Alkaline earth metal isotopes as a novel tool to constrain water sources and changes in carbonate precipitation in the lagoon-estuarine environments

Y. (Mandy) Shao1,*, J. Farkaš1,2, L. Mosley3, J. Tyler1, H. Wong4, M. Samanta1, C. Holmden5, B. M. Gillanders3, A. Kolevica6 and A. Eisenhauer6

1Department of Earth Sciences, University of Adelaide, Australia
2Department of Environmental Geosciences, Czech University of Life Sciences, Czech Republic
3Department of Ecology and Evolutionary Biology, University of Adelaide, Australia
4Australian Nuclear Science and Technology Organisation, Australia
5Department of Earth Sciences, University of Saskatchewan, Canada
6GEOMAR, Helmholtz Centre for Ocean Research Kiel, Germany
*correspondence: yuexiao.shao@adelaide.edu.au
A broad picture…

Fossil shells

Tracers
\(^{87}\text{Sr}/^{86}\text{Sr},\ \delta^{88}/^{86}\text{Sr}\)

Land-ocean interface

Past
- Paleo-hydrology
- Water source mixing

Refer back

Decision making

Modern/Future
- Climate change
- Anthropogenic (human) disturbances

- water cycle
- water resources
- environmental sustainability
Alkaline earth metal elements??

Our Tools:

Strontium (Sr)
- $^{87}\text{Sr}/^{86}\text{Sr}$ – radiogenic
- $^{88}\text{Sr}/^{86}\text{Sr}$ – stable
The Coorong— a natural isotope laboratory

- Unique geomorphology and large salinity gradient!

Modified from Shao et al. (2018)
Know the past for a better future…

• Problems of the wetland site
  ➢ Difficulties in freshwater management
  ➢ The Millennium Drought (late 90s to 2010)
  ➢ Changes to ecological condition
  ➢ Decreased tourism

• Murray-Darling Basin Plan: “$8 billion spent and still the Coorong wetland is dying”

• What was the past like?
  More saline or fresh?
In this talk:

• Introduction to strontium isotope systems ($^{87}$Sr/$^{86}$Sr and $\delta^{88/86}$Sr)

• Application of strontium isotopes in the modern Coorong
  ➢ Water source mixing and carbonate fluxes
  ➢ The role of the South Coorong Lagoon as a sink of DIC – linked to blue carbon

• Application of strontium isotopes in paleo-hydrology studies
  ➢ Calibration of $\delta^{88/86}$Sr against $\delta^{44/40}$Ca and salinity in the Coorong water
  ➢ Calibration of $\delta^{88/86}$Sr in shells (A. helmsi) and local waters in the Coorong
  ➢ $^{87}$Sr/$^{86}$Sr and $\delta^{88/86}$Sr in shells (A. helmsi) from a South Lagoon sediment core

Water samples

Shell samples

Arthritica helmsi (aragonitic)
(Chamberlayne, 2015)
Stable Strontium Isotope Systematics

Radiogenic Strontium Isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) System

Tracer of radiogenic processes:
- Provenance identification
- Global weathering
- Water source mixing

$^{87}\text{Rb} \rightarrow ^{87}\text{Sr} + \beta^-$
- Not sensitive to chemical processes

- Higher Rb content
- Continental waters
- Modern seawater
- Lower Rb content

4.5 Billion yrs ago

Time → Present

Bulk Earth

$^{87}\text{Sr}/^{86}\text{Sr}$

Continental Crust

Oceanic Crust
Stable Strontium Isotope System

\[ \delta^{88/86}\text{Sr} = \left( \frac{^{88}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{sample}} \left( \frac{^{88}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{standard}} - 1 \right) \times 10^3 \]

Standard used: SRM/NBS987

- Measured by TIMS with Double-Spike correction
- Sensitive to mass-dependent isotope fractionation processes (e.g., carbonate precipitation/dissolution)
- \( \Delta^{88/86}\text{Sr} (\delta^{88/86}\text{Sr}_{\text{carb}} - \delta^{88/86}\text{Sr}_{\text{water}}) \) – independent of environmental parameters (i.e., temperature, pH, salinity or carbonate ion concentration) (Raddatz et al., 2013; Vollstaedt et al., 2014; Fruchter et al., 2016)
- Good indicator of paleo-water Sr isotope signatures
The two-dimensional isotope tracers – $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$ in the modern Coorong

