The Fredy and Nadine Hermann Institute of Earth Sciences

Sr Isotopes at the Onset of the Ice Ages at the Northern Apennines

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Introduction

The Sr isotope system comprises stable isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr. The ^{87}Sr/^{86}Sr ratio has been traditionally used to quantify the inputs of Sr from marine and continental sources (Fig. 1A) and the ^{88}Sr/^{86}Sr ratio expressed as $\delta^{88/86}$Sr has been recently developed as "process tracer".

The Sr geochemical signal in carbonate shells is determined by several factors: i) shell mineralogy (*Terebratula*, *Ostrea* and the innermost and outermost layer of the *Aequipecten* are calcite and *Glycymeris*, *Arctica* and the middle layer of the *Aequipecten* are aragonite), which determines the concentration of the co-precipitated element (e.g., distribution coefficient of Sr in biogenic calcite is ~0.14); ii) "vital effects" that modulate the element's distribution coefficient; iii) diagenetic loss/gain of elements in the shell; iv) "contamination" with external material (e.g. of sediment in the punctae of the brachiopods or incorporated in oyster shells; Fig. 1B).

We aim to assess the applicability of the marine biogenic carbonates from our sections as reliable paleoenvironmental recorders regarding Sr isotopes and trace element ratios. Then, we aim to evaluate the Sr fluxes from marine and continental sources to the Po embayment and in particular to establish the temporal changes in $\delta^{88/86}$Sr during the late Pliocene-early Pleistocene, at the onset of the Ice Ages.

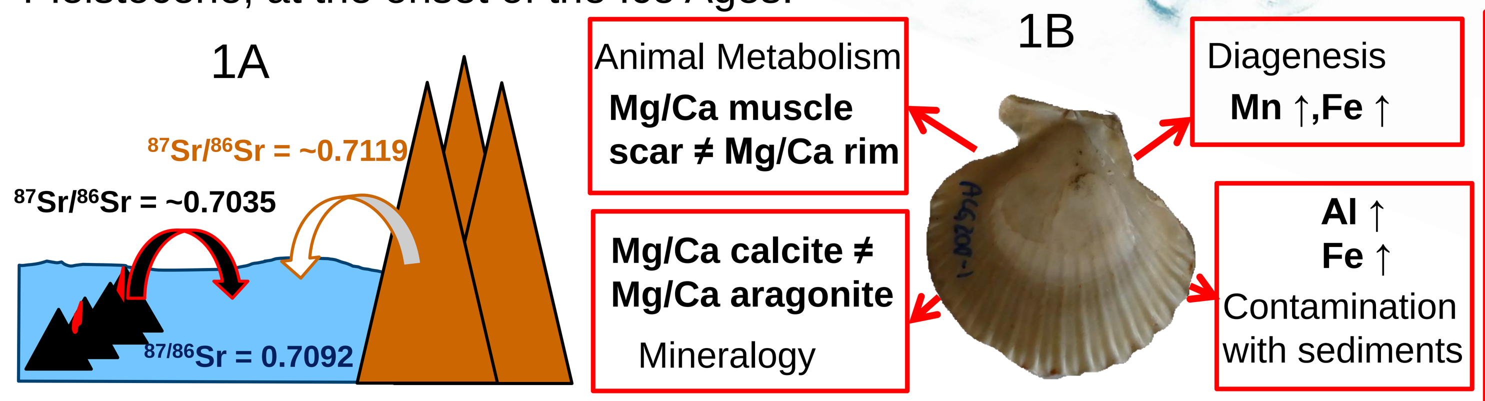

Fig. 1: A: Mixing of Sr from MORB alteration and from continental weathering results in ^{87}Sr/^{86}Sr of coeval seawater; **B**: Processes controlling the isotope and trace element composition of marine biogenic carbonates.

