

Supplemental Material A: Methods

The methods applied to characterize the samples from the Duo Lake Formation are whole rock lithogeochemistry, scanned electron microscopy, X-ray diffraction, and electron microprobe analyses. They are described in detail below.

Attempts to further characterize the carbonaceous matter besides XRD were made including using reflectance (different colors are visible, Fig. 4b) and organic matter speciation by SGS. However, the former was inconclusive, whereas the latter did not result in meaningful data. Further, whole rock lithogeochemistry (Supplemental Material) analyzed for both C_{graphite} and C_{org} with C_{org} exceeding C_{graphite} in all samples (exception: no data available for Hf05-35); hence, the presence of more than one carbonaceous matter phase (i.e., graphite) is strongly suggested.

Whole rock lithogeochemistry.

In November 2021, ALS Geochemistry at North Vancouver, British Columbia, Canada, analyzed six samples from the Van Property for major, minor and trace element composition. Prior to analyses, samples were weighted crushed with 70% <2mm, split, and pulverized with 85% <75 μm . Between samples, equipment was washed to avoid any contamination. Major and minor element (SiO_2 , TiO_2 , Al_2O_3 , MnO , MgO , Fe_2O_3 , CaO , Na_2O , K_2O , P_2O_5) analyses was done using inductively coupled plasma atomic emission spectrometry (ICP-AES; code ME-ICP06). Loss on ignition (LOI) was determined at 1000°C using WST-SEQ (code OA-GRA05). Carbon was analyzed as (1) total carbon via induction furnace spectroscopy (code C-IR07), (2) non-carbonate carbon by induction furnace spectroscopy after the sample was treated with 25% HCl at high temperature for one hour to expel carbonates as CO_2 (code C-IR06a), and (3) graphite by induction furnace spectroscopy after the sample was treated with 50% HCl to leach of carbonates and

followed by roasting to remove organic carbon (code C-IR18). Total sulfur was analyzed using induction furnace spectroscopy (Code S-IR08). Both carbon and sulfur analyses were done using LECO analyzers.

Trace elements were analyzed using (1) four acid digestion with inductively coupled mass spectrometry (ICP-MS; Ag, Cu, Zn, Pb; code ME-4ACD81), (2) Li borate fusion prior to acid dissolution with ICP-MS finish (Ba, Cr, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, W, Y, Zr; and REE: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu; code ME-MS81), and (3) aqua regia with ICP-MS finish (As, Bi, Hg, In, Re, Sb, Sc, Se, Te, Tl; code ME-MS42). Detection limits for the analyzed elements and used methods are summarized by ALS Global (2023).

Precision and accuracy were monitored using reference materials. For major and minor elements including C and S, precision and accuracy were excellent to very good ($\leq 5\%$). For trace elements, precision and accuracy ranged from excellent ($\leq 3\%$) to very good ($\leq 7\%$) and to good (7–10%).

Scanned electron microscopy.

Scanned electron microscopy (SEM) was used to define the mineralogy and texture, and V host phases of siliceous argillites of the OSD. Elemental maps were obtained using a FEI Quanta 650 FEG SEM at the Manitoba Institute for Materials, University of Manitoba (UofM) in November 2022 and March 2023. The SEM was equipped with an Octane Super energy dispersive X-ray detector, and concentric backscattered electron detection was used in high vacuum mode at a pressure of 10^{-7} Pa, a voltage of 20 kV, a working distance of approximately 10 mm, and an aperture of 30 μm . Elemental maps of selected phases were obtained using K emission lines to detect K, Si, Al, S, Zn, Ca, Fe, Ti, and V. Maps were performed at 64 counts for approximately 20 min per map. In order to detect possible interferences (e.g., Ti K_{β} interfering with V K_{α}), the

mineral of interest was scanned, and alternative emission lines were then used to check for any elemental overlaps (e.g., K_{α} for Ti). If an overlap occurred, the alternate, interference-free emission line was used for semiquantitative energy dispersive x-ray (EDX) scans. These scans allow for the detection of individual elements within minerals, but the elemental maps produced via EDX do not provide specific elemental concentrations; instead, they are based on raw counts per second. However, as the measured intensity for each element is proportional to its concentration, this approach is semiquantitative.

X-ray diffraction.

X-ray diffraction (XRD) was done at SGS Lakefield, Ontario, Canada, in April 2022 on a total of six samples using method ME-LR-MIN-MET-MIN-D04 and is accredited to the requirements of ISO-IEC 17025. Prior to analyses, samples were crushed and pulverized with a 75 % fraction < 2 μ m. The powdered fraction was further treated by centrifuge and several steps involving the addition of ethylene glycol and high temperature heating to identify different clay species. The powdered samples were oriented prior to scanning. Clay minerals are identified by their individual diffraction patterns and changes in their diffraction patterns after treatments and details can be found in the Supplemental Material (XRD spectra).

