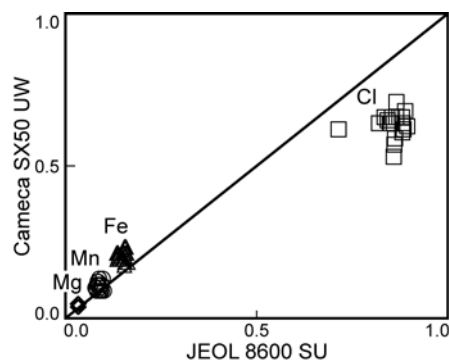


A. Reproducibility Results

Analytical precision for EPMA was assessed using a secondary standard (NMNH 104021 apatite) from the Smithsonian National Museum of Natural History. Major (Ca and P) and minor element (F and Cl) concentrations for most Ordovician samples were determined for several crystals from each sample. Totals of all oxides plus volatiles were between 96 and 101 weight percent. To ensure reproducibility of our results we have measured trace elements in an apatite standard NMNH 104021 as well as apatite crystals from the Fish Canyon Tuff (see Sell and Samson, 2011b) that are widely available in fission track counting laboratories.

The same crystals from a single relatively homogeneous apatite sample (Core sample 75NY-2 #2) were analyzed using WDS on the University of Wisconsin-Madison Cameca SX 50 and the Syracuse University JEOL JXA 8600 Superprobe. Reproducibility between Mn and Mg are within analytical error (Supplementary Fig. 1); however, Fe analyses were lower and Cl analyses were higher for the analyses acquired with the JEOL JXA 8600 Superprobe. The analytical precision of the measured elements is similar for both of the laboratories. Also, mounted apatite crystals from Emerson et al. (2004) were reanalyzed to test for reproducibility. Despite differences in absolute values, trace elements in apatite from the same samples provide the same trends at similar levels of precision (Emerson et al., 2004). K-bentonites reported in Samson et al. (1995) were recollected and analyzed with similar findings.



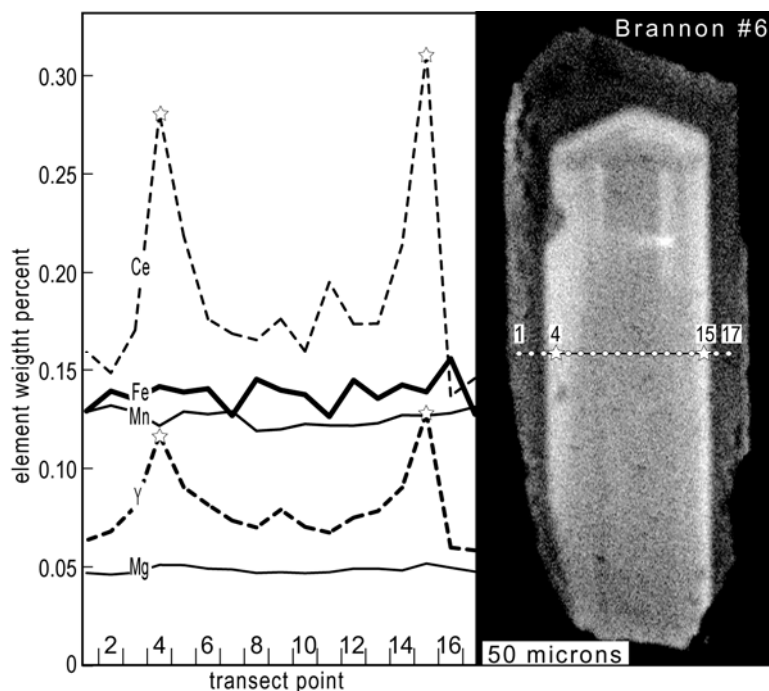
Supplementary Fig. 1.

Single crystals were tested for variations in trace element concentration by analytical transects across polished sections of crystals (Supplementary Figs. 2 and 3). Nearly all crystals examined from K-bentonites displayed variations in Ce and Y concentrations, and in most cases these variations coincided with separate zones identified by cathodoluminescence (CL). Even where CL did not show any visible zonation, analytical transects and three-point analyses across polished crystal sections still showed some systematic variation in all elements analyzed by electron microprobe for some crystals from complex samples.

