# Geochemical Fingerprinting of Yellowstone Hotspot Track (YHT) Eruptions from Ash Beds in the Central United States 

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#### Abstract

Volcanic ash beds have been shown to be reliable stratigraphic marker beds because they can be radiometrically dated using magmatic minerals: e.g. zircon, sanidine, etc. This can be utilized in any region containing ash beds and can be especially helpful where beds are laterally discontinuous, such as in the Ogallala Formation in western Kansas and Nebraska and overlying Pliocene and Pleistocene strata. These contain abundant volcanic ashfall beds, but regional correlations of these have so far been limited, due to their non-continuous outcrops and complex stratigraphy. U-Pb dating of zircon by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at The University of Kansas from several ash outcrops has confirmed the correlation of these ashes with Yellowstone hotspot track (YHT) eruptions.

Volcanic glasses from individual eruptions exhibit unique geochemical signatures, therefore lending each eruption its own distinct geochemical fingerprint. This tephrochronological approach yields robust correlations between the ash beds in the Great Plains strata of Kansas and Nebraska and their YHT source eruptions. The YHT eruptions Lava Creek B ( 0.6 Ma ) and Huckleberry Ridge ( 2.1 Ma ) of the Yellowstone Plateau and the Ibex Hollow (11.93 Ma) eruption of the Bruneau-Jarbidge (10.5-12.7 Ma) eruptive center on the Snake River Plain have previously been correlated to ash beds in western and central Kansas as well as northeastern Nebraska by major and trace element concentrations. Ash samples were collected in Norton, Smith, Jewell, and Meade Counties in Kansas and the Ashfall Fossil Beds State Historical Park in northeastern Nebraska. Trace element data trends of the Norton and Smith county, KS ashes can be correlated to the Ibex Hollow eruption (11.93 Ma) of the BruneauJarbidge YHT eruptive center when compared to published values. Trace elements in volcanic glass shards from an ash bed in Jewell county correlate to Lava Creek B ( 0.6 Ma ). Samples from


different locations in Meade County, KS can be correlated with Huckleberry Ridge (2.1 Ma) and Lava Creek B ( 0.63 Ma ), respectively. The sample taken from the basal unit of the deposit in Ashfall Fossil Bed State Historical Park, NE correlates with the Ibex Hollow eruption of the Bruneau Jarbidge eruptive center. Utilizing single shard analysis to generate bivariate elemental plots, chemical trends, and multi-element correlation coefficients proved to be more useful for determining correlations as opposed to comparing average measured values to published average values.

The insight from this research into the provenance of volcanic glass helps to further refine the understanding of dispersal of volcanic ash and other minerals from their associated eruptive centers, and the chronostratigraphy of High Plains, especially the Ogallala Formation. Research discussed here strives to demonstrate advantages in both processing time and overall analytical cost compared to traditional $\mathrm{U}-\mathrm{Pb}$ techniques. This technique is also applicable to deposits that are too young to be reliably dated using U-Pb dating. The demonstrated high efficiency of the geochemical fingerprinting approach will allow researchers to have a denser coverage of the hundreds of ash deposits throughout the Central United States, and elsewhere, to improve stratigraphic correlations.

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## INTRODUCTION

Reconstructing the chronostratigraphy and depositional history of continental basins is a difficult task. Volcanic ash beds play an important role as relative and absolute time markers in many of these studies where biostratigraphy is generally not applicable or does not supply the necessary time resolution, as for example for the Neogene Ogallala Formation of the Central USA and overlying strata (Swinehart, 1974; Sweet, 1999; Ludvigson et al., 2009). The present study uses geochemical "fingerprinting" of individual volcanic glass shards by laser ablation inductively coupled mass spectrometry (LA-ICP-MS) to test the robustness of this approach and methodology, and compares it to the previously used bulk chemical approach of solution ICPMS (e.g. David, 2009), to Electron Microprobe (EMP) for major and minor elements and X-Ray Fluorescence (XRF) for minor and trace elements (e.g. Perkins 1988, Perkins \& Nash 2002), and to the LA-ICP-MS data of Pearce et al. (2004). Geochemical fingerprinting takes advantage of a volcanic eruption's unique chemical signature by comparing multiple major, minor, and trace elements of an unknown ash deposit to the chemistry of an ash deposit of known origin in order to effectively identify an ash deposit of unknown origin (details below). Coupled with physical identification methods (e.g. petrography) and/or mineral ages, geochemical fingerprinting provides robust correlations between ash units (e.g. Lowe, 2011). Methods defined here are applied to the Ogallala Formation in the High Plains region of the US and overlying Pleistocene strata in effort to produce robust chronologic correlations.

The stratigraphy of many continental sedimentary units throughout the central US is difficult to reconstruct due to lack of continuous beds or defined stratigraphic units across wide regions. One such case is the Ogallala Formation in the Central US (Fig 1, Fig 3) and overlying Pleistocene units. These are continental deposits in which classic lithostratigraphy is difficult to
perform outside of localized basins or small regions. Bedding is laterally discontinuous, therefore, defining consistently identifiable units for the entire reach of a formation is impossible (Ludvigson et al., 2009). Biostratigraphy can give insights into a specific age range, but the age uncertainty (estimated $\sim 3 \mathrm{Ma}$ for the Ogallala Fm.) associated with this evidence is too high to be of much utility where precise ages of units are needed to understand stratigraphic architecture (Fig 1) (Diffendal, 1982).

Volcanic ash beds can be used as marker beds in many depositional environments, e.g. marine sediments, lacustrine and continental basins (Boellstorff 1976; Perkins et al., 1995; Hannan \& Totten, 1996; Perkins 1998; Perkins \& Nash, 2002). Assigning a volcanic ash layer to a specific source eruption age allows lateral correlations to be made. Several minerals in these deposits, such as zircon, sanidine, and apatite can be reliably dated using U-Pb or Ar-Ar geochronology (Harley \& Kelly 2007; Gehrels 2011; Rivera et al, 2014; Matthews et al, 2015).

Additionally, since each eruption contains a unique geochemical signature, minor and trace element data from volcanic glass shards and minerals found in ash bed deposits can be used to recognize each eruption from a particular eruptive center with relative certainty (e.g. Perkins \& Nash, 2002; Pearce et al., 2004; Tomlinson et al., 2010; Lowe, 2011). This method of characterizing volcanic ash deposits is known as geochemical fingerprinting. Geochemical fingerprinting is a method that takes advantage of the unique major and trace element compositions of separate volcanic eruptions. Because no two eruptions - even from the same volcanic center - are the same, we can resolve the differences using their geochemical fingerprint (e.g. Perkins \& Nash, 2002; Pearce, 2007; David, 2009; Tomlinson et al., 2010). Studies using this tephrochronological technique have been successful in correlating proximal regions to major volcanic centers, such as those in Wyoming, Montana, and Idaho (e.g. Perkins \& Nash, 2002)
with respect to the Yellowstone Hotspot Track (YHT) and in many other studies worldwide (e.g. Pearce et al., 2007; Steinhauser et al., 2010; Kraus et al., 2013; Monteath et al., 2019).

Geochemical fingerprinting is also useful for ash deposits distal to possible eruption locales and has been successfully performed in regions such as Nebraska, Utah, and the Gulf of Mexico (e.g. Perkins et al., 1998; Perkins and Nash, 2002; Pearce, 2004; Totten et al., 2005). It specifically has utility in locales where stratigraphic correlations have otherwise been difficult to obtain, such as the focus of this study, the Ogallala Formation and overlying Pleistocene units in the Central United States (e.g. David, 2009; Ludvigson et al., 2009). Eruptions of interest for stratigraphic work in near-surface Neogene strata of the Ogallala Formation and overlying Pleistocene units in Kansas and Nebraska include ashes from the Lava Creek B ( 0.63 Ma ), and Huckleberry Ridge (2.1 Ma) eruptions, and from the Bruneau-Jarbidge (10.5-12.7 Ma) eruptive center of the YHT (Fig. 2) (Izett, 1981; David, 2009; Ludvigson et al., 2009). U-Pb geochronology of zircons at The University of Kansas has dated ash beds in the Ogallala Fm. from locations in central Kansas (Hallman, 2015) at $11.7 \pm 0.1 \mathrm{Ma}$, and in NE Nebraska within uncertainty to the same age at $11.86 \pm 0.13 \mathrm{Ma}$ (Turner, 2018; Smith et al. 2018). These ages fall into the age range of the Ibex Hollow eruption of the Bruneau-Jarbidge eruptive center of the YHT.

This study focuses on establishing and testing a method and workflow for geochemical fingerprinting of volcanic glass by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at The University of Kansas. The approach is tested on volcanic glass from ash beds in six selected locations of Kansas and Nebraska, selected based on previously documented ages and chemical analyses (Izett and Wilcox, 1981; Ludvigson, et al., 2009; Wan, 2008, pers. comm. to Ludvigson; David, 2009; Hallman, 2016; Turner, 2017; Smith et al. 2018;) (Table 1). The goal of this research is to take advantage of recorded age and geochemical data to provide
robust correlations for the chosen samples. Whether the method is able to yield unique geochemical characteristics for each eruption event that deposited ashes in the central United States will be tested, and also which minor and trace elements are best suited in this approach. It is hypothesized that geochemical fingerprinting of glass shards by LA-ICP-MS is less laborintensive and therefore faster and less expensive than $\mathrm{U}-\mathrm{Pb}$ zircon geochronology. The results will help correlate time equivalent units of the Ogallala Fm. and overlying strata across the Central US and to reevaluate the mapped extents of these formations.

The YHT eruptions Lava Creek B ( 0.6 Ma ), Huckleberry Ridge (2.1 Ma) of the Yellowstone Plateau and the Bruneau-Jarbidge (10.5-12.7 Ma) eruptive center of the Snake River Plain, have previously been correlated to ash beds in western and central Kansas using major and trace element concentrations (Pearce et al., 2004; David, 2009; Ludvigson et al., 2009). Ash samples were collected in Norton, Smith, Jewell, and Meade Counties in Kansas and Ashfall Fossil beds State Historical Park in Northeastern Nebraska.

The insight from this research into the provenance of volcanic glass will help further refine the understanding of dispersal of ash and other minerals from their associated eruptive centers, and the Neogene chronostratigraphy of the Central US. The results of this study on geochemical fingerprinting of individual volcanic glass shards by LA-ICP-MS will test three main hypotheses: (1) can distal ash deposits be positively correlated to their source eruptions using LA-ICP-MS analytical methods, (2) can differences in chemistry due to alteration or other petrologic process be identified, (3) can the obtained results be used to make stratigraphic correlations across units that span across large areas, such as the Ogallala Fm. and overlying Pleistocene units in the Central US.

## GEOLOGICAL SETTING

## Ogallala Formation

The Ogallala Formation consists of fluvial and eolian sediments shed from the uplifting Rocky Mountains onto the Great Plains during the Miocene-earliest Pliocene (Fig. 1). This formation covers the modern-day High Plains region in the central United States extending from New Mexico and Texas in the south to Wyoming and South Dakota in the north (Fenneman, 1917) (Fig 3). The formation is largely made up of gravels, sand, and clays, and contains abundant lenticular ashfall beds of limited extent. Minerals found in ashfall beds make them well-suited for methods related to dating continental deposits (e.g. Swineford, 1963; Frye et al., 1956; Gutentag et al., 1984; Ludvigson, 2009). Most of the volcanic ashes in these units are sourced from large-scale explosive eruptions related to the Yellowstone Hotspot Track (YHT). The Ogallala Formation also hosts the High Plains aquifer, which is the source of much of the drinking and agricultural water used in this expansive region of the central United States (Sophocleous, 2009). The Ogallala is overlain by Pleistocene strata in the Western region of Kansas, which consists of terrace deposits, loess, and dune sands (Kansas Geological Survey, 2008) and locally contain volcanic ash lenses (Ludvigson et al., 2009).

## Yellowstone Hotspot Track

The Yellowstone Hotspot Track (YHT) (Pierce \& Morgan 1992; Ellis et al, 2013) is defined by a line of volcanic caldera eruptions thought to be caused by a mantle plume under the Northwestern United States. Eruptions began near the Nevada-Oregon border at ca.16.4-16.7 Ma (e.g. Bruesecke et al. 2008; Coble \& Mahood, 2012) and occur with a frequency of about 600,000 years. The most recent eruption occurred in the western portion of Wyoming and is
called the Lava Creek B eruption, recently re-evaluated to have an age of ca. 630 ka (Matthews et al. 2015). Caldera eruptions are known to be extremely explosive in nature and can produce over $300 \mathrm{~km}^{3}$ of material in a single eruption (Perkins \& Nash, 2002). Ash injected into the stratosphere from these eruptions can travel thousands of kilometers before being deposited in regions far away from any appreciable volcanic activity, i.e. for the YHT eruptions in Kansas and Nebraska (Totten et al., 2005). Ashfall deposits of interest for this study include Ibex Hollow (11.93 Ma), Huckleberry Ridge (2.1 Ma), and Lava Creek B ( 0.6 Ma ). Suspected source eruptions are selected based on previously reported age and geochemical data available for these sample locations (Table 1).

## Sample Locations

Volcanic ashes were collected from 5 locations across the state of Kansas and one sample was collected at Ashfall Fossil Beds State Historical Park in Nebraska (Fig 3). The following paragraphs briefly describe the locations, suspected source eruptions, and previously documented information about these locations.

Samples HP14-05b and HP14-07 were initially collected for the zircon U-Pb geochronologic study of Hallman (2016) from the Calvert Ash mine located in Norton County, KS (Fig 3, locality \#2). The ash deposit here is light grey and poorly lithified, with abundant glass shards, and a calcrete cement at the top. Sample HP14-07 is a fine-grained vitric ash collected from an abandoned face of the Calvert ash mine (Appendix A, Pic \#1). HP14-05b is a massively bedded, fine-grained vitric ash also located at the Calvert ash mine (Appendix A, Pic \#2).

This ash deposit is suspected to be sourced from the Bruneau-Jarbidge eruptive center of the YHT (11.93 Ma) (e.g. Swineford, 1963; Potter, 1991; Ludvigson et al., 2009; Smith \& Ludvigson, 2011). This is further supported by the zircon $\mathrm{U}-\mathrm{Pb}$ dating yielding ages of about 11.7 Ma for both HP14-05b and HP14-07 (Hallman, 2016). These samples will serve as a control to help demonstrate the robustness of the correlations determined using the methods outlined in this study.

Sample SCS-KMI-16 was collected in Smith County, KS (Fig 3. locality 3, Pic 4). The exposed deposit is poorly lithified and grey, containing abundant glass shards with a minor amount of calcrete cement. The exposed ash deposit is currently mapped outside of the extent of the Ogallala Formation in Western Kansas, due to bedrock exposure being limited to roadcuts and incised streambeds (Hallman, 2016). Because bedrock exposures are rare in this area, the ash bed has previously been assumed to be part of the Early Miocene sediments that dominate Eastern Kansas (Ludvigson et al., 2009). To test this assumption, we sampled the same ash deposit from the Wanner family ranch outside of Smith Centre in Smith County, KS to determine its origin. Generally, ashfall samples in Kansas found outside of the Ogallala Formation are assumed to correlate with either the Pleistocene Lava Creek B, the Quaternary Huckleberry Ridge eruptions of the YHT or the Quaternary Long Valley caldera (Bishop Tuff) eruption in California (Izett and Wilcox, 1982). However, major and trace element geochemical fingerprinting performed by the USGS tephrochronology lab have verified samples taken in this location to correlate with the Ibex Hollow eruption of the YHT, contradicting the expected age correlation for this location (Ludvigson, 2009).

Sample number AFB-00 is taken from the basal unit of a section of volcanic ash in Ashfall Fossil Beds Historical State Park, near Royal, NE (Fig 3., location 1). This ashfall bed
has been correlated to the Bruneau-Jarbidge eruptive center of the YHT (Perkins et al., 1998; Tucker et al., 2014), based on the diverse faunal succession of mammals and plant remains found there. Recent $\mathrm{U}-\mathrm{Pb}$ zircon dating from the same basal unit sample of the Ashfall deposit (Turner, 2017; Smith et al., 2018) yields an age of $11.86 \pm 0.13 \mathrm{Ma}$, suggesting the likely source eruption for this deposit is also the Ibex Hollow eruption of the YHT.

Sample JCS-KMI-16 was collected in Jewell County, KS from the Mankato Ash Mine (Fig 3, location 4). This ash is mapped outside of the extent of the Ogallala Formation as shown by the most recent surficial map produced by the Kansas Geological survey (KGS, 2008). The ashfall deposit has previously been correlated to the Lava Creek B (0.6 Ma) eruption of the YHT (Wan, 2008, pers. comm. to Ludvigson; David, 2009).

Multiple ash deposits have been identified in Meade County, KS (Bayne, 1976; Izett \& Wilcox, 1982; David, 2009; Ludvigson, 2009). Two sample locations were chosen for this study based on their documented volcanic sources (Table 1). These samples were collected as part of an ongoing study by the KGS. Sample number BOR-S2-01 (Fig 3, locality \#5), here referred to as Borcher's Badlands (see Table 1), has been correlated with the Huckleberry Ridge (2.1 Ma) YHT eruption based on zircon fission-track ages (Naeser et al., 1973) and geochemical fingerprinting by bulk glass solution ICP-MS (David, 2009). Sample number MC-CA-01 (Fig 3, locality \#6), known as the Cudahy Camp ash deposit has been previously correlated to the Lava Creek B (ca. 0.6 Ma ) eruption of the YHT, also using bulk glass geochemical fingerprinting (David, 2009) and zircon fission-track ages (Naeser et al., 1973).

