Volcanic ash provenance from zircon dust with an application to Maya pottery

Kevin T. Coffey, Axel K. Schmitt, Anabel Ford, Frank J. Spera, Constance Christensen and Jennifer Garrison

Geology 2014;42:595-598
doi: 10.1130/G35376.1

Email alerting services click www.gsapubs.org/cgi/alerts to receive free e-mail alerts when new articles cite this article

Subscribe click www.gsapubs.org/subscriptions/ to subscribe to Geology

Permission request click http://www.geosociety.org/pubs/copyrt.htm#gsa to contact GSA

Copyright not claimed on content prepared wholly by U.S. government employees within scope of their employment. Individual scientists are hereby granted permission, without fees or further requests to GSA, to use a single figure, a single table, and/or a brief paragraph of text in subsequent works and to make unlimited copies of items in GSA's journals for noncommercial use in classrooms to further education and science. This file may not be posted to any Web site, but authors may post the abstracts only of their articles on their own or their organization's Web site providing the posting includes a reference to the article's full citation. GSA provides this and other forums for the presentation of diverse opinions and positions by scientists worldwide, regardless of their race, citizenship, gender, religion, or political viewpoint. Opinions presented in this publication do not reflect official positions of the Society.

Notes

© 2014 Geological Society of America
Volcanic ash provenance from zircon dust with an application to Maya pottery

Kevin T. Coffey1, Axel K. Schmitt1, Anabel Ford2, Frank J. Spera3, Constance Christensen4, and Jennifer Garrison5

1Department of Earth, Planetary, and Space Sciences, University of California–Los Angeles, 595 Charles Young Drive East, Box 951567, Los Angeles, California 90095-1567, USA
2Department of Anthropology, University of California–Santa Barbara, Santa Barbara, California 93106, USA
3Department of Earth Science, University of California–Santa Barbara, Santa Barbara, California 93106, USA
4Geoscience Department, Ventura Community College, 4667 Telegraph Road, Ventura, California 93003, USA
5Department of Geosciences and Environment, California State University–Los Angeles, Los Angeles, California 90032, USA

ABSTRACT
When analyzed using secondary ion mass spectrometry, dust-sized (<63 µm) zircon in distal ash deposits of the Tierra Blanca Joven (TBJ) eruption of Ilopango Volcano (El Salvador) yielded results consistent with ages obtained from those in proximal deposits. This finding indicates insignificant age sorting of zircon crystals during their dispersal in the TBJ ash plume. As a result, analysis of zircons may permit reliable source identification of distal tephra marker beds commonly found in terrestrial and marine environments. This technique was applied to test whether an enigmatic volcanic ash used to manufacture Late Classic Maya pottery from El Pilar is from distal TBJ ash deposits, a hypothesis supported by the location, extent, and timing of the TBJ eruption, and the matching high silica content and trace element ratios between TBJ glass and glass in the archaeological samples. The exclusively older than 1 Ma ages of the archaeological zircons compared with the dominantly 20–50 cm of ash accumulating more than 100 km to the northwest of Ilopango, in the Central American Volcanic Arc (CAVA; Fig. 1). Its most recent caldera-forming eruption produced the TBJ deposit, which consists of six units, A (oldest) through F (youngest; Lexa et al., 2011). The TBJ eruption released a massive quantity of tephra (18 km3 dense-rock equivalent; Rose et al., 1999), with an estimated 20–50 cm of ash accumulating more than 100 km to the northeast of Ilopango (Dull et al., 2001). TBJ ash has also been found in lacustrine deposits ~175 km to the northeast of Ilopango (Mehringer et al., 2005). Radiocarbon dating originally placed the TBJ eruption at A.D. 260 ± 114 (1σ; Sheets, 1983), but new and recalibrated 14C dates vary by ~200 yr (Dull et al., 2001; Mehringer et al., 2005; Kitamura, 2010), with exact calendar dating confounded by a multivalued 14C age versus calendar age calibration curve in the interval of A.D. 440–540 (e.g., IntCal09; Reimer et al., 2009).

