

## **APPENDIX A. PROTEROZOIC ROCKS OF EASTERN NORTH AMERICA**

### **Southern and Eastern Granite-Rhyolite provinces (GRP in general)**

A large NE-SW-trending belt of Mesoproterozoic (1.49-1.34 Ga) felsic granitoid rocks and associated rhyolitic volcanic rocks stretches from Ontario southwest to New Mexico and is divided, based on U/Pb crystallization ages, into a Southern Granite-Rhyolite province (SGRP) and an Eastern Granite-Rhyolite province (EGRP) (Van Schmus et al., 1993). The EGRP consists predominately of ca. 1.47 Ga volcanic and plutonic felsic rocks intruded locally by ca. 1.38 Ga plutonic rocks. The SGRP consists of similar felsic volcanic and plutonic rocks, but it is about 100 m.y. younger (1.40 to 1.34 Ga). Exposures of the EGRP are limited to the St. Francois Mountains, Missouri and of the SGRP to the Arbuckle Mountains, Oklahoma, but drill-hole samples from many basement drill cores and geophysical data show that coeval rocks exist throughout the midcontinent region (Fig. 1; cf. Van Schmus et al., 1993, 1996; Lidiak et al., 1996, Rohs and Van Schmus, 2007).

Plutonic rocks coeval with the EGRP (1.49-1.42 Ga) extend northward and westward across the midcontinent and throughout the southwestern U.S. Plutonic rocks coeval with the SGRP extend northward into Kansas and Missouri, and a few coeval plutons exist in Colorado. The subsurface boundary between predominately EGRP rocks and predominantly SGRP rocks at the top of the Precambrian basement runs roughly E-W through southern Kansas and southern Missouri, south of the St. Francois Mountains (Van Schmus et al, 1993), but its continuation eastward is unconstrained due to lack of sufficient data.

Both granite-rhyolite provinces can be subdivided further along a NE-SW-trending boundary based on Sm-Nd depleted mantle model ages ( $T_{DM}$ ), which imply the age of the crustal source.  $T_{DM}$  ages in the western portions of the EGRP (Michigan, Indiana, Illinois, Missouri) and in western to northern portions of the SGRP (Missouri, Kansas, Oklahoma, Texas) are uniformly  $>1.55$  Ga (see thick dashed line in Fig. 1.), while those to the east or south are  $<1.55$  Ga (Van Schmus et al., 1993, 1996; Rohs and Van Schmus, 2007). East of the 1.55 Ga  $T_{DM}$  line the similarities between  $T_{DM}$  and U-Pb zircon ages suggests that these rocks were essentially juvenile, that is, they incorporated little crust of appreciably greater age. On the other hand, GRP rocks west or north of the 1.55 Ga  $T_{DM}$  line have significantly older TDM ages that approximate the U-Pb zircon ages of the host Paleoproterozoic crust (1.89 to 1.63 Ga), showing that their magmas incorporated a significant amount of (or were wholly derived from) remelted Paleoproterozoic crust. Thus, Van Schmus et al. (1996) suggested that this isotopic boundary is a fundamental crustal feature marking the southeastern limit of Paleoproterozoic crust from cratonic Laurentia in the North American basement.

Previous whole rock Pb isotopic data from the GRP are limited to southeast Missouri and northern Illinois (Doe et al., 1983). Two samples analyzed for Pb isotopic composition come from southeast Missouri, an outcrop sample of the 1.38 Ga Graniteville granite and an undated drill core sample from Shannon County. Northern Illinois samples come from 1.46 Ga granite encountered in two drill holes, UPH-2 (2 analyses) and UPH-3 (9 analyses), from Stephenson County, NW Illinois. Whole rock compositions were measured at various depths in the UPH-3 core (Doe et al., 1983).

The whole-rock data for these samples plot at lower  $^{207}\text{Pb}/^{204}\text{Pb}$  (for a given  $^{206}\text{Pb}/^{204}\text{Pb}$ ) than the average crustal evolution curve of Stacey and Kramers (1975) (Fig. 2).