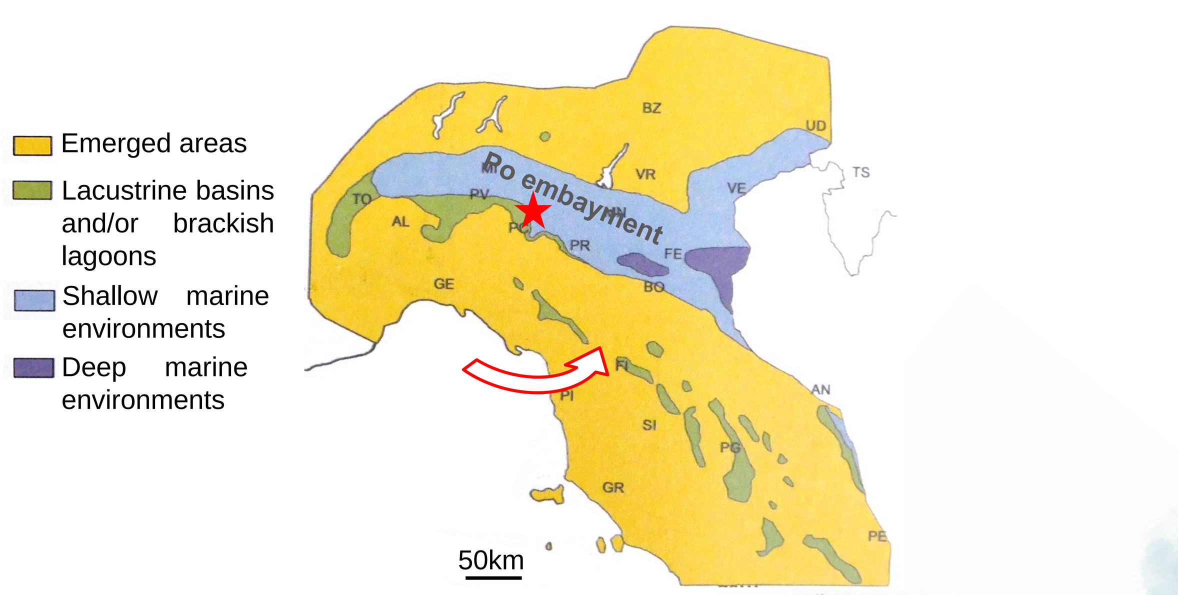

Fig. 2: Palaeogeographic setting of the Arda and Stirone valleys (red asterisk) during the late Pliocene. Tectonic movement of the Apennines is marked by the red arrow (Raineri 2007).

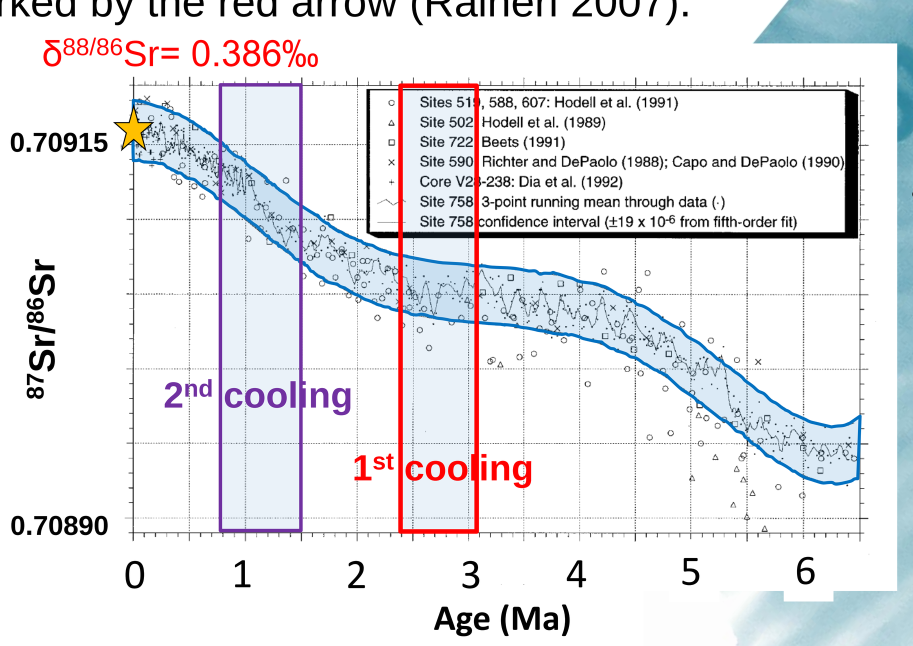

Fig. 3: Evolution of the ^{87}Sr/^{86}Sr ratio over the last 6.5 million years (Farrell et al. 1995). The cooling events during the Late Pliocene and Mid-Pleistocene are outlined by the red and purple boxes. Only the value of the modern oceanic $\delta^{88/86}$Sr (red font) was measured for this time period (Vollstaedt et al., 2014). We use fossils from the Arda and Stirone sections to reconstruct the $\delta^{88/86}$Sr for this period.