Enigmatic Ash in Maya Pottery
Coexisting with the Late Classic Period of Maya civilization (A.D. 600–900) is the widespread use of volcanic ash as a temper, or stabilizing

INTRODUCTION
Investigation of fine volcanic ash has become an indispensable tool in tephrachronology. The advantage of using zircon crystals, which are resistant to alteration, to directly date and correlate tephra deposits has long been recognized (e.g., Compston et al., 1992), but for Quaternary tephras, correlation is largely based on glass or mineral chemical indicators (e.g., Lowe, 2011). In some cases, fission-track methods have been applied to date zircon in late Cenozoic tephras (e.g., Naeser et al., 1981), but these are only effective for crystals >75 µm, and the results are generally fraught with impractically large uncertainties for ages younger than 100 ka. Zircon ages for Quaternary volcanic rocks are now routinely determined by U-Th disequilibrium isotopic analysis to address time scales of pre-eruptive crystallization and crystal residence (e.g., Reid et al., 1997; Schmitt et al., 2006; Claiborne et al., 2010). Most of these studies have targeted large zircon crystals, extracted from lava flows and pumice clasts from proximal pyroclastic deposits. Here we explore the potential of the small spot size and high sensitivity that secondary ion mass spectrometry (SIMS) affords for determining the crystallization ages of zircon with the grain size of fine ash (dust; <63 µm) recovered from distal ash fallout deposits.

Little is known about zircon sorting during atmospheric dispersal of fine ash. If size-controlled differences between age populations were absent, then zircon ages could be used for correlating distal deposits with their proximal equivalents. This study tests this possibility using tephra from the Tierra Blanca Joven (TBJ) eruption (Dull et al., 2001, 2010) of Ilopango Volcano, El Salvador. This technique is then applied to evaluate the proposed correlation between TBJ tephra and distal ash found as a major constituent of Maya pottery manufactured at approximately the same time as the eruption that produced the TBJ deposit.

GEOLOGICAL AND GEOARCHAEOLOGICAL BACKGROUND
TBJ Eruption of Ilopango
Ilopango is one of several calderas in the Central American Volcanic Arc (CAVA; Fig. 1). Its most recent caldera-forming eruption produced the TBJ deposit, which consists of six units, A (oldest) through F (youngest; Lexa et al., 2011). The TBJ eruption released a massive quantity of tephra (18 km3 dense-rock equivalent; Rose et al., 1999), with an estimated 20–50 cm of ash accumulating more than 100 km to the northwest of Ilopango, in the Central American Volcanic Arc (CAVA; El Salvador) ash sample locations, and relevant ash-fall isopachs of Ilopango TBJ (after Dull et al., 2001) and El Chichón (Mexico) 1982 (after Varekamp et al., 1984) eruptions.
additive, in pottery from the Maya lowlands (e.g., Ford and Glicken, 1987; Ford and Rose, 1995; Fig. 1). Prior to that time, lowland pottery was made largely from local, carbonate-rich materials. Explaining the presence of volcanic ash in the pottery is problematic. The region lacks nearby volcanoes, the closest being 360–410 km distant (Fig. 1), and it is devoid of known volcanic deposits containing fresh, unaltered ash. Furthermore, it is improbable that small eruptions from distant volcanoes could have produced the estimated 800 m³/a of ash (Ford and Glicken, 1987) consumed by the lowland Maya during the Late Classic Period for pottery manufacture. Trade has been proposed as the source of this ash (Simmons and Brem, 1979; Jones, 1986; Sunahara, 2003), but the large volume used, the steep transportation costs associated with the ~300 km distance to the CA VA, and the use of human rather than draft animal transportation (Feldman, 1985; Hassig, 1985), collectively render this explanation implausible. The location, extent, and age of the TBJ eruption are all consistent with it being the source of the pottery ash (Ford and Spera, 2007), a correlation that has been suggested by other researchers (Gifford, 1976; Dull et al., 2001; cf. Deevey et al., 1983). Here we show conclusively that this is not the case.