## METHODS

Seven samples were collected from six field sites with exposed volcanic ash layers throughout Kansas and Nebraska (Fig 3). All ash samples are poorly lithified and samples were
dug with a shovel from outcrops after exposing fresh surfaces to avoid surface contamination or contamination from overlying strata.

While volcanic glass is abundant in these ash bed deposits, it is also fragile and subject to alteration and surface contamination (e.g., Pearce et al., 2004; Blockley et al., 2005; Steinhauser \& Bichler, 2008). Samples studied here are poorly lithified, so we eliminated the possibility of destroying viable shards by not using hard rock processing techniques (crushing, sieving, aggressive acid etching). Glass shard samples were separated from sediments for laser ablation analysis using techniques similar to those outlined in Blockley et al. (2005). Techniques were modified to be more appropriate for analysis by LA-ICP-MS, as opposed to electron microprobe analysis. Approximately 5 grams of each sample were then treated with 1.5 M HCl solution overnight to dissolve any surrounding carbonate cement or surface contamination on glass shards. Samples were then sieved using a $196 \mu \mathrm{~m}$ mesh and glass shards were selected from the $>196 \mu \mathrm{~m}$ size fraction. Shards selected for analysis based on size, transparency and shape (e.g. Fig 4). Shards that were either very thin ( $<20 \mu \mathrm{~m}$ thickness), very curved, cloudy, contained large cracks or bubbles, or with pitted surfaces were not selected for analysis. Between 30-50 glass shards chosen per sample for analysis were mounted on double-sided tape on 1-inch epoxy mounts.

Analysis was performed using a Photon Machines Analyte G2 193nm excimer laser coupled with a Thermo Element2 Inductively Coupled Plasma Mass Spectrometer (LA-ICPMS). Laser and mass spectrometer settings are defined in Appendix B. Elements selected for analysis include $\mathrm{Ca}, \mathrm{Ti}, \mathrm{V}, \mathrm{Mn}, \mathrm{Rb}, \mathrm{Y}, \mathrm{Zr}, \mathrm{Nb}, \mathrm{Ba}, \mathrm{Ce}, \mathrm{Nd}, \mathrm{Sm}, \mathrm{Eu}, \mathrm{Gd}, \mathrm{Dy}, \mathrm{Yb}, \mathrm{Hf}, \mathrm{Pb}, \mathrm{Th}$, and U, based on their petrological significance to identify source eruptions (Perkins \& Nash, 2002; Pearce et al., 2007; Tomlinson et al., 2010). Isotopes chosen for analysis were based on relative
abundance and avoidance of significant mass interferences that could occur during analysis (Appendix B).

Data was reduced using Igor Pro and Iolite software packages using the Trace ElementIS data reduction scheme (Paton et al. 2010; 2011). ${ }^{43} \mathrm{Ca}$ is used as internal standard because it is relatively abundant in both the standards and unknown samples and free of major isobaric interferences. ${ }^{43} \mathrm{Ca}$ was chosen as the internal standard based on tests carried out with ${ }^{44} \mathrm{Ca}$ and ${ }^{29} \mathrm{Si}$ as internal standards. Other LA-ICP-MS studies use ${ }^{29} \mathrm{Si}$ as internal standard, but in the case of this study, ${ }^{29} \mathrm{Si}$ produced data that was not reproducible when compared to ATHO-G (Hu et al. 2009, Jochum et al. 2010), possibly due to an isobaric interference with several nitrogen, oxygen, carbon and hydrogen molecules at this mass. Using ${ }^{43} \mathrm{Ca}$ as the internal standard gave results within <5\% of published best estimates for the NIST 612 glass (Fig 5a) (Jochum et al, 2011). Values for ATHO-G produced results with $\leq 10 \%$ bias for all reported elements except for Ti ( $+11.9 \%$ bias) and Eu ( $-12 \%$ bias) (Jochum et al, 2006) (Fig 5b). Data generated in these method tests can be found in Appendix C. ${ }^{43} \mathrm{Ca}$ as an internal standard is sensitive to contamination from plagioclase micro inclusions, with significantly higher Ca content than the rhyolitic glass (Pearce et al., 2004). The total CPS yield and calculated ${ }^{44} \mathrm{Ca}$ were monitored and analyses outside of the expected data range were not used for final reporting (see Appendix E for details).

Data were excluded based on duration of analysis, internal standard error, and ${ }^{43} \mathrm{Ca}$ count rates. A combination of calculated similarity coefficients (SC) (Borchardt et al. 1974) and discrimination diagrams are generated to provide correlations between ash samples and literature data. A minimum SC of 0.86 was defined as a positive correlation (Borchardt et al., 1974).

Elemental data trends were also compared and evaluated against literature data where possible.

## RESULTS

Results for major and trace element concentrations obtained by LA-ICP-MS for seven volcanic ash samples are listed in Appendix E. The results are also presented in sets of element correlation plots and element ratio correlation plots for each set of samples (Figs 6-11). Data were excluded based on duration of analysis, internal standard error, and ${ }^{43} \mathrm{Ca}$ count rates. The sample sets are organized in text sections according to the source eruption they have been correlated with, based on previously published geochemical or geochronological data or stratigraphic correlation assumptions.

## Samples assigned to Lava Creek B (JCS-KMI-16 and MC-CA-01)

The two samples discussed in this section (from Jewell County and Meade County, KS) have been designated as sourced from the Lava Creek B eruption based on their previously published geochemistry (David 2009, Ludvigson 2009) (See Table 1). Thirty-five analyses were obtained from JCS-KMI-16 and 40 data points were collected from MC-CA-01. Data are presented as individual data points instead of reporting average values because reporting a singular average value for each element may omit important petrological information, such as correlated concentrations. In the case of these two samples, two distinct populations of glass shards were identified based on Ba concentrations, one with $\mathrm{Ba}<150 \mathrm{ppm}$ and one with $>150 \mathrm{ppm}$ (here referred to as "high Ba" and "low Ba") (Fig 6a). Nineteen of thirty-five data points for JCS-KMI-16 fell into the low Ba population with the remaining sixteen segregated into the high Ba population. Thirteen of the forty data points for MC-CA-01 fell into the low Ba population with the remaining twenty-seven points falling into the high Ba population. Bimodal element concentrations have also been reported for Lava Creek B ashes by Pearce et al. (2004) based on Fe concentrations, which correlate with the Ba groups. Other element vs. element plots display
correlated (6b: Nd-Zr) or anti-correlated (6c: Y-Zr; 6d: Nb-Zr) trends. As a fluid-immobile HFS element that generally increases with fractional crystallization, zircon was chosen for the x -axis of these plots. It is notable that in the $\mathrm{Ba}-\mathrm{Zr}$ and $\mathrm{Nd}-\mathrm{Zr}$ plots, the reference average values of Pearce et al. (2004) lie on the same trends as the data presented here, whereas for Nb and Y the concentrations calculated here are significantly higher than the reference average values.

Plots of element concentration against $\mathrm{Ce} / \mathrm{Zr}$ (because both are weathering-resistant HFS elements increasing with fractional crystallization, the $\mathrm{Ce}-\mathrm{Zr}$ ratio should be a robust value constant for a particular magma) vs other HFS (Y, Nb, Nd) and LIL (Ba) elements show overlapping data populations for JCS-KMI-16 and MC-CA-01. Fig 7a, c and d show bimodal distributions for $\mathrm{Y}, \mathrm{Ba}$, and Nd , respectively. The strongest separation of the modes is in Ba (Fig. 7c) with differences of a factor of 5, whereas differences in Y and Nd are more subtle (ca. $20 \%$ ). The Nb vs. Ce/Zr plot (Fig. 7b) does not show such a grouping but a positive correlation, similar to the low and high Ba and Fe shard populations (Pearce et al., 2004). Plots presented in figures 6 and 7 show both populations of glass shards (JCS-KMI-16 and MC-CA-01) bear a possible correlation to the Lava Creek B ( 0.6 Ma ) YHT eruption values from Pearce, et al. (2004).

Similarity coefficients (SC) were calculated between the data populations of JCS-KMI-16 and MC-CA-01 and LA-ICP-MS literature data of Pearce et al. (2004) from a sample of Lava Creek B tephra from Idaho (Appendix D). SC was calculated using elemental concentrations of $\mathrm{Rb}, \mathrm{Zr}, \mathrm{Nd}, \mathrm{Ba}$, and Ce . Grain populations for JCS-KMI-16 and MC-CA-01 overlap well with one another and can be correlated to one another. Glass shards from both samples, JCS-KMI-16 and MC-CA-01, in the low Ba population correlate with the $>1.6 \% \mathrm{Fe}$ population of Pearce et al. (2004) (average SC values 0.87 and 0.86 , respectively). Glass shards in the high Ba population
correlate with the $<1.6 \%$ Fe population of Pearce et al. (2004), with average SC values 0.89 and 0.86 , respectively (See Appendix D).

Samples assigned to the Tuff of Ibex Hollow (HP14-05b, HP14-07, AFB-00, SCS-KMI-16)

Samples described in this section have been interpreted to be sourced from the same eruption, described in the literature as Tuff of Ibex Hollow (Table 1; e.g. Perkins \& Nash, 2002). Based on this hypothesis, element vs. element (Fig. 8a-d, Ba, Nb, Y, Rb vs. Zr ) and element vs elemental ratio (Fig. 9a-d, $\mathrm{Ba}, \mathrm{Nb}, \mathrm{Y}, \mathrm{Rb}$ vs $\mathrm{Ce} / \mathrm{Zr}$ ) plots were generated to compare measured values with literature data (Perkins \& Nash, 2002). Thirty viable data points were obtained from HP14-05b, 32 from HP14-07, 43 from AFB-00, and 32 from SCS-KMI-16. Fig 8a and 8d (Zr vs Ba and Rb vs Zr ) show no appreciable correlated trend in the data. The 3 samples HP14-05b, HP14-07 and SCS-KMI-16 show indistinguishable, overlapping data ranges, whereas AFB-00 plots towards higher Ba and within the upper $50 \%$ percentile range of Zr . Niobium vs Zr and Y vs Zr (Fig 8b, and 8c, respectively) trends are consistent between all samples, suggesting a common source. Perkins \& Nash (2002) data plotted on Fig 8a, b, and d overlap well with experimental data ranges while the lower half of the Y value overlap with experimental data (Fig 8c). Fig 9 also displays experimental data that does not overlap with Perkins \& Nash (2002) due to a decreased Ce concentration in our experimental data. Positive correlation trends, especially for Y and Zr for samples from the Calvert ash mine (HP14-05b, HP14-07) in these plots may be related to fractional crystallization processes (Pearce et al., 2004).

Similarity coefficients calculated for all four samples to literature data of Perkins \& Nash (2002) obtained by electron microprobe were above 0.86 (Appendix D). Elements used to calculate SC were $\mathrm{Ti}, \mathrm{Mn}, \mathrm{Zr}, \mathrm{Nb}, \mathrm{Ba}$, and Th . As observed in other YHT eruptions (Pearce et
al., 2004), element vs. element plot trends are interpreted as evidence for fractional crystallization of plagioclase (Fig 8a-d).

Sample assigned to Huckleberry Ridge tephra (BOR-S2-16)

Forty-seven viable data points were collected for sample BOR-S2-16. Element vs. element (Fig. 10) and element vs ratio (Fig. 11) plots were generated to compare measured values with literature data (Pearce et al., 2004) for the Huckleberry Ridge tephra (e.g. $2.003 \pm 0.014 \mathrm{Ma}$, Gansecki et al. 1998; $2.059 \pm 0.004 \mathrm{Ma}$, Lanphere et al. 2002; $2.0794 \pm 0.0046$ Ma, Riviera et al. 2014) of the YHT. Figure 10 a and d ( Ba vs Zr and Nd vs Zr ) display a positive correlation trend while fig 10 b and $\mathrm{c}(\mathrm{Nb} \mathrm{vs} . \mathrm{Zr}$ and Y vs Zr ) display a negative correlation. Multiple populations of grains were defined based on Ba values in the same manner as for the Lava Creek B samples described above. These are clearly defined in the distribution of data shown in Fig 11 a. One population of thirty-one grains can be observed at 75-200 ppm, another of sixteen grains at $\mathrm{Ba}>200 \mathrm{ppm}$. Multiple populations of Ba such as this within a sample have been interpreted by the presence of plagioclase microphenocrysts within the glass shard by Pearce et al. (2004). The scatter of data in Fig 11b and 11c. may also be explained by such microphenocrysts.

For illustrative purposes, averages of values for this study are plotted on bivariate element plots along with average values reported in Pearce et al. (2004) (Fig 10a-d). While the plotted averages mostly both fall within the overall population of individual measured values (with the exception of 10 d , for which the literature data of Nd are higher than the values reported here), it is apparent that the distribution of the data populations of the individual measured grains strongly influences the reported average value. This demonstrates the problems inherent with only reporting and comparing average values for geochemical fingerprinting.

Similarity coefficients were calculated for BOR-S2-16 compared to a sample from the same geographic location reported in Pearce et al. (2004). Similarity coefficient calculation yielded an average $\mathrm{SC}=0.87$ (Appendix D) positively correlating this ash to the Huckleberry Ridge eruption of the YHT. Elements used to calculate the SC were $\mathrm{Rb}, \mathrm{Zr}, \mathrm{Nb}$, and U .

## DISCUSSION

Using geochronological methods such as $\mathrm{U}-\mathrm{Pb}$ zircon or $\mathrm{Ar}-\mathrm{Ar}$ feldspar dating to identify and correlate volcanic ash beds has utility in many instances. However, this can be both expensive and time-consuming because of the need to extract minerals from the volcanic ashes, e.g., by heavy liquid separation techniques. For large regional studies that aim to correlate marker beds/stratigraphic units across large areas, such as the Ogallala Formation and overlying Neogene units in the central US, the geochronology approach is therefore impractical. This study confirms that it is possible to positively correlate volcanic ash beds with their source eruptions using geochemical fingerprinting of individual glass shards via LA-ICP-MS in a relatively quick, cost-effective manner. Separate aspects of this procedure will be discussed in this chapter.

The results of this study on geochemical fingerprinting of individual volcanic glass shards by LA-ICP-MS test three main hypotheses: Using individual shard LA-ICP-MS, (1) can distal ash deposits be positively correlated to their source eruptions, (2) can differences in chemistry due to alteration or other petrologic process be identified, (3) can the obtained results be used to make stratigraphic correlations across units that span across large areas, such as the Ogallala Fm. and overlying Plio-Pleistocene units in the Central US. The following paragraphs explore and discuss the evidence for these hypotheses in the light of published literature.

## Correlating Distal Ashes to Source Eruptions

While rhyolitic glasses from different volcanic eruptions generally have inherent geochemical similarities in relative abundance of major elements, every eruption has its own unique geochemical fingerprint of trace elements or combination of major and trace elements (e.g. Pearce et al. 2004), which is the very basic tenet of geochemical fingerprinting applied to volcanic ash deposits (Lowe, 2011). Using individual glass shard analyses, a positive correlation of samples to their source can be made based on their geochemical fingerprints. Elements such as $\mathrm{Ti}, \mathrm{Mn}, \mathrm{Rb}, \mathrm{Zr}, \mathrm{Nb}, \mathrm{Ba}$, and REEs provide the framework for building fingerprints for unknown ashes. Due to differences in instrumentation, limits of detection, and statistical variations, it is not feasible to simply compare average concentration values to reported literature values. For example, reference data from Perkins \& Nash (2002) were obtained using electron microprobe (EMP) analysis and X-ray fluorescence (XRF) spectroscopy. While these methods are typically used to measure major and minor elements, LA-ICP-MS is limited in major element analysis (i.e. cannot measure Fe or K ), but it is very useful for measuring minor and trace elements, providing a broader range of elements than XRF and EMP. Instead, comparisons are made by plotting elemental ratios (Figs 7, 9, and 11). Statistical correlations of samples based on multiple elements have been performed using a correlation coefficient calculation approach (Borchardt et al., 1972) (Appendix D).

Earlier studies have demonstrated that multiple eruptions from the same caldera may produce chemical trends that are similar due to the similarities in petrogenesis (Pearce et al., 1999). It can be argued that correlation coefficient calculations may not be enough to definitively correlate ashes to their source eruptions if multiple eruptions of the source volcano of similar composition have to be considered. To test whether samples from the YHT are similar enough to
make an incorrect correlation, SC values were calculated for all samples versus all reference data (Appendix D) (Perkins \& Nash 2002; Pearce et al., 2004). The calculations (Appendix D) of the correlation coefficients show only one possible 'false positive' correlation of JCS-KMI-16 (high Ba) to Huckleberry Ridge (Pearce et al., 2004). This correlation is likely due to the relatively wide range of the comparative data values for JCS-KMI-16 (Appendix E).

