Rare Earth Elements of modern shelf and deep-water articulated brachiopods: evaluation of seawater masses

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or carbonate-rock facies) from the Carboniferous to the Permian indicates that the body size changes of *Neochonetes* were not controlled by the substrate. The body size of *Neochonetes* decreased in the Middle Permian and increased in the Wuchiapingian (early Late Permian), which is inferred to respectively link to the temperature rising in the Middle Permian and the transgression in the early Late Permian. Comparison of the occurrence frequency of *Neochonetes* and *Tethyochonetes* in three different facies (shallow-water clastic-rock facies and carbonate-rock facies and deep-water siliceous-rock facies) demonstrates that both genera occurred more commonly in the shallow-water facies, and in the deep-water facies *Tethyochonetes* dominates and has a larger average size, which means that *Tethyochonetes* could perform better in deep-water environments than *Neochonetes*. More interestingly, *Tethyochonetes* occurred more frequently in the Early Triassic than *Neochonetes* did, suggesting *Tethyochonetes* coping with the end-Permian crisis stress better and surviving more during the Early Triassic.

A new sample processing protocol: an important update for procuring reliable ree signatures

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Cleaning of brachiopod shells is a fundamental step that should be conducted with great care and attention to detail prior to processing their rare earth element (REE) contents. Without cleaning, the concentrations would represent the REE compositions not only of the shells calcitic structure but also of lattice bound oxides, detritus, particulates and organic remnants. Developing a sensitive and precise analytical protocol is of utmost importance required for isolating contaminants on biogenic and abiogenic carbonates in order to acquire a robust REE signal that enhances our confidence in oceanographic applications. To achieve this goal, 26 shell fragments separated from recently dead *Liothyrella neozelanica* shells, recovered from the deep water's of the southwest Pacific, north of New Zealand, were extensively washed and rinsed with distilled water. Five parts did not receive any further cleaning; protocol – 1 (P-1). A set of four parts was physically cleaned using a sharp stainless-steel blade (P-2). Another set of four parts was immersed in 2.5 % hydrogen peroxide (H_2O_2) for three continuous days (P-3). A further set of four parts was physically cleaned then dropped into 10% hydrochloric acid (HCl) until the fragments were deemed clean (P-4). The last nine parts were processed using all cleaning protocols: water washed, physically cleaned, H_2O_2 immersed, and then HCl leached (P-5).

Attached detritus and nano-particulates adsorbed on the calcitic structure of brachiopod shells besides the organic tissue, proteinaceous periostracum (Carpenter and Lohmann, 1995) may lead to elevated ΣREE, anomalous Ce anomaly (Fig. 1A) and elevated Mn, Fe (Fig. 2A) and U concentrations as documented by the P-1 set. Physical cleaning removes mainly the adsorptive nano-particulates and the periostracum. This protocol leads to depleted ΣREE and lower Mn, Fe, and U concentrations but with a slight Ce anomaly: set P-2. Hydrogen peroxide eliminates primarily the organic tissue; however it requires physical cleaning to remove the periostracum or the nano-particulates, which leads to partial depletion in the Ce anomaly: set P-3. Physical cleaning followed by chemical cleaning removes adsorptive particulates, organic remnants, periostracum and the primary layer. This protocol is reflected in the drastic reductions of the ΣREE, Mn, Fe, U concentrations and 'normal' Ce anomalies in the P-4 and P-5 sets (Figs. 1A, 2A).

Protocol P-4 was applied to Ordovician, Silurian, Pennsylvanian and Permian brachiopods and their enclosing lime matrix collected from Canada, USA and China to test for the reliability of REEs in fossil and Deep-Time carbonates. The immersion in H_2O_2 was omitted since no organic tissue was documented in any fossil samples. The fossil shells display ΣREEs, Mn, Fe, U concentrations and Ce anomalies comparable to their modern counterparts, while the lime matrixes are slightly to extensively enriched (Figs. 1B& 2B). This unequivocally documents the veracity of the processing protocols and if we expect, want reliable REEs, the need for its rigorous application to fossil material such as brachiopods, conodonts, corals, molluscs, foraminiferas and whole rock.

