Petrology and Geochronology of 1.48 to 1.45 Ga Igneous Rocks in the St. Francois Mountains Terrane, Southeast Missouri
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Prepared in cooperation with the Missouri Geological Survey

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U.S. Geological Survey
Acknowledgments

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**Conversion Factors**

International System of Units to U.S. customary units

<table>
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<th>Multiply</th>
<th>By</th>
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<tr>
<td>Length</td>
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</tr>
<tr>
<td>millimeter (mm)</td>
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<td>inch (in.)</td>
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<tr>
<td>meter (m)</td>
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<td>foot (ft)</td>
</tr>
<tr>
<td>kilometer (km)</td>
<td>0.6214</td>
<td>mile (mi)</td>
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U.S. customary units to International System of Units

<table>
<thead>
<tr>
<th>Multiply</th>
<th>By</th>
<th>To obtain</th>
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<tr>
<td>Mass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ounce, avoirdupois (oz)</td>
<td>28.35</td>
<td>gram (g)</td>
</tr>
</tbody>
</table>

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

\[
°F = (1.8 \times °C) + 32.
\]

Ages are expressed in Ga, for giga-annum (billion years), Ma for mega-annum (million years), and time intervals are in m.y. for million years.

**Abbreviations and Acronyms**

- **HFSE**: High-field-strength element
- **HREE**: Heavy rare earth element
- **LREE**: Light rare earth element
- **LILE**: Large-ion lithophile element
- **REE**: Rare earth element
- **USGS**: U.S. Geological Survey
- **MSWD**: mean square of weighted deviates
- **NIST**: National Institute of Standards and Technology
- **ppm**: parts per million

**Chemical Compounds**

- **Al₂O₃**: Aluminum oxide
- **CaO**: Calcium oxide
- **FeO***: Total iron expressed as ferrous oxide
- **K₂O**: Potassium oxide
- **MgO**: Magnesium oxide
- **MnO**: Manganese oxide
- **Na₂O**: Sodium oxide
$N_2$  Nitrogen
$P_2O_5$  Phosphorus pentoxide
$SiO_2$  Silicon dioxide
$TiO_2$  Titanium dioxide
$UO$  Uranium oxide
$UO_2$  Uranium dioxide

**Elements**

Ag  Silver
Ar  Argon
As  Arsenic
Au  Gold
Ba  Barium
Ca  Calcium
Ce  Cerium
Co  Cobalt
Cr  Chromium
Cs  Cesium
Cu  Copper
Eu  Europium
Fe  Iron
He  Helium
Hg  Mercury
La  Lanthanum
Nb  Niobium
Nd  Neodymium
Ni  Nickel
O  Oxygen
Pb  Lead
Rb  Rubidium
Sc  Scandium
Sn  Tin
Sr  Strontium
Ta  Tantalum
Th  Thorium
U  Uranium
V  Vanadium
Y  Yttrium
Zr  Zirconium
Petrology and Geochronology of 1.48 to 1.45 Ga Igneous Rocks in the St. Francois Mountains Terrane, Southeast Missouri


Abstract

The igneous geology of the St. Francois Mountains terrane in southeast Missouri is dominated by the products of 1.48 to 1.45 billion year old volcanic and plutonic magmatism but also includes volumetrically minor, compositionally bimodal contributions added during plutonism between 1.34 and 1.27 billion years ago. The 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane are bimodally distributed between volumetrically dominant felsic rocks and volumetrically minor rocks with mafic to intermediate compositions. All of these rocks are ferroan, which like most of their trace element abundances, suggests a genesis associated with farfield intraplate extensional tectonism and decompression-related magmatism. The diversity of compositions among 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane probably reflects mixtures of mantle-derived mafic inputs and low-degree partial melting of more evolved crustal protoliths. Newly determined ages define essentially continuous magmatism during the 30-million-year period between 1.48 and 1.45 billion years ago. The products of this magmatism are essentially coeval, whether intrusive or extrusive or having mafic, intermediate, or felsic compositions. In addition, the iron oxide-apatite (for example, Pea Ridge) and likely the iron oxide-copper gold (Boss) deposits in the St. Francois Mountains terrane have ages coincident with this magmatic episode. Spatial and temporal relations between 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane and the mineral deposits they host suggest the associated magmatic and mineralization processes are also genetically related.

Introduction

Mesoproterozoic igneous rocks (fig. 1) constitute the basement beneath a relatively thick (greater than 400 meters [m]) Paleozoic sedimentary rock sequence in the southern midcontinent region of the United States in the St. Francois Mountains terrane of southeast Missouri (Kisvarsanyi, 1981; Tolman and Robertson, 1969). The 1.48 to 1.45 giga-annum (Ga) rocks of southeast Missouri are unique in hosting coeval and cospatial iron oxide-apatite ± rare earth element (IOA) and iron oxide-copper ± gold ± cobalt (IOCG) mineral deposits. These igneous rocks represent a significant component of a broadly early Mesoproterozoic igneous terrane, intruded by a middle Mesoproterozoic bimodal sequence of granite and gabbro at about 1.3 Ga in southeast Missouri, that crops out extensively in North America (Anderson and Bender 1989; Bickford and others, 2015; du Bray and others, 2018a). The petrogenesis and tectonic regime that prevailed during Mesoproterozoic magmatism in the United States remain elusive.

Our study focuses on the characteristics of early Mesoproterozoic igneous rocks in the St. Francois Mountains terrane in order to establish their petrogenesis and potential role in formation of associated IOA and IOCG deposits of the Missouri metallic province (Kisvarsanyi and Proctor, 1967). Recent investigations by Bickford and others (2015), du Bray and others (2018a), and Frost and Frost (2008, 2011) define the conditions favorable for ferroan granitoid, broadly within-plate magmatism that extends across the North American craton and Ayuso and others (2016) and Day and others (2016) review the factors that fostered approximately 1.4 Ga magmatism specifically in the St. Francois Mountains terrane. However, the tectonic setting that prevailed during Mesoproterozoic magmatism in the St. Francois Mountains terrane is uncertain and relations between
Figure 1. Map showing the spatial distribution of Mesoproterozoic igneous rocks in the St. Francois Mountains terrane, southeast Missouri. A, Geochemical and geochronologic sample sites. B, Locations and names of mines and prospects. [Ga, giga-annum (billion year old)]
Figure 1. Map showing the spatial distribution of Mesoproterozoic igneous rocks in the St. Francois Mountains terrane, southeast Missouri. A, Geochemical and geochronologic sample sites. B, Locations and names of mines and prospects. [Ga, giga-annum (billion year old)]
—Continued
the resulting igneous rocks and analogous but more widely distributed 1.4 Ga Mesoproterozoic igneous rocks across the United States are not well established.

Many relatively specific studies of Mesoproterozoic igneous rocks in the St. Francois Mountains terrane contributed to presently available knowledge about the character and petrogenesis of these rocks (Bickford and others, 1981; Cullers and others, 1981; Day and others, 2016; Lowell, 1991; Menuge and others, 2002; Sides and others, 1981; Walker and others, 2002). Ultimately, these studies constrain the geologic framework prevailing during magma genesis. Pioneering work by Anderson (1962) established the presence of widely distributed, voluminous rhyolitic ash-flow tuffs, and identified and defined the areal extent of calderas from which the associated volcanic rocks erupted. Similar studies by Berry (1970) and Brown (1988) added considerable detail concerning the character and distribution of igneous, principally volcanic rocks, exposed in the St. Francois Mountains terrane. The conceptual synthesis by Kisvarsanyi (1981) and systematic compilation efforts (Day and others, 2016; Pratt and others, 1979; Sides and others, 1981) considerably refined the distribution and character of these rocks; these investigations are critical to defining the geologic architecture prevailing during magmatism. The recently completed (2016), exhaustive study of the Pea Ridge IOA deposit, in particular, and igneous rocks and mineral deposits in the St. Francois Mountains terrane, in general, produced a significant volume of modern, high-quality whole-rock geochemical, radiogenic isotope tracer, and geochronologic data (Slack and others, 2016, and references therein). Similarly, Bickford and others (2015) have produced important new hafnium-in-zircon isotope data applicable to the study of these rocks. With completion of the compilation of whole-rock geochemical data for broadly 1.4 Ga igneous rocks in the conterminous United States (du Bray and others, 2015), including those in the St. Francois Mountains terrane, additional data compilation, and acquisition of data for newly collected samples (du Bray and others, 2018b; Granitto and others, 2018), the data necessary to better define the petrogenetic and tectonic processes responsible for 1.48 to 1.45 Ga magmatism in the St. Francois Mountains terrane are now available.

Rock unit names used throughout this report correspond to formal and informal stratigraphic nomenclature developed by Anderson (1962), Berry (1970), Brown (1988), Pippin (1996), Sides (1981), and Sylvester (1984). Mafic extrusive and hypabyssal intrusive units include the Lake Four Winds basalt, basalt in the Cope Hollow Formation, Boss basaltic trachyandesite, basalt of Kratz Spring, Silver Mines basaltic andesite, lower andesite of Marble Creek campground, Bourbon basalt, upper andesite of Marble Creek campground, trachyte host of Camels Hump IOA deposit, Boss trachyandesite, and trachyte of Kratz Spring. The sole recognized mafic intrusive unit is the diorite host of the Boss IOCG deposit. Intermediate composition extrusive and hypabyssal intrusive units include the trachyandesite of Floyd Tower/Indian Creek, trachyte of South Crane Mountain, Bourbon trachydacite, and trachyte of Kratz Spring. The sole intermediate composition intrusive unit is the Tiemann quartz diorite. Felsic extrusive and hypabyssal intrusive rocks include the Iron Mountain Lake rhyolite, Ironon Rhyolite, rhyolite at South Crane Mountain, Little Rock Creek rhyolite, Boss rhyolite, Russell Mountain Rhyolite, Shepherd Mountain Rhyolite, Upper Ridge rhyolite, Pond Ridge Rhyolite, Lower Ridge rhyolite, Tile Red ash-flow tuff, Pea Ridge 1825 rhyolite porphyry, Bourbon rhyolite, Ketcherside Mountain rhyolite, Grassy Mountain Ignimbrite, Royal Gorge Rhyolite, Lake Killarney Formation, Ironon Hollow-Cedar Bluff Rhyolite, lower campground tuff at Marble Creek campground, Taum Sauk Rhyolite, and Cuthbertson Mountain rhyolite. Felsic intrusive units include the Big Spring granite, Boss granite, Breadtray Granite, Brown Mountain granite porphyry, Bunker granite, Butler Hill Granite, Knoblick Granite, Silvermine Granite—fine grained, Silvermine Granite—medium grained, Slabtown Granite, and Stono Granite.

Nature of Mesoproterozoic Igneous Rocks in the St. Francois Mountains Terrane

Igneous rocks in the St. Francois Mountains terrane define two distinct episodes of Mesoproterozoic magmatism: (1) about 1.48 to 1.45 Ga, and (2) about 1.34 to 1.28 (Aleinikoff and others, 2016; Bickford and Mose, 1975; du Bray and others, 2018a; Thomas and others, 2012; and Van Schmus and others 1996). The St. Francois Mountains terrane is a Mesoproterozoic large felsic igneous province. The extent of the earlier (Calymmmian) episode is dramatically greater than that of the later (Ectasian) episode (Kisvarsanyi, 1981; Pratt and others, 1979). The older magmatic episode consists of dominantly felsic volcanic and volcaniclastic rocks and associated intrusions with volumetrically lesser amounts of basalt, basaltic andesite, and andesite and their associated hypabyssal intrusions (for example, the Silver Mines mafic suite of Sylvester, 1984). The younger magmatic episode consists of a compositionally bimodal assemblage of volumetrically relatively minor mafic intrusions epitomized by the Skrainka suite (Sylvester, 1984) and its equivalents and a volumetrically more significant assemblage, exemplified by the Graniteville Granite, of mostly hypersolvus granites, most of which are concealed by overlying Paleozoic sedimentary rocks (Kisvarsanyi, 1981). All known magmatic-associated IOA and IOCG mineral deposits in the St. Francois Mountains terrane are coeval and cospatial with the products of and hosted in volcanic rocks of the older magmatic episode. Consequently, we focus on the petrogenesis and tectonic setting of the older Mesoproterozoic igneous rock assemblage in the St. Francois Mountains terrane. However, we present limited new geochronologic data for several plutons representative of the younger magmatic episode.

Mafic through felsic rocks, manifest as intrusive and extrusive masses, are represented among 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane. However,
relative proportions of each of these various igneous rock types are quite dissimilar. The two most complete and useful regional-scale maps portraying the relative distribution of various igneous rock types in the St. Francois Mountains terrane were produced by Kisvarsanyi (1981) and Pratt and others (1979). Kisvarsanyi (1981) produced an interpretive map, based on geologic and geophysical data, portraying presumed continuous bedrock geologic relations beneath Paleozoic sedimentary rocks exposed throughout much of the St. Francois Mountains terrane. In contrast, Pratt and others (1979) produced a map that portrays the observed distribution and character of exposed Mesoproterozoic igneous rocks. For this study and following the guidance of Hildreth (2007), we classify mafic, intermediate, and felsic igneous rocks as those consisting of basalt through basaltic andesite, andesite through dacite, and rhyodacite through rhyolite, respectively. Accordingly, approximations of the relative areal extents of various igneous rock types in the St. Francois Mountains terrane were determined in a geographic information system context by applying these classification criteria to the maps of Kisvarsanyi (1981) and Pratt and others (1979) (table 1). Although results derived from the two maps are not identical, 1.48 to 1.45 Ga magmatism in the St. Francois Mountains terrane is dominated (95 to 99 percent) by felsic magmatism; the relative proportions of mafic and intermediate composition igneous rocks are minor (table 1). A similar classification of rock geochemistry verifies that the igneous rock population is dominated by felsic compositions but also reveals the compositions of these rocks are bimodally distributed, with respect to silica content, between a dominant felsic population and a much smaller mafic- to intermediate-composition population.

Several intrinsic features of igneous rocks in the St. Francois Mountains terrane further characterize these rocks. Importantly, except for outcrops in the Hawn State Park area (Lowell, 1976), none of the Mesoproterozoic igneous rocks in the St. Francois Mountains terrane exhibit deformation that resulted in penetrative fabrics. Rather, brittle deformation, as exemplified by fracture cleavage and brittle faulting, dominates throughout the terrane (Day and others, 2016). Most noticeably, felsic igneous rocks are much more abundant than either intermediate or mafic igneous rocks in this area (table 1). Although both the outcrop map of Pratt and others (1979) and the conceptual map of Kisvarsanyi (1981) indicate that the extent of felsic extrusive rocks is more than twice that of their intrusive equivalents (table 1) our updated compilation of St. Francois Mountains terrane geology (fig. 1) suggests the opposite. Also, many of the felsic Mesoproterozoic intrusions in the St. Francois Mountains terrane form large, essentially circular plutons. These intrusions, principally the Breadtray and Butler Hill Granites but also including the Bunker and Big Spring granites, constitute the massif-type intrusions of Kisvarsanyi (1981). In contrast, the Stono, Knoblick, Silvermine, and Slabtown Granites constitute the ring-type intrusions of Kisvarsanyi (1981), many of which form broadly annular bodies surrounding the massif-type intrusions. Finally, most of the mafic and intermediate igneous rocks in this area consist of small subvolcanic or hypabyssal intrusions, although some formed lava flows. The diorite that hosts the Boss IOCG deposit is the best documented example of a volumetrically significant mafic 1.48 to 1.45 Ga intrusion in the St. Francois Mountains terrane. Similarly, the Tiemann quartz diorite, an intrusion in the east-central part of the St. Francois Mountains terrane, constitutes the sole known example of a volumetrically significant intermediate composition 1.48 to 1.45 Ga intrusion in the St. Francois Mountains terrane.

Detailed geologic mapping by Anderson (1962), Berry (1970), Brown (1988), and Sides (1981) first characterized the eruptive styles and types of volcanoes that dominated the Mesoproterozoic geologic landscape in the St. Francois Mountains terrane. Caldera-derived rhyolite ash-flow tuffs constitute the vast majority of volcanic units mapped in the St. Francois Mountains terrane (Day and others, 2016); their exceedingly large distribution and volumes markedly surpass the minor volume of rhyolite erupted as rhyolite flow dome complexes. The mafic and intermediate composition volcanic rocks, including the upper and lower andesites of Marble Creek

### Table 1

<table>
<thead>
<tr>
<th>Rock type</th>
<th>Outcrop map</th>
<th>Conceptual map</th>
<th>This study (fig. 1)</th>
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</table>

1Pratt and others (1979).
3du Bray and others (2018b).
isotope Laboratory at the University of California, Santa Cruz.

tion mass spectrometry (CA-ID-TIMS) at the W.M. Keck

mined by chemical abrasion-isotope dilution-thermal ioniza-

Uranium and lead ages for these two samples were also deter-

geochronology of 1.48 to 1.45 ga igneous rocks in the st. francisco mountains terrane

49 samples of zircon and two samples (table 2) of
titanite (CLT-1-13; ICM-1-13) from Mesoproterozoic igneous
rocks in the St. Francois Mountains terrane of southeast Missouri
were analyzed using the U.S. Geological Survey (USGS)-Stanford
sensitive high resolution ion microprobe-reverse geometry
(SHRIMP-RG). In addition, titanite sample CLT-1-13 was
analyzed using the USGS laser ablation-inductively coupled
plasma mass spectrometry (LA-ICPMS) technique in Denver,
Colo. The ages of two additional samples were determined by
uranium-lead (U-Pb) surface analysis using the SHRIMP-RG.
Uranium and lead ages for these two samples were also deter-
mained by chemical abrasion-isotope dilution-thermal ioniza-
tion mass spectrometry (CA-ID-TIMS) at the W.M. Keck
Isotope Laboratory at the University of California, Santa Cruz.

Methods

The procedures used to prepare samples for analysis are
described in the following sections.

Sample Preparation

Samples for dating were collected either at outcrops or
from drill core archived at the McCracken Core Library and
Research Center, Rolla, Mo. At outcrop sample sites, about
4–6 kilogram (kg) samples were collected, whereas drill core
samples consist of 0.5–2 m of half-split drill core. Zircon
was extracted using standard mineral separation techniques
including crushing, pulverizing, processing over a Wilflley
table, and passing the heavy mineral suite through a Frantz
Isodynamic Magnetic Separator. Nonmagnetic grains were
then poured into methylene iodide (density of 3.3 grams per
cubic centimeter) for density separation. Zircon (plus titanite
and pyrite, if present) sunk, whereas apatite (plus quartz and
feldspar, if present) floated. For SHRIMP analyses, individual grains of zircon and
titanite were handpicked under a binocular microscope. Selected
grains were placed onto double-sided tape, mounted in epoxy,
ground to about half thickness using 2,500-grit wet-dry sandpaper,
and polished sequentially using 6 micrometer (μm) and 1 μm
diamond suspensions. All grains were imaged in reflected
and transmitted light on a petrographic microscope. Using the
USGS JEOL 5800LV scanning electron microscope (SEM) in
Lakewood, Colo., zircon was imaged in cathodoluminescence
(CL), whereas titanite was imaged using backscattered electrons
(BSE) (fig. 2).

For the U-Pb surface analyses, individual euhedral crystals
were adhered to a glass slide coated with a thin (<10 μm) film
of agave nectar. After the [010] crystal faces were oriented in
the plane of the glass slide, the slide was flipped to press all
crystals into indium metal containing pre-polished standard
grains, resulting in flat, non-polished zircon surfaces exposed
parallel to the mount surface (Matthews and others, 2015). All
grains were imaged with reflected light on a petrographic
microscope to identify inclusions and physical defects such as
fractured crystal faces. Prior to introduction into the SHRIMP-RG,
the indium-mounted zircons were soaked in soapy water, fol-
hewed by a 10 percent ethylenediaminetetraacetic acid wash
for about 2 minutes each, thoroughly rinsed in distilled water,
and dried at 50 degrees Celsius (°C) in a vacuum oven. The
sample surface was coated with about 100 nanometers of gold
prior to analysis.

For LA-ICPMS analyses, fragments or single crystals of
titanite from sample CLT-1-13 were handpicked, mounted in
epoxy, and imaged in transmitted and (or) reflected light on a
petrographic microscope. BSE imaging on the USGS FEI Quanta
FEG 450 SEM in Lakewood, Colo revealed internal textures
(core-rim structures) and inclusions in individual grains.

For CA-ID-TIMS analyses, zircon crystals were plucked
from indium grain mounts and thermally annealed in a quartz
crucible at 900 °C for 60 hours. Following thermal annealing,
each zircon crystal was placed into a 200 microliter Teflon®
microcapsule and leached in 29 M (molar) hydrofluoric
acid inside a high-pressure Parr® vessel held at 220 °C for
12 hours, a procedure modified after the chemical abrasion
partial-dissolution procedure of Mattinson (2005). Grains were
then transferred to 3 mL Savillex® perfluoroalkoxy beakers
and rinsed with 16 M nitric acid and 6 M hydrochloric acid,
fluxed in the acid at 80 °C, followed by an approximately
30-minute ultrasonic bath. Between acid washes, grains were
rinsed three times with Milli-Q® water. Single zircon crystals
were loaded with clean water into Teflon® microcapsules and
spiked with the EARTHTIME 205Pb,231U,235U (ET535) tracer
crystal solution and dissolved in 29 M hydrofluoric acid at 220 °C
for 48 hours. Upon dissolution, aliquots were dried down on
a hotplate and redissolved under pressure in 6 M hydrochloric
acid overnight at 180 °C. Sample solutions were then dried
and redissolved at 180 °C in 3 N (normal) hydrochloric
acid. Lead and uranium were separated using a miniaturized
hydrochloric acid-based ion-exchange chromatography
SHRIMP U-Pb Analysis

Zircon and titanite from the St. Francois Mountains terrane were analyzed using the USGS-Stanford SHRIMP-RG ion microprobe following methods described in Ireland (1995) and Williams (1998). The primary ion beam was operated at about 4–6 nA with an analytical spot size of about 20–25 µm in diameter. The magnet was cycled through the appropriate mass stations five times. Measured $^{206}$Pb/$^{238}$U for zircon was normalized to the accepted value for zircon standard R33 (419 Ma; Black and others, 2004). For samples dated during 2013–2014, zircon standards FC-1 (1099 Ma; Paces and Miller 1993) or OG-1 (3441 Ma; Stern and others, 2009) were run as secondary standards to verify accuracy of $^{206}$Pb/$^{238}$Pb ages. For samples run after 2014, zircon standard Z1242 (2679 ± 1 Ma; Davis and others, 2018) was analyzed on all mounts with unknowns; any divergence from the accepted $^{206}$Pb/$^{238}$Pb age of the standard was used to normalize measured values of $^{207}$Pb/$^{206}$Pb for unknowns. Titanite was dated using titanite standard BLR-1 (1047 ± 1 Ma; Aleinikoff and others, 2007) to normalize measured $^{206}$Pb/$^{238}$U ages.