## Discerning Multiple Geochemical Shard Populations Within One Sample

In the case of both primary and secondary ash deposits, there is a possibility for material from multiple eruptions being present in one outcrop (i.e. Trapper Creek, Idaho or Borcher's Badlands, Kansas). Analyzing individual shards instead of using bulk geochemical techniques, we were able to discern populations of grains from the same eruption with different trace element geochemical fingerprints. While major element analysis could prove indistinguishable for these glass shards, incompatible elements would be more strongly affected by fractional crystallization processes. Such is the case when caldera eruptions sample both fractionated upper parts and the less evolved deeper parts of a magma chamber (e.g. Pearce et al., 2004). Three samples from this study contain such different glass shard populations, JCS-KMI-16, MC-CA01, and BOR-S2-01 (see Table 1 for detailed descriptions). Similarly, Pearce et al. (2004) identified two populations in Lava Creek B glass shards from Idaho based on their Fe concentrations. While this study was not able to measure Fe , two populations of grains could be identified using Ba concentrations (Fig. 6a) within both Lava Creek B correlative samples JCS-KMI-16 and MC-CA-01. Using elemental concentrations and similarity coefficient calculations (Appendix D ), the low Ba concentration population from this study correlates with the high Fe population from Pearce et al. (2004) and the high Ba data correlates to the low Fe group from that same study.

Although glass is subject to alteration via cation exchange in aqueous solutions (e.g. Steinhauser \& Bichler, 2008) the effect of aqueous alteration from depositional environments or during sample preparation ( $<1 \%$ of ion absorption for elements $\mathrm{Rb}, \mathrm{Ba}, \mathrm{La}, \mathrm{Ce}, \mathrm{Nd}, \mathrm{Sm}$ ) would not be enough to account for the differences in concentration within the grain populations of this study. In this case, it is surmised that the difference in Ba concentrations is the result of two populations of grains sourced from different phases of the same eruption or different parts of the magma chamber as discussed in previous studies (e.g. Pearce et al., 2004; Leeman et al., 2008; Seligman, 2012).

The ability to observe two (or more) populations of glass shards within an ash sample is an advantage unique to using individual spots instead of bulk methods or simple averaging of results to interpret the data. Any chemical inhomogeneity-including cracks, inclusions, and surface contamination-would also be impossible to detect. Chemical variation due to analysis of micro-inclusions within the glass may also go undetected. Instead reported average values would fall within neither discrete population of grains and would produce a high RSD (>15\%). In this study, the average Ba concentration of the two samples correlated with the Lava Creek B eruption would be 130 ppm with $69 \%$ RSD for JCS-KMI-16 and 159 ppm with $53 \%$ RSD for MC-CA-01. After splitting the results of both samples into high and low Ba populations, the $\%$ RSD values are much lower (7.1 and $7.62 \%$ for high Ba averages, respectively).

Individual shard analysis may show trends reflective of crystal fractionation. Therefore, the use of element ratio plots may distinguish YHT eruptions from each other more distinctively than bivariate element concentration plots. This lends added robustness to correlations due to eliminating influences from systematic uncertainties in calibrations of absolute concentration. To be fully confident in the produced correlations, a reasonable minimum number of analyses
should be performed and included in correlation calculations. For this study, 30-50 individual shard analyses were considered enough to produce a robust dataset.

## Applications to Stratigraphic Correlations

Findings of this study support both expected and unexpected correlations with respect to the extent of the Ogallala Formation in Western Kansas and Nebraska, a formation where lithostratigraphic correlations are difficult to perform and correlations rely heavily on the use of expensive radiometric mineral age and relatively imprecise fossil stage data (Ludvigson, 2009). Samples were chosen based on published correlations of their provenance, and their proximity to the mapped edges of the exposed Ogallala Formation. In the following paragraphs, we will discuss the correlations of volcanic ash deposits that have been confirmed by this study and one correlation that contradicts the stratigraphy as it is currently mapped.

The samples taken from Meade County (BOR-S2-01 and MC-CA-01) were collected from units overlying the Ogallala Fm. and were previously correlated with the Huckleberry Ridge (2.1 Ma) and Lava Creek B (0.6 Ma) eruptions, respectively (Izett \& Wilcox 1982; Pearce et al., 2004; Ludvigson et al., 2009). Our results confirm these correlations. Sample JCS-KMI-16 from Jewell County was collected from an area beyond the extent of the Ogallala and, like many other ashes in Central and Eastern KS, correlated to the Lava Creek B ( 0.6 Ma ) eruption of the YHT (Izett, 1982; David, 2009; Ludvigson et al., 2009). This was supported by tephrochronologic analysis of a core sample from the same locale done at the USGS Tephrochronology Lab in Menlo Park, California (Wan, 2008, pers. comm. to Ludvigson) of the same outcrop, which agrees with our findings.

We also demonstrate the possibility to use geographically close samples to provide better spatial resolution of geologic unit boundaries. This applies to the samples from Norton (HP1405b and HP14-07), Smith (SCS-KMI-16) and Jewell (JCS-KMI-16) counties in Kansas. The Smith and Jewell county sites are mapped as being outside of the Ogallala Fm. and should logically correlate to the Lava Creek B YHT eruption (Izett, 1981; David, 2009, Ludvigson, 2009). However, data collected here as well as previously analyzed surface samples support a correlation of the Smith county sample (SCS-KMI-16) with the Ibex Hollow eruption. This supports correlation of the Smith County ash deposits with the Calvert Ash mine in Norton County, KS, a site that lies approximately 55 miles to the West, mapped within the extent of the Ogallala formation. Correlation between these two ash deposits suggests that the erosional extent of the formation might need to be reevaluated.

Similarly, the sample from Ashfall Fossil Beds State Historical Park in Nebraska (AFB$00)$ is mapped near the northeastern boundary of the Ogallala formation. It correlates well with the results of samples HP14-05b, HP14-07, and SCS-KMI-16 from Norton and Smith county ashes (Fig 08a-d, Fig 09a-d), suggesting these are all derived from the same eruptive source, which is supported by U-Pb zircon ages of ca. 11.9 Ma (Hallman 2015; Turner, 2016; Smith et al., 2018). Previous tephrochronology reports (Wan, 2008, pers. comm. to Ludvigson) and faunal succession correlations for the Ashfall site (Tucker et al., 2014) together with LA-ICP-MS geochemical analyses from this study lead us to correlate these ashes with the Ibex Hollow (11.93 Ma) eruption of the YHT.

This study shows that the approach used here can be used to define the boundaries of the Ogallala Fm. in Kansas and Nebraska more precisely. This may be difficult as outcrop exposures along the edge of the formation are not well exposed and are likely to be only located along
stream beds or roadcuts. However, with the detailed ash locality maps previously established (Izett \& Wilcox, 1982) and the use of satellite imagery, localities of interest for future stratigraphic work can be carefully chosen. Additionally, because sampling to obtain these ashes is relatively quick and does not require heavy drilling equipment, may make it more likely for property owners to allow sampling.

## Limitations of the geochemical fingerprinting approach

Reference literature data for comparison that analyzed the same elements is a limitation of the approach. For the YHT, most of the published data available for correlations are major and minor element concentrations measured using different instrumentation (EMP, XRF, etc.) (e.g. Perkins 1998, Perkins \& Nash, 2002, David 2009). Major element analysis can be difficult for high sensitivity LA-ICP-MS configurations, unless minor isotopes can be used, as applied to Si when used as an internal standard (e.g. Tomlinson et al., 2010), so those literature values were not usable for correlations in this study. For the Lava Creek B and Huckleberry Ridge eruptions, there is published LA-ICP-MS data (e.g. Pearce et al., 2004). Collecting vitric ash samples of known origin proximal to the eruption site and analyzing them alongside the distal samples of known and unknown origin, as done by Pearce et al. (2004) was outside the scope of this study but is recommended.

## CONCLUSIONS

For Ogallala Formation and overlying Neogene strata in the central US, abundant lenticular ash beds can be used to make stratigraphic correlations across units spanning thousands of kilometers. $\mathrm{U}-\mathrm{Pb}$ dating of zircons from the units of interest can provide accurate matches to source eruptions (e.g. Hallman 2016; Turner 2017; Smith et al., 2018), but this method involves labor-intensive mineral separation and analytical time and is expensive when
regional scale studies require dozens of samples to be correlated. Since the ash bed deposits are found throughout the Ogallala Formation and overlying Neogene strata in Kansas, Nebraska, and Oklahoma, there is utility in having a faster, less expensive way of analyzing samples to make effective correlations between many sites. Geochemical fingerprinting of glass shards from these ash beds can be used to correlate them across Kansas and Nebraska by tracing their provenance back to known large scale eruptions, e.g. along the Yellowstone hotspot track (YHT). Individual volcanic eruptions have been shown to have unique geochemical fingerprints (major and trace element signatures), yielding unique results and robust correlations (e.g. Perkins,1988; Perkins \& Nash, 2002; Pearce et al., 2007; Tomlinson et al., 2010; Lowe, 2011). Geochemical fingerprinting of volcanic ashes has been performed with success in other regions of the High Plains (e.g. Perkins, 1998), but few studies have been published about the Kansas Pearlette ash beds (Potter, 1991; David, 2009; Ludvigson et al., 2009). Pearlette ash beds have been defined by Izett \& Wilcox (1982) as undifferentiated ash beds with distinctive characteristics (e.g. light grey/white color, finely bedded, poorly lithified).

Previous studies on geochemical fingerprinting of volcanic ash in the area have used bulk methods that produced average values, either by solution ICP-MS (David, 2009) or by atomic absorption spectroscopy (AAS, Potter, 1991). The AAS results did not yield trace element data useful for correlating these ashes to potential source eruptions (Potter, 1991). Solution ICP-MS was successful for some correlations (David, 2009), but the preparation and analysis can be expensive and since this is a bulk analytical technique there is some uncertainty in the assumption that all measured material is from the same eruptive event, and other caveats about using bulk techniques as mentioned above. In the study by David (2009), 20 grams of sample material were required. In the LA-ICP-MS technique, individual glass shards are analyzed,
which allows discrimination between potential different shard populations within a deposit, observation of trends of magma fractionation between analyses, or detection of microscopic contamination with K-feldspar, as previously shown by Pearce et al (2004). In summary, the rapid analysis of multiple individual glass shard per sample by LA-ICP-MS allows insights into sample homogeneity and details of magma evolution that are not possible with any bulk technique.

Elemental concentrations from LA-ICP-MS spot analyses were used to construct bivariate and elemental ratio plots. Direct comparisons to reference literature values (mostly given as averages only) proved to be problematic where a range of values were found to be present in the glass shard population (i.e. Ba concentration in Lava Creek B samples). Therefore, similarity coefficient (SC) calculations based on multiple elements were performed for all samples (Appendix D) and matches were determined based on an average SC value $>0.86$ as recommended by Borchardt (1972). The possibility of false positive correlations was effectively excluded by comparing literature data from ash deposits of different eruptions.

Results produced here correlate three ash beds from Kansas and one from Nebraska (Ashfall Fossil Beds) to the tuff of Ibex Hollow eruption of the Bruneau-Jarbidge eruptive center of the YHT (Fig 02). Independent analysis of a sample from Smith County (Kansas) by the USGS Tephrochronology Lab (Wan 2008, pers comm. to Ludvigson) also determined a correlation to the Ibex Hollow eruption of the YHT. Geochronological evidence provided by UPb zircon ages from the Nebraska Ashfall Fossil Beds (Turner, 2016; Smith et al. 2018) and the Calvert Ash mine (Hallman, 2016) support this interpretation.

One sample from Smith County (Kansas) and one sample from Meade County (Kansas) correlate to the Lava Creek B eruptive center of the YHT. Independent analysis of samples from

Smith County by the USGS Tephrochronology Lab (Wan, 2008, pers. comm. to Ludvigson) also determined a correlation to the Lava Creek B eruption of the YHT. One sample from Meade County (Kansas) correlates to the Huckleberry Ridge eruptive center of the YHT. This is confirmed by Pearce, et al. (2004).

Future work toward a large-scale mapping initiative could be very beneficial to correlate and reconstruct the chronostratigraphy and development of the Ogallala Formation in the High Plains region. To improve the accuracy of the correlations proposed here, it would be worthwhile to collect and analyze vitric ash samples taken proximal to the source eruptions of interest in order to build a reference database obtained with the same analytical technique. This would be preferable to comparing with literature values because it would eliminate any complications that may arise in comparing results produced from different analytical methods (e.g. electron microprobe), calibration approaches (e.g. different reference materials, different internal standard elements) or sample preparation techniques.

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## FIGURES



Figure 1. Summary of tephrochronologic and biostratigraphic data constraining the Neogene age of the Ogallala Formation. While the North American Land Mammal Ages (NALMA) are useful for determining a general depositional age range of this formation, the ages ranges are very broad and have been unhelpful in distinguishing different members or performing extensive correlations (Ludvigson et al., 2009) of the Ogallala Fm. throughout the entire High Plains. U-Pb dates from zircons (Hallman, et al 2015; Turner, 2018; Smith et al. 2019) have constrained ash deposits in the region to a more confined age range ( $12.7-10.5 \mathrm{Ma}$ ) that fall into the age range of the Bruneau-Jarbidge YHT eruptions. Modified from Ludvigson et al. (2009).


Figure 2a. Map of the estimated ashfall extent of three major YHT eruptions relevant to the study, the Tuff of Ibex Hollow (ca 11.9 Ma) of the Bruneau-Jarbidge eruptive field (green), Huckleberry Ridge (red), and Lava Creek B (purple). Inset (blue rectangle) is shown in Fig. 2b. State borders of Kansas and Nebraska outline broadly the area of study.


Figure 2b. Subset from Fig. 2a, map of the Yellowstone Hotspot Track (YHT) eruptive centers, from Link \& Phoenix (1996) with calderas marked with eruption age ranges. Eruptions are younging from Southwest to

Northeast. YHT eruptive centers of interest for this research are Bruneau-Jarbidge (Br-Ja) Huckleberry Ridge (HR) and Lava Creek (LC). Colored stars have been placed near the areas of interest. Modified from Rose and Durant (2009) and Izett and Wilcox (1982).


Figure 3. Map of the extent of the Ogallala Formation (grey), associated with late Tertiary and Quaternary units (dappled), and sample locations of this study (red triangles). 1. Nebraska Ashfall Fossil Bed State Park, 2. Calvert Mine 3. Smith County, 4. Jewell County, 5. and 6. Meade County, KS. Modified from Sophocleous (2009).


Figure 4. Microscope image of glass shard from sample HP14-07 taken after laser ablation analysis.
Shards pictured here were chosen based on size, flatness, and lack of cracks, pits or bubbles. Laser ablation pits are $50 \mu \mathrm{~m}$ diameter. Some minor surface dust can be observed, which is eliminated from inclusion in the collected data by three pre-ablation laser shots.

Table 01. Summary of Sample names, ID\#, Location, Suspect sources, and supporting literature.

| Sample Name | Sample ID \# | Location | Suspected <br> source <br> eruption | literature |
| :--- | :--- | :--- | :--- | :--- |
| Calvert Ash | HP14-05b <br> HP14-07 | Norton County, <br> KS | Ibex Hollow <br> BJ YHT (ca <br> 11.93 Ma)* | Hallman, 2016 <br> Ludvigson et al., <br> 2009 <br> Izett \& Wilcox, 1981 <br> David, 2009 <br> Rose et al, 2003 <br> Swineford,1963 <br> Smith, 2011 |
| Smith County | SCS-KMI-16 | Smith County, <br> KS | Ibex Hollow <br> BJ YHT (ca <br> 11.93 Ma) | Ludvigson et al, 2009 <br> Izett \& Wilcox, 1981 <br> David, 2009 <br> Wan, E., 2008 |
| Ashfall Fossil Beds State | AFB-00 | Royal, NE | Ibex Hollow <br> BJ YHT (ca. <br> 11.93 Ma) | Tucker, et al 2014 <br> Perkins \& Nash, 2002 |
| Reference for source material: Perkins \& Nash, 2002; Pearce et al., 2004 |  |  |  |  |



Figure $5 \mathrm{a} \& \mathrm{~b}$. Reproducibility plots for the primary (NIST 612) and secondary (ATHO-G) reference materials. Fig a. shows \%bias values for elements measured agreed with published values within $\pm 5 \%$.Fig b. shows ATHO-G \% bias values for elements measured agreed with published values within $\pm 8 \%$ with the exception of $\mathrm{Ti}(+12 \%)$ and $\mathrm{Eu}(-12 \%)$.


Figure 6a-d. Bivariate element plots ( $\mathrm{Ba}, \mathrm{Nd}, \mathrm{Y}, \mathrm{Nb}$ vs Zr ) for samples suspected to be sourced from the Lava Creek B eruption (0.6 Ma). Published values for Huckleberry Ridge (2.1 Ma) and Bishop Ash (0.76 Ma ) are also plotted. Bishop Ash values for Y and Nb were outside of the area of the plots.


Figure 7a-d. Elemental ratio plots for volcanic ashes suspected to be sourced from the Lava Creek B eruption. Reference data from Pearce et al. (2004).