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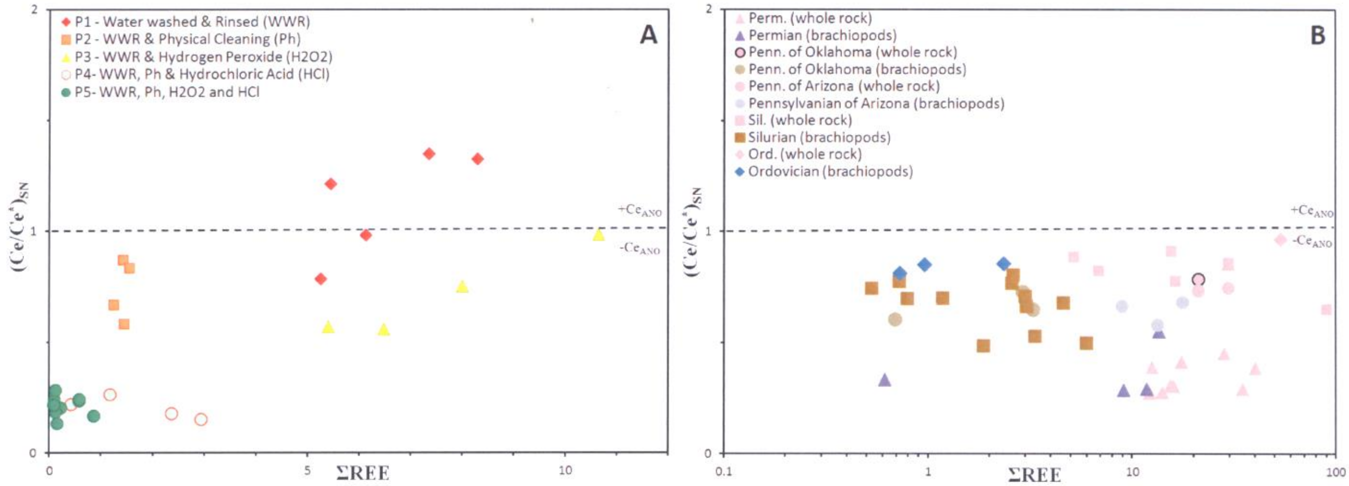

Fig. 1: Ce anomaly $(Ce/Ce^*)_{SN}$ - ΣREE evaluation of the different cleaning protocols conducted with a modern brachiopod shell (A) and on Ordovician, Silurian, Pennsylvanian and Permian brachiopods and their whole rock.

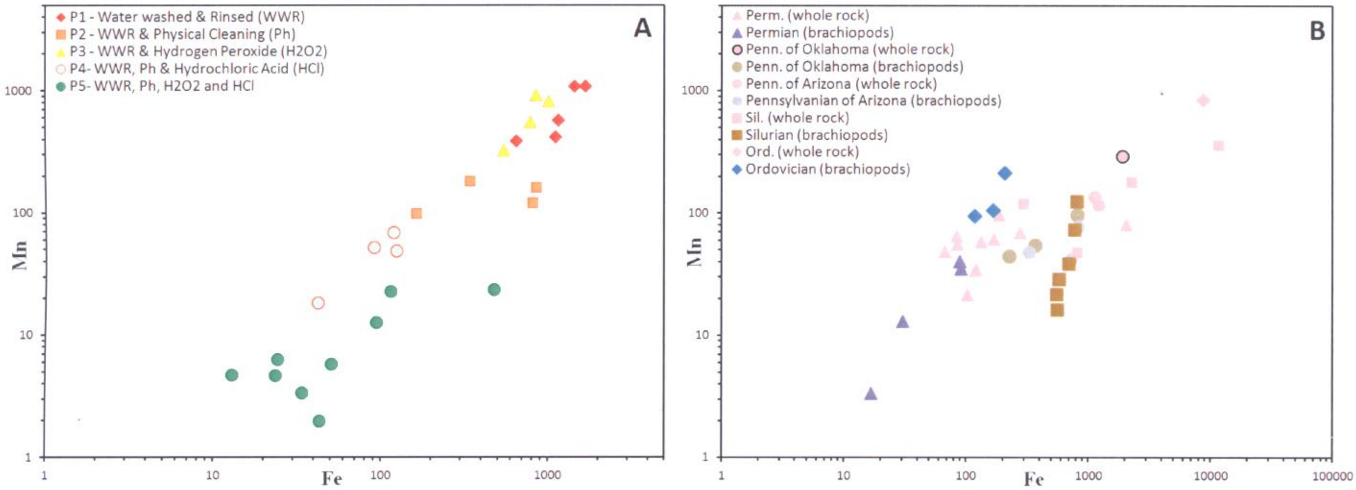

Fig. 2: Distribution of Mn and Fe contents with the different cleaning protocols of the modern brachiopod shell (A) and in their Paleozoic counterparts and enclosing whole rock (B).