- Major water components - fresh, brackish, marine and hypersaline
- $^{87}\text{Sr}/^{86}\text{Sr}$ – water source mixing
- $\delta^{88/86}\text{Sr}$ – carbonate precipitation/dissolution
Carbonate fluxes in the Coorong – Saturation indices (SI) by PHREEQC

Saturation Index (SI)

\[ SI = \log \left( \frac{\left\{\text{Ca}^{2+}\right\}\left\{\text{CO}_3^{2-}\right\}}{K_S} \right) \]

- \( SI \approx 0 \pm 0.2 \) just saturated
- \( SI > 0 \) supersaturated
- \( SI < 0 \) undersaturated
Carbonate precipitation in the Coorong – field evidence

\[ \text{Ca}^{2+} + 2\text{HCO}_3^- = \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \]  (Zeebe and Wolf-Gladrow, 2001)

The South Lagoon acts as an efficient sink of carbon due to ongoing \( \text{CaCO}_3 \) formation (mostly as aragonite)
Coorong $\delta^{88/86}\text{Sr}$ vs $\delta^{44/40}\text{Ca}$ and salinity

$\delta^{44/40}\text{Ca}$ data extracted from Shao et al. (2018)
Fractionation of $\delta^{88/86}\text{Sr}$ – biogenic carbonates ($A. \text{helmsi}$ shells) vs. water

$\Delta^{88/86}\text{Sr} (\delta^{88/86}\text{Sr}_{\text{carb}} - \delta^{88/86}\text{Sr}_{\text{water}}) = -0.09 \%o \text{ (constant)}$

The basis of the paleo-hydrology reconstruction!
Coring site C18


Age Model by C-14 dating

(Chamberlayne, 2015)
Paleo-hydrology of the Coorong

- Gentle increasing trends
- ~600-year cycles?
- Has never been purely marine in the past 2500+ yrs
Paleo-hydrology of the Coorong

Sediment core C18

Fossil A. helmsi

Increased continental influence, evaporation/salinity and carbonate precipitation?
Summary

• Coupling $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$ can constrain water mixing and carbonate precipitation/dissolution in the modern Coorong, also forms a two-dimensional tracers to understand the controlling processes of the local hydrology in the modern Coorong.

• $\delta^{88/86}\text{Sr}$ and mineral saturation modelling suggests that the South Lagoon acts as an efficient sink of carbon due to ongoing CaCO$_3$ formation (mostly as aragonite).

• Similar fractionation behaviour in stable Sr and Ca isotopes (i.e., $\delta^{88/86}\text{Sr}$ and $\delta^{44/40}\text{Ca}$) is confirmed, and results suggest systematic increasing trend of $\delta^{88/86}\text{Sr}$ with salinity in the Coorong waters.

• Fractionation between living A. helmsi shells and local water in the Coorong $\Delta^{88/86}\text{Sr}$ ($\delta^{88/86}\text{Sr}_{\text{carb}} - \delta^{88/86}\text{Sr}_{\text{water}}$) = -0.09 ‰ (constant), forming the basis of paleo-hydrology reconstruction.

• $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$ in the A. helmsi shells from the sediment core C18 indicate more continental input and increasing carbonate precipitation in the South Lagoon since ~2000 yrs BP (more measurements to be done).
Acknowledgements

- Adelaide Graduate Research Scholarship (AGRS)
- CRC LEME Regolith Science Scholarship
- EU funding from Dr. Juraj Farkaš
- Staff from the University of Adelaide

Dr. Juraj Farkaš
Dr. Jonathan Tyler
Prof. Bronwyn Gillanders

Prof. Luke Mosley
Ms. Briony Chamberlayne
Dr. Moneesha Samanta

Dr. John Tibby
Mr. David Bruce
Ms. Deborah Haynes
Thank you for listening!!

- The end ☺
References