Figure 8a-d. Bivariate element plots- Zr vs. $\mathrm{Ba}, \mathrm{Nb}, \mathrm{Y}$, and Rb , respectively- for volcanic ashes suspected to be sourced from the Ibex Hollow eruption (see text for discussion). Ibex Hollow reference data averages are from Perkins \& Nash, (2002).


Figure $9 \mathrm{a}-\mathrm{d}$. $\mathrm{Ce} / \mathrm{Zr}$ vs. elemental concentration plots for $\mathrm{Ba}, \mathrm{Y}, \mathrm{Nb}$, and Nd , respectively. Plots show data from samples of this study and Perkins \& Nash (2002) average values for the Bruneau Jarbidge (11.93 Ma) YHT eruption.


Figure 10a-d. Element vs. element concentration plots for BOR-S2-01 (see locality 5 , fig 02 ) of Zr vs Y , $\mathrm{Nb}, \mathrm{Ba}$, and Nd. Average values for sample BOR-S2-16 (Fig 2. Location 5) were plotted against Pearce (2004) reported averages for Huckleberry Ridge tephra.


Figure $11 \mathrm{a}-\mathrm{d}$. Ce/Zr vs. Ba, $\mathrm{Y}, \mathrm{Nb}$, and Nd (respectively) plots for sample BOR-S2-01 (Fig 2, location 5) and averages reported by Pearce (2004) for Huckleberry Ridge tephra.

## APPENDICES

Appendix A: Annotated Outcrop Photographs


Picture 01. Photo courtesy of Jason Hallman. Sample HP14-07 (Fig 3, locality \#2) is a fine-grained vitric ash collected from an abandoned face of the Calvert ash mine.


Picture 02. HP14-05b is a massively bedded, fine-grained vitric ash also located at the Calvert ash mine
(Fig 3., locality 2). Photo courtesy of Jason Hallman


Picture 03. Fine-grained vitric ash sample MC-CA-01 collected from the Cudahy Camp location (Fig 3,
locality 5), Meade County, KS. Photo courtesy John J. Smith.


Picture 04. Fine-grained vitric ash sample SCS-KMI-16 collected from Smith County location (Fig 3, locality 3 ).

Table B-01. Operating parameters for the LA-ICP-MS. Parameters such as spot size, repetition rate, and energy density were chosen to maximize sample collection time and analytical precision without drilling through the thin volcanic glass shards.

| LA-ICP-MS operating procedures |  |
| :---: | :---: |
| Laser parameters- Photon machines Analyte G2 |  |
| 193nm ArF excimer |  |
| Energy Density | $4.0 \mathrm{~J} / \mathrm{cm}^{2}$ |
| Pulse Duration | 5 ns |
| Repetition Rate | 5 Hz |
| Spot size | $50 \mu \mathrm{~m}$ |
| He cell gas flow | $0.511 / \mathrm{min}$ |
| $\mathrm{N}_{2}$ cell gas flow | $0.51 / \mathrm{min}$ |
| Sampling | Spot |
| ICP-MS settings | Thermo Element2 Sector Field |
| RF Power | 1230 W |
| Plasma gas flow | $0.93 \mathrm{l} / \mathrm{min}$ |
| Carrier gas flow | $1.095 \mathrm{l} / \mathrm{min}$ |
| Torch | Garnet |
| Cones | Garnet |
| Data acquisition parameters |  |
| Count time on sample | 22 sec |
| Count time on background | 20 sec |
| Sweeps per reading (passes) | 1 |
| Replicates (runs) | 90 |
| Sample time | 42 |
| Isotopes | ${ }^{43} \mathrm{Ca},{ }^{44} \mathrm{Ca},{ }^{49} \mathrm{Ti},{ }^{51} \mathrm{~V},{ }^{55} \mathrm{Mn},{ }^{86} \mathrm{Rb},{ }^{89} \mathrm{Y},{ }^{90} \mathrm{Zr}$, <br> ${ }^{93} \mathrm{Nb},{ }^{137} \mathrm{Ba},{ }^{140} \mathrm{Ce},{ }^{146} \mathrm{Nd},{ }^{147} \mathrm{Sm},{ }^{153} \mathrm{Eu},{ }^{157} \mathrm{Gd}$ <br> ${ }^{163} \mathrm{Dy}{ }^{172} \mathrm{Yb}{ }^{178} \mathrm{Hf},{ }^{208} \mathrm{~Pb},{ }^{232} \mathrm{Th},{ }^{238} \mathrm{U}$ |
| External calibration standard | NIST 612, ATHO-G |
| Comment: | SQUID signal smoothing device used. |

## Appendix C: LA-ICP-MS Reference Material Validation

Table C-1: Average measured values for NIST-612 for all experiments, listed against reference values from Jochum et al. (2011). Percent bias is calculated in the same manner as Tomlinson et al. 2010.

| Element | mean value <br> $(\mathrm{ppm})$ | \%standard <br> Deviation | Reference values <br> (Jochum et al., 2011) | \%bias |
| :---: | :---: | :---: | :---: | :---: |
| Ca | 85200 | 1.3 | 85000 | $0.2 \%$ |
| Ti | 44.06 | 2.9 | 44 | $0.1 \%$ |
| V | 39.02 | 1.0 | 38.8 | $0.6 \%$ |
| Mn | 38.00 | 1.1 | 38.7 | $-0.8 \%$ |
| Rb | 31.42 | 1.2 | 31.4 | $0.1 \%$ |
| Y | 38.02 | 1.1 | 38.3 | $-0.7 \%$ |
| Zr | 38.01 | 1.4 | 37.9 | $0.3 \%$ |
| Nb | 40.03 | 1.1 | 38.9 | $2.8 \%$ |
| Ba | 39.70 | 1.6 | 39.3 | $1.0 \%$ |
| Ce | 38.73 | 1.2 | 38.4 | $0.9 \%$ |
| Nd | 35.92 | 2.2 | 35.5 | $1.2 \%$ |
| Sm | 38.10 | 2.2 | 37.7 | $1.1 \%$ |
| Eu | 35.01 | 1.0 | 35.6 | $-0.7 \%$ |
| Gd | 36.72 | 1.8 | 37.3 | $-0.6 \%$ |
| Dy | 36.01 | 1.3 | 35.5 | $1.4 \%$ |
| Yb | 39.19 | 1.1 | 39.2 | $0.0 \%$ |
| Hf | 35.02 | 1.4 | 36.7 | $-0.8 \%$ |
| Pb | 38.61 | 1.7 | 38.57 | $0.1 \%$ |
| Th | 37.79 | 1.1 | 37.79 | $0.0 \%$ |
| U | 37.41 | 1.4 | 37.38 | $0.1 \%$ |

Table C-2: Average measured values for ATHO-G for all experiments, listed against reference values from Jochum et al, (2006). Percent bias is calculated in the same manner as Tomlinson et al., 2010.

| Element | Reference <br> Values <br> (Jochum et al., <br> 2006) | Mean <br> Value <br> (ppm) | $\%$ <br> Standard <br> deviation | \% bias |
| :--- | :--- | :--- | :--- | :--- |
| Ca | 12000 | 11575.6 | 4.8 | $-3.5 \%$ |
| Ti | 1528.7 | 1711 | 7.3 | $11.9 \%$ |
| V | 3.9 | 3.58 | 6.04 | $-8.4 \%$ |
| Mn | 821.1 | 843.89 | 5.13 | $2.8 \%$ |
| Rb | 65.3 | 65.50 | 6.38 | $0.3 \%$ |
| Y | 94.5 | 88.27 | 3.28 | $-6.6 \%$ |
| Zr | 512.0 | 491.77 | 2.60 | $-4.0 \%$ |
| Nb | 62.4 | 64.72 | 6.61 | $3.7 \%$ |
| Ba | 547.0 | 508.18 | 2.71 | $-7.1 \%$ |
| Ce | 121.0 | 115.04 | 2.12 | $-4.9 \%$ |
| Nd | 60.9 | $\mathbf{5 7 . 5 0}$ | $\mathbf{3 . 3 9}$ | $-5.6 \%$ |
| Sm | 14.2 | 13.47 | 4.87 | $-5.1 \%$ |
| Eu | 2.8 | 2.43 | 3.83 | $-12.1 \%$ |
| Gd | 15.3 | 14.06 | 3.43 | $-8.1 \%$ |
| Dy | 16.2 | 15.90 | 3.41 | $-1.8 \%$ |
| Yb | 10.5 | 10.03 | 3.84 | $-4.4 \%$ |
| Hf | 13.7 | 12.74 | 3.71 | $-7.0 \%$ |
| Pb 208 | 5.7 | 5.63 | 8.50 | $-0.6 \%$ |
| Th | 7.4 | 7.20 | 3.02 | $-2.7 \%$ |
| U | 2.4 | 2.29 | 6.24 | $-3.5 \%$ |

## Appendix D: Similarity Coefficient

Similarity coefficient formula used to produce Table E. (Borchardt et al., 1972).

$$
\begin{aligned}
& d(A, B)=\frac{\sum_{i=1}^{n} R_{1}}{n} \\
& d_{(A, B)=\text { similarity coefficient for comparison }} \\
& \text { between sample } A \text { and sample } B . \\
& \mathrm{i}=\text { element number } \\
& \mathrm{n}=\text { number of elements } \\
& \mathrm{Ri}=\mathrm{Xi}_{\mathrm{i} A} / \mathrm{XiB}_{\mathrm{i} B} \text { if } \mathrm{XiB} \geq \mathrm{XiA} \\
& \mathrm{Ri}=\mathrm{Xi}_{\mathrm{i} B} / \mathrm{XiA}_{\mathrm{i}} \text { if } \mathrm{XiA}>\mathrm{XiB}_{\mathrm{i}} \\
& \mathrm{Xi}=\text { concentration of element } \mathrm{i} \text { in sample } A \\
& \mathrm{Xi}=\text { concentration of element } \mathrm{i} \text { in sample } B .
\end{aligned}
$$

Table E-1: Average Similarity Coefficients calculated for measured values vs. reference literature values. Numbers in bold are above the 0.86 threshold for positive correlation defined by Borchardt, et al 1972.

| Reference material |  | Perkins and Nash, 2002 | Perkins and Nash, 2002 | Perkins and Nash, 2002 |  | Pearce et al., 2004 | Pearce et al., 2004 | Pearce et al., 2004 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Source |  | YHT | YHT | YHT |  | YHT | YHT | YHT |
| Eruption |  | Tuff of Ibex Hollow | Lava Creek B | Huckle berry Ridge Tuff |  | Lava Creek B | Lava Creek B | Huckleberry Ridge |
| Sample name |  |  |  |  |  | $\begin{gathered} \text { UA256 } \\ (\mathrm{Fe}<1.6 \%) \end{gathered}$ | $\begin{gathered} \mathrm{UA} 256 \\ (\mathrm{Fe}>1.6 \%) \end{gathered}$ | UA598 |
|  | Elements used |  |  |  | Elements used |  |  |  |
| HP14-05b | Ti, Mn, Zr, Nb, Ba, Th | 0.93 | 0.65 | 0.72 | Rb, Zr, Nd, Ba, Ce | 0.73 | 0.62 | 0.81 |
| HP14-07 | Ti, Mn, Zr, Nb, Ba, Th | 0.94 | 0.64 | 0.71 | Rb, Zr, Nd, Ba, Ce | 0.74 | 0.62 | 0.81 |
| $\begin{gathered} \hline \text { SCS-KMI- } \\ 16 \\ \hline \end{gathered}$ | Ti, Mn, Zr, Nb, Ba, Th | 0.93 | 0.65 | 0.73 | Rb, $\mathrm{Zr}, \mathrm{Nd}, \mathrm{Ba}, \mathrm{Ce}$ | 0.72 | 0.64 | 0.8 |
| AFB-00 | Ti, Mn, Zr, Nb, Ba, Th | 0.87 | 0.66 | 0.71 | Rb, Zr, Nd, Ba, Ce | 0.66 | 0.62 | 0.73 |
| $\begin{gathered} \text { JCS-KMI- } \\ 16 \text { (low Ba) } \\ \hline \end{gathered}$ | Ti, Mn, Zr, Nb, Th | 0.64 | 0.83 | 0.74 | Rb, Zr, Nd, Ba, Ce | 0.71 | 0.87 | 0.63 |
| $\begin{aligned} & \text { JCS-KMI- } \\ & 16 \text { (high } \\ & \text { Ba) } \\ & \hline \end{aligned}$ | Ti, Mn, Zr, Nb, Th | 0.70 | 0.88 | 0.85 | Rb, Zr, Nd, Ba, Ce | 0.89 | 0.56 | 0.87 |
| $\begin{gathered} \text { MC-CA-01 } \\ \text { (low Ba) } \\ \hline \end{gathered}$ | Ti, Mn, Zr, Nb, Th | 0.53 | 0.80 | 0.72 | Rb, Zr, Nd, Ba, Ce | 0.69 | 0.86 | 0.61 |
| $\begin{gathered} \text { MC-CA-01 } \\ \text { (high Ba) } \\ \hline \end{gathered}$ | Ti, Mn, Zr, Nb, Th | 0.63 | 0.85 | 0.84 | Rb, $\mathrm{Zr}, \mathrm{Nd}$, Ba, Ce | 0.86 | 0.56 | 0.85 |
| BOR-S2-01 | Ti, Mn, Zr, Nb, Th | 0.63 | 0.82 | 0.86 | $\mathrm{Rb}, \mathrm{Zr}, \mathrm{Nb}, \mathrm{U}$ | 0.81 | 0.65 | 0.87 |

## Appendix E. LA-ICP-MS elemental concentration data

Notes on data exclusion: samples were sorted and rejected based on the following criteria

1) Sample duration $<7$ seconds were excluded
2) ${ }^{43}$ Ca count rates too low or too high (determined on a sample-by-sample basis)
3) ${ }^{44}$ Ca concentrations with errors $>10 \%$
4) Data outliers were also addressed on a sample-by-sample basis


