Tracking voluminous Permian volcanism of the Choiyoi Province into central Antarctica

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ABSTRACT

Permian volcanic deposits are widespread throughout southwestern Gondwana and record voluminous silicic continental arc volcanism (e.g., Choiyoi Province) that may have contributed to Permian global warming and environmental degradation. Many Permian volcanic deposits of southwestern Gondwana (southern South America, southern Africa, West Antarctica and eastern Australia), however, remain to be accurately correlated to magmatic source regions along the active paleo-Pacific margin of Gondwana, and this lack of correlation limits our understanding of the timing and distribution of voluminous volcanism. Here we present detrital zircon U-Pb and Hf isotope data for Permian volcaniclastic sedimentary rocks from the Ellsworth Mountains, Pensacola Mountains, and the Ohio Range of central Antarctica in southwestern Gondwana used to determine their volcanic source along the paleo-Pacific margin of Gondwana. Rocks in central Antarctica record Permian (ca. 268 Ma) volcanism with a mean zircon $\varepsilon$Hf of $-0.04 \pm 4.8$ (2 standard deviation). Comparison of these zircon age and Hf data with compilations for adjacent regions along the Gondwana margin suggest derivation of the Antarctic zircons from a major episode of Permian explosive arc volcanism that is broadly synchronous with, and geochemically similar to, the voluminous Choiyoi Province in South America. This correlation also relates the source of synchronous volcaniclastic deposits in the Karoo Basin, South Africa, to the same major Permian volcanic episode associated with the Choiyoi Province. In aggregate, geochemical data from Permian zircon in central Antarctica support an along-arc variation in geochemistry, with isotopically enriched high-flux magmatism associated with thicker crust and lithospheric mantle in South America, and isotopically depleted magmatism and thinner crust and lithospheric mantle in Australia. The timing of inferred Choiyoi-related explosive arc volcanism recorded in the Antarctic sector, South African sector, and South American sector is contemporaneous with a documented increase in global arc flux, an increase in atmospheric CO$_2$, a decrease in $\delta^{13}$C of benthic marine fossils, and mass extinction events. We suggest that the Choiyoi Province and correlated arc volcanism along the Gondwana margin contributed to increased global arc flux in the Permian leading to elevated background levels of atmospheric CO$_2$, conducive to producing an environmental crisis during mafic large igneous province emplacement, and may serve as an example of continental arc outgassing exerting a first order control on climate.

INTRODUCTION

There is evidence for widespread explosive continental arc volcanism during the Permian throughout southwestern Gondwana (southern South America, southern Africa, West Antarctica and eastern Australia, Fig. 1; Rocha-Campos et al., 2011; Sato et al., 2015; Castillo et al., 2016; Elliot et al., 2016, 2017; McKay et al., 2016). In South America, Permian arc volcanism resulted in exceptionally high volume silicic volcanism of the Choiyoi Province (estimated volume of ~1.3 Mkm$^3$) that may have contributed to global climate change, Permian mass extinctions and biotic crises (e.g., Henry et al., 2009; Hermann et al., 2011; Henry, 2013; Limarino et al., 2014; Kimbrough et al., 2016; Spalletti and Limarino, 2017; Luppo et al., 2018). Correctly correlating Permian volcanic deposits in southwestern Gondwana to the Choiyoi Province, therefore, is critical to determining the timing and distribution of one of the largest silicic provinces along the paleo-Pacific margin of Gondwana and its relationship to Permian global warming and environmental degradation.

Constraints on the timing and geochemistry of regional Permian volcanism in the proto–Weddell Sea segment of the paleo-Pacific margin (Fig. 1) have been greatly improved by the application of zircon geochronology and geochemistry (i.e., petrochronology) in detrital studies of volcaniclastic sediments (Canile et al., 2016; McKay et al., 2016; Nelson and Cottle, 2017; Fanning et al., 2011; Castillo et al., 2016; Kylander-Clark, 2017). In particular, detrital zircon U-Pb geochronology and Hf isotopic investigations of sedimentary rocks from the Paraná Basin and accretionary complexes of the Antarctic Peninsula and Patagonia (Fig. 1) have identified Permian volcanic detritus that may have been sourced from the Choiyoi Province or correlative continental arc magmatism (Canile et al., 2016; Castillo et al., 2016; Fanning et al., 2011). In contrast, distal volcanic deposits in the Karoo Basin of South Africa (Fig. 2), although synchronous with the Choiyoi Province, have instead been correlated to volcanic deposits and detrital zircon in the Ellsworth and Transantarctic mountains (Figs. 1 and 2) of Antarctica based on detrital zircon Th/U ratios (McKay et al., 2016). Zircon Th/U ratios alone, however,

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are poor proxies for determining provenance because Th/U ratios vary
due to magma temperature and fractional crystallization (e.g., Kirkland
et al., 2015). Thus, in the absence of combined isotopic data, it remains
unclear whether explosive volcanic deposits correlative to the Choiyoi
Province extend into South Africa and the Ellsworth and Transantarctic
mountains of Antarctica. This limits our understanding of the volume
and distribution of distal ashes from one of the largest silicic volcanic
provinces in Earth’s history.