Measured SHRIMP U-Pb data (Aleinikoff, 2021) were reduced using Squid 2 (Ludwig, 2009) and plotted using Isoplot 3 (Ludwig, 2003) (fig. 2). Ages of these Mesoproterozoic zircon samples were determined using one of two methods: (1) for discordant data (mostly less than 10 percent discordant), the weighted mean of selected $^{207}$Pb/$^{206}$Pb ages was calculated; or (2) for concordant data, a Concordia Age (CA) (Ludwig, 1980; 2003) was calculated. Unless otherwise noted, ages were calculated by method (1). Concentrations of uranium and thorium (Th), determined by analysis of zircon standard MADDER, are believed to be accurate to about ±20 percent (Ireland, 1995).

SHRIMP U-Pb Surface Analysis

Uranium and Pb isotopic measurements (table 3) were performed on the Stanford-USGS SHRIMP-RG using an O$_2$- primary beam with an intensity ranging from 6.0 to 7.2 nanoamps and spot dimension of approximately 35 x 32 x 2 µm (length x width x depth). Calculated U/Pb dates (fig. 3) are standardized relative to zircon standard 91500 (1065 million years old [Ma]; Wiedenbeck and others, 1995) calibrated from the ratio of uranium oxide to uranium (UO/U) (Schmitt and Zack, 2012), which was determined repeatedly throughout the duration of the analytical session. Ion intensities were measured on a single ETP® discrete-dynode electron multiplier operated in pulse counting mode and corrected for deadtime. Measurements were performed at mass resolutions of 6,500–7,500 (10 percent peak height), which eliminates interfering molecular species at lead, thorium, and uranium peaks. Data reduction for geochronology follows the methods described by Ireland and Williams (2003) using the spreadsheet add-in program Squid 2.51 (Ludwig, 2009, 2012). Individual spots are reported as $^{206}$Pb/$^{238}$U dates that were corrected for common Pb using $^{207}$Pb and with application of an age-appropriate-modeled Pb composition from Stacey and Kramers (1975), and for initial $^{230}$Th disequilibrium using the method of Scharer (2002). Uranium and thorium concentrations were calculated relative to MAD-559 zircon (uranium = 3940; Coble and others, 2018). Some analyses were omitted from the final dataset based on common Pb concentration (greater than 5 percent $^{207}$Pb-corrected for sample MO16-015, greater than 2 percent for sample MO16-001), and run quality, which varied depending on the degree of surface contamination, grain size, surface topography (cracks or significant undulation), secondary ion yield, and uranium concentration.

LA-ICPMS Analysis

Titanite from sample CLT-1-13 was analyzed using a LA-ICPMS method because this titanite has an unusual composition (resulting in matrix effect problems for SHRIMP analysis) and low concentrations of uranium and high common lead contents, also problematic for SHRIMP analysis.

We used an LA-ICPMS system that includes a Teledyne Photon Machines Excite-Analyte™ 193 nm excimer ArF (argon fluoride) laser and a Nu Instruments AttoM ES™ high resolution-sector field ICPMS to acquire U-Th-Pb isotopic data. Prior to analysis, the system was optimized using NIST (National Institute of Standards and Technology) 610 glass (National Institute of Standards and Technology, 1992) ablated in raster mode to achieve maximum signal intensity, optimal peak shape at mass 238, and low interelement fractionation monitored by Th/U (typically approximately 0.8). Approximate uranium and thorium concentrations (table 4) were obtained using the Iolite™ U-Pb geochronology data reduction scheme (U_Pb_Geochronology3; Paton and others, 2011), using NIST 610 glass as the primary standard reference material (461.5 parts per million [ppm] uranium and 457.2 ppm thorium). NIST glasses can exhibit substantially different elemental fractionation behavior than many common geological matrices, resulting in degraded precision and accuracy for concentrations of some elements (Jackson, 2008; Sylvester, 2008). Because of the matrix difference between the NIST 610 glass and titanite, we assume an accuracy of uranium and thorium concentrations in titanite to be ±20 percent based on results by Jochum and others (2011). We used the Pb/U isotopic values in NIST 610 from Baker and others (2004) and Stern and Amlin (2003). Additional instrumental and data acquisition parameters are defined in table 5.
Raw data were reduced using a combination of Iolite™ and spreadsheet calculations using Isoplot software (Ludwig, 2012). We used NIST 610 glass as a primary matrix-mismatched standard and titanite standard BLR-1 (1047 Ma; Aleinikoff and others, 2002) as a secondary matrix-matched standard. Normalization to the primary standard was done using Iolite™, which calculates accurate titanite lead-isotope ratios and biased U/Pb values because the matrix-mismatched primary standard was used. Biased 208Pb/206Pb age for the BLR-1 standard was calculated by Isoplot using Stacey-Kramers 1.05 Ga common lead correction (Stacey and Kramers, 1974) and Tera-Wasserburg isochron diagram (Tera and Wasserburg, 1972). Measured U/Pb for titanite sample CLT-1-13 were corrected for instrumental bias by applying a correction factor F calculated from the difference between the measured biased age and known “true” age for the BLR-1 matrix-matched standard. Two-sigma uncertainties were appropriately propagated. The validity of this approach was verified by analyzing secondary titanite standards Khan (approximately 520 Ma; Heaman, 2009) and OL-T-1 (approximately 1015 Ma; Kennedy and others, 2010). More details on the analytical techniques and data reduction protocols are described by Neymark and others (2018).

CA-ID-TIMS Analysis

Measurement of isotopic ratios of uranium and lead was done on an IsotopX X62 thermal ionization mass spectrometer at the W.M. Keck Isotope Laboratory at the University of California at Santa Cruz. Isotopes of lead were measured by peak-hopping on a single Daly/photomultiplier detector system (table 6). Isotopes of uranium were measured as uranium dioxide (UO₂) on Faraday detectors in static mode. Isotope ratios of lead were corrected for mass dependent fractionation by empirically determining alpha-lead based on long-term measurements of the NBS−981 common-lead standard. Isotopes of uranium were corrected for mass fractionation during analysis using the ET535 tracer solution. Data reduction was done using the Tripoli and U/Pb Redux software packages (Bowring and others, 2011; McLean and others, 2011). Zircon analyses were corrected for initial thorium disequilibrium by using the measured 208Pb for the Th/U of the zircon crystal and assuming a Th/U of the magma of 4.

Results

For each of the analyzed samples, we compiled the data (table 7), including source of the rock sample, age (including 2-sigma uncertainty), and method of age calculation (Concordia Age or 207Pb/206Pb weighted mean age); also, we present a representative CL or BSE image and concordia plot, pertinent to each geochronologic age determination. All of the previously published, high precision ages for Mesoproterozoic igneous rocks in southeast Missouri are given in table 8.

Fifty samples, regionally distributed throughout the St. Francois Mountains terrane, were dated as part of this study. Of these, 25 are samples from drill core obtained from the McCracken Core Library, whereas 25 samples were collected at outcrops (table 7). Unless otherwise noted, zircon grains from Mesoproterozoic igneous rocks in the St. Francois Mountains terrane are euhedral, prismatic, doubly terminated, and display concentric oscillatory zoning (see representative CL images in figure 2A–5).

Samples are grouped by geographic location and geologic association and by age. As shown by Van Schmus and others (1996) and confirmed by Thomas and others (2012), Mesoproterozoic rocks of the St. Francois Mountains terrane define two broad age groups, approximately 1.46 Ga and approximately 1.32 Ga. Our new data, discussed from youngest to oldest (table 7), define these same two magmatic episodes.

1.34–1.27 Ga Bimodal Plutonic Rocks

Six samples of granitic rocks (five from drill core and one collected from outcrop) from the middle Mesoproterozoic bimodal plutonic rock group (Day and others, 2016) were dated. The three youngest plutonic rocks of this age group in the study area are the Greenville pluton (sample 63W20; weighted mean age 1275 ± 13 Ma, mean square of weighted deviations (MSWD) = 1.6), Van Buren pluton (sample CT-5; weighted mean age 1278 ± 10 Ma, MSWD = 0.65) and Piedmont pluton (sample 82MO-8; weighted mean age 1290 ± 15 Ma, MSWD = 1.2) (fig. 2A1–2A6). All of these granites are in the southern part of the study area (fig. 1). Slightly older granite rocks, the Graniteville Granite (sample GVG-1-13; weighted mean age 1311 ± 13 Ma, MSWD = 1.2) and the Buick pluton (sample FED3; 1317 ± 8; Concordia Age) (fig. 2B1–2B4), are in the central part of the study area. An alkali-feldspar granite sample (sample 124-14A; weighted mean age 1338 ± 10 Ma, MSWD = 1.12) (fig. 2B5, 2B6) was collected from core derived from a hole drilled southwest of the study area, in the area coincident with the regional Missouri gravity low (Guiness and others, 1982; Hildenbrand and others, 1996).

The Graniteville Granite had previously been dated by two studies. Our SHRIMP age of 1311 ± 13 Ma is within uncertainty of the 1317 ± 2 Ma age determined by CA-ID-TIMS (Thomas and others, 2012). Multigrain TIMS data (Van Schmus and others, 1996) yielded an older and less precise age of 1358 ± 25 Ma.

The alkali-feldspar granite sample was dated as part of an investigation of the Missouri gravity low (MGL), which forms a belt about 125 kilometers wide and about 600 kilometers long across the Mesoproterozoic eastern granite-rhyolite province and the Central Plains orogen. Historically, the MGL has been most commonly and plausibly attributed to either (1) an approximately 1.3 Ga granite batholith related to a mantle plume (Hildenbrand and others, 1996), or (2) a failed Precambrian rift (Guiness and others, 1982). An age was also determined for a second granite intrusion coincident with the MGL (see text in the Regional Granitoids and Rhyolite section of this report; table 7).
Table 2. Samples of igneous rocks in the St. Francois Mountains terrane, southeast Missouri for which ages were determined by SHRIMP U-Th-Pb analysis of zircon and titanite.

[Aleinikoff (2021) presents SHRIMP U-Pb geochronologic data for the analyzed samples]

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<th>Map number (fig. 1)</th>
<th>Sample number</th>
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<th>West longitude</th>
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Petrology and Geochronology of 1.48 to 1.45 Ga Igneous Rocks in the St. Francois Mountains Terrane, Southeast Missouri

Figure 2. Representative cathodoluminescence images of zircon and backscattered electron images of titanite from igneous rocks in the St. Francois Mountains terrane, southeast Missouri. Zircon uranium-lead isotope data are plotted on Wetherill (1956) concordia curves, whereas titanite uranium-lead isotope data are plotted on Tera-Wasserburg (1972) concordia curves. Insets show weighted means of selected $^{207}\text{Pb}/^{206}\text{Pb}$ ages. [Ma, million years; Ga, billion years]
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Results

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**Results**

1450 ± 19 Ma

1477 ± 21 Ma

WY032

207Pb/206Pb age

1466 ± 19 Ma

M-DT-3-1

Mean 207Pb/206Pb age

1467 ± 17 Ma

1442 ± 20 Ma

MO17-001

Quartz-alkali feldspar andesite dike

1456 ± 8 Ma

Concordia Age

1456 ± 8 Ma

Age = 1464 ± 8 Ma

(Mean square of weighted deviates, MSWD= 0.83)

1360

1440

1520

1600

1700

1600

1500

1200

1000

MO17-001

Quartz-alkali feldspar andesite dike

1700

1600

1500

1400

1300

1200

1100

1000

1100

1000

0.16

0.18

0.20

0.22

0.24

0.26

0.28

1.6 2.0 2.4 2.8 3.2 3.6 4.0 4.4

1300

1400

1500

1600

1600

1500

1200

1400

1300

1200

1100

1000

1100

1000

207Pb/235U

206Pb/238U

0.16

0.18

0.20

0.22

0.24

0.26

0.28

0.30

1.6 2.0 2.4 2.8 3.2 3.6 4.0 4.4

Age = 1468 ± 10 Ma

(MSWD= 1.05)

1442± 20 Ma

207Pb/ 206Pb age

Figure 2. Representative cathodoluminescence images of zircon and backscattered electron images of titanite from igneous rocks in the St. Francois Mountains terrane, southeast Missouri. Zircon uranium-lead isotope data are plotted on Wetherill (1956) concordia curves, whereas titanite uranium-lead isotope data are plotted on Tera-Wasserburg (1972) concordia curves. Insets show weighted means of selected 207Pb/206Pb ages. [Ma, million years; Ga, billion years]—Continued
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Results

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Results

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Table 3. SHRIMP-RG U-Th-Pb isotopic data and dates for two samples of Mesoproterozoic igneous rock from the St. Francois Mountains terrane, southeast Missouri.

[Errors are 1 sigma unless otherwise specified. Strutthrough data are omitted from the weighted mean based on percent common Pb. Pb* denotes radiogenic lead. 204Pb/206Pb, ratio of the abundances of the mass 204 isotope of lead to that of the mass 206 isotope of lead; %, percent; 207Pb/206Pb, ratio of the abundances of the mass 207 isotope of lead to that of the mass 206 isotope of lead; 206Pb/238U, ratio of the abundances of the mass 206 isotope of lead to that of the mass 238 isotope of uranium; 207Pb, mass 207 isotope of lead; U ppm, uranium abundance in parts per million; Th ppm, thorium abundance in parts per million; 207U/206U, ratio of the abundances of the mass 207 isotope of thorium to that of the mass 238 isotope of uranium; Ma, million years; 207Pb corrected, ratio of the abundances of the mass 207 isotope of lead to that of the mass 206 isotope of lead; 206Pb corrected common, ratio of the abundances of the mass 206 isotope of lead to that of the mass 235 isotope of lead.]

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<th>error</th>
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<th>error</th>
<th>207Pb-corrected common (%)</th>
<th>error</th>
<th>U ppm</th>
<th>Th ppm</th>
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<th>207Pb corrected</th>
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Table 3. SHRIMP-RG U-Th-Pb isotopic data and dates for two samples of Mesoproterozoic igneous rock from the St. Francois Mountains terrane, southeast Missouri.—Continued

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CA-ID-TIMS
Weighted mean = 1465.52 ± 0.71 million years, Ma
Mean square of weighted deviates, MSWD = 1.3, n = 9

207Pb/206Pb, Th, Pa-corrected

Wetherill (1956) Concordia curve, along which 206Pb/238U and 207Pb/235U ages are equal
Concordia curve error envelope associated with uncertainties in the 238U and 235U decay constants

SHRIMP-RG
207Pb/206Pb ages
Weighted mean = 1490 ± 20 Ma
MSWD = 2.3, n = 12

206Pb/238U ages
Upper intercept = 1478 ± 60 Ma
MSWD = 2.6 n = 17

EXPLANATION
Error ellipse (representing two-sigma errors)
Pb/U data used to calculate zircon ages
Discordant Pb/U data excluded from age calculations
Wetherill (1956) Concordia curve, along which 206Pb/238U and 207Pb/235U ages are equal
Mean 207Pb/206Pb age
1-sigma uncertainty envelope
2-sigma uncertainty envelope

Error bar (2-sigma) of selected 207Pb/206Pb ages derived from CA-ID-TIMS data—Used to calculate a weighted average age and uncertainty

Error bar (2-sigma) of selected 207Pb/206Pb ages derived from SHRIMP data—Used to calculate a weighted average age and uncertainty

Figure 3. CA-ID-TIMS and SHRIMP-RG zircon Pb/Pb weighted mean and U/Pb concordia plots for two samples of Mesoproterozoic igneous rock from the St. Francois Mountains terrane, southeast Missouri. Preferred dates shown in bold type. [CA-ID-TIMS, chemical abrasion-isotope dilution-thermal ionization mass spectrometry; SHRIMP-RG, sensitive high resolution ion microprobe-reverse geometry; Pb, lead; U, uranium]
Figure 3. CA-ID-TIMS and SHRIMP-RG zircon Pb/Pb weighted mean and U/Pb concordia plots for two samples of Mesoproterozoic igneous rock from the St. Francois Mountains terrane, southeast Missouri. Preferred dates shown in bold type. [CA-ID-TIMS, chemical abrasion-isotope dilution-thermal ionization mass spectrometry; SHRIMP-RG, sensitive high resolution ion microprobe-reverse geometry; Pb, lead; U, uranium]—Continued
Table 4. LA-ICPMS analyses of titanite from sample CLT-1-13.

[U ppm, uranium in parts per million; Th ppm, thorium in parts per million; Th/U, ratio of thorium and uranium abundances; 238U/206Pb, ratio of the abundances of the mass 238 isotope of uranium to that of the mass 206 isotope of lead; +/- 2SE, two standard errors; 207Pb/206Pb, ratio of the abundances of the mass 207 isotope of lead to that of the mass 206 isotope of lead; Rho, correlation coefficient between 238U/206Pb and 207Pb/206Pb. Values in italics are outliers not used in age calculations]

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Table 4. LA-ICPMS analyses of titanite from sample CLT-1-13.—Continued

[U ppm, uranium in parts per million; Th ppm, thorium in parts per million; Th/U, ratio of thorium and uranium abundances; 238U/206Pb, ratio of the abundances of the mass 238 isotope of uranium to that of the mass 206 isotope of lead; +/- 2SE, two standard errors; 207Pb/206Pb, ratio of the abundances of the mass 207 isotope of lead to that of the mass 206 isotope of lead; Rho, correlation coefficient between 238U/206Pb and 207Pb/206Pb. Values in italics are outliers not used in age calculations]

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Median values                  1.8    0.45   0.32
Table 4. LA-ICPMS analyses of titanite from sample CLT-1-13.—Continued

[U ppm, uranium in parts per million; Th ppm, thorium in parts per million; Th/U, ratio of thorium and uranium abundances; 238U/206Pb, ratio of the abundances of the mass 238 isotope of uranium to that of the mass 206 isotope of lead; +/- 2SE, two standard errors; 207Pb/206Pb, ratio of the abundances of the mass 207 isotope of lead to that of the mass 206 isotope of lead; Rho, correlation coefficient between 238U/206Pb and 207Pb/206Pb. Values in italics are outliers not used in age calculations]

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<td>0.08</td>
<td>20.09</td>
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<td>Median values</td>
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</table>

¹ Time-resolved analysis (TRA) session number. Correction factor (F) value is given with ±2SE uncertainty.
² U/Pb ratio corrected for instrumental mass-bias using BLR-1 titanite standard (see text for details).
³ Ratio corrected for Pb-isotope fractionation using NIST 610 glass standard.
Table 5. LA-ICPMS instrumental and data acquisition parameters.

