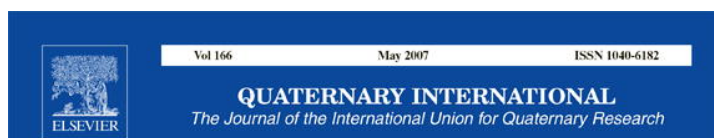
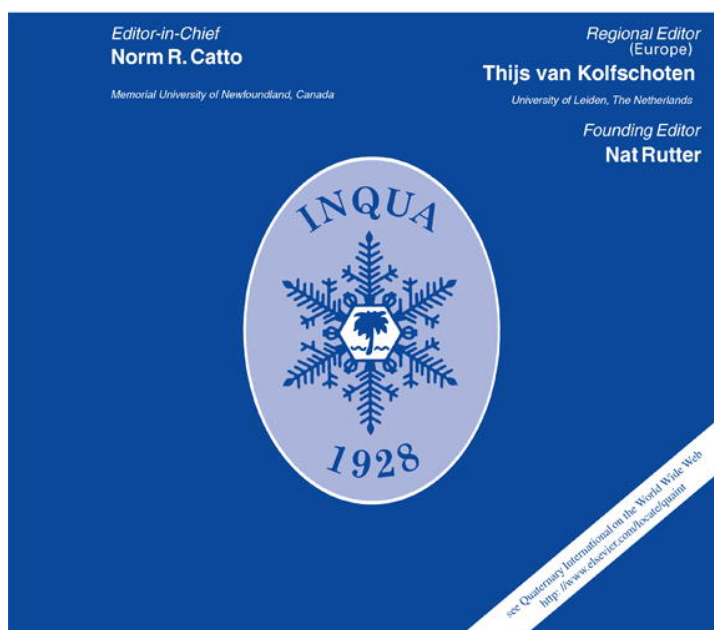


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**DATING QUATERNARY SEDIMENTS  
AND LANDFORMS IN DRYLANDS**

*Guest Editors*  
**J.R. KNOTT and L.A. OWEN**



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# Differentiating the Bishop ash bed and related tephra layers by elemental-based similarity coefficients of volcanic glass shards using solution inductively coupled plasma-mass spectrometry (S-ICP-MS)

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## Abstract

Volcanic glass samples from the same volcanic center (intra-source) often have a similar major-element composition. Thus, it can be difficult to distinguish between individual tephra layers, particularly when using similarity coefficients calculated from electron microprobe major-element measurements. Minor/trace element concentrations in glass can be determined by solution inductively coupled plasma mass spectrometry (S-ICP-MS), but have not been shown as suitable for use in large tephrochronologic databases. Here, we present minor/trace-element concentrations measured by S-ICP-MS and compare these data by similarity coefficients, the method commonly used in large databases. Trial samples from the Bishop Tuff, the upper and lower tuffs of Glass Mountain and the tuffs of Mesquite Spring suites from eastern California, USA, which have an indistinguishable major-element composition, were analyzed using S-ICP-MS. The resulting minor/trace element similarity coefficients clearly separated the suites of tephra layers and, in most cases, individual tephra layers within each suite. Comparisons with previous instrumental neutron activation analysis (INAA) elemental measurements were marginally successful. This is an important step toward quantitative correlation in large tephrochronologic databases to achieve definitive identification of volcanic glass samples and for high-resolution age determinations.

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## 1. Introduction

Tephrochronology is an important correlative dating tool used for age control in many arid land paleoclimate and paleogeography studies where volcanic glass shards are commonly preserved (e.g., Sarna-Wojcicki and Davis, 1991; Katoh et al., 2000). Correlations are typically made by statistical comparison of the glass shard major-element concentrations (expressed as oxides) determined by electron-microprobe analysis (EMA) supplemented by stratigraphic data and/or other correlative age control methods (e.g., paleontology or paleomagnetism). However, a single, detritally contaminated tephra bed found in unfossiliferous sediments not suitable for paleomagnetic analysis may be datable by tephrochronologic correlation alone. To com-

plicate matters, tephra layers from the same volcanic center (intra-source) have a similar glass shard composition and EMA may only narrow the correlation to the volcanic center (e.g., Long Valley, Yellowstone) with a substantial age range (e.g., 1–2 Ma). In such cases, minor and trace element concentrations are required to make a more accurate correlation (Sarna-Wojcicki et al., 1991; Sarna-Wojcicki, 2000).