### **Adirondack Mountains**

The Grenville-age rocks of the Adirondack Mountains are mainly granitic and anorthositic gneisses that intruded a predominantly carbonate sedimentary sequence (Daly and McLelland, 1991; McLelland et al., 2001). U-Pb zircon ages range from ~1.35 Ga for tonalitic arc-related rock to 1.04 Ga for younger intrusions (McLelland et al., 1996; McLelland et al., 2001; McLelland et al., 2004). Sm-Nd  $T_{\text{DM}}$  ages of the tonalites are 1.37-1.40 Ga, within ~70 Ma of their U-Pb zircon ages, suggesting derivation from the mantle. Younger rocks typically have  $T_{\text{DM}}$  ages similar to those of the tonalites (1.5-1.3 Ga), suggesting that they were derived by remelting the magmatic arc crust (Daly and McLelland, 1991; McLelland et al. 1993). Pb isotopic data from the Adirondacks form a coherent array plotting at lower  $^{207}\text{Pb}/^{204}\text{Pb}$  (at a given  $^{206}\text{Pb}/^{204}\text{Pb}$ ) than the average crustal evolution curve of Stacey and Kramers (1975) (Fig. 2) (Sinha and McLelland, 1999).

### **Central and Southern Appalachian Orogen**

Grenville-age igneous or meta-igneous rocks are exposed throughout the SCAB, from Pennsylvania to Alabama (Fig. 1). The Grenville age rocks in the Appalachian orogen are divided into the central Appalachian basement, which includes exposures north of the North Carolina-Virginia border, and the southern Appalachian basement which includes exposures south of the North Carolina-Virginia border. Although this division has historically been a geographic one, a geologically reasonable division can be made based on Nd isotopic data (see discussion below).

### ***Central Appalachians***

Grenville-age rocks of the central Appalachian basement discussed here are limited to those with pre-existing Pb isotopic data (Sinha et al., 1996). These include rocks of the Honey Brook Uplands of Pennsylvania, the Baltimore Gneiss of Maryland, and numerous massifs in Virginia that are exposed in two roughly NE-SW trending belts: the Virginia Blue Ridge and the Goochland terrane (Fig. 1).

Throughout the central Appalachian basement, magmatic ages range from 1.25-1.02 Ga (e.g., Aleinikoff et al., 2000; Aleinikoff et al., 2004; Tollo et al., 2004). A relatively small range of  $T_{DM}$  ages (1.5-1.3 Ga) is reported from the Virginia Blue Ridge and Goochland terrane (Pettingill et al., 1984; Owens and Sampson, 2004). With the exception of the Stage Road Layered Gneiss of Virginia, which defines a steeper slope, Pb isotopic data from the central Appalachians define a coherent array that overlaps and has slightly higher  $^{207}\text{Pb}/^{204}\text{Pb}$  (at a given  $^{206}\text{Pb}/^{204}\text{Pb}$ ) than the average crustal evolution curve of Stacey and Kramers (1975) (Fig. 2) (Sinha et al, 1996).

### ***Southern Appalachians***

A majority of the Mesoproterozoic basement in the southern Appalachians is exposed in a NE-SW trending belt along the Tennessee-North Carolina border (Hatcher et al., 2004). Smaller exposures are also found to the south and east including the Sauratown Mountains window, Trimont Ridge complex, Toxaway dome, Tallulah Falls dome, and the Pine Mountain window (Hatcher et al. 1984; 2004) (Fig. 1).