| Table E-2 LA-ICP-MS Elemental Concentration Data: HP14-05 B (continued) |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Spot \# | $\begin{aligned} & \mathrm{Zr} 90 \\ & \mathrm{ppm} \end{aligned}$ | Int2SE | $\begin{gathered} \text { Nb93 } \\ \text { ppm } \end{gathered}$ | Int2SE | $\begin{gathered} \text { Ba137 } \\ \text { ppm } \end{gathered}$ | Int2SE | $\begin{gathered} \text { Ce140 } \\ \text { ppm } \end{gathered}$ | Int2SE | $\begin{gathered} \mathrm{Nd} 146 \\ \mathrm{ppm} \end{gathered}$ | Int2SE | $\begin{gathered} \text { Sm147 } \\ \text { ppm } \end{gathered}$ | Int2SE | Eu153 ppm | Int2SE |
| 1 | 315 | 15 | 44.2 | 1.8 | 395 | 19 | 145.2 | 7.1 | 55.4 | 2.6 | 10.89 | 0.73 | 0.645 | 0.042 |
| 2 | 289.6 | 9.7 | 43 | 1.4 | 473 | 15 | 142.1 | 4.7 | 50.2 | 1.9 | 9.58 | 0.79 | 0.686 | 0.036 |
| 3 | 334 | 11 | 39.4 | 1.1 | 611 | 17 | 122.7 | 4.6 | 48.6 | 2.2 | 9.23 | 0.65 | 0.806 | 0.043 |
| 4 | 288 | 13 | 46 | 2.3 | 389 | 14 | 144.5 | 5.8 | 52.1 | 2.1 | 9.76 | 0.81 | 0.615 | 0.04 |
| 5 | 295 | 10 | 44.2 | 1.8 | 447 | 18 | 143.7 | 6.3 | 53.9 | 2.1 | 10.01 | 0.66 | 0.677 | 0.038 |
| 6 | 290 | 12 | 41.7 | 1.5 | 369 | 17 | 135.7 | 5.1 | 51.6 | 2.2 | 9.71 | 0.7 | 0.62 | 0.037 |
| 7 | 286.5 | 9.6 | 42.7 | 1.4 | 357 | 12 | 138.3 | 4.9 | 52 | 2 | 9.74 | 0.67 | 0.598 | 0.035 |
| 8 | 292 | 14 | 43.7 | 2.2 | 357 | 18 | 139.6 | 6.5 | 51.1 | 2.8 | 9.86 | 0.73 | 0.552 | 0.035 |
| 9 | 299 | 13 | 44.1 | 1.7 | 399 | 16 | 145.5 | 6.3 | 54 | 2.4 | 10.3 | 0.83 | 0.612 | 0.038 |
| 10 | 302 | 14 | 46.3 | 2.2 | 431 | 22 | 152.4 | 8.1 | 54.5 | 2.8 | 10.14 | 0.64 | 0.63 | 0.051 |
| 11 | 301.6 | 9.4 | 45.6 | 1.5 | 378 | 13 | 148.3 | 6.1 | 55.9 | 2 | 10.27 | 0.58 | 0.563 | 0.039 |
| 12 | 290 | 11 | 40.9 | 1.7 | 400 | 14 | 135.3 | 4.5 | 51.5 | 2 | 9.79 | 0.61 | 0.637 | 0.041 |
| 13 | 285 | 12 | 43.4 | 1.8 | 416 | 20 | 144.1 | 7.3 | 50.9 | 2.7 | 9.51 | 0.97 | 0.62 | 0.038 |
| 14 | 304 | 16 | 40.4 | 2.8 | 536 | 33 | 136.5 | 9.3 | 50.5 | 3.6 | 8.4 | 1.4 | 0.731 | 0.082 |
| 15 | 288 | 14 | 48.2 | 2.5 | 490 | 28 | 164 | 11 | 55.9 | 3.5 | 9.89 | 0.75 | 0.648 | 0.053 |
| 16 | 277 | 14 | 45.9 | 2.5 | 355 | 22 | 149.3 | 8.5 | 49.6 | 3.1 | 9.48 | 0.71 | 0.567 | 0.054 |
| 17 | 277 | 10 | 46.1 | 2.2 | 421 | 16 | 145.4 | 6.5 | 51.6 | 2.2 | 9.47 | 0.59 | 0.584 | 0.035 |
| 18 | 269 | 17 | 46.4 | 3.8 | 410 | 28 | 146 | 12 | 51.4 | 4.2 | 8.82 | 0.96 | 0.652 | 0.061 |
| 19 | 296 | 11 | 41.4 | 1.5 | 411 | 16 | 139.7 | 5.6 | 53.2 | 2.6 | 10.22 | 0.61 | 0.604 | 0.039 |
| 20 | 285 | 11 | 42.7 | 1.8 | 386 | 17 | 141.8 | 6.3 | 52.2 | 2.6 | 9.67 | 0.62 | 0.59 | 0.037 |
| 21 | 299 | 11 | 40.2 | 1.7 | 420 | 18 | 134.1 | 5.8 | 53.1 | 2.3 | 9.49 | 0.73 | 0.656 | 0.044 |
| 22 | 281 | 14 | 39.4 | 2.1 | 379 | 19 | 133.4 | 6.5 | 51.1 | 3.1 | 9.78 | 0.84 | 0.607 | 0.03 |
| 23 | 299 | 11 | 45.7 | 1.9 | 349 | 14 | 148 | 5.7 | 54.1 | 2.2 | 10.24 | 0.63 | 0.605 | 0.039 |
| 24 | 286 | 12 | 43.6 | 1.7 | 396 | 17 | 142.9 | 6.3 | 50.6 | 2.4 | 9.43 | 0.63 | 0.637 | 0.041 |
| 25 | 288 | 11 | 45.6 | 1.9 | 413 | 16 | 150.8 | 7.4 | 54.3 | 2.7 | 10.73 | 0.79 | 0.619 | 0.046 |
| 26 | 291 | 12 | 43 | 1.7 | 368 | 15 | 142.9 | 6.9 | 50.3 | 2.6 | 9.65 | 0.76 | 0.635 | 0.038 |
| 27 | 297 | 13 | 41.8 | 1.5 | 391 | 15 | 140.2 | 5.4 | 52.5 | 2.3 | 10.53 | 0.72 | 0.613 | 0.043 |
| 28 | 309 | 13 | 46.4 | 2 | 312 | 13 | 152.5 | 6.6 | 55.1 | 2.2 | 10.79 | 0.73 | 0.576 | 0.039 |
| 29 | 286 | 13 | 42.2 | 2.1 | 325 | 15 | 136.4 | 6.1 | 50.6 | 2.9 | 10.06 | 0.61 | 0.563 | 0.036 |
| 30 | 299 | 14 | 43.9 | 1.9 | 429 | 19 | 145.5 | 6.6 | 54.1 | 2.9 | 10.44 | 0.83 | 0.631 | 0.044 |
| 31 | 292 | 14 | 43.2 | 2.2 | 439 | 22 | 143 | 7.6 | 55.2 | 4 | 10.25 | 0.83 | 0.656 | 0.05 |
| Average | 293 |  | 44 |  | 408 |  | 143 |  | 52 |  | 10 |  | 1 |  |
| Standard Dev | 12.02 |  | 2.24 |  | 58.60 |  | 7.29 |  | 1.96 |  | 0.54 |  | 0.05 |  |
| \% Standard | 4.10 |  | 5.14 |  | 14.36 |  | 5.10 |  | 3.73 |  | 5.44 |  | 8.02 |  |




|  | $\begin{aligned} & \mathrm{Zr} 90 \\ & \mathrm{ppm} \\ & \hline \end{aligned}$ | Int2SE | $\begin{aligned} & \mathrm{Nb} 93 \\ & \mathrm{ppm} \\ & \hline \end{aligned}$ | Table E-5 LA-ICP-MS Elemental Concentration Data: HP14-07 (continued) |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{gathered} \text { spot } \\ \# \end{gathered}$ |  |  |  | Int2SE | $\begin{gathered} \text { Ba137 } \\ \text { ppm } \end{gathered}$ | Int2SE | $\begin{gathered} \text { Ce140 } \\ \text { ppm } \end{gathered}$ | Int2SE | Nd146 <br> ppm | Int2SE | $\begin{gathered} \text { Sm147 } \\ \text { ppm } \end{gathered}$ | Int2SE | $\begin{gathered} \text { Eu153 } \\ \text { ppm } \end{gathered}$ | Int2SE |
| 1 | 299.00 | 13.00 | 44.70 | 2.10 | 413.00 | 19.00 | 147.50 | 7.10 | 54.70 | 3.00 | 10.08 | 0.83 | 0.61 | 0.04 |
| 2 | 316.00 | 14.00 | 44.60 | 2.00 | 428.00 | 20.00 | 147.60 | 7.10 | 55.90 | 2.50 | 10.67 | 0.61 | 0.66 | 0.06 |
| 3 | 297.00 | 12.00 | 42.10 | 1.80 | 482.00 | 22.00 | 141.50 | 6.20 | 54.10 | 2.50 | 10.23 | 0.66 | 0.67 | 0.04 |
| 4 | 290.00 | 13.00 | 44.10 | 2.10 | 393.00 | 18.00 | 146.40 | 6.80 | 53.50 | 3.10 | 9.57 | 0.73 | 0.66 | 0.04 |
| 5 | 274.00 | 10.00 | 41.00 | 1.40 | 463.00 | 16.00 | 136.90 | 5.20 | 50.40 | 2.10 | 9.42 | 0.66 | 0.62 | 0.04 |
| 6 | 306.00 | 18.00 | 43.30 | 2.60 | 419.00 | 24.00 | 149.20 | 8.70 | 60.20 | 4.00 | 10.32 | 0.81 | 0.67 | 0.05 |
| 7 | 284.00 | 10.00 | 43.30 | 2.00 | 361.00 | 12.00 | 143.40 | 4.50 | 53.20 | 2.60 | 9.90 | 0.65 | 0.58 | 0.04 |
| 8 | 293.00 | 14.00 | 44.70 | 2.00 | 480.00 | 21.00 | 146.10 | 6.80 | 55.80 | 2.30 | 9.70 | 0.65 | 0.66 | 0.04 |
| 9 | 296.60 | 9.50 | 42.80 | 1.40 | 436.00 | 17.00 | 143.20 | 5.50 | 54.00 | 2.20 | 10.47 | 0.56 | 0.65 | 0.05 |
| 10 | 296.00 | 15.00 | 43.40 | 2.30 | 422.00 | 21.00 | 144.90 | 7.50 | 55.80 | 2.70 | 9.45 | 0.78 | 0.66 | 0.04 |
| 11 | 310.00 | 15.00 | 46.90 | 2.50 | 453.00 | 20.00 | 154.60 | 8.00 | 57.30 | 3.30 | 11.03 | 0.83 | 0.69 | 0.04 |
| 12 | 288.00 | 14.00 | 44.80 | 2.00 | 433.00 | 20.00 | 144.80 | 6.70 | 51.70 | 2.20 | 10.19 | 0.72 | 0.62 | 0.04 |
| 13 | 300.00 | 14.00 | 40.40 | 1.90 | 411.00 | 20.00 | 138.60 | 6.70 | 55.30 | 3.00 | 9.88 | 0.66 | 0.62 | 0.05 |
| 14 | 278.00 | 11.00 | 42.30 | 1.70 | 476.00 | 18.00 | 140.20 | 6.20 | 51.10 | 2.50 | 9.42 | 0.74 | 0.63 | 0.04 |
| 15 | 276.90 | 8.80 | 42.60 | 1.70 | 382.00 | 12.00 | 140.00 | 4.90 | 53.00 | 2.10 | 10.37 | 0.69 | 0.58 | 0.04 |
| 16 | 289.00 | 16.00 | 44.50 | 2.30 | 502.00 | 26.00 | 143.40 | 7.00 | 52.50 | 2.70 | 10.18 | 0.84 | 0.67 | 0.06 |
| 17 | 285.00 | 11.00 | 43.70 | 1.90 | 431.00 | 16.00 | 141.70 | 5.90 | 53.60 | 2.50 | 9.99 | 0.66 | 0.60 | 0.04 |
| 19 | 277.00 | 10.00 | 41.70 | 1.60 | 448.00 | 21.00 | 136.20 | 6.50 | 49.90 | 2.10 | 8.99 | 0.64 | 0.63 | 0.05 |
| 20 | 288.00 | 14.00 | 43.70 | 2.30 | 413.00 | 21.00 | 146.20 | 7.40 | 53.80 | 2.60 | 10.45 | 0.78 | 0.60 | 0.05 |
| 21 | 290.00 | 17.00 | 43.10 | 2.30 | 476.00 | 23.00 | 140.90 | 6.70 | 52.90 | 3.00 | 9.95 | 0.86 | 0.61 | 0.05 |
| 22 | 283.00 | 15.00 | 43.00 | 2.30 | 483.00 | 24.00 | 145.20 | 7.70 | 53.70 | 2.80 | 10.00 | 0.64 | 0.69 | 0.04 |
| 23 | 306.00 | 15.00 | 47.30 | 2.30 | 462.00 | 24.00 | 152.00 | 7.70 | 55.40 | 3.00 | 10.01 | 0.88 | 0.64 | 0.05 |
| 24 | 293.00 | 11.00 | 44.90 | 1.90 | 466.00 | 20.00 | 151.10 | 6.50 | 53.50 | 2.90 | 9.73 | 0.78 | 0.66 | 0.04 |
| 25 | 296.00 | 13.00 | 45.50 | 2.10 | 297.00 | 12.00 | 150.90 | 6.30 | 55.40 | 2.70 | 9.90 | 0.60 | 0.56 | 0.03 |
| 26 | 302.00 | 17.00 | 44.80 | 2.30 | 458.00 | 23.00 | 149.10 | 7.40 | 56.00 | 3.60 | 10.06 | 0.78 | 0.63 | 0.05 |
| 27 | 288.00 | 13.00 | 42.30 | 1.80 | 402.00 | 16.00 | 142.70 | 5.30 | 51.40 | 2.70 | 9.82 | 0.69 | 0.57 | 0.04 |
| 28 | 301.00 | 13.00 | 43.70 | 1.90 | 456.00 | 21.00 | 146.80 | 6.60 | 54.40 | 2.80 | 10.67 | 0.64 | 0.69 | 0.05 |
| 29 | 284.00 | 11.00 | 43.10 | 1.70 | 460.00 | 17.00 | 144.00 | 6.20 | 52.00 | 2.20 | 9.40 | 0.72 | 0.63 | 0.04 |
| 30 | 293.00 | 12.00 | 45.70 | 1.90 | 429.00 | 15.00 | 150.90 | 5.50 | 53.60 | 2.60 | 10.34 | 0.65 | 0.63 | 0.03 |
| 31 | 279.00 | 11.00 | 43.60 | 1.90 | 459.00 | 20.00 | 142.80 | 6.20 | 51.10 | 2.10 | 9.33 | 0.74 | 0.64 | 0.04 |
| 32 | 282.00 | 11.00 | 44.20 | 1.80 | 404.00 | 16.00 | 140.20 | 6.10 | 49.80 | 1.90 | 9.25 | 0.81 | 0.58 | 0.03 |
| Average | 291.63 |  | 43.74 |  | 435.42 |  | 144.81 |  | 53.71 |  | 9.96 |  | 0.63 |  |
| Standard deviation | 10.20 |  | 1.51 |  | 41.25 |  | 4.46 |  | 2.22 |  | 0.46 |  | 0.04 |  |
| \% standard deviation | 3.50 |  | 3.45 |  | 9.47 |  | 3.08 |  | 4.14 |  | 4.63 |  | 5.63 |  |


| Table E-6 LA-ICP-MS Elemental Concentration Data: HP14-07 (continued) |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| spot | Gd157 |  | Dy163 |  | Yb172 |  | Hf178 |  | Pb208 |  | Th232 |  | U238 |  |
| \# | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE |
| 1 | 8.94 | 0.52 | 9.84 | 0.70 | 5.41 | 0.30 | 9.26 | 0.47 | 29.00 | 1.60 | 32.20 | 1.70 | 8.16 | 0.41 |
| 2 | 8.97 | 0.65 | 9.98 | 0.58 | 5.57 | 0.34 | 9.17 | 0.59 | 27.90 | 1.30 | 33.20 | 1.70 | 7.93 | 0.38 |
| 3 | 8.76 | 0.60 | 9.32 | 0.53 | 5.28 | 0.35 | 8.64 | 0.55 | 27.20 | 1.40 | 32.70 | 1.80 | 7.48 | 0.33 |
| 4 | 9.04 | 0.58 | 8.92 | 0.53 | 5.26 | 0.33 | 8.65 | 0.51 | 32.40 | 1.80 | 31.30 | 1.50 | 8.57 | 0.41 |
| 5 | 8.04 | 0.52 | 8.33 | 0.46 | 5.03 | 0.28 | 7.93 | 0.33 | 28.40 | 1.10 | 29.80 | 1.10 | 7.86 | 0.4 |
| 6 | 9.16 | 0.81 | 9.35 | 0.62 | 5.74 | 0.43 | 9.22 | 0.64 | 29.30 | 1.60 | 33.00 | 1.90 | 8.09 | 0.49 |
| 7 | 8.25 | 0.47 | 9.07 | 0.38 | 5.36 | 0.25 | 8.35 | 0.51 | 29.50 | 1.40 | 31.00 | 1.10 | 8.05 | 0.35 |
| 8 | 9.03 | 0.45 | 9.80 | 0.58 | 5.15 | 0.32 | 8.78 | 0.56 | 30.90 | 1.50 | 32.10 | 1.60 | 8.26 | 0.4 |
| 9 | 9.03 | 0.57 | 9.19 | 0.39 | 5.31 | 0.28 | 8.75 | 0.50 | 28.60 | 1.20 | 31.90 | 1.20 | 8.01 | 0.36 |
| 10 | 8.93 | 0.60 | 9.29 | 0.63 | 5.44 | 0.33 | 8.78 | 0.55 | 28.90 | 1.60 | 32.00 | 1.50 | 8.02 | 0.41 |
| 11 | 8.94 | 0.57 | 9.44 | 0.53 | 5.74 | 0.40 | 9.22 | 0.56 | 30.90 | 1.60 | 33.00 | 1.50 | 8.85 | 0.5 |
| 12 | 8.48 | 0.56 | 8.71 | 0.58 | 5.35 | 0.31 | 8.37 | 0.49 | 31.00 | 1.60 | 31.30 | 1.60 | 8.92 | 0.41 |
| 13 | 8.46 | 0.53 | 9.26 | 0.67 | 5.54 | 0.35 | 8.92 | 0.57 | 25.10 | 1.40 | 31.70 | 1.80 | 7.26 | 0.41 |
| 14 | 8.70 | 0.45 | 8.40 | 0.49 | 5.13 | 0.27 | 8.18 | 0.46 | 29.00 | 1.50 | 30.20 | 1.30 | 8.06 | 0.35 |
| 15 | 8.00 | 0.39 | 8.72 | 0.41 | 5.01 | 0.31 | 8.26 | 0.38 | 28.80 | 1.30 | 30.20 | 1.20 | 8.11 | 0.32 |
| 16 | 8.34 | 0.55 | 8.77 | 0.66 | 5.05 | 0.32 | 8.53 | 0.50 | 29.30 | 1.50 | 31.00 | 1.80 | 8.40 | 0.46 |
| 17 | 7.94 | 0.51 | 8.65 | 0.42 | 4.95 | 0.29 | 8.41 | 0.35 | 30.40 | 1.90 | 30.30 | 1.20 | 8.20 | 0.39 |
| 19 | 7.86 | 0.52 | 8.45 | 0.47 | 5.04 | 0.26 | 8.39 | 0.59 | 27.60 | 1.30 | 29.90 | 1.60 | 8.10 | 0.43 |
| 20 | 8.26 | 0.64 | 8.82 | 0.47 | 5.18 | 0.30 | 8.72 | 0.74 | 29.10 | 1.70 | 31.10 | 1.50 | 8.35 | 0.42 |
| 21 | 8.70 | 0.51 | 8.87 | 0.46 | 5.28 | 0.30 | 8.32 | 0.49 | 28.70 | 1.50 | 31.10 | 1.60 | 8.36 | 0.42 |
| 22 | 8.82 | 0.64 | 9.27 | 0.53 | 5.38 | 0.38 | 8.46 | 0.51 | 30.60 | 1.50 | 30.90 | 1.40 | 8.34 | 0.42 |
| 23 | 9.35 | 0.56 | 9.45 | 0.58 | 5.34 | 0.33 | 9.01 | 0.60 | 31.60 | 1.80 | 32.50 | 1.90 | 8.98 | 0.5 |
| 24 | 8.82 | 0.51 | 9.11 | 0.60 | 5.29 | 0.26 | 9.33 | 0.50 | 29.90 | 1.50 | 32.30 | 1.60 | 8.41 | 0.38 |
| 25 | 8.83 | 0.60 | 9.24 | 0.53 | 5.46 | 0.27 | 8.64 | 0.43 | 30.30 | 1.40 | 32.00 | 1.10 | 8.64 | 0.35 |
| 26 | 8.41 | 0.55 | 9.66 | 0.66 | 5.52 | 0.38 | 8.74 | 0.57 | 30.00 | 1.60 | 32.40 | 1.80 | 8.52 | 0.44 |
| 27 | 8.34 | 0.44 | 9.07 | 0.53 | 5.19 | 0.30 | 8.34 | 0.40 | 28.60 | 1.50 | 31.30 | 1.60 | 8.05 | 0.39 |
| 28 | 8.53 | 0.60 | 9.34 | 0.58 | 5.64 | 0.28 | 8.73 | 0.60 | 29.40 | 1.50 | 32.30 | 1.50 | 8.39 | 0.32 |
| 29 | 8.75 | 0.56 | 8.93 | 0.45 | 5.00 | 0.27 | 8.44 | 0.49 | 29.40 | 1.30 | 31.20 | 1.20 | 8.18 | 0.34 |
| 30 | 8.66 | 0.53 | 9.11 | 0.52 | 5.34 | 0.25 | 8.56 | 0.51 | 30.40 | 1.30 | 31.50 | 1.20 | 8.62 | 0.3 |
| 31 | 8.49 | 0.55 | 9.10 | 0.47 | 5.22 | 0.28 | 8.30 | 0.45 | 29.20 | 1.30 | 30.30 | 1.20 | 8.34 | 0.3 |
| 32 | 8.25 | 0.40 | 8.87 | 0.53 | 5.18 | 0.22 | 8.21 | 0.55 | 29.70 | 1.40 | 31.30 | 1.10 | 8.30 | 0.37 |
| Average | 8.62 |  | 9.11 |  | 5.30 |  | 8.63 |  | 29.39 |  | 31.52 |  | 8.25 |  |
| Standard deviation | 0.38 |  | 0.40 |  | 0.21 |  | 0.35 |  | 1.37 |  | 0.93 |  | 0.36 |  |
| \% standard deviation | 4.36 |  | 4.41 |  | 3.94 |  | 4.07 |  | 4.68 |  | 2.94 |  | 4.38 |  |




