water indicates a missing Sr source, which we attribute to the inflow of brackish submarine groundwater discharge from the continents.