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Is Mid-Late Paleozoic ocean-water chemistry coupled with epeiric seawater isotope records?

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SUPPLEMENTARY INFORMATION

Methods

A total of 42 samples (7 – whole rock/matrix: mAC); 35 – brachiopods: bLMC) from Japan and China were examined for this study. The biogenic components were manually separated from their enclosing host rock, cleaned and powdered for chemical analysis. Trace chemistry was determined on a Varian 400P atomic absorption spectrophotometer. The accuracy and precision of results relative to NBS 633 was for Ca (1.00, 3.49), Mg (1.13, 2.86), Sr (2.08, 6.44), Mn (2.42, 2.95), and Fe (3.39, 5.16) relative percent, respectively. A subset of samples was analyzed for carbon, oxygen (Memorial University) and strontium isotopes (Ruhr University – Bochum). The C and O isotope results are expressed as delta permil relative to PDB. The precision and accuracy of analyses are better than 0.05 ‰ and 0.1‰, respectively (NBS 19-IAEA). Processing for strontium isotope values followed standard analytical procedures for carbonate powders. Strontium isotope results of samples were adjusted to an average value of 0.710247 relative to NBS 987. All results are presented in Appendix 1, and the data set from China was supplemented by results of Lee and Wan, 2000 (uppermost horizons of Stratum 120).

Diagenetic Evaluation

The preservational integrity of carbonates is paramount in using geochemical results for constructing trends of a global importance. A multi-faceted approach is used to evaluate the integrity of biogenic and abiogenic allochems, including a visual inspection of diagenetic alteration (e.g., discoloration – nacreous shell luster turning dull/white; fractures filled with cement), a microstructural evaluation of internal shell features by scanning electron microscope, trace element re-distribution and divergence of isotope values from 'normal' parameters (e.g., Brand and Veizer, 1980, 1981; Marshall, 1992; Banner and Kaufman, 1994; Brand, 2004).

The microstructures of two specimens showing the whole spectrum of preservation/alteration are depicted in Supp. Fig. DR1. Plate A shows that the fibers and possibly the prisms of the secondary and tertiary layer in a specimen of *Isogramma millepunctata* (OMI-374) have been replaced by diagenetic coarse-mosaic calcite. Plate B is an example of preservation of both the fibers of the secondary layer (upper portion of scan) and the prisms of the tertiary layer (lower portion) in a *Neospirifer* sp. (OMI-394; Supp. Fig. DR1). These two SEM scans are typical of the preservation, in a majority, and alteration observed in the specimens from Japan (this study) and China (cf. Lee and Wan, 2000).

Diagenesis of carbonate allochems leads to increases in Mg, Mn and Fe and concomitant decreases in Sr contents if alteration proceeded in a partly-open to open system controlled by meteoric water (cf. Brand and Veizer, 1980; Brand, 2004). In such a diagenetic system, the carbon and oxygen isotope values of the pristine material tend to be more positive than that of their altered counterparts (cf. Brand and Veizer, 1981).

Identification of preserved and altered specimens is followed with the additional testing of trace element and isotope trends. Supp. Fig. DR2 shows the chemical trends for samples from the *Fusulina-Fusulinella biconica* Zone (Moscovian) of the Akiyoshi Limestone, Akiyoshi Terrane sampled at OMI, Japan (Tazawa, 2007). Brachiopod samples deemed preserved cluster closely about sample OMI-394 for Sr and Mg, whereas altered brachiopods and matrix/whole rock show decreasing Sr contents with increasing Mg values with progressive diagenetic alteration (Supp. Fig. DR2A). In contrast are the trends for Mn and Fe with relatively low values of both recorded in the pristine material and concomitant higher contents in diagenetically altered samples and material (Supp. Fig. DR2B). The overall small change in Mn and Fe contents speaks to the fact that probably water other than strictly meteoric water was responsible or the driving force for the diagenetic alteration of the carbonate materials from Japan (cf. Walter et al., 1993; work in prep).