Combined zircon geochronology and geochemistry, e.g., U-Pb and
Hf isotopes, provide a means to investigate volcanic provenance along
the paleo-Pacific margin. Comprehensive zircon geochemistry data does
not exist for Permian volcanic deposits of the Ellsworth and southern
Transantarctic mountains (TAM), referred to here as central Antarctica
(Fig. 2). An important utility of combined geochronology and geochemi-
cal data (i.e., petrochronology) for accessory minerals such as zircon
(e.g., Kylander-Clark, 2017) is the ability to stitch together a fragmented
temporal, geochemical, and geodynamic history of a convergent margin
using both igneous and sedimentary rocks. Furthermore, the addition of
isotopic geochemical tracers provides increased reliability to provenance
studies that otherwise rely solely on geochronologic data. A petrochrono-
logic approach, therefore, is particularly useful in Antarctica where the
tectonic evolution is highly fragmented due to inaccessibility and poor
exposure (Fig. 2). For this reason, we focus on key sections of Permian
strata in central Antarctica, i.e., Ellsworth Mountains and southern TAM
(Fig. 2; Elliot et al., 2016, 2017), with the goal of characterizing the age
and isotopic geochemistry of Permian-aged zircon. These data are com-
pared with a new compilation of zircon Hf data for surrounding crustal
blocks to determine potential temporal and geochemical correlations with
other Permian-aged rocks along the Gondwana margin. These data support
the contention that some Permian volcanic strata from central Antarctica
and the Karoo Basin represent distal components of continental arc vol-
canism temporally and geochemically characteristic of South America
and the Choiyoi Province.

GEOLOGIC BACKGROUND

The source of widespread Permian distal volcanic deposits and detri-
tal zircon within the proto–Weddell Sea region is generally considered
to be the outboard active continental paleo-Pacific margin of Gondwana,
including the Choiyoi Province (Fig. 1; Sato et al., 2015; Canile et al.,
2016; Elliot et al., 2016). However, this segment of the Gondwana mar-
gin has been highly fragmented due to supercontinent breakup in the
Jurassic through Cretaceous and, consequently, reconstructing the pre-
breakup arrangement of the various crustal blocks has been considered
the “problem child” of paleo-Pacific margin tectonics (Dalziel and Elliot,
1982; Grunow et al., 1987; Storey et al., 1988). This problem has been
further complicated by the inaccessibility and poor exposure of areas of
interest in southern Patagonia and ice-covered regions in West Antarctica.
For these reasons, potential sources of Permian-aged detrital zircon in volcaniclastic sediments in the Paraná Basin, southern Patagonia, West Antarctica, and South Africa have been limited to abundant Permian subduction-related magmatic and volcanic rocks of the Choiyoi Province, or sparse occurrences of subduction-related Permian granites in the crustal blocks of West Antarctica (e.g., Antarctic Peninsula, Marie Byrd Land, Thurston Island; Fig. 2) (Canile et al., 2016; Castillo et al., 2016; Fanning et al., 2011; Elliot et al., 2016, 2017; McKay et al., 2016).

The Choiyoi Province (Fig. 1) is principally characterized by widespread Permian subduction-related andesitic to rhyolitic volcanic rocks (primarily ignimbrites) erupted over an area of ~1.7 Mkm² of Chile and Argentina, with an average thickness of 700 m emplaced between ca. 282 and 251 Ma with a major flare-up at 269–263 Ma (e.g., Rocha-Campos et al., 2011; Kimbrough et al., 2016; Spalletti and Limarino, 2017). The plutonic components of the Choiyoi Province are broadly defined as tonalities–granodiorites to granites emplaced between 286 and 247 Ma (e.g., Sato et al., 2015). Plutonic and volcanic rocks of the Choiyoi Province are distributed across the Chilean Coastal Cordillera, the Chilean Precordillera, the Principal and the Frontal Andean Cordillera, the Argentinian Precordillera, the San Rafael–Las Matras–Chadileuvú Blocks, and northern Patagonia, including the North Patagonian Massif. Contemporaneous Permian plutonic rocks have also been discovered in Tierra del Fuego (Fig. 1). Proposed distal volcanic ashes of the Choiyoi Province are found throughout late Paleozoic Gondwana basins in South America and South Africa including the Paraná and Karoo basins, respectively (Fig. 1). Voluminous calc-alkaline volcanism and magmatism of the early stage of the Choiyoi Province at ca. 280–265 Ma is generally syntectonic with transpression during the San Rafael compressional event and Gondwancide Orogeny (e.g., Kleiman and Japas, 2009). The later stage of Choiyoi Province is characterized by anorogenic magmatism from ca. 265 to 250 Ma associated with extensional collapse of the San Rafael orogen and Gondwancide Orogeny at ca. 265 Ma (Kleiman and Japas, 2009; Sato et al., 2015; Rocha-Campos et al., 2011).

Definitive volume estimates for the Choiyoi Province, volcanic and plutonic, are lacking but there is broad consensus that the Choiyoi Province represents the largest silicic magmatic event in southwestern Gondwana (e.g., Rocha-Campos et al., 2011; Sato et al., 2015; Kimbrough et al., 2016; Spalletti and Limarino, 2017). The age of the Choiyoi Province (ca. 286–247 Ma) overlaps with the Permian–Triassic and End Guadalupian mass extinction events, carbon isotope excursions, and a shift from icehouse to greenhouse conditions associated with increases in atmospheric greenhouse gases (Spalletti and Limarino, 2017). For these reasons the Choiyoi Province has been proposed as a major source of volcanicogenic greenhouse gases (e.g., CO₂) during volcanism and magmatism that heated organic-rich Paleozoic sedimentary rocks, releasing additional greenhouse gases and contributing to Permian global warming and environmental crises (Kimbrough et al., 2016; Spalletti and Limarino, 2017; Henry et al., 2009; Henry, 2013; Hermann et al., 2011; Luppo et al., 2018; Limarino et al., 2014).

