

Additional file

This file contains Table S1 and Figures S1–S8.

Table S1 v_1 peak center position (peak center) and FWHM of the studied brachiopod shells

Sample ID	Species	n	Min.	Max.	Average	SD
Peak center						
Modern shells						
BL_1v, 2v	<i>Basiliola lucida</i>	111	1088.53	1088.74	1088.63	0.03
TCr100_1v, 2v	<i>Terebratulina crosseii</i>	42	1088.47	1088.78	1088.63	0.09
TCr70_1v, 2v, 3v	<i>Terebratulina crosseii</i>	71	1088.34	1088.83	1088.61	0.09
TCo100_1v, 2v, 3d	<i>Terebratalia coreanica</i>	75	1088.32	1088.77	1088.58	0.09
LB100_1v, 2v, 3d	<i>Laqueus blanfordi</i>	79	1088.37	1088.80	1088.54	0.08
LB70_1v	<i>Laqueus blanfordi</i>	30	1088.43	1088.69	1088.56	0.06
LR100_1v, 2v, 3d	<i>Laqueus rubellus</i>	91	1088.33	1088.70	1088.54	0.05
Fossil shells						
SMTTCo3–5	<i>Terebratalia coreanica</i>	84	1088.42	1088.83	1088.59	0.08
MNTCo1–3	<i>Terebratalia coreanica</i>	144	1088.39	1088.88	1088.56	0.09
MNLR1–3	<i>Laqueus rubellus</i>	187	1088.47	1088.91	1088.61	0.07
TY	<i>Tylopecta yangtzeensis</i>	88	1088.52	1088.91	1088.73	0.08
FWHM						
Modern shells						
BL_1v, 2v	<i>Basiliola lucida</i>	111	1.94	2.59	2.21	0.06
TCr100_1v, 2v	<i>Terebratulina crosseii</i>	42	2.96	7.18	3.81	0.75
TCr70_1v, 2v, 3v	<i>Terebratulina crosseii</i>	71	2.96	7.30	3.84	0.79
TCo100_1v, 2v, 3d	<i>Terebratalia coreanica</i>	75	2.36	5.55	3.19	0.60
LB100_1v, 2v, 3d	<i>Laqueus blanfordi</i>	79	2.67	5.10	3.29	0.48
LB70_1v	<i>Laqueus blanfordi</i>	30	2.71	4.60	3.17	0.40
LR100_1v, 2v, 3d	<i>Laqueus rubellus</i>	91	2.41	4.70	2.88	0.34
Fossil shells						
SMTTCo3–5	<i>Terebratalia coreanica</i>	84	2.20	4.07	2.64	0.31
MNTCo1–3	<i>Terebratalia coreanica</i>	144	2.10	3.61	2.49	0.27
MNLR1–3	<i>Laqueus rubellus</i>	187	1.96	3.77	2.43	0.32
TY	<i>Tylopecta yangtzeensis</i>	88	2.07	3.14	2.66	0.24

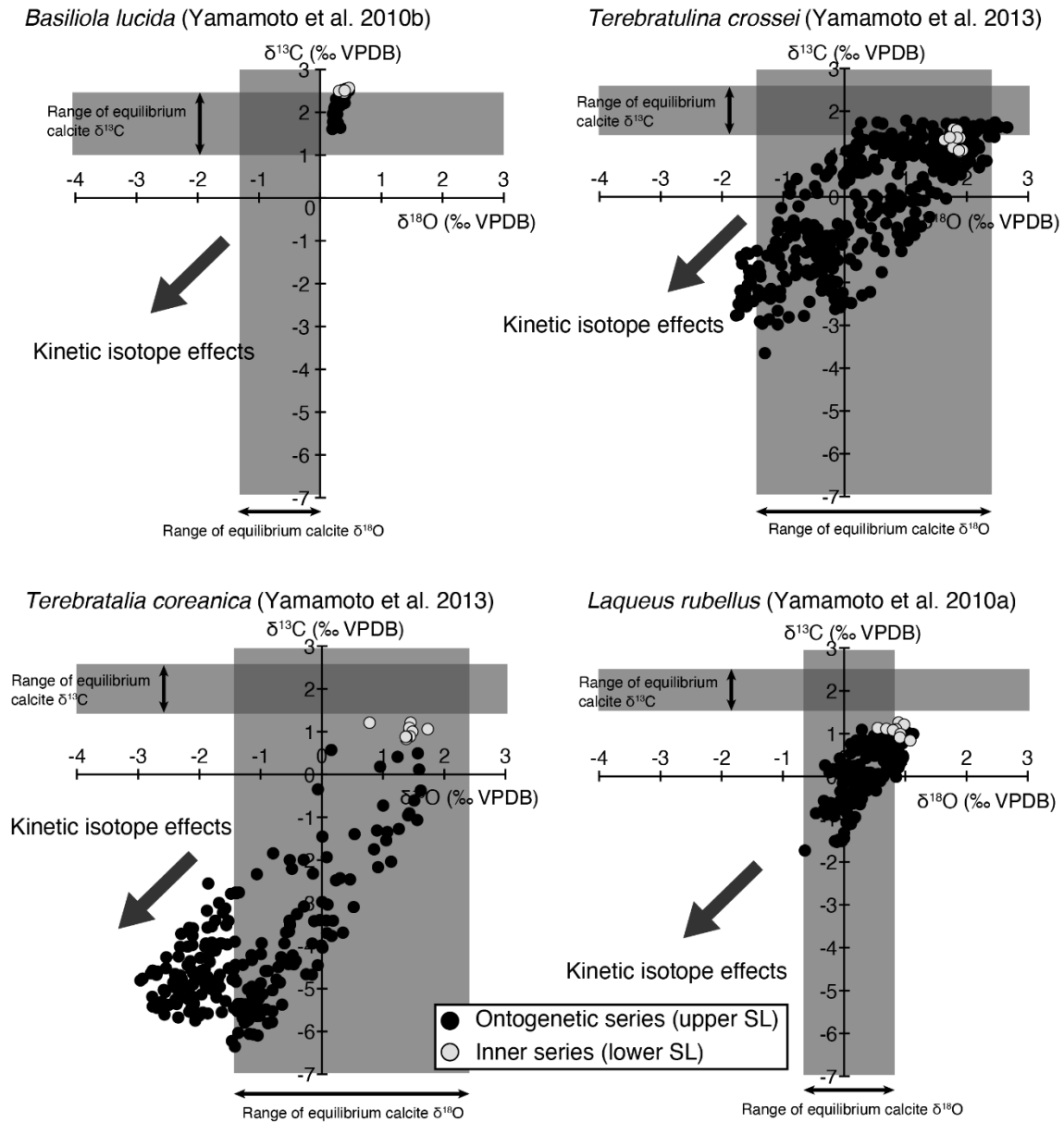


Fig. S1 Cross plot of $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ of four modern brachiopod species: *Basiliola lucida* (Yamamoto et al., 2010b), *Terebratulina crosseii* (Yamamoto et al. 2013), *Terebratalia coreanica* (Yamamoto et al. 2013), and *Laqueus rubellus* (Yamamoto et al. 2010a). Shaded areas represent estimated ranges for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of calcite precipitated in isotopic equilibrium with ambient seawater. The terms “ontogenetic series” and “inner series” follow Auclair et al. (2003). For a schematic overview of how these sampling categories relate to the shell portions analyzed in this study, see Fig. S2