The stable isotope (carbon and oxygen) trends follow the expected decrease with increasing diagenetic stabilization in a partly closed system in the presence of some carbon dioxide-charged meteoric water and/or fluid of increased temperature (Supp. Fig. DR2C). The slight decreases in carbon isotope values may be the result of more complex diagenetic processes other than meteoric water such as pore water in the shallow burial environment (cf. Patterson and Walter, 1994; Walter et al., 2007) or some other fluids (waters) of unknown composition and origin.

The Sr isotope trends of pristine to diagenetic altered material observed in this study and the results of Nishioka et al., 1991) are in contrast to conventional observations, which suggest that diagenesis leads to more radiogenic values in the altered product (e.g., Veizer, 1989; Denison et al., 1994). However, in special circumstances, it has been observed that diagenesis actually has the opposite impact and leads to less radiogenic values in the diagenetically affected carbonate allochems (cf. Brand, 1991; Gröcke et al., 2007). This effect may be the outcome of diagenetic alteration in the presence of pore-waters in the shallow burial environment of platforms and/or shelves noted for mineralogy, trace chemistry and isotopes (Hu and Burdige, 2007; Swart and Eberli, 2005; Hover et al., 2001). More work will be done to explore this diametrically opposed trend of Sr isotope re-distribution with diagenesis on the full suite of carbonate allochems from the Mino and Akiyoshi terranes of Japan.

All samples in the appendix have been evaluated for their preservational status, and the pristine material and results are highlighted by sample #s in bold (Appendix 1), whereas altered material and results are in normal font.

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Supplementary Figure DR1. Photomicrographs of microstructures in brachiopods (bLMC) from the Akiyoshi Terrane at Omi, Japan. A is representative of the microstructural destruction (obliteration) by diagenetic processes of the features in specimen OMI-374; recrystallized calcite has replaced the original material. B shows the two-layer structure in a well-preserved specimen (OMI-394) from the same horizon as OMI-374. The layers show good fibers of the secondary layer, and prisms of the tertiary layer. SEM scans were taken with an AMRAY 1500 scanning electron microscope.

Supplementary Figure DR2. Diagenetic evaluation of brachiopods (bLMC) and whole rock/matrix (mAC) from the Akiyoshi Terrane, Japan. Scatter diagrams show the distribution of trace elements, stable isotopes and Sr isotopes with progressive diagenetic alteration of original carbonate allochems. A shows the distribution of Sr and Mg contents of preserved brachiopods (bLMC; including OMI-394), altered brachiopods (including OMI-374) and corresponding whole rock/matrix (mAC). B shows the distribution of Mn and Fe with progressive diagenetic alteration. C shows the enrichment in lighter isotope in both the carbon and oxygen isotope values with diagenetic alteration. D shows the change in strontium isotope values with diagenesis, in this case of less radiogenic values in the microstructurally (Supp. Fig. 1) and chemically altered samples (cf. Brand, 1991; Gröcke et al., 2007).

