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Marine carbonates dissolution and recrystallization close the oceanic Sr isotope balance during the Plio-Pleistocene

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Temporal changes in the Sr isotopes (88, 87, 86, 84) in the oceans reflect the input and output fluxes of Sr from various sources and sinks. It appears that the input fluxes of Sr from rivers and hydrothermal sources at the mid-ocean ridges, which are estimated to be ~$60 \cdot 10^9$ mol/y, are not in balance with the huge output fluxes, mainly co-deposition with marine carbonates, which is estimated to be ~$255 \cdot 10^9$mol/y (a gross deposition rate). Previous studies suggested that this imbalance reflects a delay in the Sr input stemming from differences in the weathering regime of continental material during glacial and interglacial periods. Here, we analyze Sr-isotopic ratios and chemical compositions of fossils collected from marine sedimentary sequences of the late Neogene-Pleistocene Mediterranean (spanning ~5.3 to 0.8 Ma). These marine sequences (containing brachiopods, mollusks, and foraminifers) are exposed at the banks of the Stirone and Arda Rivers that currently flow from the Apennines to the Po Valley. During the studied time interval, the $^{87}Sr/^{86}Sr$ ratios follow the global array, with a significant excursion to lower ratios around ~5 Ma, attributed to the contribution of continental groundwater in the early Pliocene. The $\delta^{88/86}Sr$ values, however, remain virtually constant during the past ~5 Myr. Simulations of the oceanic $^{87}Sr/^{86}Sr$ ratios and the $\delta^{88/86}Sr$ values according to the abovementioned input and output fluxes are not consistent with these observed ratios. The Sr imbalance can also be closed by considering that ~75% of the solid carbonate pool is re-dissolved, with Sr flux of ~$190 \cdot 10^9$ mol/yr, $^{87}Sr/^{86}Sr$ of 0.7092 and $\delta^{88/86}Sr$ value of $0.22^o/_{oo}$. Small but significant positive/negative shifts in marine $^{87}Sr/^{86}Sr$ ratios measured in interglacial and glacial carbonate sediments, respectively, are consistent with the deposition/dissolution of shallow carbonates on continental shelves, trends that are also reflected in atmospheric CO_2 variations.