Supplemental Material for

Methanogen microfossils and methanogenesis in Permian lake deposits

Funing Sun, Wenxuan Hu*, Xiaolin Wang, Jian Cao, Bin Fu, Haiguang Wu, and Shengchao Yang

This PDF file includes:

● **Geological Background**

● **Samples and Methods**

● **References**

● **Figures S1–S7**

Figure S1. Geological setting of the methanogen microfossils.

Figure S2. Carbonate beds and nodules within the upper Lucaogou Formation.

Figure S3. Energy dispersive X-ray spectrum of the deformed carbonaceous individual.

Figure S4. Typical XRD spectra of the microfossil-bearing dolomite.

Figure S5. Cross-plot of the $\delta^{13}\text{C}$ values of dolomite versus the microfossil numbers (groups 1 and 2) per square millimeter observed in each thin section.

Figure S6. Cross-plot of $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ values from different settings and ages.

Figure S7. Conceptual model of microbial methanogenesis in the Permian lake sediments.

● **Tables S1–S3**

Table S1. Diameter range statistics of the spheroidal methanogen microfossils.

Table S2. Bulk-rock $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and methanogen microfossil numbers per square millimeter in thin sections.

Table S3. *In situ* isotopic and elemental compositions of zoned dolomite and calcite.

1. Geological Background

During the early stages of the Middle Permian, affected by the closure and subsequent basement uplift of the West Bogda Trough, the southern Junggar region changed from a marine environment to a closed epicontinental offshore lacustrine environment (Wang et al., 2018). These regions subsequently received deposits in a rapidly subsiding, collisional foreland basin (Sharps et al., 1992), which developed (from bottom to top) into the Wulapo Formation, Jingjingzigou Formation, Lucaogou Formation, and Hongyanchi Formation during the Middle Permian (Fig. S1). The Lucaogou Formation can be subdivided into lower and upper members. The lower Lucaogou Formation consists of laminated mudstone, siltstone, and dolomitic sandstone (Fig. S1C). The upper Lucaogou Formation consists mainly of laminated and organic carbon-rich shale interbedded with dolomite and limestone beds and nodules (Fig. 4A; Figs. S1D and S2).

During the deposition of the Lucaogou Formation, the basement subsided and the lacustrine environment gradually changed to a semi-deep to deep lake (Carroll et al., 1992; Carroll, 1998; Wang et al., 2018). The organic-rich profundal mudstone facies of the Junggar–Turpan–Hami Basins cover an area of more than 900×300 km, which is comparable to the area of the Caspian Sea (Carroll and Wartes, 2003). This unit was deposited in a moderately saline to brackish water environment (Tao et al., 2013; Liang et al., 2014) at middle palaeolatitudes (39–43° N; Carroll et al., 1992; Sharps et al., 1992). An extensive faunal assemblage of non-marine ostracods and molluscs has been reported (Zhang, 1981; Carroll, 1998).

The upper Lucaogou Formation is the focus of this study and contains abundant spheroidal microfossils interpreted as methanogens. The oil shale of the upper Lucaogou Formation in the Urumqi–Jimsar area is distributed at the northern foot of the Bogda Mountains

and is 134 km long and 10–20 km wide (Bai, 2008). The Hongyanchi section (43°43'53" N, 87°39'37" E) is located at the northern foot of the West Bogda Mountains on the southern margin of the Junggar Basin (Figs. S1A and S1B). The total thickness of the upper Lucaogou Formation is ~400 m at the Hongyanchi section. These sequences are rich in organic matter, with up to 20.78% total organic carbon, and were deposited in a persistently deep, stratified, and anoxic lake that may have exceeded 100 m in depth (probably up to several hundred meters; Carroll et al., 1992; Carroll, 1998). The microfossil-bearing dolomite is restricted to the upper Lucaogou Formation and occurs as beds and lenticular nodules (Figs. S2A and S2B).

