Tephra without Borders: Far-Reaching Clues into Past Explosive Eruptions

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This review is intended to highlight recent exciting advances in the study of distal (>100 km from the source) tephra and cryptotephra deposits and their potential application for volcanology. Geochemical correlations of tephra between proximal and distal locations have extended the geographical distribution of tephra over tens of millions square kilometers. Such correlations embark on the potential to reappraise volume and magnitude estimates of known eruptions. Cryptotephra investigations in marine, lake, and ice-core records also give rise to continuous chronicles of large explosive eruptions many of which were hitherto unknown. Tephra preservation within distal ice sheets and varved lake sediments permit precise dating of parent eruptions and provide new insight into the frequency of eruptions. Recent advances in analytical methods permit an examination of magmatic processes and the evolution of the whole volcanic belts at distances of hundreds and thousands of kilometers from source. Distal tephrochronology has much to offer volcanology and has the potential to significantly contribute to our understanding of sizes, recurrence intervals and geochemical make-up of the large explosive eruptions.

Keywords: tephra, tephrochronology, cryptotephra, explosive eruptions, volcanic glass

INTRODUCTION

Modern humankind has limited experience of living through a large explosive volcanic eruption. Of the ∼30 largest explosive eruptions known to have occurred in the last 2000 years (Brown et al., 2014) only a few were described by witnesses (e.g., AD 1883 Krakatau or AD 1815 Tambora) and only one (1991 Pinatubo) was monitored with the help of ground-based, air- and satellite-borne instruments. The others were reconstructed based on tephra deposits left by the eruptions. Pinatubo was not the largest in this list as its tephra production was an order of magnitude less than that of Tambora (Wiesner et al., 2004; Kandlbauer and Sparks, 2014). Although the impacts of the Tambora eruption have been reconstructed based on contemporary evidence and climate proxies (e.g., Oppenheimer, 2003; Stoffel et al., 2015), we still do not have sufficient knowledge of how similar event could affect the modern world.

The infamous Eyjafjallajökull eruption ash cloud that disrupted air travel over Europe and North Atlantic in April-May 2010 caused an economic loss of €5 billion (Oxford Economics, 2010). The total magma volume for this eruption was estimated at ∼0.18 km^3 (Gudmundsson et al., 2012). In contrast, Pinatubo magma volume was roughly estimated at 4.8–6 km^3 (Wiesner et al., 2004) and that of Tambora—at ∼41 km^3 (Kandlbauer and Sparks, 2014), and so based on magma volume these eruptions were one and two orders of magnitude larger than Eyjafjallajökull, respectively.

In the intricately interconnected modern world, both immediate and long-term effects of similar future events on various human activities are hard to predict.

One of the prerequisites of predicting future giant eruptions is the understanding of sizes and recurrence times of past similar events (Self and Gertisser, 2015). The existing global catalog of the large explosive eruptions, however, is far from complete (e.g., Brown et al., 2014). Even for the last millennium, new findings are frequently added to the growing list of eruptions and it is thought that only 40% of explosive eruptions are reported between AD 1500 and 1900 (Deligne et al., 2010; Brown et al., 2014). One of the most recent additions includes the previously unknown caldera-forming eruption of Samalas volcano in AD 1257 (Lavigne et al., 2013). Furthermore, the source of the AD 1809 eruption, which preceded Tambora and left a sulfate signal both in Greenland and Antarctic ice (Dai et al., 1991), is still unknown. What is more, the size of documented explosive eruptions is often poorly constrained and the majority of estimates are based solely on proximal deposits. Despite ongoing efforts aimed to improve our knowledge of past eruptions we still do not know how many large explosive eruptions happened on Earth, even in the Quaternary period. As Self and Gertisser (2015) conclude in their paper dedicated to the Tambora bicentennial: "It is high time for a systematic exploration of all available eruption archives. . . so that we have a better chance to understand potential future hazards" (pp. 249–250).

A continuous effort is, however, underway to add more eruptions to the existing catalogs and to significantly contribute to their size estimates. For the Quaternary time, this effort is largely undertaken by geographers and archeologists in their pursuit of distal tephra and cryptotephra deposits in areas that are remote to the active volcanoes. A widespread tephra isochron holds considerable promise for the correlation and dating of disparate depositional successions. Several recent papers provide a review of the significance of tephra for paleoenvironmental and archeological studies (e.g., Lowe, 2011; Riede and Thastrup, 2013; Lane et al., 2014; Lowe and Alloway, 2014; Davies, 2015), and the quickly developing field of cryptotephra studies has been considered a revolution in correlation and precision dating of Quaternary deposits (Davies, 2015). In this review we briefly summarize the most recent advances in distal tephra and cryptotephra research that embark on challenges but also offer new opportunities for volcanologists and petrologists. Distal tephra investigations have been successfully executed on tephras as old as the Proterozoic (e.g., Saylor et al., 2005), however we focus mostly on Quaternary tephras.

NEW ADVANCES IN TEPHRA RESEARCH

Tephra is fragmental material produced by a volcanic eruption regardless of composition, fragment size or emplacement mechanism (Thorarinsson, 1950). During the eruption, an eruptive cloud is transported and dispersed by the wind, and tephra particles settle mantling the landscape. In this way tephra forms an isochron that directly links various sedimentary successions and permits synchronization of disparate paleoenvironmental archives (e.g., Lowe et al., 2012; Albert et al., 2015). An eruptive cloud has the most far-reaching impact affecting distal areas both with solid and aerosol particles. Near the source, tephra forms a visible deposit but in distal areas the volcanic grains can be deposited in low concentrations and become mixed within the sediments or other host material. These distal shards do not form clear layers that are visible to the naked eye and are referred to as cryptotephra (Lowe and Hunt, 2001).

Extensive geochemical fingerprinting of single volcanic glass shards buried in marine, lake, cave and peat deposits as well as in the ice has led to the discovery of cryptotephra deposits in regions where tephra research has never been attempted. Several tephra and cryptotephra deposits have recently been identified at distances of 5000–7000 km from their source volcanoes (e.g., Coulter et al., 2012; Narcisi et al., 2012; Pyne-O'Donnell et al., 2012; Lane et al., 2013b; Jensen et al., 2014). Such far-traveled ash clouds may not initially seem surprising, given the long-distance transport of dust particles (e.g., Garrison et al., 2003; Delmonte et al., 2010). Volcanic ash, found far from the source, however, is different from dust. First, it signals a strong explosive eruption; second, many tephras can be connected to their source volcanoes or volcanic zones via their unique geochemical fingerprint (e.g., Kutterolf et al., 2008a; Gudmundsdóttir et al., 2011; Lane et al., 2011; Smith et al., 2011b, 2013; Tomlinson et al., 2015). With recent advances in microanalytical techniques, the composition of micron-sized individual ash particles can be characterized. Electron microprobe and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) permit the determination of major, minor and trace-element abundances and lead (Pb) isotope data (Tomlinson et al., 2010; Kuehn et al., 2011; Hayward, 2012; Pearce et al., 2014; Kimura et al., 2015; Maruyama et al., in press). These techniques allow characterization of glass, minerals, and melt inclusions in minerals to support correlations between widely dispersed locations as well as to the source areas (e.g., Lowe, 2011; Matsu'ura et al., 2011; Smith et al., 2011c). Such long-distance correlations present new opportunities for reconstructing past eruptive history, eruptions size estimates as well as geochemical specifics of the erupted products.