X-ray fluorescence (Jack and Carmichael, 1968; Sarna-Wojcicki et al., 1979) and instrumental neutron activation analysis (INAA) (Borchardt et al., 1972; Sarna-Wojcicki et al., 1979; Izett, 1981; Izett et al., 1988) have been used to measure minor and trace element concentrations in glass shards. Sarna-Wojcicki et al. (1984) reported minor and trace element variations of  $\pm 1$ –4% on replicate samples of glass shards measured by INAA. They deemed this variability as sufficiently accurate for use in comparative calculations. Westgate et al. (1994) reported a range of

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2.9%–>15% for INAA analysis of glass shards as well. However, INAA is costly, time consuming, and requires a nuclear reactor.

Solution and laser ablation ICP-MS (S-ICP-MS and LA-ICP-MS, respectively) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) have been used to distinguish between compositionally similar inter-source and intra-source tephra layers (Kikkawa et al., 1989; Westgate et al., 1994; Pearce et al., 1996, 1999, 2004). Initial studies showed that LA-ICP-MS results are within 15% accuracy and >20% precision of INAA and S-ICP-MS (Westgate et al., 1994). Pearce et al. (1996) reported  $\pm 5\%$  accuracy for most elements measured by S-ICP-MS. Pearce et al. (1999) reported a precision of  $\pm 10\%$  for most trace elements using LA-ICP-MS on single shards, which was equivalent to the precision for S-ICP-MS (Pearce et al., 1996). Pearce et al. (1999, 2004) illustrated the differences between intra-source tephra layers using variation diagrams of minor and trace elements and elemental ratios.

Both S-ICP-MS and LA-ICP-MS have their advantages and disadvantages. The greater precision and accuracy favors S-ICP-MS. The ability to use polished slides and analyze individual shards, however, makes LA-ICP-MS more efficient and eliminates any homogenization caused by dissolving the sample. The ground breaking studies by Westgate et al. (1994) and Pearce et al. (1996, 1999, 2004) answer many questions and raise several others. As we start to build databases of minor and trace element concentrations in volcanic glasses for correlation, (1) Is S-ICP-MS or LA-ICP-MS sufficiently precise and accurate for these inevitably large databases? (2) Does dissolving the glass shards in acid for S-ICP-MS analysis create a homogenized sample that could yield a spurious correlation due to the dissolution of microlite inclusions? (3) Is the precision and accuracy of S-ICP-MS sufficient for use with similarity coefficient calculations such that intra-source tephra layers may be distinguished from each other?

To address the questions raised above, we measured minor and trace element concentrations by S-ICP-MS. We chose S-ICP-MS rather than LA-ICP-MS because of its reported higher accuracy and precision (Totland et al., 1992). We measured two trial volcanic glass samples of the Bishop Tuff and five trial samples from its (stratigraphically distal equivalent) ash bed. Then we evaluated the analyzed data using similarity coefficients. For further comparison, we measured the minor and trace elements concentrations of volcanic glass samples from different suites of tephra layers known to have great differences in age, but with a similar major-element composition. We then compared the results using similarity coefficients.

If similarity coefficients derived from S-ICP-MS data are suitable for large tephrochronologic databases, then there should be high similarity, or good chemical correlation, among the Bishop Tuff and its distal ash bed equivalents. In addition, there should be low similarity among the intra-source, or similar, suites of tephra layers. If these results are not attainable or reproducible using the more accurate

and precise S-ICP-MS technique, then, presumably, the less accurate and precise LA-ICP-MS technique will not be suitable for large tephrochronologic databases.

## 2. Methods

Volcanic glass shards were processed at the US Geological Survey Tephrochronology Laboratory in Menlo Park, California using methods outlined in Sarna-Wojcicki et al. (1984, 1997, 2005). All of the samples underwent EMA to determine the major-element composition using the methods described by Sarna-Wojcicki et al. (2005). Samples for S-ICP-MS were dissolved at the Carbonate Petrology Laboratory at the University of California, Riverside under clean room conditions, and S-ICP-MS analysis was completed at the Aqueous Analytical Laboratory at the University of Minnesota.