The southern Appalachian Mesoproterozoic basement has been divided into the eastern and western Blue Ridge (EBR, WBR) based on lithologic differences (Fig. 3) (e.g., Hatcher, 1978). However, the combined U/Pb zircon ages and Sm-Nd and Pb

whole-rock isotopic data show significant overlap between the eastern and western Blue Ridge, similar to the data from metaclastic rocks (Carrigan et al. 2003; Ownby et al. 2004; Bream et al., 2004; Hatcher et al., 2005; Berquist 2005), and thus no distinction is made here. Additionally, the Mars Hill terrane, located in the western Blue Ridge (Fig. 3), has been distinguished from the surrounding basement on the basis of apparent older age (Monrad and Gulley, 1983; Carrigan et al., 2003), more ancient isotopic signatures (Sinha et al., 1996; Carrigan et al. 2003; Ownby et al., 2004), well-preserved Mesoproterozoic granulite-facies metamorphism (Mersch, 1977; Gulley, 1985), and lithologic diversity (Mersch, 1977; Raymond et al., 1989). However, recent investigations of the Mars Hill terrane have demonstrated that the oldest magmatic and  $T_{DM}$  ages are confined to the Roan Mountain area, Tennessee-North Carolina border (Fig. 1). Based on the pre-Grenvillian history of Roan Mountain we discuss it separately from the remainder of the southern Appalachian basement including the Mars Hill terrane.

The Grenville-age basement of the southern Appalachians consists primarily of orthogneisses of predominantly granitic composition (Carrigan et al., 2003). U-Pb zircon SHRIMP ages range from 1.27 to 1.02 Ga with the exception of a single granitoid (gneiss) at 1.38 Ga (Heatherington et al., 1996; Carrigan et al., 2003; Ownby et al., 2004; Steltenpohl et al., 2004; Berquist et al., 2005).  $T_{DM}$  ages show no systematic variation with U-Pb age, and range from 1.78 to 1.34 Ga; (Heatherington et al., 1996; Fullagar et al., 1997; Carrigan et al., 2003; Hatcher et al. 2004). Available Pb isotopic data are limited to the Corbin Gneiss, Sauratown Mountains, Tallulah Falls dome, and the Pine Mountain terrane (Fig. 1), and overlaps and lie at slightly lower  $^{207}\text{Pb}/^{204}\text{Pb}$  (at a given

$^{206}\text{Pb}/^{204}\text{Pb}$ ) than the average crustal evolution curve of Stacey and Kramers (1975) (Fig. 2) (Sinha et al., 1996). No Pb data have been published from the widespread exposures of Grenville-age basement along the Tennessee-North Carolina border, within the Watauga, Globe, and Elk River massifs of Bartholomew et al. (1984).

**Roan Mountain.** The Roan Mountain area contains the most ancient crust thus far identified in the Appalachian orogen and is considered to be exotic to Laurentia (Carrigan et al. 2003; Ownby et al. 2004; Hatcher et al., 2005). Meta-igneous rocks exposed at Roan Mountain yield distinctive age and isotopic characteristics. Monrad and Gulley (1983) determined a 1.8 Ga whole rock Rb/Sr isochron based on five meta-igneous samples. A magmatic age of 1.8 Ga was confirmed by U-Pb zircon dating by secondary ion mass-spectrometry (SIMS), although recent studies have demonstrated that most magmatic ages are between 1.2 and 1.3 Ga (Carrigan et al. 2003; Ownby et al. 2004).  $T_{\text{DM}}$  ages range from 2.32-1.65 Ga, the oldest known in the Appalachians (Carrigan et al., 2003; Ownby et al. 2004). The unusual Pb isotopic characteristics cited above for the Mars Hill Terrane were determined from samples collected on the flanks of Roan Mountain (Fig. 2) (same as Carvers Gap granulite gneiss; Sinha et al. 1996). The slope of the composite array corresponds to an age of ~3.0 Ga (Sinha et al., 1996), much older than any magmatic ages identified thus far. While this array may also be the result of mixing or complex U/Pb history, similar compositions are not observed in any SCAB samples.

