NERC BIO-Carbon Workshop - 7th March 2023

Fish gut carbonates and the control of ocean alkalinity

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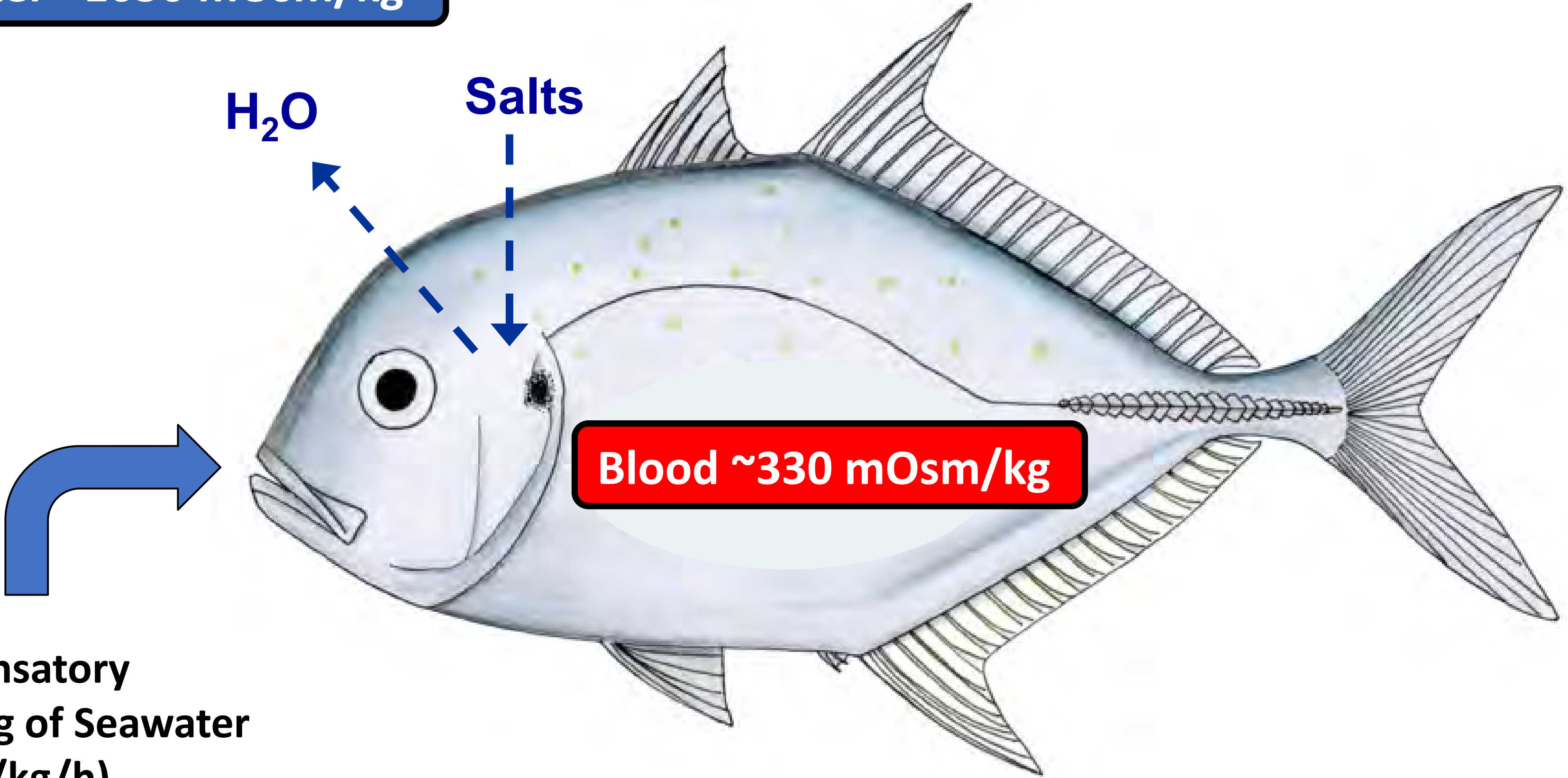
1) How and why do fish produce gut carbonates?

(Answer = Osmoregulation)

Seawater Ions (mM):

Na^{+}	~ 470	Cl^{-}	~ 550
Mg^{2+}	~ 53	SO_4^{2-}	~ 28
Ca^{2+}	~ 10		
K^{+}	~ 10		

Sea Water ~1050 mOsm/kg

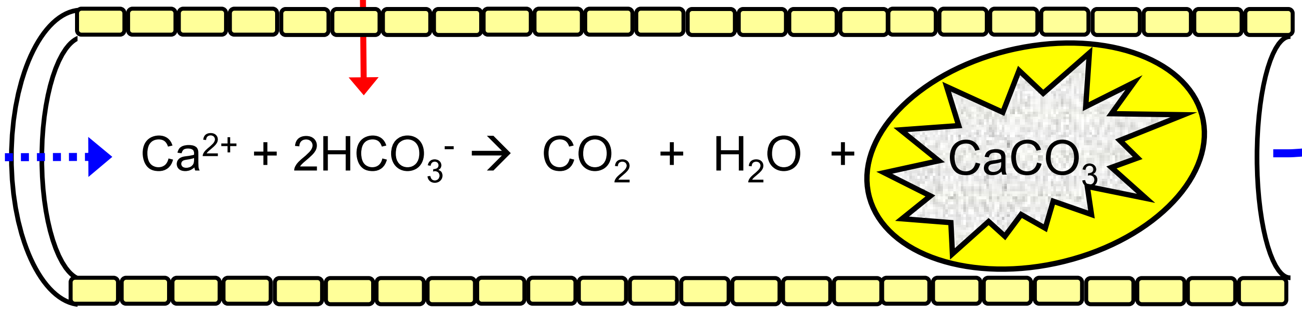


Compensatory
Drinking of Seawater
(1-5 ml/kg/h)

How? - Alkaline precipitation of ingested Ca^{2+} in the intestine

HCO_3^- secretion (intestinal cells)

Ingestion of Ca^{2+}-rich seawater (and Mg^{2+})



Excrete mucus-coated $CaCO_3$ pellets (and $MgCO_3$)

