Supercontinental Inheritance and its Influence on Supercontinental Breakup: The Central Atlantic Magmatic Province and the Breakup of Pangea

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ABSTRACT

The Central Atlantic Magmatic Province (CAMP) is the large igneous province (LIP) that coincides with the breakup of the supercontinent Pangea. Major and trace element data, Sr-Nd-Pb radiogenic isotopes, and high-precision olivine chemistry were collected on primitive CAMP dikes from Virginia (VA). These new samples were used in conjunction with a global CAMP data set to elucidate different mechanisms for supercontinent breakup and LIP formation. On the Eastern North American Margin, CAMP flows are found primarily in rift basins that can be divided into northern or southern groups based on differences in tectonic evolution, rifting history, and supercontinental inheritance. Geochemical signatures of CAMP suggest an upper mantle source modified by subduction processes. We propose that the greater number of accretionary events, or metasomatism by sediment melts as opposed to fluids on the northern versus the southern Laurentian margin during the formation of Pangea led to different subduction-related signatures in the mantle source of the northern versus southern CAMP lavas. CAMP samples have elevated Ni and low Ca in olivine phenocrysts indicating a significant pyroxenite component in the source, interpreted here as a result of subduction metasomatism. Different collisional styles during the Alleghanian orogeny in the North and South may have led to the diachroneity of the rifting of Pangea. Furthermore, due to a low angle of subduction, the Rheic Plate may have underplated the lithosphere then delaminated, triggering both the breakup of Pangea and the formation of CAMP.

Dedication

This thesis is dedicated to my husband for reading me his geology textbook when I couldn't fall asleep in the hope that it would help. I've been wide-awake ever since with my mind stimulated by the wonderful complexity of our planet.

Acknowledgements

I would like to thank my husband, William Whalen for his support and encouragement at every step – I couldn't have done this without you. My brother, Daniel Ashley showed me that graduate school could be done and was worth it. My dad, Rick Ashley supported me through tough times and gave great advice. My mom, Laurie Ashley supported me early on in my college endeavor and instilled in me a love of the outdoors and science at an early age.

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Attributions

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L. Whalen prepared sample powders that were then sent for analysis for major and trace elements at the GeoAnalytical Lab at Washington State University and at the Center for Elemental Mass Spectrometry at the University of South Carolina by M. Bizimis for radiogenic isotopes. L.Whalen also prepared samples to be sent to the New Mexico Geochronology Research Laboratory for age dating. L. Whalen mapped thick sections that were then analyzed with the electron microprobe for olivine phenocryst data by C. Vidito at Rutgers University. J. Puffer and B. Henika provided samples and valuable input on sample locations. L. Whalen drafted the manuscript and figures. All coauthors provided input on the drafting of the manuscript and figures. All interpretation and modeling of the data was done by L. Whalen and E. Gazel.

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Introduction

1.1 Large Igneous Provinces

Wilson cycles, or the formation and breakup of supercontinents, are an integral part of plate tectonics [Wilson, 1965, 1966]. However, a mechanism or trigger for initiating the breakup of the continental lithosphere is a fundamental missing piece of this unifying theory. Although large igneous province (LIP) formation has been linked to supercontinent breakup [Storey, 1995; Courtillot et al., 1999], the formation mechanisms of LIPs are still debated [King and Anderson, 1995; Lustrino, 2005; Campbell, 2007]. Nevertheless, some of the most significant mass extinction events in Earth's history correlate with LIPs [Courtillot and Renne, 2003] making LIP formation important not only for understanding mantle dynamics, but also for elucidating relationships between geological and biological processes during the evolution of our planet.

1.2 The Central Atlantic Magmatic Province

The Central Atlantic Magmatic Province (CAMP, Figure 1) is the LIP temporally related to the breakup of Pangea ~200 Ma [Marzoli et al., 1999; Blackburn et al., 2013] and is one of the largest LIPs in the geologic record, with a volume of 2.3 x 10 $\frac{5}{10}$ km and a surficial area of 10 $\frac{7}{10}$ km [McHone, 2003]. Thus, understanding the formation mechanism of CAMP can provide explanations for the formation of LIPs that share similar characteristics. Assessing the role of CAMP in the breakup of Pangea can also help to clarify the triggering mechanism responsible for the breakup of supercontinents. Some models for CAMP suggest that it may have formed from the impingement of a mantle plume on the lithosphere [e.g., May, 1971; Morgan, 1983; Anderson, 1982; White

and McKenzie, 1989; Hill, 1991; Wilson, 1997; Courtillot et al., 1999; Ernst and Buchan, 2002; Fokin, 2003]. In this scenario, a hot mantle upwelling impacts the lithosphere, the plume head undergoes decompression, melts, and emplaces the LIP [e.g., White and McKenzie, 1989; Wilson, 1997]. This mechanism is problematic for CAMP because no active hot spot or hot spot trail can be linked to the province, nor are there clear geochemical signatures to indicate plume activity or excess mantle potential temperatures [McHone, 2000; Puffer, 2001; Herzberg and Gazel, 2009]. Thus, alternative explanations such as edge-driven convection (EDC) [King and Anderson, 1995] have also been proposed for CAMP initiation [McHone, 2000; Deckart et al., 2005; Merle et al., 2011].

EDC relies on the difference in thickness between the thinner edge of the continent and the thicker interior, forming a temperature gradient that drives small-scale convection cells [King and Anderson, 1995]. Delamination is another shallow formation mechanism that has been proposed for some continental LIPs [Lustrino, 2005]. Delamination occurs when denser lower crust, lithospheric mantle, or underplated material separates or breaks away as either a planar feature or a Rayleigh-Taylor instability and sinks into the asthenospheric mantle [Bird, 1979; Houseman et al., 1981; Conrad and Molnar, 1997; Houseman and Molnar, 1997; Kay and Kay, 1993; Schott and Schmeling, 1998]. The resulting influx of hot asthenosphere will melt due to decompression, producing uplift, extension, and rifting [Bird, 1979; Houseman et al., 1981; Conrad and Molnar, 1997; Houseman and Molnar, 1997; Kay and Kay, 1993; Schott and Schmeling, 1998].

The goal of this study was to provide a viable formation mechanism for CAMP that explains the large volume of melt produced, the relatively cool mantle potential

temperatures, temporal and chemical evolution, as well as the relationship of this LIP to the breakup of Pangea. Despite the large amount of data available for some parts of CAMP there are limited data available for CAMP in Virginia. Therefore, diabase dikes were sampled from different locations around the Danville Triassic rift basin and in the Shenandoah Valley in southwest Virginia (GPS locations in Table 1). Our new data were combined with a more complete data set to address the formation mechanism of CAMP and its relationship to both the assembly and the breakup of Pangea. Additionally, our new samples from Virginia were used to assess the source components of CAMP using high-precision olivine chemistry [Sobolev et al., 2007] never applied to the LIP before.

1.3 Previous Work

Any attempt at assessing how Pangea broke up must examine if any of the inherited structures and/or chemical signatures from the breakup of the previous supercontinent, Rodinia, or protracted subduction leading to the formation of Pangea played a role. While previous authors [Schlische et al., 2003; Hatcher, 2010; Hibbard et al., 2010] have made huge strides toward a large-scale, integrated view of the breakup of Pangea, we combined their conclusions with some relatively new, relevant geophysical results [Benoit et al., 2014] and the results from our characterization of the source composition of CAMP samples from Virginia, allowing for a new look at the formation mechanism for CAMP and the breakup of Pangea.

1.4 Formation of Pangea: Differences in the Northern and Southern Appalachians

The Paleozoic Appalachian Orogeny records the multistage formation of the most

recent supercontinent, Pangea through several accretionary events [Hatcher, 2010]. After the Middle Ordovician-age Taconic Orogeny [e.g., Hibbard et al., 2007; van Staal et al., 2009; Hatcher, 2010; Hibbard et al., 2010] these accretionary events are not evenly distributed across the Laurentian margin, thus Hibbard et al. [2010] suggested the use of the New York promontory as the division between the northern and southern Appalachians. During the Late Ordovician through the Early Devonian, the northern margin records the accretion of the Ganderia and Avalonia terranes while the southern margin records the accretion of the Carolina terrane [van Staal et al., 2009; Hibbard et al., 2010]. The terminal step in the formation of Pangea was the Alleghanian Orogeny that occurred during the Carboniferous period when Gondwana collided obliquely with the northern portion of the Laurentian margin, then rotated clockwise eventually resulting in a head-on collision between Gondwana and the southern portion of the Appalachians. This resulted in the accretion of the Meguma Terrane in the North and the Suwannee Terrane in the South [Hatcher, 2002].