2. Samples and Methods

Sample collection

There are 38 preserved carbonate beds and nodules at the Hongyanchi section (43°43'53" N, 87°39'37" E), Urumqi, Xinjiang, northwestern China (Fig. S1). A total of 55 samples, including 49 dolomite samples and 6 limestone samples, were collected from this section of the upper Lucaogou Formation (Table S2).

Optical microscopy

Standard 30- μ m-thick, polished thin sections of each sample were examined using a Nikon ECLIPSE LV100N POL transmitted-light microscope equipped with a CCD camera to determine the petrological compositions of the carbonates and the morphological characteristics of the microfossils. This was undertaken at the School of Earth Sciences and Engineering, Nanjing University, China. In the light micrograph images, the abundances of methanogen microfossils (groups 1 and 2) were counted.

Scanning electron microscopy

A field-emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray spectrometer (EDS) was used to characterize the morphologies and mineral compositions of the microfossils. The samples were coated with a few nanometers of gold or platinum prior to the SEM observations. Analyses were carried out at the State Key Laboratory of Palaeobiology and Stratigraphy of Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences, using a TESCAN MAIA 3 FE-SEM with an accelerating voltage of 20 kV and a beam current of 10 nA. In the SEM images that used a secondary electron (SE) mode, the diameters of the well-exposed spheroidal microfossils were measured.

Powder X-ray diffraction

Powder X-ray diffraction (XRD) analyses of bulk samples were performed on a Rigaku Dmax Rapid II X-ray diffractometer at the State Key Laboratory for Mineral Deposits Research of Nanjing University, China. Analyses were carried out using a rotating anode Mo target X-ray source with an accelerating voltage of 50 kV and a beam current of 90 mA. Data processing and mineral identification were performed using the Jade 6.0 software. The relative abundances of dolomite and calcite in each bulk sample were estimated from the intensities of the (104) peaks (Zevin, 1977). The degree of order of dolomite was calculated following: $R = I(015)/I(110)$, where I is the intensity of the (015) or (110) peak (Graf and Goldsmith, 1956).

Electron microprobe analyses

Major elemental analyses of the carbonate minerals were performed on polished thin sections using a JEOL JXA-8100 electron microprobe analyzer (EMPA) at the State Key Laboratory for Mineral Deposits Research of Nanjing University, China. Analyses were carried out using an accelerating voltage of 15 kV, a beam current of 20 nA, and a beam spot diameter of 2 μm . All data were corrected using a standard ZAF program.

Bulk-rock C-O isotope analyses

Carbon and oxygen isotopes of bulk samples were measured using a Thermo Finnigan Delta V Plus continuous flow isotope ratio mass spectrometer (IRMS) at the State Key Laboratory for Mineral Deposits Research of Nanjing University, China. Approximately 80–120 µg of carbonate powder was dissolved with orthophosphoric acid at 70 °C for more than 12 h in a continuous flow sample preparation device (Gas Bench II) connected to the IRMS. All isotopic ratios are reported as per mil relative to the Vienna Pee Dee belemnite (V-PDB) reference. The internal precision (1SD) was less than ±0.1‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, and the external precision was better than ±0.5‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values.