The Bishop Tuff (BT11A1 and BT11D2) and upper tuff of Glass Mountain D (BT-2C) and G (BT-1A) samples were collected at the south end of the Volcanic Tableland, ~11 km north of Bishop, California (Sarna-Wojcicki et al., 2005). Here, an  $^{40}\text{Ar}/^{39}\text{Ar}$  age (sanidine) of  $0.759 \pm 0.002$  Ma was determined for the Bishop Tuff. The upper tuffs of Glass Mountain in this same area are of reverse polarity and underlie a tephra layer with an  $^{40}\text{Ar}/^{39}\text{Ar}$  (sanidine) age of  $1.13 \pm 0.19$  Ma (Sarna-Wojcicki et al., 2005). The Bishop ash bed samples from Death Valley (JRK-DV-42, -43, -58, -62, and -93) are reliably identified by their position stratigraphically below the 0.639 Ma Lava Creek B ash bed (Knott et al., 1999, 2002) or direct  $^{40}\text{Ar}/^{39}\text{Ar}$  dating (Deino, 1997, written communication). The lower tuff of Glass Mountain (JRK-DV-89) sample was collected in southern Death Valley where it overlies the Shoreline Butte basalt, which has an age of ~1.7 Ma (whole rock K/Ar; Wright et al., 1991). This tephra layer is probably equivalent to <1.7 Ma altered lower tuffs of Glass Mountain found by Sarna-Wojcicki et al. (2005) three kilometers south in the Confidence Hills. Snow and Lux (1999) determined  $^{40}\text{Ar}/^{39}\text{Ar}$  ages (sanidine) of  $3.35 \pm 0.13$  Ma (JRK-DV-71) and  $3.35 \pm 0.07$  Ma (JRK-DV-80) for the Mesquite Spring tuffs (informal suite name) in Death Valley.

For INAA comparison, the mean ( $n = 8$ ) for the Bishop Tuff samples from Izett et al. (1988) was selected. These samples were selected because they are the greatest number of analyses from one subunit of the Bishop Tuff (basal 4 m, air-fall).

### 2.1. Separating and cleaning volcanic glass shards

Methods of separating and cleaning volcanic glass shards are described in Sarna-Wojcicki et al. (1984). In brief, samples were disaggregated with a mortar and pestle and wet sieved through 100 (150  $\mu$ ), 200 (80  $\mu$ ) and 325 (30  $\mu$ ) mesh screens. The >100–<200 mesh fraction is the optimum size for instrumental analysis. Next, authigenic materials were removed by ultrasonic baths, 10 s

treatments in 8% hydrofluoric (HF) acid, and 30s treatments in 10% hydrochloric (HCl) acid. After the acid wash treatments, glass shards were separated from the remaining minerals and composite grains (mineral/glass or glass with inclusions) using a magnetic separator and by density using heavy liquid mixtures of methylene iodide/acetone. Volcanic glass samples analyzed by EMA were composed of >95% isotropic glass shards, while S-ICP-MS samples were >99% glass shards by petrographic examination.

## 2.2. Dissolution for S-ICP-MS

Dissolution of earth materials for S-ICP-MS analysis may be done by alkali fusion, microwave digestion or HF/HClO<sub>4</sub> acid dissolution (Totland et al., 1992). Because our samples are already >99% glass, we chose acid dissolution. Facility limitations did not permit the use of HClO<sub>4</sub>, so we modified our dissolution process to use heated 1:1 HF:HNO<sub>3</sub> solution and HNO<sub>3</sub> instead.

Thirty milligram samples were placed in Teflon plastic beakers with 1.5 ml of 2:1 solution of highest purity, 5 M seastar-grade HF:HNO<sub>3</sub>. Heating to 80–100 °C on a hot plate caused most of the shards to dissolve in less than one hour. Once dissolved, the acid was evaporated (1 h or less), leaving a white, chalky powder residue. Some samples formed a “gel” rather than a powder. This gel was dissolved by reheating with an additional milliliter of 5 M HF:HNO<sub>3</sub>. Then, the acid mixture was evaporated until a powder residue remained.

To volatilize F<sup>-</sup>, 1 ml of seastar-grade, 4 M HNO<sub>3</sub> was added to the powdery residue and the samples were heated at 180 °C until all of the liquid was again evaporated leaving a yellow to yellow-brown solid. One sample chosen randomly was brought back into solution using 1% HNO<sub>3</sub> and tested for F<sup>-</sup> by ion chromatography and found to contain 0.03% (volume/volume) of F<sup>-</sup>, a sufficiently low concentration for S-ICP-MS analysis.

