Appendix 1 DR1. Description of samples and methods used in *rhyolite-MELTS* modeling

Samples

DEL10-30: The lowest Zr granite (322 ppm) is a typical ca. 1150 Ma, protomylonitic basement augen orthogneiss from the southern Blue Ridge province, eastern Great Smoky Mountains. Zircon crystals analyzed via SHRIMP are prismatic and either oscillatory zoned without inclusions, or irregularly zoned with inclusions (Fig. 1). The original magmatic assemblage is K-feldspar + plagioclase + quartz + biotite. The whole rock major and trace element (Zr = 332 ppm) analysis was collected in the Kentucky Geological Survey XRF lab on a split of the sample used to extract zircons for geochronology. Further details relevant to this sample, including U-Pb zircon geochronology, are reported in Quinn (2012), which is available at http://uknowledge.uky.edu/ees_etds/7/.

SF98-1: The State Farm orthogneiss of the Grenvillian Goochland terrane (Virginia) is a high-Zr (540 ppm, Table DR1), ca. 1050 Ma porphyritic granitic orthogneiss. Zircon crystals in the State Farm gneiss are exceptionally large (up to 1 mm in length: Moecher and Samson, 2006), contain an inclusion assemblage of $Qtz \pm Kfs \pm Ap \pm Hbl \pm Mt$ (Fig. 1), typically exhibit sector zoning, and contain apparent antecrystic interiors (Fig. 1). Magmatic assemblage interpreted to be quartz + K-feldspar + biotite + plagioclase + garnet + titanite. Sample is an 'augen gneiss' with relict porphyroclasts of Kfs enveloped by a matrix of feldspar + biotite + quartz (Owens and Tucker, 2003; Owens and Samson, 2004).

VA12-1: Lovingston Massif (Virginia), Stage Road Suite orthogneiss, sample locality HP-4 of Hughes et al. (2004) which they report as having Zr = 1685 ppm; mesoperthite + quartz + biotite + plagioclase + orthopyroxene. We resampled this outcrop, and prepared a thin section from the slab used for extracting zircons and for major and trace element analysis carried out by the Washington State University GeoAnalytical Lab. The latter analysis returned a Zr concentration of 1201 ppm. The sample exhibits a weak foliation defined by parallelism of biotite folia wrapping porphyroclasts of K-feldspar. The assemblage in thin section is Kfs + biotite + quartz + muscovite + plagioclase. Rutile and ilmenite are absent, but the sample contains a high relief phase comprised of a microcrystalline intergrowth containing a Ti-bearing phase. Zircon grains in this sample contain single mineral inclusions (equant grains with 20-30 micron diameter) of apatite, hornblende, quartz, alkali feldspar, and a ternary feldspar composition. Two composite inclusions in zircon consist of amphibole + alkali feldspar + apatite and quartz + biotite + ilmenite. Zircon grains with inclusions were not among those analyzed by SHRIMP for Ti concentration.

VA12-2: "low silica charnockite" (monzogranite to quartz monzodiorite) as from locality SNP - 99-91 of Tollo et al. (2004), Shenandoah massif (Virginia) who report Zr = 1676 ppm; original assemblage interpreted to be microcline microperthite + quartz + plagioclase + ilmenite + opx + cpx + hornblende. The sample collected for this study is relatively massive in hand sample but is mylonitic in thin section with considerable dynamic recrystallization of quartz, recrystallization of the matrix to fine-grained muscovite and biotite, and formation of fractured and rotated grains of feldspar, hornblende, and ilmenite. Zircon grains do not exhibit evidence of deformation-induced recrystallization. The slab used to prepare the thin section and crushed to extract zircon was also used for XRF analysis at Washington State University. Only one mineral inclusion was found among the zircon grains imaged by CL, and it consisted of apatite + quartz + biotite.