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Rare earth elements of modern shelf and deep-water articulated brachiopods: evaluation of seawater masses

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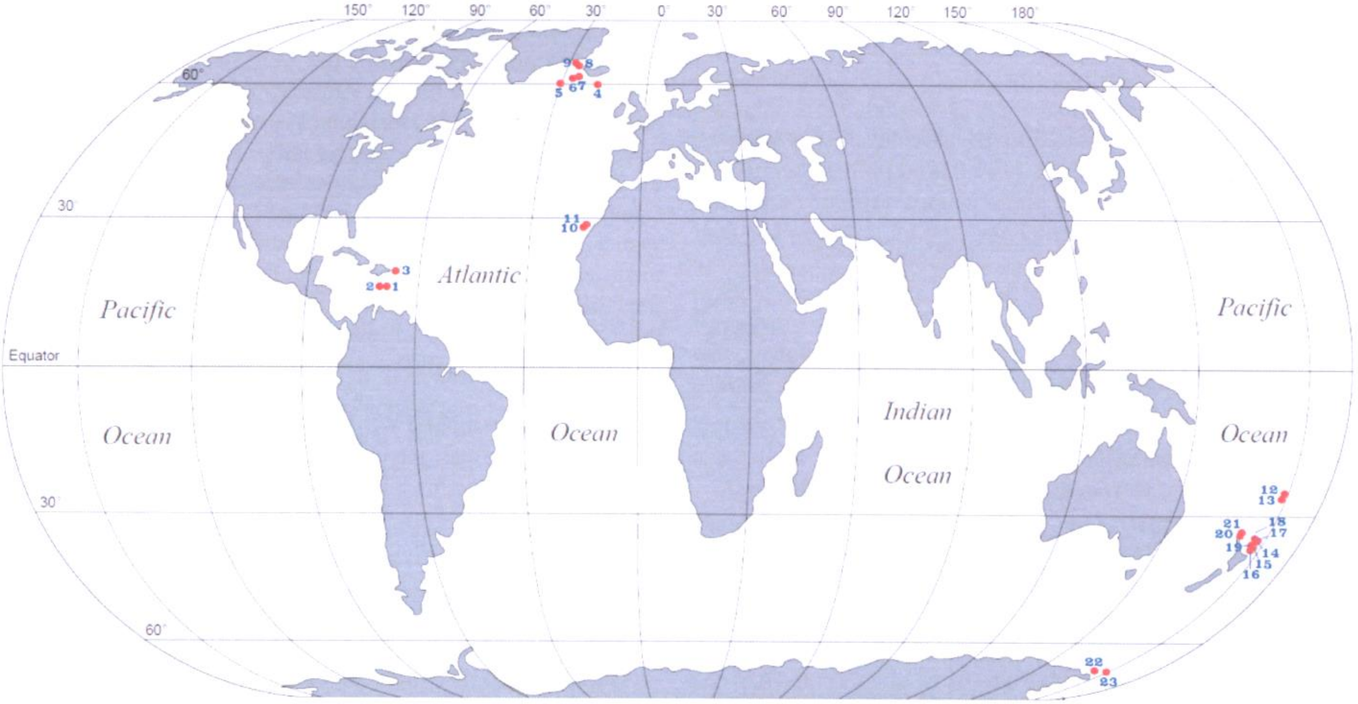

Fig. 1: Geographic distribution of the shelf and deep-water collection stations of the investigated brachiopod archives.

Table 1: Location, setting and depth of the shelf and deep-water stations and brachiopod taxonomy.