| Table E-9 LA-ICP-MS Elemental Concentration Data SCS-KMI-01 (continued) |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Spot | Gd157 |  | Dy163 |  | Yb172 |  | Hf178 |  | Pb208 |  | Th232 |  | U238 |  |
| \# | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE |
| 2 | 8.33 | 0.68 | 9.27 | 0.73 | 5.19 | 0.37 | 8.92 | 0.45 | 27.4 | 1.9 | 31 | 1.8 | 8.18 | 0.59 |
| 4 | 8.25 | 0.71 | 9.2 | 0.81 | 5.16 | 0.48 | 8.3 | 0.65 | 28.1 | 1.8 | 31.7 | 2.2 | 8.1 | 0.53 |
| 5 | 7.6 | 0.71 | 8.4 | 0.83 | 4.88 | 0.53 | 8.66 | 0.93 | 26 | 3.1 | 29.1 | 1.9 | 7.21 | 0.5 |
| 6 | 8.63 | 0.76 | 9.57 | 0.79 | 5.5 | 0.43 | 8.99 | 0.51 | 31 | 2.1 | 32.8 | 2.1 | 8.74 | 0.66 |
| 9 | 8.18 | 0.58 | 8.53 | 0.6 | 5.28 | 0.46 | 8.42 | 0.8 | 30.3 | 3.2 | 30.5 | 2.2 | 8.13 | 0.79 |
| 10 | 8.36 | 0.81 | 8 | 1.1 | 4.86 | 0.52 | 8.5 | 1.1 | 31.4 | 3.9 | 30.5 | 3.3 | 8.7 | 1.1 |
| 12 | 8.8 | 1.1 | 9.8 | 1.2 | 5.33 | 0.62 | 9.2 | 1.5 | 28 | 7.4 | 31.7 | 4.5 | 8 | 1.5 |
| 13 | 7.7 | 2.1 | 8.2 | 2.4 | 4.09 | 0.88 | 8.6 | 3.4 | 19.5 | 5.7 | 27.2 | 8.4 | 5.9 | 1.8 |
| 14 | 7.61 | 0.5 | 8.6 | 0.47 | 4.87 | 0.25 | 7.82 | 0.57 | 31.7 | 1.6 | 29.4 | 1.1 | 8.84 | 0.54 |
| 15 | 7.72 | 0.63 | 8.57 | 0.72 | 5.24 | 0.44 | 7.8 | 0.54 | 28.5 | 1.9 | 30 | 1.8 | 8.11 | 0.43 |
| 20 | 7.64 | 0.55 | 8.71 | 0.4 | 4.65 | 0.32 | 8.11 | 0.5 | 27.3 | 1.4 | 29.9 | 1.4 | 7.62 | 0.36 |
| 21 | 8.1 | 1.1 | 8.61 | 0.85 | 5.27 | 0.38 | 7.99 | 0.6 | 31.7 | 3.3 | 29.7 | 2.7 | 8.9 | 0.85 |
| 22 | 7.96 | 0.63 | 8.9 | 0.8 | 4.66 | 0.45 | 7.75 | 0.77 | 29.2 | 3 | 29.5 | 2.4 | 8.43 | 0.74 |
| 23 | 9.19 | 0.79 | 9.34 | 0.85 | 5.19 | 0.51 | 8.78 | 0.77 | 34.3 | 2.9 | 33.4 | 2.5 | 10.06 | 0.83 |
| 26 | 7.87 | 0.84 | 8.35 | 0.59 | 4.89 | 0.41 | 8.74 | 0.74 | 24.9 | 1.9 | 24.8 | 1.9 | 6.53 | 0.49 |
| 27 | 8.1 | 1 | 8.9 | 1.3 | 5.23 | 0.63 | 8.88 | 0.88 | 32.3 | 3.1 | 33.2 | 2.8 | 8.95 | 0.83 |
| 29 | 7.05 | 0.64 | 8.37 | 0.89 | 4.3 | 0.3 | 7.64 | 0.85 | 28.4 | 2.7 | 27.4 | 1.8 | 8.6 | 1.2 |
| 3 | 7.12 | 0.77 | 7.8 | 0.64 | 5.11 | 0.6 | 8.32 | 0.68 | 29.90 | 2.80 | 29.80 | 2.60 | 7.8 | 0.82 |
| 4 | 8.02 | 0.98 | 8.3 | 0.63 | 5.09 | 0.48 | 8.08 | 0.69 | 22.90 | 1.80 | 30.80 | 2.00 | 6.09 | 0.43 |
| 5 | 8.35 | 0.94 | 9.38 | 0.59 | 4.88 | 0.55 | 8.35 | 0.82 | 31.70 | 2.40 | 30.50 | 2.50 | 8.69 | 0.78 |
| 6 | 8.9 | 1.1 | 8.71 | 0.65 | 5.04 | 0.46 | 8.44 | 0.78 | 30.50 | 2.40 | 30.30 | 1.70 | 8.13 | 0.7 |
| 7 | 10.28 | 0.86 | 9.18 | 0.54 | 5.48 | 0.34 | 8.83 | 0.45 | 30.60 | 2.40 | 30.80 | 1.40 | 7.84 | 0.44 |
| 8 | 8.68 | 0.81 | 8.86 | 0.55 | 4.84 | 0.38 | 8.48 | 0.75 | 33.40 | 2.70 | 31.20 | 2.40 | 8.41 | 0.53 |
| 13 | 8.76 | 0.99 | 7.82 | 0.97 | 4.71 | 0.42 | 7.46 | 0.73 | 29.2 | 2.7 | 28 | 2.4 | 8.17 | 0.89 |
| 14 | 7.6 | 1 | 8.23 | 0.74 | 5.16 | 0.41 | 8.2 | 1 | 33.2 | 2.3 | 29.5 | 1.9 | 9.73 | 0.82 |
| 15 | 8.57 | 0.56 | 8.23 | 0.38 | 4.75 | 0.3 | 7.99 | 0.56 | 29.1 | 1.7 | 29.3 | 1.4 | 7.57 | 0.43 |
| 16 | 7.94 | 0.78 | 8.51 | 0.82 | 5.14 | 0.54 | 7.58 | 0.95 | 28.5 | 2.9 | 28.7 | 2.6 | 7.65 | 0.74 |
| 17 | 9.5 | 1 | 9.6 | 1 | 5.36 | 0.38 | 9.23 | 0.9 | 34.7 | 2.8 | 33.6 | 3.4 | 8.95 | 0.87 |
| 18 | 7.97 | 0.82 | 8.79 | 0.67 | 5.15 | 0.53 | 7.38 | 0.56 | 25 | 2 | 29.2 | 2.1 | 6.57 | 0.54 |
| 19 | $9.06$ | 0.88 | 8.74 | 0.9 | 4.76 | 0.58 | 8.11 | 0.94 | 32.5 | 2.6 | 30.5 | 2.1 | 8.55 | 0.77 |
| Average | 8 |  | 9 |  | 5 |  | 8 |  | 29 |  | 30 |  | 8 |  |
| Standard <br> Deviation | 0.69 |  | 0.51 |  | 0.32 |  | 0.50 |  | 3.33 |  | 1.85 |  | 0.94 |  |
| $\begin{aligned} & \text { \% standard } \\ & \text { dev } \end{aligned}$ | 8.30 |  | 5.89 |  | 6.35 |  | 6.01 |  | 11.34 |  | 6.15 |  | 11.55 |  |





| Spot | Duration | Ca43 |  | Ca44 | 兂 | Ti49 | , | V51 |  | Mn55 |  | Rb85 |  | Y89 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| \# | Seconds | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE |
| 1 | 18.4 | 7110 | 330 | 4630 | 250 | 860 | 42 | 0.025 | 0.03 | 287 | 14 | 222 | 11 | 74 | 3.8 |
| 2 | 14.9 | 7360 | 380 | 4420 | 250 | 805 | 43 | 0.14 | 0.069 | 268 | 14 | 210 | 12 | 72.7 | 3.8 |
| 3 | 9.8 | 8210 | 420 | 4480 | 310 | 755 | 34 | 0.099 | 0.063 | 271 | 13 | 218.2 | 9.2 | 73.9 | 4.1 |
| 5 | 18.4 | 5770 | 450 | 4220 | 370 | 997 | 91 | 0.57 | 0.13 | 307 | 29 | 155 | 18 | 55 | 4 |
| 6 | 15.2 | 8240 | 550 | 4280 | 240 | 896 | 50 | 0.058 | 0.037 | 276 | 16 | 188 | 10 | 70.8 | 4 |
| 7 | 18.4 | 6980 | 390 | 4520 | 240 | 834 | 42 | 0.055 | 0.047 | 296 | 17 | 235 | 16 | 65 | 3.5 |
| 8 | 18.4 | 7940 | 540 | 4220 | 290 | 726 | 45 | 0.087 | 0.045 | 249 | 17 | 206 | 14 | 72 | 5.1 |
| 10 | 15.1 | 8240 | 390 | 4270 | 190 | 992 | 56 | 0.097 | 0.035 | 296 | 15 | 185.4 | 8.1 | 63.6 | 3.3 |
| 11 | 18.4 | 8150 | 400 | 4340 | 200 | 766 | 40 | 0.06 | 0.031 | 271 | 14 | 239 | 12 | 78.8 | 4.4 |
| 12 | 18.4 | 7610 | 420 | 4400 | 250 | 855 | 51 | 0.076 | 0.031 | 284 | 15 | 231 | 14 | 73 | 4.5 |
| 13 | 9.4 | 7270 | 540 | 4670 | 460 | 882 | 88 | 0.115 | 0.048 | 311 | 25 | 239 | 23 | 63.1 | 3.8 |
| 14 | 12.1 | 7980 | 360 | 4390 | 230 | 817 | 46 | 0.043 | 0.05 | 271 | 13 | 205.6 | 9.6 | 72.7 | 3.6 |
| 15 | 18.4 | 7770 | 430 | 4190 | 220 | 773 | 46 | 0.41 | 0.17 | 247 | 12 | 195 | 11 | 68.7 | 3.6 |
| 16 | 13.8 | 9080 | 570 | 4220 | 300 | 1016 | 65 | 0.126 | 0.041 | 294 | 21 | 158 | 10 | 54.9 | 4 |
| 17 | 18.4 | 8300 | 390 | 4530 | 220 | 1070 | 61 | 0.154 | 0.042 | 304 | 15 | 177.6 | 6.7 | 57.6 | 3.2 |
| 18 | 10.2 | 8030 | 290 | 4560 | 250 | 830 | 45 | 0.09 | 0.059 | 275 | 13 | 214.7 | 9.9 | 73.6 | 2.6 |
| 19 | 18.4 | 8000 | 370 | 4490 | 260 | 831 | 41 | 0.096 | 0.042 | 275 | 12 | 212.4 | 9.8 | 73.9 | 4.2 |
| 20 | 7.2 | 8180 | 770 | 4210 | 420 | 1040 | 100 | 0.156 | 0.048 | 299 | 33 | 158 | 19 | 57.5 | 5.7 |
| 21 | 18.4 | 6760 | 360 | 4310 | 260 | 705 | 41 | 0.129 | 0.041 | 256 | 13 | 248 | 16 | 84 | 4.4 |
| 23 | 13.0 | 7660 | 530 | 4550 | 390 | 833 | 64 | 0.093 | 0.032 | 285 | 20 | 219 | 18 | 72.8 | 5.1 |
| 24 | 14.3 | 7820 | 410 | 4420 | 250 | 756 | 45 | 0.129 | 0.076 | 271 | 14 | 226 | 12 | 80.3 | 4 |
| 25 | 18.4 | 7420 | 450 | 4690 | 260 | 872 | 54 | 0.033 | 0.035 | 290 | 16 | 237 | 16 | 75.4 | 5.1 |
| 26 | 18.4 | 7990 | 410 | 4400 | 270 | 873 | 49 | 0.142 | 0.052 | 268 | 12 | 190.9 | 9.6 | 72.6 | 3.7 |
| 27 | 13.6 | 7350 | 470 | 4580 | 360 | 840 | 58 | 0.114 | 0.066 | 298 | 22 | 218 | 17 | 71.5 | 5.4 |
| 28 | 18.4 | 8230 | 410 | 4180 | 200 | 1021 | 51 | 0.34 | 0.19 | 295 | 13 | 158.3 | 8.3 | 56.3 | 2.9 |
| 29 | 18.4 | 5320 | 440 | 4370 | 310 | 776 | 58 | 0.27 | 0.086 | 267 | 18 | 228 | 17 | 77 | 5 |
| 30 | 17.1 | 5990 | 490 | 4000 | 290 | 704 | 47 | 0.44 | 0.2 | 259 | 16 | 202 | 15 | 80.3 | 5 |
| 31 | 8.0 | 7680 | 620 | 4620 | 310 | 787 | 59 | 0.053 | 0.055 | 283 | 20 | 242 | 19 | 75.4 | 5.3 |
| 32 | 16.1 | 7120 | 490 | 4170 | 290 | 1158 | 93 | 0.69 | 0.1 | 260 | 17 | 212 | 15 | 68.3 | 4.8 |
| 33 | 16.6 | 7360 | 500 | 4400 | 310 | 894 | 63 | 0.123 | 0.042 | 284 | 19 | 193 | 13 | 69.7 | 4.6 |
| 34 | 18.4 | 8280 | 330 | 4360 | 190 | 983 | 43 | 0.095 | 0.039 | 288 | 12 | 180.6 | 7.2 | 62.1 | 2.8 |
| 35 | 18.4 | 8470 | 390 | 4330 | 240 | 1039 | 56 | 0.132 | 0.035 | 301 | 15 | 161.6 | 9.5 | 54.8 | 2.8 |
| 36 | 13.4 | 6560 | 480 | 4480 | 390 | 823 | 89 | 1.1 | 0.64 | 279 | 20 | 234 | 19 | 76.8 | 6.6 |
| 37 | 11.3 | 7320 | 510 | 4660 | 420 | 847 | 74 | 0.039 | 0.04 | 304 | 26 | 265 | 23 | 74.4 | 5.7 |
| 38 | 18.4 | 8180 | 410 | 4380 | 280 | 1032 | 63 | 0.204 | 0.064 | 293 | 16 | 164.8 | 9.1 | 58.3 | 2.9 |
| 39 | 10.4 | 8090 | 430 | 4490 | 300 | 960 | 54 | 0.097 | 0.062 | 280 | 14 | 167.2 | 8.2 | 65.3 | 3.5 |
| 40 | 18.4 | 8970 | 400 | 4140 | 220 | 766 | 32 | 0.095 | 0.035 | 257 | 13 | 195.6 | 9.1 | 72.6 | 3.7 |
| 41 | 18.4 | 7990 | 360 | 4430 | 220 | 830 | 34 | 0.08 | 0.038 | 283 | 13 | 222.4 | 9.8 | 68.9 | 3.2 |
| 42 | 18.4 | 7790 | 430 | 4640 | 200 | 867 | 42 | 0.082 | 0.038 | 290 | 13 | 233.1 | 9.2 | 76.9 | 4.3 |
| 43 | 18.4 | 8680 | 340 | 4190 | 210 | 998 | 43 | 0.251 | 0.053 | 307 | 13 | 170.3 | 7.8 | 62.5 | 2.4 |
| 44 | 18.4 | 8320 | 530 | 4480 | 250 | 787 | 51 | 0.062 | 0.038 | 271 | 15 | 230 | 14 | 77.3 | 4.2 |
| 45 | 11.5 | 8660 | 450 | 4230 | 190 | 715 | 36 | 0.095 | 0.071 | 249 | 12 | 208.2 | 9.5 | 74.4 | 3.5 |
| 46 | 14.1 | 9150 | 640 | 4130 | 240 | 764 | 51 | 0.04 | 0.051 | 253 | 16 | 197 | 12 | 72.5 | 4.2 |
| 47 | 18.4 | 7240 | 500 | 4330 | 230 | 768 | 45 | 0.064 | 0.024 | 267 | 16 | 226 | 15 | 79.2 | 5 |
| 48 | 18.4 | 7640 | 390 | 4400 | 250 | 908 | 46 | 0.074 | 0.032 | 279 | 12 | 192.7 | 9.8 | 70.3 | 3.6 |
| 49 | 18.4 | 8240 | 460 | 4370 | 270 | 943 | 57 | 0.41 | 0.48 | 281 | 17 | 179 | 10 | 63.2 | 3.7 |



