MATERIALS AND METHODS

The opal samples were provided by R. Zielinski and D. Lindsey from the U.S. Geological Survey and were previously characterized by Ludwig et al. (1980) in terms of their U concentration and U-Pb age (Table 1). One altered rhyolite and three uraniferous opal samples are examined in this study using a combination of Electron Microprobe analysis (EMPA), Laser Ablation ICP-MS, Secondary-Ion Mass spectroscopy (SIMS), X-ray Photoelectron Spectroscopy, Scanning Electron Microscopy (SEM), X-ray powder diffraction and Raman Spectroscopy. Table 1 lists the sample location, paragenesis, appearance, U-Pb age and the analytical methods used to characterize each sample.

Scanning Electron Microscopy (SEM), Electron MicroProbe Analysis (EMPA) and X-Ray Diffraction (XRD)

Scanning Electron Microscopy (SEM) was done using a JEOL 6400 SEM operated at 20 kV and with a beam current of ~ 1 nA. The microscope is equipped with both backscattered (BSE) and secondary electron (SE) detectors and an Energy Dispersive X-ray Spectrometer (EDS) and is located in the Central Analytical Facility (CAF) at Laurentian University.

The samples *M3N and DL-U18B* were characterized with a Cameca SX-100 in the Ontario GeoScience Laboratories (Table 1). A wavelength-dispersive spectrometer (WDS) was used to collect data for Na, Mg, Al, Si, K, Ca, Mn, Fe and U at 20kV and 10nA using a focused beam. A PAP correction (Pouchou and Pichoir, 1985) was applied to all data and a decomposition study was done to monitor count-rate changes over time.

Powder X-ray diffraction was done with a Philips PW 1729 X-ray diffractometer using Co $K\alpha$ radiation (1.79 Å) at a voltage and current of 40Kv and 30mA, respectively. Spectra from smear-mounted powdered samples were collected over a scan range of 10-70° 2θ with a step size of 0.02 ° 2θ and a dwell time of 2 s.

Conventional stable isotope analyses of the UO_2 standards

The oxygen isotopic composition of pyrolusite, MnO_2 was isotopically characterized by conventional methods at Queen's University, Canada to calibrate it for potential use as an SIMS standard. Oxygen was liberated from multiple fractions of finely powdered (<350 μm) material derived from a single crystal by using the BrF_5 technique of Clayton and Mayeda (1963) and analyzed via dual inlet on a Thermo-Finnigan Delta Plus XP isotope ratio mass spectrometer (IRMS). Oxygen isotopic compositions are reported in units of ‰ relative to Vienna Standard Mean Ocean Water (V-SMOW). Replicate analyses for $\delta^{18}O$ are reproducible to ±0.1‰, and the $\delta^{18}O$ value of NIST-28 quartz is 9.6‰. The oxygen yield for the MnO_2 crystal was 10.7+/-0.2 micro moles of O/mg and multiple measurements (3) gave a $\delta^{18}O$ value of -6.8±0.3 ‰.

Secondary Ion Mass Spectrometer (SIMS)

Prior to SIMS analysis, the mounts were re-polished and cleaned to remove the carbon coatings and subsequently coated with Au. The mounts were

placed in stainless-steel sample holders, and the entire assembly was then placed in the SIMS sample lock and held at high vacuum for a minimum of 8 h prior to the start of the analysis. The oxygen isotopic composition and relative fluorine concentrations of uraniferous opals, the in-house pyrolusite standard, and crystals and finely disseminated pyrolusite (MnO_2) was measured with a CAMECA ims 7f. Secondary-Ion Mass Spectrometer (SIMS) at the University of Manitoba using a Cs^+ primary beam with extreme energy filtering of 200 eV. The ~2 nA primary-ion beam was focused to a 10 x 20 μm spot using a 100 μm aperture in the primary column. The Brazil quartz standard has a $\delta^{18}O_{V-SMOW}$ value of 15.1±0.3‰. The spot-to-spot reproducibility on the quartz standard was ±0.6‰ (1σ). The overall precision and accuracy for each isotope analysis include errors arising from counting statistics of each individual analysis, calibration to a known standard, and uncertainty in deadtime corrections arising from variable count rates. In general, the overall precision is ±1‰ (2σ), including the spot-to-spot reproducibility of the in-house pyrolusite standard. Values are reported in units of ‰ relative to Vienna-Standard Mean Ocean Water (V-SMOW) (Table 2).