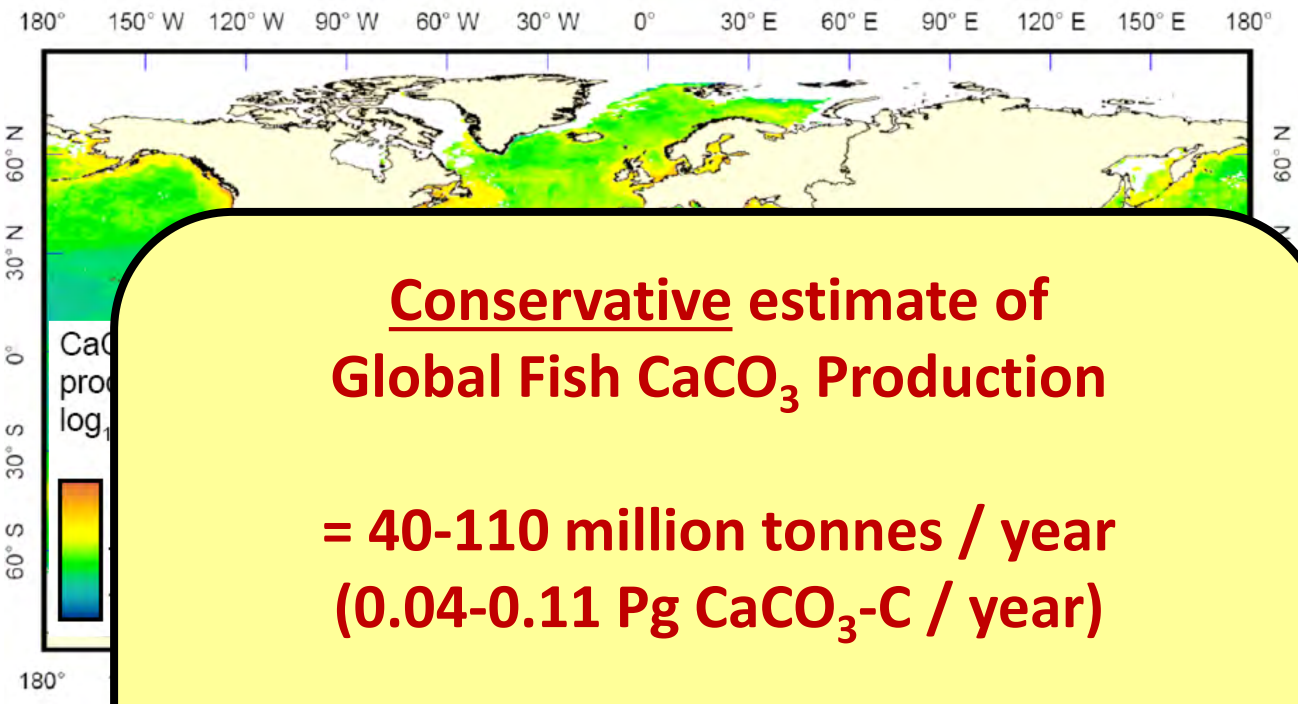
	Seawater	Intestinal Fluid
pH	8.1	8.3-9.2
$[HCO_3^-]$	2 mM	30 to >100 mM

Excreted pellets break down → high Mg calcite crystals (varied morphology and size) in mud fraction (< 63 µm) of shallow tropical sediments (Perry et al., 2011; Salter et al. 2012)

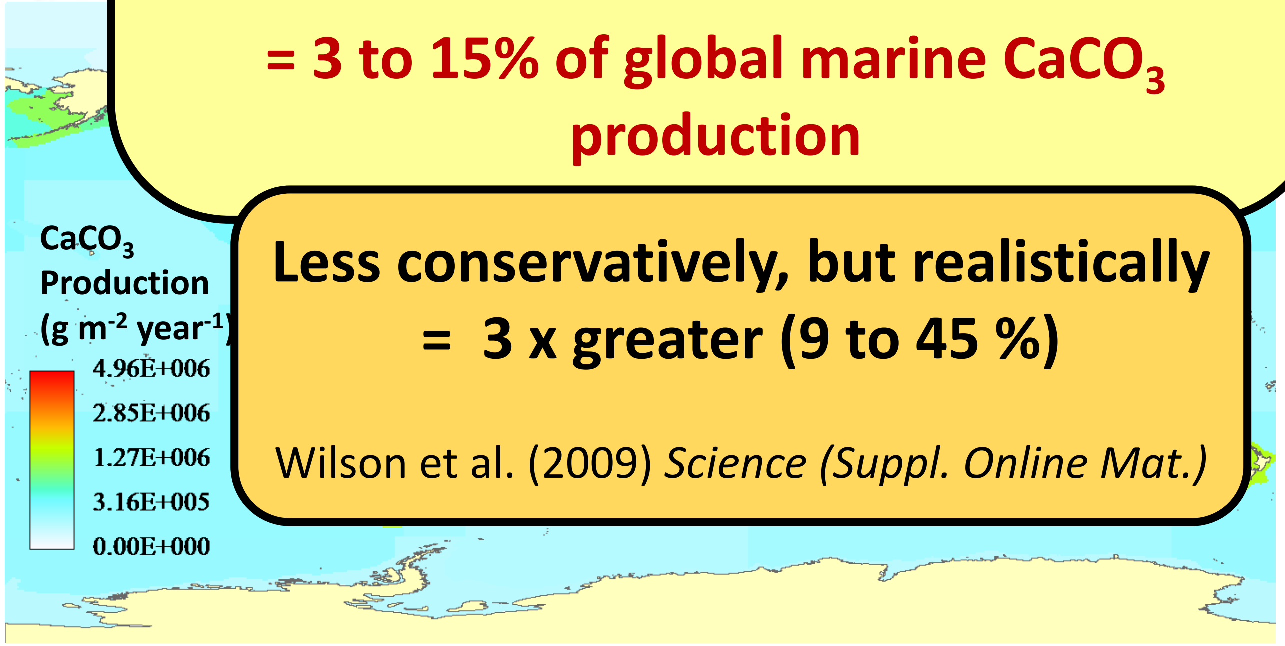
Ellipsoidal | **Straw-bundle** | **Dumbbell** | **Semi-spheres** | **Spheres**

< 1 µm → 10-20 µm

Size-based Macroecological Model (Simon Jennings)



Large Marine Ecosystems (LMEs) Model (Villy Christensen)



<u>Conservative</u> estimate of Global Fish $CaCO_3$ Production

= 40-110 million tonnes / year
(0.04-0.11 Pg $CaCO_3$-C / year)

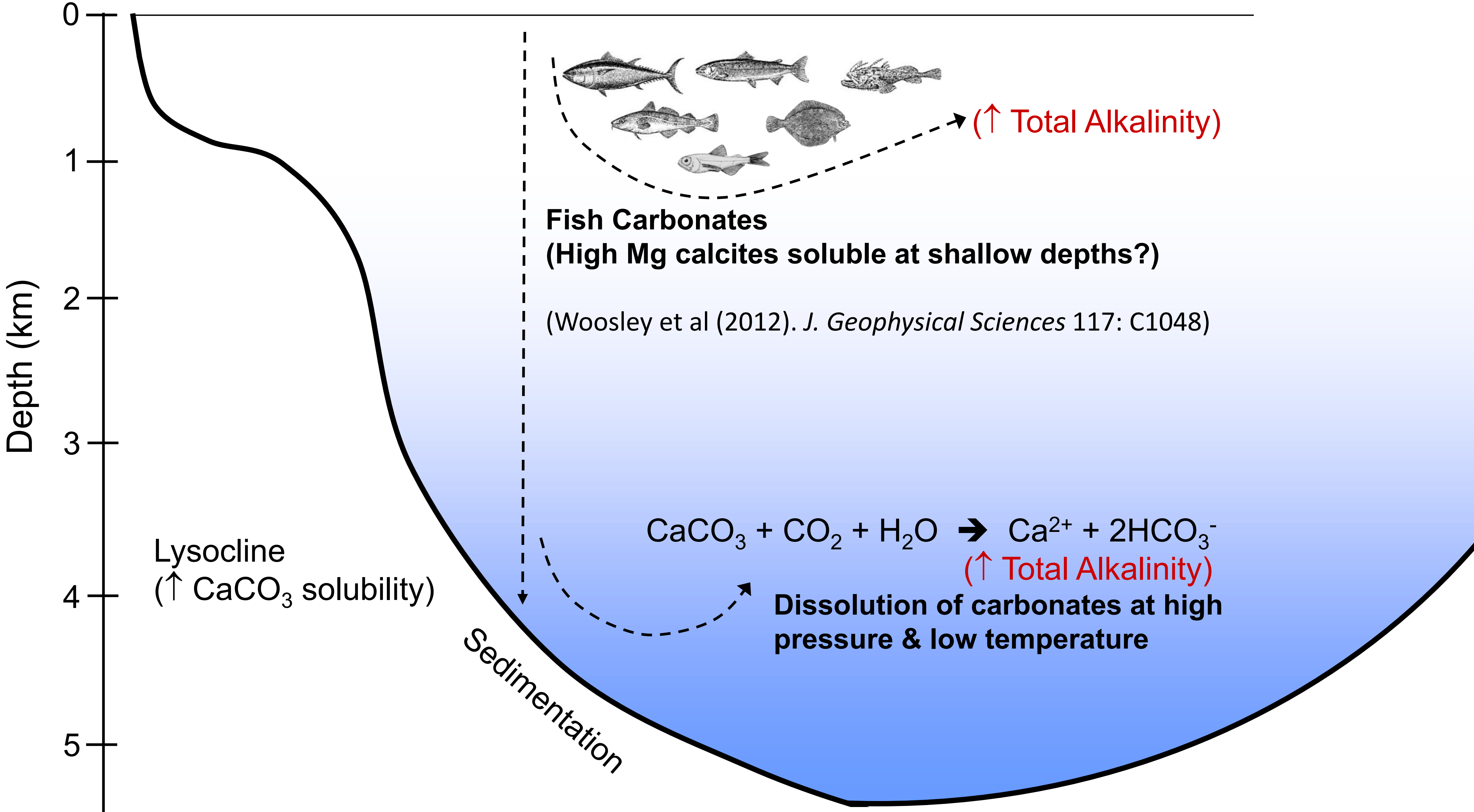
= 3 to 15% of global marine $CaCO_3$ production