	Station	Depth (m)	Bathymetry	Order	Taxon
CARIBBEAN SEA					
VENEZUELA					
Venezuela Basin	1	3986	Deep Sea	*Terebratulida*	*Chlidonophora incerta*
	2	3998			
US VIRGIN ISLANDS					
Vigin Islands Basin	3	3940	"	"	"
NORTH ATLANTIC OCEAN					
ICELAND					
Iceland Basin	4	2567.7-2568.5	"	"	*Waldheimia cranium*
Irminger Basin	5	2504.7-2531.8	"	"	"
	6	698.1-678.5	Continental shelf	"	"
	7	724.4-704.9			
Denmark Strait	8	742.5-603.1	"	"	"
	9	696.9-706.4			
CANARY ISLANDS					
Continental slope of northwest Africa	10	1265	Deep Sea	"	*Dallina septigera*
	11				Hispanirhynchia cornea
SOUTHWEST PACIFIC OCEAN					
TONGA					
Lau Arc (Tonga-1)	12	589	Lau Arc	"	*Basiliola beecheri*
Colville Arc (Tonga-2)	13	660	Colville Arc	*Terebratulida*	*Dallina sp.*
NEW ZEALAND					
Kermadec Arc (New Zealand-1)	14	1244	Thomson seamount	"	*Stenosarina crosnieri*
	15	1460	Clark Seamount, south cone	"	*Dallina triangulari,* *Stenosarina crosnieri*
	16	1583	Clark Seamount south flank	"	*Dallina triangularis*
Havre Trough (New Zealand-2)	17	1740	Brothers Seamount West	"	*Goniobrochus ewingi*
	18	1172-1115	Seamount west of Volcano L	"	*Liothyrella neozelanica*
	19	1520	Seamount west of Rumble II West	"	*Goniobrochus ewingi*
Northland Plateau (New Zealand-3)	20	1293	Seamount #441 "Ballance Seamount"	*Rynchonellida* *Terebratulida*	*Basiliola pompholyx* *Stenosarina sp.*
	21	1583	Unnamed volcanic peak	"	*Abyssothyris wyvillei*
SOUTHERN OCEAN					
ANTARCTICA					
Balleny Spreading Corridor	22	547	Northeastern knoll of Admiralty seamount	"	*Magellania fragilis*
	23	1130	Seamount close to Scott Island	"	*Liothyrella sp.*

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Modern Rhynchonellids and Terebratulids, obtained from water depths below the neritic zone (>500m) at 23 stations in the Caribbean Sea, North Atlantic, South Pacific and Southern Oceans, were investigated for their rare earth element (REE) contents (Fig. 1, Table 1). The ΣREE of shelf (500-1000 m) or deep-water (>1000 m) brachiopod populations do not vary significantly between oceans/seas irrespective of water mass origins or influences by major currents.

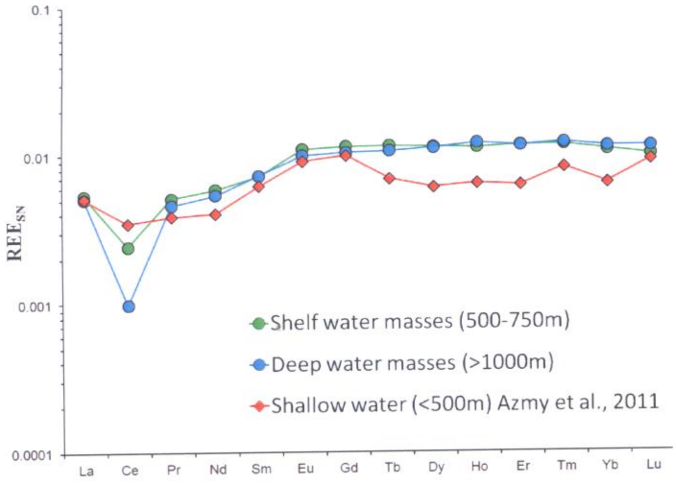

Fig. 2. Mean REE_{SN} patterns of the shelf and deep-water masses revealed by articulated brachiopods, and the REE_{SN} pattern of shallow water articulated brachiopods (<500m) of Azmy et al. (2011).

Four brachiopod populations from the shelfs of the Irminger Basin and Denmark Strait (North Atlantic) and from the Lau and Colville Arcs (South Pacific) display a mean REE_{SN} pattern of gradual enrichment with increasing atomic number punctuated by negative Ce excursions (Fig. 2). In contrast to the four above, the population from the Ross Sea (Southern Ocean) is relatively depleted in ΣREE reflecting local sea ice formation and consequent down-flow of saline water. Although similar in pattern to the four shelf populations, the REE_{SN} trend of the five deep-water brachiopod populations from the Venezuela Basin (Caribbean Sea), Iceland Basin (North Atlantic) and from the Kermadec Arc, Havre Trough and Northland Plateau (South Pacific) is more pronounced as well as its Ce excursion is more prominent (Fig. 2). Furthermore two populations from the Irminger Basin and Canary Islands are influenced by local environmental parameters such as deep convection and the remineralization of bottom sediments enhanced by turbidity current flows, respectively. Overall, the REE patterns of the shelf and deep-water brachiopod populations are similar to that of open ocean seawater, but remarkably different to that of shallow water counterparts.

Acknowledgements: We thank the National Institute of Water and Atmospheric research in New Zealand (NIWA) for supplying us with some of the brachiopods, and NSERC for financial support to UB.

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A Katian (Late Ordovician) minute *Foliomena* fauna from the Sibumasu paleoplate

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