[LA-ICPMS, laser-ablation inductively coupled plasma mass spectrometry; ArF, argon fluoride; Hg, mercury; He, helium; Ar, argon; N₂, nitrogen; Ni, nickel]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
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<tbody>
<tr>
<td>Mass spectrometer:</td>
<td>AttoM ES™ sector field ICPMS</td>
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<tr>
<td>Laser:</td>
<td>Teledyne Photon-Machines Excite-Analyte™ 193 nanometer ArF excimer with HelEx cell</td>
</tr>
<tr>
<td>General parameters</td>
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</tr>
<tr>
<td>RF generator power</td>
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<tr>
<td>Acceleration voltage</td>
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<tr>
<td>Auxiliary gas flow rate</td>
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<tr>
<td>Instrument resolution</td>
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<tr>
<td>Analysis mode</td>
<td>Deflector jump</td>
</tr>
<tr>
<td>Acquisition mode</td>
<td>Time resolved analysis</td>
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<tr>
<td>Peak center mass</td>
<td>²⁰⁶Pb</td>
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<tr>
<td>Peak integration time durations (per sweep)</td>
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<td>²³⁸U (250 microseconds)</td>
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<tr>
<td>²³⁵U (500 microseconds)</td>
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</tr>
<tr>
<td>²³²Th (500 microseconds)</td>
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<td>²⁰⁸Pb (500 microseconds)</td>
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<tr>
<td>²⁰⁷Pb (1.5 milliseconds)</td>
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<tr>
<td>²⁰⁶Pb (500 microseconds)</td>
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<td>²⁰⁴Pb (500 microseconds)</td>
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<td>²⁰⁲Hg (500 microseconds)</td>
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<td>Total peak integrations (per cycle)</td>
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<td>Total signal acquisition time per spot</td>
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<tr>
<td>Total baseline acquisition time per spot</td>
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<td>Laser-mode parameters</td>
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<td>Laser energy</td>
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<tr>
<td>Energy density</td>
<td>4-5 joules per square centimeter</td>
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<tr>
<td>Spot size</td>
<td>50 microns</td>
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<tr>
<td>NIST 610, the titanite secondary reference ma-</td>
<td></td>
</tr>
<tr>
<td>terial (BLR-1), and the titanite unknown (CLT-</td>
<td></td>
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<tr>
<td>1-13) were analyzed with the same laser spot</td>
<td>for a single analytical session</td>
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<tr>
<td>Repetition rate</td>
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<tr>
<td>Cell and carrier He gas flow rate</td>
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<tr>
<td>Make-up Ar gas flow rate</td>
<td>0.25-0.45 liters per minute</td>
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<tr>
<td>Accessory N₂ gas</td>
<td>5.5-6.0 milliliters per minute</td>
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<tr>
<td>Ni sampler cone</td>
<td>“Dry” plasma type, X (regular) or Y (ES) millimeter orifice</td>
</tr>
<tr>
<td>Ni skimmer cone</td>
<td>“Dry” plasma type, X (regular) or Y (ES) millimeter orifice</td>
</tr>
<tr>
<td>Total U sensitivity (SRM-610, 50 micron spot)</td>
<td>Approximately 3-4 ×10⁷ counts per second per part per million</td>
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</table>
Table 6. Uranium and lead isotopic concentrations and ages, determined by chemical abrasion-isotope dilution-thermal ionization mass spectrometry, for two samples of Mesoproterozoic igneous rock from the St. Francois Mountains terrane, southeast Missouri.

| Sample | ²⁰⁶Pb/²³⁸U | ²⁰⁷Pb/²³⁵U | ²⁰⁷Pb/²⁰⁶Pb | ²⁰⁶Pb/²³⁸U absolute age, Ma | ²⁰⁷Pb/²³⁵U absolute age, Ma | ²⁰⁷Pb/²⁰⁶Pb absolute age, Ma | Th/U | Pb* | Pb*/Pb | ²⁰⁶Pb/²⁰⁴Pb | ²⁰⁶Pb/²³⁸U | ²⁰⁷Pb/²³⁵U | ²⁰⁷Pb/²⁰⁶Pb |
|--------|-----------|-----------|-----------|----------------------------|----------------------------|----------------------------|-------|------|-------|----------------|----------------|----------------|-------|------|-------|
| MO16-001 |            |           |           |                            |                            |                            |       |      |       |               |               |               |       |      |       |
| z1     | 1,452.77  | 0.95      | 1,457.69  | 1.30                        | 0.60                        | 1.60                        | 0.44  | 26.00 | 1,564.95 | 0.2528          | 0.0733          | 3.2022         | 0.0919 | 0.1329 |
| z2     | 1,465.20  | 1.66      | 1,465.95  | 1.52                        | -0.05                       | 0.4145                      | 0.44  | 41.21 | 0.85    | 2,901.06       | 0.2553          | 0.0784         | 3.2343 | 0.0919 | 0.0780 |
| z3     | 1,461.43  | 1.44      | 1,461.13  | 1.43                        | 0.70                        | 0.46                        | 0.46  | 20.60 | 0.70    | 1,760.29       | 0.2544          | 0.1105         | 3.2248 | 0.0920 | 0.2354 |
| z4     | 1,460.91  | 0.94      | 1,463.32  | 0.99                        | 0.80                        | 0.44                        | 0.44  | 51.26 | 0.86    | 3,582.87       | 0.2552          | 0.0787         | 3.2315 | 0.0919 | 0.0713 |
| z5     | 1,466.40  | 2.01      | 1,466.15  | 2.08                        | 0.57                        | 0.45                        | 0.45  | 12.21 | 0.76    | 16.07           | 0.2554          | 0.1534         | 3.2373 | 0.0920 | 0.2180 |
| z6     | 1,466.40  | 0.75      | 1,466.32  | 0.79                        | 0.76                        | 0.44                        | 0.44  | 51.26 | 0.86    | 5,828.72       | 0.2552          | 0.0872         | 3.2315 | 0.0919 | 0.0713 |
| z7     | 1,466.40  | 2.01      | 1,466.15  | 2.08                        | 0.57                        | 0.45                        | 0.45  | 12.21 | 0.76    | 16.07           | 0.2554          | 0.1534         | 3.2373 | 0.0920 | 0.2180 |
| z8     | 1,466.40  | 0.75      | 1,466.32  | 0.79                        | 0.76                        | 0.44                        | 0.44  | 51.26 | 0.86    | 5,828.72       | 0.2552          | 0.0872         | 3.2315 | 0.0919 | 0.0713 |
| z9     | 1,466.40  | 0.75      | 1,466.32  | 0.79                        | 0.76                        | 0.44                        | 0.44  | 51.26 | 0.86    | 5,828.72       | 0.2552          | 0.0872         | 3.2315 | 0.0919 | 0.0713 |
| z10    | 1,466.40  | 0.75     | 1,466.32  | 0.79                        | 0.76                        | 0.44                        | 0.44  | 51.26 | 0.86    | 5,828.72       | 0.2552          | 0.0872         | 3.2315 | 0.0919 | 0.0713 |

1 Corrected for initial Th/U disequilibrium using radiogenic ²⁰⁶Pb and Th/U[magma] = 4.0.
2 Isotopic dates calculated using λ²³⁸U = 1.55125E-10 (Jaffey and others, 1971) and λ²³⁵U = 9.8485E-10 (Jaffey and others, 1971).
3 Corrected for initial Pa/U disequilibrium using initial fraction activity ratio [²³¹Pa]/[²³⁵U] = 1.1.
4 Th contents calculated from radiogenic ²⁰⁶Pb and ²⁰⁶Th-corrected ²⁰⁶Pb/²³⁸U date of the sample, assuming concordance between U-Pb Th-Pb systems.
5 Total mass of radiogenic Pb.
6 Total mass of common Pb.
7 Ratio of radiogenic Pb (including ²⁰⁸Pb) to common Pb.
8 Measured ratio corrected for fractionation and spike contribution only.
9 Measured ratios corrected for fractionation, tracer and blank.
Table 7. Summary of stratigraphic relations and new U-Pb ages for Mesoproterozoic igneous rocks in the St. Francois Mountains terrane, southeast Missouri.

<table>
<thead>
<tr>
<th>Rock unit (sample number)</th>
<th>Sample source</th>
<th>Age (Ma) [± 2 sig]</th>
<th>Age calc. method</th>
<th>Figure</th>
<th>Map no. (fig. 1)</th>
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<tbody>
<tr>
<td><strong>1.34-1.27 Ga Bimodal Plutonic Rocks</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Greenville pluton (63W20)</td>
<td>c</td>
<td>1,275 ± 13</td>
<td>76</td>
<td>2A1, 2A2</td>
<td>1</td>
</tr>
<tr>
<td>Van Buren pluton (CT-5)</td>
<td>c</td>
<td>1,278 ± 10</td>
<td>76</td>
<td>2A3, 2A4</td>
<td>2</td>
</tr>
<tr>
<td>Piedmont pluton (82MO-8)</td>
<td>c</td>
<td>1,290 ± 15</td>
<td>76</td>
<td>2A5, 2A6</td>
<td>3</td>
</tr>
<tr>
<td>Graniteville Granite (GVG-1-13)</td>
<td>o</td>
<td>1,311 ± 13</td>
<td>76</td>
<td>2B1, 2B2</td>
<td>4</td>
</tr>
<tr>
<td>Buick pluton (FED3)</td>
<td>c</td>
<td>1,317 ± 8</td>
<td>CA</td>
<td>2B3, 2B4</td>
<td>5</td>
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<tr>
<td>Alkali-feldspar granite, Missouri gravity low (124-14A)</td>
<td>c</td>
<td>31,338 ± 10</td>
<td>CA</td>
<td>2B1, 2B2</td>
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<tr>
<td><strong>1.49-1.44 Ga Volcanic and Associated Plutonic Rocks</strong></td>
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<td>Volcanic rocks of Marble Creek area</td>
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<tr>
<td>Rhyolite of South Crane Mtn. (CLT-1-13)</td>
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<td>1,380 ± 27</td>
<td>Lower intercept age</td>
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<tr>
<td>Tuff at Crane Pond (MO14-053)</td>
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<td>3.1460 ± 17</td>
<td>76</td>
<td>2A3, 2A4</td>
<td>8</td>
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<tr>
<td>Lower campground tuff at Marble Creek campground (MO14-043)</td>
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<td>3.1473 ± 9</td>
<td>76</td>
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<td>Volcanic rocks of Taum Sauk caldera</td>
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<td>Royal Gorge Rhyolite (RGR-1-13)</td>
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<td>1,459 ± 4</td>
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<td>Breadtray Granite (BTG-1-13)</td>
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<td>Butler Hill Granite (BH-1-13)</td>
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<td>76</td>
<td>2E3, 2E4</td>
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<td>Slabtown Granite (STG-1-13)</td>
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<td>Knoblick Granite (KLG-1-13)</td>
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<td>1,463 ± 7</td>
<td>CA</td>
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<td>Stono Granite (MO17-013)</td>
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<td>2G2, 2G3</td>
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<td>Regional granitoids and rhyolite</td>
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<td>Massif-type granite (RE060)</td>
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<td>1,456 ± 5</td>
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<td>Biotite granite (MO17-002)</td>
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<td>3.1448 ± 12</td>
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<td>2H5, 2H6</td>
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<td>Quartz-alkali feldspar andesite dike (MO17-001)</td>
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<td>3.1456 ± 8</td>
<td>CA</td>
<td>2J1, 2J2</td>
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<td>Trachyandesite at Buford Mountain (PcF-076)</td>
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<td>1,463 ± 9</td>
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<td>2K3, 2K4</td>
<td>49</td>
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<td>3.1464 ± 8</td>
<td>76</td>
<td>2L3, 2L4</td>
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<td>Rhyolite at Middlebrook Hill (PcF-077)</td>
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<td>3.1465 ± 6</td>
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<td>2L5, 2L6</td>
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<tr>
<td>Trachyandesite at Iron Mountain (PcF-075)</td>
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<td>3.1465 ± 6</td>
<td>76</td>
<td>2L1, 2L2</td>
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<td>Granite near Piedmont pluton (WY-032)</td>
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<td>1,468 ± 10</td>
<td>76</td>
<td>2L5, 2L6</td>
<td>27</td>
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<td>Megacrystic granite, Missouri gravity low (W-6-2578)</td>
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<td>3.1467 ± 8</td>
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<td>2K1, 2K2</td>
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<td>Massif-type granite (RE05)</td>
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<tr>
<td>Massif-type biotite granite (MH-1)</td>
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<td>3.1471 ± 5</td>
<td>76</td>
<td>2L5, 2L6</td>
<td>30</td>
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<tr>
<td>Stouts Creek Rhyolite (GMI-1-13)</td>
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<td>3.1471 ± 5</td>
<td>76</td>
<td>2L1, 2L2</td>
<td>31</td>
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<tr>
<td>Granite of Castor River Shut-Ins (MO17-006)</td>
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<td>3.1472 ± 8</td>
<td>76</td>
<td>2L3, 2L4</td>
<td>32</td>
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<tr>
<td>Rhyolite near Silver Mines (OZ-5)</td>
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<td>3.1479 ± 4</td>
<td>76</td>
<td>2L5, 2L6</td>
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<tr>
<td>Biotite granite (MF-1-1)</td>
<td>c</td>
<td>3.1484 ± 7</td>
<td>76</td>
<td>2M1, 2M2</td>
<td>34</td>
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</table>
Table 7. Summary of stratigraphic relations and new U-Pb ages for Mesoproterozoic igneous rocks in the St. Francois Mountains terrane, southeast Missouri.—Continued

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<thead>
<tr>
<th>Rock unit (sample number)</th>
<th>Sample source&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Age (Ma) [± 2 sig]</th>
<th>Age calc. method&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Figure</th>
<th>Map no. (fig. 1)</th>
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</thead>
<tbody>
<tr>
<td>1.49-1.44 Ga Volcanic and Associated Plutonic Rocks</td>
<td></td>
<td></td>
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<tr>
<td>Volcanic and intrusive rocks of Eminence area</td>
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<tr>
<td>Upper unit of Coot Mountain (MO14-007)</td>
<td>o</td>
<td>1,464 ± 6</td>
<td>CA</td>
<td>2N1, 2N2</td>
<td>35</td>
</tr>
<tr>
<td>Lower unit of Coot Mountain (MO14-009)</td>
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<td>1,463 ± 5</td>
<td>CA</td>
<td>2N3, 2N4</td>
<td>36</td>
</tr>
<tr>
<td>Rhyolite of Steggal Mountain (MO14-003)</td>
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<td>1,462 ± 6</td>
<td>CA</td>
<td>2N5, 2N6</td>
<td>37</td>
</tr>
<tr>
<td>Biotite-hornblende granodiorite (SV-3)</td>
<td>c</td>
<td>1,467 ± 7</td>
<td>CA</td>
<td>2O1, 2O2</td>
<td>38</td>
</tr>
<tr>
<td>Hypabyssal rocks related to Pea Ridge deposit</td>
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<td></td>
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<tr>
<td>Trachyandesite at Floyd Tower (MO13-006)</td>
<td>o</td>
<td>1,463 ± 2</td>
<td>76</td>
<td>2P1, 2P2</td>
<td>39</td>
</tr>
<tr>
<td>Trachyandesite of Indian Creek mine (ICM-1-13)&lt;sup&gt;4&lt;/sup&gt;</td>
<td>o</td>
<td>1,459 ± 13</td>
<td>76</td>
<td>2P3, 2P4</td>
<td>40</td>
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<td>Intrusive rocks related to Boss deposit</td>
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<tr>
<td>Rhyolite host (USA-50)</td>
<td>c</td>
<td>1,470 ± 10</td>
<td>76</td>
<td>2Q1, 2Q2</td>
<td>41</td>
</tr>
<tr>
<td>Trachyte host (J22-1541-1562)</td>
<td>c</td>
<td>1,477 ± 17</td>
<td>76</td>
<td>2Q3, 2Q4</td>
<td>42</td>
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<tr>
<td>Post-mineralization diorite (S5)</td>
<td>c</td>
<td>1,471 ± 8</td>
<td>76</td>
<td>2Q5, 2Q6</td>
<td>43</td>
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<tr>
<td>Granite dike (S5-gr)</td>
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<td>1,322 ± 10</td>
<td>76</td>
<td>2R1, 2R3</td>
<td>44</td>
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<tr>
<td>Biotite granite (J15)</td>
<td>c</td>
<td>1,327 ± 11</td>
<td>76</td>
<td>2R2, 2R4</td>
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<td>Volcanic rocks related to Bourbon deposit</td>
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<tr>
<td>Rhyolite (Bourb-435)</td>
<td>c</td>
<td>1,472 ± 11</td>
<td>76</td>
<td>2S1, 2S2</td>
<td>46</td>
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<tr>
<td>Trachydacite (Bourb-204)</td>
<td>c</td>
<td>1,463 ± 12</td>
<td>76</td>
<td>2S3, 2S4</td>
<td>47</td>
</tr>
</tbody>
</table>

<sup>1</sup> Sample source: c (sample collected from core), o (sample collected from outcrop).

<sup>2</sup> Age calculation method: CA (Concordia Age of Ludwig, 1980; 2003), 76 (weighted mean of selected 207Pb/206Pb ages).

<sup>3</sup> 207Pb/206Pb normalized to isotopic data obtained from concurrently analyzed secondary standard Z1242. 207Pb/206Pb for other samples validated by subjective comparison to data from secondary standards FC-1 (Paces and Miller, 1993) or OG1 (Stern and others, 2009).

<sup>4</sup> Titanite; all other ages from zircon.

<sup>5</sup> CA-ID-TIMS 207Pb/206Pb age (MO16-015) of 1468.28 ± 0.71 Ma (table 6) for Tile Red ash-flow tuff, which is interlayered with the tuff at Crane Pond (Brown, 1988).

<sup>6</sup> CA-ID-TIMS 207Pb/206Pb age (MO16-001) of 1465.52 ±0.71 Ma (table 6).
Table 8. Previously published ages for Mesoproterozoic igneous rocks in the St. Francois Mountains terrane, southeast Missouri.

[TIMS, thermal ionization mass spectrometry; CA-TIMS, chemical abrasion-thermal ionization mass spectrometry]

<table>
<thead>
<tr>
<th>Rock unit</th>
<th>Age (Ma)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graniteville Granite</td>
<td>1,358 ± 25</td>
<td>TIMS U-Pb zircon</td>
<td>Van Schmus and others (1996)¹</td>
</tr>
<tr>
<td>Graniteville Granite</td>
<td>1,317 ± 2</td>
<td>CA-TIMS U-Pb zircon</td>
<td>Thomas and others (2012)</td>
</tr>
<tr>
<td>Munger Granite Porphyry</td>
<td>1,378 ± 6</td>
<td>TIMS U-Pb zircon</td>
<td>Van Schmus and others (1996)</td>
</tr>
<tr>
<td>Munger Granite Porphyry</td>
<td>1,323 ± 2</td>
<td>CA-TIMS U-Pb zircon</td>
<td>Thomas and others (2012)</td>
</tr>
<tr>
<td>Devil’s Tollgate Gabbro</td>
<td>1,323 ± 1</td>
<td>CA-TIMS U-Pb baddeleyite</td>
<td>Thomas and others (2012)</td>
</tr>
<tr>
<td>Skrainka Diabase</td>
<td>1,300 ± 10</td>
<td>TIMS Pb-Pb baddeleyite</td>
<td>Rämö and others (1994)</td>
</tr>
<tr>
<td>Muddy Knob gabbro, Skrainka Diabase</td>
<td>1,316 ± 6</td>
<td>TIMS Pb-Pb baddeleyite</td>
<td>Rämö and others (1994)</td>
</tr>
<tr>
<td>Shepherd Mountain Gabbro</td>
<td>1,333 ± 56</td>
<td>Sm-Nd isochron age</td>
<td>Lowell and Rämö (1999)</td>
</tr>
<tr>
<td>Cope Hollow Formation</td>
<td>1,462 ± 1</td>
<td>CA-TIMS U-Pb zircon</td>
<td>Thomas and others (2012)</td>
</tr>
<tr>
<td>Johnson Shut-ins rhyolite</td>
<td>1,464 ± 3</td>
<td>CA-TIMS U-Pb zircon</td>
<td>Thomas and others (2012)</td>
</tr>
<tr>
<td>Taum Sauk Rhyolite</td>
<td>1,466 ± 3</td>
<td>CA-TIMS U-Pb zircon</td>
<td>Thomas and others (2012)</td>
</tr>
<tr>
<td>Hawn Park Gneiss</td>
<td>1,478 ± 43</td>
<td>TIMS U-Pb zircon</td>
<td>Van Schmus and others (1996)</td>
</tr>
<tr>
<td>Hawn Park Gneiss</td>
<td>1,462 ± 1</td>
<td>CA-TIMS U-Pb zircon</td>
<td>Thomas and others (2012)</td>
</tr>
<tr>
<td>Rhyolite of Shut-In Mountain</td>
<td>1,470.4 ± 2.7</td>
<td>TIMS U-Pb zircon</td>
<td>Harrison and others (2000)</td>
</tr>
<tr>
<td>Royal Gorge Rhyolite</td>
<td>1,503 ± 20</td>
<td>TIMS U-Pb zircon</td>
<td>Van Schmus and others (1996)</td>
</tr>
<tr>
<td>Silvermine Granite</td>
<td>1,484 ± 7</td>
<td>TIMS U-Pb zircon</td>
<td>Van Schmus and others (1996)</td>
</tr>
<tr>
<td>Butler Hill Granite</td>
<td>1,465 ± 32</td>
<td>TIMS U-Pb zircon</td>
<td>Van Schmus and others (1996)</td>
</tr>
<tr>
<td>Breadtray Granite</td>
<td>1,480 ± 30</td>
<td>TIMS U-Pb zircon</td>
<td>Van Schmus and others (1996)</td>
</tr>
<tr>
<td>Knoblick Granite</td>
<td>1,491 ± 18</td>
<td>TIMS U-Pb zircon</td>
<td>Van Schmus and others (1996)</td>
</tr>
</tbody>
</table>

¹Van Schmus and others (1996) list samples from cores according to the drill hole name. Although we used a similar naming convention, it is not known if the same units were sampled within the drill core. Thus, age comparisons are made only on samples collected at outcrops.
Petrology and Geochronology of 1.48 to 1.45 Ga Igneous Rocks in the St. Francois Mountains Terrane, Southeast Missouri

1.48–1.45 Ga Volcanic and Associated Plutonic Rocks

Volcanic Rocks of the Marble Creek Area

Near the summit of South Crane Mountain, a large outcrop area contains two compositionally distinct volcanic rock types (Brown, 1988). Rhyolite contains 68–71 weight percent SiO₂, whereas trachydacite contains 64–66 weight percent SiO₂ (du Bray and others, 2018b). Both rock types were sampled for geochronology, but neither sample yielded zircon. However, the rhyolite (sample CLT-1-13) does contain pale yellow, anhedral titanite. The color of this titanite is unusual (titanite commonly is honey-brown colored). BSE imaging identifies cores with concentric, wedge shaped, oscillatory zoning (consistent with an igneous origin), and unzoned or weakly patchy zoned overgrowths (fig. 2C1). Preliminary SHRIMP analysis indicated that this titanite has low uranium contents (mostly less than 10 ppm) and many grains have a high proportion of common lead contents (2–100 percent common ²⁰⁶Pb). Additionally, a significant matrix mismatch between titanite standard BLR-1 and CLT-1-13 unknowns results in unusable SHRIMP data for this sample. To circumvent these issues, we used the USGS AttoM LA-ICPMS to analyze oscillatory-zoned cores and unzoned rims.

Three sessions of U-Pb analysis of CLT-1-13 titanite by LA-ICPMS (117 spot analyses total; table 4) indicate low concentrations of uranium in cores and rims, 0–9 and 0–20 ppm, respectively, and high proportions of common lead, confirming preliminary SHRIMP results. A regression through the data for cores (n = 74; 6 data points excluded) yields a Tera-Wasserburg lower intercept age of 1380 ± 27 Ma (fig. 2C2). However, because most of the data plot near the y-axis (indicative of high common lead content), the lower intercept age constitutes a large extrapolation, mostly controlled by only a few discordant data points. The geologic accuracy of the calculated age is suspect, especially because of a lack of similar-age rocks in the region. Although the BSE zoning of the cores suggests an igneous origin, we are unable to determine a crystallization age for the rhyolite at South Crane Mountain.