In situ C-O isotope analyses

In situ carbon and oxygen isotopes were examined using secondary ion mass spectrometer (SIMS, SHRIMP SI) at the Research School of Earth Science of Australian National University, Australia. Thin section samples were extracted by Soxhlet extraction using chloroform/methanol (97:3) for 72 h to remove the soluble organic matter. Samples were then cast in 25-mm-diameter epoxy resin, as were several reference materials, including NBS-19 calcite ($\delta^{13}\text{C}_{\text{V-PDB}} = 1.95\text{‰}$, and $\delta^{18}\text{O}_{\text{V-SMOW}} = 28.64\text{‰}$), UWC-3 calcite ($\delta^{13}\text{C}_{\text{V-PDB}} = -0.91\text{‰}$, and $\delta^{18}\text{O}_{\text{V-SMOW}} = 12.49\text{‰}$; Kozdon et al., 2009), UW-6220 dolomite ($\delta^{13}\text{C}_{\text{V-PDB}} = 0.84\text{‰}$, and $\delta^{18}\text{O}_{\text{V-SMOW}} = 22.60\text{‰}$; Śliwiński et al., 2016a, b), and Hammerfall dolomite ($\delta^{13}\text{C}_{\text{V-PDB}} = -0.28\text{‰}$, and $\delta^{18}\text{O}_{\text{V-SMOW}} = 21.43\text{‰}$; Ian S. Williams, personal communication). The epoxy resins were polished and coated with a few nanometers of gold prior to SIMS analyses.

The analytical procedures for this method have previously been described (Ickert et al., 2008; Hu et al., 2018). A Cs^+ primary ion source with an accelerating potential of 15 kV was focused over areas with diameters of ~25 µm or ~15 µm for C isotopic analyses, and ~15 µm for

O isotopic analyses. The SIMS C-O isotopic analyses of the samples (typically four measurements) were bracketed by three to four analyses of reference materials.

The analytical accuracies of the SIMS $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses are affected by instrumental mass fractionation and sample matrix effects, which are systematically related to the chemical compositions and crystal structures of carbonates (Śliwiński et al., 2016a, b). A calibration of the SIMS $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ bias for carbonate minerals along the dolomite–ankerite solid solution series was performed. The measured C isotopic ratios are reported as per mil relative to the V-PDB reference, with analytical precisions (2SD) of $\pm 0.6\text{‰}$ (25- μm -diameter spot size) and $\pm 1.8\text{‰}$ (15- μm -diameter spot size). The O isotopic ratios are reported as per mil relative to the V-PDB reference, with analytical precisions (2SD) of $\pm 0.4\text{‰}$ (15- μm -diameter spot size). The $\delta^{18}\text{O}$ values are also presented relative to the Vienna standard mean ocean water (V-SMOW) in Table S3; calculations were performed following the equation $\delta^{18}\text{O}_{\text{V-SMOW}} = 1.03091 \times \delta^{18}\text{O}_{\text{V-PDB}} + 30.91$ (Coplen et al., 1983).

REFERENCES

- Alqattan, M.A., and Budd, D.A., 2017, Dolomite and dolomitization of the Permian Khuff-C reservoir in Ghawar field, Saudi Arabia: American Association of Petroleum Geologists Bulletin, v. 101, p. 1715–1745, <https://doi.org/10.1306/01111715015>.
- Bai, Y., 2008, Prospects for development of oil shale deposits in southern margin of Junggar Basin: Xinjiang Petroleum Geology, v. 29, p. 462–465.