### **Llano Uplift and West Texas**

Texas exposures of Mesoproterozoic basement occur in both the Llano Uplift of central Texas (cf. Mosher et al., 2008), in the Franklin and Van Horn Mountains, and within

xenoliths hosted in Tertiary volcanic rocks at Rancherias Canyon and the Forbidden Mountains of west Texas (Fig. 1a) (Smith et al., 1997; Cameron and Ward, 1998; Bickford et al., 2000). Surface exposures in west Texas contain younger (1.12-1.07 Ga) granitic rocks intruded into predominantly 1.38-1.32 Ga sedimentary-volcanic sequences of the SGRP (Smith et al., 1997; Bickford et al., 2000), while 1.12 Ga granitic rocks in central Texas are intruded into the 1.28-1.23 Ga Packsaddle and Valley Creek domains considered to represent the southern extension of the SGRP (Reese et al., 2000; Mosher et al., 2008). Both the granitic intrusions and older SGRP units in west and central Texas, and the xenoliths in west Texas, have a narrow range of  $T_{DM}$  ages ( $\sim 1.4$ -1.1) Ga suggesting that the older volcanic units were likely derived from depleted mantle, whereas the younger granitic intrusions and xenoliths may have incorporated both depleted mantle and remelted material from the slightly older Texas rocks (Patchett and Ruiz, 1989; Smith et al., 1997; Whitefield, 1997; Cameron and Ward, 1998; Roller 2004). Pb isotopic data from both the Llano uplift and west Texas samples form a coherent linear array plotting at slightly lower  $^{207}\text{Pb}/^{204}\text{Pb}$  (at a given  $^{206}\text{Pb}/^{204}\text{Pb}$ ) than the average crustal evolution curve of Stacey and Kramers (1975) (Fig. 2) (Smith et al., 1997; Roller 2004; R.C. Roback, personal communication; Cameron and Ward, 1998).

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## **APPENDIX B. Analytical Methods**

### **Whole-rock Isotopic data**

New southern Appalachian whole-rock Sm-Nd and Pb isotopic data presented in this study (Tables 2 and 3) come from samples originally collected by Carrigan et al., 2003, Ownby et al., 2004, and Berquist, 2005. New whole rock Pb isotopic for the Granite-Rhyolite province are from samples originally used in the study of Van Schmus et al., 1996, as well as two new drill core samples presented here (OH-DC and CO-DC). In the case of southern Appalachian basement samples, thin slabs were cut from representative 1-5 kg samples (parallel to lineation and perpendicular to foliation, where applicable) and powdered in an alumina ceramic shatterbox. Drill core samples were cut into smaller slabs, or consisted of cuttings and were pulverized in an alumina ceramic mortar and pestle.

New whole rock Sm/Nd and Pb isotopic analyses presented here were performed at the University of North Carolina-Chapel Hill on a VG Sector 54 mass spectrometer. For Pb analysis, 300 mg aliquots of the pulverized powder were washed in 1N HNO<sub>3</sub> for 30 minutes on a warm hotplate before dissolution in Teflon™ dissolution bombs. Samples were dissolved in two stages using HF/HNO<sub>3</sub> and 6N HCl. Pb was isolated using an HBr anion exchange technique, loaded onto standard Re filaments with a mixture of silica gel and phosphoric acid. Twenty analyses of NBS981 indicate fractionation of 0.12% per amu with measured isotopic ratios within 0.05%. For Sm/Nd analyses, 300 mg aliquots of pulverized powder were spiked with <sup>147</sup>Sm/<sup>150</sup>Nd mixed spike and dissolved in the same manner as the Pb samples, except the powders were not washed in HNO<sub>3</sub>. Rare earth elements (REE) were isolated using REE-SPECTM column

chemistry. Sm and Nd were subsequently isolated using LN-spec columns. Analyses were normalized to  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ . Twenty-seven analyses of JNdi yielded an average  $^{143}\text{Nd}/^{144}\text{Nd}$  of  $0.512108 \pm 0.0006\%$  std error.  $T_{\text{DM}}$  ages are calculated using the theoretical isotopic decay constant ( $6.54 \times 10^{-12}/\text{yr}$ ) of Lugmair and Marti (1978) and the depleted mantle model of DePaolo (1981;  $\epsilon_{\text{Nd}} = 0.25T^2 - 3T + 8.5$ ).