Isotopic data from titanite rims of sample CLT-1-13 indicate somewhat higher uranium content and lower proportions of common lead than was found for the cores, resulting in less discordant data (in other words, data that plot closer to the lower intercept). Regression through 37 rim analyses yields a lower intercept age of 1319 ± 28 Ma (fig. 2C3). This sample was collected just east of the interpreted occurrence of the buried Sabula pluton (fig. 1), which is considered a member of the 1.3 Ga igneous suite (Kisvarsanyi, 1981). Thus, the titanite rims may have formed by regional magmatic-hydrothermal activity related to emplacement of the Sabula pluton.

Three samples were collected from outcrops in the Marble Creek area (table 7). Zircon from the tuff at Crane Pond (sample MO14-053) have parallel (but not concentric) oscillatory zoning and yielded a weighted mean age of 1460 ± 17 Ma, MSWD = 1.5 (fig. 2C4, 2C5). The unit represented by this sample is interlayered with rhyolite of the Tile Red ash-flow tuff (Brown, 1988). CA-ID-TIMS data for seven grains from a sample (MO16-015) of Tile Red ash-flow tuff, collected about 35 m from our sample of tuff at Crane Pond, yielded a weighted mean age of 1468.28 ± 0.71 Ma, MSWD = 1.8 (table 6); data for an eighth analyzed grain were omitted from the age calculation because of poor analytical run characteristics.

Few zircons were extracted from a sample of the lower campground tuff at Marble Creek campground (sample MO14-043). These grains are relatively small (50–100 µm in length) and subhedral to euhedral; they yielded a weighted mean SHRIMP age of 1473 ± 9 Ma, MSWD = 1.6 (fig. 2D1, 2D2). Because of the paucity of zircon in this rock, a second sample (MO16-001) was collected from an adjacent layer (about 60 m from the first sample). This sample yielded better-preserved zircon grains; five of nine grains result in a weighted mean CA-ID-TIMS age of 1465.52 ± 0.71 Ma, MSWD = 1.3 (table 6); data for four grains were not included in the age calculation because data for these grains show evidence of lead loss.

Volcanic Rocks of the Taum Sauk Caldera

Two samples of rhyolite were collected from outcrops associated with the Taum Sauk caldera. Zircon extracted from the Royal Gorge Rhyolite (RGR-1-13) are subhedral to euhedral, blocky, and have faint, broad, irregular zoning (fig. 2D3). Most of the data points are concordant, enabling calculation of a Concordia Age of 1459 ± 4 Ma (fig. 2D4). Van Schmus and others (1996) obtained an age of 1503 ± 20 Ma for another sample of Royal Gorge Rhyolite. Slightly discordant data from zircon of the Shepherd Mountain Rhyolite (sample MO15-008) yielded a weighted mean age of 1466 ± 8 Ma, MSWD = 0.88 (fig. 2D5, 2D6).

Volcanic and Intrusive Rocks of the Butler Hill Caldera

Six samples of granite and one sample of felsic volcanic rock were collected from outcrops associated with the Butler Hill caldera in the east-central part of the study area. Based on our new SHRIMP data, intrusive and extrusive rocks in this group define a narrow age range (table 7). SHRIMP ages for the Breadtray Granite (sample BTG-1-13; weighted mean age 1453 ± 11 Ma, MSWD = 0.88) (fig. 2F1, 2F2), and Butler Hill Granite (sample BHG-1-13; weighted mean age 1453 ± 8 Ma, MSWD = 0.6) (fig. 2F3, 2F4) are younger and more precise than previous age data (1480 ± 30 Ma and 1465 ± 32 Ma, respectively; Van Schmus and others, 1996) for these rocks. The Grassy Mountain Ignimbrite (sample GMI-2-13) yielded a weighted mean age of 1460 ± 6 Ma, MSWD = 1.32 (fig. 2E5, 2E6) and the Slabtown Granite (sample STG-1-13) yielded a Concordia Age of 1462 ±7 Ma (fig. 2F3, 2F4). SHRIMP
Concordia Ages for Silvermine Granite (sample SMG-1-13; 1461 ± 8 Ma; fig. 2F1, 2F2) and Knoblick Granite (sample KLG-1-13; 1463 ± 7 Ma; fig. 2F5, 2F6) are younger than previous age data (1484 ± 7 Ma and 1491 ± 18 Ma, respectively; Van Schmus and others, 1996) for these rocks.

The Stono Granite is regionally unusual because it contains many mafic inclusions (up to 5 cm in diameter; fig. 2G1). In addition, δ18O values for the Stono Granite are uncharacteristically low compared to all other Mesoproterozoic granite rocks in the St. Francois Mountains terrane (King and others, 2008; Wenner and Taylor, 1996). The sampled granite (sample MO17-013) contains a minor but unavoidable amount of fine-grained mafic inclusions. Two types of CL zoning were observed in zircon from the Stono Granite: (1) typical light to dark grains with concentric, fine oscillatory zoning, and (2) dark, unzoned grains (fig. 2G2). Both types of zircon are partially resorbed and somewhat fractured. Type 1 grains have relatively low uranium concentrations (approximately 100–600 ppm) and Th/U (approximately 0.40–0.65), whereas type 2 grains have higher uranium (approximately 650–1,700 ppm) and higher Th/U (approximately 0.65–2.7). Analyses of five zircon grains with concentric oscillatory CL zoning and relatively high uranium concentrations yield concordant Pb/U data that result in a calculated Concordia Age of 1465 ± 9 Ma (fig. 2G3). Because the origin of the unzoned low-uranium zircon is uncertain, analytical data for those grains were excluded from the age calculation for the Stono Granite.

Regional Granitoids and Rhyolite

Ten samples of granite and two samples of rhyolite were collected from drill core and seven samples (two granites, two rhyolite, two trachyandesites, and one petrographically unusual andesite dike) were collected from outcrops for rocks of this group. These rocks have been divided into four subgroups, including (1) nine samples of massif-type granitoids (biotite granodiorite to granite on fig. 1), (2) two granitoids interpreted as ring-type intrusions surrounding 1.3 Ga plutons (homblende-biotite granodiorite on fig. 1; Kisvarsanyi, 1981), (3) four rhyolites, two trachyandesites, and one hypabyssal andesite dike, and (4) one megacrystic granite that occurs at depth within the MGL, southwest of the study area.

Rocks within subgroup 1 range in age from about 1455 to 1485 Ma (table 7). All of these samples contain zircon with typical euhedral morphology, and concentric oscillatory CL zoning. Specific zircon U-Pb ages are a Concordia Age for sample RE060—1456 ± 5 Ma (fig. 2H1, 2H2) and weighted mean ages for sample MO17-002, 1448 ± 12 Ma, MSWD = 0.66 (fig. 2H5, 2H6); sample SV-5, 1458 ± 7 Ma, MSWD = 1.09 (fig. 2F3, 2F4); sample VB-23-2153, 1455 ± 11 Ma, MSWD = 1.9 (fig. 2F5, 2F6); sample M-DT-3-1, 1464 ± 8 Ma, MSWD = 0.83 (fig. 2F3, 2F4); sample RE05, 1469 ± 7 Ma, MSWD = 0.97 (fig. 2L3, 2L4); sample MH-1, 1471 ± 5 Ma, MSWD = 1.09 (fig. 2L5, 2L6); sample MO17-006, 1472 ± 8, MSWD = 0.93 (fig. 2M3, 2M4); and sample M-FK-1-1, 1484 ± 7 Ma, MSWD = 0.6 (fig. 2N1, 2N2).

Geophysical data (Kisvarsanyi, 1980, 1981) suggest that several granitoid units form annular intrusions surrounding Graniteville-type plutons representative of caldera-related resurgent magmatism. This model requires that the annular or ring-type intrusions are approximately coeval with hypothesized resurgent granitoid intrusions. To test this interpretation, ages were determined for two drill core samples of annular, ring-type intrusions. Sample RE037 is from an intrusion that surrounds the undated Redford pluton (fig. 1) and has a Concordia Age of 1457 ± 7 Ma (fig. 2H3, 2H4). Although the locations of some core holes are coincident with the projected areal extent of the Redford pluton, none of these holes penetrate to the granite. Thus, although the Redford pluton has not been dated, its age is presumed to be approximately 1.3 Ga based on its geophysical characteristics (Kisvarsanyi, 1981). Consequently, magmatism represented by the Redford pluton and its presumed ring intrusion do not seem to be coeval or co-genetic. Sample WY032 is from a granite intrusion that surrounds the Piedmont pluton and has a weighted mean age of 1468 ± 10 Ma, MSWD = 1.05 (fig. 2J5, 2J6). Similarly, because the Piedmont pluton crystallized at about 1290 ± 15 Ma (table 7), the annular intrusion cannot be petrologically associated with the Piedmont pluton, but rather represents basement into which the Piedmont pluton was subsequently intruded.

Six of the volcanic rock units in subgroup 3 were dated. Zircon grains from rhyolite tuff (sample MR-3-1556) are elongate to acicular (length-to-width ratios of 5–7), lack terminations, and have parallel CL zoning (fig. 2I1). These grains yielded a weighted mean age of 1456 ± 9 Ma, MSWD = 1.6 (fig. 2I2). This group of dated volcanic rocks also includes an unusual quartz-alkali feldspar-bearing andesite dike (sample MO17-001) that yielded a Concordia Age of 1456 ± 8 Ma (fig. 2J1, 2J2). Weighted mean ages of other dated felsic volcanic rocks within this subgroup include trachyandesite at Buford Mountain (sample PcF-076, 1463 ± 9 Ma, MSWD = 1.17; fig. 2K3, 2K4), rhyolite at Middlebrook Hill (sample PcF-077, 1465 ± 6 Ma, MSWD = 1.02; fig. 2K5, 2K6), trachyandesite at Iron Mountain (sample PcF-075, 1465 ± 6 Ma, MSWD = 1.12; fig. 2K1, 2K2), the Stouts Creek Rhyolite (sample GMI-1-13, 1471 ± 5 Ma, MSWD = 1.08; fig. 2M1, 2M2) and rhyolite that hosts Mesoproterozoic sphalerite mineralization near Silver Mines (sample OZ-5, 1479 ± 4 Ma, MSWD = 0.63; fig. 2M5, 2M6). The andesite dike intruded biotite granite (sample MO17-002—1448 ± 12 Ma, fig. 2H5, 2H6); the mapped intrusive relationship is plausible given analytical uncertainties associated with the relevant age determinations.

Subgroup 4 consists solely of a megacrystic granite from within the MGL. This sample of drill core (sample W-6-2578) was collected for comparison with age data for sample 124-14A (1338 ± 10 Ma, in text above in the 1.34–1.27 Ga bimodal plutonic rocks section), also coincident with the MGL. Zircon from the megacrystic granite yielded a weighted mean age of 1467 ± 8 Ma, MSWD = 1.33 (fig. 2L1, 2L2), demonstrating that both 1.3 and 1.4 Ga intrusions are spatially associated with the MGL.
Volcanic and Intrusive Rocks of the Eminence Area

Ages of volcanic rocks near Eminence, Mo. were determined by analysis of three samples collected from outcrops in the southwest part of the study area (fig. 1, table 7). In addition, we determined the age of a sample of granodiorite collected from core derived from a hole drilled in this area. The granodiorite forms an aeromagnetic high that encircles the rhyolite exposed near Eminence, Mo., and was interpreted as a ring-type intrusion associated with a caldera (Harrison and others, 2000, 2002; Kisvarsanyi, 1981). The volcanic rocks include samples of rhyolite tuff collected from the upper and lower units of Coot Mountain (Orndorff and others, 1999) and the rhyolite of Stegall Mountain located a few kilometers to the southeast (Harrison and others, 2002). Concordia Ages were determined for zircon from the upper unit of Coot Mountain (sample MO14-007; 1464 ± 6 Ma; fig. 2O1, 2O2) and from the lower unit (sample MO14-009; 1463 ± 5 Ma; fig. 2O3, 2O4). The rhyolite of Stegall Mountain (sample MO14-003) yielded a Concordia Age of 1462 ± 6 Ma (fig. 2O5, 2O6); it is considered correlative with the rhyolite of Shut-In Mountain (Harrison and others, 2002), whose stratigraphic relationship with the upper and lower units of Coot Mountain is indeterminate (Orndorff and others, 1999). The rhyolite of Shut-In Mountain was previously dated by multigrain and single grain TIMS analysis at 1470.4 ± 2.7 Ma (Harrison and others, 2000). Biotite-hornblende granodiorite sample SV-3 from the ring-type intrusion that surrounds the rhyolitic rocks of the Eminence caldera structure yielded a Concordia Age of 1467 ± 7 Ma (fig. 2P1, 2P2).

The maximum total age range (including analytical uncertainties) for volcanic rocks of the Eminence area is about 1456 to 1470 Ma, as determined from SHRIMP U-Pb zircon ages. (table 7). The individual uncertainty associated with each age determination (between 5 and 6 million years [m.y.]) is not sufficiently precise to constrain their relative stratigraphic positions. However, geologic relations suggest that rocks included in the upper and lower units of Coot Mountain may be slightly younger than the rhyolite of Stegall Mountain. The age of the biotite-hornblende granodiorite (sample SV-3) is consistent with it being part of a ring-type intrusion associated with the Eminence caldera of Harrison (2000) and Kisvarsanyi (1981).

Hypabyssal Rocks Related to the Pea Ridge Deposit

Geophysical data (Kisvarsanyi, 1981) suggest the presence of an arcuate mass of trachyandesite (previously termed trachyte) in the vicinity of the inferred Pea Ridge granitoid pluton, which presumably lies deeply buried beneath the Pea Ridge IOA deposit (Day and others, 2016). However, relative age relations and petrogenic kinship of the trachyandesite and the hypothesized Pea Ridge granitoid pluton are unknown. Previous geochronologic investigations have shown that rare earth element (REE)-bearing dikes within approximately 1475-Ma rhyolitic rocks at Pea Ridge were emplaced at ~1465 Ma and that both of these rock types were subsequently intruded by felsic dikes at about 1440 Ma (Aleinikoff and others, 2016). These felsic intrusive rocks may represent apophyses of the concealed granitoid intrusion beneath the rhyolite host rocks at Pea Ridge deposit.

Two samples of trachyandesite were collected in order to constrain the age of these intermediate composition igneous rocks. Sample MO13-006 (from near Floyd Tower) was collected at a surface outcrop, whereas sample ICM-1-13 was collected from an extensive mine dump composed of rock excavated as part of mining activities associated with the Mississippi Valley-type deposit at the Indian Creek Mine. Both samples are fine grained and indurated. Zircon was not identified in the least magnetic fraction (its typical residence) from either sample, but it was recovered in the approximately 1.8 Amp magnetic fraction. These grains are dark gray, subhedral, elongate, and highly fractured. CL images show that these grains are composed of medium-gray (relatively low uranium) fragments bounded by cracks filled with unidentified black material with a high uranium content (fig. 2Q1, 2Q2). In sample MO13-006, the homogeneous gray areas are sufficiently large to accommodate SHRIMP analytical spots. In sample ICM-1-13, the grains are more highly fractured and do not preserve areas that have the requisite size and homogeneity required for SHRIMP analysis.

SHRIMP U-Pb data for gray (in CL) areas in zircon from sample MO13-006 indicate that these fragments contain between about 1,400 and 4,500 ppm uranium and have unusually high Th/U values of 0.7–2.0. Zircon with high uranium contents (greater than 2,500 ppm) tend to yield 206Pb/238U ages that are too old, probably because of matrix mismatch between standards and unknowns (White and Ireland, 2012; Williams and Hergt, 2000). However, in order to date the zircon in sample MO13-006, we used 206Pb/207Pb systematics (which are not affected by matrix effects) to calculate a weighted mean age of 1463 ± 2 Ma, MSWD = 1.4 (fig. 2Q2). Although no dateable zircon was obtained from ICM-1-13, we did extract titanite suitable for SHRIMP U-Pb geochronology. The titanite grains are medium brown, anhedral, and in BSE display oscillatory zoning, which suggests an igneous origin. These grains yielded a weighted mean age of 1459 ± 13 Ma, MSWD = 2.1 (fig. 2Q4). As described by Day and others (2017), this age is equivalent to the timing of mineralization at the Pea Ridge IOA deposit.

Intrusive Rocks Related to the Boss Deposit

The Boss deposit, in the west-central part of the study area, is unusual. Whereas other iron ore occurrences in southeast Missouri are IOA deposits, the mineralized rock at Boss constitutes an IOCG deposit (Day and others, 2016). Five rock samples associated with the Boss deposit were collected from drill core and dated by SHRIMP U-Pb geochronology in order to constrain the age of the deposit. These samples include rhyolite
(sample USA-50) and trachyandesite (sample J22-1541-1562), both of which host iron-copper ore. Both samples contain euhedral zircon with fine, concentric, and oscillatory zoning. Zircon grains from sample USA-50 are well-preserved, terminated prisms (fig. 2R1), whereas the grains from sample J22-1541-1562 are partially resorbed and have irregular outer edges (fig. 2R3). Zircon from the rhyolite yielded a weighted mean U-Pb age of 1470 ± 10 Ma, MSWD = 1.7 (fig. 2R1, 2R2), whereas zircon from the trachyandesite yielded a weighted mean age of 1477 ± 17 Ma, MSWD = 0.86, (fig. 2R3, 2R4). Sample S5 represents a diorite pluton that intruded magnetite mineralized rock, and therefore crystallized after ore deposition. Most of the few grains of zircon obtained from the diorite are unzoned and have CL features that are consistent with partial internal replacement (fig. 2R5). Zircon from this sample yielded a broad array of discordant data with a weighted mean 207Pb/206Pb age of 1471 ± 8 Ma, MSWD = 1.3 (fig. 2R6). Together, these three samples bracket the timing of IOCG ore mineralization at the Boss deposit to between about 1480 and 1465 Ma.

Two younger, crosscutting granitic dikes at Boss were also dated. Sample S5-gr is a relatively fresh granite dike that clearly intrudes diorite sample S5. Sample J15 is a biotite granite dike that intrudes the host rhyolite. Zircon from both granite dike samples contains oscillatory-zoned cores and black (in CL) overgrowths, some of which are broad enough to accommodate a SHRIMP spot (fig. 2R1, 2R2). U-Pb data for S5-gr and J15 zircon cores yield weighted mean ages of 1322 ± 10 Ma, MSWD = 1.6 and 1327 ± 11 Ma, MSWD = 1.17, respectively (fig. 2S3, 2S4). As suggested by CL imagery, dark zircon rims from both samples are significantly enriched in uranium (3,000–13,000 ppm). On a standard concordia plot, U-Pb data for rims form arrays with lower intercept ages of about 300 Ma and upper intercept ages of about 1.3 Ga. These data suggest that the rims formed in the late Paleozoic, possibly in association with regional Mississippi Valley type Pb-Zn ore formation, as epitomized by mineralized rock in the nearby Buick Mine. Determining a more precise and accurate lower intercept age was precluded by considerable data scatter. The measured isotopic systematics may have been affected by three independent processes including: (1) inheritance (for example, overlap of the SHRIMP analytical spots on core and narrow rim zones), (2) lead loss from very metamict zones (resulting in younger ages), and (3) matrix effects caused by compositional differences between standard and unknowns (likely resulting in older ages). These processes produce discrete trajectories in U-Pb space (fig. 2R5, 2R6).

### Volcanic Rocks Related to the Bourbon Deposit

The Bourbon IOA deposit is approximately 20 km west of the Pea Ridge IOA deposit (fig. 1). It is associated with a bimodal sequence of early Mesoproterozoic basalt to basaltic andesite and trachydacite to high-silica rhyolite. Two samples were collected from drill core in order to constrain the ages of volcanic rocks associated with the Bourbon IOA deposit. These include a rhyolite (sample Bourb-435) associated with magnetite ore and a trachydacite unit, represented by sample Bourb-204, that is stratigraphically beneath the rhyolite (C. Meighan, written communication, 2018). Both samples yielded euhedral, slightly resorbed, oscillatory-zoned zircon (fig. 2S1, 2S3); because of the possibility of inheritance in cores (Watts and Mercer, 2020), only zoned mantles were analyzed. The SHRIMP U-Pb weighted mean age for the trachydacite is 1463 ± 12 Ma, MSWD = 0.65 (fig. 2T4), whereas the weighted mean age of the rhyolite is 1472 ± 11 Ma, MSWD = 1.5 (fig. 2T2). Within error, these new data suggest that the Bourbon rhyolite and Bourbon trachydacite are coeval.