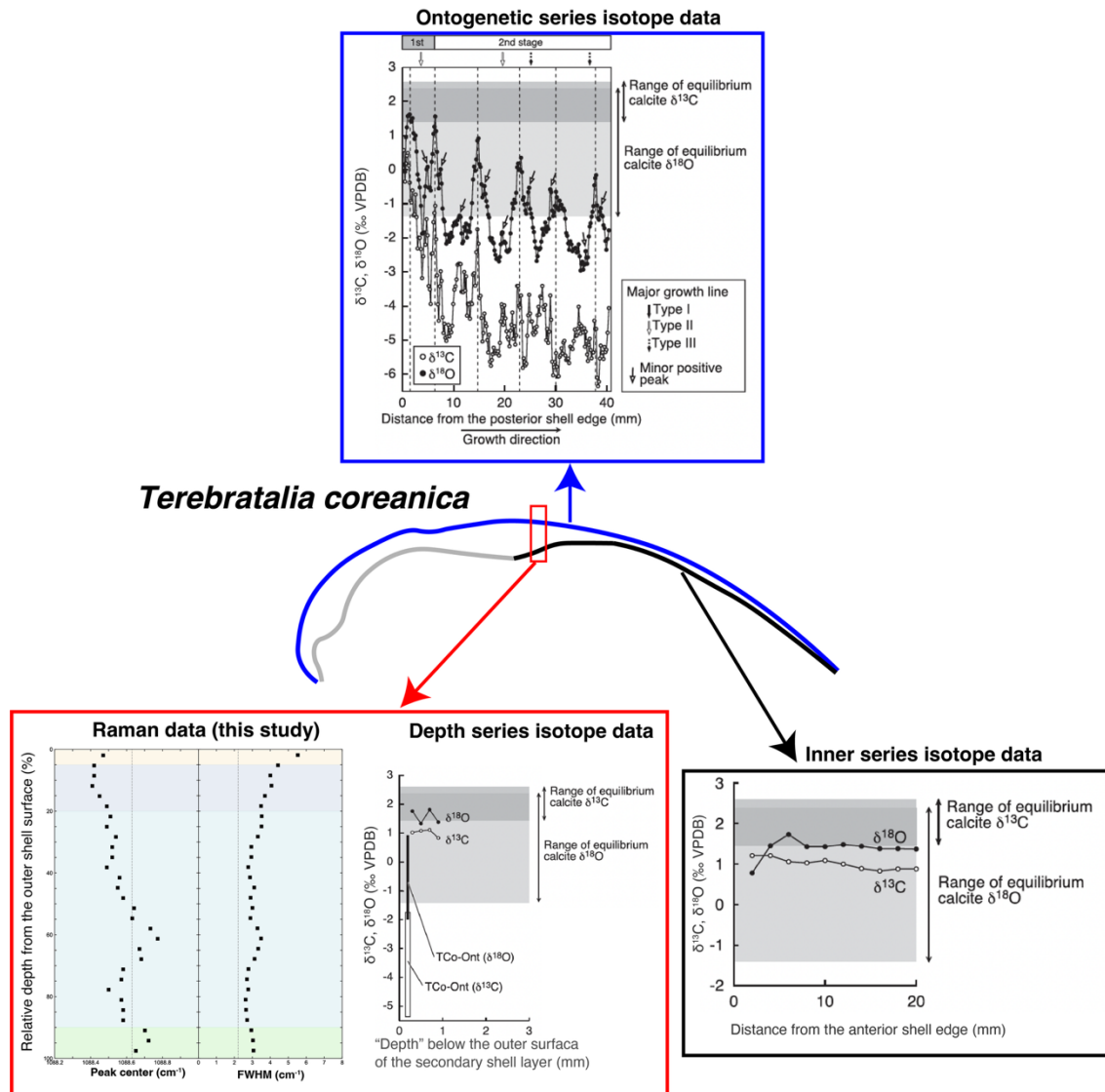


Fig. S2 Schematic diagram illustrating differences in isotope profiles between sampling transects using *T. coreanica* shells as examples (profiles from Yamamoto et al. 2013). Also shown is a location where a depth profile of Raman data was acquired in this study, along with the corresponding profiles

