Supplementary Materials for

APPENDIX S1. Methods of Sampling Tephra in the Field and the Utility of Volcanic Glass in Tephrochronology

When an explosive volcanic eruption occurs, ash from the eruption is injected into the troposphere, sometimes above the tropopause (altitudes of ~9–11 km), and during particularly energetic eruptions, into the upper atmosphere (the stratosphere). Prevailing winds transport tephra downwind, often in complicated patterns due to wind shear, to sites of deposition on land and under water. The tephra particles fall out at different velocities, the larger and denser particles closer to the vent, the finer particles at greater distances. Thus, larger pumice clasts and accidental lithic fragments fall out closer to the vent, while the smaller pumice, rock fragments, mineral crystals, mineral fragments, and glass shards tend to fall out farther from the vent. At any particular location, there is often a gradation in particle size and density, with the coarsest and densest particles which fell fastest being at the base of the unit, and progressively finer material located above due to differences in settling times of the particles. Tephra deposited in water may show reverse grading because pumice clasts are often more buoyant than rock fragments, minerals, and unvesiculated glass shards. During eruptive episodes, when several eruptions may occur, the initial areal fallout patterns, and bedding characteristics at any particular site, can be quite complicated, with alternating "rhythmic"

repetitions of coarser and finer clasts. These bedding characteristics may reflect the eruptive history of an eruption or an eruptive episode, or a history of reworking of a single tephra layer from the landscape, and it may be difficult to resolve which of these possible origins apply in any particular case.

Large areas may be covered by a continuous blanket of ash, but wind and water begin to transport and redeposit the ash from sloping terrains to lower and more level areas after the eruption, so that the air-fall layer may soon be buried by reworked tephra. Multiple sets of reworked tephra may be deposited above the initial air-fall layer, each succeeding set less pure as the blanket of tephra is removed by erosion from the surrounding highlands by successive storms, and underlying older material is exposed and incorporated by erosion into the reworked tephra (Fig. 1). Thus, for the purpose of tephrochronology, the best place to sample a

Figure 1. Photo of an exposure of air-fall ash and reworked ash. A basal layer of pure white ash, ~1.5 cm thick, is expose at the base of this unit, and is the result of direct air-fall. Above this is a ~3-cm thick layer composed of finer laminae and layers, less pure than the basal layer; this is reworked ash that has been brought into this depositional basin from surrounding highlands by streams and wind (?). Above the latter, there is a ~9-10 cm thick layer or layers and laminae of progressively less pure ash, which is mixed in with the local detrital sediment lithology. Above the latter is sediment that is the same in color as the sediment underlying the ash, indicating that the ash has been mostly cleared out from the nearby highlands during successive storms. Tuff of Blind Spring Valley, ~2.19 Ma, in the Beaver Basin of southwestern Utah, erupted near and east of Long Valley caldera in east-central California
(Sarna-Wojcicki and others, 2005)

tephra layer is close to the base of the unit, where the original comagmatic components, the

volcanic glass and minerals, are most likely to be present, but sufficiently above the base of the

layer so that contamination from underlying material is avoided. Additional coarse layers within a compound tephra layer may be sampled, to determine whether multiple eruptions occurred, and to check for variations in chemical composition and mineralogy vertically within the sampled unit. This will help in determining whether compositional zonation existed in the magma chamber before eruption. Air-fall tephra layers have clast-supported textures, with the larger clasts in contact with each other, and finer clasts filling interstices between larger clasts.

In areas close to the volcanic source, multiple layers of an eruptive episode may be present that are not represented at greater distance (Sarna-Wojcicki and others, 1981a; Waitt and Dzurisin, 1981), and it becomes a matter of judgment, resources, and time to determine which units should be sampled near the eruptive sources. Fine layers might be ignored, but fine layers from distal sources could provide additional vital age and stratigraphic sequence information that would otherwise not be available. Initial sampling can often be followed-up, if necessary, after initial analytical results are available, except in areas where rapid urban growth is taking place, or where return to the field area or site are otherwise not possible.

Tephra layers formed by ash flows (ignimbrites) are generally present in areas close to the volcanic source areas and may extend for distances of several tens to as much as several hundred kilometers away from the source. Ash flows have matrix-supported textures, with larger pumice fragments and generally somewhat finer lithic fragments surrounded by a finer ash and pumice matrix. The grain size in ash flows also decreases with distance from the eruptive source by comminution within the ash flow sheets. The ash flows often overlie the Plinian (air fall) deposits near the eruptive source areas. Samples of ash flows can be taken from any homogeneous part of a bed, preferably from both pumice clasts and the finer matrix, but

care has to be taken to avoid contamination from older material that may have been present

on the land surface and became entrained into the ash flow before the ash flow came to rest.

In our studies, tests of vertical and lateral variation or homogeneity of tephra layers

were made, particularly in the early stages of sampling in the study area (1967 and on),

together with description of bedding features, thickness of tephra units and subunits, and

stratigraphic relations to overlying and underlying beds. Such initial tests were done, for

example, on the Lawlor Tuff, a compound tephra unit in the study area that has both a basal

pumice fall unit and an overlying ash flow. This unit is exposed continuously over a distance of

~15 km on the northeast flank of Mount Diablo, so that possible lateral as well as vertical

variations in glass chemical composition and mineral content could be determined. The range

of the mineral and chemical parameters determined for this unit could be compared with the

ranges obtained for tephra layers found stratigraphically above and below the Lawlor Tuff.

Those parameters (*e.g.*, specific element or oxide concentrations in the volcanic glass), the

ranges of which were systematically and significantly different from those of the underlying and

overlying units, were then identified as the parameters useful in identification of this tephra

layer and distinguished it from other tephra layers. Although the presence or absence of certain

minerals were often a useful secondary set of parameters, the quantitative abundance of

mineral species in the tephra was quite variable with both distance and manner of

emplacement of the tephra (tephra "facies"), and was not generally useful in identification.

Downwind abundance of specific mineral species does not appear to vary in any

straightforward manner, in part because of the differences in mineral content within pumice

clasts and finer aggregates of volcanic shards and mineral particles, as well as the different ways tephra is emplaced: air-fall, ash-flow, or water transported.