Recent work has utilized zircon geochronology and geochemistry to unlock the history of Permian magmatism and volcanism in southwestern Gondwana contemporaneous with the Choiyoi Province. U-Pb ages and Hf isotopes of detrital zircon within volcaniclastic rocks from the Paraná Basin are reported to be temporally and geochemically comparable to the Choiyoi Province (Canile et al., 2016). Similarly, Fanning et al. (2011) and Castillo et al. (2016) utilized zircon Hf-O isotopes to demonstrate a correlation in Permian detrital zircon Hf isotope compositions between the Antarctic Peninsula, Patagonia, and the Choiyoi Province. They argued that similarities in age and zircon Hf isotope composition for detrital zircon from the Antarctic Peninsula and Patagonia suggest they may be sourced directly from the Choiyoi Province or a temporally and geochemically related southern extension of the Permian magmatic arc into southern Patagonia and the Antarctic Peninsula.

Distal volcanic tuffs from the Karoo Basin, South Africa (Fig. 1), overlap in age with Permian zircon from South America and may represent distal ash deposits of the Choiyoi Province (e.g., McKay et al., 2016). Whole-rock geochemistry for Karoo Basin tuffs indicates a possible intraplate magmatic source consistent with back-arc magmatism rather than continental arc magmatism (McKay et al., 2016). Whole-rock data for Karoo Basin tuff samples, however, are contaminated by admixed detritus consisting of possibly multiple geochemically distinct signatures and require zircon geochemistry for reliable time-integrated geochemical interpretations. Similarities in zircon Th/U ratios were interpreted to indicate that Karoo Basin tuffs are genetically related to volcanicogenic sediments in the Ellsworth Mountains and TAM, Antarctica (Figs. 1 and 2), rather than Permian zircon from South America, i.e., Choiyoi Province (McKay et al., 2016). Zircon Th/U ratios, however, may vary greatly within a single magma system due to temperature and differentiation which make Th/U a potentially unreliable geochemical tracer for zircon provenance (e.g., Kirkland et al., 2015; Yakymchuk et al., 2018). Instead, Hf isotopes provide a more reliable geochemical signature of the magma source because Hf isotopic ratios do not vary with magma temperature and fractionation. Zircon Hf isotopic data, unfortunately, do not currently exist for Permian zircon from either the Karoo Basin or Permian strata of central Antarctica (McKay et al., 2016; Elliott et al., 2016, 2017). In this contribution, we investigate the geochronology and Hf isotopic composition of Permian zircon from Permian strata (Figs. 2 and 3; >500 km between each locality) of the Ellsworth Mountains (Polarstar Formation), and

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### Figure 3. Simplified geologic columns for Carboniferous to Triassic strata in central Antarctica and central Transantarctic Mountains with the stratigraphic positions of samples (modified from Storey et al., 1996; Elliott et al., 2016, 2017).
the Ohio Range (Mt. Glossopteris Formation) and Pensacola Mountains (Pecora Formation) of the southern TAM to clarify correlations with the Karoo Basin, Choiyoi-related flare-up in South America, or petrogenetically distinct magmatism recorded in the central TAM, Marie Byrd Land, Zealandia, and Australia. Our data, combined with a new compilation for adjacent regions along the Gondwana margin, demonstrate that Permian zircon from central Antarctica and the Karoo Basin has a strong temporal and geochemical similarity to arc magmatism within the South American sector and the Choiyoi Province.

**Polarstar Formation, Ellsworth Mountains**

The Polarstar Formation is the youngest formation of the Paleozoic strata in the Ellsworth Mountains (Figs. 2 and 3; Elliot et al., 2016; Castillo et al., 2017a; Craddock et al., 2017). A minimum thickness of 1.2 km for the intensely folded strata of the Polarstar Formation has been estimated by combining several measured sections. The Polarstar Formation has been divided into a lower Argillite Facies, middle volcanioclastic Sandstone-Argillite Facies, and upper Glossopteris-bearing Coal Measures Facies (Collinson et al., 1992; Elliot et al., 2016). Our sample is from the middle volcanioclastic sandstone facies (Fig. 3). Comparable Permian strata to the Polarstar Formation have been identified in eastern Ellsworth Land, Karoo Basin of South Africa, Falkland Islands, and central TAM (Elliot et al., 2016). Based on geochronology and facies comparisons, the Polarstar Formation has been interpreted as an extension of the Permian–Triassic Transantarctic Basin and separate from the Karoo Basin of South Africa and Permian deposits in the Falkland Islands (Elliot et al., 2016). Volcanogenic Permian detrital zircon for volcanioclastic sandstones of the Polarstar Formation generally range in age from 270 to 260 Ma and three zircon U-Pb ages have been determined for tuff beds: 258 ± 2 Ma, 263 ± 2 Ma, and 263 ± 1 Ma (Elliot et al., 2016; Craddock et al., 2017). 