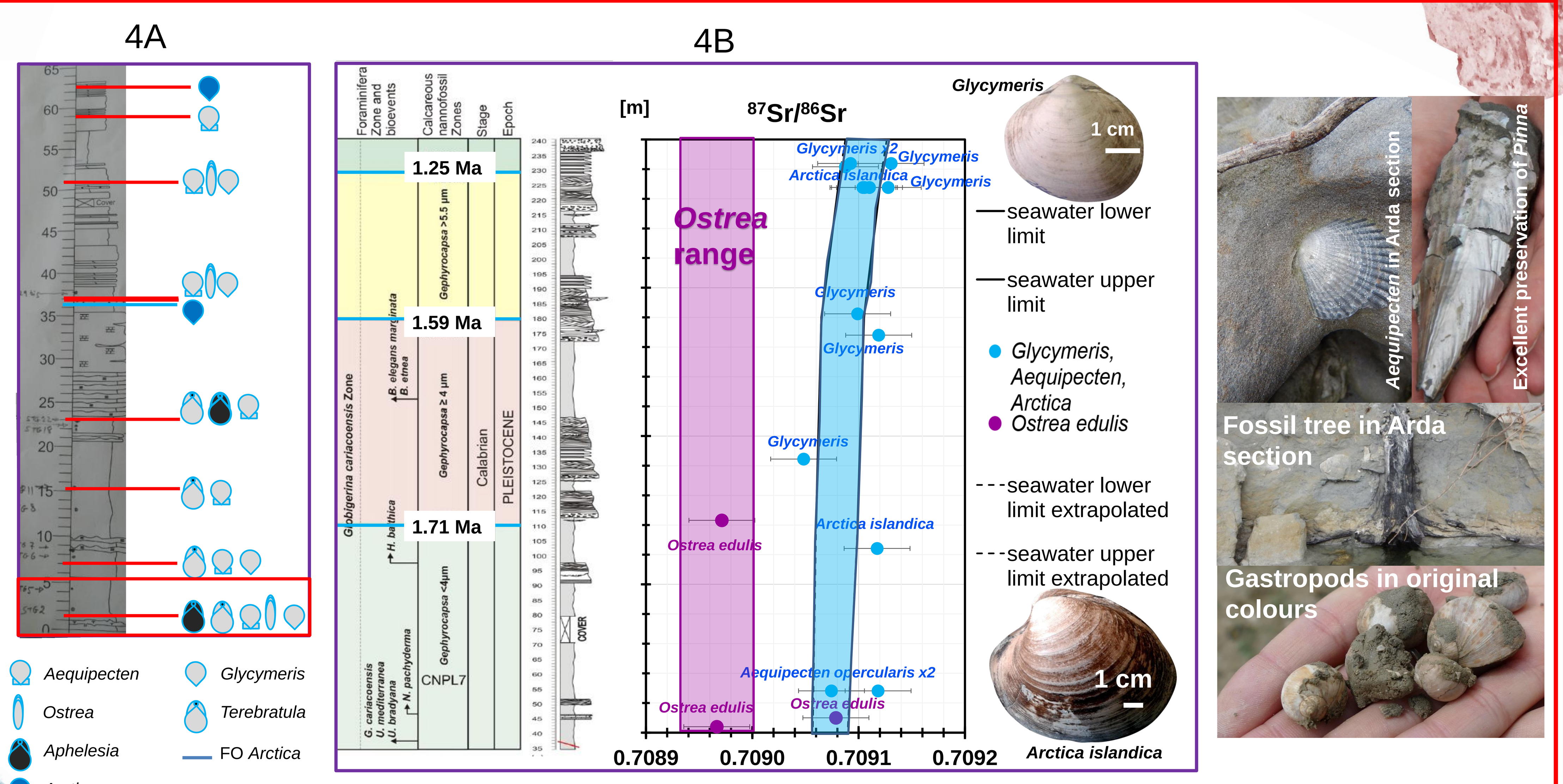

Fig. 4: Stratigraphic sections of **A**: Stirone River showing sampled horizons and fossil types; **B**: Arda River showing stratigraphic anchor ages that were determined using foraminifera and calcareous nannoplankton (Crippa et al. 2016). The ^{87}Sr/^{86}Sr of *Glycymeris* and *Arctica islandica* along the Arda section follow nicely the seawater curve for that period (blue shaded area). Most of the oysters were affected by a secondary process, probably diagenesis (purple shaded box).

<u>The late Pliocene-early Pleistocene transition</u>: The northern hemisphere changed from being mostly free of ice to large scale glaciation during mid Pleistocene. Cooling happened in two steps: i) the Late Pliocene Transition characterized by 41ky climate cycles and ii) since the mid Pleistocene there was a dominance of the 100ky climate cycles. The temporal variation in the marine ^{87}Sr/^{86}Sr ratio during the past 6My is shown in Fig. 3.

<u>Sampling sites and fossil shells</u>

Lower Pleistocene shells were collected in the outcrops of the Arda and Stirone Rivers, Northern Italy (Fig. 2). The sediments comprising the sections are of marine origin that were deposited in the large Po embayment between 1.8-1.2 Ma (Arda) and ~2-1 Ma (Stirone). At ~1Ma the study area was exposed due to the counter-clockwise rotation of the Apennines toward the western Alps (Fig. 2).

Sampled fossils are all marine: *Terebratula scillae* (brachiopod), *Ostrea edulis* (bivalve), *Aequipecten opercularis* (bivalve), *Glycymeris inflata* and *insubrica* (bivalve) and *Arctica islandica* (bivalve) (Fig. 4A).