RECORD OF EXPLOSIVE ERUPTIONS: IDENTIFICATION AND DATING OF THE LARGE EXPLOSIVE EVENTS

Near vent deposits from the largest explosive eruptions usually form packages that are tens to hundreds of meters thick. In regions of highly explosive volcanism these packages from different volcanoes may overlap forming pyroclastic successions. However, stratigraphic relationships of individual units in such successions may be very complex and the deposits can be partly or completely eroded especially in glaciated or coastal areas (e.g., Rawson et al., 2015). Proximal deposits of near-coast volcanoes are also spread and hidden under water. As a result, near-vent deposits of large explosive eruptions in many cases cannot be put into detailed and reliable stratigraphic context. Tephra deposited

and preserved in distal environments, however, often provide a well-resolved stratigraphic sequence and considerable insight into the frequency of large eruptions that are sometimes not recognized in proximal sequences.
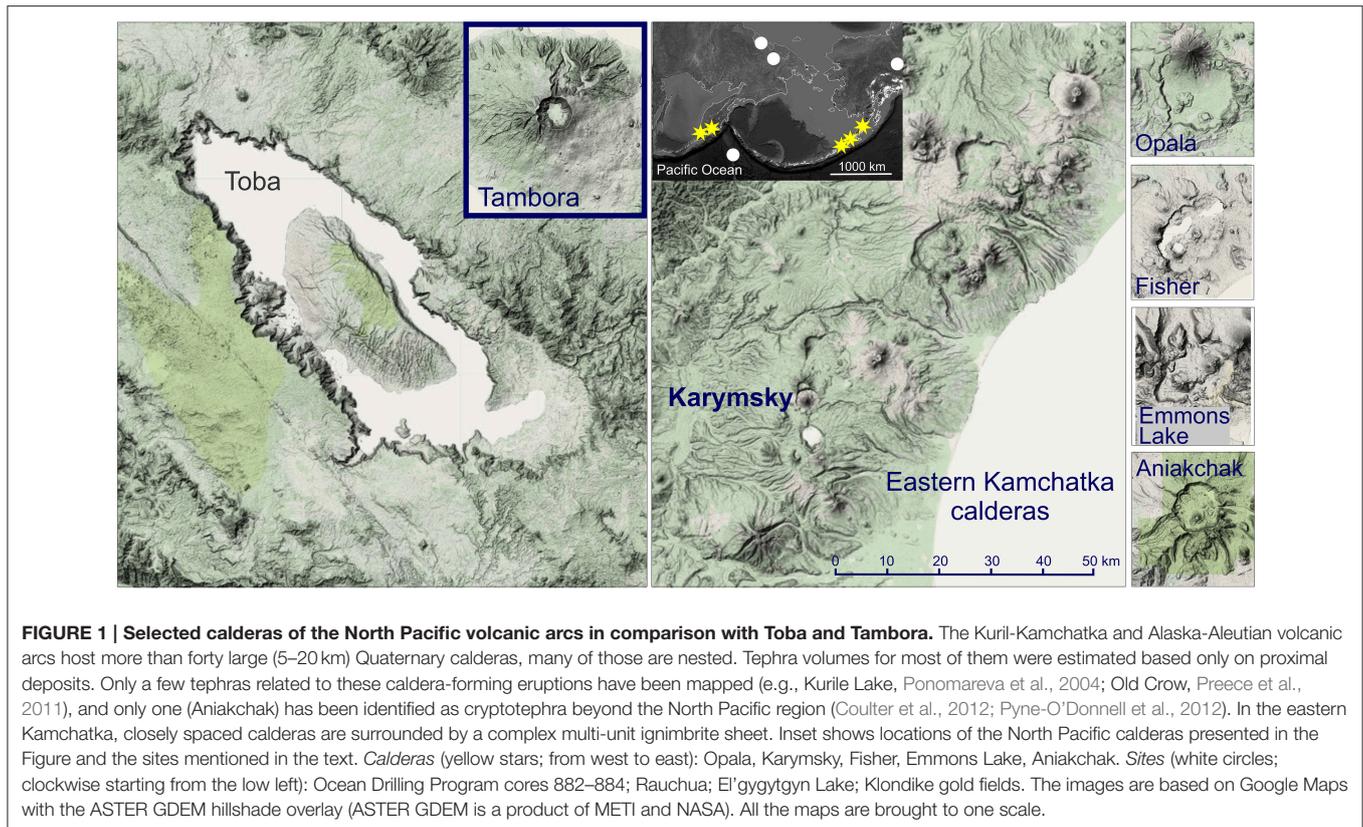
Large (M>7) and well-studied Quaternary eruptions originate from eruptive centers such as Toba, Taupo, Changbaishan (Tianchi), Campi Flegrei, Mazama, Tambora, and Santorini, yet many more large eruptions remain undiscovered. Indeed, according to analysis of the Smithsonian Volcanoes of the World database (Siebert et al., 2010) only about 30% of the world's volcanoes have eruptive records before 1500 AD (Loughlin et al., 2015). North Pacific volcanic arcs, especially Kurile-Kamchatka and Alaska-Aleutians, definitely hosted many large eruptions, the magnitudes of which are not known. The Alaska-Aleutian volcanic arc hosts at least 14 calderas >5 km in diameter, with some being nested (**Figure 1**; www.avo.alaska.edu). Tephra volumes for some of these eruptions have been roughly estimated at 10–50 km^3 based on proximal deposits (Miller and Smith, 1987). Prevailing westerly winds, however, indicate a common transport pathway from the Alaska-Aleutian arc over Alaska where distal tephras provide evidence of these large eruptions. For example, studies of Old Crow tephra (∼124 ka) allowed Preece et al. (2011) to identify a Tambora-size or even larger eruption and tentatively associate it with the Emmons Lake volcanic center. In fact, the Klondike goldfields in northwestern Canada lying ∼330 km downwind from the closest volcano can be considered a tephra bonanza. Fifty late Cenozoic tephra layers in this area have been cataloged, each likely to represent large but previously undocumented explosive eruptions from the Wrangell volcanic field and eastern Aleutian arc (Westgate et al., 2011). Further mapping of these tephras and identification of their source volcanoes will significantly contribute to a global catalog of large explosive eruptions.