**Mt. Glossopteris Formation, Ohio Range**

The Permian Mt. Glossopteris Formation is the youngest formation in the Ohio Range of the Transantarctic Mountains (Figs. 2 and 3; Elliot et al., 2017). It is composed of a lower marine succession (shale and siltstone) and a thick upper fluvial succession consisting of sandstones and coal (Collinson et al., 1994). The Mt. Glossopteris Formation is a member of the Beacon Supergroup that comprises Devonian-Triassic sediments of the TAM and correlates with the Buckley and Fairchild formations in the central TAM and the Weller Formation in south Victoria Land (Elliot et al., 2017). Recent detrital zircon geochronology for the Mt. Glossopteris Formation reported high proportions of air-fall–transported volcanic detritus and Permian zircon ranging in age from 280 to 245 Ma derived from the outboard active Gondwana margin. We selected a sample from a stratigraphic position close to their reported volcanioclastic sandstone in order to target Permian zircon (Fig. 3).

**Pecora Formation, Pensacola Mountains**

The Pecora Escarpment, the type locality for the Permian Pecora Formation, is the southernmost extension of the Pensacola Mountains (Figs. 2 and 3, Williams, 1969; Barrett et al., 1986; Collinson et al., 1994). Rocks of the Pecora Formation include abundant sandstones, siltstones, and shales. Minor carbonaceous and coal beds contain Permian Glossopteris fossil leaves indicative of a Permian age for the Pecora Formation (Williams, 1969). The Pecora Formation of the Pensacola Mountains has been correlated to Beacon Supergroup sediments of the TAM, including the Mt. Glossopteris Formation in the Ohio Range and the Buckley Formation in the central TAM (Barrett et al., 1986; Collinson et al., 1994). Detrital zircon studies have not previously reported Permian zircon in the Pecora Formation, and no radiometric dates are available.

**ANALYTICAL METHODS**

One sample from each Permian unit, the Mt. Glossopteris Formation, Pecora Formation, and Polarstar Formation (Figs. 2 and 3) were selected from the Polar Rock Repository (polar rock and dredge samples are available for research and educational use at https://doi.org/10.7289/V5RF5S18) to determine the age and geochemistry of Permian zircon. Zircon were separated using standard mineral separation techniques (i.e., disk milling, water table, magnetic separation, and heavy liquids), mounted in epoxy, and polished to expose equatorial sections. Prior to isotopic analysis, zircon were imaging using cathodoluminescence on an FEI Quanta400f scanning electron microscope (SEM) and used to guide selection of locations for laser ablation split stream (LASS) analysis (U-Pb and trace elements) and Lu-Hf measurements.

Zircon U-Pb isotopes and trace-element concentrations were obtained simultaneously with using the “split stream” approach (Kylander-Clark et al., 2013) at the University of California at Santa Barbara under standard operating conditions (McKinney et al., 2015). Instrumentation consists of a 193 nm ArF excimer laser ablation (LA) system coupled to Nu Plasma high-resolution multi collector–inductively coupled plasma–mass spectrometer (MC-ICP-MS) for U/Pb and an Agilent 7700S Quadrupole ICPMS for trace elements. A selection of 64 zircon grains was measured for U-Pb and trace-element analysis from each sample. Subsequent Lu-Hf analyses were performed by LA-ICP-MS exclusively on zircon younger than Ordovician (n = ~25 per sample) to better characterize the geochemistry of post–Ross-aged zircon. All data reduction was performed using Iolite v2.5 ( Patton et al., 2011, 2010) and 207Pb corrected 206Pb/238U ages were calculated for zircon younger than ca. 800 Ma using the method of Andersen (2002) and ISOPLOT/EX (Ludwig, 2003). Detailed analytical methods, data reduction protocols, and results of reference zircon analyses and unknown data are provided in the Data Repository Supplementary Text S1, and Datasets S1 and S2 (Jackson et al., 2004; Sláma et al., 2008; Liu et al., 2010; Thirlwall and Anczkiewicz, 2004; Chu et al., 2002; Patchett and Tatsumoto, 1980, 1981; Woodhead and Hergarten, 2005; Blichtert-Toft, 2008; Wiedenbeck et al., 1995, 2004).

**RESULTS**

All zircon U-Pb and geochemical data are provided in Datasets S1 and S2 (see footnote 1). Zircon U-Pb Tera-Wasserburg concordia, 207Pb/206Pb corrected error-weighted mean 206Pb/238U crystallization ages, representative cathodoluminescence (CL) images of zircon, and kernel density/ histogram plots for Permian-aged zircon are provided in Figure 4. Permian zircon from all formations have euhedral prismatic and elongate zircon with both oscillatory and sector zoning in CL. Histogram plots of zircon Hf isotope data are given in Figure 5. Zircon trace-element concentrations fall within the range of continental arc zircon and have “igneous” Th/U ratios (>0.1) (Grimes et al., 2015; Rubatto, 2002). Calculated weighted mean crystallization ages with two sigma uncertainties and mean squared weighted deviation (MSWD) for samples from this study are discussed below. Calculated weighted mean εHf values are provided alongside their
two standard error uncertainties below. All εHf values were calculated using chondritic uniform reservoir (CHUR) parameters of Bouvier et al. (2008) and 176Lu decay constant from (Söderlund et al., 2004).