Uranium and silica concentrations were also obtained with the CAMECA 7f. A ~7 nA primary ion beam of O^-, accelerated at 12.5 kV, was focused to a 30 x 30 μm spot using a 100 μm aperture in the primary column. The sample accelerating voltage was +7.95 kV, with electrostatic analyzer in the secondary column set to accept +8.00 kV. The entrance and exit slits were narrowed to obtain flat-top peaks at a mass resolving power of about 1300. Ions were detected with a Balzers SEV 1217 electron multiplier coupled with an ion-counting system with an overall deadtime of 31 ns. The following species were detected sequentially by switching the magnetic field: $^{30}Si^+$ and $^{238}U^+$. A typical analysis lasted ~5 minutes, comprising 15 cycles of analysis. NIST 610, 612 and 614 glass standards were used to construct calibration curves and correct for instrumental mass fractionation.

X-ray Photoelectron Spectroscopy

The near-surface chemical composition of the sample *M3N* was characterized with a Kratos Axis Ultra X-ray Photoelectron Spectrometer (XPS) at the University of Manitoba which is equipped with a magnetic-confinement charge-compensation system. The advantages of this system for insulators (*e.g.* uranyl minerals) have been described in detail by Schindler et al. (2009b, c). Spectra of the U 4f electrons were collected at high resolution using monochromatic Al$K\alpha$ radiation (1486.6 eV) and the charge-compensation system. Spectra were recorded using 20 sweeps, scan rates per sweep of 200 ms with analyzer pass-energies of 160 eV (U 4f), and large spot sizes and with an aperture size of 110 μm. Resolution for the different pass energies, spot sizes and aperture are listed in detail in Schindler et al. (2009b, c). Shirley background corrections (Shirley 1972) and Gaussian-Lorentzian peak shapes of 60 ± 10% were used to fit the U 4f spectra. The electrostatic sample-charging (which was not completely compensated by the charge neutralizer) was corrected by setting the binding energy of the C 1s electrons of adventitious C-H species on the sample surface equal to 285 eV (Wagner et al., 1979, Handbook of X-ray photoelectron spectroscopy). The presence and relative proportions of U^{6+} and U^{4+} were determined by peak fitting of the U $4f_{7/2}$ spectra using the software Vision 2.2.6. The FWHM values of the bands in the U 4f spectrum vary in the range 1.70-2.00 eV, but were constrained to be equal in each individual spectrum. More

details on fitting of the U $4f_{7/2}$ spectra and standard deviations of the binding energies and relative proportions of the U bands are given by Schindler et al. (2009b).

Laser Ablation Inductively Coupled Plasma Spectroscopy

The major and trace-element composition of opal DL-N22 was measured by laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) using a New Wave Nd-YAG 213 nm laser coupled to a quadrupole Thermo X II mass spectrometer. Ablation was done in a He atmosphere and Ar was mixed to the carrier gas before it entered the ICP-MS. Line scans were recorded with a spot size of 10 μm, respectively, using a repetition rate of 10 Hz and an energy density of 11 Jcm^{-2}. The synthetic glass standard NIST610, which contains a nominal trace-element abundance of ~500 $mgkg^{-1}$ was used as the external standard. The standard was ablated under the same conditions at the beginning of each analytical run, intermittently during acquisition, and at the end of each sample. Detection limits for elements depend on the experimental setting of the laser scan and are listed for a similar experimental setting in Durocher and Schindler (2011). Line scans were designed to traverse the different zones of the opal. Integration areas were selected based on chemical differences between the coatings and matrix composition as obtained by SEM-EDS analyses. The breadth of each integration area was determined by monitoring the inflection points of the rise and fall of the Ca and Si peaks. Laser Ablation ICP-MS data are usually quantified by calibrating the counts per second (CPS) with respect to an internal standard as well as an external standard (e.g. NIST glasses). However, as the samples analyzed in this study are heterogeneous and partly hydrated, no single element could be used as a suitable standard, so only external standards were used. Molar ratios of the elements were calculated from the total counts obtained and the known concentrations in the NIST glass. These were then used to calculate element concentrations by normalizing the sum of the moles to 100%, the underlying assumption being that the samples dominantly contains Si and Ca (as was observed in SEM-EDS analyses). The mole-proportion of H_2O and F^- was estimated on the basis of the number of F^- and H_2O groups per Ca and Si in fluorite and opal-CT. This procedure resulted in a semi-quantitative data set based on the uncertainty of the amount of fluorite and (H_2O) present in the opal.

Raman spectroscopy

Raman spectra recorded at Laurentian University were obtained over the range of 100 to 4000 cm^{-1} and collected in backscattered mode with a HORIBA JobinYvon XPLORA spectrometer interfaced with an Olympus BX 41 microscope, 100x magnification (estimated spot size of 2 μm), a 1200 cm^{-1} grating and an excitation radiation of λ = 532 nm. Calibration was done using the 521 cm^{-1} line of a silicon wafer.