Results of such sampling studies as those made on the Lawlor Tuff indicated that the chemical composition of untreated bulk samples of the tephra, or mineral-frequency counts of samples, were not consistently good identifiers. The chemical composition of the volcanic glass, however, was quite uniform over long distances of aerially and fluvially transported tephra (Sarna-Wojcicki, 1971; Sarna-Wojcicki and others, 1979, 1981b). There is some suggestion of variation of tephra composition, as seen in its glass composition, with phase of eruption: early vs. late (Sarna-Wojcicki and others, 1985, 2000). We recognize volcanic glass composition as the most distinctive and compositionally homogeneous component of tephra layers. When the glass of a tephra layer is devitrified or altered, that's a whole different ball game. Older tephra layers tend to be more frequently altered or devitrified, and the state of preservation of the volcanic glass as well as cogenetic minerals depends on both the natural storage environment of the tephra and the length of storage. The most common form of alteration of tephra after deposition is hydration of the glass. This generally does not affect the composition of the glass, other than to decrease the weight percent of the elements of oxides. This can be corrected by summing the analyzed oxides to 100 percent. The difference between the total on analysis and the recalculated total (to 100 percent) is an approximation of the amount of water of hydration present in the glass. When this amount approaches or exceeds 10 percent, there are usually other indications that the original glass composition has changed. Such changes are usually accompanied by variations in the alkalis. For example, Na_2O and K_2O are often depleted, but sometimes the opposite happens, and one or the other of the alkalis is enriched in the glass.

Such changes depend on the "storage" environment of the tephra layer, and amount of time since deposition. With further alteration, the glass may become anisotropic due to the growth of diagenetic phases, and the glass becomes partly or wholly birefringent under the microscope, using crossed-Nichol polarizers and analyzers. The composition of the glass at this stage is sufficiently altered, so that the original composition of the glass is changed and may no longer be recognized.

Most evolved (*i.e.*, the most highly differentiated, most silicic) volcanic glass is most often derived from the initial, explosive Plinian phase of a volcanic eruption. This initial phase is most often found at distal sites of an eruptive unit but is not always represented near-source; it may be buried under later products of the same eruptive episode, or by tephra and lavas erupted later. Ash flows may be the same composition as the early-erupted Plinian material (based on glass shard composition), but in some cases the ash flows are less evolved, indicating that there was zonation in the pre-eruptive magma chamber. For example, the volcanic glass of the Bend Pumice (~0.43 Ma), from near the town of Bend, Oregon (Sarna-Wojcicki and others, 1988) (Fig. 2) is chemically identical in composition to the overlying Tumalo Tuff, the associated

Figure 2. Bend Pumice tuff and the Tumalo Tuff exposed in quarry face. The white layer at about the level of the white belt of the man standing by the cliff is a traction layer or surge layer, at the base of the Tumalo Tuff, an ash flow. The tephra below these is the Bend Pumice, a coarse air-fall pumice layer. In the latter unit, the pumice clasts are in contact with each other, and finer ash fills the interstices between them. A rough layering can be seen in this lower unit. The overlying Tumalo Tuff consists of an ash matrix, with clasts of pumice and rock suspended within the matrix. These clasts are not in contact with each other. The dark-brown rock above the ash-flow is a partly-welded upper part of the Tumalo Tuff. The Bend-Tumalo Tuff is ~435 Ka in age, with K-Ar and $^{40}Ar/^{39}Ar$ ages ranging from 400 to 470 Ka. The chemical composition of the fall pumice and overlying ash flow are essentially the same. Location east of Triangle Hill, west of Bend, in central Oregon. We assigned stratigraphic number (SN) 31 to this unit in northern California and the greater San Francisco Bay area.

ash flow phase of this eruption. The Bishop Tuff air-fall pumice (erupted from the Long Valley Caldera in east central California), however, has slightly different composition from the overlying ash flow (Sarna-Wojcicki and others, 2021, their Fig. 26), the latter being somewhat less evolved, and containing pyroxene rather than the biotite that is present in the air-fall unit (Sarna-Wojcicki and others, 2000). The ash flows usually follow the initial, Plinian eruption, as the volcanic vent is enlarged by erosion during the eruption, and the volcanic plume collapses to form ash flows extending away from the vent. However, the differences in chemical composition of the glass observed in products from a major volcanic eruption (in both air-fall and ash flow) are usually smaller than differences among tephra layers of demonstrably different ages, as determined from studies of the chemical compositions and stratigraphic positions of the tephra layers within the San Francisco Bay area and elsewhere. At distal sites, the eruptive products of the air-fall and ash-flow phases can mix and become indistinguishable from each other, and complex stratigraphy observed near the eruptive source may become simpler at distal sites for the same tephra layer (Sarna-Wojcicki and others, 1981; Waitt and Dzurisin, 1981).

Sampling strategies as related to laboratory treatment of samples

Trial and error were involved in developing sampling strategies and methods of analysis for the San Francisco Bay tephrochronology project. These methods were eventually used in developing successful procedures for tephra sampling, analysis, and identification. Because the Lawlor Tuff, on the northeast flank of Mount Diablo, is exposed almost continuously for a distance of ~20 km, and because several facies of this tuff are present along its length—pumice fall, ash-flow, water transported, and fine ash-flow elutriate—this tephra was chosen for initial

tests in 1966-1967 to develop and validate sampling and analytical protocols (Sarna-Wojcicki, 1971, 1976, 2000; Sarna-Wojcicki, and others, 1979, 2011). Initially, multiple samples were taken laterally and vertically in this unit to determine its internal variability with regard to a number of parameters: stratigraphic characteristics, mineralogy, quantitative determination of mineral abundances, both cogenetic and detrital, bulk chemical composition, and composition of the volcanic glass in the tephra, and cogenetic minerals as determined by wavelength-dispersive X-ray fluorescence (WDXRF) and electron-microprobe analysis (EMA) of the volcanic glass in pumice and glass shards. From these initial tests, the senior author was able to show that the chemical composition of glass shards remained essentially constant from site to site, as determined by the elemental and oxide abundances in the glass, while most other parameters varied from site to site, or as in the case of most of the minerals analyzed, had wide ranges of composition due to solid solution that made it harder to distinguish tephra units of different age or stratigraphic position because of compositional overlap (Sarna-Wojcicki, 1971).