A sandstone from the Mt. Glossopteris Formation (specimen PRR-11683, Fig. 4) of the Ohio Range yielded Permian-aged zircon with a unimodal distribution on a kernel density plot. Given the acceptable MSWD of 1.5, we use the error-weighted mean of 266 ± 1 Ma (n = 55) as the best estimate for the minimum age of this sample. The zircon εHf ranges from –3.2 to 0.7 with a unimodal distribution and a mean of –0.6 ± 1.7 (2SD) (Fig. 5). Only one zircon within this sample yielded a concordant U-Pb age older than the Permian (ca. 508 Ma). Permian zircon from the Mt. Glossopteris Formation have an average Th/U = 0.62, Gd/Yb = 0.07, and U/Yb = 0.58.

A sandstone sample from the Pecora Formation (PRR-33218, Fig. 4) in the Pensacola Mountains contained Permian zircon with a weighted mean age of 267 ± 1 Ma (MSWD = 1.2, n = 39). The kernel density plot looks similar to that for the Mt. Glossopteris sample with a unimodal distribution and a slight skew toward younger dates. The zircon εHf ranges from –4.2 to +5.6 with a mean of +0.7 ± 5.4 (2 standard deviation [SD]). The zircon εHf histogram plot demonstrates a bimodal distribution of εHf, with peaks at ~−0.5 and +3 (Fig. 5). Concordant ages for PRR-33218 older than the Permian include four Carboniferous ages, a ca. 512–489 Ma (n = 11) range, and a single age of ca. 632 Ma. Permian zircon from the Pecora Formation have an average Th/U = 0.93, Gd/Yb = 0.08, and U/Yb = 0.60.

A sandstone from the Polarstar Formation (PRR-299; Fig. 4) of the Ellsworth Mountains yielded a population of Permian-aged zircon with a weighted mean of 270 ± 1 Ma (MSWD = 1.5 for n = 37). The kernel density plot for PRR-299 indicates a unimodal distribution, justifying the error-weighted mean as the best estimate of the minimum depositional age of this rock. The zircon εHf ranges from –5.4 to +4.5 with a mean of −0.2 ± 6.0 (2SD) (Fig. 5). Concordant ages for PRR-299 older than the Permian include a single age of ca. 308 Ma, an age range of ca. 520–486 Ma (n = 9), and seven Proterozoic ages from ca. 1735 to 541 Ma. Permian zircon from the Pecora Formation have an average Th/U = 0.75, Gd/Yb = 0.06, and U/Yb = 0.54.

DISCUSSION

Regional Temporal Correlations of Permian Volcanism

Our new detrital zircon data for Polarstar, Mt. Glossopteris, and Pecora formations indicate a period of Permian volcanism between ca. 277 and 260 Ma (the maximum age range of all detrital zircon in the three samples;
The age range for Permian zircon from the central TAM are comparable to detrital zircon ages from Australia and New Zealand which demonstrate a broad difference in the timing of Permian arc magmatism between Australia/Zealandia and South America (see compilation in Nelson and Cottle, 2017). In summary, detrital zircon ages for Mt. Glossopeteris, Polarstar, and Pecora formations in central West Antarctica are contemporaneous with the Choiyoi igneous province, Patagonia, the Antarctica Peninsula, and South Africa, and are generally older than Permian arc magmatism recorded in the central TAM that is itself contemporaneous with arc activity in Zealandia and Australia. Consequently, central Antarctica defines the southernmost distal component of widespread Permian volcanism contemporaneous with the Choiyoi Province along the Gondwana margin and may have been directly sourced from a major high-flux period of Choiyoi-related volcanic activity (Kimbrough et al., 2016).

**Hf Isotopic Constraints on Provenance**

The Hf isotopic composition of zircon from the central Antarctica samples exhibit similarly enriched εHf values that overlap within uncertainty and have a combined εHf range of −5 to +5 (mean of all data = −0.04 ± 4.8 (2SD, n = 85), Fig. 5), reinforcing a shared geochemical and temporal history for these rocks. At least two geologically plausible scenarios can explain the lack of juvenile Hf isotopic compositions (εHf > +5) in central Antarctica samples. The evolved signature may result from contamination of depleted mantle melts by assimilation of enriched Cambrian (e.g., Ross Orogen) and/or Proterozoic (Grenville-aged cratonic basement) crustal reservoirs (Hagen-Peter et al., 2015; Hagen-Peter and Cottle, 2018) that are ubiquitous along the Gondwana margin (Nelson and Cottle, 2018). Alternatively, enriched compositions may have resulted from enriched lithospheric mantle melting followed by crustal assimilation. Permian zircon from the Antarctic Peninsula contain enriched Hf isotope compositions (εHf = −1.3 to +5.2), similar to that of central Antarctica, and mantle-like oxygen isotope compositions (δ18O = 4.5–6.4‰), consistent with a shared enriched lithospheric mantle source for central Antarctica and the Antarctic Peninsula (Castillo et al., 2016). Evidence for proximal
magmatism with an enriched lithospheric mantle source recorded in Permian zircon from the Antarctic Peninsula and the absence of zircon $\varepsilon_{Hf} > +5$ in central Antarctica suggest an enriched lithospheric mantle source for central Antarctica.