The remaining samples were then re-dissolved by pipetting 1 ml of 1% seastar-grade HNO<sub>3</sub> into capped Savillex beakers and allowing the beakers to stand for 24–48 h. After 1–2 h, most samples consisted of a clear solution with gel at the bottom of the beaker. Over the next 24–48 h the vials were occasionally stirred to break up the gel.

After two days, most, if not all of the gel in each sample was dissolved and the solutions were poured into 50 ml screw-capped plastic tubes. Any remaining solution or gel was removed from the beakers by rinsing with 1% HNO<sub>3</sub> or wicked into a pipette tip. The plastic tubes were filled with 1% HNO<sub>3</sub> was added to reach a total volume of 30 ml. This solution was then analyzed by ICP-MS.

## 2.3. Analytical conditions for ICP-MS

Samples were analyzed using a Perkin-Elmer/Sciex Elan 5000 ICP-MS run in high resolution mode. The concentrations and standard deviations (2σ) listed are an average of

five replicate analyses on each sample. The internal standard was <sup>115</sup>In.

## 2.4. Similarity coefficient

From the electron microprobe data, we used the standard suite of Si, Al, Fe, Ca, and Ti oxide concentrations for the similarity coefficient calculations. These oxides are generally abundant, but show sufficient variability to allow correlations and are immobile, unlike K or Na, at earth-surface temperatures. For minor/trace-element similarity coefficients, we selected 14 elements (Sc, Ti, Mn, Fe, Rb, Cs, La, Ce, Sm, Tb, Yb, Lu, Hf, and Th). Sarna-Wojcicki et al. (1984) used 12 of these elements and showed that these elements have sufficient compositional variability to allow discrimination of individual intra-source tephra layers.

Sarna-Wojcicki et al. (1984) found tantalum (Ta) to be a useful trace element, however, we have omitted Ta in this study because Ta volatilizes to tantalum pentafluoride when heated in HF (Remy, 1956). As a result, Ta concentrations were unreliable and not reproducible. We included manganese (Mn) and titanium (Ti) because both elements are known to vary in Long Valley eruptives (Sarna-Wojcicki et al., 1984; Metz and Mahood, 1985). Similarity coefficients for replicate analyses range from 0.93 to 0.99 (Sarna-Wojcicki et al., 1984) due to inhomogeneities in the glass, purity of the glass separations (presence of microlites) or analytical errors (Sarna-Wojcicki et al., 1984).

The similarity coefficient equation used in this study (after Borchardt et al., 1972) is

$$d_{(A,B)} = \frac{\sum_{i=1}^n R_i}{n},$$

where  $d_{(A,B)} = d_{(B,A)}$  is the similarity coefficient for comparison between sample A and sample B,  $i$  is element number,  $n$  is number of elements,  $R_i$  is  $X_{iA}/X_{iB}$  if  $X_{iB} \geq X_{iA}$ ; otherwise  $X_{iB}/X_{iA}$ ,  $X_{iA}$  is concentration of element  $i$  in sample A, and  $X_{iB}$  is concentration of element  $i$  in sample B.

As described in Sarna-Wojcicki et al. (1984), the similarity coefficient is an average of the element concentrations in two samples. From the two samples being compared, the lower concentration for each element is always in the numerator so that the ratio is always  $\leq 1$ . A chemically identical pair would yield a similarity coefficient of 1.

## 3. Results

Similarity coefficients for major-element concentrations for the Bishop Tuff and ash bed measured by EMA range from 0.9365 to 0.9855 (Table 1). All of these similarity coefficients exceed the 0.93 minimum threshold for replicate analyses of tephra layers (Sarna-Wojcicki et al. 1984).

Table 1  
Electron-microprobe analysis of volcanic glass shards of Bishop Tuff and ash bed

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	MnO	CaO	TiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	T <sub>(o)</sub>	SC
BT11A1	77.6	12.7	0.69	0.03	0.04	0.43	0.06	3.69	4.78	94.4	1.0000
BT11D2	77.2	13.1	0.76	0.02	0.04	0.42	0.05	3.73	4.66	93.9	0.9365
JRK-DV-58	77.50	12.30	0.74	0.03	0.04	0.44	0.06	3.46	5.39	93.20	0.9754
JRK-DV-93	76.80	13.24	0.70	0.03	0.03	0.43	0.05	3.54	5.21	91.90	0.9536
JRK-DV-43	77.30	12.90	0.76	0.03	0.03	0.44	0.06	4.20	4.34	93.90	0.9732
JRK-DV-42	77.60	12.60	0.72	0.03	0.03	0.44	0.06	3.78	4.20	94.30	0.9855
JRK-DV-62	77.90	12.40	0.77	0.03	0.03	0.43	0.06	4.00	4.39	92.00	0.9737