135 Blättler, C.L., Miller, N.R., and Higgins, J.A., 2015, Mg and Ca isotope signatures of authigenic
 136 dolomite in siliceous deep-sea sediments: *Earth and Planetary Science Letters*, v. 419, p.
 137 32–42, <https://doi.org/10.1016/j.epsl.2015.03.006>.
 138 Carroll, A.R., 1998, Upper Permian lacustrine organic facies evolution, Southern Junggar Basin,
 139 NW China: *Organic Geochemistry*, v. 28, p. 649–667, <https://doi.org/10.1016/S0146->
 140 6380(98)00040-0.
 141 Carroll, A.R., and Wartes, M.A., 2003, Organic carbon burial by large Permian lakes, northwest
 142 China, *in* Chan, M.A., and Archer, A.W., eds., *Extreme Depositional Environments:*
 143 *Mega End Members in Geologic Time*: Boulder, Colorado, Geological Society of
 144 America Special Paper 370, p. 91–104, <https://doi.org/10.1130/0-8137-2370-1.91>.
 145 Carroll, A.R., Brassell, S.C., and Graham, S.A., 1992, Upper Permian lacustrine oil shales,
 146 Southern Junggar Basin, Northwest China: *American Association of Petroleum*
 147 *Geologists Bulletin*, v. 76, p. 1874–1902, <https://doi.org/10.1306/BDFF8B0A-1718->
 148 11D7-8645000102C1865D.
 149 Coplen, T.B., Kendall, C., and Hopple, J., 1983, Comparison of stable isotope reference samples:
 150 *Nature*, v. 302, p. 236–238, <https://doi.org/10.1038/302236a0>.
 151 Graf, D.L., and Goldsmith, J.R., 1956, Some hydrothermal syntheses of dolomite and
 152 protodolomite: *The Journal Geology*, v. 64, p. 173–186, <https://doi.org/10.1086/626332>.
 153 Hu, W.X., Kang, X., Cao, J., Wang, X.L., Fu, B., and Wu, H.G., 2018, Thermochemical
 154 oxidation of methane induced by high-valence metal oxides in a sedimentary basin:
 155 *Nature Communications*, v. 9, 5131, <https://doi.org/10.1038/s41467-018-07267-x>.
 156 Ickert, R.B., Hiess, J., Williams, I.S., Holden, P., Ireland, T.R., Lanc, P., Schram, N., Foster, J.J.,
 157 and Clement, S.W., 2008, Determining high precision, in situ, oxygen isotope ratios with

158 a SHRIMP II: Analyses of MPI-DING silicate-glass reference materials and zircon from
159 contrasting granites: *Chemical Geology*, v. 257, p. 114–128,
160 <https://doi.org/10.1016/j.chemgeo.2008.08.024>.

161 Jost, A.B., Mundil, R., He, B., Brown, S.T., Altiner, D., Sun, Y., DePaolo, D.J., and Payne, J.L.,
162 2014, Constraining the cause of the end-Guadalupian extinction with coupled records of
163 carbon and calcium isotopes: *Earth Planetary Science Letters*, v. 396, p. 201–212,
164 <https://doi.org/10.1016/j.epsl.2014.04.014>.

165 Kozdon, R., Ushikubo, T., Kita, N.T., Spicuzza, M., and Valley, J.W., 2009, Intratest oxygen
166 isotope variability in the planktonic foraminifer *N. pachyderma*: Real vs. apparent vital
167 effects by ion microprobe: *Chemical Geology*, v. 258, p. 327–337,
168 <https://doi.org/10.1016/j.chemgeo.2008.10.032>.

169 Liang, J., Tang, D., Xu, H., Tao, S., Li, C., and Gou, M., 2014, Formation condition of Jimusaer
170 oil shale at the northern foot of Bogda Mountain, China: *Oil Shale*, v. 31, p. 19–29,
171 <https://doi.org/10.3176/oil.2014.1.03>.

172 Loyd, S.J., Berelson, W.M., Lyons, T.W., Hammond, D.E., and Corsetti, F.A., 2012,
173 Constraining pathways of microbial mediation for carbonate concretions of the Miocene
174 Monterey Formation using carbonate-associated sulfate: *Geochimica et Cosmochimica*
175 *Acta*, v. 78, p. 77–98, <https://doi.org/10.1016/j.gca.2011.11.028>.

176 Lu, X., Shi, J., Zhang, S., Zou, N., Sun, G., and Zhang, S., 2015, The origin and formation model
177 of Permian dolostones on the northwestern margin of Junggar Basin, China: *Journal of*
178 *Asian Earth Sciences*, v. 105, p. 456–467, <https://doi.org/10.1016/j.jseaes.2015.02.024>.

179 Sharps, R., Li, Y., McWilliams, M., and Li, Y., 1992, Paleomagnetic investigation of Upper
180 Permian sediments in the South Junggar Basin, China: *Journal of Geophysical Research*,
181 v. 97, p. 1753–1765, <https://doi.org/10.1029/91JB02741>.