Less conservatively, but realistically = 3 x greater (9 to 45 %)

Wilson et al. (2009) *Science (Suppl. Online Mat.)*

Wilson et al. (2009) *Science* 323: 359-362.

Rapid dissolution of fish carbonates – may explain surface alkalinity-depth profile



Wilson et al. (2009) *Science* 323: 359-362.

Seawater drinking not only calcium source for intestinal carbonate precipitation

Seawater Ions (mM):

Na^+	~ 470	Cl^-	~ 550
Mg^{2+}	~ 53	SO_4^{2-}	~ 28
Ca^{2+}	~ 10		
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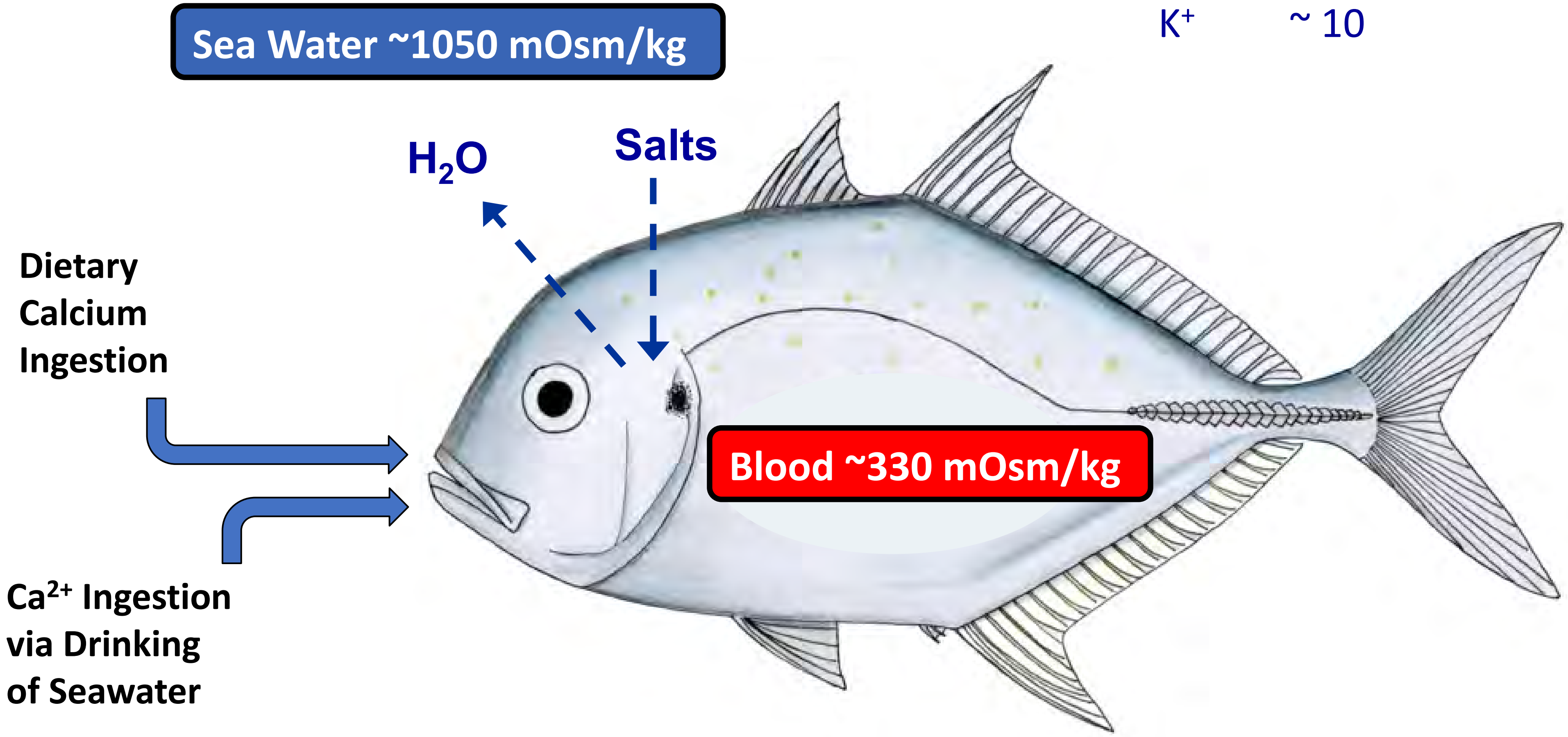


OBJECTIVE 1 (WP1):

Test hypothesis that fish carbonate production rate is proportional to both **feeding rate and dietary calcium content**.

First attempt to quantify carbonate production by **epipelagic** fish species (Prediction = higher production due to active lifestyles/metabolic rates).

Effect of Feeding on $CaCO_3$ excretion rate

Proportional to individual feeding rates in juvenile sea bass

...and ~10-fold higher than when starved

@ 15 °C

Unpublished data removed:

Showed graph of gut $CaCO_3$ excretion rate v. food intake rate in sea bass

Effect of diet calcium content?

- Fish-based ($Ca_3(PO_4)_2$ - rich)
- Shellfish-based ($CaCO_3$ - rich)
- Soft-bodied inverts (Low Ca)

Carbonate and phosphate co-precipitation in fish that are feeding?

Gut precipitates - ***Fasted*** barracuda:

High Mg calcite

+

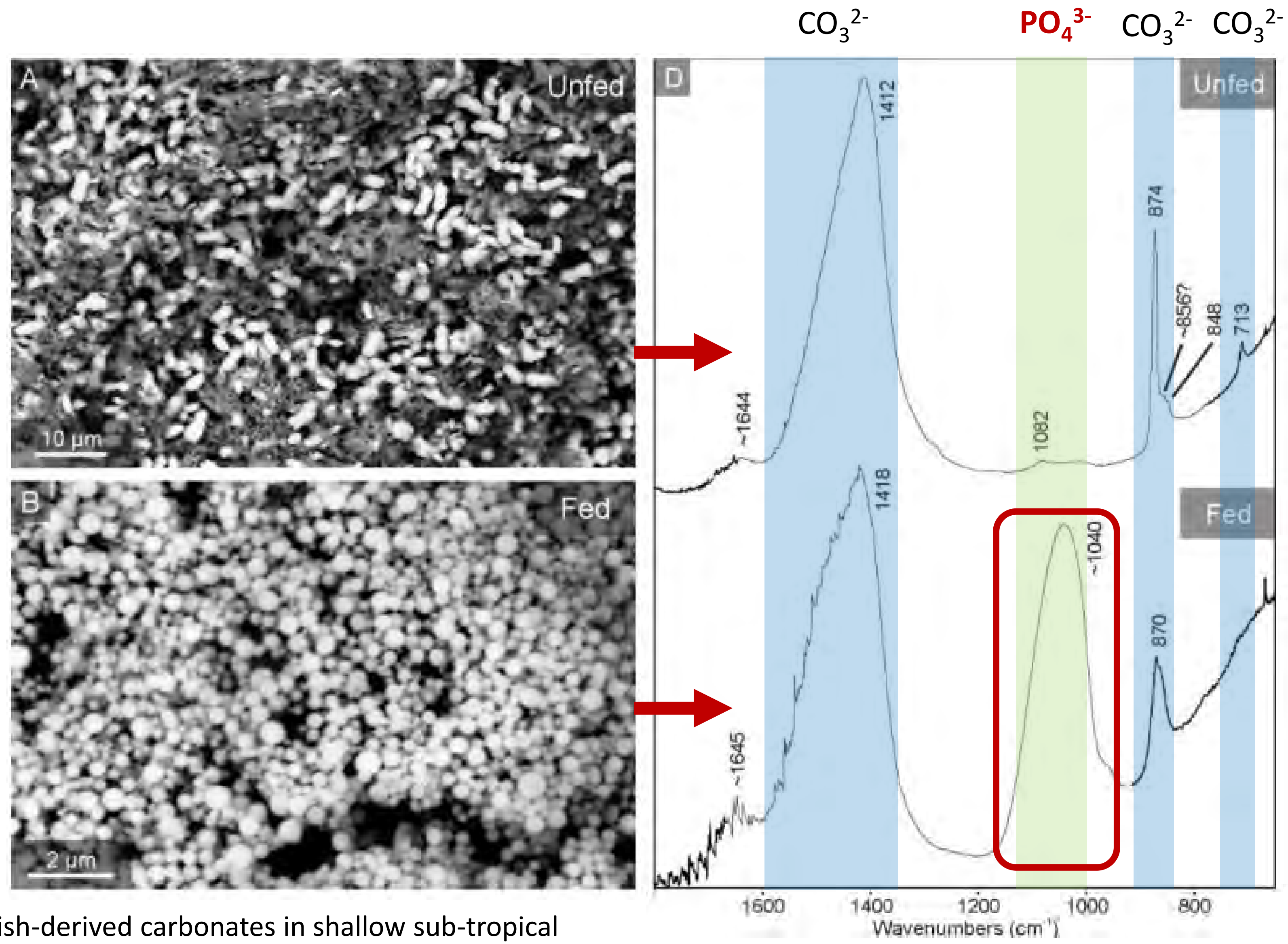
Mg-rich amorphous carbonate

Gut precipitates - ***Fed*** barracuda:

Mg-rich amorphous carbonate

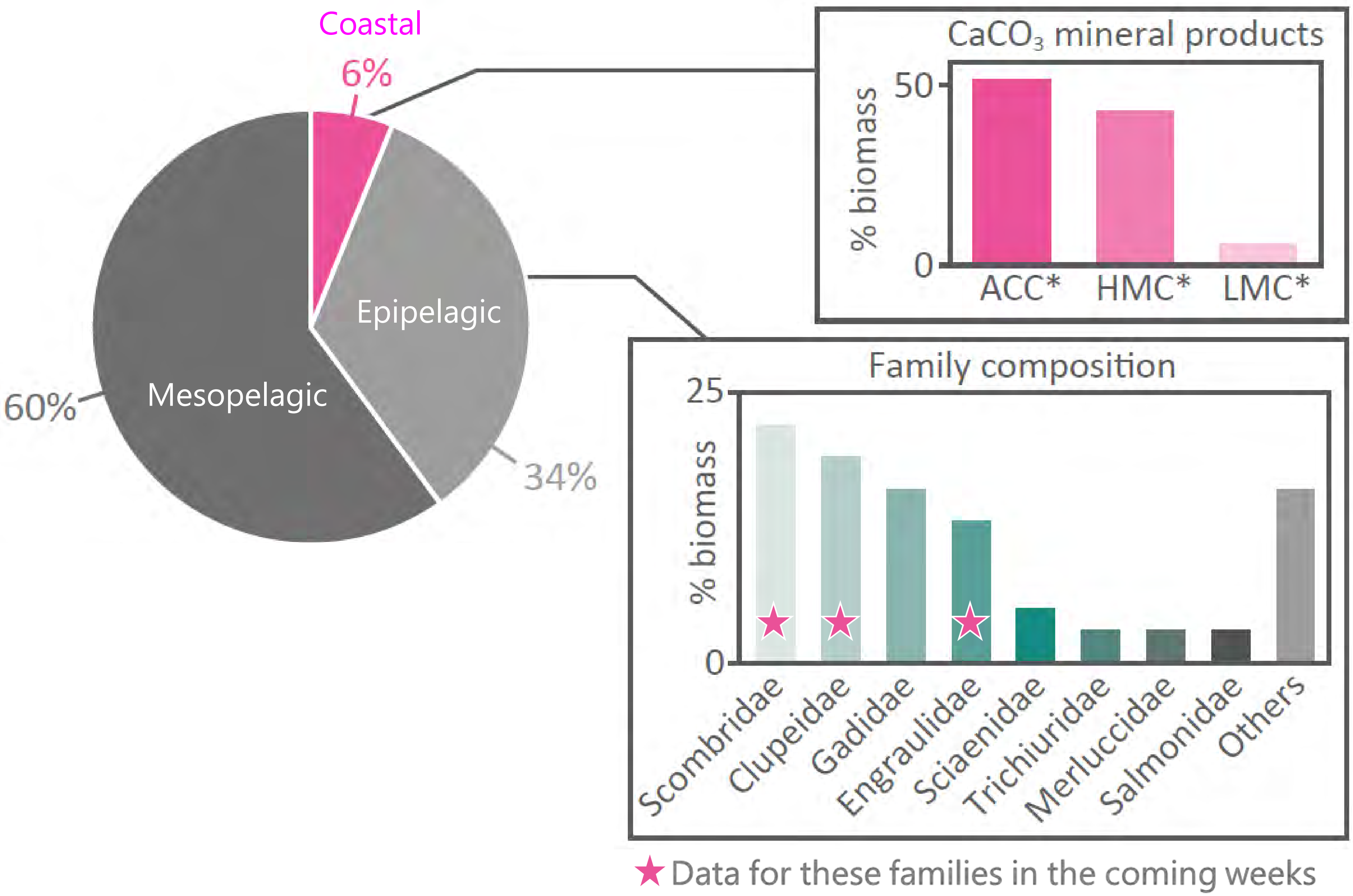
+

phosphate



Salter, M.A., 2013. The production and preservation of fish-derived carbonates in shallow sub-tropical marine carbonate provinces (PhD Thesis, Manchester Metropolitan University, UK).
https://e-space.mmu.ac.uk/314039/1/M%20Salter_PhD%20Thesis_Final%20amended%20version.pdf

Little Known about Carbonates from Most Abundant Fish Species



ACC – Amorphous $CaCO_3$
HMC - High Mg Calcite
LMC – Low Mg Calcite

OBJECTIVE 2 (WP2):

Characterise biogeochemical properties relevant to solubility of gut carbonates of most globally significant fish taxa

- **epipelagic** and **mesopelagic** fishes (key data gaps)

Analyse intestinal carbonates from frozen wild-caught fish* for:

- morphology, mineralogy, composition, solubility & sinking rates

* From international project partners (US, Bahamas, Gran Canaria, Germany and UK)

New Collaborations

Mesopelagic fish sources			
David Wells	Texas A&M University (USA)	Gulf of Mexico	Original PP
Heino Fock	Thünen Institute of Sea Fisheries (Germany)	Benguela upwelling region and Tropical Atlantic	Original PP
Webjørn Melle	Institute of Marine Research (Norway)	Iceland Basin, Norwegian Sea and North Sea	**New PP**
Pietro Battaglia	Stazione Zoologica Anton Dohrn (Italy)	Mediterranean Sea	**New PP**
via Clive Trueman/Jethro Reading (Southampton)	Marine Institute/Foras na Mara (Ireland)	Irish Sea	**New PP**

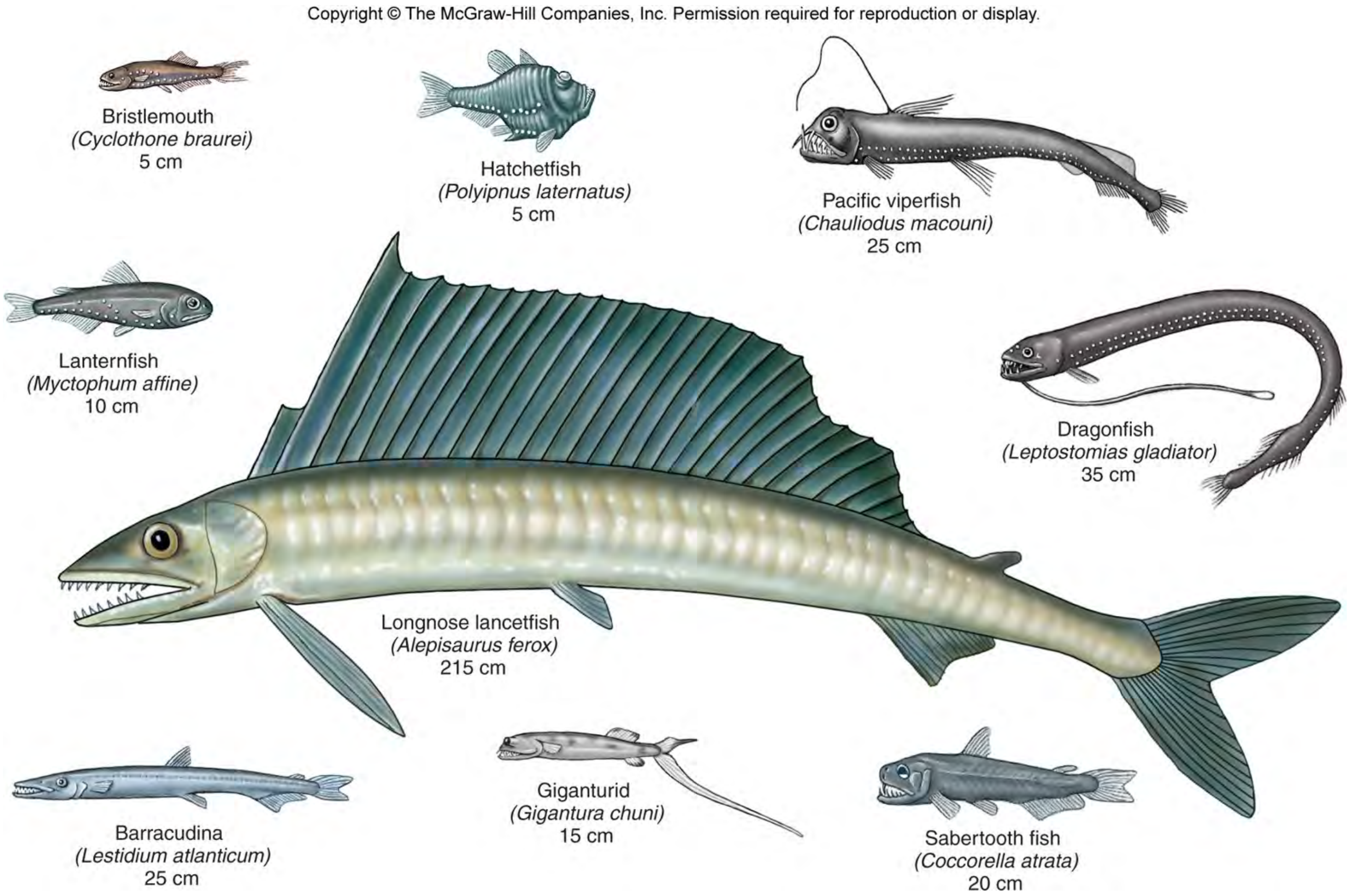
Other NERC BIO-Carbon Projects:

Constraining respiration rates of mesopelagic fishes - NE/X00869X/1
PI – Clive Trueman (Southampton)

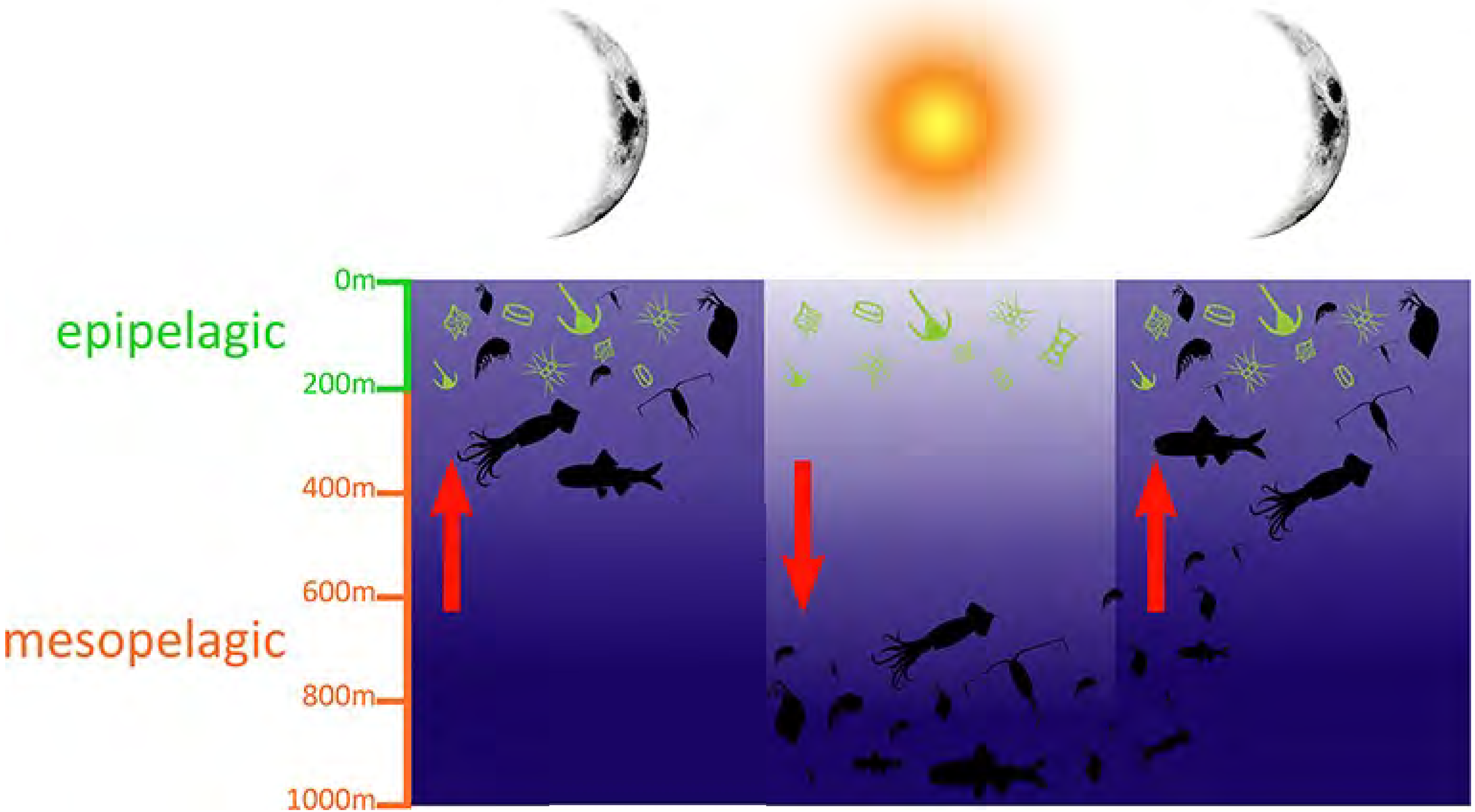
Future global ocean Carbon storage: Quantifying warming impacts on zooplankton (C-QWIZ) - NE/X008622/1
PI – Dan Mayor (Previously NOC, now Exeter Uni)