The second phase of these initial tests was to determine if the range of chemical compositions of the glass shards were significantly different in tephra layers that were of demonstrably different ages, as, for example, within a set of tephra layers stratigraphically superposed in a single or in multiple outcrops. This test proved to work well as, for example, the differences in chemical composition of glass shards between the Lawlor Tuff and the underlying Alves Quarry Tuff, or between the overlying Huichica Tuff and, in turn, the Tuff of Napa on the northeast flank of Mount Diablo, were significantly greater than the internal variability of each as determined by multiple analysis at the same and at different sites. The chemical composition of volcanic glass has become the most important factor in correlating

tephra layers among sites between which they are not continuously exposed. With the validation of the method, it was possible to utilize it to analyze and correlate other tephra layers within the San Francisco Bay area, and eventually to expand this methodology to other areas in the western United States. During the following years, other scientists conducting tephrochronological work came to similar conclusions, some independently and some by sharing of information (Czamanske and Porter, 1965; Smith and Westgate, 1969; Westgate and others, 1970; Izett and others, 1972; Borchardt and others, 1972; Davis, 1978; Izett, 1981; Knott, 1998; Perkins and others, 1995, 1998).

The treatment of tephra samples for laboratory analysis evolved by trial and error from the early days of reconnaissance studies to the systematic sampling and analysis of tephra layers in the San Francisco Bay area (Sarna-Wojcicki, 1971). Early studies by Sarna-Wojcicki had indicated that certain groups of elements tended to accumulate in specific mineral phases, or in authigenic coatings on tephra particles, and these factors could distort or mask the original composition of the volcanic glass. Initial analysis of bulk (whole tephra) samples was then supplanted by separation of the main components of tephra, and separation and cleaning of the volcanic glass for chemical analysis. Small amounts of tephra sample scraped from its surface were initially examined under a petrographic microscope in optic oil to determine whether the volcanic glass was fresh (as indicated by its optical clarity and isotropism), or altered or devitrified (as, indicated by presence of incipient crystals and anisotropism), so that a decision could be made whether to attempt an analysis, and if so, to determine the best approach for the separation of the components of the tephra sample. Microporphyritic or microlitic glass presents problems in both the separation and analysis of volcanic glass, while

low-order birefringence of the glass indicates its incipient alteration or devitrification, indicating that the original composition of the glass may have changed.

Laboratory treatment of tephra samples for analysis

After disaggregation, or crushing in a mullite mortar, the tephra particles are sieved to a convenient size range for separation and analysis, generally 100 to 200 mesh size, with openings of ~120 to 80 μm of the nylon screens used. Use of metal screens and sieves was abandoned when contamination was detected, with high concentrations of several metallic elements such as Cu, Zn, and Ni, showing up on analysis—elements present in high concentrations in the screens, screen holders, and solder used to fasten the screens to the sides of the holders. After removing the highly magnetic minerals (magnetite and ilmenite) with a hand magnet, the sieved fraction was then passed through a Frantz magnetic separator twice, first at a low amperage to separate the more magnetic particles (pyroxenes, amphiboles, biotite, and metallic oxides) from the less magnetic clasts (lithic fragments, volcanic glass, and non-magnetic crystal grains such as quartz, feldspars, zircon, and apatite). Then the non-magnetic fraction was run through again at a high amperage setting to separate the non-magnetic particles from those of intermediate magnetic susceptibility (the non-magnetic crystal grains from the volcanic glass, the latter usually having more iron in it than the non-magnetic crystal grains). Subsequently, the volcanic glass, lighter than other components of the tephra, was separated from other tephra components using heavy liquids (bromoform or methylene iodide) mixed with acetone in sufficient amounts to cause the heavier particles to sink and the volcanic glass to hover or float in the liquid (the glass particles are generally in the specific-gravity range of ~2.0–2.4 g/cm^3; comagmatic crystals and crystal fragments are heavier). The

gravity separation was accomplished in a long, vertical separatory tube developed for this purpose. Many aspects of these separating procedures were pioneered by William Eastwood, in his study of upper Miocene tephra in western Nevada (Eastwood, 1969), and some even earlier, in techniques developed for the separation of minerals for K-Ar dating at the Earth Sciences and Physics Departments at the University of California, Berkeley beginning around 1956 (Evernden and others, 1964; Jack and Carmichael, 1968). The separated glass shards were rinsed in acetone to remove any traces of bromoform or methylene iodide (both bromine and iodine showed up in X-ray fluorescence scans of samples that were not sufficiently dried in the oven; their spectra masked those of certain other trace or minor elements present in the glass. The separated glass was next treated briefly (~30 seconds) with 10% hydrochloric acid (HCl) to remove authigenic carbonate coatings that might have formed on the glass particles, and quickly rinsed in distilled water. Then it was etched briefly (~15 seconds) with 8% dilute hydrofluoric acid (HF) to remove any altered rinds that may have been present on the glass particles, quenched with distilled water, and rinsed. Authigenic carbonate contains Sr as well as Ca, and the altered rims of glass particles or coatings may contain clays and other low-temperature minerals such as zeolites, that are crystallizing at the expense of the volcanic glass. These alteration phases are often leached or depleted in certain trace and minor elements in the clay and zeolite phases. The acid treatments were terminated quickly in distilled water to prevent further dissolution of the glass. X-ray fluorescence scans were run on the separates at each step of the treatment procedure, to determine the effect of each step on the composition of the separate. The separation procedures that evolved from the early experiments were those that resulted in progressively tighter clustering of data points for glasses of tephra layers

of different age, and clear separation of the scatter fields for the elements (or oxides) that were eventually chosen as the best discriminants, when plotted on binary or ternary graphs, or analyzed statistically by factor analysis with dendrograms derived from the chemical data (Sarna-Wojcicki, 1971, 1976; Sarna-Wojcicki and others, 1979, 1984, 2005, 2011).

Altered or devitrified volcanic glass shards generally do not retain their original composition, and thus cannot be used for the purpose of identification and correlation. The authigenic minerals within tephra, however, tend to be more stable over time than the volcanic glass in many depositional environments. Thus, the chemical composition of these minerals can be used for identification as well as for direct dating.

Proper names for tephra layers

The names of tephra layers are ephemeral and varied because they have been found at different times, at multiple sites, and are often named for the places at which they were found. Thus, a tephra layer sampled at different times and at different sites may have multiple names. Conversely, tephra layers that are not continuous may be assigned the same name based on field criteria, but later are shown to be different. Tephra names in such cases can only be simplified or standardized once correlations among the various sites have been well established by mapping or chemical and petrographic analysis, or by radiometric dating. Once the volcanic field or source vent from which a tephra has been erupted is identified, either by the actual presence of that tephra near its eruptive source or by close chemical and age similarity between a proximal unit in the source area and a specific distal tephra layer, it has been our practice to choose a name reflecting its source area.