1.5 Timing and Age Progression of CAMP Magmatism

Recent work by Blackburn et al. [2013] using high-precision U-Pb geochronology on zircons from CAMP basalts definitively linked CAMP with the End-Triassic Extinction as well as constrained the initiation of CAMP to the North as opposed to the South, as previously thought [Wilson, 1997; Schlische et al., 2003]. Furthermore, CAMP lavas decrease in age from North to South. High-titanium quartz normative lavas represent the first pulse of CAMP magmatism with an age of 201.566 6 0.031 (North Mt. Basalt, Fundy, Nova Scotia) [Blackburn et al., 2013]. Olivine normative lavas, found

mostly in the South, are the youngest pulse and have an age of 200.916 6 0.064 (Butner intrusive, Deep River Basin, North Carolina) [Blackburn et al., 2013]. The rifting of Pangea proceeded in the opposite direction to CAMP magmatism, beginning first in the South [Schlische et al., 2003] (Figure 2).

1.6 Breakup of Pangea and CAMP Emplacement: Differences Between the Northern and Southern Appalachians

A series of fault-bounded rift basins related to the initial rifting of Pangea exist along the eastern margin of North America and the western margin of Africa [Olsen, 1997]. Significant differences between the basin history of the northern versus the southern Appalachians are evident through a comparison of the timing of sediment deposition between rift basins (Figure 2) [Olsen, 1997; Schlische et al., 2003]. In general, rifting began in the South and ended prior to the emplacement of CAMP basalts, depositing only Late Triassic-age strata [Schlische et al., 2003]. In the North, most CAMP flows thicken toward the upper border faults of rift basins indicating that they are late synrift flows [e.g., Olsen et al., 1989; Withjack et al., 1995]. Strata in the northern basins span the Triassic and Early Jurassic [Olsen et al., 1989; Olsen, 1997] with accelerated rates of sedimentation in the Jurassic [Olsen et al., 1989; Schlische and Olsen, 1990].

1.7 Supercontinental Inheritance From Rodinia

Rodinia, the supercontinent preceding Pangea, formed during the Grenville Orogeny (1.2–0.9 Ga) [Hatcher, 2010] and broke up over a 200 myr timespan, during which rifting occurred along what would become the eastern Laurentian margin [McClellan and Gazel, 2014]. Supercontinental inheritance, the geologic history of a previous supercontinent directing the evolution of its successor, is observed in the rifting record of the Newark, Gettysburg, Culpepper and Barboursville basins (Figures 1 and 2). Similarities between these basins have led to the suggestion that they represent one continuous basin [Faill, 2003] and collectively share specific traits with both the northern and southern rift basins. Like the southern basins, deposition in the Newark, Gettysburg, and Culpepper basins began in the Late Triassic, but in common with the northern basins they also contain Jurassic-age strata and synrift CAMP flows [Olsen, 1997].

These basins are located adjacent to the Pennsylvania salient, where the central Appalachian Mountains undergo a drastic change in strike [e.g., Lefort and Van der Voo, 1981; Wise, 2004; Ong et al., 2007]. Hibbard et al. [2010] suggested that the New York promontory, which separates first order distinctions between the two portions of the Appalachian orogen, might reflect an inherited structure related to the Neoproterozoic rifting of Rodinia. A failed Neoproterozoic rift was recently imaged adjacent to the Pennsylvania salient using wide-angle reflection and temporary broadband seismic data [Benoit et al., 2014]. The Scranton Rift is buried in the subsurface and based on adjacent fold and fault geometry, may have acted as a collisional ''backstop'' during the Alleghanian accretionary event, effectively shaping the Appalachian Orogeny [Benoit et al., 2014].

This Rodinia-related relic rift and associated underplated dense material [Benoit et al., 2014] were probably responsible for the change from oblique collision in the North to rotation and eventual head-on collision in the South during the Alleghanian Orogeny.

Furthermore, we propose that the transitional nature of the Newark, Gettysburg, and Culpepper basin histories [Schlische et al., 2003] are also due to this subsurface inherited feature which acted as a rigid ''buffer'' and effectively negated much of the uplift, which may have affected the northern and southern Appalachians throughout the Mesozoic [Frizon de Lamotte et al., 2015]. In this study we use the Scranton Rift to separate northern CAMP (located to the north of the Scranton Rift) [Dostal and Durning, 1998; Marzoli et al., 2011; Merle et al., 2013], southern CAMP (located to the south of the Scranton Rift [Callegaro et al., 2013; Mazza et al., 2014] and transitional CAMP (located within or nearby the Newark, Gettysburg, and Culpepper basins) [Marzoli et al., 2011; Merle et al., 2013].

Materials and Methods

2.1 Methods for Collected Data

Sample SPG-111 was selected for $\frac{40}{Ar}$ Ar geochronology because it contained ample biotite, an ideal mineral to date with this method. The sample was crushed, and sieved. Biotite was separated using a magnetic separator, heavy liquids, and hand picking. After being washed with HCl, phenocryst biotite separates and the standard Fish Canyon tuff sanidine (FC-2) (assigned age = 28.02 Ma [Renne et al., 1998]) were irradiated for 40 hours at the USGS TRIGA reactor in Denver, Colorado. Bulk separates were analyzed using the incremental heating age spectrum method (15 steps per analysis) utilizing a Argus VI mass spectrometer and a defocused 50 watt diode laser at the New Mexico Geochronology Research Laboratory.

Rock chips free of alteration (oxides, zeolites, etc.) were selected under a stereoscopic microscope and powdered in an alumina mill at Virginia Tech. Samples were analyzed for major (wt. %) and trace elements (ppm) at the GeoAnalytical Lab at Washington State University. Major elements were collected by x-ray fluorescence (XRF) on a ThermoARL XRF following standard XRF procedures [Johnson et al., 1999]. Trace elements were collected on solutions by an Agilent model 4500 ICP-MS. Data from two additional samples (042 Singers Glen and 12DJ Mosque 1) are from [Mazza et al., 2014].

Analyses of Sr, Nd, and Pb radiogenic isotope ratios were carried out at the Center for Elemental Mass Spectrometry, University of South Carolina following established techniques for this lab [e.g., Bizimis et al., 2013; Khanna et al., 2014].

Sample powders from the same aliquots used for major and trace elements were digested in sub-boiling Teflon-distilled 3:1 HF:HNO₃ (v/v) mixture, and the isotopes were analyzed on aliquots of a single digestion. Pb was separated on an anion resin in HBr, HNO₃ acids [e.g. Mahnes et al., 1984]. Sr and REE were separated from the bulk rock washes of the Pb chemistry on a cation resin in HCl. Sr was further purified on a Sr-spec resin and Nd on an Ln-resin (both from EICHROM, USA). The radiogenic isotope ratios were determined on a Thermo Neptune multi collector ICPMS with the PLUS upgrade. Sample introduction was with an APEX enhanced sensitivity spray chamber and high sensitivity cones (JET and X-skimmer configuration) resulting in Nd sensitivities in the order of 1400-1500 V / ppm. The NIST SRM-987 Sr standard was determined at 87 Sr 86 Sr $= 0.710320 \pm 0.000012$ (n=12) using ${}^{87}Sr/{}^{86}Sr = 0.1194$ for instrumental fractionation correction. All Sr-isotope ratios are reported relative to the 87 Sr⁸⁶Sr = 0.710250 for the NIST standard to correct for instrument bias. The LaJolla Nd standard was determined at ¹⁴⁴ Nd of 0.511858 ± 0.000007 (n = 10) using ¹⁴⁴ Nd = 0.7219 for fractionation correction. Pb isotope ratios were determined using the TI-addition technique [White et al., 2000]. The standard NBS-981 was determined at $^{206}Pb/^{204}Pb =$ 16.936 ± 0.001 , 207 Pb/ 204 Pb = 15.940 ± 00.1 , 208 Pb/ 204 Pb = 36.694 ± 0.003 (n=13).

A modified version of the high precision method of [Sobolev et al., 2007] was used to analyze 71 olivine phenocrysts from 7 different dikes in Virginia using only the most primitive, unfractionated (samples in olivine control) basalts. Data was collected at Rutgers University on a JEOL JXA-8200 Superprobe. Many of the olivine phenocrysts exhibited compositional zoning so 4-point traverses were done on several phenocryts

from each sample (resulting in 247 individual analyzes). A focused beam $(\sim 1 \text{ um})$ of 20 kV and 300 nA was used with peak count times: Si: 50s; Mg: 80s; Fe: 100s; Ni: 150s; Ca: 150s and Mn: 150s. To correct for instrumental drift the San Carlos olivine standard was analyzed at regular intervals during each analysis. Primary standards, statistics for the secondary standards and statistics for the olivine analyses are given in Tables 6 and 7. The average relative 2σ error for major and trace elements were: Si ~0.14%, Mg ~0.15%, Fe \sim 0.19% and Ni \sim 0.74%, Mn \sim 1.85, and Ca 1.39%. Detection limits (3 σ) for the major and trace elements were: Si ~0.004%, Mg ~0.004%, Fe ~0.003%, Ni ~0.001%, Mn \sim 0.002% and Ca \sim 0.002%. 2 standard errors for the San Carlos olivine standard (n=48) were Si ~0.17%, Mg ~0.12%, Fe ~0.08% and Ni 40 ppm, Mn 33 ppm, and Ca 15 ppm.