Values are given in mean weight-percent oxide, recalculated to 100% fluid free basis; Meyer (1977–1996), US Geological Survey, Menlo Park, CA, analyst. Original oxide totals ( $T_{(o)}$ ) before calculation are given to indicate approximate degree of hydration of volcanic glass. All similarity coefficients are calculated using Si, Al, Fe, Ca and Ti oxides relative to BT11A1, where 1.0000 represents a perfect match. See text for sample locations.

Table 2  
Concentration in mg/kg (parts/million) of elements in glass shards analyzed by S-ICP-MS

Element	Bishop Tuff		Bishop ash bed					INAA
	BT11A1	BT11D2	JRK-DV-58	JRK-DV-93	JRK-DV-43	JRK-DV-42	JRK-DV-62	Bishop Tuff
Sc*	2.99±0.09	3.12±0.09	3.05±0.05	2.87±0.10	2.98±0.08	2.61±0.08	2.95±0.07	2.8±0.1
Ti*	349±1.4	353±3.7	341±3.9	344±1.8	344±2.7	349±6.9	336±5.3	n.d.
Mn*	249±3.8	257.3±3.0	247.6±1.9	249.7±2.4	252.9±1.1	251.7±3.2	250.9±2.2	256±14
Fe*	4770±39.5	4880±50.7	4732±34.4	4683±40.3	4719±40.0	4769±38.7	4670±63.1	4800±30
Rb*	175.5±1.6	179.0±1.7	172.8±1.5	174.1±1.7	178.3±1.5	176.9±1.3	176.1±1.6	160±6
Cs*	6.21±0.09	6.39±0.09	6.13±0.07	6.07±0.08	6.27±0.14	6.26±0.12	6.27±0.06	5.3±0.3
La*	17.5±0.13	18.1±0.11	17.7±0.20	17.3±0.21	17.8±0.13	17.9±0.18	17.3±0.08	16.8±0.9
Ce*	39.8±0.45	41.3±0.53	40.6±0.34	39.9±0.39	40.8±0.31	40.7±0.18	40.2±0.29	36.2±4.4
Nd	16.5±0.13	16.9±0.26	16.6±0.22	16.4±0.39	16.9±0.35	16.5±0.28	16.4±0.32	17±2
Sm*	3.9±0.14	3.9±0.09	3.9±0.20	3.8±0.12	4.0±0.15	3.86±0.17	3.9±0.09	3.9±0.3
Eu	0.02±0.007	0.05±0.01	0.03±0.004	0.04±0.01	0.03±0.007	0.03±0.00	0.02±0.00	0.04±0.01
Gd	3.85±0.21	4.13±0.09	3.84±0.08	3.83±0.09	3.99±0.20	3.96±0.14	4.02±0.13	4.1±0.9
Tb*	0.64±0.02	0.67±0.02	0.64±0.03	0.67±0.02	0.69±0.02	0.66±0.02	0.67±0.03	0.6±0.07
Dy	4.04±0.09	4.03±0.17	3.98±0.11	4.07±0.14	4.06±0.09	3.97±0.06	4.06±0.09	3.8±0.3
Yb*	2.70±0.12	2.65±0.07	2.61±0.10	2.64±0.08	2.71±0.09	2.67±0.11	2.60±0.08	2.6±0.2
Lu*	0.41±0.02	0.43±0.02	0.42±0.02	0.41±0.02	0.44±0.01	0.42±0.02	0.42±0.02	0.38±0.04
Hf*	3.51±0.05	3.67±0.09	3.58±0.09	3.52±0.08	3.67±0.11	3.69±0.09	3.67±0.09	3.1±0.2
Ta	0.69±0.01	0.54±0.07	0.28±0.02	1.48±0.15	1.67±0.14	0.79±0.00	1.86±0.05	2.5±0.1
Pb	28.9±0.53	29.9±0.35	28.9±0.25	29.3±0.44	29.7±0.28	30.1±0.27	29.4±0.35	n.d.
Th*	18.7±0.24	19.2±0.22	18.1±0.30	18.6±0.44	18.8±0.16	18.2±0.23	18.7±0.14	19.4±0.8
U	7.52±0.13	7.58±0.07	7.42±0.15	7.42±0.12	7.61±0.13	7.56±0.10	7.51±0.12	7.7±0.3

Standard deviation is based on five analyses of the same sample. Asterisk (\*) indicates element used in calculation of similarity coefficient. See Table 1 for sample localities. Ave. Bishop Tuff ( $n = 8$ ) is the average concentration reported for the Bishop Tuff measured by INAA (Izett et al., 1988). n.d. = not determined.

