Appendix 1: Detailed material and methods information on the XRF-derived concentrations of elements, and the statistical analyses.

1. Vegetation reconstruction

The pollen record from Chickaree Lake was used unmodified from Dunnette et al. (2014).

2. Tests on XRF-derived concentrations

We tested the trends between count data, ratios on Ti, and calibrated data for all of the 10 elements (Table S1). The correlation coefficient between ratios of elements to Ti count, and the calibrated elemental concentrations is overall lower than the count and calibrated element concentrations correlation coefficient (Table S1). Example is shown with Ca in Figure S1.

We quantified concentrations of eight trace elements and 19 rare Earth elements on 13 samples by Inductively Coupled Plasma mass spectrometry (ICP-MS, conducted at the GeoAnalytical Lab at Washington State University) to estimate biases with the standard XRF calibration technique (Fig. S2). Because ICP-MS requires a sample mass of at least 1 g, sediment samples were chosen throughout the core based on their weight, minimizing the number of contiguous samples needed to attain this mass. These eight trace elements represent a small portion of the sediment composition, and their concentrations are the lowest recorded (30 to 300 times lower than the base cation concentrations). Because of low sample mass in several elements (e.g., Th, U, and Nb), many samples are close to the detection threshold; thus, the calibration results for those elements are the least accurate.

The eight trace elements quantified both by ICP-MS and calibrated XRF were compared with linear regressions. Pb, U, Th, Nb were present in the lowest
concentrations, and also had the lowest correlations between ICP-MS and XRF-derived concentrations (Table S2). Y, Zr, Sr, Rb displayed concentrations close to or over 0.01 mg/100 mg, and the two methods were strongly correlated ($r^2 > 0.80$; Table S2). The mean absolute percentage error calculated for these four elements is 4.8% (Table S2).

3. Superposed Epoch Analysis (SEA)

To assess the impacts of wildfires on geochemical proxies, we followed methods described in Dunnette et al. (2014) for superposed epoch analysis. A slightly modified version of these methods are provided here for reference, taken from Dunnette et al.:

“We assessed the biogeochemical impacts of fire using superposed epoch analysis (SEA), a nonparametric method used to evaluate the average response to multiple events in a time series (Adams et al. 2003). The analysis was conducted on high-severity catchment fires ($n = 11$ [17 in the current study]) and a subset of lower severity/extra local fires ($n = 9$ [13 in the current study]) using custom scripts written in MATLAB (available online at http://dx.doi.org/10.6084/m9.figshare.988687). Response variables [of the 10 elements measured in this study (Mg, Al, Si, P, S, K, Ca, Ti, Mn, and Fe)] were sampled every 0.5 cm for c. 5 cm before and after each fire event. Outside of this window, subsamples from two consecutive 0.5-cm samples were analyzed at c. 1-cm intervals. The high-resolution sampling window represents c. 50–125 yr (depending on local sediment accumulation rates). The SEA was performed specifically on samples from 50 yr pre-fire to 75 yr post-fire (a span selected based on trends during lodgepole pine stand development (Pearson et al. 1987). Because many samples c. 50–75 yr post-fire were not included in high-
resolution sampling, composite patterns over this span may be more muted than if they were sampled at higher resolution.

Before SEA, samples were interpolated to the median sample resolution (for biogeochemical samples) of 5 yr, and low-frequency trends were summarized with a 500-yr locally weighted regression robust to outliers (Fig. S3). To minimize bias arising from long-term changes in response variables, we subtracted the low-frequency trends from the interpolated time series to obtain residual series. Residuals were averaged across events to produce composite time series (hereafter ‘response series’) showing each variable’s mean response to fire events, in 5-yr bins.

To assess the statistical significance of the response series, confidence intervals (CIs) were generated with a Monte Carlo randomization method. For each response variable, 10,000 time series were created by randomly shuffling samples in five-sample blocks to account for temporal autocorrelation. Each random time series was sampled via the same method used to generate the observed response series, producing random composites. The $0.5^{th}$, $2.5^{th}$, $97.5^{th}$, and $99.5^{th}$ percentiles from the 10,000 random composites were used to construct 95% and 99% CIs.

In the current study, all high severity catchment fires were included in the SEA. Although there were four high severity catchment fires that occurred within 100 years of another high severity catchment fire, the direction and significance of SEA results did not differ if those fires were excluded from the SEA. Response of elements to high severity catchment fires, and low severity/extra local fires are presented in Figure S4.