Tephra layers in the stratigraphic record can be widespread, sometimes continental in areal distribution, but their preservation after eruption and emplacement is usually quite variable, so outcrops of tephra are often lenticular and isolated, even though they may be present in many different formations and in many areas. For this reason, and for the difficulties associated with the naming of tephra layers over large areas by different investigators at different times, we have found it most convenient to use informal names, giving preference to those names having close association with the eruptive source area. However, we also include other names that may have been given to tephra layers in the past, to avoid confusion between older and newer names.

Chemical types of tephra and their relation to source areas

There are several orders of variability in the range of glass compositions of tephra, as determined from statistical analyses such as factor, cluster, and principal components analysis (e.g., Sarna-Wojcicki, 1971, 1976), and the variation in these indicates that the greatest differences exist between tephra of silicic compared to basaltic composition. Among silicic tephra, the greatest differences exist within the glasses of tephra erupted from different volcanic provinces. Smaller differences are found in tephra erupted from the same volcanic field or province. Smaller differences yet are observed for tephra layers erupted from the same source (i.e., vent or volcano, or volcanic field), and the shorter the interval of time between erupted units, as observed from their stratigraphic separation or direct numerical ages, the greater the chemical similarity. The similarity is greatest in replicate samples obtained from the same tephra unit or layer.

There are only a few areas in the conterminous United States that were the centers of

major volcanic eruptions of *silicic* tephra in Cenozoic time, producing widespread deposits

(Izett, 1981; Sarna-Wojcicki and others, 1983; Sarna-Wojcicki and Davis, 1991; Sarna-Wojcicki

and others, 1991; Sarna-Wojcicki, 2000; Cassel, 2009, Henry and others, 2012). These centers

are each situated within a specific volcano-tectonic area, and their magmas have tapped

specific types of source rocks (Sarna-Wojcicki and others, 2021, their Fig. 1). Thus, the major

source areas for the most widespread tephra layers in the conterminous United States are now

well known, with regard to both their compositions and their age ranges, and the compositions

of tephra erupted from these sources are characteristic of the sources (also see Izett, 1981, and

Perkins and others, 1998, for both graphic and qualitative classifications of tephra layers and

their source areas). These source areas are shown in Fig. 1 of Sarna-Wojcicki and others, 2021).

Methods of Chemical Analysis of Tephra

The senior author began analysis of tephra in the greater San Francisco Bay area using a

Norelco wavelength-dispersive X-ray fluorescence (WDXRF) spectrometer at the Earth Sciences

Department of the University of California, Berkeley (Carmichael and McDonald, 1961; Jack and

Carmichael, 1969). Rapid scans made it possible to determine the effects of separation

procedures and chemical treatment of the tephra samples, and selection of the most

dependable variables for the identification of tephra. Initial rapid-scan analyses and graphic

comparisons for the elements Rb, Sr, Y, Zr, Nb, were supplanted by quantitative WDXRF

analyses for Fe, Ti, Ba, Mn, Zr, Rb, Sr, Zn, Y, Ga, Nb, Cu, and Ni. Only some of these elements,

Fe, Ti, Ba, Mn, Zr, Rb, Sr, Zn, Y, and Nb proved to be useful for high-silica tephra, but all were

useful to some degree in identification of the whole compositional spectrum of tephra layers,

from basaltic to high silica tephra (Sarna-Wojcicki, 1971). WDXRF required the preparation of a two-gram sample of pure glass separated from the original tephra sample, ground to a powder in a mortar made of non-contaminating materials, usually agate or mullite, together with a specific weight of cellulose as a binder. This procedure required much labor and time.

In the mid- to late 1960s, electron microprobe analysis (EMA) of volcanic glass was also initiated, as were EMA of individual grains of minerals contained in the tephra. These analyses were expressed in oxides as SiO_2, Al_2O_3, Fe_2O_3, MgO, MnO, CaO, TiO_2, Na_2O and K_2O. On occasion, Cl, P, and S were also determined. Results of mineral analyses indicated that these had broad ranges of compositions, particularly for the solid-solution minerals like the feldspars, amphiboles, and pyroxenes, and were thus more difficult to use for identification of tephra layers than the volcanic glass because of broad compositional overlaps among minerals from tephra layers of different age. After 1971, and particularly after 1976, use of the microprobe became a standard technique for the analysis of volcanic glass at the USGS Tephrochronology Project Laboratory in Menlo Park, California with Charles E. Meyer as Project analyst. EMA then evolved into the main technique employed on new samples. When chemical differences could not be resolved by EMA other more discriminating analytical techniques (*e.g.*, instrumental neutron activated analysis [INAA]) were employed. Samples for EMA were still prepared by separating the volcanic glass from the rest of the tephra sample. But the separations did not need to be as thorough, and the chemical treatment of the glass shards could be avoided because specific glass shards could be selected in the polished mount prepared for EMA. Fresh internal surfaces of the glass grains could be selected and analyzed by positioning a 6–12 μm electron beam within the glass grains. EMA is one of the techniques that provides consistent

results largely independent of the instrument used. At the U.S.G.S. in Menlo Park, California, we have successively used four different EMA instruments over a period of about 50 years, and the results have been consistent on replicates of the same samples or the same tephra units, and reference standards, perhaps with the exception of values for Na_2O and, to a lesser extent, K_2O. The light alkalis, particularly Na_2O, present a special analytical problem; the sodium in volcanic glass in particular appears to be fairly mobile, with the light positive ions being repelled by the electron beam. Thus, lower beam current, scanning across an area of a glass specimen, or use of a glass standard, are required to obtain reliable results for Na_2O (Smith and Westgate, 1969). Also, samples of the same tephra layer collected from different sites may have different concentrations of alkalis due to leaching or enrichment of these elements in the volcanic glass over time, as seen in samples of the same tephra layer collected from different depositional environments (Tephrochronological Database, Tephrochronology Project Laboratory, U.S. Geological Survey, Menlo Park, CA). The identity of tephra layers can be determined without using the alkali data, either by using the other oxides determined by EMA, or by additionally using other techniques, such as INAA. Identities of tephra layers can also be independently confirmed when characteristic sequences of several tephra layers are identified at different localities. The odds of mistaken identities based on chemical compositions of tephra layers become very low when three or more tephra layers are found in a stratigraphic sequence. Although homotaxial successions are observed in nature and need not be unique in a chronological sense (for example, Bouma sequences), in the case of volcanic layers with specific chemical characteristics related to each layer that are present within a stratigraphic sequence of tephra layers, it is unlikely that two such sequences could be replicated at different times,

and the odds against this duplication increase exponentially with the increase in the number of tephra layers within such sequences (Sarna-Wojcicki, 2000).