These four samples were selected based either on their reportedly high Zr content (VA12-1 and -2) or because geochemical and zircon U-Pb geochronological data available from previous work (SF98-1 and DEL10-30; Owens and Samson, 2004). The Virginia samples are from granitoid suites that were found to have the highest Zr content in a survey of Grenville granitoids from North America. All four samples exhibit mineralogic and textural evidence for varying degrees of post-magmatic Grenville or Paleozoic metamorphism and ductile deformation, which is typical for Grenville basement rocks in eastern Laurentia (Tollo et al., 2010). Grenville rocks comprising Appalachian massifs have also undergone Paleozoic deformation at varying grade, often within high strain zones (Tollo et al., 2004). In all cases the Grenville rocks retain their Mesoproterozoic U-Pb age systematics, and zircon grains exhibit only minor modification from Paleozoic events (e.g., thin overgrowths interpreted to be metamorphic: Tollo et al., 2004, 2010; Southworth et al., 2010), suggesting magmatic zircon trace element contents should be retained through the later events as well. The CL zoning patterns of zircon in the two VA12- samples are similar to those observed in some other felsic systems that do not have a post-magmatic metamorphic history (e.g., Pamukcu et al., 2013).

All these samples occur within the part of the southern Appalachian Grenville massifs that have been inferred, based on Pb isotopes, to be exotic to Laurentia (i.e., an Amazonian/Gondwanan affinity). New Pb data of Quinn (2012) for sample DEL10-30 support an Amazonian affinity. We do not have Pb data for the Goochland terrane sample.

Ti-in-Zircon Thermometry

The calibration experiments (Watson et al., 2006; Ferry and Watson, 2007) were conducted with quartz and rutile present during zircon crystallization ($a_{SiO_2} = 1$, $a_{TiO_2} = 1$). In natural systems where quartz or rutile was absent during zircon crystallization, reasonable estimates of a_{SiO_2} and a_{TiO_2} are necessary for reliable calculation of temperature. Values of $a_{SiO_2} = 1$ (quartz is present in all samples) and $a_{TiO_2} = 0.7$ (Ghiorso and Gualda, 2013) were assumed for initial *T* calculation, and then re-examined further in the Results section. The temperature range

associated with an a_{TiO_2} range of 0.6–0.8 is 30–45°, and that associated with an a_{SiO_2} range of 0.8–1.0 is 20–35°. If a_{TiO_2} is overestimated, temperature is underestimated, so we consider temperatures calculated using a value of $a_{TiO_2} = 0.7$ to be minima.

Modeling Methods Using rhyolite-MELTS

The phase assemblage for each sample was monitored at 25° intervals starting from the liquidus. In addition to calculating the crystallizing phase assemblage, *rhyolite-MELTS* calculates the composition of the remaining melt at each temperature step. The remaining melt composition was then used to calculate the M value of the melt at each step, from which a predicted zircon saturation temperature was calculated for each M at each 25° temperature step using the relation:

$$Zr_{M,T} = 496000exp\{[3.8 + (0.85^{*}(M-1))] - 12,900T(K)\}$$

$$M = (Na+K+2Ca)/(Al^{*}Si),$$
[1]

where the elemental symbol is the cation fraction (Watson and Harrison, 1983). The Zr concentration of the evolving melt is calculated according to:

$$Zr_{melt} = C_0/F$$
^[2]

where C_0 is the initial Zr content (from the bulk rock Zr content) and F is the fraction of melt remaining at each temperature, which is also an output from *rhyolite-MELTS*. In the modeling, Zr is considered to be perfectly incompatible until zircon saturation is reached. The temperature at which $Zr_{M.T} = Zr_{melt}$ is the predicted onset of zircon crystallization (Fig. 2).

Although *rhyolite-MELTS* is viewed as an improvement over MELTS for modeling the crystallization of silicic melt compositions, there remain limitations in the program's ability to handle hydrous phase crystallization (biotite, hornblende; see other limitations in Appendix 1).

Other limitations of this modeling approach include: (1) Bulk rock analyses do not reflect magmatic H_2O contents. We used nominal H_2O concentrations of 0.5 to 1.1 wt % (Table DR1), but evaluated the effect of higher modeling results H_2O in some samples. Grenville magmatic rocks, particularly charnockites of the AMCG suite that have affinity to A-type magmas, are commonly interpreted to have been relatively anhydrous (McClelland et al., 2010). Higher H_2O will lower the liquidus temperature ($25^{\circ}C$ reduction for 1 vs. 2 wt. % H_2O for sample VA12-1) but was found to not markedly change the onset of zircon crystallization; (2) many bulk plutonic rock compositions are not melt compositions, which also needs to be considered in interpretation of zircon saturation temperatures (Miller et al., 2003); (3) depth of crystallization is unknown (0.5 GPa is assumed); (4) some zircon may be xenocrystic, which would lead to overestimation

of Zr in melt and therefore to overestimation of zircon saturation temperatures; however, Grenville granites rarely show evidence for an appreciable fraction of xenocrysts.