Powdered mineral preparate were analyzed using a BRUKER AXS D8 Advance Diffractometer with a Co radiation tube. Analyses conditions were 35kV, 40mA using LYNXEYE detector. The X-ray diffractograms were acquired at 4-75° 2 θ range with step conditions of 0.02° and 0.03 s per step. The detection limit ranged between 0.5-2% and is a function of crystallinity. Mineral identification and interpretation were performed by matching data from the sample material to single phase reference material. The reference patterns were assembled by the Joint Committee on Powder Diffraction Standards—International Centre for Diffraction Data and released on

Diffraction Plus Eva software as PDF2/PP4 databases of Powder Diffraction Files (PDF). Semiquantitative analysis using the reference intensity ratio (RIR) method was performed by analyzing the minerals peak height and their respective I/I_{cor} values using corundum as internal standard; the I/I_{cor} values were accessed through the PDF database to determine mineral composition. The mineral abundance of each sample, expressed in wt%) was generated using Bruker-EVA software and the data were reconciled with the whole rock lithochemistry analyzed by ALS Geochemistry, North Vancouver, Canada.

Electron probe micro-analyses

Spectral maps of illite and compositional analyses of illite and rutile were done in April 2023 using Camaca SX-100 electron probe micro-analyzer at the Department of Earth Sciences, University of Manitoba, Winnipeg, Canada. The instrument is equipped with five detectors, a W filament, Be window, and Faraday cup. Raw analyses were recalculated to wt% of elements and oxides using a standardized PAP correction (Pouchou and Pichoir 1984).

For spectral maps, emphasis was on illite previously analyzed at the SEM and with a V signal. Conditions for spectral analyses were the following: All spectrometers were used to map the relative abundance of Si (spectrometer 2, TAP crystal), Ti (spectrometer 4, PET crystal) and V (spectrometer 1: LIF crystal; spectrometer 3: LLIF crystal; spectrometer 5: LIF crystal) in illite and rutile. Emission lines used for all three phases were K_{α} . All V is reported as K_{α} and the sum of all three used detectors to detect V. Prior to spectral maps, abundance of Cr, Nb and Ta were checked in illite and rutile and their concentrations were at or below the detection limit. Maps were collected using a beam of $1\mu\text{m}$ at a step size of $0.2\mu\text{m}$ with a dwell time of 0.2 s at 15keV and 20.1 nA. Mapped areas did not exceed $20\mu\text{m} \times 20\mu\text{m}$ and took approximately 1hr per area. Abundances of elements are reported in counts per second (cps) on the analyzed maps. Potential zoning in illite

(higher counts in center compared to rim, Fig. 11F) are an artifact due to beam overlap and do not present original zoning of V in high-V illite (personal communication P. Yang).

For compositional analyses, a beam of 1 μm at 15 keV and 2 nA was used to detect Al, Mg, Si, Na, Ca, K, Ti, Fe, Mn and V in both illite and rutile. Calibration for these elements involved the following reference materials (first order element lines, crystal used, detection limit [DL] based on 46 analyses for illite and 14 analyses for rutile): Al – pyrope (K_{α} , LTAP, DL: 0.23 ± 0.06 wt% for illite and 0.02 ± 0.0 wt% for rutile), Mg – olivine (K_{α} , LTAP, DL: 0.08 ± 0.03 wt% for illite and 0.02 ± 0.0 wt% for rutile), Si – diopside (K_{α} , TAP, DL: 0.49 ± 0.10 wt% for illite and 0.05 ± 0.03 wt% for rutile), Na – albite (K_{α} , TAP, DL: 0.08 ± 0.04 wt% for illite, not analyzed in rutile), Ca – diopside (K_{α} , LPET, DL: not analyzed in illite, 0.03 ± 0.01 wt% in rutile), K – orthoclase (K_{α} , LPET, DL: 0.25 ± 0.07 wt% for illite, not analyzed in rutile), Ti – titanite (K_{α} , DL: 0.05 ± 0.01 wt% for illite and 0.46 ± 0.03 wt% for rutile), Fe – fayalite (K_{α} , LIF, DL: 0.40 ± 0.18 wt% for illite, not analyzed in rutile), Mn – spessartine (K_{α} , LIF, DL: 0.10 ± 0.11 wt% for illite and 0.07 ± 0.07 wt% for rutile), and Vi – VP2O7 (K_{α} , LLIFDL: 0.25 ± 0.09 wt% for illite and 0.06 ± 0.06 wt% for rutile). Total analyses time per element was 60s with 40 s on peak time and 20 s on background.

Water concentrations of illite was calculated by subtracting analyzed totals in wt% from 100%. Some illite grains have lower water concentrations than commonly reported for illite which is caused by H₂O loss due to beam damage on the small area of illite analyzed. Illite analyses exceeding 4wt% H₂O and stoichiometrically representing illite were used for data interpretation. Due to the small size of the analyzed phases, especially rutile, contaminations with neighboring phases (e.g., Si from quartz, Fe, Al, Ca, Mg from neighboring clays, carbonate and sulfides) could

not be completely avoided. Rutile analyses with a Total of > 96.5 wt%, potential contaminants totaling < 2wt%, and stoichiometrically representing rutile composition were deemed acceptable.

References:

- ALS Global (2023) Geochemistry: Schedule of services and fees 2023, CAD. 50 pages. Retrieved in October 2023 from: <https://www.alsglobal.com/en/geochemistry/geochemistry-fee-schedules>
- Pouchou, J.L., and Pichoir, F. (1984) A new model for quantitative X-ray microanalysis, Part II: Application to in depth analysis of heterogeneous samples: La recherche aérospatiale, 5, 349-367.