1 ANALYTICAL METHODS

2 Carbon and oxygen isotope analyses on carbonates were performed at Hatch Labs, University of

3 Ottawa and at SIFIR laboratory, University of Manitoba. Carbonates were microdrilled with 1

4 mm diameter diamond drill bits from the least-altered (i.e., lacking veins, discoloration,

5 weathering rinds, and silicification) and finest-grained portions of polished thick sections.

6 Carbonate powders were reacted at 70°C with anhydrous phosphoric acid using a GasBenchII

7 carbonate device and delivered in a stream of high-purity He to a Thermo Finnigan^{TM} Delta V

8 Plus Isotope-Ratio Mass-Spectrometer via an open-split interface (ConFlo IV, Thermo

9 Finnigan^{TM}) at SIFIR laboratory of the Department of Geological Sciences, University of

10 Manitoba, Canada. Carbonate powders analyzed at Hatch Labs were reacted at 50°C for 48 hours

11 with anhydrous phosphoric acid using a GasBenchII carbonate device and delivered in a stream

12 of high-purity He to a Thermo Finnigan^{TM} Delta XP Isotope-Ratio Mass-Spectrometer.

13 All C isotope ratios are reported in delta notation

$$\delta^{13}C = \left(\frac{^{13}R_{\ carbonate\ C}}{^{13}R_{\ V-PDB}} - 1 \right) \times 1000$$

14 relative to international standards on the *Vienna-Pee Dee Belemnite (V-PDB)* scale. Sample

15 normalization was performed using the two-point (NBS-18 and NBS-19 international calcite

16 standards analyzed at the beginning, middle and end of each run) calibration described in Coplen

17 et al. (2002). A calibration line was calculated by least squares linear regression using the known

18 and measured isotope values of the calibration standards. To check the quality of analysis

19 performance at SIFIR lab, one calibrated internal calcite standard (CHI, $\delta^{13}C$ = -8.01‰ and $\delta^{18}O$

20 = -11.67‰) and one calibrated internal dolomite standard (Tytyri, $\delta^{13}C$ = +0.78‰ and $\delta^{18}O$ = -

21   7.07‰) were analyzed together with unknown samples. Replicate analyses of internal standards

22   yielded the results of $\delta^{13}C$ = -7.96±0.11‰ and $\delta^{18}O$ = -11.64±0.12‰ (n=146) for CHI, and $\delta^{13}C$

23   = +0.73±0.08‰ and $\delta^{18}O$ = -5.97±0.17‰ (n=209) for Tytyri. Correction based on difference

24   between the known and measured oxygen isotope values for the Tytyri dolomite standard was

25   performed for $\delta^{18}O$ values of dolomite samples. At Hatch Labs, internal calcite standard C-44

26   ($\delta^{13}C$ = -1.81‰ and $\delta^{18}O$ = -22.04‰) was analyzed with unknowns, producing $\delta^{13}C$ = -1.84‰ (σ

27   = 0.02‰) and $\delta^{18}O$ = -22.00‰ (σ = 0.05‰), n=4. Correction was performed for $\delta^{18}O$ values of

28   dolomite samples.

29   Sulfur isotope analyses of evaporite material were performed at SIFIR Laboratory, University of

30   Manitoba. Approximately 0.2 to 0.4 mg of sample powder was weighed into Sn cups (5x3.5

31   mm), wrapped and analyzed for S isotope ratios on a Costech^{TM} 4010 Elemental Analyzer (EA)

32   coupled to a Thermo Finnigan^{TM} Delta V Plus isotope-ratio mass-spectrometer (IRMS) via an

33   open-split interface (ConFlo IV, Thermo Finnigan^{TM}).

34   In the EA, the sample Sn cup was dropped to the 1st reaction column, containing both oxidation

35   (upper part) and reduction (lower part) chemicals. The sample Sn cup was combusted at 1050°C,

36   with O_2 supplied to enhance the combustion efficiency. The produced SO_2, together with other

37   gases, passed through the reduction chemicals (ultra-pure Cu) with the ultra-pure He to remove

38   unconsumed O_2 and to reduce SO_3 to SO_2. The gas mixture passed through the water trap, and

39   then the 2nd reaction column. The 2nd column was filled with quartz chips (890°C) and this was

40   to minimize the uncertainty in corrections related to oxygen isotopes (cf. Fry et al., 2002). The

41   SO_2 was separated from other gases by passing through the GC column (at 100°C) before being

42   transferred to the IRMS through the open split interface.

43   The S isotope ratios are reported in delta notation relative to international standards on the V-

44   CDT scale. Sample normalization was performed using the two-point calibration described in

45   Coplen et al. (2006). Three international standards (IAEA-SO-5, IAEA-SO-6 and NBS127) were

46   analyzed at the beginning, middle and end of each run. Calibration line was calculated for each

47   run by least-squares linear regression using the known and measured isotope ratios of the

48   calibration standards. To monitor the quality of analysis performance, three internal $BaSO_4$

49   standards (FE-1; +11.7±0.4‰ (n=20), BN-2; +4.2±0.5‰ (n=20), and Aldrich $BaSO_4$;

50   +5.1±0.7‰ (n=22)) were analyzed with unknown samples, with the results of $\delta^{34}S$ =

51   +11.5±0.3‰ (n=8), FE-1; +4.2±0.6‰ (n=10), BN-2; and 5.1±0.8‰ (n=9), Aldrich $BaSO_4$.

52   Total organic and inorganic carbon contents, sulfate content, and carbon isotope composition of

53   organic carbon in five sulfate samples from the first and second white intervals and the grey

54   interval were analysed at SIFIR Laboratory, University of Manitoba. Samples were washed with

55   deionized water, dried, acidified, washed with deionized water to reach neutral pH, and dried

56   again. Weight loss was recorded to calculate TIC and TOC. Analyses of $\delta^{13}C_{organic}$ on a split of

57   the residue with sulfate and carbonate removed were performed using a Costech^{TM} 4010

58   Elemental Analyzer (EA) coupled to a Thermo Finnigan^{TM} Delta V Plus isotope-ratio mass-

59   spectrometer via an open-split interface (ConFlo III, Thermo Finnigan^{TM}). Temperature in the

60   oxidation column was set at 1050°C, and a 'macro' O_2 injection loop was utilized. Tin cups were

61   used as a catalyst to increase the combustion temperature through exothermic reaction. All C

62   isotope ratios are reported in delta notation relative to international standards on the *Vienna-Pee*

63   *Dee Belemnite (V-PDB)* scale. Sample normalization was performed using the two-point

64   calibration described in Coplen et al. (2006). Two international standards (USGS40 and

65   USGS41) were analyzed at the beginning, middle and end of each run. A calibration line was

66   calculated for each run by least-squares linear regression using the known and measured isotope

67   values of the calibration standards. To monitor the quality of sample preparation and analysis

68   performance, the international standard USGS Green River shale SGR-1b ($\delta^{13}C_{org}$ = -29.3 ±

69   0.1‰ V-PDB) was treated and analyzed as an unknown. Replicate analyses of SGR-1b standard

70   yielded the δ13Corg value of -29.5 ± 0.2‰ (n=9).

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