2.2 Data from the Literature

Our new data were incorporated into the geochemical data set from the literature for CAMP dikes and flows collected in Africa, Europe, and North and South America (Figure 1) [Bertrand, 1991; Dostal and Durning, 1998; Puffer and Volkert, 2001; Cebria et al., 2003; Jourdan et al., 2003; Marzoli et al., 2004; Deckart et al., 2005; Verati et al., 2005; Mahmoudi and Bertrand, 2007; Martins et al., 2008; Marzoli et al., 2011; Merle et al., 2011; Callegaro et al., 2013; Merle et al., 2013; Callegaro et al., 2014; Mazza et al., 2014]. We also compiled available radiogenic isotope data for the Coastal New England Magmatic Province (CNE) that overlaps with the onset of CAMP [McHone and Butler, 1984; McHone, 1992; Pe-Piper et al., 1992; Pe-Piper and Reynolds, 2000] and for the accreted terrenes where CAMP was emplaced [Pettingill et al., 1984; Sinha et al., 1996; Currie et al., 1998; Pe-Piper and Piper, 1998].

Results

3.1 Age Data

A single $\frac{40}{Ar}$ $\frac{39}{Ar}$ are was obtained for sample SPG111, making this the first CAMP sample dated in southwest Virginia. After evaluating the mean calculated age of 202.81 ± 0.55 Ma with the inverse isochron technique, the calculated age was 201 ± 2 Ma (Figure 3). This confirms the connection of this dike with the CAMP event of 201.566±0.031 Ma [Blackburn et al., 2013].

3.2 Major and Trace Elements

New major and trace element data are reported in Table 1, 2 and 3. Following nomenclature originally defined for CAMP lavas [Weigand and Ragland, 1970], the samples analyzed consist of low-Ti tholeiites: olivine normative and quartz normative basalts, which we will call here low-Ti basalts and basaltic andesites, respectively. The low-Ti basalt samples have primitive Mg#s ([molar MgO/FeO1MgO]*100) ranging from 64 to 73. SiO_2 , CaO and Al_2O_3 decrease with increasing MgO, while the opposite occurs for NiO, suggesting that olivine was the main fractionating phase. A primary magma was calculated from the most primitive low-Ti basalt sample, SPY681 (that required <10% olivine addition). Liquid lines of descent (LLDs) were modeled for CAMP low-Ti basalts using Petrolog3 [Danyushevsky and Plechov, 2011] showing that they are in olivine control (Figure 4a–4c). The Mg#s of the low-Ti basaltic andesites range from 42 to 53. CaO decreases with decreasing MgO, while K_2O increases and Al_2O_3 remains relatively unchanged, suggesting a cotectic crystallization of olivine and clinopyroxene (Figure 4), followed by other phases (e.g., plagioclase) as fractionation proceeded. The same primary

starting composition used for the Petrolog3 LLD models was too low in silica to replicate the trends of the low-Ti basaltic andesites. Primary magmas of varying degrees of enrichment in silica were estimated and then modeled in Petrolog3. A primary magma with 50.0 wt.% SiO_2 and 0.5 21.0 wt.% H_2O replicated the low-Ti basaltic andesite trends the best (Figure 4g–4i).

Our new CAMP samples, plotted in a primitive mantle normalized multi-element diagram [McDonough and Sun, 1995] (Figure 5) show relative high field strength element (e.g., Nb, Ta and Ti) depletions as well as large-ion lithophile element (LILE) enrichments. As expected, the low-Ti basaltic andesites are more enriched in trace elements relative to the basalts as a result of fractional crystallization discussed above.

3.3 Radiogenic Isotopes

Measured radiogenic isotope ratios, associated errors, and age-corrected isotope ratios (corrected to 200 Ma) are reported in Table 4. Age corrected isotope ratios are plotted in Figure 6. The basalts have lower $\frac{^{143}}{Nd}$ $\frac{^{144}}{Nd}$ $\frac{^{144}}{200Ma}$ (0.51221–0.51234), 206 204 207 207 207 204 208 208 208 204 208 204 209 204 209 204 209 204 209 209 209 209 209 209 20 38.27) and higher 87 Sr⁸⁶ Sr_{200Ma} ratios (0.70587–0.71075) than the basaltic andesites, which have $\frac{^{143} \text{Nd}^{144} \text{Nd}}{^{200} \text{Ma}}}$ 0.51230–0.51243; $\frac{^{206} \text{p}^{204} \text{Pb}}{^{200} \text{Ma}}}$ 18.52–18.65; 207 204 204 ${}^{15.60-15.64}$; 208 204 204 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 10 0.70625. Both the low-Ti basalts and basaltic andesites from Virginia sampled for this study plot in the range of published southern CAMP [Callegaro et al., 2013; Mazza et al., 2014] except for one basalt (sample PHT911Table 4), which has a high 87 Sr $>^{86}$ Sr $_{200Ma}$

value of 0.71075. Sample BLR531B, a low-Ti basaltic andesite increases the range of 206 Pb Pb _{200Ma} for southern CAMP to 18.65. Sample STS971, also a low-Ti basaltic 204 andesite is a radiogenic end-member for southern CAMP as it has a $^{207}Pb/^{204}Pb_{200Ma}$ value of 15.64, and a 208 Pb/ Pb_{200Ma} value of 38.44.

3.4 Mineral Data

New high-precision major and trace element data from olivine phenocrysts (Figure 7 and Table 5) show elevated Ni and Fe/Mn as well as low Ca and Mn relative to the values expected for peridotite derivative magmas [Sobolev et al., 2007; Qin and Humayun, 2008; Herzberg, 2011; Foley et al., 2013].

Discussion

4.1. Trace Element Signatures of CAMP Magmas

CAMP samples from Virginia analyzed for this study are similar to CAMP samples from the literature from all along the Eastern North American Margin [Dostal and Durning, 1998; Puffer and Volkert, 2001; Marzoli et al., 2011; Callegaro et al., 2013; Merle et al., 2013; Mazza et al., 2014] in that they display large-ion lithophile element (LILE) (e.g., Ba, Pb, K, Figure 5) and light rare earth element (LREE) enrichments and high-field strength element (HFSE) (e.g., Nb and Ta, Figure 5) depletions typical of arc magmas. Elevated LREE/heavy rare earth element (HREE) ratios alone do not necessarily imply a subduction-modified source, but taken together with low HFSE contents and no significant differences in melt fraction [Herzberg and Gazel, 2009], enrichment in LREE compared to HREE can be used as evidence of mantle metasomatism in subduction systems [Pearce and Peate, 1995]. This signature suggests, in accordance with Puffer [2001] that from a geochemical perspective CAMP lavas are broadly more arc-like than plume-like.

Subduction-sensitive Th/Yb and fluid-immobile Nb/Yb element ratios are particularly useful for distinguish- ing between subduction and mantle plume influenced environments. In Figure 8a, these element ratios from CAMP samples are compared to the mantle array as defined by global mid-ocean ridge basalt (MORB) and intraplate ocean island basalt (OIB) data. Like lavas from the Lesser Antilles, Marianas and Cascades arcs, most CAMP lavas (including the new samples from Virginia) plot above the mantle array, suggesting a subduction-modified source. We divide CAMP terranes (Figure 1) into northern, southern and transitional groups based on their location with

respect to the Scranton Rift. Southern CAMP lavas plot nearest to or within the mantle array indicating less of a subduction component in the South. High Th/Yb and Nb/Yb ratios of transitional and northern CAMP suggest mixing between relatively depleted and enriched arc- modified sources. Ce/Yb ratios of CAMP lavas show an increase in Ce/Yb from South to transitional to North (Figure 8b). In terms of Nb/U, another trace element ratio that is indicative of source compositions, northern and transitional CAMP have lower values than southern CAMP samples (Figure 8b) placing them in the same Nb/U space as lavas from an arc-modified source (Nb/U \leq 20) [Hofmann et al., 1986; Hofmann, 2007]. Southern CAMP spans the entire range of Nb/U ratios including those derived from nonsubduction modified sources such as MORB and OIB [Hofmann et al., 1986; Hofmann, 2007]. Most of the new samples from Virginia plot within the bounds of published southern CAMP [Callegaro et al., 2013], with the exception of a few low-Ti basaltic andesites that plot at slightly higher Th/Yb and Nb/Yb ratios suggesting a stronger subduction influence for these samples. In Nb/U - Ce/Yb space, the low-Ti basalts collected in Virginia for this study plot within the confines of published southern CAMP data, with the low-Ti basaltic andesites plotting as the high Ce/Yb end-member of southern CAMP.