### Synthesis of Geochronologic Data

Our new geochronologic data better constrain the role of magmatism in the Mesoproterozoic geologic evolution of southeast Missouri. As shown by Van Schmus and others (1996) and Thomas and others (2012), this area was the locus of magmatism during two Mesoproterozoic episodes (fig. 4.4). The first of these, the principal subject of findings reported herein, was volumetrically dominant and spanned 1.48 to 1.45 billion years ago. A second, volumetrically less significant episode, consists of intrusions emplaced between 1.33 and 1.28 billion years ago and may exhibit a systematic north-to-south younging progression. Importantly, magmatism between 1.48 and 1.45 billion years ago was essentially continuous; no significant temporal gaps were detected using presently available technology. The new data also suggest that no particular period within this 30 m.y. episode was characterized by a disproportionate magmatic volume (fig. 4B). The older magmatic episode was succeeded by a volumetrically minor magmatic component depicted by late, crosscutting dikes emplaced at about 1440 Ma (Aleinikoff and others, 2016; Neymark and others, 2016). Significantly, on a regional basis, intrusive and extrusive magmatic products of the older magmatic episode are coeval (fig. 4), as are the ring- and massif-type intrusions of Kisvarsanyi (1981). The observation that granitic rocks intrude rhyolite (Kisvarsanyi, 1981; Sides and others, 1981) establishes their relative age relations but our data do not indicate a significant time gap between the emplacement of volcanic and granitic rocks in the St. Francois Mountains terrane. Our geochronologic data also confirm that rocks previously interpreted (on the basis of geophysical studies by Kisvarsanyi, 1980, 1981) as ring-type intrusions associated with 1.3 Ga plutons are in fact part of the 1.4 Ga magmatic episode. Importantly, our geochronologic data demonstrate that the Pea Ridge iron ore deposit formed between about 1475 and 1460 Ma (Aleinikoff and others, 2016; Neymark and others, 2016) and therefore is entirely coeval with the older period of Mesoproterozoic magmatism in southeast Missouri (fig. 4).
Figure 4. Compilation of age data for Mesoproterozoic igneous rocks in the St. Francois Mountains terrane, southeast Missouri. A, Relative probability plot of all high precision ages displaying two major episodes of magmatism (Harrison and others, 2000; Lowell and Rämö, 1999; Rämö and others, 1994; Thomas and others, 2012; this study). B, Comparison of ages (± 2-sigma errors) for samples of approximately 1400 Ma extrusive and intrusive rocks, each shown in chronologic order.
Petrographic Characteristics

Approximately 1.4 Ga Mesoproterozoic igneous rocks in the St. Francois Mountains terrane are principally rhyolite (Le Maitre, 1989) and granite (Streckeisen, 1976) but also include lesser amounts of mafic- to intermediate-composition rocks. The data compilation of du Bray and others (2015) shows that the phenocryst assemblage in rhyolite tuffs and lavas is dominated by variable amounts of plagioclase, alkali feldspar, and quartz, of which plagioclase is dominant (table 9). Primary mafic silicate phenocryst phases are relatively minor in the rhyolites and are usually replaced by secondary iron-titanium (Fe-Ti) oxide minerals, which reflect pervasive postdepositional alteration that affects all crystalline phases and commonly obscures primary mafic phases. Most of the 1.48 to 1.45 Ga mafic to intermediate composition volcanic rocks in the St. Francois Mountains terrane, principally lavas or hypabyssal intrusions, contain fewer phenocrysts than their felsic volcanic counterparts and some are aphyric. Most phenocrysts in these rocks consist of plagioclase but include clinopyroxene, hornblende, and minor biotite.

Modal data compiled by du Bray and others (2015) indicate that phaneritic intrusive rocks in the St. Francois Mountains terrane are composed of alkali-feldspar granite, syenogranite, monzogranite, and minor granodiorite (fig. 5). Most of these rocks are medium to coarse grained, hypidiomorphic, and inequigranular. These rocks contain both albite-twinned plagioclase and variably exsolved microcline-twinned alkali feldspar, which is consistent with their cooling and solidification from relatively hydrous crustal reservoirs favorable for subsolvus feldspar crystallization. Biotite, 1 to 3 modal percent, is the principal mafic silicate mineral in the 1.48 to 1.45 Ga intrusive rocks in the St. Francois Mountains terrane, although 1 to 2 percent hornblende is sometimes present. Although biotite is the principal mafic silicate mineral in the massif-type intrusions, hornblende is dominant among the ring-type intrusions (Day and others, 2016; Kisvarsanyi, 1981). Fine-grained primary Fe-Ti oxide crystals account for about 0.5 to 1.5 percent of both the extrusive and intrusive rocks. Accessory mineral assemblages in these rocks commonly include apatite, zircon, allanite, and titanite; monazite is a less common accessory constituent. Secondary epidote, chlorite, actinolite, and sericite reflect weak postmagmatic alteration of most of these rocks.

Whole-Rock Geochemistry

Whole-rock geochemical data were compiled from available literature sources and additional, new analyses were obtained for samples collected in support of this investigation (du Bray and others, 2018b; Granitto and others, 2018). Obviously altered samples were eliminated from the interpreted database. Other altered samples were identified as samples with any of the following characteristics: SiO2 abundances greater 78 weight percent, Na2O abundances greater than 6.5 weight percent or less than 0.5 weight percent, K2O abundances greater than 8 weight percent, Na2O/K2O greater than 5, K2O/Na2O greater than 1.5, CO2 concentrations greater than 0.35 weight percent, or total volatile concentrations greater than 3 weight percent. Analyses with any of these characteristics were eliminated from the interpreted data compilation because samples with any of these characteristics probably do not preserve primary igneous rock compositions. In addition, samples with analytical totals greater than 103 or less than 97 probably reflect inaccurate analyses; data for these samples were also eliminated. Although many of the 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane have been affected by alkali metasomatism (Slack and others, 2016), resulting dominantly in sodium losses and potassium gains, the alkali data interpreted herein constitute the best available and quite plausible values for the abundances of these constituents. The identities of samples that convey representative compositions of individual 1.48 to 1.45 Ga igneous rock units exposed in the St. Francois Mountains terrane are listed in table 10.

Formal and informal stratigraphic nomenclature for rock unit names used in this report (table 10) are consistent with those defined in previous investigations (Anderson, 1962; Berry, 1970; Brown, 1988; Pippin, 1996; Sides, 1981; Sylvester, 1984). However, the data compiled by du Bray and others (2018b) indicate that the compositional designations included in some extrusive or hypabyssal intrusion rock units, for example, trachyte in the trachyte of Kratz Spring, are either inconsistent with available geochemical data and (or) are not in agreement with the standard major oxide abundance classification schema of Le Maitre (1989). In these instances, we assigned correct compositional designations for previously defined but inaccurate rock unit names, as appropriate (table 11).

Major Oxide Data

The compositions of 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane are essentially bimodally distributed with respect to silica content. The great majority of both the extrusive and intrusive igneous rocks constitute a felsic end member; this population is dominated by rhyolite with 72 to 78 weight percent SiO2 but includes rhyolite with SiO2 contents as low as about 69 weight percent. In the St. Francois Mountains terrane, a small but important mafic end member is composed of samples that contain about 49 to 57 weight percent SiO2 and includes basalt, basaltic andesite, and basaltic trachyandesite. An even smaller group of samples, with compositions intermediate between those of the felsic and mafic populations, represents just four geologic units; these trachyandesites and trachydacites contain about 60 to 68 weight percent SiO2. Compositions of intrusive rocks across the St. Francois Mountains terrane are almost exclusively felsic and essentially indistinguishable from those of cospatial rhyolitic rocks. With the exception of the fine-grained phase of the Silvermine Granite, all of the ring-type intrusive rocks in
Table 9. Average phenocryst abundances, in percent, in extrusive and shallow hypabyssal geologic units of the St. Francois Mountains terrane, southeast Missouri; averages calculated from the data of du Bray and others (2015). [N, number of samples; Pl, plagioclase; AFS, alkali feldspar; Qtz, quartz; Hbl, hornblende; Cpx, clinopyroxene; Bt, biotite; Opq, opaque Fe-Ti oxides; —, species not present]

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the St. Francois Mountains terrane have SiO₂ contents that are less than those characteristic of the massif-type intrusive rocks as defined by Kisvarsanyi (1981) (fig. 6; table 10). However, major oxide compositions of the ring-type intrusions are distinct from those of the massif-type intrusive rocks only because they extend geochemical arrays or fields to less evolved, lower silica compositions that are continuous or collinear with trends defined by the massif-type intrusive rocks (Cullers and others, 1981). Most igneous rocks in the St. Francois Mountains terrane, including the intrusive rocks, are subalkaline (Irvine and Baragar, 1971) although compositions of the trachyte that hosts the Kratz Spring IOA deposit and the trachyandesite host of the Boss IOCG deposit appear to be alkaline (fig. 6). Similarly, melt inclusions in zircon from some samples of the Pea Ridge 1825 rhyolite porphyry, the upper and lower units of Coot Mountain, and the rhyolite of Stegall Mountain are alkaline, whereas the majority of inclusions in these units and those in zircon from the Bourbon trachydacite are subalkaline (Watts and Mercer, 2020). Na₂O/K₂O values for extrusive rocks, a significant majority are weakly peraluminous, whereas the majority of inclusions in these units and those in zircon from the Bourbon trachydacite are subalkaline (Watts and Mercer, 2020). Na₂O/K₂O values for extrusive rocks, a significant majority are weakly peraluminous, whereas the majority of inclusions in these units and those in zircon from the Bourbon trachydacite are subalkaline (Watts and Mercer, 2020). Na₂O/K₂O values for extrusive rocks, a significant majority are weakly peraluminous, whereas the majority of inclusions in these units and those in zircon from the Bourbon trachydacite are subalkaline (Watts and Mercer, 2020). Na₂O/K₂O values for extrusive rocks, a significant majority are weakly peraluminous, whereas the majority of inclusions in these units and those in zircon from the Bourbon trachydacite are subalkaline (Watts and Mercer, 2020). Na₂O/K₂O values for extrusive rocks, a significant majority are weakly peraluminous, whereas the majority of inclusions in these units and those in zircon from the Bourbon trachydacite are subalkaline (Watts and Mercer, 2020). Na₂O/K₂O values for extrusive rocks, a significant majority are weakly peraluminous, whereas the majority of inclusions in these units and those in zircon from the Bourbon trachydacite are subalkaline (Watts and Mercer, 2020). Na₂O/K₂O values for extrusive rocks, a significant majority are weakly peraluminous, whereas the majority of inclusions in these units and those in zircon from the Bourbon trachydacite are subalkaline (Watts and Mercer, 2020). Na₂O/K₂O values for extrusive rocks, a significant majority are weakly peraluminous, whereas the majority of inclusions in these units and those in zircon from the Bourbon trachydacite are subalkaline (Watts and Mercer, 2020). Na₂O/K₂O values for extrusive rocks, a significant majority are weakly peraluminous, whereas the majority of inclusions in these units and those in zircon from the Bourbon trachydacite are subalkaline (Watts and Mercer, 2020). Na₂O/K₂O values for extrusive rocks, a significant majority are weakly peraluminous, whereas the majority of inclusions in these units and those in zircon from the Bourbon trachydacite are subalkaline (Watts and Mercer, 2020). Na₂O/K₂O values for extrusive rocks, a significant majority are weakly peraluminous, whereas the majority of inclusions in these units and those in zircon from the Bourbon trachydacite are subalkaline (Watts and Mercer, 2020). Na₂O/K₂O values for extrusive rocks, a significant majority are weakly peraluminous, whereas the majority of inclusions in these units and those in zircon from the Bourbon trachydacite are subalkaline (Watts and Mercer, 2020).
Table 10. Identification and characteristics of igneous rock samples from the St. Francois Mountains terrane, southeast Missouri for which representative geochemical analyses are presented by du Bray and others (2018b) and Granitto and others (2018).

<table>
<thead>
<tr>
<th>Sample number</th>
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### Table 10. Identification and characteristics of igneous rock samples from the St. Francois Mountains terrane, southeast Missouri for which representative geochemical analyses are presented by du Bray and others (2018b) and Granitto and others (2018).—Continued

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metaluminous and all but one are mafic and compositionally primitive (figs. 7, 9, and 10; table 11). Four of these units have compositions that are calc alkalic and one is calcic (table 11). Within this composition-based classification schema, extrusive and intrusive rocks are indistinguishable.

Major oxide compositions of individual 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane form diffuse clusters or irregular arrays, each somewhat diagnostic of particular geologic units (fig. 11). These overlapping clusters and arrays define two discrete major oxide composition populations, one mafic and the other felsic; the previously identified third population consists of samples from just four intermediate-composition geologic units that also form distinct major oxide compositional clusters and arrays. Among 1.48 to 1.45 Ga igneous rocks, TiO$_2$, MgO (magnesium oxide), CaO (calcium oxide), and P$_2$O$_5$ (phosphorous pentoxide) abundances vary considerably at SiO$_2$ abundances less than about 60 weight percent but scatter less and decrease with increasing SiO$_2$ contents. Similarly, Al$_2$O$_3$ abundances vary considerably at lower SiO$_2$ abundances; Al$_2$O$_3$ abundances vary irregularly in samples with less than about 60 weight percent SiO$_2$, but decrease significantly and consistently, forming a concave downward data array, in samples with more than 70 weight percent SiO$_2$. Concentrations of FeO* (total iron expressed as ferrous oxide) and MnO decrease systematically with increasing SiO$_2$. Abundances of Na$_2$O and K$_2$O vary considerably at all SiO$_2$ contents, but particularly at high SiO$_2$ contents (fig. 11). At any given SiO$_2$ content, Na$_2$O abundances vary by as much as about 3 weight percent. Similarly, at any given SiO$_2$ content among the mafic rocks, K$_2$O abundances vary by about 2 weight percent and by as much as 4.5 weight percent among the felsic rocks. These highly variable Na$_2$O and K$_2$O abundances do not systematically correlate with SiO$_2$ content and may reflect cryptic alkali metasomatism of some of these rocks. K$_2$O abundances of the 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane are broadly coincident with the high potassium (Le Maitre, 1989) and shoshonitic (Ewart, 1982) fields. Major
oxide compositions of the 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane are indistinguishable (fig. 11) from those of all other Mesoproterozoic granitoid rocks exposed throughout the United States (du Bray and others, 2018a). However, mafic to intermediate composition rocks in the St. Francois Mountains terrane have no analog in the compilation of du Bray and others (2015), which was restricted to rocks with >56 weight percent SiO₂.

With the exception of loss on ignition data, relatively limited information is available concerning volatile component abundances in 1.48 to 1.45 Ga igneous rocks of the St. Francois Mountains terrane. Median loss on ignition values and chlorine and fluorine abundances in these rocks are 0.88, 0.03, and 0.08 weight percent, respectively. Low halogen contents imply that H₂O is the principal volatile constituent in these rocks. Inferred H₂O abundances, ranging from 0.1 to about 3 weight percent and symmetrically and unimodally distributed about a maximum frequency value of about 0.7 weight percent, are similar to abundances in subalkalic silicic obsidians (Macdonald and others, 1992), which are compositionally similar to 1.48 to 1.45 Ga felsic igneous rocks of the St. Francois Mountains terrane. One attribute of A-type igneous rocks, which are grossly similar to the ferroan 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane, is their low volatile content (Loiselle and Wones, 1979). Although H₂O contents of 1.48 to 1.45 Ga felsic igneous rocks of the St. Francois Mountains terrane are not especially low relative to values characteristic of A-type igneous rocks nor to the obsidians, they are significantly lower than the >4 weight percent H₂O characteristic of hornblende-bearing andesitic arc magmas (Rutherford and Hill, 1993). Fluorine abundances determined for about 60 samples of 1.48 to 1.45 Ga felsic igneous rocks from the St. Francois Mountains terrane range from about 0.01 to 0.3 weight percent and define a maximum frequency value of 0.05 weight percent (500 ppm). The median fluorine content of these rocks, 800 ppm, is comparable to the average (850 ppm) for low-calcium granites (Turekian and Wedepohl, 1961), somewhat elevated relative to abundances (average, 500 ppm) in silicic obsidians associated with magmatic arcs, and low relative to average abundances (1,500 ppm) in intracontinental silicic obsidians (Macdonald and others, 1992). Chlorine abundances determined for about 40 samples of these rocks range from 0.01 to about 0.13 weight percent and are strongly skewed to values between 0.01 and 0.02 weight percent. The maximum frequency value is 0.01 weight percent (100 ppm) and the median chlorine abundance of these rocks, 300 ppm, is similar to the average chlorine content (200 ppm) of low-calcium granite (Turekian and Wedepohl, 1961) and low relative to abundances in most silicic obsidians (Macdonald and others, 1992).

### Trace Element Data

Trace element abundances of the 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane vary widely but certain of these characteristics are consistent among particular rock types and inform our understanding of the petrogenesis and tectonic setting pertinent to the associated magmatism. Relative to the average low-calcium granite (Turekian and Wedepohl, 1961), most of the felsic 1.48 to 1.45 Ga igneous rocks from the St. Francois Mountains terrane contain elevated Hf and Zr and low Cu, Nb, Sr, Ta, Th, and V. In contrast, relative to average basaltic rocks (Turekian and Wedepohl, 1961), mafic rocks in the St. Francois Mountains terrane contain low Cr, Cu, Nb, Ni, Sr, and Th. Abundances of Ba, Hf, La, Nb, Rb, Th, U, Y, and Zr in igneous rocks of the St. Francois Mountains terrane increase slightly with increasing silica content; those for Co, Cr, Cu, Ni, Sc, Sr, V, and Zn decrease with increasing silica content; and abundances of Be, Cs, Ga, Pb, Sn, and Ta display no consistent covariation with SiO₂ content.

Among 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane, representative REE abundances vary by nearly a full order of magnitude; however, their chondrite-normalized REE patterns are grossly similar (fig. 12). These representative patterns are moderately negatively sloping; most have Laₐ/Ybₐ (ratio of the chondrite-normalized abundances of lanthanum and ytterbium) that varies from about 2.5 to 8.7 (median, 4.7) (table 12). In contrast, negative europium (Eu) anomaly magnitudes vary systematically with respect to whole-rock composition. The median Eu/Eu⁎ (ratio of determined europium abundance to europium abundance interpolated from the abundances of samarium and gadolinium) for mafic igneous rocks of the St. Francois Mountains terrane is 0.89; those for the intermediate and felsic rocks are 0.66 and 0.43, respectively (table 12). The extent of REE abundance variation within each geologic unit, expressed as chondrite-normalized pattern dispersion, is conveyed by standard deviation values calculated from the REE data for each unit. For any given unit, standard deviations calculated for each of the REE vary within relatively narrow ranges, which suggests that the standard deviation for any particular REE (such as La, which is abundant and easily determined with high precision) depicts REE abundance dispersion for each unit. The standard deviation of La abundance calculated for each unit, divided by its associated average La abundance, yields a consistent, normalized REE dispersion metric (table 12, Dispersion). Among 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane, calculated REE dispersion, Laₐ/Ybₐ, and total REE do not vary systematically with respect to SiO₂ content, although the mafic rocks, as group, have systematically lower total REE contents than the intermediate and felsic igneous rocks.

Representative chondrite-normalized REE patterns for 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane exhibit some similarities, regardless of whole-rock
Figure 6. Total alkali-silica variation diagrams showing compositions of 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri. Alkaline-subalkaline dividing line from Irvine and Baragar (1971). Extrusive rock classification grid from Le Maitre (1989).
A. Extrusive and hypabyssal intrusive rocks

- Bell Mountain Rhyolite
- Black rhyolite
- Boss diorite
- Boss andesite
- Boss rhyolite
- Boss trachyte
- Bourbon basalt
- Bourbon rhyolite
- Bourbon trachydacite
- Brown Mountain
- Brown's rhyolite
- Brushy rhyolite
- Trachyte host of Camels Hump IOA deposit
- Cedar Bluff Rhyolite
- Clearcut rhyolite
- Lower unit of Coot Mountain
- Basalt in Cope Hollow Formation
- Rhyolite in Cope Hollow Formation
- Tuff at Crane Pond
- Creekbed rhyolite
- Cuthbertson Mountain rhyolite
- Fenceline rhyolite
- Forked Creek rhyolite
- French Mills felsite
- Goggin's Mountain rhyolite
- Grassly Mountain Ignimbrite
- Green rhyolite
- Hogan Mountain rhyolite
- Trachyandesite of Floyd Tower/Indian Creek
- Iron Mountain Lake rhyolite
- Ironton Rhyolite
- Ironton Hollow Rhyolite
- Johnson shut-ins rhyolite
- Ketcherside Mountain rhyolite
- Kratz Spring basalt
- Kratz Spring rhyolite
- Kratz Spring trachyte
- Lake Four Winds basalt
- Lake Killarney Formation
- Little Rock Creek rhyolite
- Logroad rhyolite
- Lower campground tuff at Marble Creek campground
- Lower Ridge rhyolite
- Marble Creek rhyolite
- Mountain View rhyolite
- Mudlick rhyolite
- Oak Mountain rhyolite
- Pea Ridge rhyolite
- Pea Ridge trachyte
- Pond Ridge Rhyolite
- Reader Hollow rhyolite
- Royal Gorge Rhyolite
- Russell Mountain Rhyolite
- Saddle rhyolite
- Sawmill rhyolite
- Shepherd Mountain Rhyolite
- Silver Mines basaltic andesite
- Rhyolite at South Crane Mountain
- Trachydacite at South Crane Mountain
- Stouts Creek rhyolite
- Taum Sauk Rhyolite
- Tile Red ash-flow tuff
- Tilk Hollow rhyolite
- Transition rhyolite
- Upper and Lower andesites of Marble Creek campground
- Upper Orchard rhyolite
- Upper Ridge rhyolite

B. Intrusive rocks

- Massif intrusions
  - Big Spring granite
  - Buford Granite Porphyry
  - Butler Hill Granite
  - Breadtray Granite
  - Bunker granite
  - Granite of Castor River Shut-Ins

- Ring intrusions
  - Knoblick Granite
  - Slabtown Granite
  - Silvermine Granite—Medium grained
  - Silvermine Granite—Fine grained
  - Stono Granite
  - Tiemann quartz diorite

- Minor intrusion
  - Brown Mountain granite porphyry

Figure 6. Total alkali-silica variation diagrams showing compositions of 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri. Alkaline-subalkaline dividing line from Irvine and Baragar (1971). Extrusive rock classification grid from Le Maitre (1989). —Continued
Figure 7. Variation diagrams showing molar major-oxide compositions of 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri as a function of relative alumina and alkali saturation.
A. Extrusive and hypabyssal intrusive rocks

**EXPLANATION**

- Bell Mountain Rhyolite
- Black rhyolite
- Boss diorite
- Boss andesite
- Boss rhyolite
- Boss trachyte
- Bourbon basalt
- Bourbon rhyolite
- Bourbon trachydacite
- Brown Mountain
- Brown’s rhyolite
- Brushy rhyolite
- Trachyte host of Camels Hump IOA deposit
- Cedar Bluff Rhyolite
- Clearcut rhyolite
- Lower unit of Coot Mountain
- Basalt in Cope Hollow Formation
- Rhyolite in Cope Hollow Formation
- Tuff at Crane Pond
- Creekbed rhyolite
- Cuthbertson Mountain rhyolite
- Fenceline rhyolite
- Forked Creek rhyolite

- French Mills felsite
- Goggins Mountain rhyolite
- Grassy Mountain ignimbrite
- Green rhyolite
- Hogan Mountain rhyolite
- Trachyandesite of Floyd Tower/Indian Creek
- Iron Mountain Lake rhyolite
- Ironon Rhyolite
- Ironon Hollow Rhyolite
- Johnson shut-ins rhyolite
- Ketcherside Mountain rhyolite
- Kratz Spring basalt
- Kratz Spring rhyolite
- Kratz Spring trachyte
- Lake Four Winds basalt
- Lake Killarney Formation
- Little Rock Creek rhyolite
- Logroad rhyolite
- Lower campground tuff at Marble Creek campground
- Lower Ridge rhyolite
- Marble Creek rhyolite
- Mountain View rhyolite
- Mudlick rhyolite
- Oak Mountain rhyolite
- Pea Ridge rhyolite
- Pea Ridge trachyte
- Pond Ridge Rhyolite
- Reader Hollow rhyolite
- Royal Gorge Rhyolite
- Russell Mountain Rhyolite
- Saddle rhyolite
- Sawmill rhyolite
- Shepherd Mountain Rhyolite
- Silver Mines basaltic andesite
- Rhyolite at South Crane Mountain
- Trachydacite at South Crane Mountain
- Stouts Creek rhyolite
- Taum Sauk Rhyolite
- Tile Red ash-flow tuff
- Tilk Hollow rhyolite
- Transition rhyolite
- Upper and Lower andesites of Marble Creek campground
- Upper Orchard rhyolite
- Upper Ridge rhyolite

B. Intrusive rocks

**EXPLANATION**

**Massif intrusions**
- Big Spring granite
- Buford Granite Porphyry
- Butler Hill Granite
- Breadtray Granite
- Bunker granite
- Granite of Castor River Shut-Ins

**Ring intrusions**
- Knoblick Granite
- Slabtown Granite
- Silvermine Granite—Medium grained
- Silvermine Granite—Fine grained
- Stono Granite
- Tiemann quartz diorite

**Minor intrusion**
- Brown Mountain granite porphyry

---

*Figure 7.* Variation diagrams showing molar major-oxide compositions of 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri as a function of relative alumina and alkali saturation.