The fourteen minor/trace-element concentrations used for similarity coefficient calculations (Table 2) have standard deviations around the mean of five S-ICP-MS analyses of individual samples typically <1% (Table 2). The similarity coefficients for the Bishop Tuff and ash bed samples are  $\geq 0.97$  (Table 3). Similarity coefficients calculated between the mean INAA Bishop Tuff from Izett et al. (1988) and the S-ICP-MS Bishop Tuff and ash bed samples range between 0.9145 and 0.9381.

The upper tuffs of Glass Mountain (BT-2C and BT-1A), lower tuffs of Glass Mountain (JRK-DV-89), and tuffs of Mesquite Spring (JRK-DV-71 and -80) all have similar major-element compositions (Table 4). Major-element similarity coefficients for these tephra layers range from

0.9185 to 0.9879 (Table 5). Only two of the similarity coefficients are below the 0.93 threshold. Thus, major-element similarity coefficients alone are unsuccessful at differentiating among these tephra layers known to be of different ages from different suites.

The S-ICP-MS analyses of the Bishop/upper Glass Mountain, lower Glass Mountain and Mesquite Spring tephra beds generally showed <1% standard deviation around the five-analysis means (Table 6). Similarity coefficients calculated using the 14 minor/trace elements measured by S-ICP-MS range from 0.6781 to 0.9996 when samples from all of the various suites are compared (Table 7). In other words, using the minor/trace-element similarity coefficients, we can quantitatively separate the

Table 3

Minor/trace-element (Sc, Ti, Mn, Fe, Rb, Cs, La, Ce, Sm, Tb, Yb, Lu, Hf, and Th) similarity coefficients comparing Bishop Tuff (S-ICP-MS), Bishop ash bed (S-ICP-MS), and Bishop Tuff (INAA)

	Bishop Tuff		Bishop ash bed					INAA
	BT11A1	BT11D2	JRK-DV-58	JRK-DV-93	JRK-DV-43	JRK-DV-42	JRK-DV-62	Bishop Tuff
BT11A1	1	0.9710	0.9815	0.9845	0.9773	0.9742	0.9818	0.9383
BT11D2	—	1	0.9720	0.9664	0.9806	0.9722	0.9749	0.9207
JRK-DV-58	—	—	1	0.9791	0.9768	0.9727	0.9791	0.9304
JRK-DV-93	—	—	—	1	0.9738	0.9745	0.9863	0.9408
JRK-DV-43	—	—	—	—	1	0.9767	0.9825	0.9198
JRK-DV-42	—	—	—	—	—	1	0.9753	0.9255
JRK-DV-62	—	—	—	—	—	—	1	0.9330
INAA Bishop Tuff	—	—	—	—	—	—	—	1

A perfect match is 1.0000.

Table 4

Electron-microprobe analysis of volcanic glass shards from the upper tuffs of Glass Mountain, lower tuffs of Glass Mountain and tuffs of Mesquite Spring suites

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	MnO	CaO	TiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	T <sub>(o)</sub>
BT-2C	77.6	12.7	0.74	0.03	0.03	0.43	0.07	3.66	4.73	94.8
BT-1A	77.5	12.6	0.74	0.03	0.04	0.42	0.06	3.71	4.81	95.4
JRK-DV-89	77.5	12.7	0.74	0.02	0.06	0.42	0.05	4.30	4.17	92.3
JRK-DV-71	77.3	12.7	0.73	0.04	0.08	0.48	0.05	3.48	5.21	93.9
JRK-DV-80	76.8	12.7	0.75	0.04	0.08	0.48	0.06	2.84	6.21	93.3

Values are given in mean weight-percent oxide, recalculated to 100% fluid free basis; Meyer (1977–1996), US Geological Survey, Menlo Park, CA, analyst. Original oxide totals ( $T_{(o)}$ ) before calculation are given to indicate approximate degree of hydration of volcanic glass. Similarity coefficients are shown on Table 5; see text for sample locations.