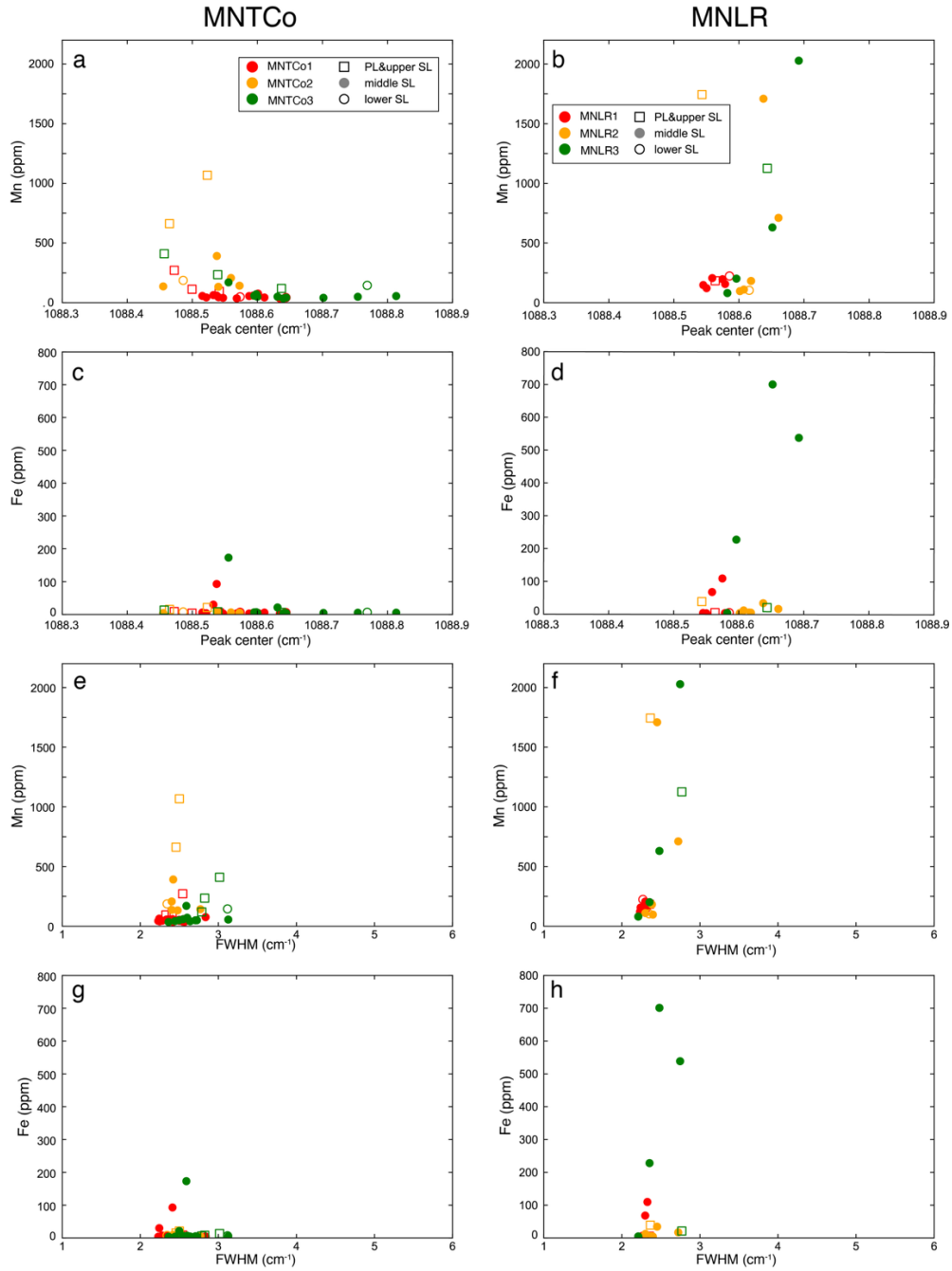


Fig. S3 Cross plot of Raman data (peak center and FWHM) vs. metal element (Mn, Fe) concentrations in studied Pliocene *T. coreanica* (left panels) and *L. rubellus* shells (right panels). **a, b** Peak center vs. Mn concentration. **c, d**, Peak center vs. Mn concentration. **e, f** FWHM vs. Mn concentration. **g, h** FWHM vs. Fe concentration. We processed the Raman data to match the spatial resolution of the microsampling for metal element analysis, calculating averages at each relative depth. Open squares represent data from the primary shell layer (PL) and upper secondary shell layer (upper SL; 0–20% relative depth). Colored solid circles denote data from the middle and lower secondary shell layers (middle and lower SL; 20–100% relative depth).

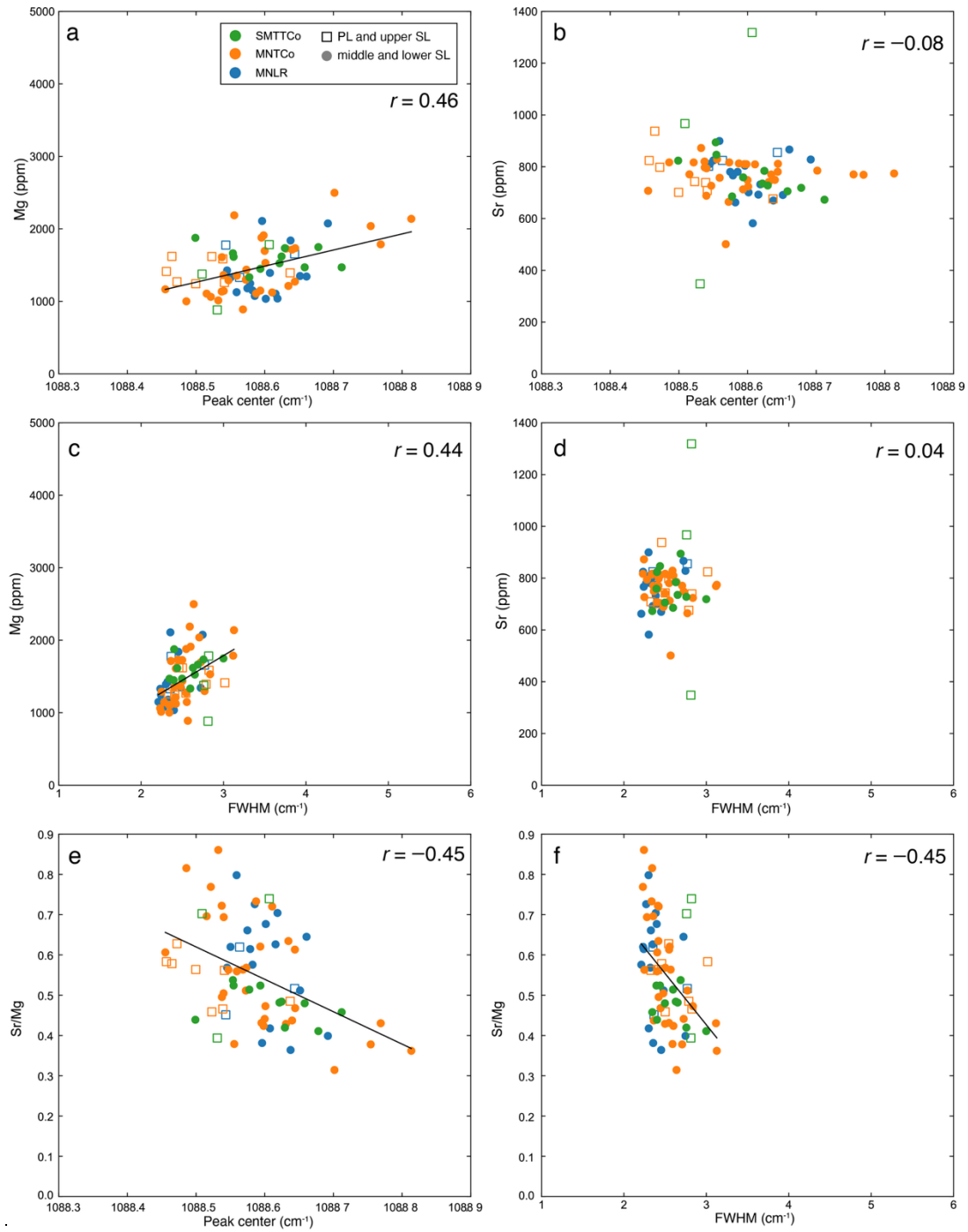


Fig. S4 Cross plot of Raman data (peak center and FWHM) vs. metal element (Mg, Sr) concentrations in studied Pliocene *T. coreanica* and *L. rubellus* shells. **a** Peak center vs. Mg concentration. **b** Peak center vs. Sr concentration. **c** FWHM vs. Mg concentration. **d** FWHM vs. Sr concentration. **e** Peak center vs. Sr/Mg. **f** FWHM vs. Sr/Mg. We processed the Raman data to match the spatial resolution of the microsampling for metal element analysis, calculating averages at each relative depth. For symbols, see Fig. S3