—Continued
Figure 8. $\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO}$ relative to SiO$_2$ variation diagram showing the compositions of 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri relative to boundaries between alkalic, alkali-calcic, calc-alkalic, and calcic rock series. Boundaries between various rock series from Frost and others (2001).
A. Extrusive and hypabyssal intrusive rocks

**EXPLANATION**
- Bell Mountain Rhyolite
- Black rhyolite
- Boss diorite
- Boss andesite
- Boss rhyolite
- Boss trachyte
- Bourbon basalt
- Bourbon rhyolite
- Bourbon trachydacite
- Brown Mountain
- Brown’s rhyolite
- Brusky rhyolite
- Trachyte host of Camels Hump IOA deposit
- Cedar Bluff Rhyolite
- Clearcut rhyolite
- Lower unit of Coot Mountain
- Basalt in Cope Hollow Formation
- Rhyolite in Cope Hollow Formation
- Tuff at Crane Pond
- Creekbed rhyolite
- Cuthbertson Mountain rhyolite
- Fenceline rhyolite
- Forked Creek rhyolite
- French Mills felsite
- Goggins Mountain rhyolite
- Grassy Mountain Ignimbrite
- Green rhyolite
- Hogan Mountain rhyolite
- Trachyandesite of Floyd Tower/Indian Creek
- Iron Mountain Lake rhyolite
- Ironton Rhyolite
- Ironton Hollow Rhyolite
- Johnson shut-ins rhyolite
- Ketcherside Mountain rhyolite
- Kratz Spring basalt
- Kratz Spring rhyolite
- Kratz Spring trachyte
- Lake Four Winds basalt
- Lake Killarney Formation
- Little Rock Creek rhyolite
- Logroad rhyolite
- Lower campground rhyolite at Marble Creek campground
- Lower Ridge rhyolite
- Marble Creek rhyolite
- Mountain View rhyolite
- Mudlick rhyolite
- Oak Mountain rhyolite
- Pea Ridge rhyolite
- Pea Ridge trachyte
- Pond Ridge Rhyolite
- Reader Hollow rhyolite
- Royal Gorge Rhyolite
- Russell Mountain Rhyolite
- Saddle rhyolite
- Sawmill rhyolite
- Shepherd Mountain Rhyolite
- Silver Mines basaltic andesite
- Rhyolite at South Crane Mountain
- Trachydacite at South Crane Mountain
- Stouts Creek rhyolite
- Taum Sauk Rhyolite
- Tile Red ash-flow tuff
- Tilk Hollow rhyolite
- Transition rhyolite
- Upper and Lower andesites of Marble Creek campground
- Upper Orchard rhyolite
- Upper Ridge rhyolite

B. Intrusive rocks

**EXPLANATION**

**Massif intrusions**
- Big Spring granite
- Buford Granite Porphyry
- Butler Hill Granite
- Breadtray Granite
- Bunker granite
- Granite of Castor River Shut-Ins
- French Mills felsite
- Goggins Mountain rhyolite
- Grassy Mountain Ignimbrite
- Green rhyolite
- Hogan Mountain rhyolite
- Trachyandesite of Floyd Tower/Indian Creek
- Iron Mountain Lake rhyolite
- Ironton Rhyolite
- Ironton Hollow Rhyolite
- Johnson shut-ins rhyolite
- Ketcherside Mountain rhyolite
- Kratz Spring basalt
- Kratz Spring rhyolite
- Kratz Spring trachyte
- Lake Four Winds basalt
- Lake Killarney Formation
- Little Rock Creek rhyolite
- Logroad rhyolite
- Lower campground rhyolite at Marble Creek campground
- Lower Ridge rhyolite
- Marble Creek rhyolite
- Mountain View rhyolite
- Mudlick rhyolite
- Oak Mountain rhyolite
- Pea Ridge rhyolite
- Pea Ridge trachyte
- Pond Ridge Rhyolite
- Reader Hollow rhyolite
- Royal Gorge Rhyolite
- Russell Mountain Rhyolite
- Saddle rhyolite
- Sawmill rhyolite
- Shepherd Mountain Rhyolite
- Silver Mines basaltic andesite
- Rhyolite at South Crane Mountain
- Trachydacite at South Crane Mountain
- Stouts Creek rhyolite
- Taum Sauk Rhyolite
- Tile Red ash-flow tuff
- Tilk Hollow rhyolite
- Transition rhyolite
- Upper and Lower andesites of Marble Creek campground
- Upper Orchard rhyolite
- Upper Ridge rhyolite

**Ring intrusions**
- Knoblick Granite
- Slabtown Granite
- Silvermine Granite—Medium grained
- Silvermine Granite—Fine grained
- Stono Granite
- Tiemann quartz diorite

**Minor intrusion**
- Brown Mountain granite porphyry

---

**Figure 8.** $Na_2O + K_2O - CaO$ relative to $SiO_2$ variation diagram showing the compositions of 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri relative to boundaries between alkalic, alkali-calcic, calc-alkalic, and calcic rock series. Boundaries between various rock series from Frost and others (2001).  —Continued
Table 11. Chemical classification of 1.48 to 1.45 Ga igneous rock geologic map units in the St. Francois Mountains terrane, southeast Missouri.

[Units with compositions transitional between more than one category are listed in each appropriate category. Entries in parentheses represent reclassification of unit compositions based on the data of du Bray and others (2018b) and the classification schema of Le Maitre (1989)]

<table>
<thead>
<tr>
<th>Peraluminous</th>
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<tr>
<td>Alkalic</td>
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<td>Alkali-calcic</td>
<td>Calcic</td>
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</table>

<table>
<thead>
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<th>Boss trachyte (trachyandesite)</th>
<th>Bell Mountain Rhyolite</th>
<th>Butler Hill Granite</th>
<th>Cuthbertson Mountain rhyolite</th>
<th>Trachyte host of Camels Hump IOA deposit (trachyandesite)</th>
<th>Boss andesite (basaltic trachyandesite)</th>
<th>Bourbon trachyandesite</th>
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</thead>
<tbody>
<tr>
<td>Rhyolite in the Cope Hollow Fm</td>
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<td></td>
<td>Lower unit of Coot Mountain</td>
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<td>Brown's rhyolite</td>
<td>Black rhyolite</td>
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<td>Fenceline rhyolite</td>
<td>Boss rhyolite</td>
<td></td>
<td>Lower campground tuff at Marble Creek campground (rhyolite)</td>
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<td>Black rhyolite</td>
<td>Bunker granite</td>
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<td>Ironont Rhyolite</td>
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<td>Rhyolite of Kratz Spring (trachyte)</td>
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<td>Little Rock Creek rhyolite</td>
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</tbody>
</table>
Table 11. Chemical classification of 1.48 to 1.45 Ga igneous rock geologic map units in the St. Francois Mountains terrane, southeast Missouri.—Continued

[Units with compositions transitional between more than one category are listed in each appropriate category. Entries in parentheses represent reclassification of unit compositions based on the data of du Bray and others (2018b) and the classification schema of Le Maitre (1989)]

<table>
<thead>
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<th>Peraluminous</th>
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<thead>
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<th>Magnesian</th>
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<td>Basalt host of the Bourbon IOA deposit</td>
</tr>
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<tr>
<td>Silvermine Granite-medium grained</td>
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<tr>
<td>Basalt of Kratz Spring</td>
</tr>
</tbody>
</table>
Figure 9. FeO*/(FeO* + MgO) variation diagram showing the composition of 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri relative to boundaries between ferroan and magnesian rocks as well as between tholeiitic and calc-alkaline rocks. Ferroan-magnesian boundary from Frost and others (2001); tholeiitic-calc-alkaline boundary from Miyashiro (1974).
A. Extrusive and hypabyssal intrusive rocks

- Bell Mountain Rhyolite
- Black rhyolite
- Boss diorite
- Boss andesite
- Boss rhyolite
- Boss trachyte
- Bourbon basalt
- Bourbon rhyolite
- Bourbon trachydacite
- Brown Mountain
- Brown’s rhyolite
- Brushy rhyolite
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- Clearcut rhyolite
- Lower unit of Coot Mountain
- Basalt in Cope Hollow Formation
- Rhyolite in Cope Hollow Formation
- Tuff at Crane Pond
- Creekbed rhyolite
- Cuthbertson Mountain rhyolite
- Fenceline rhyolite
- Forked Creek rhyolite
- French Mills felsite
- Goggins Mountain rhyolite
- Grassy Mountain Igneous Trachyte
- Green rhyolite
- Hogan Mountain rhyolite
- Trachyandesite of Floyd Tower/Indian Creek
- Iron Mountain Lake rhyolite
- Ironton Rhyolite
- Ironton Hollow Rhyolite
- Johnson shut-ins rhyolite
- Ketcherside Mountain rhyolite
- Kratz Spring basalt
- Kratz Spring rhyolite
- Kratz Spring trachyte
- Lake Four Winds basalt
- Lake Killarney Formation
- Little Rock Creek rhyolite
- Logroad rhyolite
- Lower campground tuff at Marble Creek campground
- Lower Ridge rhyolite
- Marble Creek rhyolite
- Mountain View rhyolite
- Mudlick rhyolite
- Oak Mountain rhyolite
- Pea Ridge rhyolite
- Pea Ridge trachyte
- Pond Ridge Rhyolite
- Reader Hollow rhyolite
- Royal Gorge Rhyolite
- Russell Mountain Rhyolite
- Saddle rhyolite
- Sawmill rhyolite
- Shepherd Mountain Rhyolite
- Silver Mines basaltic andesite
- Rhyolite at South Crane Mountain
- Trachydacite at South Crane Mountain
- Stouts Creek rhyolite
- Taum Sauk Rhyolite
- Tile Red ash-flow tuff
- Tilk Hollow rhyolite
- Transition rhyolite
- Upper and Lower andesites of Marble Creek campground
- Upper Orchard rhyolite
- Upper Ridge rhyolite

B. Intrusive rocks

EXPLANATION

Massif intrusions
- Big Spring granite
- Buford Granite Porphyry
- Butler Hill Granite
- Breadtray Granite
- Bunker granite
- Granite of Castor River Shut-Ins
- Brown Mountain granite porphyry

Ring intrusions
- Knoblick Granite
- Slabtown Granite
- Silvermine Granite—Medium grained
- Silvermine Granite—Fine grained
- Stono Granite
- Tiemann quartz diorite

Minor intrusion
- Brown Mountain granite porphyry

Figure 9. FeO*/(FeO* + MgO) variation diagram showing the composition of 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri relative to boundaries between ferroan and magnesian rocks as well as between tholeiitic and calc-alkaline rocks. Ferroan-magnesian boundary from Frost and others (2001); tholeiitic-calc-alkaline boundary from Miyashiro (1974).—Continued
A. Extrusive and hypabyssal intrusive rocks

Figure 10. Ternary AFM (Na$_2$O+K$_2$O–FeO*–MgO) diagram showing compositions of 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri. Calc-alkaline and tholeiitic trend lines from Irvine and Baragar (1971).

B. Phaneritic intrusive rocks

Figure 10. Ternary AFM (Na$_2$O+K$_2$O–FeO*–MgO) diagram showing compositions of 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri. Calc-alkaline and tholeiitic trend lines from Irvine and Baragar (1971).
A. Extrusive and hypabyssal intrusive rocks

EXPLANATION

- Bell Mountain Rhyolite
- Black rhyolite
- Boss diorite
- Boss andesite
- Boss rhyolite
- Boss trachyte
- Bourbon basalt
- Bourbon rhyolite
- Bourbon trachydacite
- Brown Mountain
- Brown's rhyolite
- Brushy rhyolite
- Trachyte host of Camels Hump IOA deposit
- Cedar Bluff Rhyolite
- Clearcut rhyolite
- Lower unit of Coot Mountain
- Basalt in Cope Hollow Formation
- Rhyolite in Cope Hollow Formation
- Tuff at Crane Pond
- Creekbed rhyolite
- Cuthbertson Mountain rhyolite
- Fenceline rhyolite
- Forked Creek rhyolite
- French Mills felsite
- Goggins Mountain rhyolite
- Grassy Mountain Ignimbrite
- Green rhyolite
- Hogan Mountain rhyolite
- Trachyandesite of Floyd Tower/Indian Creek
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- Ironon Rhyolite
- Ironton Hollow Rhyolite
- Johnson shut-ins rhyolite
- Ketcherside Mountain rhyolite
- Kratz Spring basalt
- Kratz Spring rhyolite
- Kratz Spring trachyte
- Lake Four Winds basalt
- Lake Killarney Formation
- Little Rock Creek rhyolite
- Logroad rhyolite
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- Lower Ridge rhyolite
- Marble Creek rhyolite
- Mountain View rhyolite
- Mudlick rhyolite
- Oak Mountain rhyolite
- Pea Ridge rhyolite
- Pea Ridge trachyte
- Pond Ridge Rhyolite
- Reader Hollow rhyolite
- Royal Gorge Rhyolite
- Russell Mountain Rhyolite
- Saddle rhyolite
- Sawmill rhyolite
- Shepherd Mountain Rhyolite
- Silver Mines basaltic andesite
- Rhyolite at South Crane Mountain
- Trachydacite at South Crane Mountain
- Stouts Creek rhyolite
- Taum Sauk Rhyolite
- Tile Red ash-flow tuff
- Tilk Hollow rhyolite
- Transition rhyolite
- Upper and Lower andesites of Marble Creek campground
- Upper Orchard rhyolite
- Upper Ridge rhyolite
- Boss andesite
- Boss trachyte
- Bourbon basalt
- Bourbon rhyolite
- Bourbon trachydacite
- Brown Mountain
- Brown's rhyolite
- Brushy rhyolite
- Trachyte host of Camels Hump IOA deposit
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- Upper Ridge rhyolite

B. Intrusive rocks

EXPLANATION

**Massif intrusions**
- Big Spring granite
- Buford Granite Porphyry
- Butler Hill Granite
- Breadtray Granite
- Bunker granite
- Granite of Castor River Shut-Ins

**Ring intrusions**
- Knoblick Granite
- Slabtown Granite
- Silvermine Granite—Medium grained
- Silvermine Granite—Fine grained
- Stono Granite
- Tiemann quartz diorite

**Minor intrusion**
- Brown Mountain granite porphyry

---

**Figure 10.** Ternary AFM (Na₂O+K₂O–FeO*–MgO) diagram showing compositions of 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri. Calc-alkaline and tholeiitic trend lines from Irvine and Baragar (1971).—Continued
compositions (fig. 13). REE patterns for the felsic and intermediate igneous rocks are almost indistinguishable. In particular, patterns for these two groups of rocks overlap and are parallel, consistent with the interpretation of insignificant relative REE fractionation among magmas represented by these two groups of rocks. Only the magnitude of negative europium anomalies, moderate among intermediate composition rocks and more well developed among the felsic rocks, distinguish REE characteristics of these two groups of rocks. REE patterns for the mafic rocks, although parallel to, and in part overlapping with, those of the other two groups, depict abundances that are, on average, somewhat lower than those characteristic of the other two groups. In addition, the mafic rocks have small to nonexistent negative europium anomalies. Although chondrite-normalized REE patterns for the massif- and ring-type intrusions overlap considerably, the massif-type intrusions are characterized by subtly smaller negative europium anomalies and greater overall REE contents than the ring-type intrusions (fig. 12; table 12).

Essential characteristics of representative primitive-mantle normalized patterns for the 1.48 to 1.45 Ga igneous rocks of the St. Francois Mountains terrane are also generally similar (fig. 14). These patterns are gently negatively sloping, depict relative large-ion lithophile element (LILE) enrichment, and include several superimposed abundance anomalies, including variably developed negative Ba, Sr, P, and Ti anomalies, which are most- or least-well developed in the felsic and mafic rocks, respectively. The primitive-mantle-normalized patterns also include moderately well developed negative niobium and tantalum anomalies similar to those characteristic of subduction-related magmas (Gill, 1981; Pearce and others, 1984; Wood and others, 1979). Representative primitive-mantle-normalized patterns for the igneous rocks of the St. Francois Mountains terrane also include variably developed positive thorium and lead anomalies. Similar to their variable chondrite-normalized REE patterns, primitive-mantle-normalized patterns for individual igneous rock geologic units in the St. Francois Mountains terrane exhibit considerable dispersion, regardless of whole-rock bulk composition (fig. 15). In particular, the felsic and intermediate rocks are again essentially indistinguishable, except that negative trace element anomalies are somewhat less well developed among the intermediate composition rocks. This trend continues among trace element abundances for the mafic rocks, which although grossly similar to, and in part overlapping with, those of the felsic and intermediate composition rocks, are characterized by even smaller negative anomalies. Primitive-mantle-normalized patterns for massif- and ring-type intrusions are also almost indistinguishable (fig. 14). In addition to previously identified REE differences, the massif-type intrusions have somewhat lower Ba, Sr, P, and Ti contents and higher Rb, Th, and Pb contents than the ring-type intrusions. These characteristics are in agreement with the massif intrusions being somewhat more chemically evolved than the ring-type intrusions.

### Tectonic Setting During 1.48 to 1.45 Ga Magmatism in the St. Francois Mountains Terrane

Comparing volcanologic features, physical characteristics of igneous intrusions, and compositional attributes of igneous rocks helps constrain the tectonic setting that prevailed during 1.48 to 1.45 Ga magmatism in the St. Francois Mountains terrane. Previously, two principal settings have been suggested for 1.48 to 1.45 Ga magmatism (Ayuso and others, 2016; Day and others, 2016): (1) subduction-related, plate boundary convergent arc magmatism, and (2) within-plate, anorogenic magmatism. As described by Rogers and Santosh (2002), 1.4 Ga ferroan granitoid magmatism across the United States, including the St. Francois Mountains terrane, was coeval with the final fragmentation of supercontinent Columbia (Nuna) but was completed before amalgamation of the Rodinian supercontinent.

As epitomized by the Andean arc (Hildreth and Moorbath, 1988) and magmatism associated with the modern and ancestral Cascades arc (du Bray and John, 2011; Hildreth, 2007), subduction-related arc magmatism is dominated by formation of mafic- to intermediate-composition stratovolcanoes and associated lava dome complexes. The principal eruptive products associated with this arc magmatism include, lava flows, central-volcano associated pyroclastic deposits, massive debris flow deposits, and endogenous and exogenous lava dome complexes. In contrast, intraplate, anorogenic volcanism, such as that characteristic of the modern-day Yellowstone region, is dominated by bimodal, mafic-felsic volcanism. The associated products are principally those formed as a consequence of felsic, caldera-forming eruptions but also include coeval and co-spatial mafic volcanism (Christiansen and McCurry, 2008). The eruptive products associated with bimodal intraplate magmatism are dominated by large volume ash-flow tuffs, related but much less voluminous rhyolite lavas deposited proximal to intracaldera environments, and somewhat less voluminous effusive magmatism manifested as numerous relatively thin mafic lava flows and associated pyroclastic fall deposits. As previously described, the style of volcanism and types of eruptive products characteristic of 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane are unlike those typical of subduction-related arc magmatism but are consistent with those commonly encountered among the products of intraplate, anorogenic magmatism.