In the late 1970s and early 1980s, analyses of tephra were also performed using energy-dispersive X-ray fluorescence (EDXRF). A database of these analyses was developed, but the specific instrument used was breaking down frequently, and results obtained after repairs often did not match previous results. For this reason, this type of analysis was eventually abandoned. The initial numerical data obtained, however, remain useful in tephra correlation.

To date, the most precise and definitive technique used for chemical analysis of volcanic glass of tephra, and thus the one most successful in discriminating among them and identifying correlative samples (at least for the U.S. Geological Survey Tephrochronology Project Laboratory at Menlo Park, Calif.), is Instrumental Neutron Activation Analysis (INAA). This technique requires irradiation of a separate of pure volcanic glass, ~0.2 to 0.5 g, together with standards of equal weight, within a nuclear reactor. After the sample is removed from the reactor and after a waiting period for the reduction of induced radioactivity from the sample, the remaining induced activity is measured for the intensity of the characteristic wavelengths of a number of elements. A second waiting period is required to measure the radiation for a second group of elements, the spectra of which are initially masked by the intense initial radiation of the first group. Over 40 elements can be determined by this method, with high precision (Perlman and Asaro, 1969; Sarna-Wojcicki and others, 1979, 1984; Budahn, 2002). About 24 elements are particularly useful in the identification of silicic tephra (more elements are available for intermediate to basaltic tephra). Precisions as high as 2–4 percent are often obtained on replicate analyses for many of these elements. The suite chosen for identification

and correlation of silicic tephra, in order of increasing atomic number, is: Sc, Ti, Mn, Fe, Rb, Sr, Zr, Cs, and Ba, the rare-earth elements La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb, and Lu, and Hf, Ta, Th, and U. The drawback to the INAA technique is that a very pure sample of volcanic glass is required (although smaller than what is required for XRF), and long periods of time must elapse between the submission of samples, analysis, and acquisition of the analytical results, as well as the need for a special facility, a nuclear reactor, and the safety protocols required in handling and analysis of radioactive materials. Thus, delayed results and relatively high expense are methodological disadvantages.

A relatively new technique that has come into use in the analysis of volcanic glass and other components of tephra is inductively coupled plasma mass spectroscopy (ICP-MS) (Pearce and others, 2004, 2007, 2011, 2014). This technique has been applied in two ways: weighted aliquots of separated glass are digested in acids then volatilized by a monochromatic laser beam to form a plasma; the volatilized material is then passed through a spectral analyzer, alternately with standards. This is referred to as Solution S-ICP-MS. Alternatively, polished surfaces of volcanic glass are volatilized by a monochromatic laser beam to obtain a discrete volume, then the plasma thus formed is passed through the spectrometer, again alternately with standards. This method is referred to as Laser ablation (LA-ICP-MS). The precisions obtained by ICP-MS, on the average, are almost as high as those obtained by INAA, the liquid dissolution S-ICP-MS method being somewhat consistently more precise than the LA-ICP-MS. The advantages of ICP-MS analysis are that a large number of elements can be determined with high precisions within a relatively short period of time, and at a lower cost compared to INAA.

This method has now been used on some tephra layers we have sampled in the greater San Francisco Bay area (Knott and others, 2007).

Methods of $^{40}Ar/^{39}Ar$ analysis used for dating the Nomlaki and Putah Tuffs

In this study, three pumice samples, one each from the Nomlaki ($^{40}Ar/^{39}Ar$ lab. sample ROSER-2a = DCNT- through DCNT-32 in this report), the lower Putah Tuff unit A ($^{40}Ar/^{39}Ar$ lab. sample PVRD-2a = 758-287A of this report), and an upper Putah Tuff unit B ($^{40}Ar/^{39}Ar$ lab. sample PVRD-3b = 758-287D of this report), were dated by the laser incremental heating approach on multiple grains of plagioclase phenocrysts. Mineral crystals (typically feldspars) were concentrated using standard separation techniques, consisting of gentle crushing in a mortar, magnetic separations with a Frantz Isodynamic Separator, a brief dilute (5%) HF bath, distilled water rinse, and final hand-picking to obtain the clearest, inclusion free grains. Grain sizes recovered ranged from ~400 to 800 μm.

Following separation, the plagioclase concentrates were irradiated in a single batch in the CLICIT position of the Oregon State University TRIGA reactor (BGC Irradiation #191 for 2 hours). Sanidine phenocrysts from the Fish Canyon Tuff of Colorado (orbitally referenced age of 28.201 ±0.023 (1 sigma) Ma; Kuiper and others, 2008) were used as the neutron fluence monitor. Following radiological "cooling" after irradiation, all argon analyses were performed at the Berkeley Geochronology Center using an on-line extraction system employing a CO_2 laser fitted with a 6-mm integrator lens as the heating source under ultra-high vacuum. Approximately 20–40 mg of plagioclase was incrementally heated in 9–14 steps until fusion. One aliquot of Nomlaki Tuff ROSER-2a (Nomlaki Tuff DCNT 1-3), two of PVRD-2a (Putah Tuff,

lower unit A), and three of PVRD-3b (Putah Tuff, upper unit B) were analyzed. Argon gas

measurements were performed immediately after gas extraction on MAP 215 noble-gas mass

spectrometer using an analog multiplier in peak-hopping mode. Additional details of the

general analytical and data-reduction process are provided elsewhere (Best and others, 1995).

The ^{40}Ar/^{39}Ar analytical data are listed in Tables 3 and 5.