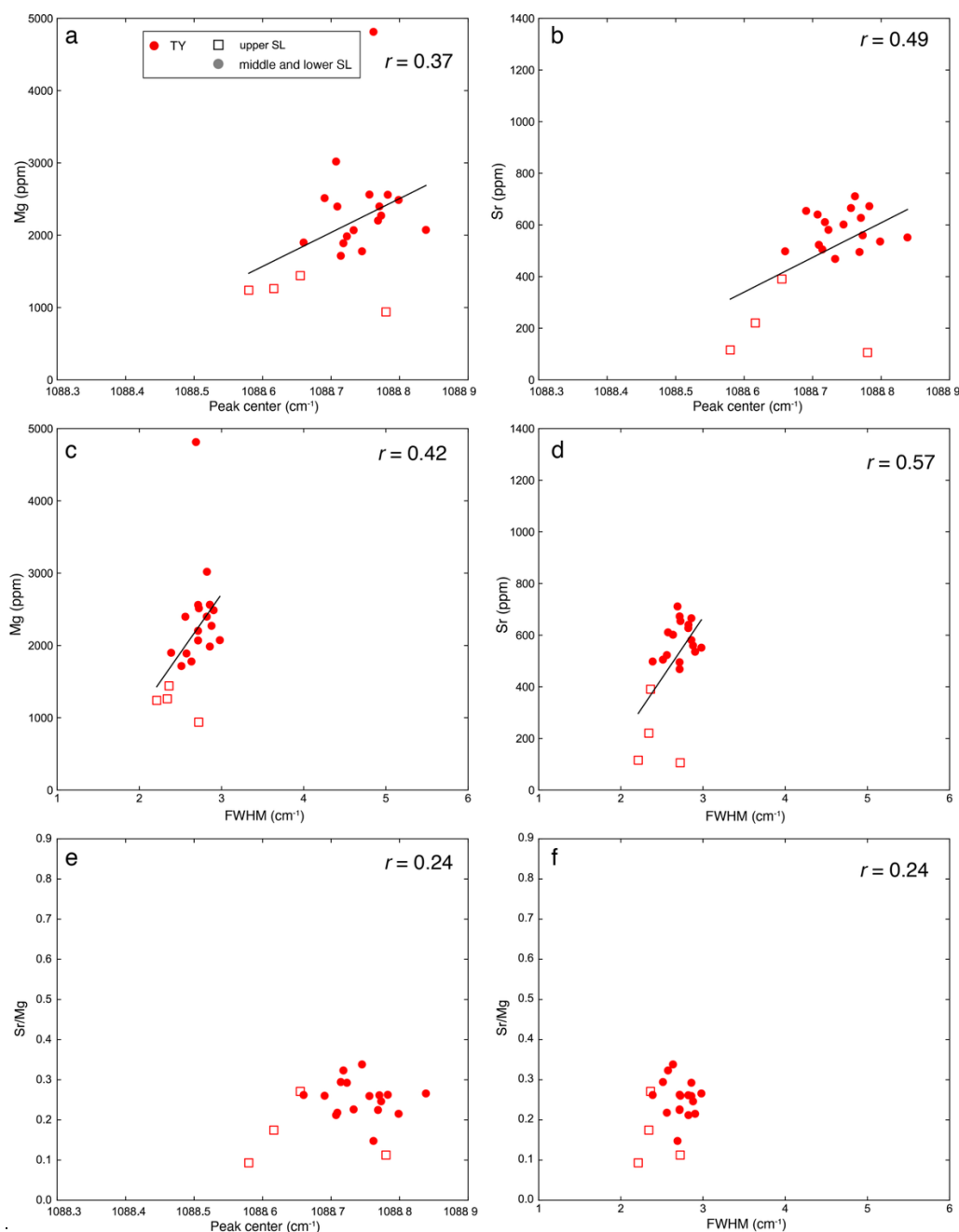


Fig. S5 Cross plot of the Raman data (peak center and FWHM) vs. metal element (Mg, Sr) concentrations for the studied Permian *Tyloplecta yangtzeensis* shell. **a** Peak center vs. Mg concentration. **b** Peak center vs. Sr concentration. **c** FWHM vs. Mg concentration. **d** FWHM vs. Sr concentration. **e** Peak center vs. Sr/Mg. **f** FWHM vs. Sr/Mg. We processed the Raman data to match the spatial resolution of microsampling for the metal element analysis and calculated their averages at each relative depth. For symbols, see Fig. S3

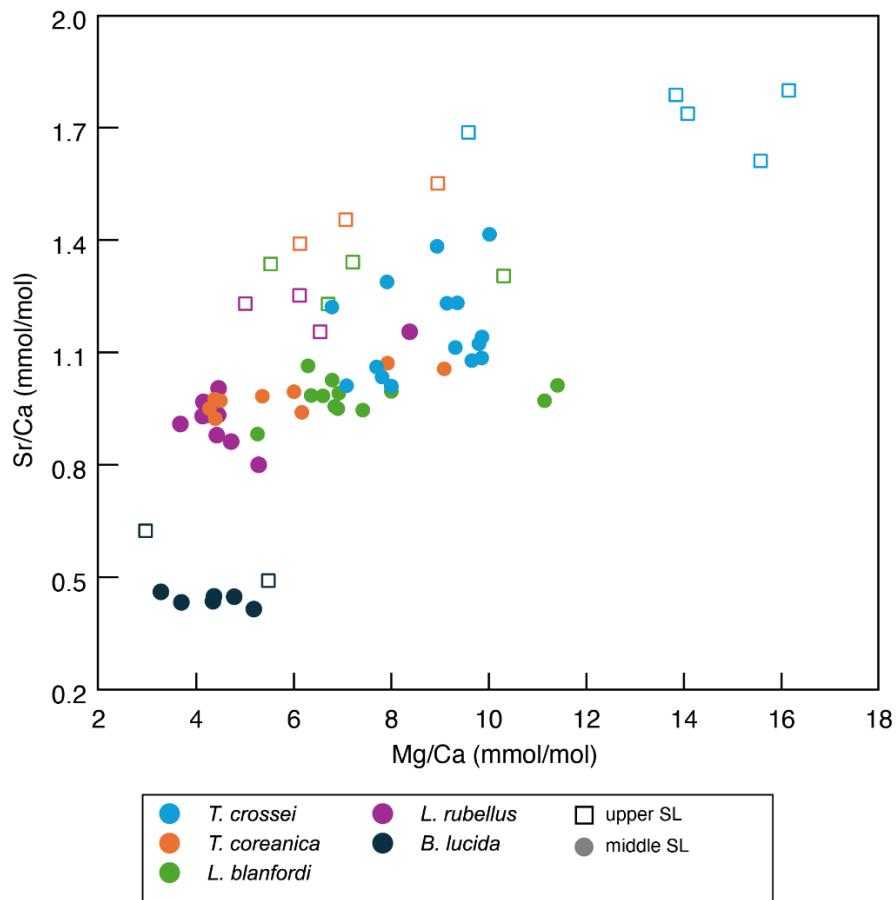


Fig. S6 Cross plot of Mg/Ca vs. Sr/Ca in the studied modern brachiopod shells. Open squares represent data from the primary (PL) and upper secondary (upper SL) shell layers (0–20% relative depth). Colored solid circles denote data from the middle and lower secondary shell layers (middle and lower SL) (20–100% relative depth)