Table 5

Major element similarity coefficients comparing volcanic glass composition of tephra layers from different suites

SUITE	Upper Glass Mountain				Lower Glass Mountain	Mesquite Spring	
TEPHRA LAYER	Bishop Tuff		UGM-D	UGM-G	LGM	Tuffs of Mesquite Spring	
	BT11-A1	BT11-D2	BT-2C	BT-1A	JRK-DV-89	JRK-DV-71	JRK-DV-80
BT11-A1	1	0.9365	0.9579	0.9800	0.9482	0.9341	0.9611
BT11-D2	—	1	0.9258	0.9530	0.9879	0.9607	0.9319
BT-2C	—	—	1	0.9649	0.9379	0.9785	0.9459
BT-1A	—	—	—	1	0.9651	0.9369	0.9690
JRK-DV-89	—	—	—	—	1	0.9718	0.9372
JRK-DV-71	—	—	—	—	—	1	0.9660
JRK-DV-80	—	—	—	—	—	—	1

Coefficients are calculated using oxides of Si, Al, Fe, Ca, and Ti measured by electron microprobe (Tables 1 and 4). Values in italic print identifies similarity coefficients below the 0.93 threshold for replicate analyses.

Mesquite Spring, lower tuff of Glass Mountain and Bishop/upper tuffs of Glass Mountain suites from each other. The minor/trace-element similarity coefficients are highest for intra-suite samples and lowest for inter-suite samples. The highest similarity coefficients are for replicate samples.

#### 4. Discussion

The benefit of measuring minor and trace elements by S-ICP-MS is clear when comparing similarity coefficient

correlations obtained by EMA data to those by S-ICP-MS data. For example, based on the EMA results, the 1.9–1.7 Ma lower tuff of Glass Mountain (JRK-DV-89) is correlative with the 0.759 Ma Bishop, the 1.2–0.8 Ma upper tuffs of Glass Mountain, and the 3.35–3.1 Ma tuffs of Mesquite Spring. Using the minor and trace element similarity coefficients, JRK-DV-89 is shown to be not correlative with any of these tephra beds. The minor/trace-element similarity coefficients also correctly correlate the replicate Bishop Tuff and Mesquite Spring tuff samples.

Table 6  
Concentration in mg/kg (parts per million) of elements in glass shards analyzed by S-ICP-MS

SUITE	Upper Glass Mountain		Lower Glass Mountain	Mesquite Spring	
TEPHRA	UGM-D	UGM-G	LGM	Tuffs of Mesquite Spring	
Element	BT-2C	BT-1A	JRK-DV-89	JRK-DV-71	JRK-DV-80
Sc*	2.68±0.04	2.98±0.05	3.19±0.10	2.64±0.08	2.71±0.06
Ti*	402±3.2	390±6.7	309±5.1	368±3.2	388±5.1
Mn*	236±1.3	279±2.5	449±5.1	522±3.9	528±6.3
Fe*	4923±59.7	5183±22.9	5008±57.6	4858±64.7	4851±35.6
Rb*	161.1±1.9	181.7±2.3	242.6±1.8	178.6±1.3	179.4±1.5
Cs*	5.27±0.06	6.11±0.05	9.63±0.15	5.72±0.13	5.69±0.05
La*	23.4±0.20	21.1±0.08	13.8±0.09	22.9±0.20	23.2±0.39
Ce*	53.3±0.67	49.9±0.44	34.6±0.38	49.1±0.36	50.0±0.71
Nd	19.9±0.29	20.4±0.25	16.8±0.26	18.0±0.67	18.1±0.21
Sm*	4.1±0.15	4.5±0.14	4.9±0.21	4.0±0.17	3.9±0.12
Eu	0.03±0.008	0.04±0.014	0.03±0.007	0.12±0.008	0.14±0.012
Gd	4.32±0.09	4.39±0.11	5.17±0.15	4.09±0.16	4.16±0.10
Tb*	0.64±0.02	0.74±0.02	0.98±0.05	0.68±0.02	0.71±0.03
Dy	3.84±0.10	4.36±0.13	6.18±0.08	4.15±0.08	4.24±0.08
Yb*	2.42±0.05	2.82±0.15	4.23±0.12	2.69±0.08	2.69±0.06
Lu*	0.41±0.02	0.46±0.02	0.68±0.03	0.39±0.03	0.43±0.01
Hf*	3.38±0.13	3.75±0.12	4.41±0.09	3.29±0.07	3.33±0.08
Ta	0.74±0.05	2.21±0.09	1.87±0.02	0.18±0.02	1.48±0.18
Pb	28.4±0.56	32.0±0.39	38.4±0.51	30.4±0.51	30.4±0.44
Th*	16.1±0.23	18.2±0.21	26.1±0.38	14.8±0.18	14.6±0.28
U	6.43±0.17	7.57±0.07	11.2±0.15	5.10±0.13	4.97±0.12

Standard deviation is based on five analyses of the same sample. Asterisk (\*) indicates element used in calculation of similarity coefficient.