**Regional Detrital Zircon Hf Isotope Comparisons**

Here we compile detrital zircon Hf isotope data to test whether Permian zircon in central Antarctica have geochemical affinities with Permian detrital zircon in the Antarctic Peninsula and South America or the central TAM (Fig. 7). Permian detrital zircon from the Paraná Basin, Patagonia, and Antarctic Peninsula all contain enriched Hf isotope compositions and lack juvenile Hf isotope compositions similar to central Antarctica (Fig. 7; Fanning et al., 2011; Canile et al., 2016; Castillo et al., 2016). Intermediate Hf compositions ($\varepsilon_{Hf} = 0$ to $+5$) for middle Permian zircon are more common in central Antarctica than the Paraná Basin, Patagonia, and Antarctic Peninsula; however, the uniformly enriched compositions ($\varepsilon_{Hf} < +5$) for all of these regions are consistent with derivation from temporally and geochemically related magmatic sources. Limited early to middle Permian zircon Hf isotope data exists for the central TAM but late Permian and Early Triassic Hf isotope compositions are significantly more juvenile ($\varepsilon_{Hf} > +14$) and there are only a minor amount of zircon with $\varepsilon_{Hf} < 0$ (Fig. 7; Nelson and Cottle, 2017). The data from central TAM, therefore, suggest zircon derived from a magmatic arc that is temporally and geochemically distinct (i.e., Marie Byrd Land, Zealandia, and Australia) from the source of central Antarctica, Paraná Basin, Patagonia, and Antarctic Peninsula (Nelson and Cottle, 2017).

**Zircon Hf Isotope Composition of Permian Magmatic Rocks**

Compilation of zircon Hf isotope data from plutonic rocks across the Gondwana margin enable identification of potential source regions for Permian zircon in central Antarctica (Fig. 8). In South America, magmatic rocks of the Frontal Andes, Coastal Batholith, North Patagonian Massif, and Tierra del Fuego generally have enriched zircon Hf isotope compositions ($\varepsilon_{Hf} < +5$) similar to that of central Antarctica (Fig. 8; Fanning et al., 2011; del Rey et al., 2016; Castillo et al., 2017b). A comprehensive study of the zircon Hf isotope composition of volcanic rocks of the Choiyoi Province is unavailable, but limited data from Choiyoi volcanic rocks and plutonic rocks from the North Patagonian Massif indicate the Choiyoi Province has an $\varepsilon_{Hf} = -7$ to $+5$ (Fig. 8; Fanning et al., 2011; Castillo et al., 2017b). The lack of zircon with $\varepsilon_{Hf} > +5$ in South America may be due to melting of an enriched lithospheric mantle, or extensive crustal contamination of depleted mantle melts. Evidence for an enriched lithospheric mantle is preserved in Permian zircon with enriched Hf isotope compositions and mantle-like O isotope compositions from Frontal Andes batholiths and the North Patagonian Massif (Fig. 8; del Rey et al., 2016; Castillo et al., 2017b). Re/Os data from Patagonian mantle xenoliths demonstrate the existence of a Proterozoic enriched lithospheric mantle source that was likely present in the Permian and related to ancient lithosphere reported in South Africa and the Shackleton Range of Antarctica (Mundl et al., 2015; Schilling et al., 2017, 2008). Together these observations provide strong evidence for a lithospheric mantle source.
for contemporaneous Permian magmatism in South America, including the Choiyoi Province, and are consistent with the Choiyoi Province or temporally and geochemically correlative arc magmatism as the source for Permian zircon from central Antarctica.

Zircon Hf isotope compositions for crystalline basement in the Antarctic Peninsula and the adjacent crustal block of Thurston Island are limited (Fig. 8; Flowerdew et al., 2006; Riley et al., 2017; Nelson and Cottle, 2018). The available data suggests they both record enriched Hf isotopic compositions in the Permian–Triassic and, therefore, may have been sourced from an enriched lithospheric mantle similar to that of South America. A Permian diorite from Thurston Island (276 ± 1 Ma) is contemporaneous with the ca. 268 Ma Permian zircon age peak for central Antarctica and has similarly enriched zircon Hf isotope compositions (mean $\varepsilon_{Hf} = +0.4 \pm 0.7 [2SE]$) suggesting Thurston Island as a potential source for Permian zircon from central Antarctica (Fig. 8; Nelson and Cottle, 2018). In contrast, there are no Permian magmatic rocks from Marie Byrd Land contemporaneous with the ca. 268 Ma central Antarctica Permian zircon (Fig. 8; Pankhurst et al., 1998; Mukasa and Dalziel, 2000; Yakymchuk et al., 2013, 2015; Nelson and Cottle, 2018). Older Permian magmatic rocks (ca. 295–283 Ma) and a Triassic granite (ca. 248 Ma) from Marie Byrd Land have zircon Hf compositions that are generally more depleted than central Antarctica (Fig. 8) and record unambiguous evidence for a depleted mantle source (Nelson and Cottle, 2018). In summary, there is currently no evidence to support Marie Byrd Land as a likely source region for Permian zircon in central Antarctica.

**Along Arc Geochemical Variation**

The depleted zircon Hf isotope compositions from Marie Byrd Land are comparable to Permian–Triassic zircon from the central TAM and compiled zircon Hf isotope data from Zealandia and Australia (Fig. 8; Nelson and Cottle, 2018). These observations have previously been used to argue for an along arc geochemical variation from depleted in Australia, Zealandia, and Marie Byrd Land to enriched in South America, Antarctic Peninsula, and Thurston Island. This along arc variation is likely caused at least in part by a thinned crust and depleted asthenospheric mantle source in Australia, Zealandia, and Marie Byrd Land and a thickened crust and ancient enriched lithospheric mantle source in South America, Antarctic Peninsula, and Thurston Island (Nelson and Cottle, 2017, 2018). The difference may have developed due to varied tectonic (i.e., geodynamic) histories of these two broad segments of the Gondwana margin. In particular, Australia, Zealandia, and Marie Byrd Land likely underwent lithospheric rejuvenation during slab rollback and/or lithospheric foundering (i.e., extensional collapse) earlier, circa mid to late Paleozoic, than South America, which did not undergo major extension and lithospheric rejuvenation until later, circa late Permian to Jurassic (Nelson and Cottle, 2018).