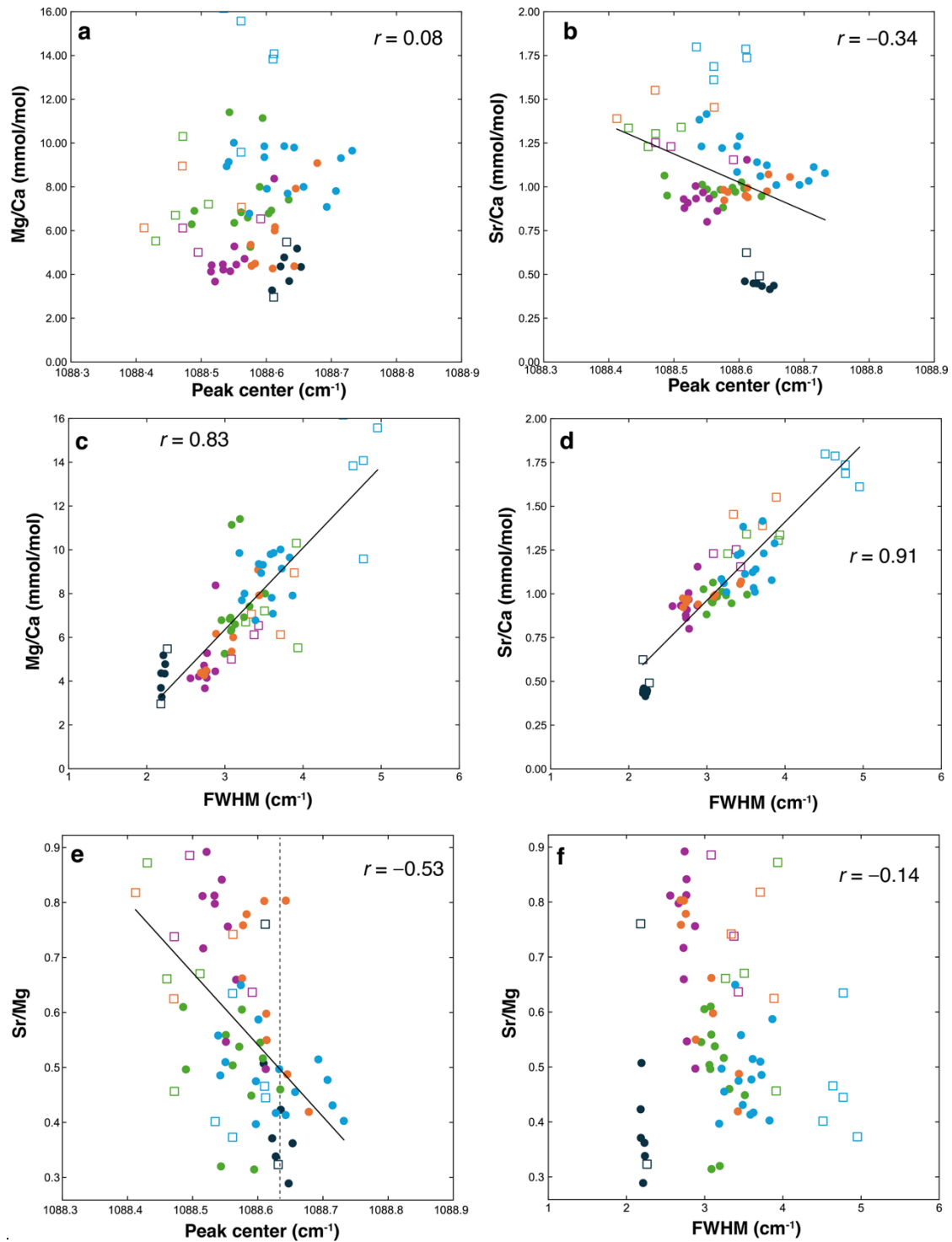


Fig. S7 Cross plot of Raman data (peak center and FWHM) vs. Me/Ca (Mg, Sr). **a** Peak center vs. Mg/Ca. **b** Peak center vs. Sr/Ca. **c** FWHM vs. vs. Mg/Ca. **d** FWHM vs. Sr/Ca. **e** Peak center vs. Sr/Mg. **f** FWHM vs. Sr/Mg. We processed the Raman data to match the spatial resolution of the microsampling for metal element analysis, calculating averages at each relative depth. For the symbols, see the caption for Fig. S6

Terebratulina crosseii

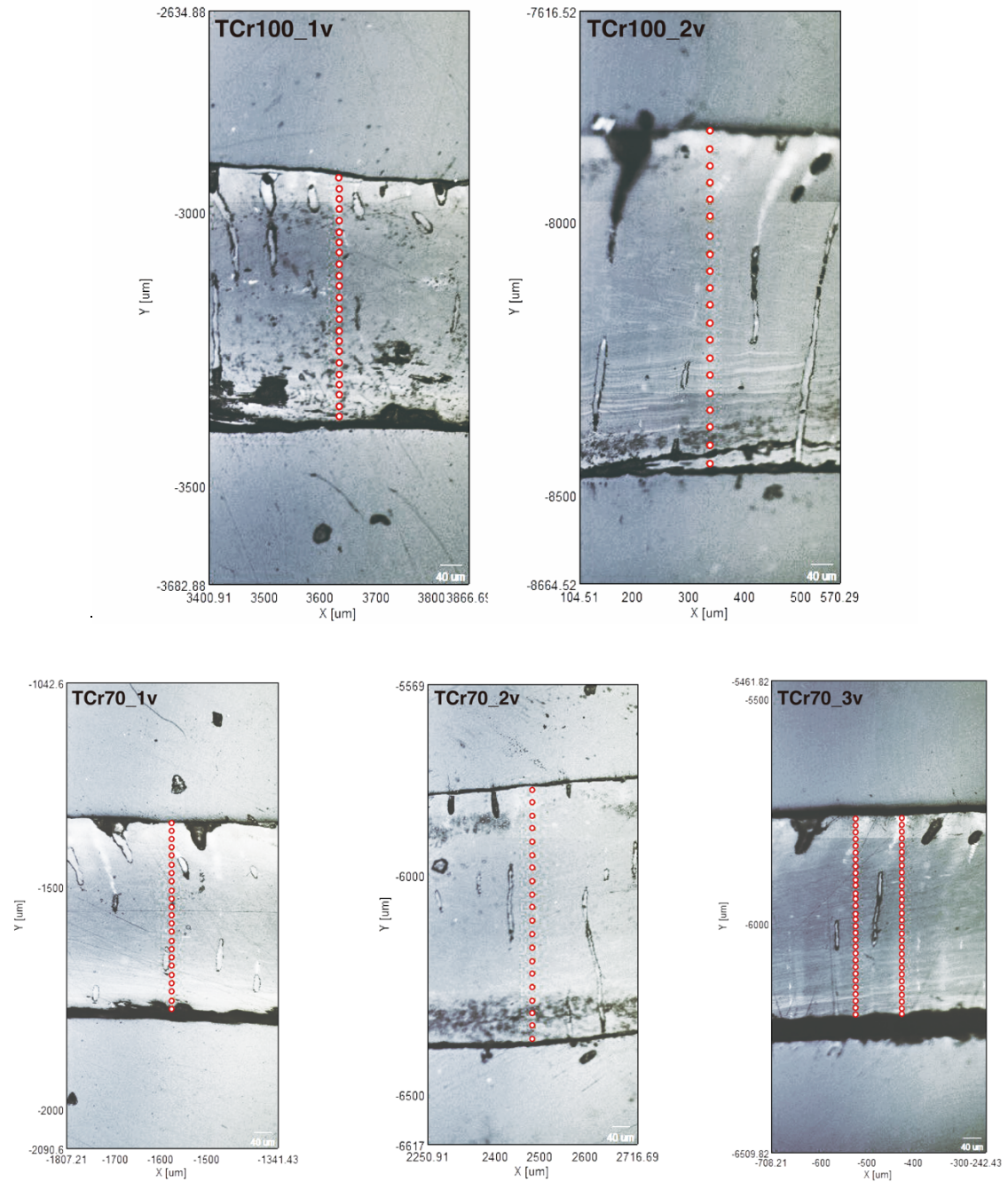


Fig. S8 Optical microscope images of the cross-sections of the studied brachiopod shells. The red dotted lines represent the transects along which depth-series Raman data were obtained.