METHODS

Sample Preparation and Analysis

TBJ pumice samples (units B, C, E, and F) collected at Ilopango caldera are termed proximal, TBJ ash collected near San Salvador (by Payson Sheets) are termed intermediate, and an ash collected ~160 km from Ilopango (by José Alexander Chavez) is termed distal (Fig. 1). Excavated Late Classic pottery samples (MAR016, MAR017, and MAR020) are from the El Pilar area (Ford, 2004; Fig. 1). We analyzed 14 volcanic-glass–bearing pottery samples for glass compositions; a subset of 3 was selected for zircon extraction from ~10–20-g sized fragments. Gentle hand-crushing produced <250 µm fines, which were reacted with cold hydrofluoric acid (HF). Zircon in the residue was separated by density in methylene iodide (ρ = 3320 kg/m³) and hand-picking. The TBJ ash and pottery samples both yielded plentiful zircon dust (10–75 µm; average = 45 µm); zircon picked from proximal pumice included a range of grain sizes (45–110 µm).

RESULTS

Zircon Geochronology

Overall, U-Th zircon rim ages range between ca. 0 ka and 250 ka in both the proximal pumice and the intermediate and distal ash samples (Fig. 3A). The ages are independent of grain size, and lack systematic differences between TBJ subunits, although some subunits were only sampled at a reconnaissance level (Table DR1). Collectively, the zircon age populations for the proximal pumice and the combined intermediate and distal ash TBJ samples are statistically identical, as indicated by Kolmogorov-Smirnov testing, which yields a probability of identity P = 0.20 (P = 0.05 being the level of acceptance; Fig. 3A). By contrast, El Pilar pottery zircons, including zircons with adherent glass analyzed in situ, lack evidence for disequilibrium, and are thus clearly distinct from the majority of TBJ zircons. Pottery U-Pb zircon ages range from ca. 1 Ma to 1324 Ma. The U-Pb zircon age populations from samples MAR016 and MAR017 closely overlap, but are distinct from those of MAR020 (Fig. 3B).

Glass Composition

The silica contents of the TBJ volcanic glass (77.0 ± 0.1 wt%, n = 3; Mehringer et al., 2005) and the El Pilar pottery samples (78.0 ± 1.1 wt% (GSA Data Repository item 2014207, Table DR3 in the GSA Data Repository1)) using 99.999% aluminum (Al) as the mounting medium for zircon dust (Fig. 2A), rather than indium (In) or epoxy. The absence of interferences with the 230Th peak when the analysis spot (~50 µm in diameter) overlaps onto Al was demonstrated by the analysis of small, Al-mounted fragments of secular equilibrium zircon AS3, which yielded (230Th)/(238U) = 1.018 ± 0.022 (mean square of weighted deviates = 1.2; n = 8). A subset of the archaeological zircons was also analyzed in situ in sectioned and polished pottery (Fig. 2B). Disequilibrium crystallization ages were calculated as two-point isochrons combining the average (230Th)/(238U) whole-rock value of 1.03 for TBJ pumice determined by Garrison et al. (2012) with zircon values. Zircons within error of secular equilibrium (the upper limit of disequilibrium dating, ca. 300 ka) were subsequently U-Pb dated following the protocols in Schmitt et al. (2003).

Figure 2. A: Zircon from sample of distal Tierra Blanca Joven (El Salvador) ash, mounted in aluminum (Al) with remnants of gold (Au) coating. B: Zircon partially encased in shard of volcanic glass in a Late Classic Maya pottery sample (MAR016). Both zircons were partly obliterated by secondary ion mass spectrometry analysis (analysis spot outlined in white).

1GSA Data Repository item 2014207, Table DR1 (U-Th disequilibrium zircon analyses), Table DR2 (U-Pb zircon analyses), and Table DR3 (major and trace element abundances in glass from El Pilar pottery), is available online at www.geosociety.org/pubs/ft2014.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
Despite its high density ($\rho = 4650$ kg/m$^3$), zircon dust is abundant in distal ash deposits, as seen in the TBJ and Maya pottery samples. This is expected, as faster settling due to zircon’s higher density is compensated for by its comparatively small crystal size. Stokes’ law settling times for volcanic glass particles ($\rho = 2300$ kg/m$^3$) and zircons are hydrodynamically equivalent if the zircon crystal radii are ~40% of those of the glass particles.