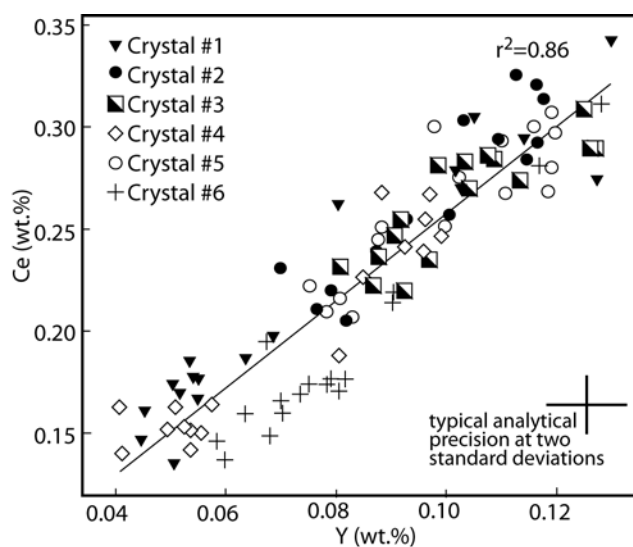
The variation in elemental concentrations did not limit our ability to define unique trends and thus characterize most samples statistical comparison. For example, some single crystals from the Brannon K-bentonite encompassed the entire range of concentrations defined by all the other crystals from that sample while other single crystals had considerably more homogenous Ce and Y contents (Supplementary Fig. 3). A few K-bentonites (e.g., Millbrig, Nittany, and Dolly Ridge K-bentonites) do show multiple clusters of Mg, Cl, Mn, and Fe concentrations in individual apatite samples, but the variance of each cluster is useful for discrimination. None of these analyses show an obvious correlation between apatite trace

Supplementary Data

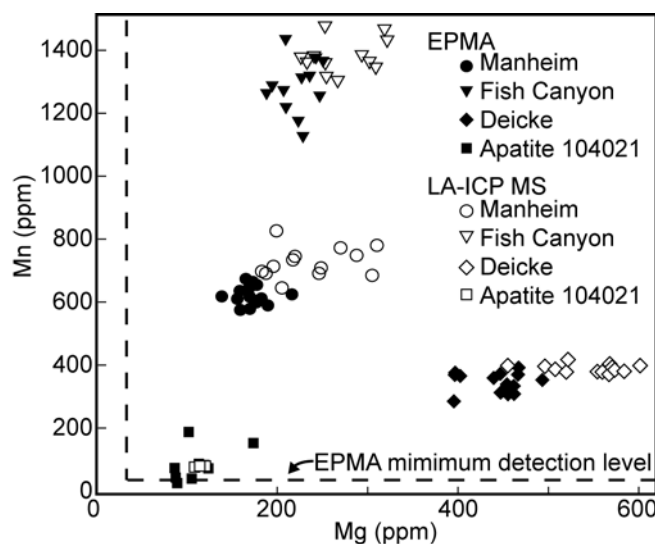
element concentrations and crystal size. The same apatite crystals of NMNH 104021 and some apatite from various tephra were analyzed both via EPMA and LA-ICP MS. Precision between the two methods for the same number of crystals was comparable for Mg and Mn (Supplementary Fig. 4).



Supplementary Fig. 2.



Supplementary Fig. 3.



Supplementary Fig. 4.

B. Statistical methods

All references herein are also in the main text. The apatite element data were subjected to a variety of statistical treatments to test for similarities among samples. We have applied ANOVA (e.g. Sell and Samson, 2011a), principle component analyses (PCA), and K-means clustering techniques (Sell and Samson, 2011b) to our data. The data presented here were examined with discriminant function analysis (DFA) using the commercially available software package called SYSTAT®, which is available as a freeware student version called MYSTAT 12 for Windows®. Discriminant function analysis is computationally similar to multivariate analysis of variance (MANOVA) and assumes that data are normally distributed and homoscedastic (equal variance among compared samples). These data assumptions of DFA are not strictly required, which is evident in the DFA of our dataset. For example, all Millbrig apatite data do not appear to be normal and homoscedastic on the basis of Shapiro-Wilk (p -value = 0.000) and Anderson-Darling normality tests and Bartlett's (p -value = 0.000) and Levine's (p -value = 0.000) tests, respectively. However, calculated F -values agree with interpretations based upon bivariate data plots. F -values calculated from the mean and variance of each multivariate sample, appear to be robust with respect to identifying potential matches (Supplementary Tables 3 and 4). The reason why DFA is robust is likely due to the large range values exhibited by apatite in tephra and their tendency for element data cluster for individual samples. Some samples with obvious multiple populations of apatite crystals could be split into separate groups using PCA and K-means clustering (Sell and Samson, 2011b). However, DFA appears somewhat less effective because n (number of analyses) becomes small for samples split into groups such that accurate comparison of variance is not possible. Supplementary Tables 3 and 4 are F -value matrices constructed on the basis of unfiltered data sets from this study, Samson et al. (1995), and Adhya (2011). All three studies broadly agree. The F -matrix does suggest some impossible correlations, and this has been shown to be a rare, but resolvable occurrence (Samson, et al., 1995). Each suggested correlation by the F -value matrix should carefully be examined by directly comparing all element data with consideration of other kinds of stratigraphic data. Using multivariate statistical methods to correlate ash-fall beds can be a perilous endeavor; see Pearce

Supplementary Data

et al. (2008) for a detailed explanation on the pitfalls of relying on multivariate statistical comparisons of geochemical data from ash-fall beds.

2015122_Sell_SuppDataB.xls