4.2 Sr-Nd-Pb Radiogenic Isotope Signatures of CAMP Magmas

Radiogenic isotopes do not fractionate by melting or crystallization processes, thus they provide key information about the geochemical signature of the melt source components. We age-corrected Sr-Nd-Pb radiogenic isotopic ratios to 200 Ma for our new data (Table 4) as well as for northern, transitional and southern CAMP, and for

CAMP sampled in Africa, Europe, and South America. Additionally, we included Sr-Nd-Pb radiogenic isotope ratios for the accreted terranes of Avalonia [PePiper and Piper, 1998], Meguma [Currie et al., 1998], and Carolina [Pettingill et al., 1984; Sinha et al., 1996]. We also included, in this isotopic comparison data from the Coastal New England magmatic province (CNE) [McHone and Butler, 1984; McHone, 1992; Pe-Piper et al., 1992; Pe-Piper and Reynolds, 2000] because its age range (255 - 202 Ma) broadly overlaps with the onset of CAMP magmatism at 200 Ma.

Northern and transitional CAMP lavas have higher $\frac{^{143}}{Nd}$ $\frac{^{144}}{Nd}$ $\frac{^{144}}{200Ma}$ and Pb isotopic ratios while southern CAMP covers a wider range for both 87 Sr 86 Sr ${}_{200Ma}$ ratios, ¹⁴³ Nd^{$/$} Nd_{200Ma} and Pb isotopic ratios (Figures 6a–6c). CAMP lavas plot in a mixing line between depleted MORB mantle (DMM) (Figure 6a), an enriched source and a HIMU-like (high $\mu = \frac{^{238} - ^{204}}{U}$ Pb) component (Figures 6b and 6c). South American CAMP also plots toward a HIMU component along with the Coastal New England lavas on a S_1^{87} S_5^{86} Sr/ S_7^{86} Sr_{200Ma} - S_7^{143} Nd/ S_7^{144} Nd_{200Ma} diagram (Figure 6a), however these high-Ti tholeiites may represent a younger pulse of CAMP magmatism recording the transition to oceanic crust [Deckart et al., 2005].

In 143 Nd^{144} $\text{Nd}_{200\text{Ma}}$ - 206 Pb^{204} $\text{Pb}_{200\text{Ma}}$, as well as in Pb isotope space, northern and transitional CAMP plot alongside the Meguma and Avalonia terranes (Figure 9), while the Carolina terrane plots closer to southern CAMP. Erosion of the Avalonia, Meguma and Carolina terranes prior to accretion could have led to sediment input during subduction, which would then be incorporated into the upper mantle through the input of sediment melts into the overlying mantle wedge beneath Laurentia, accounting for the Nd

and Pb isotopic composition of the northern and transitional CAMP lavas [Merle et al., 2013].

For northern and transitional CAMP this is evidence that the source of these magmas inherited their enriched continental-like trace element and radiogenic isotope composition from subduction-related processes as opposed to crustal contamination, which has been shown to represent a minimal contribution for any of the CAMP terranes [Puffer, 2001; Merle et al., 2011; Callegaro et al., 2013; Callegaro et al., 2014]. The low 187 Os/ 188 Os ratios of CAMP samples also argue against significant crustal contamination

processes in the generation of this LIP [Merle et al., 2011; Callegaro et al., 2013].

Furthermore, assimilation-fractional-crystallization (AFC) calculations starting with an Atlantic plume [Holm et al., 2005] or MORB [Gale et al., 2013] composition that was then contaminated with local Blue Ridge basement (detailed in section 4.3) were unsuccessful in replicating the trace element and Sr-Nd-Pb compositions of the low-Ti basalts and basaltic andesites analyzed in this study.

AFC models by Merle et al. [2013] using both a plume and a MORB starting composition also argue against crustal contamination as the models require an unrealistic amount (up to 35%) of assimilation to get close to the radiogenic isotopes of CAMP samples while keeping primitive mantle-derived major element com- positions. On the other hand, calculations to reproduce northern CAMP lavas required only 3–5% sediment [Merle et al., 2013], which is within the range (2–6%) of the sediment budget of arc lavas [Plank, 2005].

As a current example of this process, the Lesser Antilles' highly radiogenic isotope signature has been attributed to sediment derived from the South American

cratonic basement and transported by the Orinoco River [e.g., White and Dupr e, 1986] with Lesser Antilles basalts requiring a sediment component of up to 10% [Carpentier et al., 2008]. Transport of eroding sediment via rivers into the subduction trench, as well as by deep underwater currents may account for southern CAMP's isotopic range from the less evolved Carolina through Meguma and Avalonia. Alternatively sediment may have played less of a role in the metasomatization of the mantle beneath the southern margin of Laurentia.

4.3 Assimilation Fractional Crystallization Modeling

A database of local Blue Ridge basement in Virginia [*Pettingill et al.,* 1984; *Sinha et al.,* 1996] was compiled and used to assess the possible crustal contribution to our sample set. We limited our crustal samples to those with Sr, Nd and Pb radiogenic isotopes in order to check for consistency between systems. We used the average MORB composition calculated by *Gale et al.* [2013] and a basanite from Cape Verde [*Holm et al.,* 2005; *Millet et al.,* 2008] to model an Atlantic plume starting composition for modeling assimilation fractional crystallization (AFC)[*DePaolo,* 1981]. For all models using a MORB starting composition $r(r = dMa/dfc)$ was 0.5 (Figure 10a-f). For models using a plume starting composition (Cape Verde) $r = 0.7$ Figure 10g-l). The majority of the partition coefficients used are from *Rollison* [1993] with Pb from *McKenzie and O'Nions* [1991]. All isotopes were age-corrected to 200 Ma.

Using MORB as the starting composition, sample H-13-81 and similar samples out of the Blue Ridge crust database are able to reproduce our sample set in 87 Sr⁸⁶ Sr –

144 Nd/ Nd space (Figure 10a). H-13-81 is a Grenville-age ferrodiorite from the Rose's Mill Pluton in the Blue Ridge [*Pettingill et al*., 1984]. However, AFC models using H-13-81 as a contaminate fail to reproduce the CAMP sample trends in Pb isotope space (Figure 10b-d). Only sample HP-24 as a contaminate produced AFC models capable of explaining the Pb isotopes of the basaltic andesites collected for this study as the rest of the database had much too low $\frac{^{206}Pb/^{204}}{Pb}$ as well as most having too low $\frac{^{207}Pb/^{204}}{Pb}$ and 208 $Pb/^{204}$ pb. Sample HP-24 is from the Roseland Anorthosite complex, a Grenville-aged anorthosite that forms the core of the Blue Ridge anticlinorium [*Pettingill et al.,* 1984]. Sample M32 was also able to explain some of the basaltic andesite's Pb isotope composition, though not as well as HP-24. Sample M32 is a felsic dike collected in the vicinity of basaltic sample PHT 911 near Philpott Lake. Muscovite separates from sample M32 gave an 40 Ar^{/39} Ar age of 332.6 \pm 4.8 Ma. Both HP-24 and M32 fall short on a 206 $Pb²⁰⁴$ $Pb - Nd¹⁴³$ Nd diagram with M32 only replicating the samples when r is increased to 0.9, which is practically mixing. HP-24 also fails to explain the samples ${}^{87}_{\text{Sr}}$ ${}^{86}_{\text{Sr}}$ ${}^{144}_{\text{Na}}$ ${}^{143}_{\text{Na}}$ Nd. Using a plume starting composition, only AFC (using r = 0.7) with H-13-81 as a contaminant could replicate the trend of the CAMP samples in $\frac{87}{143}$ Sr^{/86} Sr – Nd^{/143} Nd space (Figure 10g). However, models with H-13-81 still failed to replicate the trend of the CAMP samples in Pb isotope space (Figure 10h-j).

Trace element data was not available for the crust samples from the Blue Ridge, so upper, middle, lower and total crust values from *Rudnick and Gao* [2003] were used in addition to sample M32. Using a MORB starting composition, upper, middle, and total crust as well as M32 can replicate subsets of the trend of the basaltic andesites on a

Ce/Yb-Gd/Yb plot, while nothing replicates the basalts as they plot at much lower Gd/Yb values than the MORB starting composition (Figure 10e). However, on a Ce/Yb-Nb/U diagram only M32 replicates the trend of the basaltic andesites (as well as the basalts) (Figure 10f). All crustal compositions on a Ce/Yb- Nb/U plot can replicate a small subset of the basalts. Using a plume starting composition, AFC models for trace element ratios were completely unsuccessful in terms of replicating the trends of the CAMP samples (Figure 10k-l).