A further example of the potential of distal work lies within the sediments of the El'gygytgyn Lake (Far East Russian Arctic). Eight visible tephra layers (0.5–7 cm thick) have been identified, seven of which have been ascribed to Kurile-Kamchatka, and one—possibly to the Alaska-Aleutian arc (van den Bogaard et al., 2014). This lake lies >1100 km from the closest island-arc volcano and in a location that is perpendicular or against the direction of the jet stream. Thus, these layers may represent eruptions that rank within the Earth's largest Quaternary events. However, only one tephra from the El'gygytgyn core was tentatively correlated to the source, which permitted identification of a previously unknown M>6.5 eruption from the Karymsky eruptive center in Kamchatka (Ponomareva et al., 2013a). Specific sources of other tephras are still unknown (van den Bogaard et al., 2014). Kamchatka has the highest concentration of Quaternary calderas per unit of arc length in the world (**Figure 1**; Hughes and Mahood, 2008). What is more, many calderas are nested and their rims overlap so the real number of caldera-forming eruptions is not known. While Holocene explosive eruptions in Kamchatka are quite well studied (e.g., Braitseva et al., 1995, 1997; Ponomareva et al., 2004, 2013b, 2015), the earlier volcanic history of the region remains incomplete. Welded tuffs surrounding caldera chains are difficult to access and even more difficult to put into stratigraphic context

so only few of those have been dated (Braitseva et al., 1995; Bindeman et al., 2010). Marine cores surrounding Kamchatka offer considerable promise to reconstruct the history of volcanic events in this region. For example, three Ocean Drilling Program cores taken in 1993 in NW Pacific ∼700 km downwind from Kamchatka, each contain 41–74 visible Pleistocene tephra layers with several displaying thicknesses of >1 m (Cao et al., 1995). Further mapping of these tephras over the northwest Pacific is likely to reveal a suite of previously unrecognized M>6 explosive eruptions.

Further afield, eruptive histories are being revisited from distal tephra studies in marine, lake and peat deposits as well as in the ice caps (e.g., Shane and Hoverd, 2002; Wulf et al., 2004, 2008, 2012; Kutterolf et al., 2008a; Kuehn and Negrini, 2010; Sulpizio et al., 2010a,b; Dunbar and Kurbatov, 2011; Abbott and Davies, 2012; Narcisi et al., 2012; Pyne-O'Donnell et al., 2012; Jensen et al., 2013; Smith et al., 2013; Davies et al., 2014; van den Bogaard et al., 2014; Bourne et al., 2015a,b; Lane et al., 2015). By now, distal tephra and cryptotephra research has been successfully undertaken in many regions including Greenland (e.g., Abbott et al., 2012; Abbott and Davies, 2012; Coulter et al., 2012; Bourne et al., 2015b); North Atlantic (e.g., Lacasse and Garbe-Schönberg, 2001; Brendryen et al., 2011; Gudmundsdóttir et al., 2012; Blockley et al., 2014; Davies et al., 2014; Griggs et al., 2014; Voelker and Haflidason, 2015); European mainland (e.g., Caron et al., 2010; Sulpizio et al., 2010a,b; Lane et al., 2011, 2015; Lawson et al., 2012); Mediterranean (Siani et al., 2004; Wulf et al., 2004, 2008, 2012; Paterne et al., 2008; Zanchetta et al., 2011; Albert et al., 2012, 2015; Bourne et al., 2015a; Çağatay et al., 2015; Wutke et al., 2015); in and around Japan (e.g., Park et al., 2003; Matsu'ura et al., 2011; Okuno et al., 2011; Smith et al., 2011b, 2013; Lim et al., 2013); New Zealand (Shane, 2000; Alloway et al., 2005; Shane et al., 2006; Allan et al., 2008; Holt et al., 2011; Shane and Wright, 2011; Lowe et al., 2013); off Central America shore (e.g., Clift et al., 2005; Kutterolf et al., 2008a,b). Many tephras found within these domains have been linked to their source volcanoes based on geochemical correlations with proximal deposits (e.g., Alloway et al., 2005; Gudmundsdóttir et al., 2011; Tomlinson et al., 2012, 2015; Lane et al., 2013a; Smith et al., 2013). Several other regions, however, have considerable promise for the identification of distal tephra deposits and require further laboratory-intensive and meticulous investigations.

Once a tephra record is established, a range of dating techniques can be employed to constrain the timing of explosive eruptions. The best archives for providing precise dates are high-resolution incremental records such as ice-core records and varved marine and lake sediments. Tephra ages can be assigned according to the incremental age and sometimes even the eruptive season can be determined (e.g., Lane et al., 2013a, 2015). The challenge, however, is to find and geochemically fingerprint tiny glass shards from these deposits, and then to correlate them to known eruptions and other occurrences of the same tephra. Despite these challenges, such work is being systematically and successfully executed for the Greenland and Antarctic ice sheets. In Greenland, shards from large eruptions such as the Millenium Changbaishan, Bona-Churchill White

FIGURE 1 | Selected calderas of the North Pacific volcanic arcs in comparison with Toba and Tambora. The Kuril-Kamchatka and Alaska-Aleutian volcanic arcs host more than forty large (5–20 km) Quaternary calderas, many of those are nested. Tephra volumes for most of them were estimated based only on proximal deposits. Only a few tephras related to these caldera-forming eruptions have been mapped (e.g., Kurile Lake, Ponomareva et al., 2004; Old Crow, Preece et al., 2011), and only one (Aniakchak) has been identified as cryptotephra beyond the North Pacific region (Coulter et al., 2012; Pyne-O'Donnell et al., 2012). In the eastern Kamchatka, closely spaced calderas are surrounded by a complex multi-unit ignimbrite sheet. Inset shows locations of the North Pacific calderas presented in the Figure and the sites mentioned in the text. *Calderas* (yellow stars; from west to east): Opala, Karymsky, Fisher, Emmons Lake, Aniakchak. *Sites* (white circles; clockwise starting from the low left): Ocean Drilling Program cores 882–884; Rauchua; El'gygytgyn Lake; Klondike gold fields. The images are based on Google Maps with the ASTER GDEM hillshade overlay (ASTER GDEM is a product of METI and NASA). All the maps are brought to one scale.

River ash, Aniakchak, Mazama, and many Icelandic tephras have been identified, which permits age assignments (Abbott and Davies, 2012; Coulter et al., 2012; Sun et al., 2014). Precision of ice dating for some intervals is biannual but even for less resolved parts of the ice cores it is still far better than for any other method. In Antarctic, numerous tephra layers have been identified in ice-core records, dated and geochemically linked to both Antarctic and South American volcanoes (Narcisi et al., 2010, 2012; Dunbar and Kurbatov, 2011).

In the absence of bioturbation, rapidly deposited tephra shards form distinct layers or sharp concentration peaks within varved sequences, so downcore counting of seasonal laminations permits direct dating of tephra with annual and sometimes even seasonal resolution (Zolitschka et al., 2015). For example, in varved sediments of Lago Grande di Monticchio, which lies >100 km downwind of the Italian volcanoes, more than 350 tephras spanning the last 135 ka have been identified and dated based on ^{14}C dating and age-depth model thus providing a continuous record of explosive volcanism in the area (Wulf et al., 2004, 2008, 2012). In a Late Glacial-Holocene varved record of Meerfelder Maar in the Eifel region of Germany two visible and 15 cryptotephras from Eifel, Icelandic, and Mediterranean sources have been identified and dated (Lane et al., 2013a, 2015). In Japan, a 150 ka long varve record from Lake Suigetsu preserves ~30 visible tephra layers that have been dated and assigned to explosive eruptions in Japan and South Korea based on their geochemical affinities (Smith et al., 2013).