The physical characteristics, especially the shape of plutons in subduction-related arc and intraplate, anorogenic settings, are also distinct. For instance, plutons of the Sierra Nevada batholith, the roots of a typical Mesozoic subduction-related magmatic arc, are typified by elongate shapes that parallel the ancestral subduction zone (Bateman, 1992). In contrast, plutons emplaced in an intraplate, anorogenic setting have circular outlines, as epitomized by ovoid postorogenic plutons emplaced into the Arabian Shield during the
Figure 11. Variation diagrams showing abundances of major oxides (weight percent) in 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri. Field boundaries on K₂O relative to SiO₂ diagram from Le Maitre (1989); high-potassium shoshonitic dividing line from Ewart (1982). For comparison, dashed green lines delineate the compositional fields defined by Mesoproterozoic intrusive rocks of the conterminous United States (du Bray and others, 2018a).
Figure 11. Variation diagrams showing abundances of major oxides (weight percent) in 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri. Field boundaries on K$_2$O relative to SiO$_2$ diagram from Le Maitre (1989); high-potassium shoshonitic dividing line from Ewart (1982). For comparison, dashed green lines delineate the compositional fields defined by Mesoproterozoic intrusive rocks of the conterminous United States (du Bray and others, 2018a).—Continued
A. Extrusive and hypabyssal intrusive rocks

EXPLANATION

- Bell Mountain Rhyolite
- Black rhyolite
- Boss diorite
- Boss andesite
- Boss rhyolite
- Boss trachyte
- Bourbon basalt
- Bourbon rhyolite
- Bourbon trachydacite
- Brown Mountain
- Brown’s rhyolite
- Brushy rhyolite
- Trachyte host of Camels Hump IOA deposit
- Cedar Bluff Rhyolite
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- Rhyolite in Cope Hollow Formation
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- Fenceline rhyolite
- Forked Creek rhyolite
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- Goggin Mountain rhyolite
- Grassy Mountain Ignimbrite
- Green rhyolite
- Hogan Mountain rhyolite
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- Iron Mountain Lake rhyolite
- Ironton Rhyolite
- Ironton Hollow Rhyolite
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- Transition rhyolite
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- Upper Orchard rhyolite
- Upper Ridge rhyolite
- Mudlick rhyolite

B. Intrusive rocks

EXPLANATION

Massif intrusions
- Big Spring granite
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- Butler Hill Granite
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- Granite of Castor River Shut-Ins
- Brown Mountain granite porphyry

Ring intrusions
- Knoblick Granite
- Slabtown Granite
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- Silvermine Granite—Fine grained
- Stono Granite
- Tiemann quartz diorite

Minor intrusion
- Brown Mountain granite porphyry

Figure 11. Variation diagrams showing abundances of major oxides (weight percent) in 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri. Field boundaries on K2O relative to SiO2 diagram from Le Maitre (1989); high-potassium shoshonitic dividing line from Ewart (1982). For comparison, dashed green lines delineate the compositional fields defined by Mesoproterozoic intrusive rocks of the conterminous United States (du Bray and others, 2018a).—Continued
Table 12. REE characteristics of the 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane, southeast Missouri.

[SiO₂, in weight percent. Total REE, in parts per million. La₃/Yb₃, ratio of the chondrite-normalized abundance of lanthanum to that of ytterbium; Eu/Eu*, ratio of determined europium abundance to europium abundance interpolated from the abundances of samarium and gadolinium; Dispersion, standard deviation of La abundance divided by average La abundance; —, no data]

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Geologic unit</th>
<th>SiO₂</th>
<th>Total REE</th>
<th>La₃/Yb₃</th>
<th>Eu/Eu*</th>
<th>Dispersion</th>
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<td>Mafic volcanic rocks</td>
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<td>WA11-1291</td>
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<td>4.49</td>
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<td>3.59</td>
<td>0.97</td>
<td>0.17</td>
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<td>Bourb-039</td>
<td>Bourbon basalt</td>
<td>53.21</td>
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<td>4.46</td>
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<td>3.59</td>
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<td>0.03</td>
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<td>CW28-1317</td>
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<td>53.83</td>
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<td>4.98</td>
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<td>0.12</td>
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<td>MO13-006</td>
<td>Floyd Tower/Indian Creek trachydacite</td>
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<td>5.44</td>
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<td>MO16-012</td>
<td>South Crane Mountain trachydacite</td>
<td>64.84</td>
<td>234</td>
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<tr>
<td>Bourb-096</td>
<td>Trachydacite associated with the Bourbon IOA deposit</td>
<td>66.72</td>
<td>313</td>
<td>5.49</td>
<td>0.59</td>
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<tr>
<td>54W159-1558</td>
<td>Trachyte of Kratz Spring</td>
<td>67.45</td>
<td>303</td>
<td>8.74</td>
<td>0.62</td>
<td>0.74</td>
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<td>Intermediate intrusion</td>
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<td>RA-MO-13-10</td>
<td>Tiemann quartz diorite</td>
<td>66.14</td>
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<td>Felsic volcanic rocks</td>
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<td>MO16-059</td>
<td>Iron Mountain Lake rhyolite</td>
<td>69.34</td>
<td>211</td>
<td>2.94</td>
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<tr>
<td>ARC5/96-9</td>
<td>Ironton Rhyolite</td>
<td>69.52</td>
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<td>8.69</td>
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<tr>
<td>MO13-001</td>
<td>Rhyolite at South Crane Mountain</td>
<td>70.38</td>
<td>204</td>
<td>3.76</td>
<td>0.61</td>
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<tr>
<td>MO15-002</td>
<td>Little Rock Creek rhyolite</td>
<td>70.93</td>
<td>240</td>
<td>5.41</td>
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<tr>
<td>USA2-1196</td>
<td>Boss rhyolite</td>
<td>71.97</td>
<td>126</td>
<td>32.08</td>
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<td>ARC5/96-4</td>
<td>Russell Mountain Rhyolite</td>
<td>72.09</td>
<td>204</td>
<td>6.01</td>
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<tr>
<td>MO14-020</td>
<td>Cedar Bluff Rhyolite</td>
<td>72.95</td>
<td>86</td>
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<td>MO16-057</td>
<td>Shepherd Mountain Rhyolite</td>
<td>73.36</td>
<td>150</td>
<td>5.04</td>
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<td>MO16-007</td>
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<td>MO93-136</td>
<td>Cuthbertson Mountain rhyolite</td>
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<td>ARC5/96-7</td>
<td>Pond Ridge Rhyolite</td>
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<td>MO16-004</td>
<td>Lower Ridge rhyolite</td>
<td>75.20</td>
<td>235</td>
<td>5.95</td>
<td>0.35</td>
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<td>MO16-015</td>
<td>Tile Red ash-flow tuff</td>
<td>75.24</td>
<td>310</td>
<td>4.43</td>
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<tr>
<td>PEA10-95-16</td>
<td>Pea Ridge 1825 rhyolite porphyry</td>
<td>75.50</td>
<td>220</td>
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<td>B-USBM2-1421</td>
<td>Bourbon rhyolite</td>
<td>76.02</td>
<td>112</td>
<td>4.62</td>
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<td>MGS28-1</td>
<td>Ketcherside Mountain rhyolite</td>
<td>76.84</td>
<td>213</td>
<td>4.42</td>
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<td>0.24</td>
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<tr>
<td>MO16-024</td>
<td>Grassy Mountain Ignimbrite</td>
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<td>284</td>
<td>4.87</td>
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<td>MGS37-4</td>
<td>Royal Gorge Rhyolite</td>
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<td>125</td>
<td>2.61</td>
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<tr>
<td>MO15-004</td>
<td>Lake Killarney Formation</td>
<td>77.48</td>
<td>237</td>
<td>3.71</td>
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<td>0.18</td>
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<td>MO16-023B</td>
<td>Ironton Hollow-Cedar Bluff Rhyolite</td>
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<td>157</td>
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<td>0.56</td>
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<td>MO14-043</td>
<td>Lower campground tuff at Marble Creek campground</td>
<td>77.65</td>
<td>307</td>
<td>6.93</td>
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<td>ARC5/96-2</td>
<td>Taum Sauk Rhyolite</td>
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</table>
Table 12. REE characteristics of the 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane, southeast Missouri.—Continued

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Geologic unit</th>
<th>SiO₂</th>
<th>Total REE</th>
<th>LaN/YbN</th>
<th>Eu/Eu*</th>
<th>Dispersion</th>
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<tr>
<td><strong>Felsic intrusions</strong></td>
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<tr>
<td>Massif-type</td>
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<td></td>
</tr>
<tr>
<td>RA-MO-13-4</td>
<td>Butler Hill Granite</td>
<td>74.28</td>
<td>303</td>
<td>5.62</td>
<td>0.25</td>
<td>0.38</td>
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<tr>
<td>RA-MO-13-3</td>
<td>Breadtray Granite</td>
<td>77.76</td>
<td>290</td>
<td>4.29</td>
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<tr>
<td>60W-183-1071</td>
<td>Bunker granite</td>
<td>76.97</td>
<td>265</td>
<td>5.65</td>
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<tr>
<td>BS 111</td>
<td>Big Spring granite</td>
<td>75.78</td>
<td>182</td>
<td>4.05</td>
<td>0.44</td>
<td>0.05</td>
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<tr>
<td>Ring-type</td>
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<tr>
<td>N6976</td>
<td>Stono Granite</td>
<td>70.64</td>
<td>153</td>
<td>3.88</td>
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<td>RA-MO-13-5</td>
<td>Knoblick Granite</td>
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<td>6.25</td>
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<td>0.07</td>
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<td>RA-MO-13−9</td>
<td>Silvermine Granite—medium grained</td>
<td>71.44</td>
<td>129</td>
<td>4.10</td>
<td>0.64</td>
<td>0.23</td>
</tr>
<tr>
<td>233</td>
<td>Silvermine Granite—fine grained</td>
<td>75.93</td>
<td>114</td>
<td>5.71</td>
<td>0.43</td>
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<tr>
<td>IGCP1-3a</td>
<td>Slabtown Granite</td>
<td>72.48</td>
<td>241</td>
<td>4.75</td>
<td>0.67</td>
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<tr>
<td><strong>Minor intrusions</strong></td>
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<tr>
<td>J4-1533</td>
<td>Boss granite</td>
<td>73.23</td>
<td>214</td>
<td>7.21</td>
<td>0.32</td>
<td>0.46</td>
</tr>
<tr>
<td>MO16-003</td>
<td>Brown Mountain granite porphyry</td>
<td>71.59</td>
<td>238</td>
<td>4.99</td>
<td>0.64</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Neoproterozoic (Stoeser and Elliott, 1980). Many of the 1.48 to 1.45 Ga igneous intrusions in the St. Francois Mountains terrane have been depicted as roughly circular masses (Kisvarsanyi, 1981) that accordingly are consistent with intraplate, anorogenic magmatism.

The spatial extent and distribution of 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane provide additional constraints on the tectonic setting that prevailed during the associated magmatism. Approximately 1.4 Ga Mesoproterozoic igneous rocks in the St. Francois Mountains terrane extend over length scales of at least 150 km (Day and others, 2016; Kisvarsanyi, 1981). Similarly, approximately 1.4 Ga igneous complexes arrayed across the continental United States have minimum extents that range from similar to significantly greater proportions (du Bray and others, 2015). In contrast, magmatic arcs associated with subduction processes are narrow; their widths range from more than 10 to, in rare case cases, as much as 100 km (du Bray and John, 2011; England and Katz, 2010; Hildreth, 2007; Hildreth and Moorbath, 1988). Accordingly, the minimum spatial extent of 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane is much greater than the width characteristic of subduction-related arcs. In addition, 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane are part of a group of coeval igneous rocks that are widely distributed across the conterminous United States (fig. 1, du Bray and others, 2018a). They extend from the northern to southern midcontinent, are abundant beneath Paleozoic sedimentary rocks throughout the Great Plains region, are voluminous across southern Arizona, extend north along the Rocky Mountains throughout New Mexico, Colorado, and southern Wyoming, and form isolated outcrops in north-central Idaho (du Bray and others, 2015). This distribution is inconsistent with these rocks being related to subduction-related magmatism, because it requires that all of these areas, dispersed across the Laurentian craton, were sites of coeval arc magmatism. A geometry that requires coeval subduction-related magmatism at each of these disparate and irregularly oriented locales is implausible. Therefore, the spatial characteristics and distribution of 1.4 Ga igneous rocks throughout the conterminous United States, including those in the St. Francois Mountains terrane, are inconsistent with an arc magmatism genesis.

The geochemical characteristics of 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane provide compelling evidence pertinent to the tectonic environment prevailing during their genesis. As previously described, the great majority of these igneous rocks are ferroan (fig. 9). Subduction-related arc magmas are characteristically magnesian or calc alkaline (du Bray and John, 2011; Hildreth, 2007; Hildreth and Moorbath, 1988); whereas intraplate, anorogenic magmas are ferroan and tholeiitic (Christiansen and McCurry, 2008; Frost and Frost, 2008, 2011). Subduction-related arc magmas follow a calc-alkaline trend, whereas those of intraplate, anorogenic rocks follow a tholeiitic trend (fig. 10).
Figure 12. Representative chondrite-normalized rare earth element patterns for 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri. Chondrite abundances from Anders and Ebihara (1982). Truncated pattern segments indicate missing data.—Continued
within-plate setting although the compositions of several geologic units extend to those characteristic of volcanic arc magmas (fig. 16). Whalen and others (1987) used the relative abundances of Zr, Ga, and Al to distinguish I (igneous source)- and S (sedimentary source)-type compositions of subduction-related arc environments from A-type compositions, which have traditionally been associated with an anorogenic, intraplate setting. Relative abundances of these components in the preponderance of 1.48 to 1.45 Ga igneous rocks from the St. Francois Mountains terrane that have been analyzed are also consistent with an intraplate, anorogenic setting though a notable few analyses plot in the I- and S-type fields (fig. 16). Finally, Grebennikov (2014) used relative abundances of several major oxide components to distinguish the compositions of magmas generated in a variety of tectonic settings. As with other geochemical criteria, compositions of the vast majority of 1.48 to 1.45 Ga rocks from the St. Francois Mountains terrane are consistent with petrogenesis in an intracratonic setting that was affected by rifting and associated mantle upwelling. Each of these geochemical criteria is in agreement with all physical, volcanologic, and distribution characteristics of 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane that are consistent with these rocks being products of intracratonic, anorogenic magmatism.

Major oxide compositions of ferroan igneous rocks define eight subtypes (Frost and Frost, 2008). These include the alkali-calcic and calc-alkalic variants of both ferroan peraluminous and ferroan peralkaline granitoids, as well as the alkalic, alkali-calcic, calc-alkalic, and calcic variants of ferroan metaluminous granitoids. Although these discrete subtypes allow unique compositional classification (Frost and Frost, 2008), each ostensibly associated with a particular petrogenetic history, compositional data (du Bray and others, 2018b; Granitto and others, 2018) suggest that many 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane have compositions that extend across subtype boundaries (figs. 7 and 8) and, therefore, reflect continuous variation of corresponding petrologic processes. Experimental petrologic investigations, for which pressure, temperature, and compositional characteristics are known, define the magma compositions that result from various combinations of these parameters (Frost and Frost, 2008) and constrain the relevant petrogenetic conditions prevailing during genesis of the magmas represented by 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane (table 11).

Low-degree dehydration partial melting of granodiorite or magnesian tonalite gneiss yields ferroan, strongly peraluminous, calc-alkalic melts (Patiño Douce, 1997; Skjerlie and Johnston, 1993). With relatively higher-degree partial melting, the resulting magmas become increasingly magnesian, metaluminous, and alkali calcic. With relatively lower
Figure 14. Representative primitive-mantle-normalized (Sun and McDonough, 1989) trace element diagrams for igneous rocks in the St. Francois Mountains terrane, southeast Missouri. Discontinuous patterns indicate missing data.
pressure melting, the resulting partial melts are magnesian, metaluminous, and calc-alkalic. These relations suggest that the large group of 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane (table 11) which have ferroan, peraluminous, and calc-alkalic to alkali-calcic compositions are consistent with high pressure (8–10 kilobar), low-degree partial melting of crustal material of granodioritic to tonalitic compositions; members of the alkali-calcic subtype probably represent partial melting at higher pressure conditions than those prevailing during genesis of the calc-alkalic subtype (Patiño Douce, 1997).

Differentiation of tholeiitic basalt can produce metaluminous ferroan granites (Frost and Frost, 2011). The balance of plagioclase relative to clinopyroxene crystallization and fractionation determines whether these partial melts are alkali calcic or calc-alkalic, or even calcic. Tholeiitic compositions are increasingly calcic with clinopyroxene crystallization as plagioclase crystallization limits residual liquid alkalinity (Frost and Frost, 2011). Consequently, (1) the alkalic and metaluminous compositions of the trachyte host of Camels Hump IOA deposit and the Johnson Shut-ins rhyolite (table 11) may represent extensive clinopyroxene fractionation, and (2) the alkali-calcic metaluminous compositions of a significant group (table 11) of 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane reflect less significant clinopyroxene fractionation, and (3) the calc-alkalic metaluminous compositions of six geologic units (table 11) in the St. Francois Mountains terrane manifests the dominance of plagioclase fractionation. Clinopyroxene crystallizes at higher pressures than those associated with plagioclase crystallization (Frost and Frost, 2011). Consequently, the most alkalic of the metaluminous 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane probably represent magma genesis in systematically higher-pressure environments than those characteristic of the calc-alkalic subtype.

A small group of 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane (table 11) have alkali-calcic and calc-alkalic metaluminous compositions that are transitionally magnesian to magnesian, not ferroan, and are therefore superficially similar to characteristically magnesian and calc-alkaline, subduction-related magmatic arc rocks (Menuge and others, 2002; Walker and others, 2002). However, many lines of evidence indicate that 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane rocks represent magmatism in an intracratonic setting (Bickford and others, 2015) rather than in a magmatic arc setting. The petrogenesis of the magnesian variants reflects variations of processes not entirely different from those responsible for ferroan granitoid petrogenesis, as indicated by a smooth and continuous transition from ferroan to magnesian compositions. Weakly magnesian compositions
may reflect relatively lower pressure partial melting conditions (Skjerlie and Johnston, 1993). Relatively high-degree partial melting (Skjerlie and Johnston, 1993) of granodioritic to tonalitic protolith compositions in relatively high-pressure, lower-crust regimes (Patiño Douce, 1997) is probably responsible for the small group of transitionally magnesian to magnesian and metaluminous 1.48 to 1.45 Ga igneous rocks. Those geologic units that have alkali-calcic compositions reflect genesis under high pressure conditions, whereas those with calc-alkalic compositions manifest magma genesis at somewhat lower pressures (Patiño Douce, 1997).

Relatively primitive Sm-Nd and Pb isotopic values (Ayuso and others, 2016; du Bray and others, 2015; Gleason and others, 2000) for 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane suggest that the petrogenesis of the associated magmas includes a significant mantle-derived component. Similarly, oxygen isotope data for zircon from the Pea Ridge 1825 rhyolite porphyry and volcanic rocks near the Bourbon deposit are commensurate with mantle inputs (Watts and Mercer, 2020). Derivation of 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane exclusively by differentiation from tholeiitic basalt magmas or by partial melting of tonalite to granodiorite in the crust is inconsistent with available geochemical data. The petrogenesis of these magmas probably requires a combination of processes. Similarly, Frost and Frost (2011) have suggested that most ferroan granites represent variable mixing of crust-derived partial melts with differentiates of mantle-derived tholeiitic magma. The heat required to initiate variable degrees of crustal melting was probably supplied by primary, mantle-derived mafic magma, which likely also contributed mass to the evolving magma reservoirs. The conclusion that most 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane represent petrogenesis in an intracratonic or continental setting (Kisvarsanyi and Kisvarsanyi, 1990) and the inference that this magmatism involved mantle-derived inputs, require extensional tectonism, mantle upwelling, and crustal underplating to initiate and sustain the observed magmatism (Day and others, 2016). Processes accompanying intracratonic extension and crustal underplating by upwelling, mantle-derived tholeiitic magma have likely also contributed directly to the worldwide spatial and temporal association of felsic ferroan granitoids and relatively mafic igneous rocks described by Anderson (1983) and Hoffman (1989).

The 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane have major oxide compositions similar to those of ferroan granites throughout the world, which are subalkaline, weakly to moderately peraluminous, alkali calcic to calc alkalic, iron enriched, have moderately evolved compositions, and major oxide abundance variations within many of these ferroan granitoid intrusions are consistent with crystallization and fractionation of their contained mineral assemblages (Dall’Agnol and others, 2012). Correspondingly, the onset of plagioclase crystallization and fractionation among the 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane is denoted by decreasing Al₂O₃, among those rocks with ≥68 weight percent SiO₂ (fig. 11). The importance of plagioclase fractionation in the petrogenesis of these more evolved rocks is consistent with moderate to large negative europium anomalies characteristic of these rocks. In contrast, the mafic rocks of the St. Francois Mountains terrane have the smallest negative europium anomalies (fig. 13). Among these rocks, systematic decreases in TiO₂, FeO*, MnO, MgO, and CaO abundances with increasing SiO₂ are consistent with hornblende, biotite, and lesser Fe-Ti oxide crystallization and fractionation from the associated magmas (fig. 11). Decreasing P₂O₅ and TiO₂ abundances with increasing SiO₂ content suggest apatite and Fe-Ti oxide crystallization and fractionation, respectively.

Abundances of zirconium in 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane increase somewhat with increasing SiO₂ content, indicating that zircon did not nucleate and fractionate from the associated magmas (Bickford and others, 2015). Zirconium abundances, as high as about 500 ppm in these rocks, are noteworthy given the 140 to 175 ppm range characteristic of granitoid rocks (Turekian and Wedepohl, 1961). Most of the 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane are subalkaline, which is inconsistent with their somewhat elevated zirconium content because the abundance of zirconium in ordinary subalkaline silicate melts is limited to about 100 ppm (Watson, 1979). Elevated zirconium abundances among 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane are unexpected. Bickford and others (2015) noted this feature and the relative lack of inherited zircon in the felsic rocks of the St. Francois Mountains terrane and concluded that the source magmas were too hot to promote zircon crystallization. Elevated zirconium abundances characteristic of these rocks contrast with their apparently low zircon content. Consequently, much of the zirconium in the 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane may reside in pyroxene, small, inseparable zircon crystals, or in some other mineral, including perhaps Fe-Ti oxides.