Terebratalia coreanica

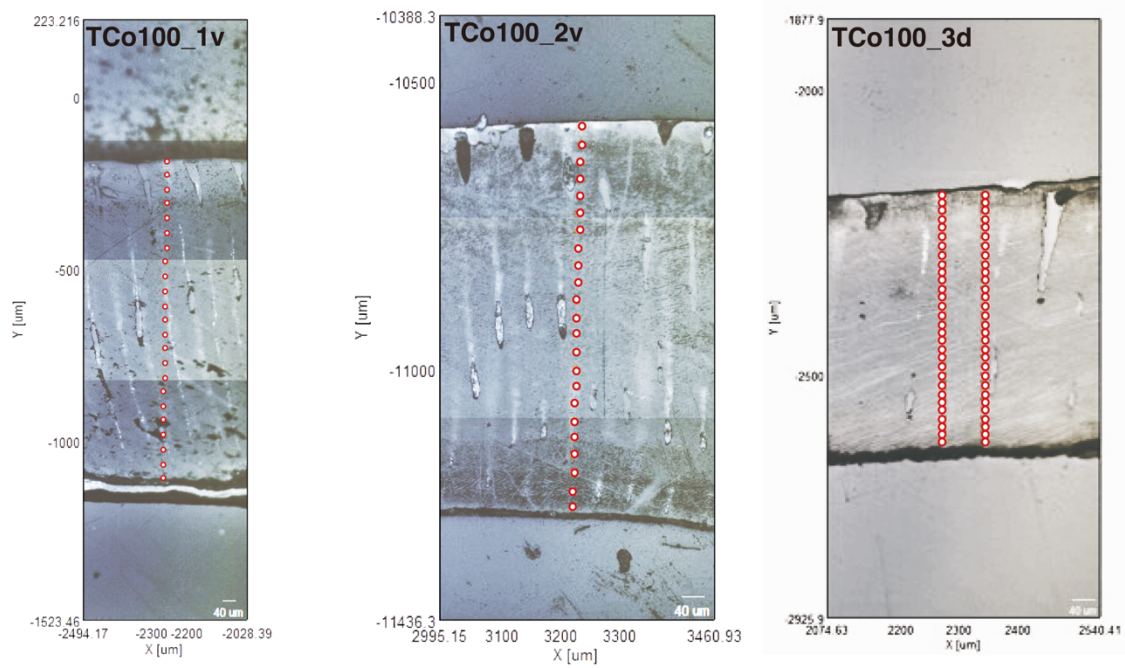


Fig. S8 (continued)

Laqueus blanfordi

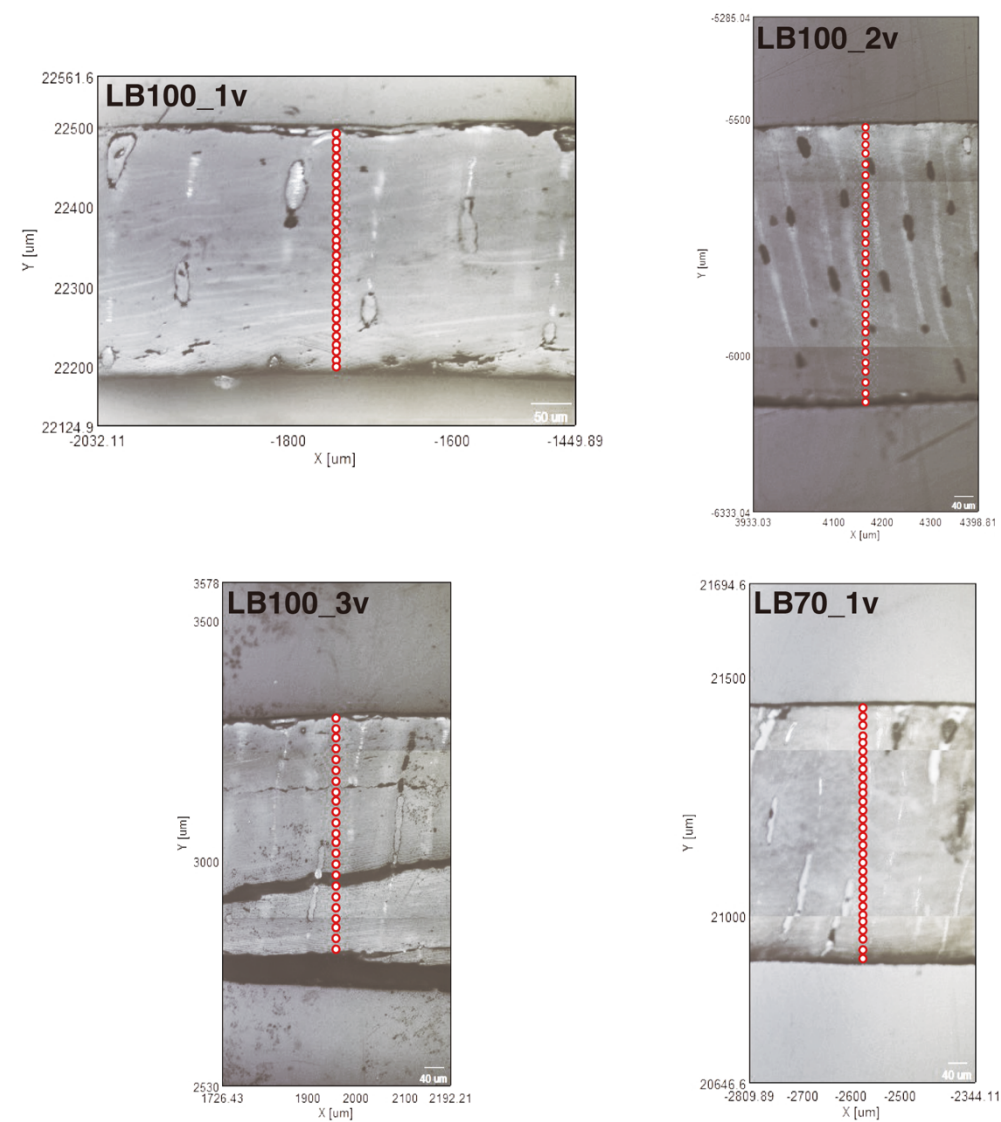


Fig. S8 (continued)

Laqueus rubellus

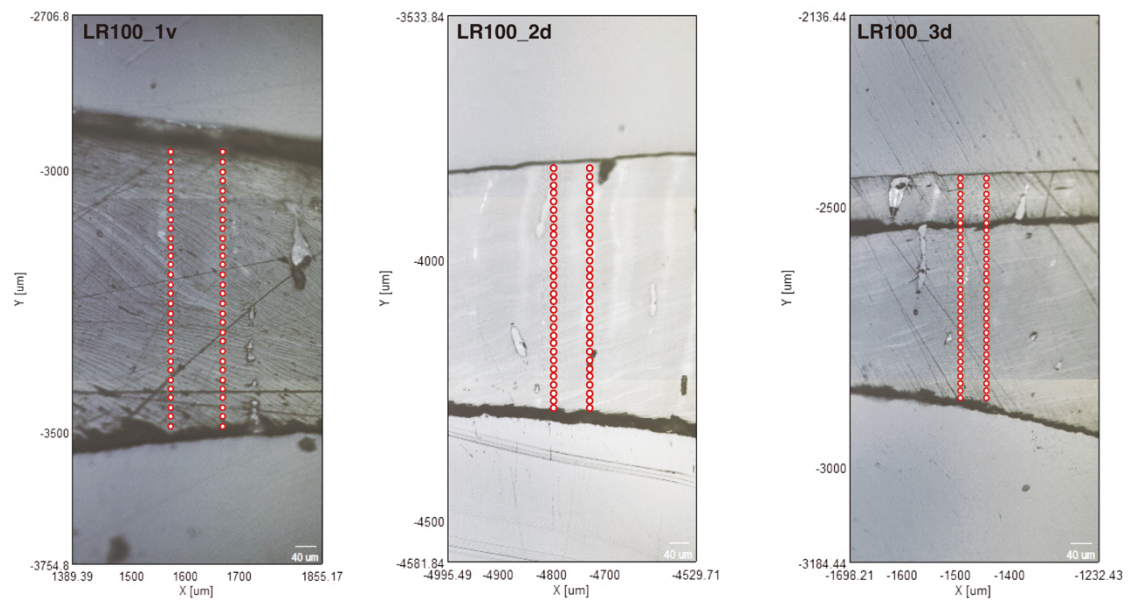


Fig. S8 (continued)