In non-laminated sequences such as marine, lake and peat deposits tephra ages are usually estimated based on core-specific age-depth models, which are in turn based on astronomic tuning, comparison to oxygen isotope stack, radiocarbon dating or other radiometric techniques etc. (e.g., Lane et al., 2013b). Alternatively, if correlation of certain tephra layers to their dated proximal counterparts is possible, then those proximal dates can be used as fix-points in an age-depth model (e.g., Smith et al., 2011b). Age estimates of the same tephra deposit found in a number of different records (e.g., marine, ice and terrestrial records) also allow a thorough comparison and refinement of ages. For instance, Bronk Ramsey et al. (2015a) and Lowe et al. (2013) adopted a Bayesian approach to refine the ages of 22 European and 24 New Zealand large explosive eruptions.

Provided age determinations can be achieved, tephras preserved within long marine records provide an interesting insight into the temporal patterns of explosive volcanism, which are crucial to inform predictions of future volcanic activity. Eruptive frequency derived from tephra deposits is thought to be highly episodic regionally and even globally, which has allowed identification and dating of regional and global pulses in explosive activity over timescales of hundreds of thousands years (e.g., Paterne et al., 1990; Cambray and Cadet, 1994, 1996; Prueher and Rea, 2001). Temporal clustering within the sequence of Holocene large explosive eruptions has been also demonstrated and statistically verified for the Kamchatka arc (Gusev et al., 2003). Causal mechanisms for this episodicity, especially on a global scale, are still unclear (e.g., Sigurdsson,

2000). Using time series analysis of tephra layers in circum-Pacific marine cores Kutterolf et al. (2013b) found obliquity-forced variability in late Pleistocene records of volcanic eruptions likely resulting from crustal stress changes associated with ice age mass redistribution. Even if visual description and count of the visible tephra layers in the cores may suffer some inconsistency (over-recording of ∼19% and under-recording of ∼10% of tephra layers) these data can be used as a valid source for data compilations (Mahony et al., 2014). Further studies that improve our volcanic catalogs of the largest explosive eruptions will definitely offer considerable promise for understanding the volcanic pulses and their causes.

ERUPTION SIZES AND TEPHRA DISPERSAL

The sizes of explosive eruptions are typically expressed as volumes of bulk tephra and/or magma, Volcanic Explosivity Index (VEI) (Newhall and Self, 1982), or magnitude (M) (Pyle, 1995, 2000). All these estimates require knowledge of tephra volume. The latter includes volumes of air-borne tephra deposits (plinian and coignimbrite) and ignimbrite. For caldera-forming eruptions the volume of caldera fill is also included (e.g., Johnston et al., 2014). The proportion of these ingredients may vary between eruptions however volume of air-borne tephra definitely constitutes a very significant part of the total tephra volume. Estimates of this part are normally based on field measurements of tephra thickness and grain-size, which are then used in sophisticated calculations and models (e.g., Bonadonna and Costa, 2012; Costa et al., 2012, 2014; Johnston et al., 2012; Daggitt et al., 2014). Tephra volumes are also used for calculating the amount of climate-affecting volatiles released into the atmosphere (e.g., Metzner et al., 2014). For many large eruptions, however, only proximal (<100 km from the source) field data are available, especially for the island arcs, which is not always sufficient for adequate volume calculations.

Distal thickness data dramatically increase the area of tephra dispersal and tephra volumes estimates based on proximal deposits (e.g., Carey et al., 2010). However, recent distal and ultra-distal (>1000 km from the source) data are still rarely used in volume calculations. Tephra volume estimates for some well-studied eruptions like Toba have been increasing steadily where more distal tephra occurrences have been added to the dataset and more sophisticated dispersal models were applied (Costa et al., 2012, 2014). Cryptotephra discoveries, however, are difficult to include due to the lack of tephra layer thickness data and low shard concentrations (Costa et al., 2014). Future work may need to consider how glass shard size and concentrations could be integrated into volume estimate models. Recent intercontinental correlations such as the findings of the White River ash (Bona-Churchill volcano in eastern Alaska) in eastern Canada, Greenland and northern Europe (**Figure 2**; Coulter et al., 2012; Pyne-O'Donnell et al., 2012; Jensen et al., 2014) will hopefully inspire new modeling efforts and lead to improved assessments of the eruptive volumes.

Even if an ultra-distal cryptotephra does not form a continuous veil but is rather deposited in patches because of atmospheric turbulence, rainflush, or some other processes, its deposition area is still far larger than that considered in previous volume calculations. The White River ash has been found along a distinct dispersal pathway from Alaska to Newfoundland, Nova Scotia, Greenland, Ireland, Scotland, Norway, and Germany (**Figure 2**; Jensen et al., 2014). We hope that other recent findings of pre-historical distal and ultra-distal tephras, for example, Aniakchak (Alaska) ash in eastern Canada and Greenland (Pearce et al., 2004; Coulter et al., 2012; Pyne-O'Donnell et al., 2012), Mazama ash (Cascades)—in many sites in Northern America and in Greenland (Zdanowicz et al., 1999), will soon lead to recalculation of these and other eruptions volumes. If justified, upgrading these eruptions to very large events with their very well-constrained Greenland ice ages will allow us to improve our knowledge of the number and size of eruptions that have occurred in the past.

An understanding of likely dispersal pathways is particularly important for hazard assessment and mitigation (e.g., Shane and Hoverd, 2002). Sulpizio et al. (2014) showed that reconstructed ash-dispersal maps from a number of eruptions can be processed in order to produce frequency maps of distal ash deposition which permits assessment of ash fall hazards over a wide area. Distal tephra records offer considerable insight into this work. In some instances, however, reconstructed dispersal pathways based on tephra occurrences show unexpected patterns. While many plinian eruptive clouds follow jet stream patterns, i.e., are dispersed eastwards, distal and ultra-distal correlations of tephra layers reveal different trajectories for quite a few large tephra plumes. For example, some high-latitude tephra plumes from Kamchatka and Aleutians were dispersed in northerly directions (**Figure 2**). Among others, Holocene tephra from M7 Kurile Lake caldera (KO) eruption was dispersed to NNW; late Pleistocene Old Crow tephra (supposedly from the Emmons Lake caldera) went to the northeast; and a middle Pleistocene M>6.5 Rauchua tephra—to the north (Ponomareva et al., 2004, 2013a; Preece et al., 2011). These examples may indicate different transport pathways that are independent of expected dispersal by the jet-stream (e.g., as in Costa et al., 2014, or in Sulpizio et al., 2008, 2013).