182 Śliwiński, M.G., Kitajima, K., Kozdon, R., Spicuzza, M.J., Fournelle, J.H., Denny, A., and
183 Valley, J.W., 2016a. Secondary ion mass spectrometry bias on isotope ratios in dolomite-
184 ankerite, part I: $\delta^{18}\text{O}$ matrix effects: *Geostandards and Geoanalytical Research*, v. 40, p.
185 157–172, <https://doi.org/10.1111/j.1751-908X.2015.00364.x>.

186 Śliwiński, M.G., Kitajima, K., Kozdon, R., Spicuzza, M.J., Fournelle, J.H., Denny, A., and
187 Valley, J.W., 2016b, Secondary ion mass spectrometry bias on isotope ratios in dolomite-
188 ankerite, part II: $\delta^{13}\text{C}$ matrix effects: *Geostandards and Geoanalytical Research*, v. 40, p.
189 173–184, <https://doi.org/10.1111/j.1751-908X.2015.00380.x>.

190 Tao, S., Tang, D., Xu, H., Liang, J., and Shi, X., 2013, Organic geochemistry and elements
191 distribution in Dahuangshan oil shale, southern Junggar Basin: Origin of organic matter
192 and depositional environment: *International Journal of Coal Geology*, v. 115, p. 41–51,
193 <https://doi.org/10.1016/j.coal.2013.05.004>.

194 Wang, J., Cao, Y.C., Wang, X.T., Liu, K.Y., Wang, Z.K., and Xu, Q.S., 2018, Sedimentological
195 constraints on the initial uplift of the West Bogda Mountains in Mid-Permian: *Scientific*
196 *Reports*, v. 8, 1453, <https://doi.org/10.1038/s41598-018-19856-3>.

197 Zevin, L.S., 1977, A method of quantitative phase analysis without standards: *Journal of Applied*
198 *Crystallography*, v. 10, p. 147–150, <https://doi.org/10.1107/S0021889877013144>.

199 Zhang, X., 1981, Regional stratigraphic chart of northwestern China, Branch of Xinjiang Uygur
200 Autonomous Region: Beijing, Geological Publishing House, 496 p.

Figure S1. Geological setting of the methanogen microfossils. A: Inset map showing the locations of the Junggar Basin and Urumqi within China. B: Geological map of the West Bogda Mountains, showing the location of the Hongyanchi section (black star). Modified from Carroll et al. (1992) and Carroll (1998). C: Stratigraphic column of the Permian Lucaogou Formation (Fm), including lower and upper members. D: Stratigraphic section of the upper Lucaogou Formation showing shale (grey), interbedded dolomite (orange), and limestone (blue) (the numbers refer to carbonate ID).

Figure S2. Carbonate beds and nodules within the upper Lucaogou Formation. A: Organic carbon-rich shale and interbedded carbonate beds and nodules. B: Dolomite nodule with an undulating base and top. C: Limestone bed with a parallel base and top. D: Photomicrograph of limestone composed of micritic calcite. The numbers refer to carbonate ID.

Figure S3. Energy dispersive X-ray spectrum of the deformed carbonaceous individual. The yellow circle marks the area analyzed by EDS.

Figure S4. Typical XRD spectra of the microfossil-bearing dolomite. The spectra indicate that poorly ordered dolomite is the dominant mineral component. The peaks refer to dolomite 'D', quartz 'Q', albite 'A', and calcite 'C', where R is the degree of order of the dolomite.

Figure S5. Cross-plot of the $\delta^{13}\text{C}$ values of dolomite versus the microfossil numbers (groups 1 and 2) per square millimeter observed in each thin section. More ^{13}C -enriched dolomite contains more abundant methanogen microfossils. The thin sections are standard 30- μm -thick and polished.