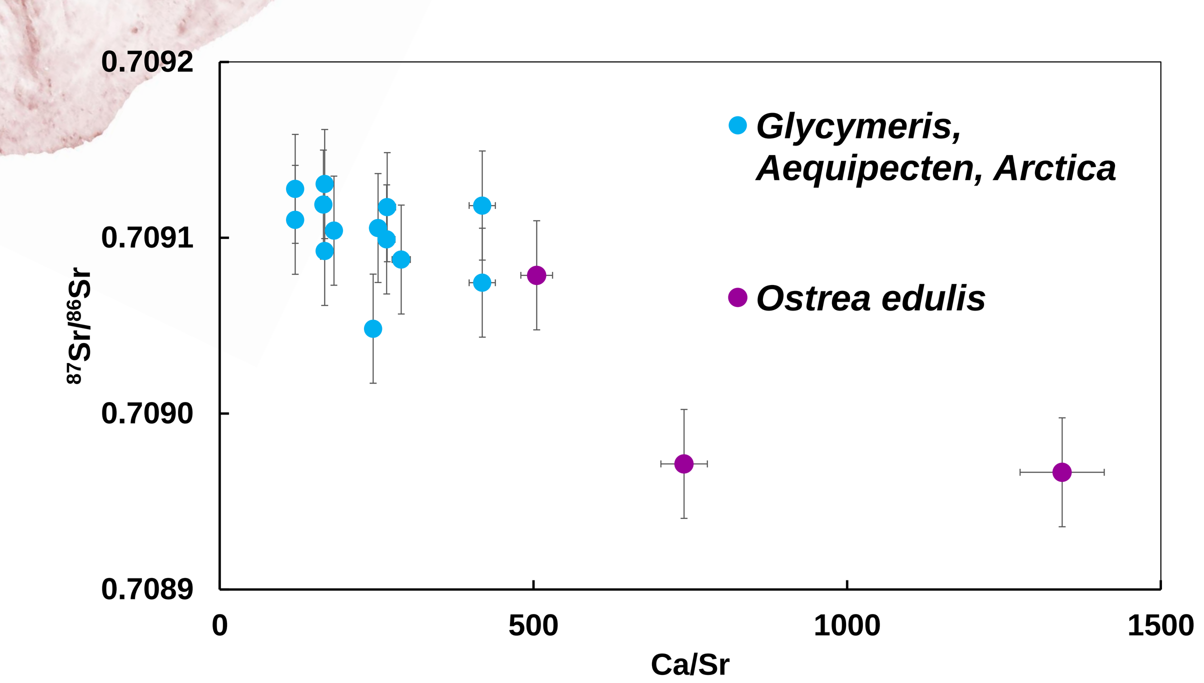

Fig. 5: ^{87}Sr/^{86}Sr vs Ca/Sr of the samples. Sr isotope mixing possibly affected the *Ostrea* shells that were probably exposed to a reservoir with low Sr and low ^{87}Sr/^{86}Sr ratio. SEM analysis revealed recrystallization of the chalky fabric (Fig. 6).

Chemical and isotopic compositions of the fossils

Sr/Ca ratios in calcite shells and Mg/Ca ratios in aragonite shells (from the same stratigraphic horizon) are uniform and reflect normal marine values (according to their distribution coefficients, $D_{X/Ca}$). Mn (<80 ppm) and Fe (<140ppm) contents in bivalves and brachiopods are as expected range for pristine shells, suggesting minor diagenetic modification. The Al content is very low (Al/Ca<0.0005) indicating no addition of external sediments. The recrystallized shell structure of *Ostrea* (Fig. 6A in comparison to 6B) reflects diagenetic effects.