TEPHRA AS A MATERIAL FOR PETROLOGICAL AND GEOCHEMICAL STUDIES

Tephra material often dominates the erupted products in terms of volume, eruption frequency, and variety of compositions some of which may never occur in lava. It is especially true for highly explosive volcanic arcs where the overwhelming majority of the magma is erupted as tephra (e.g., Kutterolf et al., 2008b). But even in the areas traditionally regarded as lava domains, tephra surprisingly dominates in terms of eruption frequency. For example, in Iceland 2/3 of all eruptions in the last 1100 years have been explosive, leaving tephra as their only product (Óladóttir et al., 2012). Similiarly on Kīlauea volcano (Hawaii),
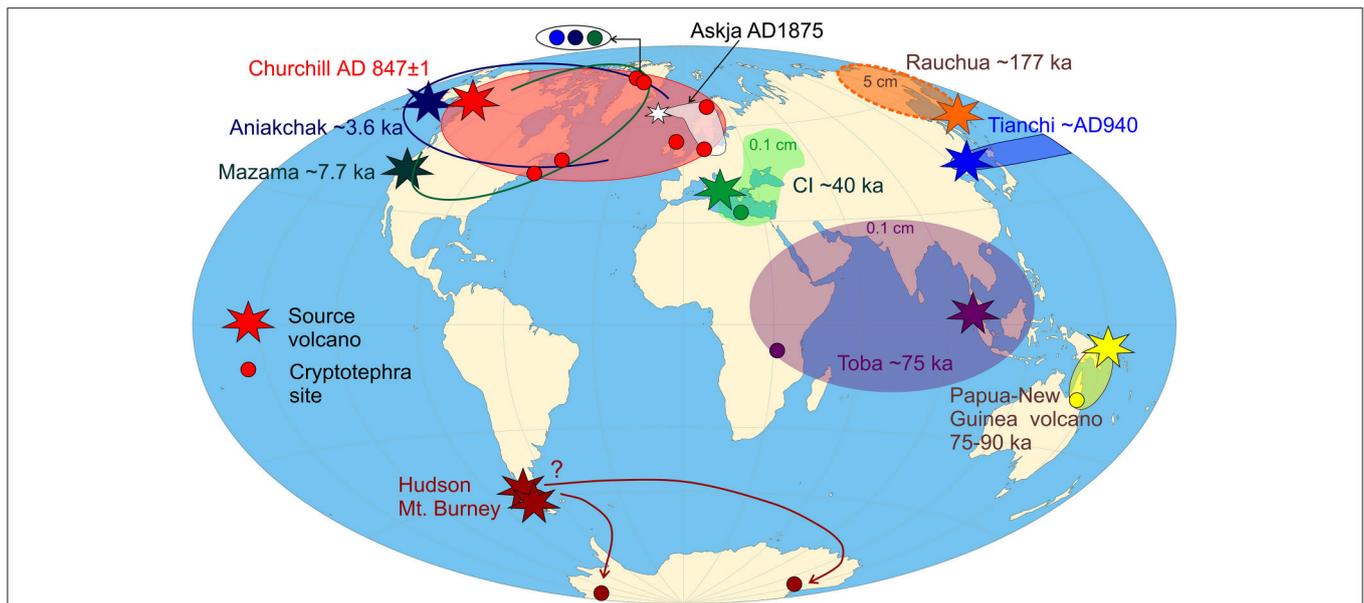
FIGURE 2 | Sketch map illustrating selected intercontinental and ultra-distal correlations of tephra discussed in the text. Tephra dispersal footprints are based on recent cryptotephra findings, and on modeling based on measured thickness of visible tephra layers. An equal area projection ensures visual comparison of the dispersal areas. Probable extent of ash plumes based on cryptotephra findings: Churchill (White River ash), Aniakchak, Mazama, a tephra from Papua-New Guinea (Zdanowicz et al., 1999; Coulter et al., 2009, 2012; Jensen et al., 2014). Ash plumes based on modeling results: Toba and Campanian Ignimbrite (CI); outer rim at 0.1 cm (Costa et al., 2012, 2014). Filled circles show selected cryptotephra sites. Tianchi tephra has been found in Greenland ice along with Aniakchak, Churchill and Mazama ones (color circles in and above Greenland; Sun et al., 2014), however, ultra-distal pathway for the Tianchi plume is not constrained. Suggested correlations of some cryptotephras found in the Antarctic ice cores to South American volcanoes (probably Mt. Burney and Hudson) based on Kurbatov et al. (2006) and Narcisi et al. (2012). Well mapped Askja 1875 plume is provided for comparison (Carey et al., 2010). The Rauchua tephra (Kamchatka) 5-cm outline (Ponomareva et al., 2013a). The Rauchua tephra as well as many others mapped only as visible layers in fact may extend well beyond known outlines.

explosive eruptions was the prevailing style for 60% of eruptions in the last 2500 years (Swanson et al., 2014).

In spite of dominance of tephra in many eruptions, its distal samples were rarely used in petrological research because of the following concerns. Distal tephra samples may be contaminated with xenogenic material, and potential sorting of crystals and glass in the eruption cloud can make the composition of a bulk tephra sample unrepresentative for erupted magma composition (e.g., Braitseva et al., 1997). Additional factor limiting interest of petrologists is that many distal tephras have unknown volcanic source. If the source is known, more rich proximal material is usually available and therefore chosen for detailed petrologic studies. Despite these factors limiting the use of distal tephra in research beyond tephrochronology, some remarkable examples of using distal tephra to study conditions of magma generation are known (e.g., Bryant et al., 2003; Straub et al., 2004, 2010, 2015). They show that the major potential for petrological and geochemical studies of distal tephra is reconstruction of long-time regional variations of composition of explosive volcanism and its correlation with macro-tectonic events. Based on these relatively rare examples, we believe that the value of distal tephra for geochemical studies is still underscored and should be reappraised.

Besides the fact that for most eruptions no other material is available for study but tephra, the petrologists' interest in tephra is triggered by two important features: robust stratigraphic control of tephra deposits and rapid cooling (quenching) upon the eruption. Stratigraphically controlled and often well-dated continuous tephra sequences provide an excellent opportunity for a time-series geochemical study, i.e., analysis of how erupted magma compositions change through time. Rapid cooling of small tephra particles ensures quenching of the melt to glass, which preserves information of the melt composition prior to eruption. The compositional changes provide insight into the variations in magma sources (e.g., Smith et al., 2005), conditions of magma fractionation, and evolution of magmatic flux through time (e.g., Rawson et al., 2015). Such studies are pertinent on time scales ranging from months to millions of years and from individual volcanoes to volcanic arcs or other tectonic arrangements of volcanoes.

Geochemical time-series studies on timescales of months to thousands of years typically address eruptive histories and magmatic evolution of individual volcanoes and mostly focus on proximal terrestrial tephra sequences (e.g., Smith et al., 2005, 2011a; Donoghue et al., 2007; Óladóttir et al., 2008, 2011a,b; Hasegawa et al., 2011; Turner et al., 2011; Firth et al., 2014; Iverson et al., 2014; Schindlbeck et al., 2014; Fontijn et al., 2015; Ponomareva et al., 2015). On a longer time scale (thousands to millions of years), tephras are more readily preserved in non-erosive marine environments that are relatively close to active volcanoes. These depositional settings preserve a continuous

record of large eruptions from one or few volcanic systems (e.g., Allan et al., 2008; Albert et al., 2012; Gudmundsdóttir et al., 2012; Lim et al., 2013; Bourne et al., 2015b), or from a large volcanic region such as a few hundred km long volcanic arc (e.g., Arculus et al., 1995; Cao et al., 1995; Clift et al., 2003, 2005; Straub, 2003; Straub and Layne, 2003a,b; Straub et al., 2004, 2010, 2015; Kutterolf et al., 2008a, 2013a). In some cases such long records are also preserved in deposits of existing or paleo-lakes (e.g., Wulf et al., 2004, 2008, 2012; Kuehn and Negrini, 2010; Smith et al., 2013).

