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Supplemental Material

S1: Analytical methods and U-Pb age interpretation

S2: U-Pb isotopic data

S3: Geochemical data

Supplemental Material -1

Analytical Methods

Geochemistry

Fresh samples were powdered by agate mortar and pestle, after weathered surfaces were removed, for elemental and stable isotopes analysis. Elemental determinations are based on total dissolution of samples using nitric, perchloric and hydrofluoric acids (2:2:1:1 acid solution of H_2O -HF- HClO_4 - HNO_3) followed by a lithium metaborate fusion of any residual material. Samples were analyzed by using a PerkinElmer mass spectrometer with $\pm 2\%$ analytical error at ACME Laboratories (Vancouver). For determination of $\delta^{13}\text{C}_{\text{org}}$, samples were washed with hydrochloric acid, and rinsed with distilled water to remove any carbonate before determination of $\delta^{13}\text{C}$ of organic carbon and analyzed using continuous flow–elemental analysis–isotope ratio mass spectrometry with a Finnigan Mat DeltaplusXL mass spectrometer interfaced with a Costech 4010 elemental analyzer. To normalize the data and correct for any instrument errors, selected internal standards were run at the beginning and end of the sample set. The results are expressed as δ -values relative to the Vienna Pee Dee Belemnite standard (V-PDB). The precision and accuracy of the analysis is 0.2‰.

Total organic carbon (TOC)

Total organic carbon (TOC) was measured by Hawk pyrolysis at the Geological Survey of Canada (Calgary). Samples were analyzed using the standard cycle of Wildcat technologies HAWK analyzer following the methods of Lafargue et al. (1998). This method involves a heating of a sample in an N_2 atmosphere pyrolysis at constant temperature of 300 °C for 3 min followed by increasing temperature at a rate of 25 °C per minute to a final temperature of 650 °C. The amount of hydrocarbons released during each heating stage is measured. The amount of free hydrocarbons released in form of gas and oil at the

isothermal stage is measured under the S1 peak. During the second stage, cracking of kerogen generates hydrocarbons measured as S2 peak (mg HC/g Rock). Simultaneously, the amount of CO₂ released within the 300-390 °C range is measured as the S3 peaks (mg CO₂/g rock) (Lafargue et al., 1998). In order to obtain the residual carbon, powdered sample is oxidized with temperatures increasing by 20 °C per minute from 300 to 850 °C. The amounts of CO₂ and CO released are measured under S4 peaks (mg CO₂/g Rock; mg CO/g Rock). TOC is calculated by summing pyrolysable organic carbon (PC%) and residual organic carbon (RC%) (Lafargue et al., 1998).

U-Pb Analytical Methods and U-Pb Age Interpretation

U-Pb Analytical Methods

Samples of ash layers were crushed and ground using jaw crusher and disk mill. Heavy mineral concentrates were prepared using a Wilfley™ table, heavy liquid (methylene iodide) density separation and a Frantz™ isodynamic magnetic separator. Methods are slightly modified from those reported in Davis et al. (2017). All fractions were prepared using the chemical leaching and annealing technique (CA-TIMS; (Mattinson, 2005)). Samples were annealed at 1000° C for 48 hours and then leached for 15 hours, in HF-HNO₃ at 190° C in Savillex 3 mL PFA capsules within a Parr digestion vessel. Individual crystals were selected under a binocular microscope, spiked with a mixed ²⁰⁵Pb-²³³U-²³⁵U tracer solution calibrated to ±0.15% against the JMM gravimetric solution and dissolved in high-pressure bombs in HF-HNO₃. Data reduction and error propagation used the ET-REDUX software (McLean et al., 2011). U and Pb isotopic ratios were measured using a Triton mass spectrometer operated in either static multi-collection mode (U) or using a secondary electron multiplier and ion counting system (all Pb and some U). A Pb mass fractionation correction of 0.155 ± 0.047%/amu was determined by analyses of the NBS982 standard. U fractionation was corrected using the ²³³U-²³⁵U double spike and was typically in the range of 0.12%/amu. Deadtime (20 ns) for the ion counting system was determined by replicate

analyses of the NBS982 solution. Age calculations used $^{238}\text{U}/^{235}\text{U}$ of 137.818 and decay constants of 1.55125e^{-10} for ^{238}U and 9.8485e^{-10} for ^{235}U . Accuracy of the method was monitored by repeated analyses of the Temora2 zircon standard. Twenty-two of twenty-four analyses gave a weighted mean age of 417.4 ± 0.3 Ma using the GSC2012 spike, relative to the age of 416.8 Ma reported by Black *et al.* (2004). Concordia plots and weighted mean calculations were made using Isoplot version 4.16 (Ludwig, 2003)