Basiliola lucida

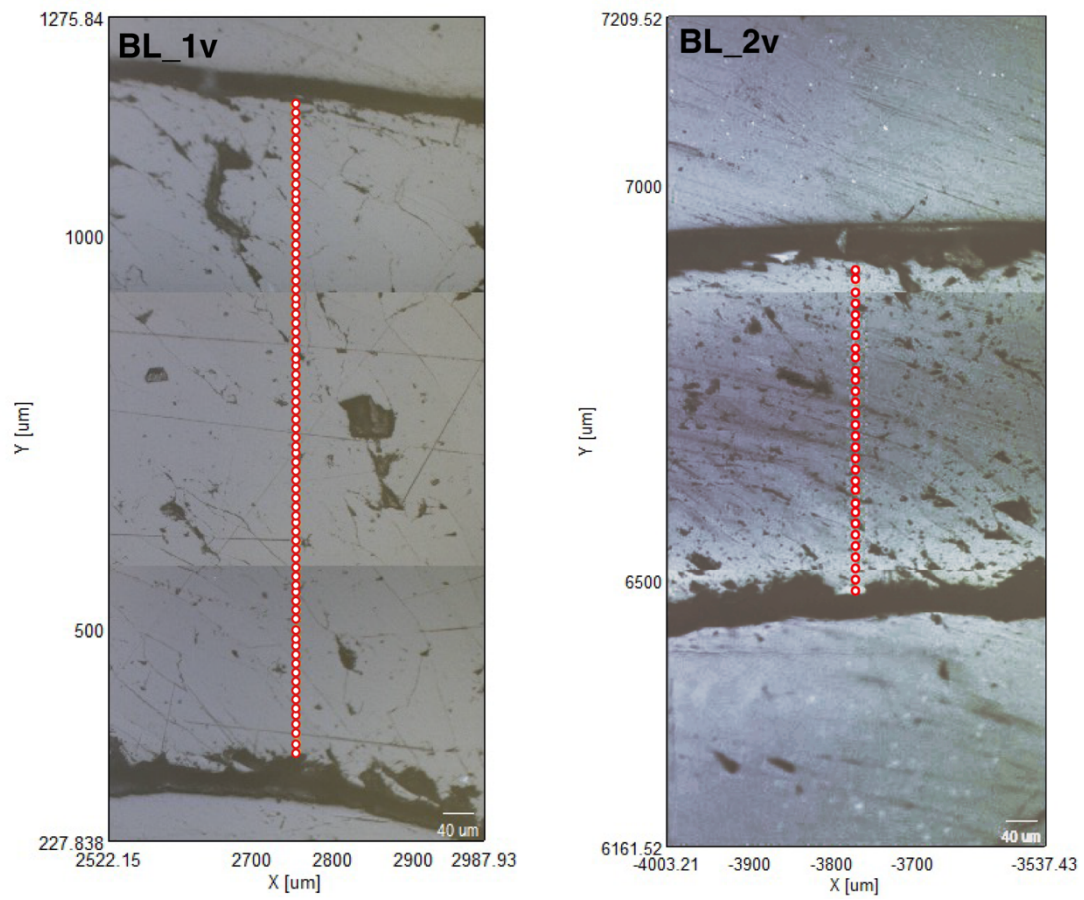


Fig. S8 (continued)

Terebratalia coreanica

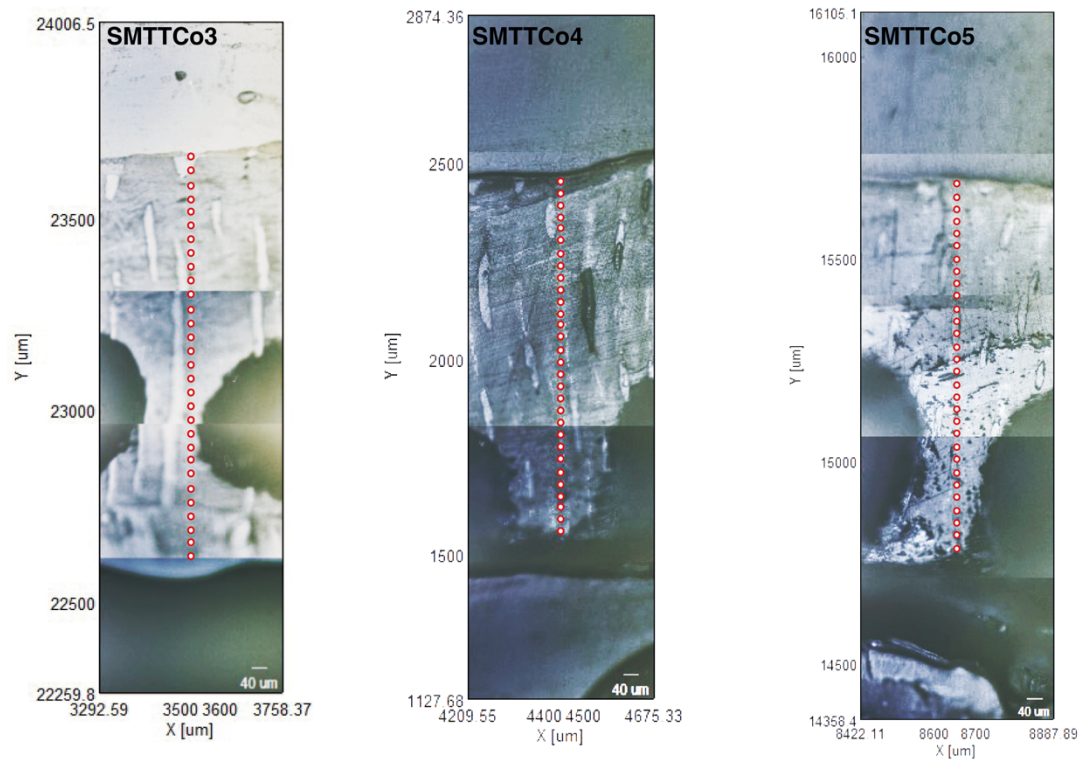


Fig. S8 (continued)