The incremental heating experiments were examined for calculated age consistency as a

function of the fraction of ^{39}Ar released (Fig. 3). Grains with a near-uniform release pattern
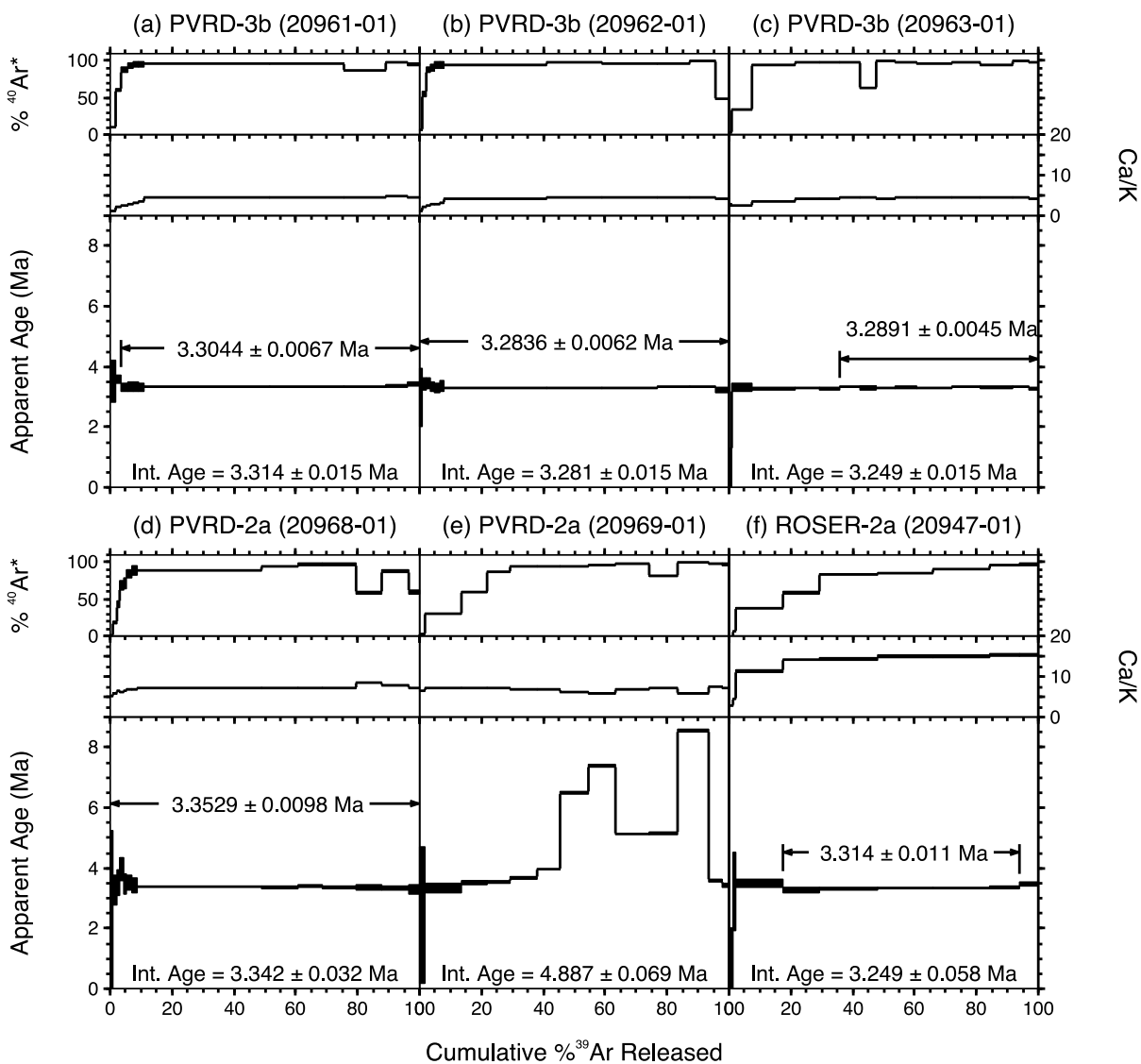
Figure 3. Incremental heating spectra of the Putah and Nomlaki Tuffs. Samples PVRD-2a are from the lower unit A of the Putah Tuff, equivalent to sample 758-287A collected for chemical fingerprinting of the volcanic glass shards; samples PVRD-3b are from the upper unit B of the Putah Tuff, equivalent to sample 758-287D. Samples were collected from the Pleasants Valley Road locality near the type locality of the Putah Tuff at Putah Creek, west side of southwestern Sacramento Valley. Sample ROSER-2a is from near the base of the Nomlaki Tuff, equivalent to samples DCNT-1 through DCNT-3 collected for chemical fingerprinting. Sample from Dry Creek, where the Nomlaki Tuff is situated near the base of the Tehama Formation, west side Sacramento Valley. The Putah and Nomlaki sample localities, both from the western margin of the Sacramento Valley and both within the Tehama Formation, are separated by ~210 km, the Nomlaki in the north.

("apparent age plateau") are considered more geologically reliable than those with irregular

age patterns. The plateau identification algorithm used here (following Fleck and others, 1977),

delineates the set of contiguous steps encompassing the greatest percent of ^{39}Ar release that

exhibit an acceptable MSWD (mean square of weighted deviates, with a threshold probability

>95% that the observed scatter is caused by analytical error alone and that geological scatter is

not demonstrated). A plateau must comprise at least 50% of the total ^{39}Ar release and consist

of at least three consecutive steps. The age and uncertainty assigned to the plateau are

weighted means (weighted by the inverse variance of each step) and modified standard error

(standard error expanded by root MSWD if MSWD >1).

The plateau data, on a sample-by-sample basis, was then plotted as an "inverse-

isochron" diagram (^{36}Ar/^{40}Ar *vs.* ^{39}Ar/^{40}Ar isotope correlation diagrams), from which the age

and presumed internal ^{40}Ar/^{36}Ar internal composition are inferred from the axis intercepts (Fig.

4). The isochron ages are preferred over the plateau ages here, as the isochron approach