U-Pb Age Interpretation

Despite treatment using the chemical abrasion method zircon from all three bentonite samples exhibit Pb-loss making interpretation of a $^{206}\text{Pb}/^{238}\text{U}$ age challenging. Nine single grain analyses from sample EOR-1 have a range of $^{206}\text{Pb}/^{238}\text{U}$ ages from 362.2 to 358.4 Ma with the younger ages exhibiting higher degrees of discordance, consistent with Pb-loss (Fig. 1a). The two oldest concordant ages overlap within uncertainty (Fig.1b) and yield a weighted mean age of 362.05 ± 0.39 Ma, which is taken as the best estimate of the bentonite age. The other two samples show similar degrees of discordance, but a single age could not be replicated. The oldest single concordant age from sample CP-1 (Fig 1c and 1d) is 363.55 ± 0.68 Ma identical to the maximum concordant age from sample JC-1 at 363.55 ± 0.76 Ma (Fig 1e and 1f). The other single grain analyses plot along Discordia lines from ~ 363.5 Ma to zero, consistent with recent Pb-loss. The upper intercept of these arrays, defined by the oldest concordant analysis, is taken as the best estimate of the age of the bentonites. It is recognised that this is a minimum estimate as it can not be demonstrated that the older analyses were not affected by small amounts of Pb-loss. However, the ages fit stratigraphically with the younger age at 362 Ma being stratigraphically highest. These ages for the Lower Exshaw Formation are also supported by previously published work. Ferri et al. (2021) reported U-Pb zircon ages for bentonites from the lower to middle Exshaw Formation in the

Liard Basin of 364.4 ± 0.3 Ma (lower Exshaw); 364.0 ± 0.3 Ma (Mid-lower Exshaw) and 363.1 ± 0.3 Ma (Mid to upper Exshaw), within uncertainty of the ages reported here.

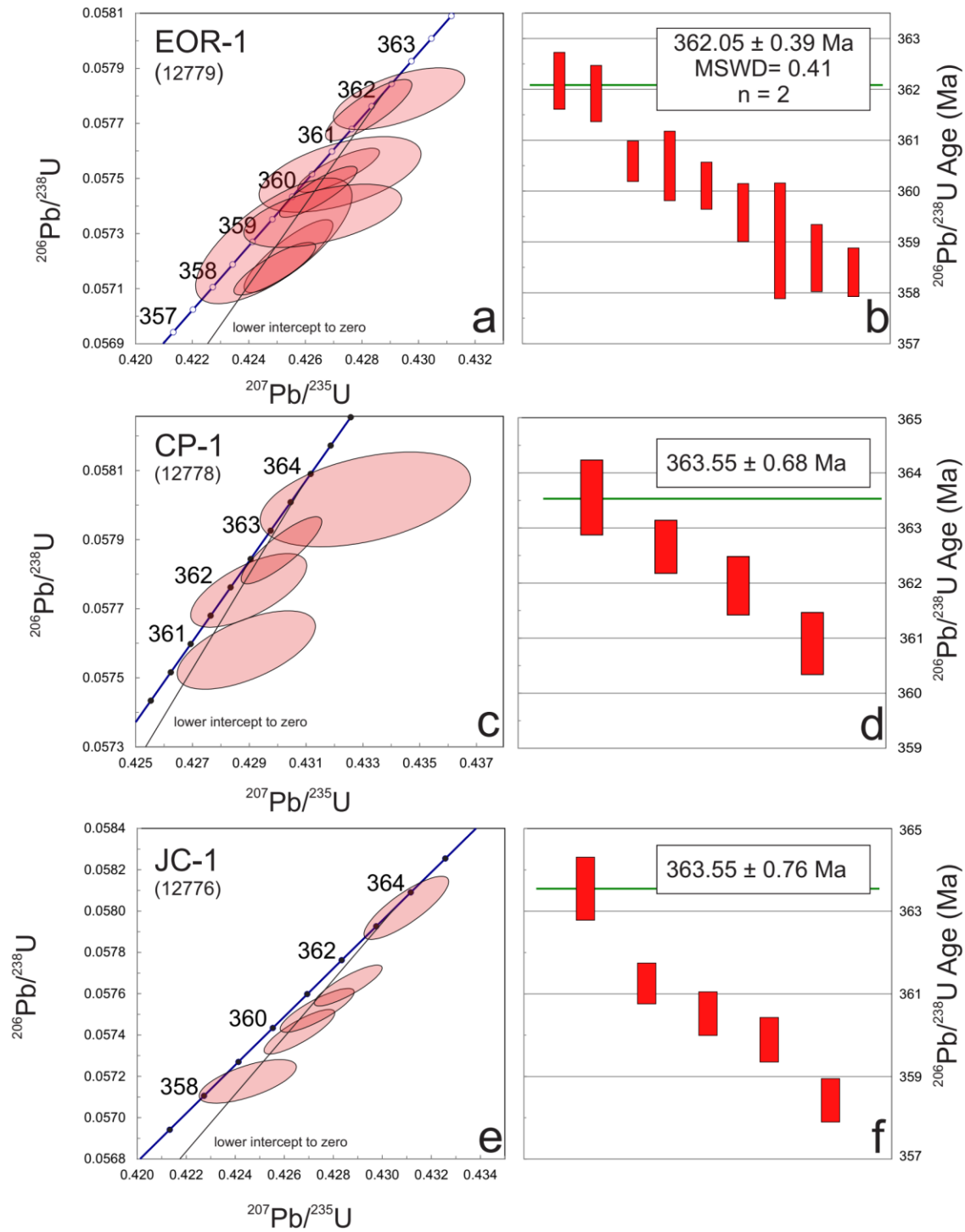


Figure 1. U-Pb Wetherill concordia and weighted mean plots for the three bentonite samples. Sample EOR-1 12779 (a, b); Sample CP-1 (12778) (c, d) and Sample JC-1 (12776) (e, f).

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