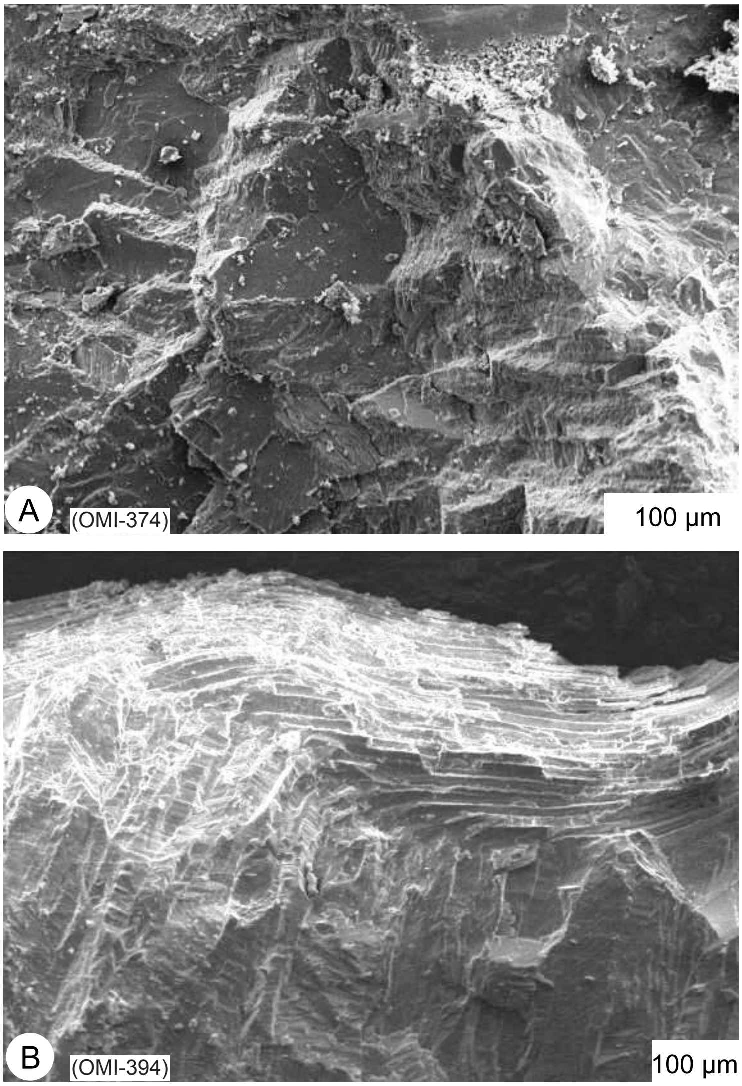

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Fig. 1

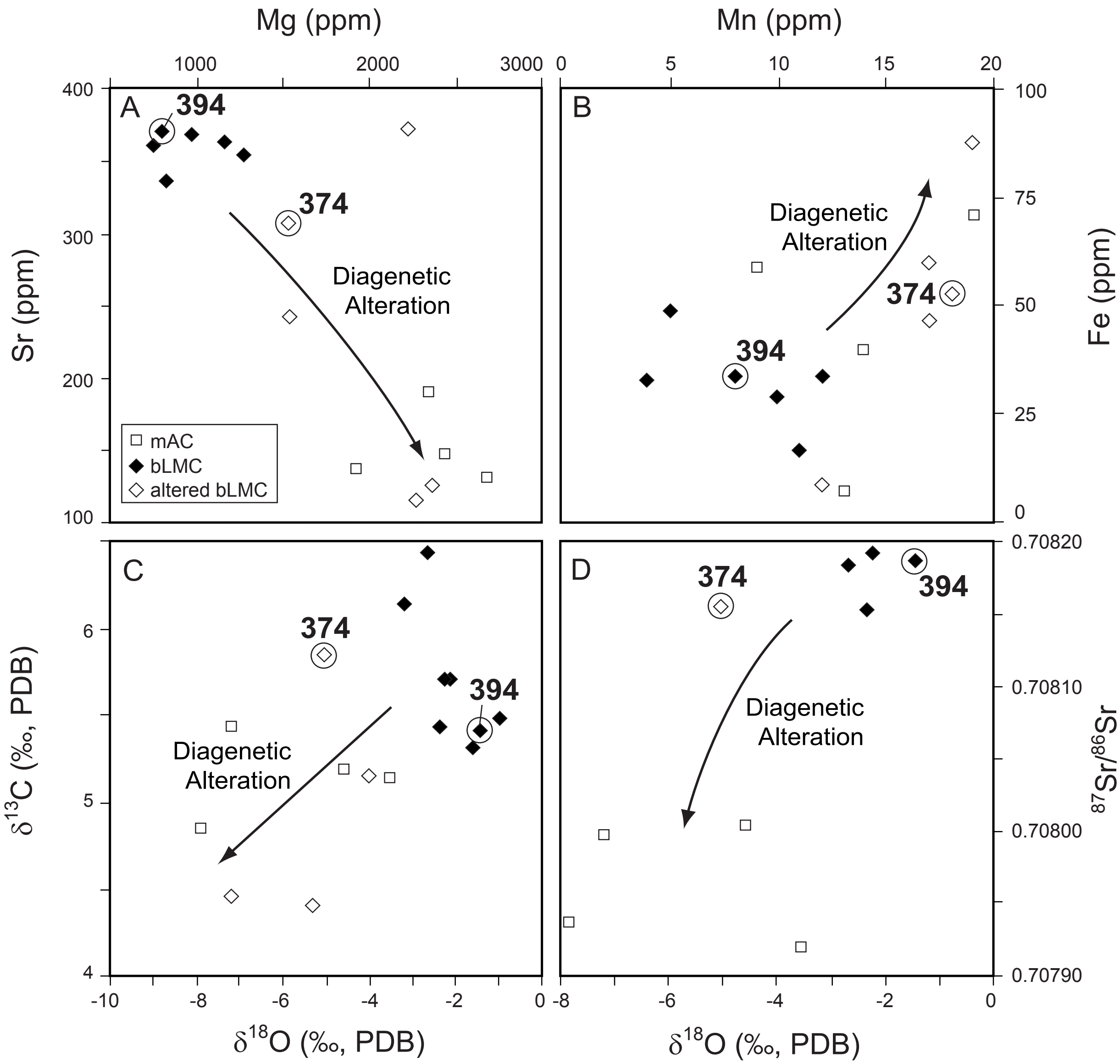

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Fig. 2

Appendix: Table DR1. Geochemistry of Permian and Carboniferous brachiopods and associated whole rock (matrix) from the Mino and Akiyoshi Terranes, Japan, and Devonian from South China.
Mineralogy (original): bLMC - biogenic low-Mg calcite, mAC - matrix (whole rock) Aragonite-Calcite. Sr isotope results adjusted to a mean value of 0.710247 relative to NBS 987.
Samples in **BOLD** are deemed to represent pristine values, based on optical, microstructural (SEM) observations, trace element trends (Sr, Mn, Fe), and concurrence of isotope values.