Figure S6. Cross-plot of $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ values from different settings and ages. The grey box marks the isotopic range of Permian marine limestone and dolomite (Jost et al., 2014; Alqattan and Budd, 2017). Other data are for the lacustrine dolomite of the Lower Permian Fengcheng Formation in the northwestern Junggar Basin (Lu et al., 2015), Miocene marine carbonate concretion (Loyd et al., 2012), Miocene deep sea authigenic dolomite (Blättler et al., 2015), and the limestone and microfossil-bearing dolomite of the upper Lucaogou Formation in the southern Junggar Basin (this study).

Figure S7. Conceptual model of microbial methanogenesis in the Permian lake sediments. The abundant organic matter provided sufficient substrate for the growth of methanogens. A large amount of CH_4 was produced through methanogenesis in the anoxic sediments, and was then released into the water column and atmosphere. The produced CO_2 was incorporated into authigenic dolomite.

240

241

Table S1. DIAMETER RANGE STATISTICS OF THE SPHEROIDAL METHANOGEN

MICROFOSSILS

Groups of spheroidal microfossils	Diameter range (μm)	Number of specimens
<u>Group 1 ($n^* = 720$, $M^\dagger = 13.1\text{ }\mu\text{m}$, and $\sigma^\S = 0.2$)</u>		
	10.5–11.0	5
	11.0–11.5	18
	11.5–12.0	69
	12.0–12.5	101
	12.5–13.0	142
	13.0–13.5	138
	13.5–14.0	123
	14.0–14.5	65
	14.5–15.0	39
	15.0–15.5	18
	15.5–16.0	2
<u>Group 2 ($n = 38$, $M = 3.6\text{ }\mu\text{m}$, and $\sigma = 0.5$)</u>		
	2.6–2.8	1
	2.8–3.0	2
	3.0–3.2	4
	3.2–3.4	6
	3.4–3.6	7
	3.6–3.8	5
	3.8–4.0	4
	4.0–4.2	3
	4.2–4.4	3
	4.4–4.6	1
	4.6–4.8	1
	4.8–5.0	1
<u>Group 3 ($n = 149$, $M = 1.7\text{ }\mu\text{m}$, and $\sigma = 0.9$)</u>		
	1.2–1.3	1
	1.3–1.4	4
	1.4–1.5	18
	1.5–1.6	26
	1.6–1.7	29
	1.7–1.8	30
	1.8–1.9	17
	1.9–2.0	15
	2.0–2.1	6
	2.1–2.2	1
	2.2–2.3	2
<i>Note:</i> Samples are stored at the School of Earth Sciences and Engineering, Nanjing University, and can be sampled from the outcrop at the Hongyanchi section, Urumqi, Xinjiang, China. [*] n is the number of specimens. [†] M is the mean diameter of specimens. [§] σ is the standard deviation.		

242 **Table S2.** BULK-ROCK $\delta^{13}\text{C}$ AND $\delta^{18}\text{O}$ VALUES AND METHANOGEN MICROFOSSIL