For intra-oceanic island-arc systems, marine tephra records provide a unique insight into the history of the arcs as their old magmatic complexes are typically buried under younger volcanics or rifted away during back-arc basin formation. For instance, near-continuous tephra records of large-scale explosive volcanism of the Izu-Bonin island arc for the last 42 Myr (Straub, 2003), the Mariana island-arc for the last 34 Myr (Straub et al., 2015), and the Kermadec arc for the last ~50 ka (Shane and Wright, 2011) were obtained by studying sediments from deep-see drilling holes. These studies provided a new and unprecedented data-set on the temporal evolution of these arc systems. New insights were derived into the composition and evolution of the mantle and slab sources involved in magma genesis and revealed possible correlations between the compositions of erupted magmas and tectonic evolution of the arcs. DSDP/ODP/IODP sediment cores have been obtained offshore many active volcanic arcs such as Kamchatka, Central America, Aleutians, Ecuador, Peru, New Zealand, Japan-Izu-Bonin-Mariana and all of those contain numerous tephra layers (Cao et al., 1995; Alloway et al., 2005; Hart and Miller, 2006); http://www-odp.tamu.edu). Geochemical fingerprinting of these tephras has been undertaken largely for reconstructions of eruptive frequency and for stratigraphic correlations between the cores. In-depth geochemical research on tephra from most of the cores is still ongoing.
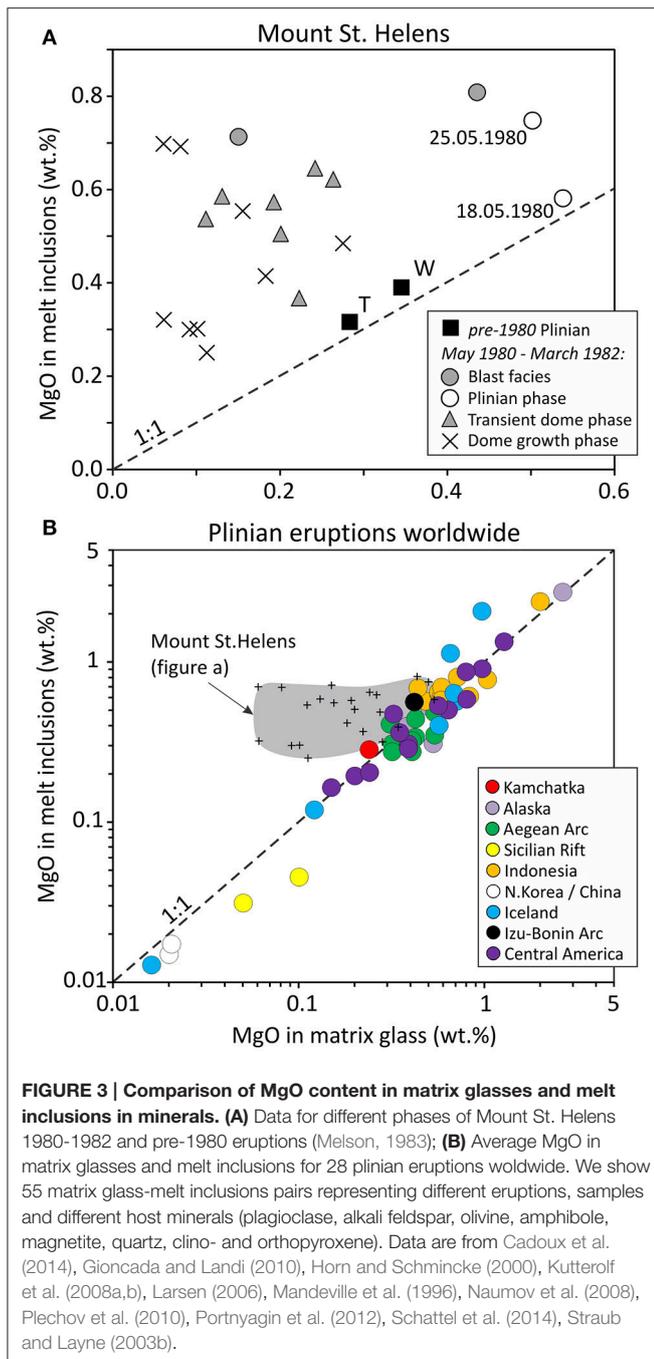
Rapid cooling upon eruption, which results in effective quenching of melt in magma to glass and preservation of pre-eruptive mineral equilibria, makes tephra a very attractive product for petrologic studies. These studies are usually aimed at quantification of physicochemical conditions of magma evolution at depth and during ascent to the surface. Several studies have focused on elucidating the volatile content in magmas prior to eruption by analysis of glassy melt inclusions in phenocrysts (e.g., Wallace, 2005; Blundy and Cashman, 2008) and on magma degassing by comparison of the compositions of matrix glasses and melt inclusions (e.g., Devine et al., 1984; Thordarson et al., 1996; Wallace, 2001; Kutterolf et al., 2015). Textural analysis of tephra particles has also been successfully used to reconstruct shallow crystallization and degassing processes occurring in magmatic systems and to correlate them to eruption dynamics (e.g., Hammer et al., 1999; Blundy and Cashman, 2008). Thermobarometric petrologic studies are commonly performed on tephra components and have an advantage over lava studies whereby rapid cooling of tephra allows preservation of magmatic equilibria between mineral phases and glasses, otherwise easily reset during slow cooling and even alteration

in more slowly cooled rocks (e.g., magnetite-ilmenite equilibria; Bacon and Hirschmann, 1988).

Distal and ultra-distal tephra produced by strong plinian eruptions consists mostly of silicic glass shards (e.g., Davies, 2015). Rarity or complete absence of crystalline phases hampers significantly the use of distal tephras in traditional petrological applications (e.g., thermobarometry, melt inclusion studies) that require both analysis of glass (in matrix and melt inclusions) and minerals. As such, petrological and geochemical studies of distal tephra are largely narrowed to study of matrix glass composition. The development of analytical techniques having high spatial resolution (electron probe, ion probe, laser ablation ICP-MS) and working with very small (pg to ng) amounts of material (MC-TIMS, MC-ICPMS, laser fluorination) permits now matrix glass multi-element and isotope analysis with high precision comparable to bulk analytical techniques (e.g., Kimura et al., 2015; Koornneef et al., 2015). Thus, analytical problems of working with distal tephra are mostly solved now and even more progress is expected in the nearest future, which would allow routine analysis of glass microparticles for wide range of trace elements and isotope ratios.