inherently accommodates departures from an assumed atmospheric $^{40}Ar/^{36}Ar$ composition of trapped argon in the plagioclase crystal interior.
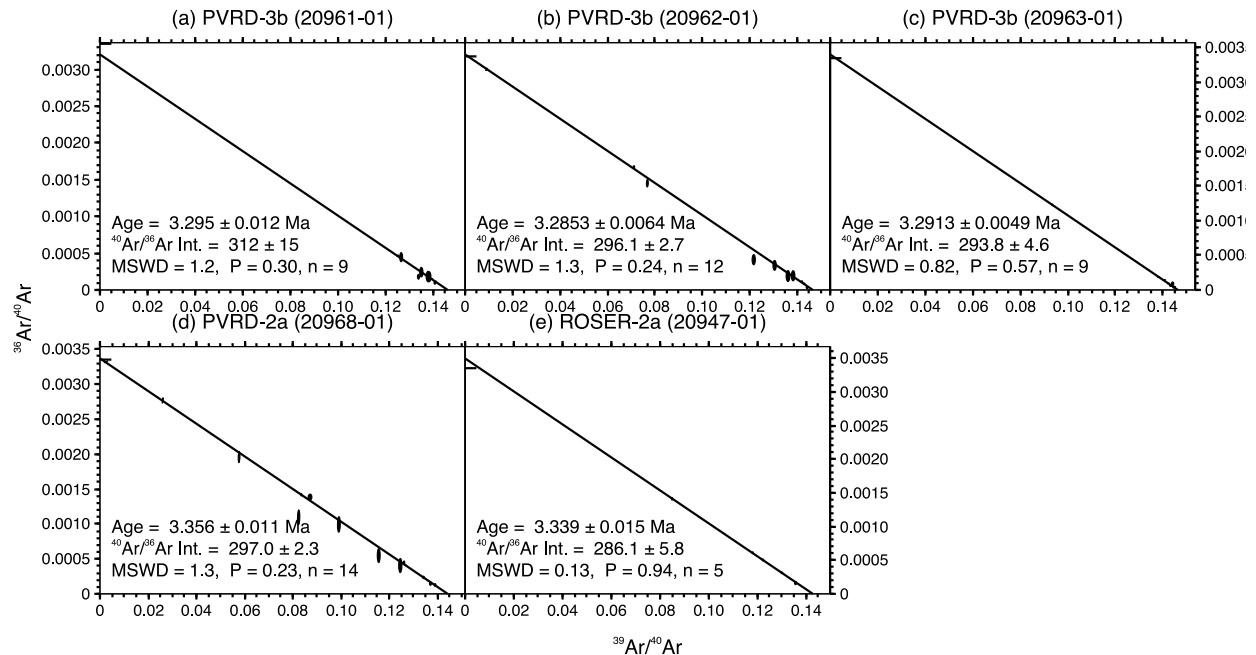

Figure 4. Isochrons for Putah and Nomlaki tuff samples. See figure 23 for sample numbers, locations and stratigraphic information.

REFERENCES

Best, M.G., Christiansen, E.H., Deino, A.L., Gromme, C.S., and Tingey, D.G., 1995. Correlation and emplacement of a large, zoned, discontinuously exposed ash flow sheet: The Ar-40/Ar-39 chronology, paleomagnetism, and petrology of the Pahranagat Formation, Nevada. Journal of Geophysical Research - Solid Earth 100(B12), p. 24593–24609.

Borchardt, G.A., Aruscavage, P.J., and Millard, H.T., Jr., 1972, Correlation of the Bishop ash, a Pleistocene marker bed, using instrumental neutron activation analysis: Journal of Sedimentary Petrology, v. 42, p. 301–306

Cassel, E.J., Calvert, A., and Graham, S.A., 2009, Age, geochemical composition, and distribution of Oligocene ignimbrites in the northern Sierra Nevada, California: Implications for landscape morphology, elevation, and drainage divide geography of the Nevdaplano. International geology review, v. 51, p. 723-742.

Budahn, J.R., and Wandless, G.A., 2002, Instrumental neutron activation by long count, *in* Taggart, J.E., Jr., ed., Analytical methods for chemical analysis of geologic and other materials: U.S. Geological Survey Open-File Report 02-0223, p. X1-X13

Czamanske, G.K., and Porter, S.C., 1965, Titanium dioxide in pyroclastic layers from volcanoes in the Cascade Range, Science, v. 150, p. 1022–1025.

Davis, J.O., 1978, Tephrochronology of the Lake Lahontan area, Nevada and California: Nevada Archaeological Research Paper 7, 137 p

Evernden, J.F., Savage, D.E., Curtis, G.H., and James, G.T., 1964, Potassium-argon dates and the Cenozoic mammalian chronology of North America. American Journal of Science, v. 262, p. 145–198.

Fleck, R.J., Sutter, J.F., and Elliot, D.H., 1977. Interpretation of discordant 40Ar/39Ar age-spectra of Mesozoic tholeiites from Antarctica. Geochimica et Cosmochimica Acta, p. 4115–4132.

Henry, C.D., Hinz, N.H., Faulds, Colgan, J.P., John, D.A., Brooks, E.R., Cassel, E.J., Garside, L.J., Davis, D.A., and Castor, S.B., 2012, Eocene-early Miocene paleotopography of the Sierra Nevada—Great Basin—Nevadaplano based on widespread ash-flow tuffs and paleovalleys: Geosphere, v. 8, no. 1, p. 1-27, https://doi.org/10.1130/GES00727.1.

Izett, G.A., 1981, Volcanic ash beds: Recorders of upper Cenozoic silicic pyroclastic volcanism in the western United States: Journal of Geophysical Research, v. 86, no. B11, p. 10,200-10,222.

Izett, G.A., Wilcox, R.E., Borchardt, G.A., 1972, Correlation of a volcanic ash bed in Pleistocene deposits near Mount Blanco, Texas, with the Guaje pumice bed of the Jemez Mountains, New Mexico: Quaternary Research, v. 1, p. 121-132.

Jack, R.N., and Carmichael, I.S.E., 1968, The chemical "fingerprinting" of acid volcanic rocks. California Division of Mines and Geology Special Report 100, p. 17–32.

Knott, J.R., 1998, Late Cenozoic tephrochronology, stratigraphy, geomorphology, and tectonics of the western Black Mountain piedmont, Death Valley, California: Implications for the spatial and temporal evolution of the Death Valley fault zone. PhD dissertation, University of California, Riverside, 407 p.

Knott, J.R., Sarna-Wojcicki, A.M., Wan, Elmira, and Montañez, I.P., 2007, Differentiating the Bishop ash bed and related tephra layers by similarity coefficients calculated from minor and trace element analysis of volcanic glass shards by solution inductively coupled plasma-mass spectrometry: Quaternary International, https://doi.org/10.1016/j.quaint.2006.12.014.

Kuiper, K.F., Deino, A., Hilgen, F.J., Krijgsman, W., Renne, P.R., and Wijbrans, J.R., 2008. Synchronizing rock clocks of Earth history. Science, v. 320(5875), p. 500–504.

Pearce, N.J., Abbott, P.M., and Martin-Jones, Catherine, 2014, Microbeam methods for the analysis of glass in fine-grained tephra deposits: a SMART perspective on current and future trends: Geological Society of London, Special Publications 398, p. 29-46, https://doi.org/10.1144/sp398.1.

Pearce, N.J., Denton, J.S., Perkins, W.T., Westgate, J.A., and Alloway, B.V., 2007, Correlation and characterization of individual glass shards from tephra deposits using trace element laser ablation ICP-MS analyses: current status and future potential: Journal of Quaternary Science, v. 22, no. 7, p. 721-736.