Continental magmatic arc rocks (du Bray and others, 2015; Hildreth and Moorbath, 1988) have considerably greater strontium abundances than those of the 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane. Because plagioclase is the principal residence of strontium in the common rock-forming minerals, its retention in the source residuum during partial melting and (or) crystallization and removal from evolving, residual silicate liquids may be responsible for relatively low strontium abundances in these rocks. Magma genesis in relatively low pressure (~20 kilobar) lower- to mid-crustal environments (Green, 1982) favors plagioclase stability, which suggests petrogenesis of the magmas represented by 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane in the lower- to mid-crust regions, at depths significantly less than those that prevail in continental magmatic arc environments. Source-region plagioclase retention and subsequent plagioclase fractionation from magmas having basaltic andesite compositions, with characteristically small negative europium anomalies, are likely responsible for moderately- to well-developed negative europium anomalies characteristic of
1.48 to 1.45 Ga intermediate to felsic igneous rocks in the St. Francois Mountains terrane.

Relative Rb and Y + Nb concentrations for most 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane are consistent with a within-plate setting (fig. 16). Y + Nb concentrations for the rhyolite in the Cope Hollow Formation and Shepherd Mountain Rhyolite, however, are low and consistent with a volcanic arc setting. Similarly, melt inclusions in zircon from the upper and lower units of Coot Mountain have Y + Nb abundances similar to those of volcanic arc compositions that have been modified by crustal contamination (Cousens and others, 2008). Consistent with a volcanic arc setting, the rocks in the St. Francois Mountains terrane that is centered in the within-plate field but ranges to compositions consistent with petrogenesis in a volcanic arc setting. As such, these low Y + Nb abundances represent compositional variants that may have hybrid geochemical signatures characteristic of inputs derived from other petrologic processes. In addition, primitive-mantle-normalized trace element plots for most 1.48 to 1.45 Ga rhyolites in the Cope Hollow Formation and Shepherd Mountain Rhyolite have high δ18O values that are consistent with arc magmatism (Watts and Mercer, 2020). Although the Y + Nb abundances for these rhyolites are low relative to within-plate igneous rocks, they are part of a continuous compositional array for 1.48 to 1.45 Ga igneous rocks of the St. Francois Mountains terrane that is centered in the within-plate field but ranges to compositions consistent with petrogenesis in a volcanic arc setting. As such, these low Y + Nb abundances represent compositional variants that may have hybrid geochemical signatures characteristic of inputs derived from other petrologic processes. In addition, primitive-mantle-normalized trace element plots for most 1.48 to 1.45 Ga igneous rocks include negative Nb-Ta anomalies that, paradoxically, resemble those characteristic of subduction-related arc magmas. By analogy, du Bray and others (2015) identified similar negative Nb-Ta anomalies among intermediate-composition rocks of the Aurora volcanic field (California and Nevada) that were erupted almost 10 m.y. after arc magmatism had ceased in this area. Negative Nb-Ta anomalies for the Aurora volcanic field rocks have been interpreted as inherited from the crustal rocks that contributed to their petrogenesis. Similarly, because all other geologic characteristics of 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane are inconsistent with arc magmatism, their negative Nb-Ta anomalies may reflect the geochemistry of older, lower crustal rocks, with an arc-related prehistory, that contributed to petrogenesis of magmas represented by the 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane, as suggested by Ayuso and others (2016). Importantly however, as shown by Bickford and others (2015), the oldest Nd model ages for igneous rocks in the St. Francois Mountains terrane are about 1.55 Ga. Correspondingly, very rare, approximately 1.55 Ga zircon xenocrysts have been identified in samples collected near the Pea Ridge and Bourbon deposits (Watts and Mercer, 2020). Given the oldest igneous rocks in this area are about 1.48 Ga, partially melted, older lower crustal sources that contributed to Mesoproterozoic magmatism in the St. Francois Mountains terrane are juvenile and can be no more than about 0.07 Ga older than exposed Mesoproterozoic igneous rocks in this area.

Compositional diversity among 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane, as reflected by several additional geochemical parameters, are also consistent with mantle-derived magmas having been variably contaminated by crustal assimilants (fig. 17). $P_{\text{O}_2}/K_{\text{O}}$ decreases with increasing $SiO_2$ content, consistent with progressive mafic magma contamination by assimilation of crustally derived inputs because crustal materials generally have $P_{\text{O}_2}/K_{\text{O}} < 0.1$ (Farmer and others, 2002). In addition, $CaO/Al_2O_3$ systematically decreases with increasing $SiO_2$, consistent with magma compositions that have been modified by crustal contamination (Cousens and others, 2008).

The petrogenetic evolution of 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane is further constrained by their relative REE abundances. These rocks have moderately steep, negatively sloping chondrite-normalized REE patterns (table 12); values of (La$_n$/Yb$_n$) in most of these rocks range from about 2 to 9, median value is 4.7. The corresponding heavy rare earth element (HREE) depletion characteristic of these rocks signifies garnet stability and HREE retention in the source region because garnet is the principal petrologically relevant residence of HREE (Hanson, 1980). Although zircon is another significant HREE residence (Hanson, 1980), the somewhat elevated zirconium abundances characteristic of these rocks precludes significant zircon crystallization and removal from the associated magmas as a cause for relative HREE depletion. The 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane, as a group, have chondrite-normalized patterns that are essentially parallel and overlapping (fig. 15), which suggests that the representative magma reservoirs evolved by similar petrogenetic processes. In particular, the mineral assemblages that crystallized and fractionated from the representative magmas must have had similar bulk mineral-melt distribution coefficients. Specifically, the relatively broad range of chondrite-normalized REE patterns suggests fractionation of variable mineral assemblages, and (or) dilution by assimilants, with relatively unfracti-nated REE abundances. Negative europium anomalies that are progressively better developed among increasingly felsic igneous rocks of the St. Francois Mountains terrane (fig. 13) suggest a significant role for progressively greater plagioclase fractionation (the principal residence of Eu, Hanson, 1980) fractionation among the most felsic of these rocks. Among most of the 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane, a relatively well developed negative correlation exists between europium anomaly magnitude and $SiO_2$ content (table 12); consequently, the most evolved magmas reflect the greatest amount of plagioclase fractionation. In contrast, among these rocks, both (La$_n$/Yb$_n$) and total REE contents are poorly correlated with $SiO_2$ content (table 12).

Among 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane, within-unit REE dispersion (table 12) is uncorrelated with $SiO_2$ content. Consequently, REE dispersion is apparently unrelated to the degree of petrogenetic evolution and likely reflects the extent of compositional homogenization achieved within the representative magma reservoirs. Many of the igneous rock units have REE dispersion values less than or equal to 0.3 (table 12) consistent with reasonably homogenous magma reservoirs; in fact, a significant subset of these have REE dispersion values ≤0.2 and are indicative of very homogenous intrusions. In contrast, a small group of these geologic units (basaltic andesite host of Kratz Spring IOA deposit,
Figure 16. Variation diagrams showing that compositions of 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri are consistent with their petrogenesis in an intraplate, anorogenic setting. A, B, From Pearce and others (1984); applicable to rocks with >56 weight percent SiO₂; C, D, After Whalen and others (1987) showing the range of compositions for typical I (igneous source)-, S (sedimentary source)-, and A (anorogenic)-type igneous rocks with >60 weight percent SiO₂. E, F, Discriminant diagram after Grebennikov (2014) showing the range of compositions for magmas, with >67 weight percent SiO₂, associated with oceanic islands and continental rifts (field A1) and those associated with intracratonic settings (field A2).
A. Extrusive and hypabyssal intrusive rocks

EXPLANATION

- Bell Mountain Rhyolite
- Black rhyolite
- Boss rhyolite
- Bourbon rhyolite
- Bourbon trachydacite
- Brown Mountain
- Brown's rhyolite
- Brushy rhyolite
- Cedar Bluff Rhyolite
- Clearcut rhyolite
- Lower unit of Coot Mountain
- Rhyolite in Cope Hollow Formation
- Tuff at Crane Pond
- Creekbed rhyolite
- Cuthbertson Mountain rhyolite
- Fenceline rhyolite
- Forked Creek rhyolite
- French Mills felsite
- Goggin Mountain rhyolite
- Grassy Mountain Ignimbrite
- Green rhyolite
- Hogan Mountain rhyolite
- Trachyanandesite of Floyd Tower/Indian Creek
- Iron Mountain Lake rhyolite
- Ironon Rhyolite
- Ironon Hollow Rhyolite
- Johnson shut-ins rhyolite
- Keicherside Mountain rhyolite
- Kratz Spring rhyolite
- Lake Killamey Formation
- Little Rock Creek rhyolite
- Logroad rhyolite
- Lower campground tuff at Marble Creek campground
- Lower Ridge rhyolite
- Marble Creek rhyolite
- Mountain View rhyolite
- Mudlick rhyolite
- Oak Mountain rhyolite
- Pea Ridge rhyolite
- Pea Ridge trachytae
- Pond Ridge Rhyolite
- Reader Hollow rhyolite
- Royal Gorge Rhyolite
- Russell Mountain Rhyolite
- Saddle rhyolite
- Sawmill rhyolite
- Shepherd Mountain Rhyolite
- Rhyolite at South Crane Mountain
- Trachydacite at South Crane Mountain
- Stouts Creek rhyolite
- Taum Sauk Rhyolite
- Tile Red ash-flow tuff
- Tilk Hollow rhyolite
- Transition rhyolite
- Upper Orchard rhyolite
- Upper Ridge rhyolite

B. Intrusive rocks

EXPLANATION

Massif intrusions
- Big Spring granite
- Butler Hill Granite
- Breadtray Granite
- Bunker granite
- Granite of Castor River Shut-Ins

Ring intrusions
- Knoblick Granite
- Slabtown Granite
- Silvermine Granite—Medium grained
- Tiemann quartz diorite

Minor intrusion
- Brown Mountain granite porphyry

Figure 16. Variation diagrams showing that compositions of 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane, southeast Missouri are consistent with their petrogenesis in an intraplate, anorogenic setting. A, B, From Pearce and others (1984); applicable to rocks with >56 weight percent SiO₂; C, D, After Whalen and others (1987) showing the range of compositions for typical I (igneous source)-, S (sedimentary source)-, and A (anorogenic)-type igneous rocks with >60 weight percent SiO₂. E, F, Discriminant diagram after Grebennikov (2014) showing the range of compositions for magmas, with >67 weight percent SiO₂, associated with oceanic islands and continental rifts (field A1) and those associated with intracratonic settings (field A2).—Continued
Figure 17. Variation diagrams showing that compositions of igneous rocks in the St. Francois Mountains terrane, southeast Missouri are consistent with primary magmas being variably contaminated by crustal assimilants. A, $\frac{P_2O_5}{K_2O}$ relative to $SiO_2$ for extrusive and hypabyssal intrusive rocks. B, $\frac{P_2O_5}{K_2O}$ relative to $SiO_2$ for phaneritic intrusive rocks. C, $\frac{CaO}{Al_2O_3}$ relative to $SiO_2$ for extrusive and hypabyssal intrusive rocks. D, $\frac{CaO}{Al_2O_3}$ relative to $SiO_2$ for phaneritic intrusive rocks. $P_2O_5$, phosphorous pentoxide; $K_2O$, potassium oxide; $SiO_2$, silicon dioxide; $CaO$, calcium oxide; $Al_2O_3$, aluminum oxide.
A. Extrusive and hypabyssal intrusive rocks

- Bell Mountain Rhyolite
- Black rhyolite
- Boss diorite
- Boss andesite
- Boss rhyolite
- Boss trachyte
- Bourbon basalt
- Bourbon rhyolite
- Bourbon trachydacite
- Brown Mountain
- Brown’s rhyolite
- Brushy rhyolite
- Trachyte host of Camels Hump
- Cedar Bluff Rhyolite
- Clearcut rhyolite
- Lower unit of Coot Mountain
- Basalt in Cope Hollow Formation
- Rhyolite in Cope Hollow Formation
- Tuff at Crane Pond
- Creekbed rhyolite
- Cuthbertson Mountain rhyolite
- Fenceline rhyolite
- Forked Creek rhyolite
- French Mills felsite
- Goggins Mountain rhyolite
- Grassly Mountain Ignyimbrite
- Green rhyolite
- Hogan Mountain rhyolite
- Trachyandesite of Floyd
- Tower/Indian Creek
- Iron Mountain Lake rhyolite
- Ironon Rhyolite
- Ironon Hollow Rhyolite
- Johnson shut-ins rhyolite
- Ketcherside Mountain rhyolite
- Kratz Spring basalt
- Kratz Spring rhyolite
- Kratz Spring trachyte
- Lake Four Winds basalt
- Lake Killarney Formation
- Little Rock Creek rhyolite
- Logrod rhyolite
- Lower campground tuff at
- Marble Creek campground
- Lower Ridge rhyolite
- Marble Creek rhyolite
- Mountain View rhyolite
- Mudlick rhyolite
- Oak Mountain rhyolite
- Pea Ridge rhyolite
- Pea Ridge trachyte
- Pond Ridge Rhyolite
- Reader Hollow rhyolite
- Royal Gorge Rhyolite
- Russell Mountain Rhyolite
- Saddle rhyolite
- Sawmill rhyolite
- Shepherd Mountain Rhyolite
- Silver Mines basaltic andesite
- Rhyolite at South Crane Mountain
- Trachydacite at South Crane Mountain
- Stouts Creek rhyolite
- Taum Sauk Rhyolite
- Tile Red ash-flow tuff
- Tilk Hollow rhyolite
- Transition rhyolite
- Upper and Lower andesites of Marble
- Creek campground
- Upper Orchard rhyolite
- Upper Ridge rhyolite

B. Intrusive rocks

EXPLANATION

<table>
<thead>
<tr>
<th>Massif intrusions</th>
<th>Ring intrusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Big Spring granite</td>
<td>Knoblick Granite</td>
</tr>
<tr>
<td>Buford Granite Porphyry</td>
<td>Slabtown Granite</td>
</tr>
<tr>
<td>Butler Hill Granite</td>
<td>Silvermine Granite—Medium grained</td>
</tr>
<tr>
<td>Breadtray Granite</td>
<td>Silvermine Granite—Fine grained</td>
</tr>
<tr>
<td>Bunker granite</td>
<td>Stono Granite</td>
</tr>
<tr>
<td>Granite of Castor River Shut-Ins</td>
<td>Tiemann quartz diorite</td>
</tr>
</tbody>
</table>

Figure 17. Variation diagrams showing that compositions of igneous rocks in the St. Francois Mountains terrane, southeast Missouri are consistent with primary magmas being variably contaminated by crustal assimilants. A, P2O5/K2O relative to SiO2 for extrusive and hypabyssal intrusive rocks. B, P2O5/K2O relative to SiO2 for phaneritic intrusive rocks. C, CaO/Al2O3 relative to SiO2 for extrusive and hypabyssal intrusive rocks. D, CaO/Al2O3 relative to SiO2 for phaneritic intrusive rocks. [P2O5, phosphorous pentoxide; K2O, potassium oxide; SiO2, silicon dioxide; CaO, calcium oxide; Al2O3, aluminum oxide]—Continued
Kratz Spring trachyte, Boss rhyolite, Bourbon rhyolite, Royal Gorge Rhyolite, Ironton Hollow-Cedar Bluff Rhyolite, and Boss granite) has REE dispersion values ≥0.4, which presumably reflects correspondingly less homogeneous magma reservoirs. Within-geologic unit chondrite-normalized REE patterns are essentially parallel, like those for the entire group of representative geologic unit REE patterns, which suggests that within-unit relative REE fractionation was minor. Consequently, evolution of magma reservoirs represented by each of the 1.48 to 1.45 Ga igneous rock units in the St. Francois Mountains terrane involved fractionation processes in which mineral assemblages and their mineral-melt REE distribution coefficients were also relatively invariant.

Among 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane, chondrite-normalized REE abundances span nearly an entire order of magnitude. Average patterns for individual intrusions are parallel, although total REE content and extent of negative europium anomaly development vary. Consequently, relatively uniform processes controlled the petrogenesis of most of the 1.48 to 1.45 Ga igneous rocks, because relative REE fractionation, as would be depicted by relative pattern rotation, is absent. Absolute REE abundances among these rocks cannot be principally related to simple differentiation processes, fractionation or accumulation of constituent minerals, because total REE and SiO₂ contents do not vary systematically. Consequently, dilution processes associated with variable crustal contaminant assimilation and compositional variations within source melt regions are likely principally responsible for the range of REE abundances characteristic of the 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane. REE pattern parallelism compatible with REE dilution relations among these rocks requires contaminants with relatively uniform compositions.

The 1.48 to 1.45 Ga Mesoproterozoic igneous rocks in the St. Francois Mountains terrane constitute a significant component of the broadly 1.4 Ga igneous rocks exposed throughout the United States (du Bray and others, 2018a). Globally, petrogenesis of ferroan granitoids involves (1) incompletely mixed mantle- and crust-derived magmas and (2) extensional tectonic settings (Dall’Agnol and others, 2012). Magmatism that yielded the 1.48 to 1.45 Ga large felsic igneous province of the St. Francois Mountains terrane was likewise in agreement with these parameters. The genesis of these igneous rocks was critically dependent on the tectonic setting prevailing during magmatism and the character of the juvenile continental crust domains in which they are hosted. The addition of hundreds of cubic kilometers of Paleoproterozoic juvenile sialic crust southward from the Laurentian core may have been a consequence of a long-lived outboard-(southward-) migrating arc system, coupled with formation and closure of successive backarc basins (Condie, 1982). Alternating subduction and slab roll-back processes, accompanied by addition of basaltic magma into the crust during lithospheric stretching and related decompression melting, may have been responsible for the continental growth manifested by 1.48 to 1.45 Ga igneous rocks across the continental United States in general, and in particular the St. Francois Mountains terrane (du Bray and others, 2018a). These processes are similar to extensional accretionary orogeny as described by Collins (2002). This type of continental augmentation is accompanied by complex extensional tectonics and reflects back-arc processes that provide the thermal energy required by bimodal intracratonic magmatism at variable distance inboard from continental margins (Karlstrom and others, 2001) and contrasts significantly with continental growth achieved by accretionary collage processes. Accordingly, 1.48 to 1.45 Ga igneous rocks in the St. Francois Mountains terrane reflect extension-driven continental augmentation and cratonization following supercontinent fragmentation.

Conclusions

The ages of Mesoproterozoic igneous rocks in the St. Francois Mountains terrane of southeast Missouri define older (1.48 to 1.45 billion years old), volumetrically dominant, and younger (1.33 to 1.28 billion years old) magmatic episodes. Magmatism associated with the older episode appears to have been fairly continuous and characterized by a fairly uniform episodicity during approximately 30 million years. Most significantly, intrusive and extrusive rocks associated with the older episode are coeval as are granitoid rocks that form the ring- and massif-type intrusions. A likely genetic association between ore formation at the Pea Ridge iron oxide-apatite ± rare earth element ore deposit and the older episode of Mesoproterozoic magmatism in southeast Missouri is borne out by the coincidence of their ages, between about 1.48 to 1.46 billion years ago and 1.48 to 1.45 billion years ago, respectively.

The 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane have somewhat diverse compositions that are diagnostic of the petrogenetic processes responsible for the associated magmatism. In particular, the occurrence of low-degree partial melting of preexisting, intermediate-composition granitoid rock at relatively elevated crustal pressures is in agreement with the abundant ferroan, peraluminous igneous rocks in the St. Francois Mountains terrane. Whether the resulting magmas are calc-alkalic or alkali calcic depends on pressure and crustal depth prevailing during magma genesis. More advanced partial melting of crustally derived, intermediate-composition granitoid rocks at lower pressure may have been responsible for the significantly less voluminous, transitionally magnesian to magnesian and peraluminous igneous rocks in this region. Extensive differentiation of tholeiitic basalt may have produced volumetrically less important ferroan but metaluminous magmas in the St. Francois Mountains terrane. The wide-ranging alkalinity among these ferroan but metaluminous rocks may reflect the balance between clinopyroxene relative to plagioclase fractionation, with the more alkalic rocks representing magmas affected by significant clinopyroxene fractionation, at
higher pressure, and the more calcic rocks reflecting relatively greater plagioclase fractionation, at lower pressure conditions. A combination of mantle-derived mafic inputs and more evolved contributions derived by partial melting of juvenile crustal protoliths are likely responsible for the diversity of compositions characteristic of 1.48 to 1.45 billion year old igneous rocks in the St. Francois Mountains terrane. As such, the petrogenesis of these rocks requires multiple, distinct source inputs. Available data are consistent with crustal melting events in an extensional, intracratonic setting that accompanied mantle upwelling and emplacement of tholeiitic basaltic magma at or near the base of the crust. Primary mafic mantle-derived magmas assimilated crustal-derived partial melts. Crystal fractionation operative in mid-crustal magma chambers further modified magma compositions, resulting in significant major and trace element compositional diversity. The resulting, variably mingled and mixed silicate liquids formed variably homogenized storage reservoirs that continued polybaric evolution in reservoirs lodged at various depths in the crust.

References Cited


Berry, A.W., Jr., 1970, Precambrian volcanic rocks associated with the Taum Sauk caldera, St. Francois Mountains, Missouri: Lawrence, University of Kansas, Ph.D. dissertation, 146 p.


Hildreth, W., and Moorbath, S., 1988, Crustal contributions to arc magmatism in the Andes of central Chile: Contributions to Mineralogy and Petrology, v. 98, no. 4, p. 455–489.


Kisvarsanyi, E.B., 1980, Granitic ring complexes and hotspot activity in the St. Francois Mountains terrane, midcontinent region, United States: Geology, v. 8, no. 1, p. 43–47.


Streickeisen, Albert, 1976, To each plutonic rock its proper name: Earth-Science Reviews, v. 12, no. 1, p. 1–33.


Watson, E.B., 1979, Zircon saturation in felsic liquids; experimental results and applications to trace element geochemistry: Contributions to Mineralogy and Petrology, v. 70, no. 11, p. 407–419.