 Beginning with either an average MORB or an Atlantic plume (Cape Verde) starting composition, no crustal composition that we tried adequately replicated the basalts, or the basaltic andesites in terms of Sr-Nd-Pb isotopes and trace elements confirming what others have found, that crustal contamination can not at this time be used to explain the geochemical trends of CAMP lavas [e.g. *Puffer,* 2001; *Merle et al*., 2011; *Callegaro et al*., 2013; *Callegaro et al*., 2014]. That the more successful models suggest not AFC, but rather mixing supports the conclusion that sediment from erosion of Grenville-age terranes may have been incorporated into the mantle through subduction [*Merle et al.,* 2013].

4.4 Discriminating Between Metasomatism by Fluids or Sediment Melt Components in CAMP

Magmas Merle et al. [2013] showed that northern and transitional CAMP were influenced by sediments or sediment melts based on LREE and Th/Yb coupled with initial Nd-isotopes [Woodhead et al., 2001]. On a Ba/La-Th/Yb diagram (Figure 11a), northern and transitional CAMP plot along the increasing Th/Yb trend observed for

several arcs, which has been interpreted as incorporation of a sediment component [e.g., Class et al., 2000]. Northern and transitional CAMP also have higher middle rare earth element (MREE) contents relative to heavy rare earth elements (HREE) than southern CAMP as indicated by higher Dy/Yb values on a Dy/Yb - Dy/Dy* diagram (Dy/Dy* = $\frac{10}{2}$ $\frac{1}{2}$ $\frac{10}{2}$ $\frac{10}{2}$ $\frac{9}{13}$ (Figure 11b) [Davidson et al., 2013]. Dy/Dy* and Th/Yb correlate with $\frac{^{143}}{Nd}$ $\frac{^{144}}{Nd_{200Ma}}$ for northern ($\frac{^{2}}{R}$ 50.77, and 0.55, respectively) and transitional (R^2 5 0.91, 0.35, respectively) CAMP (Figures 11c and 11d). Taken as a group, Th/Yb and Dy/Dy* for northern and transitional CAMP also correlate with ¹⁴³ Nd^{$/$} Nd_{200Ma} (R^2 50.81, 0.55, respectively) (Figures 11c and 11d). Th/Yb for southern CAMP does not change as Ba/La increases (Figure 11a) suggesting a limited role for sediment melt input and more of a fluid-dominated influence [McCulloch and Gamble, 1991; Woodhead et al., 2001]. There is no correlation between $\frac{^{143}}{Nd}$ $\frac{^{144}}{Nd_{200Ma}}$ and Th/Yb (Figure 11c) and only a weak correlation between $\frac{^{143}}{Nd}$ $\frac{^{144}}{Nd_{200Ma}}$ and Dy/Dy* for southern CAMP (Figure 11d) $(R^2 50.21)$.

On a Dy/Dy*-Dy/Yb plot, CAMP samples plot similarly to arc samples as they plot along the MORB array of Davidson et al. [2013], but offset toward lower Dy/Yb values (Figure 11b) [Davidson et al., 2013]. Davidson et al. [2013] suggested that the negative trend of arc data toward lower Dy/Dy* and higher Dy/Yb values as a possible influence of sediment melts. We suggest that the sediment signature was incorporated into the subcontinental mantle by sediment melts during the Paleozoic subduction that formed Pangea [Pegram, 1990; Puffer, 2001, 2003; De Min et al., 2003; Deckart et al., 2005; Dorais and Tubrett, 2008; Merle et al., 2011, 2013; Murphy et al., 2011; Callegaro

et al., 2013]. This interpretation is strengthened by the Th/Yb and Ce/Yb trends (Figure 6) [Woodhead et al., 2001; Hawkesworth et al., 1993, 1997] as well as strong correlations between Dy/Dy* and 143 Nd/ 144 Nd_{200Ma} (Figure 11d) for northern and transitional CAMP.

Northern and transitional CAMP show positive trends between Dy/Dy* and Dy/Yb (Figure 11b). A subset of mostly southern CAMP (including the Virginia basalt samples analyzed for this study) plot within the lower lefthand corner of the diagram $(Dy/Dy^* < 1.0, Dy/Yb < 1.55$) and also show a positive trend between Dy/Dy^* and Dy/Yb. Samples that plot in this corner of the diagram have U-shaped REE patterns, which Davidson et al. [2013] suggested indicates amphibole or clinopyroxene fractionation. Nevertheless, in our samples there is no correlation between Dy/Dy* and MgO, and some of these samples are in an olivine control trend, indicating instead that these U-shaped REE patterns are a feature inherited from the source. U-shaped REE patterns from mantle xenolith samples (Figure 11b) have been interpreted as the result of melt-rock reaction [e.g., Chalot-Prat and Boullier, 1997; Lenoir et al., 2000; Zhang et al., 2012; Ackerman et al., 2013; Bénard and Ionov, 2013] due to melt migration through the mantle [Navon and Stolper, 1987; Ackerman et al., 2007, 2013].

4.5 CAMP Source Lithology Composition From High-Precision Olivine Chemistry and Modeled Primary Magmas

High-precision olivine chemistry has been used as a powerful tool for the evaluation of source lithology composition [Sobolev et al., 2005, 2007; Herzberg, 2011]. Several studies have attempted to include the effects of pressure and temperature in parameterizations of D_{Ni} $O1/I$ [e.g., Li and Ripley, 2010; Niu et al., 2011; Matzen et al.,

2013] with varying degrees of success [Herzberg, 2011; Herzberg et al., 2013, 2014], however the Beattie et al. [1991] parameterization is only dependent on D_{MgO} Ol/L , which effectively accounts for temperature and will be used here. The additional terms used by other studies [e.g., Li and Ripley, 2010; Niu et al., 2011; Matzen et al., 2013] to account for pressure and temperature negatively impacted the ability of the parameterization to replicate experimentally derived D_{Ni} which may be due to these terms being model -Ol/L dependent [Herzberg et al., 2013]. The Beattie et al. [1991] model has been the most reliable choice for replicating experimentally derived Ni values in olivine as this model produces the lowest root mean square error (RMSE=1.1) while the temperature dependent model from Matzen et al. [2013] yields a RMSE of 2.5 and the pressure dependent (0–3 GPa) model of Niu et al. [2011] yields a RMSE of 2.1 [Herzberg et al., 2014]. Ni systematics in olivine phenocrysts have therefore been shown to be a viable tool for evaluating source lithology [Sobolev et al., 2005, 2007; Wang and Gaetani, 2008; Herzberg, 2011].

CAMP olivine data collected from basalts in Virginia for this study show elevated Ni and low Ca concentrations relative to peridotite-derived olivines indicating a pyroxenite source component for CAMP [Sobolev et al., 2007; Herzberg, 2011]. CAMP olivine phenocrysts systematically plot alongside data from Mauna Kea or at transitional values between data from mid-ocean ridges and Mauna Kea (Figure 7). The data from Mauna Kea have been interpreted as coming from a second-stage pyroxenite source that formed from the reaction of a high-silica melt from eclogite with peridotite. Ca and Fe/Mn values obtained for olivine phenocrysts from CAMP plot between samples from Mauna Kea and MORB and may indicate both peridotite and pyroxenite source

lithologies for CAMP [Sobolev et al., 2005]. Our new data contrast with those published by Callegaro et al. [2013], who suggested that it was unlikely that the source of CAMP contained a pyroxenite component based on their analyses of olivine phenocrysts. Our results, which utilize a modified high-precision method from Sobolev et al. [2007] indicate that a pyroxenite component probably contributed significantly to the source of CAMP.

In order to determine which type of pyroxenite was involved, CAMP primary magma compositions were calculated by taking the bulk rock compositions of lavas in olivine control and adding olivine until equilibrium with the maximum forsterite (Fo) content observed in CAMP magmas ($F_{O_{89}}$) [Callegaro et al., 2013] was achieved (using a variable Fe-Mg partition coefficient for olivine–liquid with an initial value of 0.32 [Roeder and Emslie, 1970; Toplis, 2005]) (Tables 8 and 9). These primary magma compositions contain $11.5-19.8$ wt.% MgO, and $46.93-52.43$ wt.% SiO₂. The modeled results are plotted in the pseudoternary system olivine-calcium Tschermak's (CATS) pyroxene-quartz projected from diopside [O'hara, 1968] (Figure 12). CAMP primary magmas project onto the high-SiO₂ pyroxenite side of the pyroxene-garnet plane, which acts as a thermal divide [Kogiso et al., 2004]. Source lithologies with excess silica (olivine-free source) can produce primary magmas that plot on the high-SiO₂ side of the diagram [Herzberg, 2011]. This suggests that CAMP primary magmas likely melted from a silica-rich, olivine-free pyroxenite source lithology, which could be the result of highsilica melts formed from subducted material (sediment, subducting oceanic crust) that reacted with mantle peridotite, in a process similar to that suggested by Sobolev et al. [2005, 2007].