Discussion of Zircon Zoning Patterns

In both high Zr samples studied here, the outer growth zones exhibited by zircon have higher Ti concentrations and yield higher Ti-in-zircon temperatures than the centers of most grains. The question arises as to whether the outer growth zone of zircon in the VA12- samples is magmatic or metamorphic. Granulite-facies metamorphism coincident with magmatism is a defining aspect of Grenville terranes. Metamorphic conditions approached 900–950 °C throughout large tracts of Grenville rocks in Canada and the eastern U.S. (Anovitz and Essene, 1990; Wodicka et al., 2000; Rivers, 2009; Tollo et al., 2004; 2010). It is possible that ultra-high temperature metamorphic conditions (950–1050 °C: Harley, 1998) would at least locally coexist with hot granite magmatism. However, the pattern of higher rim temperatures for zoned zircon is also apparent in hot magmatic systems such as the Cenozoic southern Black Mountains volcanic center, southwestern U.S.A. (Pamukcu et al., 2013) which did not experience a high grade metamorphic overprint and contains zircon with high-Ti rims. We thus interpret the intragrain variation of Ti content to reflect magmatic processes, e.g., two thermal events potentially reflecting recharging by pulses of high-temperature magma (e.g., Pamukcu et al., 2013), as opposed to high grade metamorphic recrystallization of igneous zircon in a magmatic protolith.

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Appendix DR2: Tables

Sample	1	2	3	4
SiO_2	64.53	64.19	61.05	68.45
TiO_2	0.68	1.45	1.87	0.86
Al_2O_3	16.78	14.63	14.38	14.12
FeO	4.08	6.00	7.20	4.36
Fe_2O_3	0.52	0.62	0.80	0.48
MnO	0.10	0.09	0.12	0.15
MgO	1.53	1.09	1.25	0.44
CaO	3.68	3.62	4.59	1.28
Na ₂ O	3.43	3.10	2.64	2.54
K ₂ O	3.62	3.97	4.32	6.00
P_2O_5	0.21	0.64	0.99	0.24
H_2O	0.83	0.48	0.79	1.08
Zr ppm	322	540	829	1201
М	1.59	1.77	1.73	1.40
T_{Zc} (°C)	835	870	915	997

Table DR1: Whole rock major element analyses andZr contents used for crystallization modeling

1: Augen orthogneiss DEL10-30 (Quinn, 2012)

2: State Farm orthogneiss SF 98-1 (Owens and Tucker, 2003)

3. Low silica charnockite VA12-2 (Tollo et al., 2004)

4. Stage Road orthogneiss VA 12-1 (Hughes et al., 2004)

Zircon saturation temperature (T_{zc}) is calculated from bulk Zr content and bulk rock M value; M = (Na+K+2Ca)/(AlSi) (Watson and Harrison, 1983).

See Appendix 1 for additional sample details.

Sample	grain.spot	Ti ppm	$T C^{0}$	U
VA12-1	1.1c	56	988	20
	1.2r	40	940	7
	2.1c	26	884	21
	2.2r	37	931	7
	3.1c	43	949	16
	4.1c	33	917	20
	5.1r	58	992	13
	5.2c	24	878	22
	6.1c	12	803	16
	7.1r	77	1035	14
	8.1c	38	935	13
	8.2r	50	971	31
	9.1c	32	911	12
	9.2r	20	853	23
VA12-2	1.1c	28	895	66
	1.2r	18	842	538
	2.1r	32	912	76
	2.2c	10	783	389
	3.1r	30	902	70
	4.1c	16	833	380
	4.2r	33	916	79
	5.1r	19	846	99
	5.2c	10	781	380
	6.1c	13	806	126
	6.2r	15	821	368

Table DR2. SHRIMP Ti analyses and calculatedTi-in-zircon temperatures

c: core; r: rim

1: temperature calculated from Ti-in-zircon thermometer discussed in text.