Tephra glass can closely approach bulk composition of rare-phyric and aphyric magma (e.g., Ponomareva et al., 2013b) or deviate strongly from bulk composition of porphyritic tephra samples (e.g., Melson, 1983; Ponomareva et al., 2015; Tomlinson et al., 2015). As such, distal tephra glasses cannot be used to reconstruct bulk magma compositions. Nevertheless, the glass represents composition of real melt existed at certain stage of magma evolution and therefore has the potential to provide valuable information about the source and magmatic conditions of explosive volcanism in the past. A common opinion, however, is that matrix tephra glasses represent residual melt after extensive magma crystallization and thus bear no or little information of parental melt at depth (e.g., Blundy and Cashman, 2008). To test this we carried out an analysis of published matrix glass compositions and melt inclusions in phenocrysts from a wide range of tephra samples. Melt inclusions enclosed in phenocrysts undoubtedly represent portions of deep melts (e.g., Wallace, 2005). Therefore, comparison of melt inclusions and matrix glasses is informative about the degree to which matrix glasses are evolved from melts existed in magma system at depth.

In **Figure 3A**, we compare matrix glasses and melt inclusions in plagioclase from tephras erupted by Mount St. Helens in 1980-1982 (Melson, 1983). A systematically more evolved (MgO-poor) composition of matrix glasses relative to melt inclusions is evident for samples representing blast facies, gray microlite-bearing pumice and dome-building phase of the eruption. All these glasses are rich in microlites and can arguably represent late-stage melts, formed after substantial crystallization following phenocryst growth and melt inclusion entrapment. In contrast, microlite-free glasses and melt inclusions from white pumice representing the plinian phase of the 1980 eruption and also pumices erupted in 1800 AD (T pumice) and 1500 AD (W pumice) have nearly identical compositions and therefore represent the same early stage of magma evolution. The only significant difference between melt inclusions and matrix glasses is lower H_2O in the latter, which was degassed from magma

FIGURE 3 | Comparison of MgO content in matrix glasses and melt inclusions in minerals. (A) Data for different phases of Mount St. Helens 1980-1982 and pre-1980 eruptions (Melson, 1983); **(B)** Average MgO in matrix glasses and melt inclusions for 28 plinian eruptions woldwide. We show 55 matrix glass-melt inclusions pairs representing different eruptions, samples and different host minerals (plagioclase, alkali feldspar, olivine, amphibole, magnetite, quartz, clino- and orthopyroxene). Data are from Cadoux et al. (2014), Gioncada and Landi (2010), Horn and Schmincke (2000), Kutterolf et al. (2008a,b), Larsen (2006), Mandeville et al. (1996), Naumov et al. (2008), Plechov et al. (2010), Portnyagin et al. (2012), Schattel et al. (2014), Straub and Layne (2003b).

during the eruption (Melson, 1983). An apparent explanation for these observations is that magma ascent rate during the plinian phase was too high (time interval too short) for nucleation and growth of microlites in the matrix melt, while the magma degassed substantially.

In **Figure 3B** we compare matrix glasses and melt inclusions in different minerals for 28 plinian eruptions (55 pairs of matrix glass—inclusions) representing a wide range of geologic settings and magma types. In most cases, the compositions of matrix glasses and inclusions are very similar. Large

differences are observed only for some mixed eruptions with wide range of matrix glasses and melt inclusions (e.g., Hekla 3; Sverrisdottir, 2007; Portnyagin et al., 2012). On the basis of these empirical observations we conclude that microlite-free matrix glasses of plinian eruptions have concentrations of non-volatile components approaching very closely those existed in melt prior to the eruptions. Far-traveled tephra are dispersed during plinian eruptions. Therefore, its matrix glass can be informative about geochemical peculiarities of melt and physicochemical conditions of its crystallization prior to eruption. Thus, geochemical analysis of distal tephra offers considerable insight into the composition and origin of parental melts for large-scale explosive volcanism on a regional scale.

In essence, the unique ability of single glass shards to preserve information on the melt crystallization conditions and on the geochemical peculiarity of magma sources makes geochemical fingerprinting possible. This application remains to be the most requested in tephrochronology. The relationships between composition of tephra glasses and magma storage conditions (pressure, temperature, oxygen fugacity, water activity) before eruption are not known in detail and need to be understood in future studies using available data from experimental petrology and geochemical modeling (e.g., Blundy and Cashman, 2008; Gualda et al., 2012; Gualda and Ghiorso, 2014). Because mineral assemblages are typically not preserved in distal tephra samples, the melt crystallization conditions cannot be estimated directly by application of two-mineral and mineral-melt thermobarometers (e.g., Anderson et al., 2008; Putirka, 2008). Alternative possibility is the use of liquidus thermobarometry, which requires knowledge of magma saturation in certain minerals and allows calculation of the conditions of its equilibrium with the melt of given composition (e.g., Roeder and Emslie, 1970; Nielsen and Dungan, 1983; Ariskin et al., 1993; Putirka, 2008; Lange et al., 2009). The methods of liquidus thermobarometry are well developed for basaltic glass compositions (e.g., Danyushevsky et al., 1996; Kelley and Barton, 2008) and are awaiting further elaboration for silicic systems commonly saturated in plagioclase - clinopyroxene - magnetite ± ilmenite ± amphibole ± quartz ± biotite. For example, Blundy and Cashman (2001) parametrized a barometer based on compositions of glasses, which can be used to constrain pressure of crystallization for melts saturated in quartz (minimum pressure for quartz-undersaturated melts). In our opinion, the studies of correlations between silicic melt (glass) composition and conditions of its equilibrium with minerals have considerable potential for improving our understanding of silicic magma origin and would pinpoint the most reliable and not just empirical but petrologically meaningful criteria for geochemical fingerprinting of tephra glass.

FUTURE CHALLENGES AND PERSPECTIVES

Although tephra studies provide important insight into past eruptions, there are also many challenges and considerations that

are critical to optimize the application of this technique. Some of the key challenges that we face include:

(1) Post-depositional processes that can affect the stratigraphic integrity of a tephra and especially a cryptotephra deposit.
(2) Pinpointing diagnostic chemical glass signatures and establishing robust matches between different sites and the source volcano.
(3) Similar compositions of tephras from different eruptions from the same volcano.
(4) Inter-lab inconsistencies in producing and reporting analytical data.
(5) Post-depositional chemical alteration of volcanic glass.

(1) Cryptotephra deposits, in particular, are prone to the influence of post-depositional processes, e.g., bioturbation, bottom current reworking and iceberg rafting (see summary in Griggs et al., 2014). Such secondary processes can result in broad zones of high shard concentrations. The real stratigraphic position and age of such cryptotephras cannot be precisely established. Moreover, tephra could be stored in the ice sheets, especially in glacial times, and then deposited from icebergs hundreds of years after the eruption (e.g., Brendryen et al., 2011). Remobilization of tephra deposits in a volcanic area by storms or fluvial reworking could also form a secondary deposit which may be misidentified as a primary fallout deposit (e.g., Liu et al., 2014; Kataoka et al., in press). In these cases, redeposited tephra does not work as an isochron, and its thickness in its final landing site may bias isopach patterns. Protocols for the identification of primary vs. reworked deposits are thus crucial for reconstructing volcanic history as well as for utilizing these deposits as isochrones in palaeo-environmental studies (e.g., Hopkins et al., 2015).
(2) Tephrochronological studies have generated large analytical datasets of silicic and mafic volcanic glass (e.g., Smith et al., 2005, 2011a, 2013; Westgate et al., 2011; Tomlinson et al., 2012, 2015). The most important task is to uniquely identify a tephra deposit based on its composition and age, and compare one tephra to another to establish robust correlations between disparate sites (Lowe, 2011). Geochemical comparisons between different samples have been implemented with the help of more and more sophisticated statistical tools (Borchardt et al., 1972; Kutterolf et al., 2008a; Green et al., 2014; Bronk Ramsey et al., 2015b).