The new olivine data together with trace element signatures and radiogenic isotopes argue for a significant sediment component in the source of CAMP lavas. As the ratio of silica-rich melt to peridotite increases, the source will change from refertilized peridotite to olivine-bearing pyroxenite, and then to an olivine-free pyroxenite. Additionally, the Ni and Fe/Mn of olivine phenocrysts crystallizing from the primary melt will also increase, while Ca decreases [Herzberg et al., 2014]. Further supporting the possibility of high-silica pyroxenite, the modeled LLD for the basaltic andesites analyzed in this study require a primary magma rich in silica (Figure 4). Northern and transitional CAMP magmas have on average even higher $SiO₂$ contents suggesting the possibility of a higher contribution of pyroxenite-derived melt in the source than those from the South, which resulted in more evolved primary magmas no longer in an olivine-control trend.

4.6 Evaluation of Mechanisms for Pangea Breakup and the Generation of CAMP

Mantle plume activity has been suggested as the formation mechanism for LIPs [White and McKenzie, 1989], but because the plume model is inconsistent with the formation of CAMP alternative explanations such as edge-driven convection (EDC) [King and Anderson, 1995] have been invoked. However, EDC does not explain the observed differences between northern and southern CAMP. More crustal thickening occurred in the South during the Alleghanian Orogeny [Hatcher, 2002], which could lead to a greater difference in the thickness between the edge of the continental lithosphere and the orogenic root. A substantial difference in lithospheric thickness can cause a localized convection cell to form in the mantle, which could explain earlier rifting in the southern basins. However, EDC does not explain why rifting was accompanied by synrift

magmatism in the North but not in the South as would be expected. Another issue with the EDC model is that Missenard and Cadoux [2012] show that EDC cannot persist if plate velocities exceed 1 cm a . Absolute plate motions are not available for North America for the Triassic, but Ruiz-Martínez et al. [2012] calculated that Pangea was moving at an average speed of 8 cm/yr at 200 Ma, using Africa as a fixed reference in order to approximate absolute velocities. This suggests that EDC would not have been viable in the mantle beneath Pangea at the time of rifting.

Continental insulation of the mantle leading to elevated mantle temperatures and magmatism has been suggested as a formation mechanism for CAMP [Anderson, 1982; Verati et al., 2005; Coltice et al., 2007, 2009; Herzberg and Gazel, 2009; Hole, 2015]. Although this model is consistent with reported mantle potential temperatures, it does not explain why rifting is asynchronous with magmatism in the South, nor the age progression of CAMP magmatism. Geodynamic models indicate the magmatism induced by continental insulation would be tectonically controlled [Coltice et al., 2009], but dikes in the South cross- cut both pre and synrift structures, indicating that magmatism was not structurally controlled [Schlische et al., 2003].

Delamination could be a formation mechanism for LIPs [Lustrino, 2005]. Ductile delamination is controlled by phase changes in the lithosphere (resulting in density instabilities) as well as low viscosity [Conrad and Molnar, 1997; Houseman and Molnar, 1997; Schott et al., 2000; Tanton and Hager, 2000; Elkins-Tanton, 2005]. Delamination may be common during supercontinent formation [Kay and Kay, 1993] as it is likely to occur in areas that have undergone crustal shortening [e.g., Kay and Kay, 1993; Schott and Schmeling, 1998; Conrad, 2000; Morency et al., 2002]. The eastern margin of

Laurentia experienced subduction related to several collisional events [Hatcher, 2010; Hibbard et al., 2010]. Both the orogenic keels formed during these events and the subducting plates themselves are likely candidates for delamination.

Reduced crustal thicknesses at the center of the Appalachian orogenic belt in Newfoundland [Hall et al., 1998] could indicate delamination. A fossil anisotropy indicative of extension perpendicular to the Appalachian Orogeny was detected using shear-wave birefringence across the New England region [Levin et al., 2000]. The anisotropy may have resulted from Late Paleozoic delamination and extension [Levin et al., 2000]. Based on the uniformity of the anisotropy layer, it must post-date the Alleghanian Orogeny. There- fore, the proposed delamination event could be related to the formation of CAMP near the Triassic-Jurassic boundary.

Finally, CAMP is part of the group of continental LIPs with arc-like geochemical signatures [Puffer, 2001]. Similarities between the LIPs with arc affinities and arc magmas may be due to the melting of subduction- metasomatized mantle [Pegram, 1990; Puffer, 2001, 2003; De Min et al., 2003; Deckart et al., 2005; Dorais and Tubrett, 2008; Merle et al., 2011, 2013; Murphy et al., 2011; Callegaro et al., 2013]. Subductionmetasomatized lithosphere is also more likely to delaminate due to heating and hydration, which lower its viscosity [Elkins- Tanton, 2005] and melt emplacement [Jull and Kelemen, 2001] and removal, which can leave behind mafic residues that can lead to density instabilities [Herzberg et al., 1983; Kay and Kay, 1993; Elkins-Tanton, 2005].

4.7 Proposed Model for the Breakup of Pangea and CAMP

Using the Scranton Rift to demarcate northern, transitional, and southern CAMP
groups, the geochemical variation between northern and southern CAMP could be attributed to a difference in the amount of subduction experienced by the northern and southern margins of Laurentia. While the Scranton Rift represents a possible structural and not a chemical control on the lavas themselves, this geochemical variation is less obvious, without separating out the CAMP flows preserved in the rift basins along the east coast of North America into groups based on their position relative to the Scranton Rift. If the Scranton Rift did act as a ''collisional backstop,'' causing a rotation in the direction of collision between Gondwana and Laurentia, this may have led to a change in the angle of subduction. This could affect the rate of subduction erosion [Keppie et al., 2009; Stern, 2011] and thus the amount of sediment incorporated into the mantle. Smaller angles of subduction favor subduction erosion of the upper plate [Keppie et al., 2009] and could explain the more prominent sediment signal in northern and transitional CAMP as opposed to southern CAMP.

We propose that differences in the accretionary history of the northern and southern Appalachians (Figure 13a) can account for the diachroneity in rifting, the chemical differences in CAMP lavas from the North and South, and could be responsible for triggering for the breakup of Pangea. Subduction of the Rheic Plate [Moran et al., 2007; Woodcock et al., 2007] at a very low angle (Figure 13b) may have resulted in the under- plating of the slab to the base of the lithosphere beneath Laurentia. During the Alleghanian collisional event, oblique subduction in the North may have led to a jamming of the subduction zone when the colli- sional front impacted the Scranton Rift and could no longer advance (Figure 13b). This blocking of the subduction zone may have led to a rotation of the subduction direction, as seen for example in the subduction

of the Hikurangi Plateau beneath New Zealand [Davy, 2014], resulting in head-on collision in the South (Figure 13c).

The head-on collision of Gondwana with the southern portion of Laurentia (Figure 13c) possibly led to greater overthickening of the crust in the South than in the North. This resulted in a denser orogenic keel surrounded by a less dense asthenospheric mantle and to earlier orogenic collapse and delamination [Sacks and Secor, 1990; Samson et al., 1995] as documented by the onset of rifting in the South at 230 Ma, probably with a similar situation in the Fundy and Argana basins in the North. While the small episodes of earliest rifting in the North were relatively restricted to the Argana and Fundy basins, rifting in the South was widespread at 230 Ma, but unaccompanied by volcanism. This initial orogenic collapse in the South may have served to heat the upper mantle as hotter material ascended to replace the foundering material permitting magmatism closer to 200 Ma [Nelson, 1992]. Additionally, the upper mantle beneath Pangea may have been warmer due to continental insulation [Anderson, 1982; Coltice et al., 2009; Herzberg and Gazel, 2009; Hole, 2015].

Subduction of the Rheic Plate continued in the North, where the slab was not constricted by the Scranton Rift, straining and eventually tearing the slab (Figure 13e). A small tear in a subducting slab can propagate laterally due to slab pull [Wortel and Spakman, 2000]. Tectonic events leading to the formation of the Central Range of New Guinea and the Talamanca Range in Central America show that the jamming of a subduction zone can lead to a slab tear, delamination, and magmatism [Cloos et al., 2005; Gazel et al., 2011]. Potentially, a tear in the Rheic slab could have led to mantle upwelling, which over time heated and destabilized the underplated oceanic slab

eventually resulting in delamination, which triggered more rifting in the North. In agreement with geodynamic models of lithospheric delamination, [Elkins-Tanton, 2005] approaching the eruption of CAMP and continuing into the Jurassic, there was active subsidence with an increase in the sedimentation rate right at the time of eruption (Figure 14) [Olsen, 1997; Schlische et al., 2003].