Sample #	species/mineralogy	locale	terrane	age	zone	Ca ppm	Mg ppm	Sr ppm	Mn ppm	Fe ppm	δ^{13}Cc ‰ VPDB	δ^{18}Oc ‰ VPDB	$^{87}Sr/^{86}Sr$
MINO3524-377m	whole rock/mAC	Akasaka	Mino	Kungurian	*Parafusulina*	384482	14000	174	28	56	3.60	-4.93	0.707324
-378	*Scacchinella gigantea/* bLMC	"	"	"	*kaerimizensis*	392467	1670	332	26	1	3.53	-3.95	
-379	"	"	"	"	"	393233	2014	329	24	5	3.50	-3.66	
-380	"	"	"	"	"	394498	1768	315	27	1	3.42	-4.07	0.707298
-382	*Scacchinella gigantea/* bLMC	"	"	"	"	396506	1614	331	29	1	3.74	-3.41	0.707274
-383	"	"	"	"	"	390154	1463	304	33	2	3.55	-3.52	
-384m	whole rock/mAC	"	"	"	"	382788	23264	190	76	111	3.49	-5.14	
NV382-368	*Martinia sp./* bLMC	Hiyomo	Mino	mid Artinskian	*Parafusulina yabei*						5.46	-5.12	0.707500
NV-B88-369	*Ledpidospirifer miyakei/* bLMC	"	"	"	"	392318	2434	449	156	102	3.39	-7.66	
OMI474-376m	whole rock/mAC	Omi	Akiyoshi	Moscovian	*Fusulina-Fusulinella*	392593	2680	130	13	7	5.14	-3.57	0.707919
-370	*Isogramma millepunctata/* bLMC	"	"	"	*biconica*						5.71	-2.24	0.708193
-371	"	"	"	"	"	389639	1538	244	12	9	5.71	-2.16	
-375	"	"	"	"	"	390501	2261	116	11	17	5.16	-3.98	
-372m	whole rock/mAC	"	"	"	"	388211	2427	147	19	71	4.85	-7.88	0.707938
-373	*Isogramma millepunctata/* bLMC	"	"	"	"	390895	1271	355	17	60	6.14	-3.19	
-374	"	"	"	"	"	390332	1527	308	18	53	5.85	-5.02	0.708155
OMI473-390	fine ribs, unid brach/bLMC	Omi	Akiyoshi	Moscovian	*Fusulina-Fusulinella*	391083	2217	372	19	88	4.47	-7.22	
-391	smooth, unid brach/bLMC	"	"	"	*biconica*	390537	2359	126	17	47	4.41	-5.29	
-392	*Neospirifer sp./* bLMC	"	"	"	"	390618	819	337	5	49	5.44	-2.33	0.708151
-393	"	"	"	"	"	395684	979	369	4	33	5.32	-1.63	
-394	"	"	"	"	"	391856	790	371	8	34	5.42	-1.46	0.708187
-395m	whole rock/mAC	"	"	"	"	391919	2344	190	9	59	5.18	-4.60	
-396	*Neospirifer sp./* bLMC	"	"	"	"	389859	741	362	10	29	5.49	-1.02	
-400	large dictyoclostus?/bLMC	"	"	"	"	390173	1153	364	12	34	6.45	-2.66	
-401m	whole rock/mAC	"	"	"	"	389160	1923	137	14	40	5.44	-7.22	0.707998
OMI382-361	*Gigantoproductus edelburgensis/* bLMC	Omi	Akiyoshi	late Visean	*Mediocris breviscula*	387234	1683	160	28	144	3.42	-7.83	
-362	"	"	"	"	"	387391	1617	212	24	210	3.29	-8.61	
-363	"	"	"	"	"	386596	1597	145	23	102	3.33	-8.79	
OMI382-364	"	"	"	"	"	387592	2146	237	23	133	3.27	-4.32	0.707805
-365	"	"	"	"	"	387328	2223	269	23	134	3.60	-4.52	0.707810
-366	"	"	"	"	"	391217	1754	174	19	154	3.98	-5.53	
OMI473-367	*Neospirifer* sp./bLMC	"	"	"	"	391370	1700	150	23	59	2.59	-11.35	
AKI-4	unid. brachiopod frag/bLMC	central	Akiyoshi	late Visean	"Uzura quarry"	394623	994	556	15	15	5.12	-2.68	
-5	"	Akiyoshi-	"	"	"	396147	1352	631	14	28	3.01	-3.34	
-6	"	dai	"	"	"	397949	1560	606	22	59	5.79	-2.19	0.708101
-7	"	Plateau	"	"	"	398625	1556	638	23	68	4.32	-2.44	
-8m	whole rock/mAC	"	"	"	"	391125	2819	202	11	34	4.32	-4.21	0.707911
-10	unid. brachiopod frag/bLMC	"	"	"	"	391579	1561	602	10	47	5.02	-3.36	0.708133
-11	"	"	"	"	"	389118	1390	650	14	58	5.55	-2.79	
-12	"	"	"	"	"	393478	1410	561	23	31	5.69	-2.45	0.708081
C-19	*Independatrypa lemma chen/* bLMC		South	mid-late	Strata 120	396319	693	498	41	127	-3.97	4.22	0.707767

C-21 **(part)**	*Desquamatia subspherica xian/* bLMC	China	Givetian	Strata 124	395090	2890	1099	21	86	-4.83	0.20	0.707791