Terebratalia coreanica

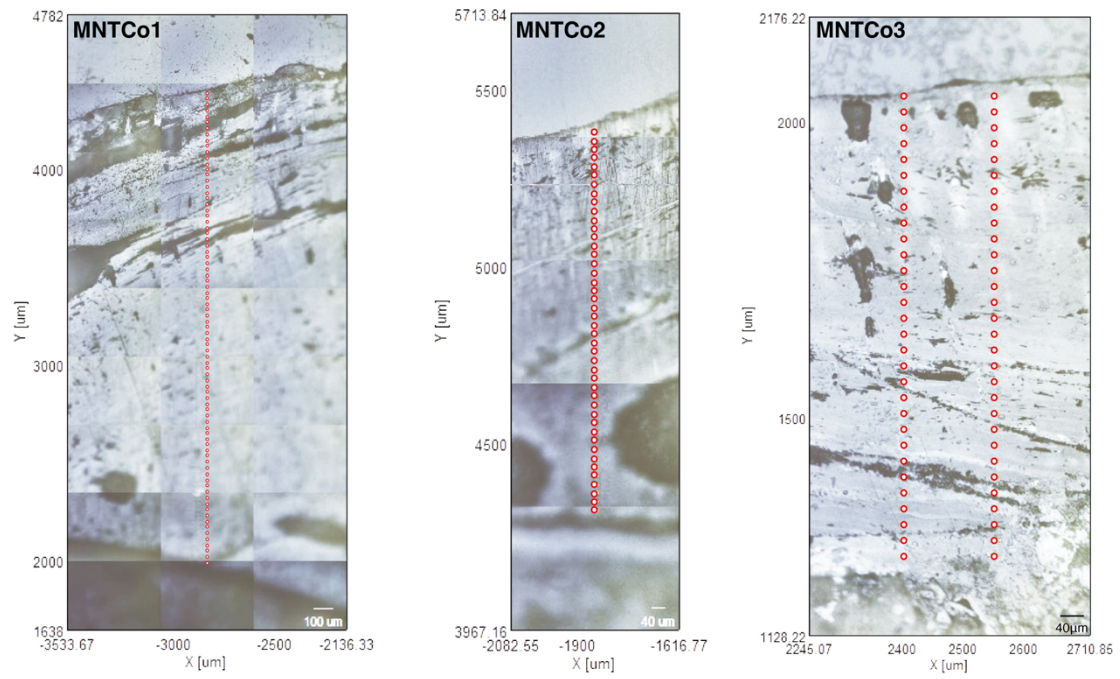


Fig. S8 (continued)

Laqueus rubellus

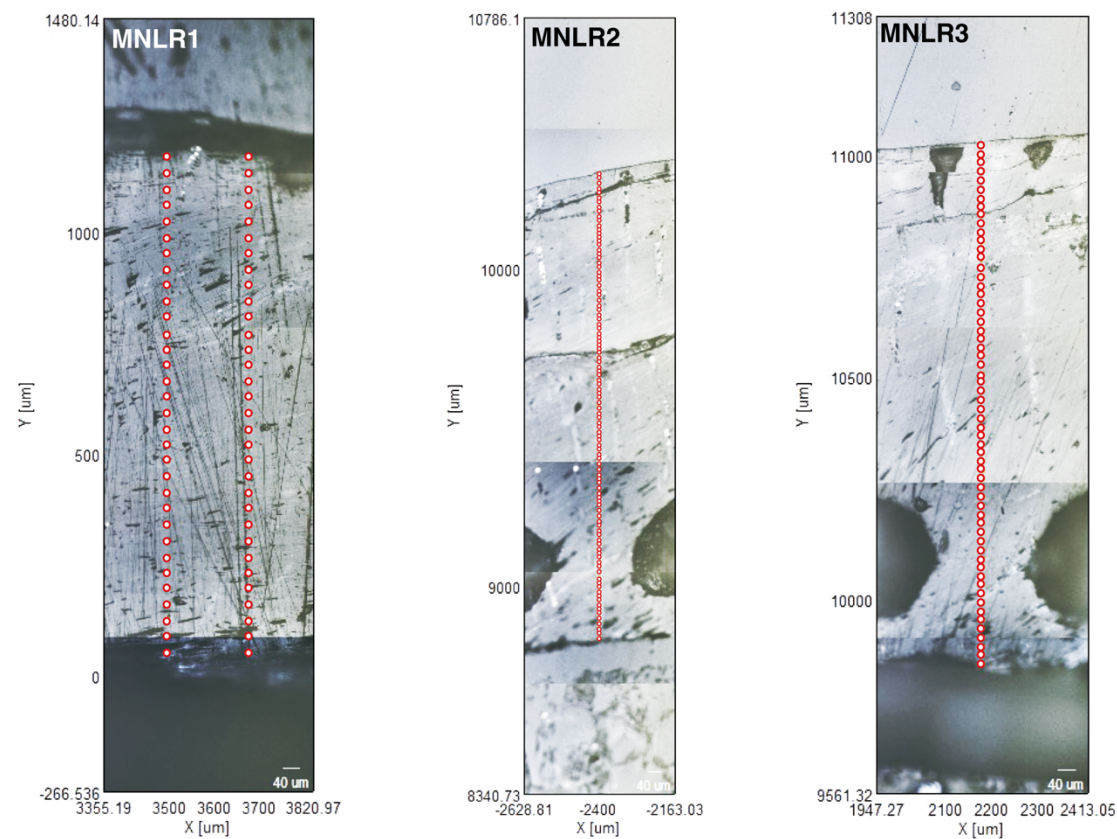


Fig. S8 (continued)

Tyloplecta yangtzeensis

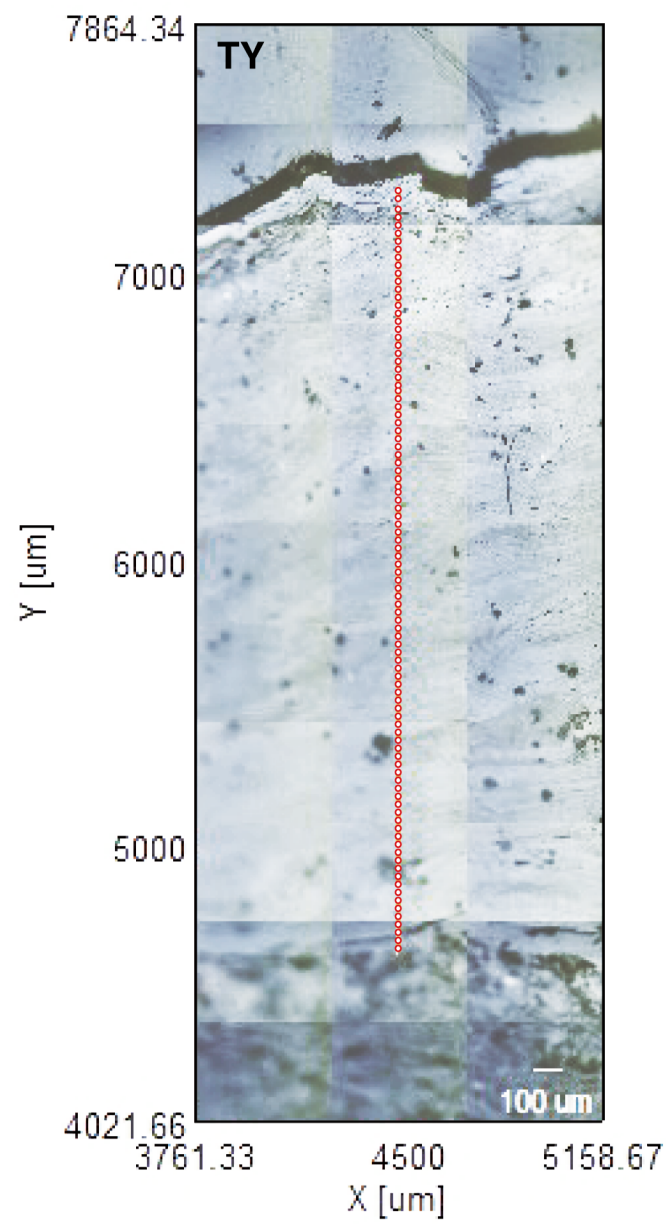


Fig. S8 (continued)