Pearce, N.J.H., Perkins, W.T., Westgate, J.A., and Wade, S.C., 2011, Trace-element microanalysis by LA-ICP-MS: The quest for comprehensive chemical characterization of single, sub 10 mm volcanic glass shards: Quaternary International, v. 246, p. 57-81.

Pearce, N.J., Westgate, J.A., Perkins, W.T., and Preece, S.J., 2004, The application of ICP-MS methods to tephrochronological problems: Applied Geochemistry, Elsevier, v. 19, Issue 3, p. 289-322.

Perlman, I., and Asaro, F., 1969, Pottery analysis by neutron activation: Archaeometry, v. 11, p. 21-52.

Sarna-Wojcicki, A. M., 1971, Correlation of late Cenozoic pyroclastic deposits in the central Coast Ranges of California: Ph.D. dissertation, University of California, Berkeley, 174 p.

Sarna-Wojcicki, A. M., 1976, Correlation of late Cenozoic tuffs in the central Coast Ranges of California by means of trace- and minor-element chemistry: U.S. Geological Survey Professional Paper 972, 32 p.

Sarna-Wojcicki, A.M., 2000, Tephrochronology, in Noler, J.S., Sowers, J.M., and Lettis, W.R., eds., Quaternary Geochronology; Methods and Applications: American Geophysical Union Reference Shelf 4, p. 357-377.

Sarna-Wojcicki, A.M., Bowman, H.R., and Russell, P.C., 1979, Chemical correlation of some late Cenozoic tuffs of northern and central California by neutron activation analysis of glass and comparison with X-ray fluorescence analysis: U.S. Geological Survey Professional Paper 1147, 15 p.

Sarna-Wojcicki, A. M., Bowman, H. R., Meyer, C. E., Russell, P. C., Woodward, M. J., McCoy, Gail, Rowe, J. J., Jr., Baedecker, P. A., Asaro, F., and Michael, H., 1984, Chemical analyses, correlations, and ages of upper Pliocene and Pleistocene ash layers of east-central and southern California. U.S. Geological Survey Professional Paper 1293, 40 p.

Sarna-Wojcicki, A. M., Champion, D. E., and Davis, J. O., 1983, Holocene volcanism in the conterminous United States and the role of silicic volcanic ash layers in correlation of latest-Pleistocene and Holocene deposits, in Wright, H. E., Jr., ed., Late-Quaternary environments of the United States, v. 2, the Holocene; University of Minnesota Press, chap. 5, p. 52-77.

Sarna-Wojcicki, A. M., and Davis, J. O., 1991, Quaternary Tephrochronology, in Morrison, R. B., ed., Quaternary nonglacial geology: conterminous United States. Geological Society of America, DNAG Series, v. K-2, p. 93-116.

Sarna-Wojcicki, A. M., and Davis, J. O., 1991, Quaternary Tephrochronology, in Morrison, R. B., ed., Quaternary nonglacial geology: conterminous United States. Geological Society of America, DNAG Series, v. K-2, p. 93-116.

Sarna-Wojcicki, A.M., Deino, A.L., Fleck, R.J., McLaughlin, R.J., Wagner, D.L., Wan, Elmira, Wahl, D.B., Hillhouse, J.W., and Perkins, M.E., 2011, Age, composition, and areal distribution of the Pliocene Lawlor Tuff, and three younger Pliocene tuffs, California and Nevada. Geosphere, v. 7, no. 3, p. 599-628, https://doi.org/10.1130/GES00609.1.

Sarna-Wojcicki, A.M., Lajoie, K.R., Meyer, C.E., Adam, D.P., and Rieck, H.J., 1991, Tephrochronologic correlation of upper Neogene sediments along the Pacific margin,

conterminous United States, in Morrison, R.B., ed., Quaternary nonglacial geology: conterminous United States. Geological Society of America, DNAG Series, v. K-2, p. 117-140.

Sarna-Wojcicki, A.M., Lajoie, K.R., Meyer, C.E., Adam, D.P., and Rieck, H.J., 1991, Tephrochronologic correlation of upper Neogene sediments along the Pacific margin, conterminous United States, in Morrison, R.B., ed., Quaternary nonglacial geology: conterminous United States. Geological Society of America, DNAG Series, v. K-2, p. 117-140.

Sarna-Wojcicki, A. M., Meyer, C. E., Bowman, H. R., Hall, N. T., Russell, P. C., Woodward, M. L., and Slate, J. L., 1985, Correlation of the Rockland ash bed, a 400,000-year-old stratigraphic marker in northern California and western Nevada, and implications for middle Pleistocene paleogeography of central California. Quaternary Research, v. 23, p. 236-257.

Sarna-Wojcicki, A.M., Meyer, C. E., Woodward, M. J., and Lamothe, P. J., 1981, Composition of air-fall ash erupted on May 18, May 25, June 12, July 22, and August 7, in Lipman, P.W., and Mullineaux, D. R., eds., The 1980 eruptions of Mount St. Helens, Washington: U.S. Geological Survey Professional Paper 1250, p. 667-680.

Sarna-Wojcicki, A.M., Pringle, M.S., and Wijbrans, Jan, 2000, New 40Ar/39Ar age of the Bishop Tuff from multiple sites and sediment rate calibration for the Matuyama-Brunhes boundary. Journal of Geophysical Research, v. 105, B9, p. 21,431-21,443.

Sarna-Wojcicki, A.M., Reheis, M.C., Pringle, M.S., Fleck, R.J., Burbank, Doug, Meyer, C.E., Slate, J.L., Wan, Elmira, Budahn, J.R., Troxel, Bennie, and Walker, J.P., 2005, Tephra layers of Blind Spring Valley and related upper Pliocene and Pleistocene tephra layers, California, Nevada, and Utah: Isotopic ages, correlation, and magnetostratigraphy. U.S. Geological Survey Professional Paper 1701, 63 p.

Smith, D.G.W., and Westgate, J.A., 1969, An electron probe technique for characterizing pyroclastic deposits: Earth and Planetary Science Letters, v. 5, p. 313-319.

Westgate, J.A., Smith, D.G.W., and Tomlinson, M.C., 1970, Late Quaternary tephra layers in southwestern Canada, in Smith, R.A., and Smith, J.W., eds., Early Man and Environments in Northwest North America", The Students' Press, Calgary, Alberta, p. 13-34.