It is possible that tephras from different (or similar) tectonic settings but originating from different geographical regions (e.g., different island arcs) can be found in the same geological sequence (e.g., Lane et al., 2011; Cullen et al., 2014). A practical guide on discrimination of glasses from different tectonic settings has been recently developed for Mediterranean, Icelandic and Azores volcanoes (Tomlinson et al., 2015). However, a more general theoretic discrimination of tephras originating from different tectonic settings and from different volcanic regions is needed. It is unclear thus far if glasses from different volcanic regions are compositionally different enough to ensure their reliable discrimination and which major and trace elements and their ratios are the most informative for the discrimination.

Abundant geochemical information is available from studies of bulk volcanic rocks (high precision major and trace element data, isotope compositions, e.g., GEOROC database, http://georoc.mpch-mainz.gwdg.de/georoc/). These data are rarely used in tephra studies. Is the information on bulk rock compositions indeed useless for tephrochronology? This is clearly not the case because volcanic glass represents the matrix of bulk rock and hosts elements which are incompatible in mineral phases. Radiogenic isotope ratios (e.g., Pb, Sr, Nd) should be identical between bulk tephra and distal glass shards. The extent to which geochemical peculiarities of bulk rocks are inherited by volcanic glass need to be investigated systematically and for different rock types and regions. Some recent data suggest a very strong heterogeneity of volcanic glass compositions in one tephra (Westgate et al., 2013) and thus decoupling of glass and bulk rock compositions. The reason for this variability is not well understood and requires attention in future studies.

(3) As well as pinpointing diagnostic features for different volcanic regions and tectonic settings, the tephrochronological community also faces a challenge when different eruptions of the same source volcano produce identical glass compositions (e.g., Siani et al., 2004; Santacroce et al., 2008; Smith et al., 2011a; Kaufman et al., 2012; Lane et al., 2012; Wutke et al., 2015). These eruptions may be separated by hundreds or even thousands of years, but if these are close in age, it may cause erroneous identification and mis-correlation of a tephra. The existence of compositionally near steady-state long-lived magma chambers in volcanically active areas is possible due to the periodic replenishment with more primitive magma, mixing, crystallization and eruption (e.g., O'Hara and Mathews, 1981; Lee et al., 2014). A search for diagnostic differences (for example, in isotope or non-traditional trace element composition, e.g., Li, B, Cl) of such eruptions is a crucial challenge for future studies. Some constraints from modeling and natural observations are also required for our general understanding of the longevity of compositionally steady-state magma chambers and of the potential uncertainty in tephra identification introduced by this natural phenomenon.
(4) Inter-laboratory comparison exercises have long been undertaken between electron microprobe laboratories (e.g., Kuehn et al., 2011) to provide a robust assessment of the data quality. Some efforts have been also made to introduce standardized protocol for laser-ablation trace element analyses (e.g., Tomlinson et al., 2010; Pearce et al., 2014). However, in contrast to microprobe analysis, the analytical conditions and equipment used for trace element analysis of single glass shards vary considerably. Further work and joint discussion are required to establish a widely accepted protocol for tephra trace element analysis. In our opinion, such protocol should necessarily include

the requirement to analyze well characterized and broadly available reference glasses and report detection limits estimated with a standardized procedure. This would enable a direct comparison of data obtained in different labs. At least one element with concentration determined by electron microprobe should be analyzed as unknown together with trace elements. Comparison of LA-ICP-MS and microprobe results for the same element permits evaluation of the consistency between major and trace element data and provides a quantitative criterion for rejection of analyses contaminated by crystal phases (Kimura et al., 2015). These obvious requirements have been adopted in solid-Earth geochemistry (e.g., Jenner and O'Neill, 2012) and are now required for routine analysis of single glass shards.

(5) In a study based on theoretical stability modeling of vitreous material Pollard et al. (2003) suggested that some volcanic glasses may be less stable than others in a given depositional environment, and may leach substantial amounts of alkali and alkaline earth elements, possibly from the entire volume of the tephra shards. Indeed, in hot and humid climates tephras can weather very quickly, within tens of thousands of years (e.g., Rawson et al., 2015). Many other researchers, however, confirm that volcanic glasses in marine and lake deposits as old as millions of years are quite fresh and have meaningful geochemical characteristics (e.g., van den Bogaard et al., 2014; Straub et al., 2015). In moderate and hot and dry climates Quaternary terrestrial tephras are also well preserved and suitable for geochemical analysis (e.g., WoldeGabriel et al., 2005; Kuehn and Negrini, 2010; Westgate et al., 2011). An assessment of post-depositional alteration is probably required on a site-specific basis.

All of these and many other problems of stratigraphic and geochemical credibility of tephra are being addressed in a wave of recent publications, particularly focused on the North Atlantic and Mediterranean regions. Not only do these studies outline the problems, but they also suggest possible approaches to overcome these issues. Multiple cores may help to fully explore the uneven nature of tephra distribution within different depositional realms (Davies, 2015) and recently applied visualization techniques (e.g., X-ray microtomography in Griggs et al., in press) also offer much promise in this respect. New developments in the analytical techniques permit analysis of a fuller range of major, volatile and trace elements from small tephra particles and melt inclusions

(e.g., Matsu'ura et al., 2011; Hayward, 2012; Pearce et al., 2014; Maruyama et al., in press).

Findings of distal tephra bring new information on earlier unrecognized large eruptions. They are helping to produce a better and more detailed record of the largest explosive eruptions than ever before and embedding these new data in tephra dispersal models and magma volume estimates provides new opportunities for quantifying eruption size. In addition, these new findings add more isochrons to a global tephrochronological framework which makes it possible to put more and more events into a tight stratigraphic and temporal context and for testing the synchronicity of major climatic shifts in different parts of the globe.

Tephra research has very quickly evolved into a global network of isochronous regional as well as hemispheric markers giving new insight into the prevailing pathways of tephra transport. Tephra deposits reveal that large explosive eruptions were a key feature of the past. Cryptotephra deposits reveal that there were many more large and far-traveled eruptions than previously realized (e.g., Coulter et al., 2012). Tephra crosses scientific disciplines, borders between land and sea, political borders and brings together multi-disciplinary research teams. New territories are being explored for their cryptotephra records (e.g., China, Sun et al., 2015; Zhao and Hall, 2015; Amazonia, Watson et al., 2015; Okhotsk and Bering Seas, Krasheninnikov et al., 2013), and there is no doubt that these efforts will result in a significant reappraisal of the power of past explosive eruptions and their temporal patterns, which will bring a better understanding of future volcanic events and their impact on humankind.

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