243 NUMBERS PER SQUARE MILLIMETER IN THIN SECTIONS

Sample ID	Bed ID	Vertical position	Lithology	$\delta^{13}\text{C}$ (‰, V-PDB)	$\delta^{18}\text{O}$ (‰, V-PDB)	Calcite (wt. %)	Dolomite (wt. %)	Microfossil number (mm ⁻²)
<u>Section A</u>								
HYC-1	1	0.22	Dolomite bed	8.97	-9.26	0.00	100.00	29
HYC-2	2	0.98	Dolomite bed	9.65	-10.09	0.15	99.85	49
HYC-3	3	8.02	Dolomite nodule	10.12	-9.53	0.00	100.00	25
HYC-4	4	9.35	Dolomite bed	11.61	-7.15	0.24	99.76	16
HYC-5	5	12.88	Dolomite bed	10.19	-7.34	0.58	99.42	142
HYC-6	6	15.53	Dolomite bed	8.36	-8.85	0.00	100.00	28
HYC-7	7	19.42	Dolomite nodule	8.40	-8.86	0.36	99.64	10
HYC-8	7	19.48	Dolomite nodule	8.56	-8.46	0.49	99.51	5
HYC-9	7	19.76	Dolomite nodule	8.46	-8.66	2.53	97.47	2
HYC-10	8	26.27	Dolomite bed	7.65	-10.55	8.47	91.53	34
HYC-11	9	29.21	Dolomite bed	8.73	-9.20	0.00	100.00	28
HYC-12	10	32.59	Dolomite bed	6.77	-12.13	0.00	100.00	31
HYC-13	11	34.57	Dolomite bed	8.51	-9.85	0.00	100.00	12
<u>Section B</u>								
HYC-14	12	309.68	Dolomite nodule	15.99	-4.09	1.73	98.27	571
HYC-15	13	310.85	Dolomite nodule	10.05	-8.37	4.45	95.55	9
HYC-16	14	312.46	Dolomite bed	17.00	-3.37	3.44	96.56	22
HYC-17	15	314.35	Dolomite bed	14.69	-5.99	0.96	99.04	278
HYC-18	16	317.24	Limestone bed	5.48	-11.62	87.45	12.55	N.D. [#]
HYC-19	17	319.06	Dolomite nodule	17.21	-5.30	1.22	98.78	1272
HYC-20	18	320.67	Dolomite nodule	14.65	-5.08	17.22	82.78	111
HYC-21	19	324.11	Dolomite bed	16.92	-3.65	1.15	98.85	552
HYC-22	20	325.82	Dolomite bed	17.42	-3.73	0.45	99.55	185
HYC-23	21	327.55	Dolomite nodule	16.43	-3.84	0.29	99.71	421
HYC-24	22	329.62	Dolomite bed	12.47	-6.03	36.42	63.58	9
HYC-25	23	331.85	Dolomite bed	15.58	-5.83	6.38	93.62	265
<u>Section C</u>								
HYC-26	25	349.20	Dolomite nodule	17.70	-2.52	9.03	90.97	944
HYC-27	26	351.05	Dolomite nodule	12.79	-6.27	2.77	97.23	98
HYC-28	26	351.14	Dolomite nodule	15.62	-5.33	2.21	97.79	733
HYC-29	26	351.23	Dolomite nodule	16.59	-4.68	2.16	97.84	682
HYC-30	26	351.32	Dolomite nodule	17.67	-3.51	2.17	97.83	2440
HYC-31	26	351.41	Dolomite nodule	16.68	-4.18	7.15	92.85	2887
HYC-32	26	351.50	Dolomite nodule	17.38	-3.65	3.50	96.50	3127
HYC-33	26	351.59	Dolomite nodule	17.63	-3.15	1.77	98.23	824
HYC-34	26	351.68	Dolomite nodule	16.49	-4.98	5.14	94.86	531
HYC-35	26	351.77	Dolomite nodule	15.27	-5.44	5.08	94.92	270
HYC-36	27	352.77	Dolomite nodule	14.28	-6.46	0.19	99.81	100
HYC-37	27	352.84	Dolomite nodule	15.73	-5.41	0.84	99.16	49
HYC-38	27	352.90	Dolomite nodule	13.52	-6.76	1.53	98.47	74
HYC-39	27	352.97	Dolomite nodule	14.05	-6.68	0.99	99.01	115
HYC-40	28	356.83	Dolomite nodule	14.60	-6.77	2.17	97.83	708