The difference in tectonic history along the Gondwana margin is particularly pronounced during the early Permian when the margin of Australia was undergoing widespread extension leading to the opening of the Sydney and Bowen basins (e.g., Rosenbaum, 2018) and the margin of South America was undergoing contraction during the San Rafael compressional event associated with the Gondwanide Orogeny (e.g., Kleiman and Japas, 2009; Sato et al., 2015). Permian volcanic and plutonic rocks of the Choiyoi Province were emplaced during contraction of the San Rafael event and continued through the initial stage of extension at ca. 265 Ma (Sato et al., 2015; Rocha-Campos et al., 2011; Spalletti and Limarino, 2017; Kleiman and Japas, 2009). The temporal and geochemical signature of this event is present in our data from central Antarctica and indicates they are sourced from the Choiyoi Province or correlative Gondwana arc rocks of Patagonia, Antarctic Peninsula, and/or Thurston...
Island. We therefore suggest that Permian volcanic and magmatic rocks in Patagonia, Antarctic Peninsula, and Thurston Island may define a southern extension of the Choiyoi Province along the Gondwanaic arc (Castillo et al., 2016; Fanning et al., 2011) and volcanic deposits in central Antarctica represent the distal expression of this southern extension of the Choiyoi Province (Fig. 9). Paleogeographic reconstructions indicate the location of the Karoo Basin was between the Paraná Basin and central Antarctica and constrain the source for Karoo Basin tuffs to aforementioned Choiyoi-related magmatism (Fig. 9). Our data from central Antarctica also support the notion that an early-Permian along arc geochemical switch occurred in the vicinity of Thurston Island and Marie Byrd Land (Nelson and Cottle, 2017, 2018) based on the difference in Permian zircon Hf isotopes of central Antarctica and central TAM.

Environmental Impacts of the Choiyoi Flare-up

Previous workers have asserted that a high magma flux during emplacement of the Choiyoi Province may have contributed significantly to an increase in atmospheric CO2 during the Permian which is associated with the end-Permian and end Guadalupian mass extinction events and a transition from icehouse to greenhouse conditions (Kimbrough et al., 2016; Spalletti and Limarino, 2017; Henry, 2013; Henry et al., 2009; Hermann et al., 2011; Limarino et al., 2014; Lippo et al., 2018). Our new geochronology data, combined with that from the Karoo Basin (McKay et al., 2016), provide an opportunity to assess correlations between peak volcanic activity associated with the Choiyoi Province (inferred as peaks in distal zircon ages) with major shifts in global continental arc flux (Cao et al., 2017; McKenzie et al., 2016), atmospheric CO2 (Berner and Kothavala, 2001), large igneous provinces and mass extinction events (Bond and Wignall, 2014), and marine fossil δ13C (Veizer et al., 1999), to evaluate the relationship between Choiyoi-related volcanism and possible environmental change (Fig. 10). Detrital zircon data and global granite surface area addition rates have been established as proxies for global arc flux through time and a correlation between high global arc flux and elevated atmospheric CO2 suggests continental arc volcanism may be the principle driver of atmospheric CO2 (e.g., McKenzie et al., 2016; Cao et al., 2017).

In particular, there is a general increase in global arc flux beginning in the Permian and continuing through the Cretaceous that aligns with an increase in atmospheric CO2 (Fig. 10; Berner and Kothavala, 2001; McKenzie et al., 2016; Cao et al., 2017). Furthermore, this increased global arc flux is broadly correlated with a shift to lighter δ13C values in brachiopod, benthic foraminifera shells (Fig. 10; Veizer et al., 1999) that may be the result of addition of light mantle carbon through prolonged increased volcanic outgassing that began in the Permian (e.g., Paulsen et al., 2017).

Our expanded data for peak Permian volcanism in the South American and Antarctic sectors of the Gondwana margin, related to the Choiyoi Province, shows that the source volcanic rocks of the zircons that we analyzed were coeval with the initial increase in global arc flux in the Permian and suggests that the Choiyoi Province and correlated arc volcanism contributed to a dramatic increase in global continental arc flux that elevated background CO2 (Fig. 10). Approximately 1022 g of CO2 is estimated to have been released over ~30 million years during the emplacement of the Choiyoi Province, corresponding to a minimum CO2 volcanic outgassing input rate of ~1016 g/m.y. (Henry, 2013; Henry et al., 2009). Significant additional CO2 and CH4 may have been released due to heating of Paleozoic organic-rich shales, peat and carbonates (decarbonation) by Choiyoi magmas and volcanics (Spalletti and Limarino, 2017). Constraints on global continental arc CO2 flux in the Permian are lacking but modern continental arc CO2 input estimates of 150 Tg/yr (on the order of 1020 g/m.y.) suggests the Choiyoi Province may have only represented a small component of the global arc CO2 flux (Lee and Lackey, 2015). However, emplacement of the Siberian Traps mafic large igneous province associated with the end-Permian mass extinction released ~30,000 Gt CO2 (Bond and Wignall, 2014) over ~800 k.y. (Burgess and Bowring, 2015), corresponding to a volcanic CO2 input rate on the order of 1019 g/m.y.—comparable to the Choiyoi Province.