4. **Principal Component Analyses (PCA)**


Principal component analyses (PCA) were conducted (R Core Team 2014) to assess (i) the relationship among elements, and (ii) to compare lake sediment composition to plant remains, organic and mineral soils, charcoals and surface lake sediments. The first PCA was conducted on the 10 element concentrations (Mg, Al, Si, P, S, K, Ca, Ti, Mn, and Fe) of the 768 sediment samples from Chickaree Lake. The second PCA was run on 9 element concentrations of the 768 sediment samples from Chickaree Lake, and 31 samples from the watershed, including pine needles (n=6), spruce needles (n=2), litter (n=4), decomposing wood (n=1), organic soil (n=9), mineral soil (n=3), surface lake sediment (n=4), terrestrial charcoal (n=1), and sedimentary charcoal (n=1). The mineral soil samples correspond to the top 20 cm, the A horizon, and the C horizon of the US soil geochemical landscape site #12891, Grand County, Colorado. The elemental concentrations were obtained by ICP-MS technique. The PCAs were centred and scaled, with no axis rotation.

5. Correlations between biochemical proxies and the 10 rock-derived elements

To test correlations between (i) previously published biochemical proxies (%N, %C, C:N, magnetic susceptibility, charcoal accumulation rate, $\delta^{15}$N, and $\delta^{13}$C) by Dunnette et al. (2014), and the 10 elements selected here (Mg, Al, Si, P, S, K, Ca, Ti, Mn, and Fe), and (ii) in between the 10 elements, we performed both a Spearman, and a Pearson correlation test (Table S3).

None of the Spearman and Pearson correlations are over 0.65 between the 10 elements and the biochemical proxies, indicating an absence of strong relationship between atmospheric source nutrients, and rock source nutrients. In addition, Ti and magnetic susceptibility, both used in the literature as erosion proxies, are not strongly
correlated (0.44 and 0.48 Spearman and Pearson correlation coefficients, respectively).

Among the 10 elements, there are strong positive correlations between the four elements responding positively to high-severity catchment fires, and explaining the PCA (i) axis 1: Ti, K, Al, and Ca (Table S3). All the negative correlations for both Spearman and Pearson tests involved Si or S in the pair comparison (Table S3), indicating that S and Si are the two elements independent to the others in their source, or loss pathways.

**Supplemental Figures and Tables**

**Fig. S1.** Comparison of elemental data from wavelength-dispersive XRF acquired with the Bruker Tracer III handheld instrument, with Ca as an example element. (A) Raw Ca raw count, (B) ratio of Ca/Ti, and (C) Ca calibrated with the Bruker Mudrock calibration dataset. Pearson correlation coefficient between Ca count and Ca calibration is 0.97. The correlation coefficient between Ca/Ti ratio and Ca calibration is 0.41 (see also table S1).

**Fig. S2.** Comparison of two methods to measure elemental concentrations in lacustrine sediments. Calibrated concentrations from XRF and Inductively Coupled Plasma for eight rare Earth elements. r-squared, p-values, and mean absolute percentage error are reported in Table S2.

**Fig. S3.** Time series for all 10 elements included in the Principal Component Analysis in Fig. 3A. Vertical solid red lines indicate the high-severity catchment fires (n = 17) and vertical dashed blue lines indicate the lower severity/extra local fires (n = 13) used in all analyses. The thick black lines are smoothed splines on 500-yr window of
element concentrations. Mann Kendall test results are reported on each graph, and indicate the significant of each element trend over time (p-value) and the direction of the slope: decreasing (positive value of tau) or increasing (negative value of tau).

**Fig. S4.** SEA for all elements for both high severity catchment fire and lower severity extra local fire events, as in Fig. 2 in the main text.

**Table S1.** Table of Pearson correlation coefficient for each of the 10 elements (Mg, Al, Si, P, S, K, Ca, Ti, Mn, and Fe) between (1) the count and the calibrated concentration, and (2) the ratio of element on Ti counts and the calibrated concentration.

**Table S2.** Table of linear regression r-square, p-values, and the mean absolute percentage error (MAPE) between the concentration obtain from ICP-MS method, and by calibrated XRF method for eight elements (Pb, Th, Rb, U, Sr, Y, Zr, and Nb).

**Table S3.** Table of correlation between (1) 10 elements, and (2) the elements and proxies presented in Dunnette et al. (2014) (%C %N, □15N, □13C, bulk density, and magnetic susceptibility (MS)).

**References**

