ANALYTICAL METHODS

Carbon and oxygen isotope analyses on carbonates were performed at Hatch Labs, University of Ottawa and at SIFIR laboratory, University of Manitoba. Carbonates were microdrilled with 1 mm diameter diamond drill bits from the least-altered (i.e., lacking veins, discoloration, weathering rinds, and silicification) and finest-grained portions of polished thick sections. Carbonate powders were reacted at 70°C with anhydrous phosphoric acid using a GasBenchII carbonate device and delivered in a stream of high-purity He to a Thermo Finnigan™ Delta V Plus Isotope-Ratio Mass-Spectrometer via an open-split interface (ConFlo IV, Thermo Finnigan™) at SIFIR laboratory of the Department of Geological Sciences, University of Manitoba, Canada. Carbonate powders analyzed at Hatch Labs were reacted at 50°C for 48 hours with anhydrous phosphoric acid using a GasBenchII carbonate device and delivered in a stream of high-purity He to a Thermo Finnigan™ Delta XP Isotope-Ratio Mass-Spectrometer.

All C isotope ratios are reported in delta notation

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

relative to international standards on the *Vienna-Pee Dee Belemnite (V-PDB)* scale. Sample normalization was performed using the two-point (NBS-18 and NBS-19 international calcite standards analyzed at the beginning, middle and end of each run) calibration described in Coplen et al. (2002). A calibration line was calculated by least squares linear regression using the known and measured isotope values of the calibration standards. To check the quality of analysis performance at SIFIR lab, one calibrated internal calcite standard (CHI, \( \delta^{13}C = -8.01\% \) and \( \delta^{18}O = -11.67\% \)) and one calibrated internal dolomite standard (Tytyri, \( \delta^{13}C = +0.78\% \) and \( \delta^{18}O = -1\)) were analyzed.
7.07‰) were analyzed together with unknown samples. Replicate analyses of internal standards yielded the results of $\delta^{13}C = -7.96\pm0.11‰$ and $\delta^{18}O = -11.64\pm0.12‰$ (n=146) for CHI, and $\delta^{13}C = +0.73\pm0.08‰$ and $\delta^{18}O = -5.97\pm0.17‰$ (n=209) for Tytyri. Correction based on difference between the known and measured oxygen isotope values for the Tytyri dolomite standard was performed for $\delta^{18}O$ values of dolomite samples. At Hatch Labs, internal calcite standard C-44 ($\delta^{13}C = -1.81‰$ and $\delta^{18}O = -22.04‰$) was analyzed with unknowns, producing $\delta^{13}C = -1.84‰$ (σ = 0.02‰) and $\delta^{18}O = -22.00‰$ (σ = 0.05‰), n=4. Correction was performed for $\delta^{18}O$ values of dolomite samples.

Sulfur isotope analyses of evaporite material were performed at SIFIR Laboratory, University of Manitoba. Approximately 0.2 to 0.4 mg of sample powder was weighed into Sn cups (5x3.5 mm), wrapped and analyzed for S isotope ratios on a Costech™ 4010 Elemental Analyzer (EA) coupled to a Thermo Finnigan™ Delta V Plus isotope-ratio mass-spectrometer (IRMS) via an open-split interface (ConFlo IV, Thermo Finnigan™).

In the EA, the sample Sn cup was dropped to the 1st reaction column, containing both oxidation (upper part) and reduction (lower part) chemicals. The sample Sn cup was combusted at 1050°C, with O2 supplied to enhance the combustion efficiency. The produced SO2, together with other gases, passed through the reduction chemicals (ultra-pure Cu) with the ultra-pure He to remove unconsumed O2 and to reduce SO3 to SO2. The gas mixture passed through the water trap, and then the 2nd reaction column. The 2nd column was filled with quartz chips (890°C) and this was to minimize the uncertainty in corrections related to oxygen isotopes (cf. Fry et al., 2002). The SO2 was separated from other gases by passing through the GC column (at 100°C) before being transferred to the IRMS through the open split interface.
The S isotope ratios are reported in delta notation relative to international standards on the V-CDT scale. Sample normalization was performed using the two-point calibration described in Coplen et al. (2006). Three international standards (IAEA-SO-5, IAEA-SO-6 and NBS127) were analyzed at the beginning, middle and end of each run. Calibration line was calculated for each run by least-squares linear regression using the known and measured isotope ratios of the calibration standards. To monitor the quality of analysis performance, three internal BaSO₄ standards (FE-1; +11.7±0.4‰ (n=20), BN-2; +4.2±0.5‰ (n=20), and Aldrich BaSO₄; +5.1±0.7‰ (n=22)) were analyzed with unknown samples, with the results of δ³⁴S = +11.5±0.3‰ (n=8), FE-1; +4.2±0.6‰ (n=10), BN-2; and 5.1±0.8‰ (n=9), Aldrich BaSO₄.

Total organic and inorganic carbon contents, sulfate content, and carbon isotope composition of organic carbon in five sulfate samples from the first and second white intervals and the grey interval were analysed at SIFIR Laboratory, University of Manitoba. Samples were washed with deionized water, dried, acidified, washed with deionized water to reach neutral pH, and dried again. Weight loss was recorded to calculate TIC and TOC. Analyses of δ¹³Corganic on a split of the residue with sulfate and carbonate removed were performed using a Costech™ 4010 Elemental Analyzer (EA) coupled to a Thermo Finnigan™ Delta V Plus isotope-ratio mass-spectrometer via an open-split interface (ConFlo III, Thermo Finnigan™). Temperature in the oxidation column was set at 1050°C, and a ‘macro’ O₂ injection loop was utilized. Tin cups were used as a catalyst to increase the combustion temperature through exothermic reaction. All C isotope ratios are reported in delta notation relative to international standards on the Vienna-Pee Dee Belemnite (V-PDB) scale. Sample normalization was performed using the two-point calibration described in Coplen et al. (2006). Two international standards (USGS40 and USGS41) were analyzed at the beginning, middle and end of each run. A calibration line was
calculated for each run by least-squares linear regression using the known and measured isotope values of the calibration standards. To monitor the quality of sample preparation and analysis performance, the international standard USGS Green River shale SGR-1b ($\delta^{13}$C$_{org} = -29.3 \pm 0.1\%$ V-PDB) was treated and analyzed as an unknown. Replicate analyses of SGR-1b standard yielded the $\delta$13Corg value of $-29.5 \pm 0.2\%$ (n=9).