| Table E-15 LA-ICP-MS Elemental Concentration Data: BOR-S2-01 (continued) |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{gathered} \text { Spot } \\ \# \end{gathered}$ | $\begin{gathered} \text { Gd157 } \\ \text { ppm } \end{gathered}$ | Int2SE | $\begin{gathered} \text { Dy163 } \\ \text { ppm } \end{gathered}$ | Int2SE | $\begin{gathered} \mathrm{Yb} 172 \\ \mathrm{ppm} \end{gathered}$ | Int2SE | Hf178 <br> ppm | Int2SE | $\begin{gathered} \mathrm{Pb} 208 \\ \mathrm{ppm} \end{gathered}$ | Int2SE | $\begin{gathered} \text { Th232 } \\ \text { ppm } \\ \hline \end{gathered}$ | Int2SE | $\begin{gathered} \hline \mathbf{U 2 3 8} \\ \text { ppm } \end{gathered}$ | Int2SE |
| 1 | 13.1 | 1.2 | 13.43 | 0.82 | 7.63 | 0.48 | 8.46 | 0.67 | 40.5 | 2 | 28.3 | 1.5 | 7.71 | 0.44 |
| 2 | 11.63 | 0.8 | 12.7 | 1 | 7.28 | 0.49 | 8.05 | 0.77 | 36.8 | 2.2 | 27.5 | 1.6 | 6.74 | 0.41 |
| 3 | 11.73 | 0.95 | 13.06 | 0.92 | 7.78 | 0.33 | 7.9 | 0.64 | 40.6 | 2.8 | 28.4 | 1.4 | 8.15 | 0.5 |
| 5 | 12.3 | 1.3 | 10.29 | 0.82 | 5.59 | 0.56 | 8.33 | 0.73 | 28.6 | 2.8 | 23.6 | 1.7 | 4.67 | 0.56 |
| 6 | 12.3 | 1.1 | 13.1 | 1.1 | 6.88 | 0.58 | 8.53 | 0.61 | 33.8 | 2.2 | 28.8 | 1.8 | 6.53 | 0.44 |
| 7 | 10.53 | 0.84 | 12.3 | 1.1 | 6.73 | 0.58 | 7.66 | 0.66 | 42.2 | 2.6 | 25.5 | 1.5 | 8.3 | 0.62 |
| 8 | 11.2 | 1 | 12.8 | 1 | 7.57 | 0.76 | 7.34 | 0.81 | 36.6 | 2.5 | 27.3 | 2 | 7.09 | 0.55 |
| 10 | 12.27 | 0.91 | 11.98 | 0.91 | 6.21 | 0.46 | 8.58 | 0.5 | 34.9 | 1.8 | 26.9 | 1.5 | 6.08 | 0.31 |
| 11 | 11.8 | 0.89 | 14.15 | 0.99 | 8.2 | 0.73 | 8.63 | 0.8 | 43 | 2.7 | 30.4 | 1.9 | 8 | 0.47 |
| 12 | 12.5 | 1.2 | 13.14 | 0.74 | 7.38 | 0.54 | 7.85 | 0.64 | 41.4 | 2.8 | 28.3 | 1.8 | 7.49 | 0.46 |
| 13 | 10.9 | 1.2 | 12.5 | 1.3 | 6.86 | 0.69 | 7.1 | 1 | 48.3 | 5.8 | 25.7 | 2.1 | 8.7 | 1.1 |
| 14 | 12.31 | 0.99 | 13.4 | 1.2 | 7.6 | 0.62 | 7.9 | 0.73 | 38.1 | 2.4 | 29.2 | 1.9 | 7.29 | 0.48 |
| 15 | 11 | 1 | 12.58 | 0.87 | 6.63 | 0.4 | 7.84 | 0.69 | 38 | 2.1 | 26.5 | 1.5 | 6.45 | 0.37 |
| 16 | 12 | 1.3 | 10.82 | 0.85 | 5.12 | 0.42 | 7.65 | 0.66 | 30.1 | 1.9 | 23.6 | 1.5 | 5.14 | 0.32 |
| 17 | 11.7 | 0.96 | 10.9 | 0.84 | 5.95 | 0.38 | 8.64 | 0.58 | 31.8 | 1.8 | 24.1 | 1.3 | 5.53 | 0.33 |
| 18 | 12.2 | 1.1 | 13.03 | 0.79 | 7.02 | 0.65 | 8.76 | 0.69 | 35.7 | 2.2 | 27.7 | 1.2 | 7.46 | 0.39 |
| 19 | 13 | 1.1 | 13.8 | 1.1 | 7.39 | 0.52 | 7.86 | 0.58 | 38.8 | 2 | 29.6 | 1.7 | 7.5 | 0.39 |
| 20 | 12.3 | 1.7 | 11.3 | 1.6 | 5.74 | 0.97 | 7.8 | 1.1 | 31 | 3.6 | 24.2 | 2.7 | 4.98 | 0.69 |
| 21 | 13.8 | 1 | 14.64 | 0.91 | 8.52 | 0.59 | 8.77 | 0.62 | 45.6 | 2.9 | 30.3 | 1.7 | 8.1 | 0.47 |
| 23 | 12.6 | 1.1 | 13.7 | 1.2 | 6.7 | 0.61 | 7.63 | 0.77 | 40.8 | 3.6 | 28.8 | 2.3 | 7.81 | 0.57 |
| 24 | 12.19 | 0.9 | 14.14 | 0.92 | 7.99 | 0.61 | 8.61 | 0.85 | 40.5 | 2.9 | 29.9 | 1.9 | 7.53 | 0.57 |
| 25 | 12.6 | 1.2 | 13.2 | 1.1 | 7.5 | 0.59 | 8.45 | 0.78 | 43.7 | 3.5 | 29.6 | 2.4 | 7.94 | 0.61 |
| 26 | 13.2 | 1.3 | 13.27 | 0.94 | 7.56 | 0.51 | 9.2 | 0.6 | 34.8 | 2.1 | 29 | 1.6 | 6.33 | 0.31 |
| 27 | 11.64 | 0.9 | 12.8 | 1 | 7.12 | 0.52 | 7.62 | 0.69 | 41.8 | 2.8 | 28.3 | 2.1 | 8.08 | 0.68 |
| 28 | 10.76 | 0.91 | 10.82 | 0.73 | 5.68 | 0.46 | 8.03 | 0.46 | 30.3 | 1.9 | 24.6 | 1.2 | 5.12 | 0.28 |
| 29 | 11.3 | 1 | 14.2 | 1.3 | 8.08 | 0.87 | 8.2 | 1 | 41.4 | 3.3 | 29.6 | 2.1 | 8.19 | 0.58 |
| 30 | 11.98 | 0.89 | 15.4 | 1.1 | 8.18 | 0.67 | 7.83 | 0.68 | 34.4 | 2.9 | 29.3 | 1.9 | 6.92 | 0.57 |
| 31 | 11.3 | 1.3 | 13.2 | 1.3 | 7.36 | 0.57 | 6.76 | 0.76 | 44.9 | 3.6 | 28.3 | 2.3 | 8.59 | 0.7 |
| 32 | 12.3 | 1.2 | 12.44 | 0.97 | 7.02 | 0.58 | 7.81 | 0.63 | 42.3 | 3.4 | 28 | 2.2 | 7.35 | 0.6 |
| 33 | 12.3 | 1.1 | 12.59 | 0.97 | 6.72 | 0.65 | 7.98 | 0.63 | 36.9 | 2.6 | 28.2 | 1.7 | 6.65 | 0.55 |
| 34 | 12 | 1 | 11.47 | 0.79 | 6.31 | 0.44 | 7.84 | 0.68 | 32.9 | 1.8 | 25.7 | 1.2 | 5.98 | 0.34 |
| 35 | 11.11 | 0.72 | 10.66 | 0.63 | 5.59 | 0.41 | 8.22 | 0.64 | 30.8 | 2.1 | 23.5 | 1.3 | 5.1 | 0.31 |
| 36 | 12.5 | 1.2 | 14.1 | 1.4 | 8.12 | 0.74 | 7.87 | 0.67 | 42.9 | 3.8 | 29 | 2.6 | 8.3 | 0.72 |
| 37 | 11.3 | 1.5 | 13.1 | 1.1 | 7.93 | 0.82 | 8.01 | 0.82 | 48 | 4.4 | 28.9 | 2 | 9.33 | 0.65 |
| 38 | 12.2 | 1 | 10.9 | 0.49 | 6.05 | 0.39 | 8.71 | 0.66 | 30 | 1.6 | 24.5 | 1.4 | 5.14 | 0.34 |
| 39 | 12.8 | 1.2 | 12.7 | 1.1 | 6.51 | 0.75 | 8.08 | 0.65 | 32.1 | 2.2 | 26.6 | 1.8 | 5.73 | 0.36 |
| 40 | 11.53 | 0.97 | 13.8 | 0.87 | 7 | 0.38 | 7.62 | 0.45 | 36.1 | 1.9 | 27.6 | 1.5 | 6.75 | 0.37 |
| 41 | 10.96 | 0.71 | 13.29 | 0.87 | 7.05 | 0.4 | 7.55 | 0.48 | 40.8 | 2.2 | 26.9 | 1.3 | 7.46 | 0.37 |
| 42 | 13.81 | 0.82 | 13.79 | 0.9 | 7.76 | 0.51 | 8.04 | 0.57 | 44.3 | 2.5 | 30.2 | 1.8 | 8.02 | 0.43 |
| 43 | 12.12 | 0.99 | 11.59 | 0.45 | 5.99 | 0.43 | 7.76 | 0.5 | 32.8 | 1.7 | 25.9 | 1.1 | 5.52 | 0.35 |
| 44 | 12.5 | 1.3 | 13.6 | 1.1 | 7.9 | 0.62 | 7.87 | 0.67 | 42.2 | 2.9 | 29.5 | 2.1 | 7.92 | 0.58 |
| 45 | 12.2 | 1.4 | 13.8 | 1.2 | 8.01 | 0.61 | 8.06 | 0.59 | 37.4 | 2.1 | 29 | 1.5 | 7.16 | 0.35 |
| 46 | 12.3 | 1.1 | 13.3 | 1.2 | 7.7 | 0.48 | 8.35 | 0.69 | 36.3 | 2.4 | 27.4 | 1.8 | 6.65 | 0.44 |
| 47 | 12.2 | 1.2 | 13.87 | 0.97 | 7.86 | 0.63 | 7.85 | 0.69 | 40.7 | 3 | 29.4 | 1.9 | 7.95 | 0.54 |
| 48 | 12.17 | 0.87 | 12.21 | 0.96 | 6.72 | 0.47 | 8.24 | 0.53 | 35.1 | 2.1 | 27.6 | 1.6 | 6.55 | 0.4 |
| 49 | 12.33 | 0.83 | 11.76 | 0.73 | 6.63 | 0.51 | 8.21 | 0.71 | 31.9 | 1.6 | 26 | 1.4 | 5.72 | 0.36 |


| Table E-16 LA-ICP-MS Elemental Concentration Data: JCS-KMI-16 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Spot \# | Duration seconds | $\begin{gathered} \mathrm{Ca} 43 \\ \text { CPS } \\ \hline \end{gathered}$ | Int2SE | $\begin{gathered} \text { Ca44 } \\ \text { ppm } \\ \hline \end{gathered}$ | Int2SE | $\begin{aligned} & \text { Ti49 } \\ & \text { ppm } \end{aligned}$ | Int2SE | $\begin{gathered} \mathrm{V} 51 \\ \mathrm{ppm} \end{gathered}$ | Int2SE | $\begin{gathered} \text { Mn555 } \\ \text { ppm } \end{gathered}$ | Int2SE | Rb85 ppm | Int2SE | $\begin{gathered} \text { Y89 } \\ \text { ppm } \end{gathered}$ | Int2SE |
| 2 | 19.1 | 10750 | 450 | 3530 | 170 | 770 | 33 | 0.27 | 0.18 | 266 | 10 | 232 | 10 | 78 | 3.2 |
| 3 | 17.8 | 9600 | 480 | 3490 | 260 | 824 | 51 | 0.60 | 0.38 | 296 | 20 | 269 | 22 | 68 | 4.4 |
| 5 | 19.1 | 8480 | 560 | 3720 | 240 | 788 | 47 | 0.25 | 0.28 | 316 | 18 | 321 | 22 | 80 | 4.4 |
| 6 | 19.1 | 11770 | 550 | 3380 | 170 | 736 | 36 | 0.04 | 0.039 | 262 | 12 | 226 | 11 | 71 | 3.2 |
| 7 | 19.1 | 11420 | 560 | 3340 | 150 | 734 | 28 | 0.02 | 0.031 | 258.6 | 9.9 | 227 | 9.6 | 71 | 3.3 |
| 11 | 19.1 | 10400 | 690 | 3340 | 200 | 621 | 41 | 0.11 | 0.058 | 278 | 19 | 299 | 18 | 85 | 5.5 |
| 12 | 19.1 | 9610 | 500 | 3540 | 230 | 795 | 44 | 0.14 | 0.14 | 278 | 12 | 244 | 15 | 71 | 4 |
| 15 | 19.1 | 11590 | 620 | 3350 | 170 | 725 | 34 | 0.07 | 0.034 | 259 | 12 | 222 | 11 | 71 | 3.9 |
| 18 | 19.1 | 11110 | 500 | 3520 | 160 | 766 | 33 | 0.13 | 0.086 | 268 | 12 | 228 | 12 | 74 | 3.4 |
| 19 | 16.0 | 10190 | 520 | 3650 | 270 | 799 | 46 | 0.19 | 0.12 | 279 | 17 | 247 | 16 | 74 | 3.8 |
| 20 | 17.0 | 9670 | 710 | 3700 | 270 | 734 | 52 | 0.20 | 0.19 | 285 | 23 | 283 | 19 | 77 | 5.6 |
| 21 | 19.1 | 10190 | 600 | 3440 | 190 | 790 | 45 | 0.09 | 0.071 | 275 | 13 | 240 | 14 | 68 | 3.9 |
| 22 | 19.1 | 10440 | 570 | 3440 | 160 | 594 | 27 | 0.07 | 0.057 | 267 | 11 | 283 | 15 | 85 | 4.1 |
| 23 | 19.1 | 10420 | 620 | 3360 | 150 | 700 | 31 | 0.02 | 0.037 | 265 | 13 | 265 | 12 | 76 | 3.7 |
| 24 | 15.0 | 11510 | 690 | 3350 | 200 | 758 | 44 | 0.22 | 0.18 | 267 | 17 | 232 | 13 | 70 | 4.1 |
| 25 | 19.1 | 9720 | 490 | 3750 | 230 | 811 | 45 | 0.07 | 0.039 | 288 | 15 | 263 | 16 | 73 | 3.5 |
| 26 | 19.1 | 10420 | 480 | 3520 | 140 | 785 | 35 | 0.21 | 0.16 | 273 | 14 | 244 | 15 | 71 | 4 |
| 29 | 19.1 | 11370 | 560 | 3440 | 180 | 740 | 36 | 0.22 | 0.23 | 259 | 13 | 230 | 11 | 71 | 3.4 |
| 30 | 19.1 | 11590 | 580 | 3350 | 150 | 746 | 35 | 0.03 | 0.032 | 265 | 12 | 230 | 13 | 71 | 3.8 |
| 1 | 14.5 | 11930 | 570 | 3220 | 140 | 902 | 38 | 0.28 | 0.36 | 277 | 14 | 160 | 7 | 58 | 2.8 |
| 4 | 19.1 | 11650 | 420 | 3320 | 130 | 893 | 31 | 0.23 | 0.16 | 268.9 | 9.9 | 167 | 8 | 59 | 2.7 |
| 8 | 19.1 | 10920 | 580 | 3730 | 180 | 956 | 48 | 0.13 | 0.052 | 303 | 16 | 180 | 10 | 62 | 3.4 |
| 9 | 19.1 | 12070 | 530 | 3310 | 130 | 886 | 38 | 0.12 | 0.048 | 281 | 13 | 160 | 7.2 | 61 | 2.4 |
| 10 | 13.8 | 11770 | 720 | 3250 | 210 | 883 | 54 | 0.18 | 0.08 | 269 | 15 | 167 | 13 | 56 | 3.5 |
| 13 | 11.6 | 11380 | 880 | 3690 | 330 | 970 | 73 | 0.19 | 0.095 | 302 | 26 | 193 | 16 | 59 | 4.5 |
| 14 | 11.0 | 12100 | 720 | 3480 | 250 | 899 | 54 | 0.07 | 0.042 | 284 | 14 | 169 | 8.3 | 60 | 4.1 |
| 16 | 19.1 | 9240 | 500 | 3210 | 170 | 861 | 59 | 0.97 | 0.26 | 252 | 15 | 140 | 8.3 | 62 | 3.7 |
| 17 | 19.1 | 11730 | 440 | 3540 | 190 | 929 | 43 | 0.33 | 0.31 | 288 | 12 | 176 | 9.1 | 62 | 2.7 |
| 27 | 12.3 | 10490 | 530 | 3670 | 290 | 1068 | 70 | 1.40 | 1.6 | 354 | 18 | 202 | 8.1 | 59 | 2.5 |
| 28 | 9.7 | 11890 | 740 | 3300 | 200 | 912 | 59 | 1.00 | 0.83 | 283 | 19 | 168 | 14 | 57 | 3.6 |
| 31 | 19.1 | 10910 | 550 | 3560 | 200 | 931 | 50 | 0.21 | 0.12 | 294 | 16 | 169 | 7.5 | 59 | 2.9 |
| 32 | 13.1 | 9910 | 600 | 3670 | 330 | 1014 | 72 | 0.36 | 0.19 | 297 | 20 | 182 | 13 | 58 | 4.3 |
| 34 | 19.1 | 11470 | 540 | 3420 | 170 | 912 | 39 | 0.09 | 0.031 | 283 | 16 | 174 | 10 | 60 | 3.5 |
| 35 | 11.9 | 11920 | 610 | 3480 | 180 | 888 | 37 | 0.16 | 0.057 | 284 | 14 | 169 | 7.5 | 60 | 2.9 |