Importance of Mesopelagic Fishes

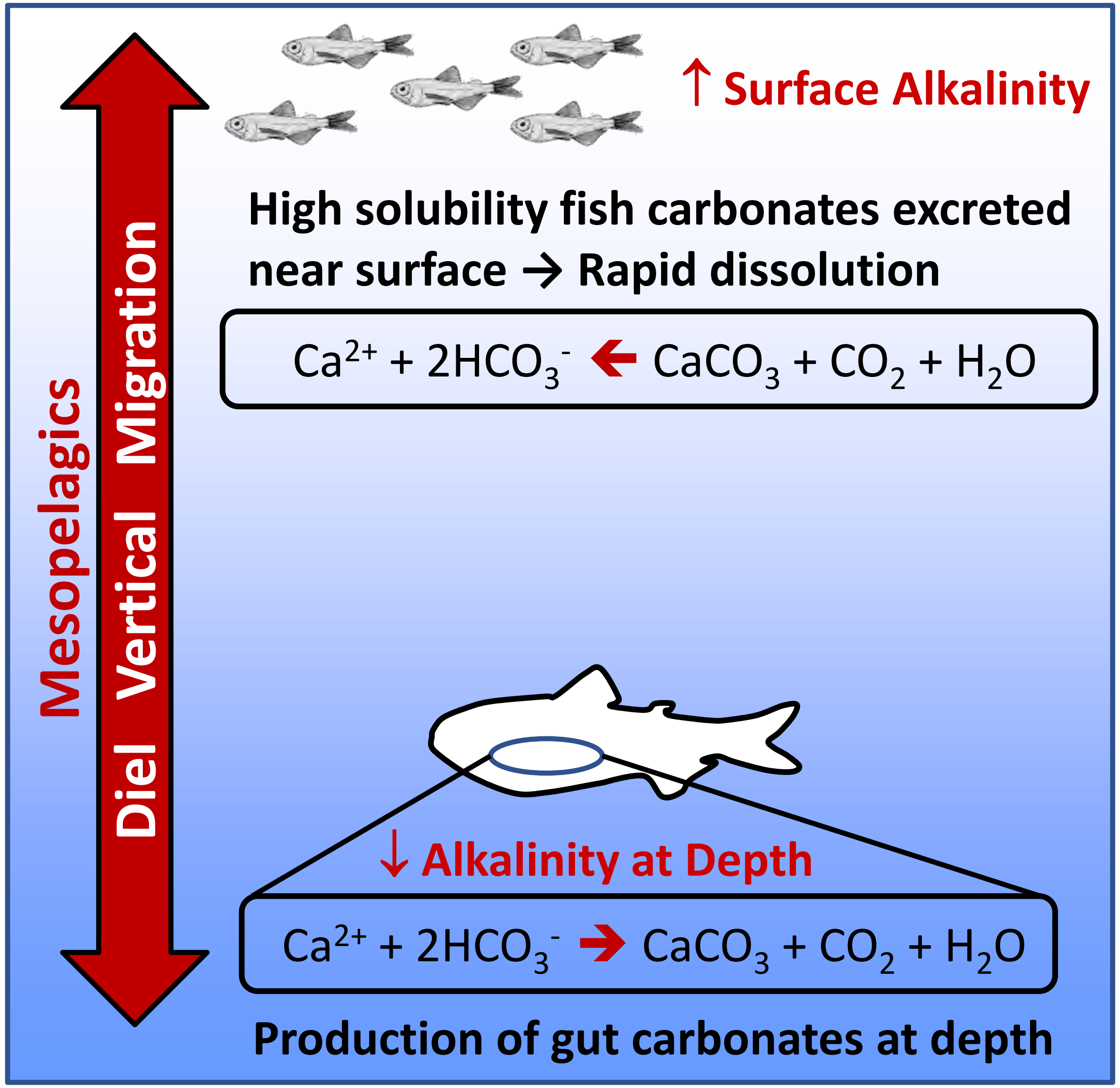
most abundant vertebrates on Earth (biomass >>1 billion tonnes)



Mesopelagic Fishes - Diel Vertical Migration (DVM)



Mesopelagic fish – Potential source of a novel "Upward Alkalinity Pump"