### **Zircon U/Pb geochronology**

Zircons from drill core sample OH-DC were liberated from ~100 grams of sample by crushing to 250µm mesh size and separation using heavy liquids and magnetic techniques. Individual grains were handpicked from non-magnetic fractions and mounted in epoxy with zircon standard R-33 and VP-10. Mounts were then polished to reveal the approximate center of the grain and imaged by cathodoluminescence (CL) to reveal internal morphology. Points on zircons (~30µm in diameter) were analyzed according to the Stanford/U.S. Geological Survey (USGS) Sensitive High-Resolution Ion Microprobe, Reverse Geometry (SHRIMP-RG) Facility procedure (Bacon et al., 2000). Data reduction was performed using the SQUID and ISOPLOT software packages of Ludwig (Ludwig 2002a, 2002b).

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# APPENDIX C. Whole-rock major and trace element geochemistry, sample description

	drill core	drill core	outcrop	Sample Descriptions:		
	CO-DC	OH-DC	RMHB			
SiO <sub>2</sub> (wt. %)	49.89	72.31	55.34	CO-DC: drill core		
Al <sub>2</sub> O <sub>3</sub>	22.55	13.40	11.73	Location:	Crab Orchard, Tennessee	
Fe <sub>2</sub> O <sub>3</sub> (T)	6.54	1.82	8.77		Ladd Oil Company #1 Drill Hole	
MnO	0.08	0.04	0.211	Depth to basement:	10,110 ft	
MgO	5.79	0.43	11.26	Sample description:	Calcic plagioclase (75%), olivine (14%),	
CaO	9.74	0.89	8.2		clinopyroxene (6%), serpentine (2%),	
Na <sub>2</sub> O	3.67	3.80	2.26		biotite (1%), opaque minerals (2%)	
K <sub>2</sub> O	0.53	4.99	1.36		trace apatite	
TiO <sub>2</sub>	0.41	0.21	0.437			
P <sub>2</sub> O <sub>5</sub>	0.25	0.06	0.09	GV-DC: drill core		
LOI	0.99	0.97	0.52	Location:	Davidson County, Tennessee	
Total	100.40	98.92	100.2		E.I. Du Pont & Co., Old Hickory Plant	
Rb (ppm)	<10	170	61	Depth to basement:	5500 ft	
Sr	982	109	234	Well name and no. :	FEE No. 1 (monitoring well)	
Ba	338	636	584	Sample description:	Granite, medium to coarsely crystalline-	
Y	4	33	30		orthoclase, quartz, plagioclase, biotote,	
Zr	10	178	71		opaques, trace zircon and apatite	
Hf	<0.2	6.6	2.1			
Nb	0.7	28.2	3.9			
Ta	<0.3	1.5	0.3	RM-HB: Roan Mountain terrane outcrop		
Zn	39	25	83	Location:	-82.145	36.093
Cu	49	3	69		latitude	longitude
V	66	14	145			
Ni	179	2	326	Sample description:	Mafic granulite, medium to course grain	
Cr	401	11.1	298		plagioclase, orthopyroxene, trace apatite, opaques	
Co	53.8	2.3	53.8			
Sc	9.39	4.14	36.6			
La	4.87	48.1	22.3			
Ce	10.6	94.1	51.4			
Pr	1.45	10.2	6.69			
Nd	6.65	34.5	26.7			
Sm	1.48	6.07	5.83			
Eu	0.89	0.99	1.27			
Gd	1.48	5.05	5.1			
Tb	0.2	1.4	0.88			
Dy	1.04	4.47	4.91			
Ho	0.19	0.99	0.99			
Er	0.49	3.48	2.95			
Tm	0.07	0.63	0.456			
Yb	0.56	4.61	2.94			
Lu	0.08	0.7	0.429			
U	0.01	6.21	0.21			
Th	0.11	19.5	2.77			