HYC-41	29	358.25	Dolomite bed	15.28	-6.15	2.50	97.50	924
HYC-42	30	359.94	Dolomite bed	15.61	-5.16	0.45	99.55	1643
HYC-43	31	363.44	Limestone bed	9.07	-11.76	98.29	1.71	N.D. [#]
HYC-44	31	363.65	Limestone bed	8.74	-11.97	98.25	1.75	N.D. [#]
HYC-45	32	365.59	Dolomite nodule	15.90	-5.54	13.05	86.95	94
HYC-46	33	370.08	Limestone bed	9.44	-10.01	100.00	0.00	N.D. [#]
<u>Section D</u>								
HYC-47	34	387.27	Dolomite bed	19.14	-1.69	1.35	98.65	2188
HYC-48	35	389.52	Dolomite bed	17.83	-4.91	4.25	95.75	437
HYC-49	35	389.67	Dolomite bed	19.10	-2.53	1.62	98.38	317
HYC-50	36	392.43	Limestone bed	6.79	-8.06	100.00	0.00	N.D. [#]
HYC-51	37	395.30	Dolomite nodule	18.90	-4.15	0.81	99.19	3911
HYC-52	37	395.38	Dolomite nodule	19.76	-3.89	1.27	98.73	3508
HYC-53	37	395.46	Dolomite nodule	17.80	-4.32	5.93	94.07	4701
HYC-54	37	395.55	Dolomite nodule	18.77	-3.96	1.43	98.57	4489
HYC-55	38	396.18	Limestone bed	1.05	-12.07	65.69	34.31	N.D. [#]

Note: Samples are stored at the School of Earth Sciences and Engineering, Nanjing University, and can be sampled from the outcrop at the Hongyanchi section, Urumqi, Xinjiang, China.

[#]N.D. = not determined.

244 **Table S3. *IN SITU* ISOTOPIC AND ELEMENTAL COMPOSITIONS OF ZONED**
245 **DOLOMITE AND CALCITE**

Mineralogy	$\delta^{13}\text{C}$ (‰, V-PDB)	2 SD	Spot size (μm)	$\delta^{18}\text{O}$ (‰, V-PDB)	$\delta^{18}\text{O}$ (‰, V-SMOW)	2 SD	Spot size (μm)	Ca (mol. %)	Mg (mol. %)	Fe (mol. %)	Mn (mol. %)	Relative distance [*]
<u>A–B</u>												
Matrix dolomite	14.0	0.3	25	−4.2	26.5	0.3	15	51.58	47.35	0.94	0.12	0.04
Matrix dolomite	12.4	0.6	25	−3.4	27.4	0.4	15	52.25	46.66	0.99	0.10	0.16
Matrix dolomite	9.2	0.6	25	−4.9	25.8	0.3	15	53.00	45.96	0.90	0.14	0.24
Matrix dolomite	16.3	0.6	25	−3.4	27.4	0.2	15	50.83	47.90	1.20	0.08	0.40
Cement dolomite	12.7	1.4	15	−2.6	28.2	0.4	15	49.96	49.73	0.31	0.00	0.50
Cement dolomite	13.1	1.8	15	−5.1	25.7	0.3	15	51.42	46.85	1.64	0.08	0.54
Cement dolomite	17.5	0.4	25	−6.3	24.4	0.3	15	51.02	48.10	0.88	0.00	0.62
Cement dolomite	17.7	0.6	25	−5.8	24.9	0.2	15	53.85	45.43	0.68	0.04	0.66
Cement calcite	−4.5	0.6	25	−17.6	12.8	0.4	15	96.94	1.88	0.97	0.21	0.77
Cement calcite	−3.5	0.4	25	−17.3	13.1	0.3	15	95.20	4.10	0.55	0.16	0.84
Cement calcite	−6.9	0.5	25	−18.2	12.1	0.4	15	96.95	1.92	0.98	0.15	0.96

Note: The sample is HYC-53, which is stored at the School of Earth Sciences and Engineering, Nanjing University.

^{*}Relative distance means the transect distance from A to an individual SIMS spot assuming that the length of A to B is one unit.

Fig. S1

Fig. S2

Fig. S3

Fig. S4

Fig. S5

Fig. S6

Fig. S7