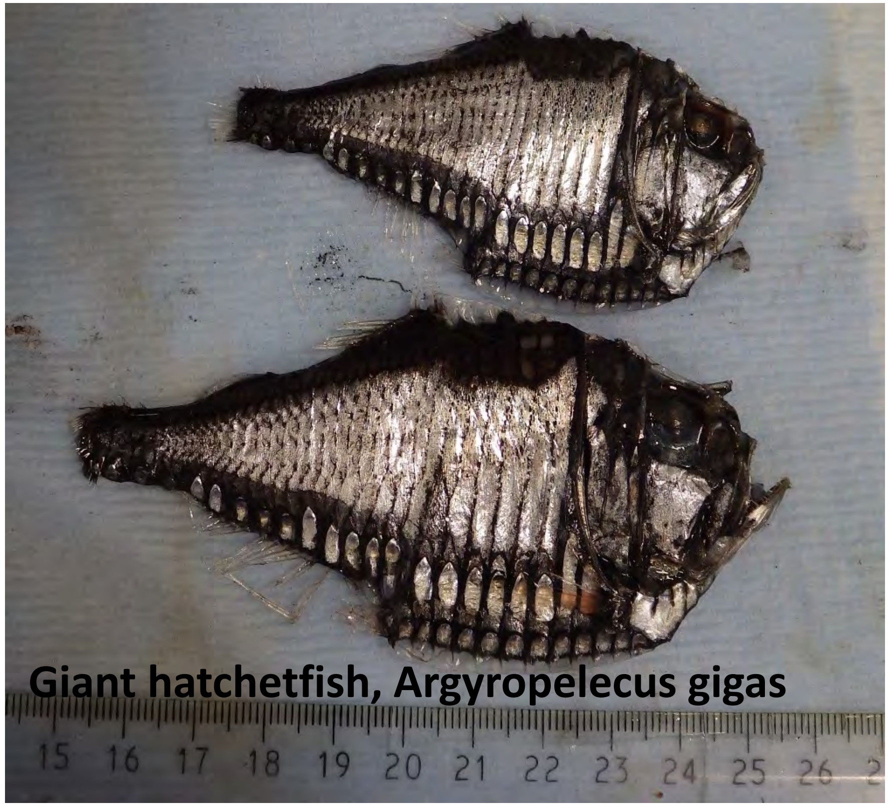


Roberts, Wilson et al. (2017). P.N.A.S. doi: 10.1073/pnas.1701262114

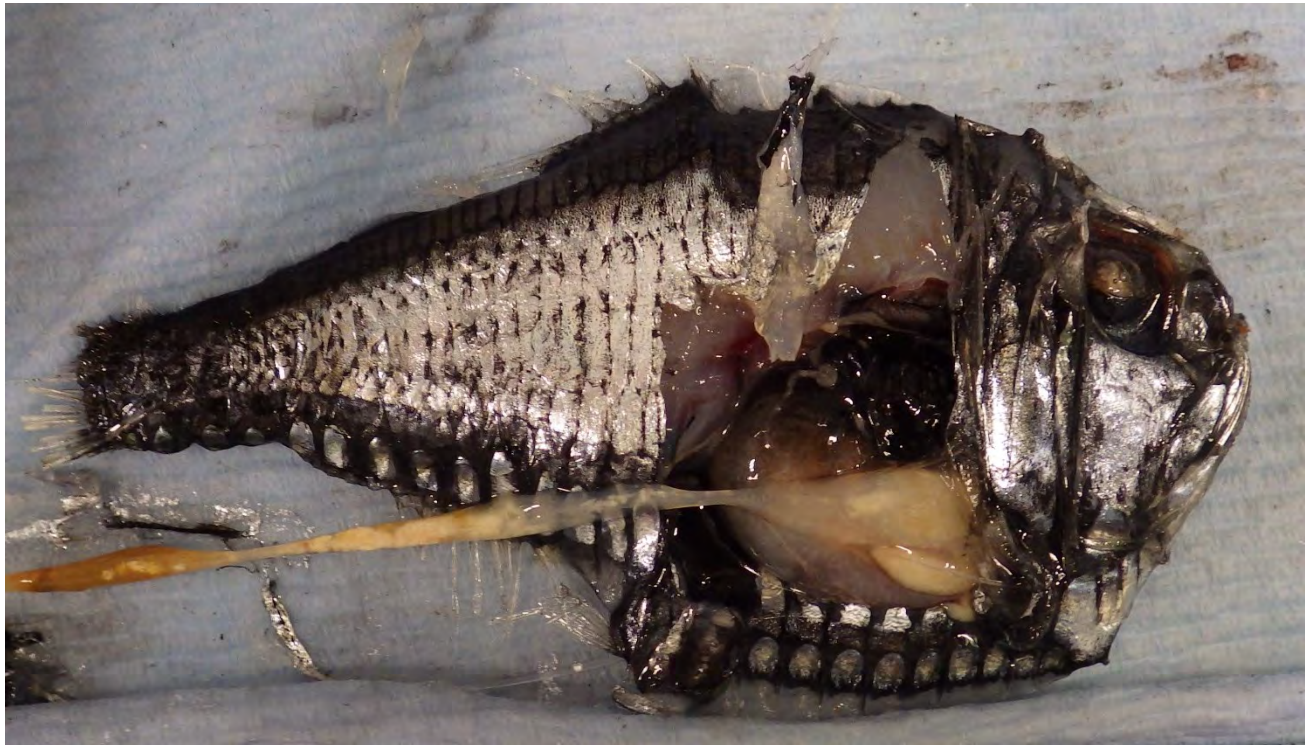
Saba et al. (2021). Toward a better understanding of fish-based contribution to ocean carbon flux. *Limnol. Oceanogr.* 9999, 2021, 1–26. doi: 10.1002/lno.11709

20 species of mid-Atlantic mesopelagic teleost fish caught at 55 and 450 m

Barbelled dragonfishes (Chauliodus sp.)

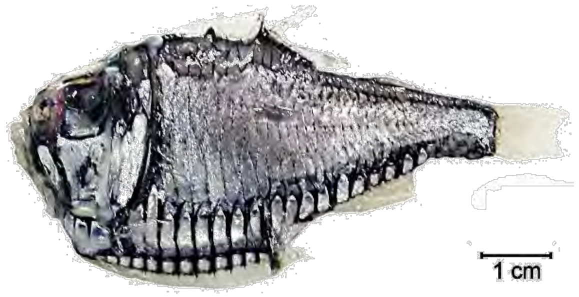


Giant hatchetfish, Argyropelecus gigas



All species had intestinal $CaCO_3$ pellets

Mesopelagic fish data so far…



Credit: Luciano Gomes Fischer (Fishbase)

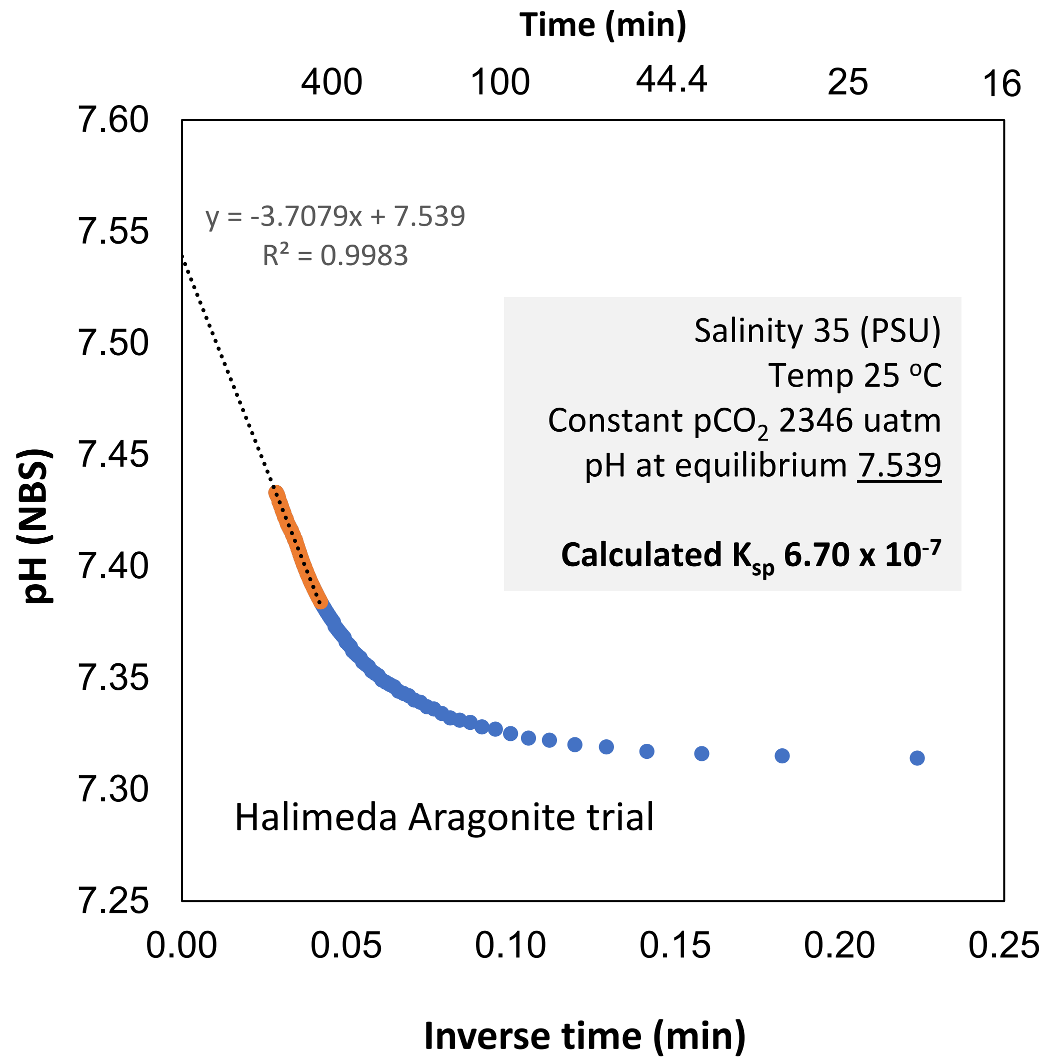
Sternoptychidae:
Argyropelecus gigas
Typical depths 400–600 m
Phosphate-rich amorphous carbonate