Table 7  
Minor and trace element similarity coefficients comparing volcanic glass composition from various tephra suites found in eastern California

SUITE	Bishop-Upper Glass Mountain			Lower Glass Mountain	Mesquite Spring		
TEPHRA	Bishop Tuff		UGM-D	UGM-G	LGM	Tuffs of Mesquite Spring	
	BT11-A1	BT11-D2	BT-2C	BT-1A	JRK-DV-89	JRK-DV-71	JRK-DV-80
BT11-A1	1	0.9690	0.9033	0.9141	0.7433	0.8835	0.8835
BT11-D2	—	1	0.8924	0.9257	0.7559	0.8845	0.8823
BT-2C	—	—	1	0.8904	0.6781	0.9117	0.9112
BT-1A	—	—	—	1	0.7539	0.8887	0.8996
JRK-DV-89	—	—	—	—	1	0.7262	0.7264
JRK-DV-71	—	—	—	—	—	1	0.9790
JRK-DV-80	—	—	—	—	—	—	1

Coefficients are calculated using Sc, Ti, Mn, Fe, Rb, Cs, La, Ce, Sm, Tb, Yb, Lu, Hf, and Th from elemental abundances measured by S-ICP-MS shown on Tables 2 and 6.

As described in earlier studies, the Bishop Tuff and upper tuffs of Glass Mountain have very similar glass shard compositions (Izett, 1981; Sarna-Wojcicki et al., 1984; Izett et al., 1988). The analyses by S-ICP-MS confirm this conclusion and the calculated similarity coefficients are insufficient to resolve these ash beds from each other. Whereas, the minor/trace-element similarity coefficients between the Bishop and upper tuffs of Glass Mountain are lower (0.8904–0.9257) than Bishop Tuff replicates (0.9690), the 0.9257 similarity coefficient may be rounded to 0.93, which is within the range of replicate analyses of Sarna-Wojcicki et al. (1984).

The similarity coefficients between samples analyzed by S-ICP-MS and INAA barely meet the 0.93 threshold for replicate analyses. The lower similarity coefficients to the INAA data may be attributable to variability within the Bishop Tuff, instrument variation, or the presence of microlites in the bulk sample used for INAA analysis. We interpret these data to illustrate that comparing older INAA data should be done cautiously.

The high similarity coefficients and low standard deviations among the Bishop Tuff and ash bed samples benefit from single instrument analysis. However, the consistency can also be interpreted as indicative of few

microlite impurities in the samples or that the microlites present do not substantially impact the results. The relatively close agreement between the S-ICP-MS and INAA methods suggests that the S-ICP-MS analyses are relatively accurate.

A more robust statistical analysis may prove useful, but the similarity coefficient is best suited for large databases (Froggatt, 1992), which we anticipate being developed. The higher precision and accuracy of the S-ICP-MS technique is suitable for such large databases; however, further studies using LA-ICP-MS and similarity coefficients, or other statistical comparison, may show that LA-ICP-MS is also suitable for large databases as well.

## 5. Conclusions

We have used similarity coefficients for minor/trace elements measured by S-ICP-MS to differentiate between the upper tuffs of Glass Mountain (including the Bishop ash bed), lower tuffs of Glass Mountain and tuffs of Mesquite Spring suites of tephra layers, all of which were indistinguishable by major element comparison. We interpret these results to indicate that S-ICP-MS analyses have sufficient precision and accuracy for incorporation into large tephrochronologic databases. Our results show the continuing difficulty in differentiating between intra-source tephra layers of very similar age (e.g., the Bishop Tuff and the upper tuffs of Glass Mountain) by glass shard composition alone. Our S-ICP-MS data are marginally suitable for comparison to previous INAA data, which may be the result of instrument variation, sample preparation or sample variability.

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