Summary

The ^{87}Sr/^{86}Sr ratios of bivalve shells (except for *Ostrea edulis*) follow remarkably well the normal marine composition for that period (Fig. 4B) suggesting that Sr signal of the early Pleistocene Mediterranean is similar to that of the contemporaneous global ocean. This finding is rather promising to the possibility of reconstructing the marine $\delta^{88/86}$Sr for the Plio-Pleistocene using a suite of organisms (*Terebratula*, *Aequipecten, Glycymeris*, *Arctica*) and evaluate diagenetic effects using *Ostrea*.

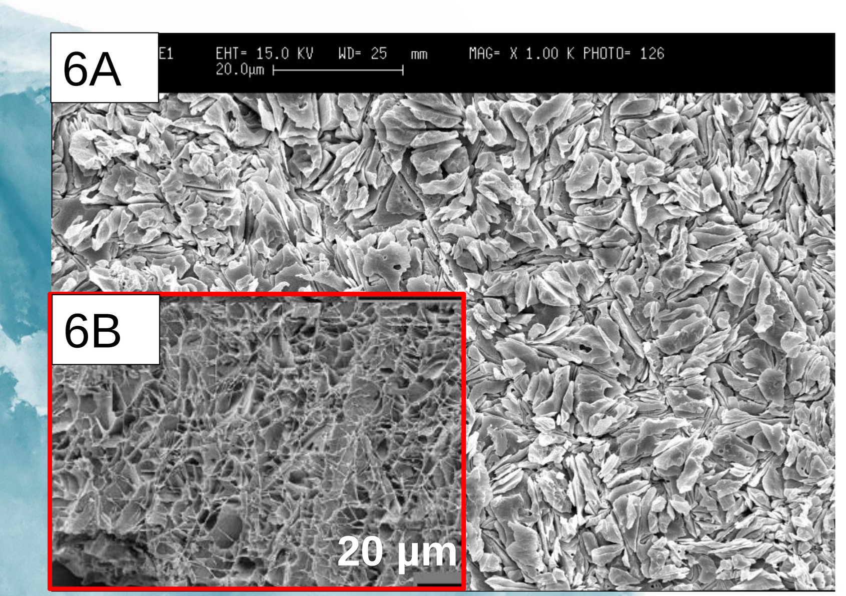

Fig. 6: Chalky fabric of *Ostrea*. **A**: Recrystallized fabric from Stirone River. **B**: Recent pristine specimen (Ullmann et al. 2010).

References

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