| Table E-17 LA-ICP-MS Elemental Concentration Data: JCS-KMI-16 (continued) |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Spot | Zr90 |  | Nb93 |  | Ba137 |  | Ce140 |  | Nd146 |  | Sm147 |  | Eu153 |  |
| \# | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE |
| 2 | 202 | 8.8 | 79 | 3.2 | 65 | 2.9 | 149 | 6.5 | 61 | 2.8 | 14.1 | 1 | 0.30 | 0.029 |
| 3 | 177 | 11 | 83 | 6 | 62 | 4.7 | 153 | 12 | 52 | 3.8 | 10.9 | 0.84 | 0.28 | 0.029 |
| 5 | 179 | 9.9 | 91 | 5.7 | 31 | 1.9 | 149 | 8.3 | 52 | 3.4 | 11.6 | 1.1 | 0.23 | 0.028 |
| 6 | 186 | 9.1 | 76 | 3.6 | 61 | 3.1 | 141 | 6.1 | 54 | 3.3 | 11.6 | 0.97 | 0.29 | 0.018 |
| 7 | 184 | 7 | 77 | 3.5 | 63 | 2.8 | 142 | 6.4 | 56 | 2.7 | 11.7 | 0.88 | 0.31 | 0.026 |
| 11 | 162 | 9.7 | 89 | 5.6 | 16 | 1.2 | 133 | 8 | 50 | 3.3 | 11.9 | 1.1 | 0.13 | 0.021 |
| 12 | 183 | 9.8 | 79 | 3.9 | 59 | 3.5 | 151 | 6.8 | 53 | 3 | 12.8 | 1 | 0.29 | 0.032 |
| 15 | 181 | 9.9 | 74 | 3.9 | 64 | 3.6 | 139 | 7.5 | 54 | 3.5 | 11.7 | 0.96 | 0.31 | 0.032 |
| 18 | 195 | 8.6 | 79 | 3.7 | 61 | 3.2 | 149 | 7.5 | 56 | 3.1 | 12.2 | 0.93 | 0.30 | 0.025 |
| 19 | 191 | 10 | 81 | 5.3 | 63 | 3.9 | 151 | 11 | 56 | 3.6 | 12.8 | 1.4 | 0.31 | 0.041 |
| 20 | 175 | 12 | 87 | 6.4 | 29 | 1.8 | 138 | 9.8 | 49 | 3.8 | 11.4 | 0.82 | 0.20 | 0.027 |
| 21 | 179 | 9.4 | 77 | 4.5 | 64 | 4 | 147 | 9.5 | 51 | 3.1 | 11.8 | 1.1 | 0.26 | 0.026 |
| 22 | 163 | 8.1 | 85 | 4.1 | 15 | 0.99 | 130 | 6.3 | 49 | 2.5 | 12.4 | 0.85 | 0.15 | 0.017 |
| 23 | 171 | 8 | 83 | 4 | 30 | 1.5 | 132 | 5.8 | 50 | 2.7 | 11.9 | 1 | 0.19 | 0.02 |
| 24 | 182 | 9.5 | 76 | 4 | 57 | 3 | 145 | 7.1 | 52 | 3.2 | 11.7 | 0.9 | 0.30 | 0.031 |
| 25 | 187 | 9 | 84 | 4.5 | 67 | 3.6 | 156 | 9 | 58 | 3.4 | 12.8 | 0.99 | 0.32 | 0.023 |
| 26 | 187 | 10 | 80 | 4.5 | 69 | 3.7 | 148 | 7.7 | 55 | 2.5 | 11.8 | 0.99 | 0.30 | 0.026 |
| 29 | 185 | 9 | 75 | 3.6 | 65 | 3.3 | 144 | 7.4 | 51 | 2.6 | 12.2 | 1.2 | 0.32 | 0.026 |
| 30 | 183 | 8.7 | 75 | 3.7 | 64 | 4.3 | 145 | 7.6 | 52 | 3.1 | 12.4 | 0.93 | 0.29 | 0.025 |
| 1 | 237 | 10 | 62 | 2.6 | 207 | 8.5 | 172 | 6.7 | 67 | 3.4 | 12.0 | 0.76 | 0.61 | 0.047 |
| 4 | 231 | 8.7 | 64 | 3.2 | 244 | 12 | 170 | 7.4 | 69 | 3.5 | 12.5 | 0.84 | 0.64 | 0.038 |
| 8 | 246 | 12 | 68 | 4 | 224 | 12 | 190 | 9.1 | 71 | 4.4 | 13.7 | 1.1 | 0.66 | 0.051 |
| 9 | 245 | 11 | 66 | 3.2 | 201 | 8.8 | 177 | 7.4 | 67 | 3.4 | 12.9 | 0.86 | 0.59 | 0.028 |
| 10 | 224 | 13 | 62 | 4 | 206 | 13 | 168 | 9.5 | 61 | 3.9 | 12.4 | 1.3 | 0.59 | 0.052 |
| 13 | 242 | 19 | 70 | 5.6 | 249 | 20 | 186 | 14 | 68 | 5.7 | 13.7 | 1.4 | 0.65 | 0.065 |
| 14 | 240 | 13 | 65 | 3.8 | 229 | 13 | 178 | 10 | 67 | 4.3 | 11.9 | 0.9 | 0.64 | 0.054 |
| 16 | 244 | 15 | 60 | 3.5 | 219 | 14 | 165 | 11 | 67 | 4.5 | 13.1 | 1.2 | 0.60 | 0.042 |
| 17 | 248 | 10 | 67 | 3.2 | 225 | 10 | 180 | 8.2 | 69 | 2.9 | 13.5 | 0.79 | 0.66 | 0.045 |
| 27 | 239 | 13 | 75 | 4.7 | 228 | 13 | 197 | 10 | 69 | 4.7 | 14.0 | 0.89 | 0.65 | 0.059 |
| 28 | 232 | 14 | 63 | 3.7 | 248 | 12 | 180 | 11 | 65 | 3.2 | 13.4 | 1.3 | 0.65 | 0.041 |
| 31 | 233 | 11 | 66 | 2.9 | 232 | 11 | 178 | 9 | 67 | 3.7 | 12.2 | 0.95 | 0.61 | 0.039 |
| 32 | 229 | 14 | 68 | 4.5 | 250 | 16 | 183 | 13 | 66 | 5.5 | 12.2 | 1.2 | 0.61 | 0.069 |
| 34 | 236 | 14 | 64 | 3.3 | 246 | 12 | 175 | 8.2 | 67 | 3 | 14.0 | 1.3 | 0.64 | 0.052 |
| 35 | 231 | 10 | 63 | 3.5 | 239 | 12 | 173 | 8.1 | 66 | 3.8 | 11.7 | 0.63 | 0.66 | 0.051 |


| Table E-18 LA-ICP-MS Elemental Concentration Data: JCS-KMI-16 (continued) |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Spot | Gd157 |  | Dy163 |  | Yb172 |  | Hf178 |  | Pb208 |  | Th232 |  | U238 |  |
| \# | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE | ppm | Int2SE |
| 2 | 11.9 | 0.75 | 14.4 | 0.58 | 8.0 | 0.5 | 7.7 | 0.45 | 36.3 | 1.8 | 29.4 | 1.3 | 8.0 | 0.34 |
| 3 | 10.3 | 0.73 | 12.5 | 1 | 7.2 | 0.63 | 6.7 | 0.54 | 45.5 | 3.8 | 26.0 | 1.7 | 9.0 | 0.7 |
| 5 | 12.0 | 0.78 | 13.9 | 0.97 | 8.1 | 0.56 | 7.3 | 0.53 | 43.9 | 2.8 | 30.5 | 2 | 10.9 | 0.78 |
| 6 | 11.1 | 0.75 | 13.1 | 0.64 | 7.1 | 0.42 | 7.4 | 0.49 | 35.1 | 1.8 | 27.4 | 1.5 | 7.8 | 0.4 |
| 7 | 11.3 | 0.8 | 12.9 | 0.62 | 7.4 | 0.43 | 7.3 | 0.41 | 36.0 | 1.5 | 27.5 | 1.3 | 7.4 | 0.34 |
| 11 | 11.5 | 0.98 | 14.7 | 1.1 | 8.8 | 0.68 | 7.0 | 0.54 | 42.7 | 2.8 | 31.7 | 1.9 | 10.3 | 0.64 |
| 12 | 11.1 | 0.62 | 12.2 | 0.68 | 7.4 | 0.55 | 6.8 | 0.53 | 36.7 | 2.4 | 27.8 | 1.6 | 8.5 | 0.47 |
| 15 | 10.9 | 0.85 | 12.6 | 0.93 | 7.1 | 0.53 | 7.1 | 0.53 | 34.7 | 2.4 | 26.9 | 1.6 | 7.4 | 0.41 |
| 18 | 11.7 | 0.79 | 13.6 | 0.73 | 7.7 | 0.47 | 7.8 | 0.52 | 37.0 | 1.8 | 28.8 | 1.3 | 7.9 | 0.46 |
| 19 | 11.8 | 0.88 | 13.4 | 0.75 | 7.5 | 0.59 | 7.9 | 0.57 | 38.9 | 2.8 | 28.2 | 1.9 | 8.7 | 0.62 |
| 20 | 11.3 | 0.98 | 13.8 | 1.1 | 8.0 | 0.63 | 7.0 | 0.52 | 40.4 | 3.2 | 29.6 | 2 | 9.7 | 0.64 |
| 21 | 10.9 | 0.86 | 13.1 | 0.94 | 7.1 | 0.43 | 7.1 | 0.47 | 36.8 | 2.2 | 26.4 | 1.5 | 8.2 | 0.51 |
| 22 | 11.8 | 0.77 | 14.8 | 0.89 | 9.1 | 0.46 | 7.2 | 0.45 | 38.8 | 2 | 31.4 | 1.6 | 9.5 | 0.52 |
| 23 | 11.9 | 0.81 | 13.8 | 0.85 | 8.2 | 0.47 | 7.4 | 0.48 | 40.5 | 2.1 | 29.4 | 1.5 | 9.0 | 0.46 |
| 24 | 10.6 | 0.83 | 12.4 | 0.83 | 7.0 | 0.4 | 7.0 | 0.43 | 36.6 | 2.2 | 27.1 | 1.3 | 7.5 | 0.42 |
| 25 | 12.1 | 0.88 | 12.8 | 0.87 | 7.5 | 0.42 | 7.1 | 0.41 | 40.0 | 3.1 | 28.3 | 1.5 | 8.5 | 0.58 |
| 26 | 11.6 | 0.85 | 13.2 | 0.78 | 7.7 | 0.53 | 7.4 | 0.55 | 38.5 | 2 | 28.6 | 1.6 | 8.0 | 0.4 |
| 29 | 10.9 | 0.79 | 12.6 | 0.75 | 7.3 | 0.41 | 7.5 | 0.36 | 35.2 | 1.9 | 26.8 | 1.3 | 7.5 | 0.4 |
| 30 | 11.1 | 0.77 | 12.6 | 0.62 | 7.5 | 0.38 | 7.1 | 0.59 | 36.2 | 2.5 | 27.2 | 1.7 | 7.5 | 0.48 |
| 1 | 11.1 | 0.74 | 11.2 | 0.7 | 6.1 | 0.38 | 7.6 | 0.41 | 27.0 | 1.3 | 24.3 | 1 | 5.2 | 0.25 |
| 4 | 11.2 | 0.73 | 11.1 | 0.65 | 6.0 | 0.34 | 7.9 | 0.41 | 27.4 | 1.5 | 23.8 | 0.98 | 5.6 | 0.29 |
| 8 | 11.4 | 0.72 | 11.8 | 0.73 | 6.4 | 0.45 | 8.0 | 0.61 | 31.5 | 1.6 | 25.5 | 1.3 | 5.8 | 0.32 |
| 9 | 10.9 | 0.53 | 11.3 | 0.59 | 5.9 | 0.33 | 7.7 | 0.44 | 27.3 | 1.5 | 24.9 | 1.3 | 5.3 | 0.28 |
| 10 | 10.1 | 0.82 | 10.6 | 0.73 | 5.6 | 0.43 | 7.5 | 0.55 | 27.1 | 1.9 | 22.7 | 1.4 | 5.4 | 0.38 |
| 13 | 11.0 | 1 | 11.4 | 1 | 6.0 | 0.53 | 7.8 | 0.77 | 31.5 | 3.3 | 24.6 | 1.9 | 5.8 | 0.55 |
| 14 | 11.3 | 1.1 | 11.1 | 0.9 | 6.1 | 0.51 | 7.8 | 0.47 | 27.6 | 1.8 | 24.0 | 1.6 | 5.4 | 0.42 |
| 16 | 11.7 | 0.82 | 11.9 | 0.84 | 6.4 | 0.52 | 8.2 | 0.52 | 23.2 | 1.5 | 25.1 | 1.6 | 4.9 | 0.37 |
| 17 | 11.7 | 0.51 | 11.8 | 0.75 | 6.4 | 0.35 | 8.2 | 0.36 | 29.1 | 1.5 | 25.2 | 1.1 | 5.6 | 0.32 |
| 27 | 10.9 | 1.1 | 11.7 | 0.9 | 6.2 | 0.48 | 8.1 | 0.72 | 34.2 | 2.1 | 25.6 | 1.4 | 6.8 | 0.48 |
| 28 | 10.7 | 0.77 | 11.2 | 1 | 6.3 | 0.6 | 8.1 | 0.89 | 29.0 | 3.3 | 23.4 | 2 | 5.2 | 0.41 |
| 31 | 11.2 | 0.73 | 11.2 | 0.71 | 5.9 | 0.26 | 7.8 | 0.43 | 28.9 | 1.7 | 23.8 | 1 | 5.3 | 0.3 |
| 32 | 10.6 | 0.82 | 10.5 | 0.93 | 6.0 | 0.44 | 7.5 | 0.62 | 30.8 | 2.6 | 23.5 | 1.5 | 6.5 | 0.65 |
| 34 | 10.6 | 0.84 | 11.2 | 0.81 | 6.1 | 0.37 | 8.3 | 0.54 | 30.3 | 1.7 | 24.1 | 1.3 | 5.5 | 0.29 |
| 35 | 11.0 | 0.87 | 11.3 | 0.71 | 6.0 | 0.49 | 7.7 | 0.7 | 26.7 | 1.4 | 24.1 | 1.3 | 5.3 | 0.31 |