Homogeneous zircon rim ages in both the ash and proximal pumice samples of the TBJ indicate that the eruption tapped a reservoir that was well mixed with regard to zircons. This finding does not address the possibility that larger crystals may record more protracted crystallization, but demonstrates that zircon rim ages can be used successfully to correlate distal tephra with proximal counterparts. Zircon rim ages are also uniformly distributed in the TBJ subunits, making the possibility of age variation in different distal tephra lobes unlikely.

Zircon geochronology can thus radically improve tephrostratigraphy in regions where ash layers are affected by alteration, and/or where an abundance of compositionally similar glass or minerals hinders tephra identification. There is a wide range of potential applications, including correlation of thin terrestrial ash beds, tephra in lake and ocean sediment cores, and even in pottery and other archaeological materials.

**DISCUSSION AND CONCLUSIONS**

**Zircon as a Tephrochronological Correlation Tool**

Despite its high density ($\rho = 4650$ kg/m$^3$), zircon dust is abundant in distal ash deposits, as seen in the TBJ and Maya pottery samples. This is expected, as faster settling due to zircon’s higher density is compensated for by its comparatively small crystal size. Stokes’ law settling times for volcanic glass particles ($\rho = 2300$ kg/m$^3$) and zircons are hydrodynamically equivalent if the zircon crystal radii are ~40% of those of the glass particles.

Homogeneous zircon rim ages in both the ash and proximal pumice samples of the TBJ indicate that the eruption tapped a reservoir that was well mixed with regard to zircons. This finding does not address the possibility that larger crystals may record more protracted crystallization, but demonstrates that zircon rim ages can be used successfully to correlate distal tephra with proximal counterparts. Zircon rim ages are also uniformly distributed in the TBJ subunits, making the possibility of age variation in different distal tephra lobes unlikely.

Zircon geochronology can thus radically improve tephrostratigraphy in regions where ash layers are affected by alteration, and/or where an abundance of compositionally similar glass or minerals hinders tephra identification. There is a wide range of potential applications, including correlation of thin terrestrial ash beds, tephra in lake and ocean sediment cores, and even in pottery and other archaeological materials.

**Maya Pottery Ash Provenance**

Examining silica contents of the volcanic glass in the pottery samples, strong similarities to those of the TBJ ash are apparent. Trace element ratios in pottery sample MAR020 are also broadly similar to the TBJ, albeit those in MAR16 and MAR17 are not (Fig. 4). At first glance, major and trace element similarities would implicate the TBJ as a potential source for at least some El Pilar ash temper, but there are severe ambiguities in such a correlation based solely on glass compositions: (1) firing experiments conducted at UCSB (Catlin, 2008) show that silica and aluminum remains unchanged while sodium decreases and calcium increases at a firing temperature $>825^\circ$ C; trace elements except for Rb decrease with firing (Catlin, 2008); (2) the variability of trace element ratios implies that multiple sources of chemically heterogeneous glasses were used to make the pottery; and (3) trace element ratios have limited discriminatory power, evident from the broad compositional similarities between TBJ and average continental crust (Fig. 4).

SIMS analysis of pottery zircons, by contrast, reveals distinct age patterns that provide a robust and characteristic fingerprint for correlation. Because in-situ zircons adhered to volcanic glass yield ages that are within the distributions of the HF-separated zircons, we have confidence that the majority of the zircons in the El Pilar pottery samples are volcanic rather than detrital, and thus significant in the quest for identifying the origin of the ash. A subset of the sampled zircons, however, is likely detrital, derived from clay that was mixed with the ash to make the pottery. Among these are the 11 ages older than 30 Ma (Fig. 3B) that match characteristic peaks in the regional detrital and basement zircon age distribution (Martens et al., 2010). On the basis of zircon age differences between the archaeological and geological samples, the TBJ eruption can be confidently ruled out as the source of the pottery ash. Eruptions from El Chichón Volcano (Mexico) (Fig. 1) can also be dismissed based on petrography (Ford et al., 2014) and preliminary zircon results (Table DR1).


Manuscript received 11 December 2013
Manuscript accepted 14 April 2014
Manuscript accepted 18 April 2014
Printed in USA