Uplift due to mantle upwelling could explain the hiatus in sedimentation in the Fundy Basin in Nova Scotia [Schlische et al., 2003] (Figures 2 and 14) during the Late Triassic (230–215 Ma). Thermal doming has been suggested to explain the Late Triassic unconformity in the CAMP basins in Nova Scotia and Morocco [Frizon de Lamotte et al., 2015]. Late Triassic alkaline Coastal New England (CNE) magmatism [McHone and Butler, 1984; McHone, 1992; Pe-Piper et al., 1992; Pe-Piper and Reynolds, 2000] peaks during the hiatus in sedimentation in the Fundy Basin (Figure 14) and could represent an early stage of rifting or uplift (Figure 13e) prior to the main phase of rifting [Ross, 1992; Swanson, 1992] as high-potassium silica-rich magmas preceding mafic, extensionally related magmas agrees with the delamination model of Kay and Kay [1993]. Alternatively CNE lavas may be from the slab tear itself, which acted as a trigger for the delamination event responsible for CAMP through heating of the underplated, now eclogitized slab, reducing its viscosity and increasing the likelihood of delamination (Figure 13e). The oldest $\frac{^{40}}{Ar}$ Ar age reported for CNE is 246 \pm 4 for a dike in Massachusetts [Ross, 2010]. While the youngest $\frac{40}{Ar}$ Ar ages reported for CNE dikes are in Plymouth, Nova Scotia of 203 ± 15 [Pe-Piper and Reynolds, 2000] with the oldest CAMP lava flows located nearby in the Fundy Basin, Nova Scotia. We suggest this decrease in age in the CNE dikes from closer to the Scranton Rift toward the site of the

onset of CAMP magmatism may indicate the direction of the initial tear in the Rheic slab.

Continued heating due to mantle upwelling through the slab tear eventually led to slab foundering in the North, culminating in the upwelling that led to CAMP magmatism (beginning in the Fundy Basin on Laurentia and in the Argana Basin on Gondwana) (Figures 1 and 13f). The magmatism was voluminous and extensive due to heating from the upwelling asthenosphere, as well as the presence of a significant pyroxenite component derived from previous subduction events (Figure 13a). Subduction-related volatiles like $H₂O$ added to the overlying mantle wedge by arc metasomatism helped to reduce the melting temperature [e.g., Hirschmann et al., 1999] increasing the amount of melting achieved at lower temperatures. Melts of the lithosphere that had been metasomatized during past subduction events could be responsible for the arc-like magmas typical of CAMP [Puffer, 2001, 2003], as well as the low $\frac{187}{\text{Os}}$ Os combined with enriched Sr-Nd-Pb isotopic ratios [Callegaro et al., 2013; Merle et al., 2013]. Upwelling in the North propagated to the South, where earlier heating may have facilitated melting [Nelson, 1992]. This upwelling could have then facilitated the weakening of the remaining slab beneath the southern portion of the margin of Laurentia

Conclusions

The northern Appalachians are the product of at least four different orogenic events terminating with the accretion of Ganderia, Avalonia and Megmua, while the southern Appalachians resulted from the accretion of Carolina, and Suwannee terranes. The difference in the number and size of accretionary events is consistent with an increase in arc-modification of the mantle beneath Laurentia in the North. Different accretionary histories may have played a part in the different trace element chemistries of the resultant CAMP lavas while the isotopic signature of the lavas reflects the incorporation of eroded sediment from adjacent accreted terranes into the mantle by subduction, particularly in northern and transitional CAMP.

The Scranton Rift, as an example of supercontinental inheritance, may have influenced the formation of Pangea by acting as a collisional backstop and leading to a rotation of the direction of subduction. The Scranton Rift may have also influenced the breakup of Pangea as the underplated rift material may have had some structural control over the basins that formed nearby. Additionally, geochemical trends showing evidence of more metasomatism of the mantle by subducted sediment melts are observed in the CAMP basalts that were emplaced in the basins north of and adjacent to the Scranton Rift versus the basins located to the South.

Major and trace element chemistry from olivine phenocrysts indicate a pyroxenite component for CAMP basalts based on elevated Ni, low Ca and some elevated Fe/Mn values. Calculated CAMP primary magmas sug- gest that the source of CAMP may be the result of a reaction between a silica-rich melt and peridotite. Due to the ubiquitous arc signature in CAMP lavas we interpret this pyroxenite component as the result of

metasomatism of the upper mantle by previous instances of subduction, possibly in the form of sediment melt.

We suggest that the combination of lithospheric delamination, slab break off, and mantle upwelling is the result of the protracted accretionary history of Pangea, although aspects of this model still require further exploration. For instance, the exact timing of delamination of the Rheic slab is complicated by the extensive erosion in the South and a general lack of consensus on the subduction direction during the final closure of Pangea.

Finally, CAMP is not responsible for the breakup of Pangea, but is itself the result of supercontinental inheritance. As supercontinents are the products of many different processes, it stands to reason that the breakup of each supercontinent will be as unique and complex as the events leading to their formation.

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Figures

Figure 1. Map of CAMP modified from Deckart et al. [2005]. Continents are in the prerift configuration of Pangea after Bullard et al. [1965]. CAMP exposures and boundary after McHone [2003]. Mesozoic rift basin loca- tions: F, Fundy; A, Argana; DF, Deerfield; H, Hartford; P, Pomperaug; N, Newark; G, Gettysburg; C, Culpepper; T,

Taylorsville; NO, Norfolk; R, Richmond; FM, Farmville; D, Danville; DR, Deep River from Schlische et al. [2003] and Olsen [1997]. Accreted terrane boundaries from Hibbard et al. [2010] and Hatcher [2010]. It should be noted that the extension of the Carolina terrane to the North and East beneath the coastal plain is based on subsurface data and is much less certain [Hatcher, 2010]. Alternatively the more northern portion of Carolina could be part of Avalonia [Hatcher, 2010]. The Scranton Rift location is from Benoit et al. [2014].

Figure 2. Rifting and sediment depositional history of Mesozoic rift basins after Olsen [1997]. Rift basins from left to right: northern basins: F, Fundy; A, Argana; DF, Deerfield; H, Hartford; P, Pomperaug; transitional basins: N, Newark; G, Gettysburg; C, Culpepper; southern basins: T, Taylorsville; R, Richmond; N, Norfolk; FM, Farmville; D, Danville/Deep River; DR, Deep River; SG, South Georgia. The average age of CAMP and timing of the End-Triassic Extinction (ETE) are from Blackburn et al. [2013]. Rifting and deposition begins and ends earlier in the southern than in the northern basins. Additionally, synrift CAMP flows are absent from the southern rift basins. Deposition in the Newark, Gettysburg, and Culpepper basins begins in the Late Triassic, as in the case with the southern basins, but continues into the Jurassic like the northern basins. Age constraints for basin fill rely on biostratigraphy, paleomagnetic data and Milankovitch cyclicity and are poorly constrained [Olsen, 1997]. Shown here are the best estimates of maximum ages based on the available information.

Figure 3. ⁴⁰ ³⁹ Ar age dating results. A) Age spectra was produced for sample

A)

B)

SPG-111. After 82% of the 39 Ar was released a weighted mean average of 202 \pm 0.55Ma was obtained. B) Evaluation with the inverse isochron technique yielded a large MSWD for the calculated age, resulting in a large error.

Figure 4. Multi-element diagram normalized to primitive mantle after McDonough and Sun [1995]. This diagram compares CAMP to a Marianas Arc average from Gazel et al. [2015] and representative samples from the Ontong Java oceanic plateau (data from the GEOROC database http://georoc.mpch-mainz.gwdg.de/georoc/). CAMP samples have both Nb and Ta depletions as well as LILE enrichments similar to the Marianas Arc average, but differing from the Ontong Java Plateau, which is plumederived [e.g., Tarduno et al., 1991].

Figure 5. Major Element variation diagrams. This diagram shows liquid lines of descent (LLD) for samples analyzed in this study. LLDs calculated with Petrolog3 software [Danyushevsky and Plechov, 2011].

Figure 6. Age corrected (200 Ma) Sr-Nd-Pb radiogenic isotopes. Samples are from Africa [Bertrand, 1991; Marzoli et al., 2004; Deckart et al., 2005; Verati et al., 2005; Mahmoudi and Bertrand, 2007] and Europe [Cebria et al., 2003; Jourdan et al., 2003; Martins et al., 2008; Callegaro et al., 2014] plot alongside northern and transitional CAMP [Dostal and Durning, 1998; Marzoli et al., 2011; Merle et al., 2013]. South Ameri- can CAMP [Deckart et al., 2005; Merle et al., 2011] lavas plot with northern and transitional CAMP or depleted MORB mantle (DMM) and Global Average MORB [Gale et al., 2013] indicative of the transition to oceanic crust [Deckart et al., 2005]. Coastal New England Province lavas are from Pe-Piper and Reynolds [2000] and Dorais et al. [2005]. Global average MORB from Gale et al. [2013]. Location of mantle reservoirs HIMU (high 1 5 238 U/ 204 Pb), depleted MORB mantle (DMM), enriched mantle I (EMI) and enriched mantle II (EMII) after Hofmann [2007]. Additional southern CAMP data from Callegaro et al. [2013] and Mazza et al. [2014]. Radiogenic isotope ratios were age corrected to initial eruptive values at 200 Ma assuming parent/daughter values reported in Table 4 using decay constants from Steiger and Jäger [1977].