Platytroctidae:
Searsia koefoedi
Typical depths 450–1500 m
Phosphate-rich amorphous carbonate

Unpublished data removed:

Showed SEM images and FTIR spectra of gut carbonates from the two mesopelagic fish species. Revealed spectra that suggest phosphate-rich amorphous carbonate in both species

Solubility Determinations in Seawater



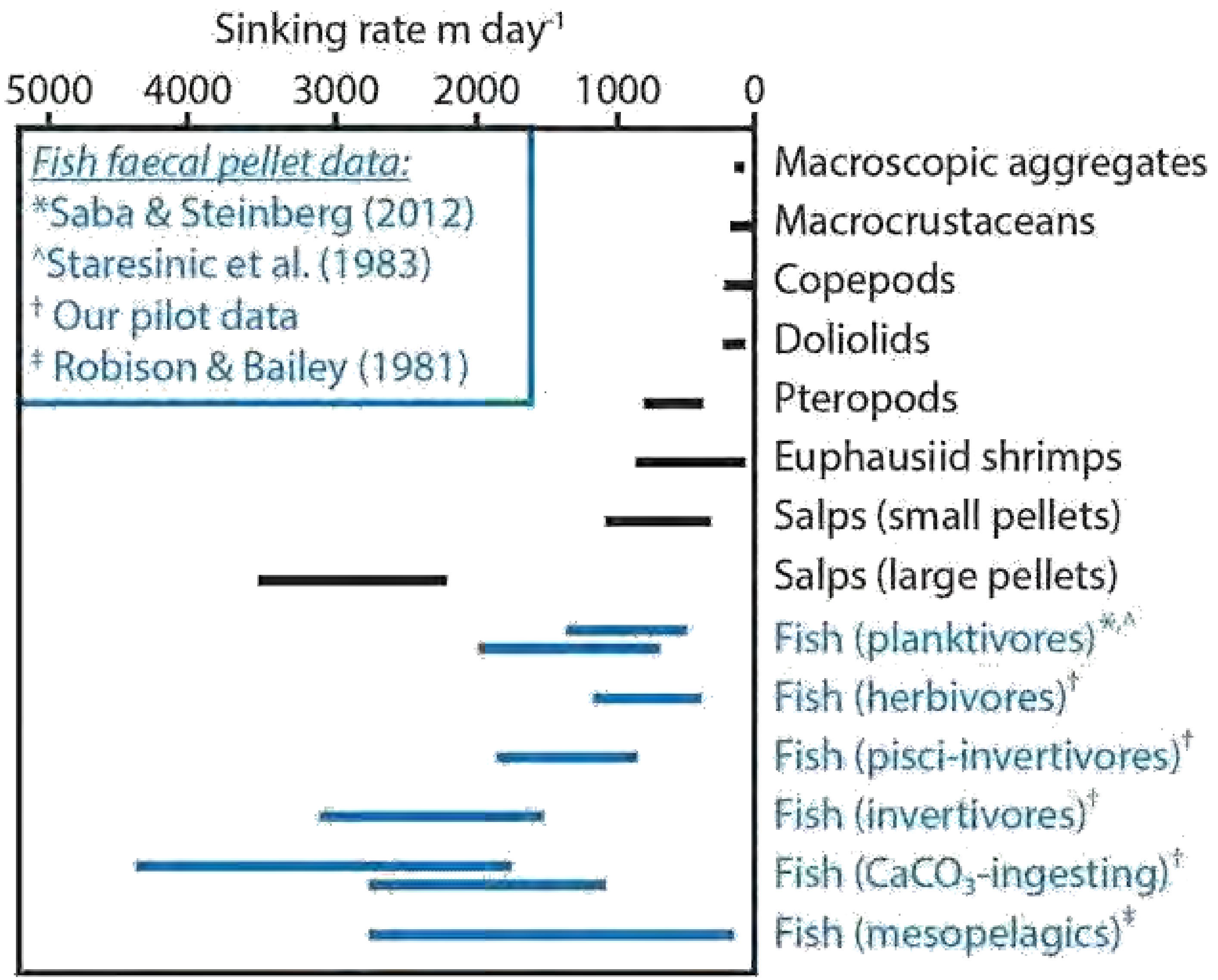
Solubility trials run at 25 °C and 35 PSU

- Solubility for different types of fish carbonate
- Range of temperature (5, 15, 25 °C) and salinity (33, 35, 37 PSU)

Will also determine **dissolution rates** in seawater

- over same temperature/salinity ranges
- over a range of Ω_{arag}

Fast dissolution rate v. Fast sinking rate ?



OBJECTIVE 3 (WP3): … to start summer 2023

Integrate outputs from WP1 and 2 to produce the first spatially- and mineralogically-resolved assessments of the role of fish $CaCO_3$ in the global marine carbon cycle.

- Will allow **predictions** of net contribution of marine bony fish to the global marine carbon cycle as a function of spatial variability in the amounts, mineral ratios and solubilities of the carbonates produced

Future Needs for Fieldwork

- Ongoing work on mesopelagic and epipelagic fish (frozen specimens)
  - Characterise $CaCO_3$ properties: mineralogy, composition, solubility
- But several significant unknowns remain:
  - $CaCO_3$ production rate *in vivo*
  - When/where (depth) most faecal pellets/carbonates are excreted
  - Sinking rates of excreted faecal pellets
- Requires working with live mesopelagic and epipelagic fishes
- Mesopelagic fish live work most challenging, but **has been done**

  e.g., Monterey Bay Aquarium deep sea exhibit;

  Messina, Sicily

Future Needs for Fieldwork

Ship-based sampling efforts targeting collection of live fish, e.g.,:

- Short, shallow, nocturnal MOCNESS tows; and/or
- Baited pressurised chambers

Lab-based sampling using specialised deep-sea research facilities, e.g.,:

- Monterey Bay Aquarium, California
- DEEP-MED-LAB, Sicily

Possibly depth-stratified sediment trap sampling to confirm and quantify presence of fish $CaCO_3$ in the marine environment:

- Adam Subhas (Wood's Hole) - currently trialling a RAMAN mapping approach with US collaborators using Bermudan sediment trap samples
  - (e.g. unidentified source with high Mg content)

Thank you

Relevant recent papers by PI or CoIs (in bold) since BIO-Carbon project started:

Ghilardi, M, **Salter, MA,** Parravicini, V, Ferse, SCA, Rixen, T, Wild, C, **Perry, CT**, **Wilson, RW**, Mouillot, D, & Bejarano, S (2023). Temperature, species identity, and morphological traits regulate carbonate excretion and mineralogy in tropical reef fishes.

Nature Communications, 14:985. https://doi.org/10.1038/s41467-023-36617-7

Davison, WG, Cooper, CA, Sloman, KA, **Wilson, RW** (2023). A method for measuring meaningful physiological variables in fish blood without surgical cannulation.

Scientific reports, 13:899. https://doi.org/10.1038/s41598-023-28061-w

Goodrich HR, Berry, AA, Montgomery, DW, Davison, WG & **Wilson, RW** (2022). Fish feeds supplemented with calcium-based buffering minerals decrease stomach acidity, increase the blood alkaline tide and cost more to digest.

Scientific Reports, 12:18468. https://doi.org/10.1038/s41598-022-22496-3