Estimates for the Choiyoi and Siberian Traps igneous provinces do not incorporate release of CO2 from decarbonation of crustal carbonates due to heating of Paleozoic organic-rich shales, peat and carbonates (decarbonation) by Choiyoi magmas and volcanics (Spalletti and Limarino, 2017). Constraints on global continental arc CO2 flux in the Permian are lacking but modern continental arc CO2 input estimates of 150 Tg/yr (on the order of 1020 g/m.y.) suggests the Choiyoi Province may have only represented a small component of the global arc CO2 flux (Lee and Lackey, 2015). However, emplacement of the Siberian Traps mafic large igneous province associated with the end-Permian mass extinction released ~30,000 Gt CO2 (Bond and Wignall, 2014) over ~800 k.y. (Burgess and Bowring, 2015), corresponding to a volcanic CO2 input rate on the order of 1019 g/m.y.—comparable to the Choiyoi Province.

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Figure 9. Paleogeographic reconstruction of supercontinent Gondwana and a cross section of Permian arc crust of South America, West Antarctica, Zealandia, and Australia summarizing the conclusions of this study (modified from Meert and Lieberman, 2008). Syd-Bow—Sydney and Bowen basins; c. TAM—central Transantarctic mountains; c. Ant—central Antarctica.

Figure 10. Compilation of Phanerozoic global arc flux proxy data (McKenzie et al., 2016; Cao et al., 2017), δ13C data from benthic marine fossils (Veizer et al., 1999), and atmospheric CO2 (Berner and Kothavala, 2001) compared with the timing of peak Choiyoi-related volcanism recorded in the Karoo Basin and central Antarctica, large igneous provinces (LIPs) and mass extinction events (Bond and Wignall, 2014; Kidder and Worsley, 2010). Global arc flux is inferred from compilations of global surface area addition rates of granitoids (red), global compilation of proportion of young detrital zircon ages within 200 million years of minimum deposition age (dashed), and global compilation of detrital zircon relative mean age calculated from difference between youngest zircon population and minimum deposition age (McKenzie et al., 2016; Cao et al., 2017). Age data for the Karoo Basin and central Antarctica are presented as a normal kernel density estimation with a bandwidth of 2 (Vermeesch, 2012). CAMP—central Atlantic magmatic province; SD—standard deviation.
to carbonate-magma interaction that may radically increase CO₂ flux during magmatism (e.g., Lee and Lackey, 2015). We suggest, therefore, that decarbonation of crustal carbonates during emplacement of the Choiyoi Province combined with global increases in continental arc flux (both volcanic outgassing and decarbonation) elevated background atmospheric CO₂ levels, creating environmental degradation and global warming in the Permian (Lee and Lackey, 2015; Cao et al., 2017; McKenzie et al., 2016; Spalletti and Limario, 2017). Punctuated mafic large igneous province emplacement, e.g., Siberian Traps and Emeishan, caused additional CO₂ input and environmental stress leading to mass extinction events (Fig. 10; Bond and Wignall, 2014). These combined effects may have occurred numerous times throughout the Phanerozoic (Fig. 10). Better constraints on the timing and volume of continental arch flare-ups and the amount of volcanic and decarbonation CO₂ outgassing throughout the Phanerozoic will enable determination of the relationship between continental arch flare-up events, global warming, and mass extinctions (e.g., Cao et al., 2017).

CONCLUSIONS

New zircon U-Pb and Hf isotopic data for Permian detrital zircon from volcaniclastic sedimentary rocks in central Antarctica record a major episode of explosive continental arc volcanism at ca. 268 Ma. Hf isotopes indicate that Permian volcanism in central Antarctica is consistent with derivation from temporally and geochemically correlated rocks in South America, Antarctica Peninsula, and Thurston Island, that likely represent a continental arch flare-up related to the Choiyoi Province. Central Antarctica therefore represents the southernmost documented extension of this broad volcanic and magmatic province that is distinct from continental arc activity recorded in central TAME, Marie Byrd Land, Zealandia, and Australia. Volcanic rocks in the Karoo Basin, South Africa, must also be sourced from Choiyoi-related igneous activity. Zircon Hf isotopes suggest an沿 arc shift from voluminous isotopically enriched arc magmatism in South America to lower volume isotopically depleted magmatism in eastern Australia during the early to middle Permian. The timing of voluminous volcanism and magmatism correlated to the Permian Choiyoi Province, recorded in central Antarctica and the Karoo Basin, is broadly synchronous with a shift from icehouse to greenhouse conditions, decreased δ¹³C in benthic marine fossils, increased atmospheric CO₂, mass extinction events, large igneous provinces, and increased global arc flux. Consequently, we suggest the Choiyoi Province was a major contributor to increased global arc flux and volcanic outgassing and decarbonation of crustal carbonates in the Permian that produced a background level of atmospheric CO₂ conducive to climatic and biotic crises during mafic large igneous province emplacement.

ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant No. 1650114 and support from NSF-ANT-1442996. NSF-ANT-1043152. This research used samples and/or data provided by the Polar Rock Repository (PRR). The PRR is sponsored by the National Science Foundation Office of Polar Programs. We are grateful to Anne Grunow and the PRR for providing samples and assisting with sample selection. We also acknowledge the original sample collectors: C. Craddock, I. Dalziel, and W. Long.

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