Figure 7. Trace element data from CAMP olivine phenocrysts. Diagram shows trace element data versus Mg# ([molar MgO/FeO1MgO]*100%). (a) CAMP samples plot alongside data from Mauna Kea and above Indian and Pacific MORB samples [Sobolev et al., 2007] suggesting a pyroxenite component. (b) CAMP data plots within the peridotite-derived field, but also at elevated Fe/Mn values indicating a pyroxenite component. (c) CAMP data plots at lower Ca values than expected for peridotite-derived melts further supporting a pyroxenite component in the source. Diagrams modified from Herzberg [2011].

Figure 8. Trace element comparison of northern, southern and transitional CAMP. The Lesser Antilles and Marianas arcs were selected for comparison as the terranes accreted to the Laurentian margin were most likely island arcs [Hatcher, 2010]. The Cascades Arc was included because it developed on previously accreted terranes [e.g., Coney et al., 1980] making it similar to the arcs that may have developed on the Laurentian margin. (a) Th/Yb-Nb/Yb diagram after Pearce [2008] showing CAMP lavas plotting above the mantle array along with arc samples. (b) Nb/U - Ce/Yb plot for northern, transitional and southern CAMP. The small group of northern and transitional CAMP samples with lower Ce/Yb, Th/Yb, and Nb/U ratios are younger pulses of CAMP [Blackburn et al., 2013]. Additional CAMP data from Bertrand [1991]; Dostal and Durning [1998]; Puffer and Volkert [2001]; Cebria et al. [2003]; Jourdan et al. [2003]; Marzoli et al. [2004]; Deckart et al. [2005]; Verati et al. [2005]; Mahmoudi and Bertrand [2007]; Martins et al. [2008]; Marzoli et al. [2011]; Merle et al. [2011]; Callegaro et al. [2013]; Merle et al. [2013]; Callegaro et al. [2014]; Mazza et al. [2014] and arc data from the GEOROC database (http:// georoc.mpch-mainz.gwdg.de/georoc/).

Figure 9. Age corrected (200 Ma) Nd-Pb radiogenic isotope comparison between northern, southern and transitional CAMP. CAMP is compared with data from Paleozoic accreted terranes: Avalonia [Pe-Piper and Piper, 1998], Meguma [Currie et al., 1998] and Carolina [Pettingill et al., 1984; Sinha et al., 1996]. For A-C northern and transitional CAMP plot with the northern accreted terranes, Avalonia and Meguma, while southern CAMP spans all three. Previous workers have shown that crustal contamination cannot account for the isotopic signature of CAMP lavas [Puffer, 2001; Merle et al., 2011; Callegaro et al., 2013, 2014]. Additional CAMP data: [Dostal and Durning, 1998; Marzoli et al., 2011; Callegaro et al., 2013; Merle et al., 2013; Mazza et al., 2014]. Radiogenic isotope ratios were age corrected to initial eruptive values at 200 Ma assuming parent/daughter values reported in Table 4 using decay constants from Steiger and Jäger

[1977].

 $\ddot{}$ Figure 10. Assimilation Fractional crystallization models. A-F shows models using MORB starting composition from Gale et al. [2013]. G-L shows models using a basanite from Cape Verde as an Atlantic plume starting composition [*Holm et al.,* 2005; *Millet et al.,* 2008].

Figure 11. Discriminating between metasomatism by fluids or sediment-melt components in CAMP magmas. (a) Ba/La-Th/Yb diagram [after Woodhead et al., 2001] shows a high Th/Yb trend indicating a sediment melt component, and a high Ba/La trend indicating a fluid component. Northern and transitional CAMP follow the high Th/Yb trend, while southern CAMP follows the high Ba/La trend. (a) CAMP plots similarly to arc magmas on a Dy/Dy*-Dy/Yb diagram (modified from Davidson et al. [2013] with REE used in the Dy/Dy^{*} calculation normalized to values from Sun and McDonough [1989]). Northern and transitional CAMP have higher middle rare earth element contents relative to heavy rare earth element contents than southern CAMP as indicated by higher Dy/Yb. Northern and transitional CAMP show positive trends between Dy/Dy* and Dy/Yb (Figure 11b). A subset of mostly southern CAMP (including the Virginia basalt

samples analyzed for this study) and one northern CAMP sample from the Caraquet dike from New Brunswick [Dostal and Durning, 1998] plot in the lower left- hand corner of the diagram $(Dy/Dy^* < 1.0, Dy/Yb < 1.55)$. Atlantic MORB averages calculated from Janney and Castillo [2001]. Mantle xenolith data from the GEOROC database (http:// georoc.mpch-mainz.gwdg.de/georoc/). Composition of subducting sediment (GLOSS-II) from Plank [2014]. As an example of possible sediment melt composition we calculated equilibrium melting (at melt fractions 0.05, 0.1, 0.20) starting from GLOSS-II in eclogite facies using the partition coefficients in Kelemen et al. [2003].

Figure 12. CAMP primary magma compositions (Table 9) on a mole% projection toward diopside into the olivine-quartz-calcium Tschermak's plane after O'hara [1968]. Reference values: mantle peridotite (KR-4003) [Walter, 1998], oceanic crust (Siqueiros Fracture Zone) [Herzberg and Asimow, 2008], and the composition of subducting sediment (GLOSS-II) from Plank [2014]. Most of the CAMP primary magmas plot on the high $SiO₂$ side of the diagram, possibly indicating a significant silica-rich, olivine-free pyroxenite component in the source. Northern CAMP could not be compared as samples are too evolved to be in olivine control.

 \bigcirc Subduction beneath Southern Margin of Laurentia ~ 300 Ma \bigcirc Formation of Pangea ~ 260 Ma

Figure 13. Schematic model for CAMP formation (not to scale). (a) Accretion of Ganderia, Avalonia and Meguma (shown here as one landmass for simplicity) resulted in metasomatization of the upper mantle beneath Laurentia as well as the formation of pyroxenite through the reaction of sediment melts with the overlying peridotite. (b) The Alleghanian collisional event begins with oblique collision and flat subduction of the Rheic plate in the North leading to more metasomatism of the mantle wedge and the production of more pyroxenite. The Scranton Rift may have been an indenter to the advancing Gondwanan plate, blocking the advancing thrust sheets [Benoit et al., 2014]. This blockage may have in turn stalled the subduction of the Rheic plate beneath Laurentia. (c) The clogging of subduction in the North leads to a rotation of the subduction zone producing head-on collision in the South. This results in metasomatism of the mantle wedge as well as the production of pyroxenite in the South. (d) Pangea is formed with the closure of the Rheic ocean. The low angle and stalling of subduction in the North results in the Rheic plate underplating the lithosphere. (e) P/T conditions cause the Rheic plate to eclogitize and begin to tear. The plate may have also been weakened by the jamming of the subduction zone. This tear initially leads to small amounts of mantle melting, which form the Coastal New England dike swarm. (f) The slab tear propagates in both directions (first toward the North, then later toward the South) due to slab pull, eventually resulting in a catastrophic delamination event. This delamination produces mantle upwelling (increasing the mantle potential temperature indicated by red in the figure), uplift and significant melting of the mantle (CAMP), which had been metasomatized by previous episodes of subduction. Accreted terrane boundaries from Hibbard et al. [2010] and Hatcher [2010]. CAMP boundary after McHone [2003]. Scranton Rift

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location from Benoit et al. [2014]. Final closure of Pangea after Hatcher [2002].

Figure 14. Histogram of ages of Late Triassic Coastal New England (CNE) dikes (purple) and plutons (light blue). Modified from McHone and Butler [1984] and updated with ages from [Pe-Piper and Jansa, 1986; Reynolds et al., 1987; Greenough et al., 1988; McHone, 1992; Pe-Piper et al., 1992; Sundeen and Huff, 1992; Pe-Piper and Reynolds, 2000; Ross, 2010]. The cumulative stratigraphic thickness for the Fundy Basin over time [Schlische et al., 2003] is shown as the blue line, which increases rapidly at the time of CAMP emplacement (indicated by red bar). CNE overlaps with CAMP magmatism in time and uplift may have occurred at the time of CNE emplacement as the majority of CNE coincides with a hiatus in sedimentation in the Fundy Basin.

Table 1 New dataset – major elements

Table 2 New dataset – trace elements

Table 3 New dataset – rare earth elements

Table 4 New dataset - radiogenic isotopes

Table 5 Olivine phenocryst analyses

Table 6 Olivine phenocryst and standard statistics

*Jarosewich et al., 1980

** All analyses of the RU SCOL standard at high currents and long count times over the last 4 years ***Jarosewich et al., 1987

Table 7 Standards used in olivine analysis

* original sample composition

Table 8 Original sample compositions used for calculated primary magmas

Table 9 Calculated primary magma