THE MOOSELOOKMEGUNTIC IGNEOUS COMPLEX, MAINE: A Pb ISOTOPIC STUDY TO CLARIFY BASEMENT SOURCES

TRACEY L. CENTORBI
GEOLOGY 394H
Adviser: Dr. Paul Tomascak

ABSTRACT

The Mooselookmeguntic Igneous Complex (MIC) is a composite granite pluton located in northern Maine which straddles the tectonite zone that separates material with principally Grenville (North American) crustal sources from the Central Maine Belt wherein granite plutons commonly derive from Avalonian (non-North American) source materials. Leached feldspars were used to derive original or 'common' Pb ratios but Pb was unable to unequivocally evaluate the relative contributions of differing basement sources until combined with existing Nd data.

With one exception, the initial Nd isotopic composition for the less evolved rocks show a limited range of Nd ($\varepsilon_{Nd(t)}$ = -2.7 to -0.7) and Pb ($^{207}Pb/^{204}Pb$ = 15.55 to 15.58), whereas the leucogranites are very heterogeneous ($\varepsilon_{Nd(t)}$ = -6.9 to -0.5; $^{207}Pb/^{204}Pb$ = 15.55 to 15.62). Combined isotope and elemental data were used to assess mantle contributions, of particular relevance among the less evolved rocks. A MORB-like mantle component was the likely primitive end-member while the more evolved end-member was likely a pelitic sediment.

Isotopic data was used in mixing models to further constrain the contributions of possible two-component mixes. A MORB-like mantle/sediment mix was the most likely mode of petrogenesis permitting for three main conclusions. Magma that formed the MIC was generated by crustal anatexis and mixed with a mantle contribution of <10%. Source isotopic heterogeneity was preserved in the MIC or later overprinting processes disturbed a homogenous source signal. The boundary between the Bronson Hill Belt (BHB) and Central Maine Belt(CMB) represent a geochemical or geophysical boundary that allows for distinct isotopic signatures within individual rock types in the complex.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Granites are important sources of information about crustal architecture in that they average the composition of large parts of the crust and bring to the surface a sample of this integrated signal (Miller et al. 1988, Tomascak 1996). Through the combination of thorough field geology, precise geochronology, and elemental and isotopic geochemistry, we can define the nature of unexposed portions of the hearts of mountain belts and shed new light on the tectonics of convergent orogens.

The Mooselookmeguntic igneous complex (MIC) is a composite pluton located in northwestern Maine. The MIC is important because it is on the border between two tectonically distinct rock associations and the crustal sources of plutons in this area are not well understood. This study is expected to not only contribute to the knowledge of the MIC itself but also add to the understanding of the regional geology, primarily because of the large sample population and strategic location of the MIC. Interpretations of the petrogenesis of this complex are enhanced by the inclusion of whole rock and Nd isotopic data conducted previously at the University of Maryland (Tian 2000).

Lead isotopic studies of plutons to the north and south across strike (Ayuso and Bevier 1991, Pressley and Brown 1999, Tomascak 1996) have demonstrated large-scale regional differences in crustal sources, based on their isotope systematics. Because the MIC straddles the tectonic boundary that may divide these crustal terranes, we did not know which isotopically distinct source it was derived from or if it represents a mixture of magmas derived from multiple sources. The hypothesis evaluated by this study in light of the data generated is: the petrographically and geochronologically distinct portions of the Mooselookmeguntic Igneous Complex were derived from an isotopically homogeneous source.

REGIONAL GEOLOGY

In the Northern Appalachians, it is particularly difficult to develop a comprehensive picture of the underlying crust due to the juxtaposition of source terranes. Basement rocks do not crop out extensively in the region so we do not have abundant direct information as to the underlying crustal structure. Regional systematics are strongly influenced by the Norumbega Shear Zone System, a dextral transpressive shear zone which runs southwest to northeast roughly paralleling the present day coast of Maine (Fig. 1). South across strike lies the Avalon Composite Terrain (ACT) that was accreted to North America during the Taconic Orogeny and the closing of the Iapetus. The MIC straddles the surficial border between the Bronson Hill Belt (BHB), an Ordovician metasedimentary and metavolcanic suite formed during the Taconic Orogeny, and the Central Maine Belt (CMB), a metasedimentary terrane, the main phase of which was formed by bulk transpression (Solar et al. 1998).

Metasedimentary rocks of the Central Maine Belt may be underlain by basement added to the North American margin during the construction of the Appalachians and closure of the Iapetus. The distance inland to which this exotic terrane extends is not precisely known, but it is at least within tens of kilometers of the surficial boundary between the Central Maine Belt (CMB) and the Bronson Hill Belt (BHB) (Pressley and Brown 1999). On the inland side of the BHB (north across strike), basement rocks crop out that belong to North America proper ("Grenville"). Zen (1983) suggested that the subsurface cratonic margin of North America extends significantly south of the Maine/Canada border but it is unlikely that Grenville basement underlies the Central Maine belt to any significant distance (Stewart 1989).

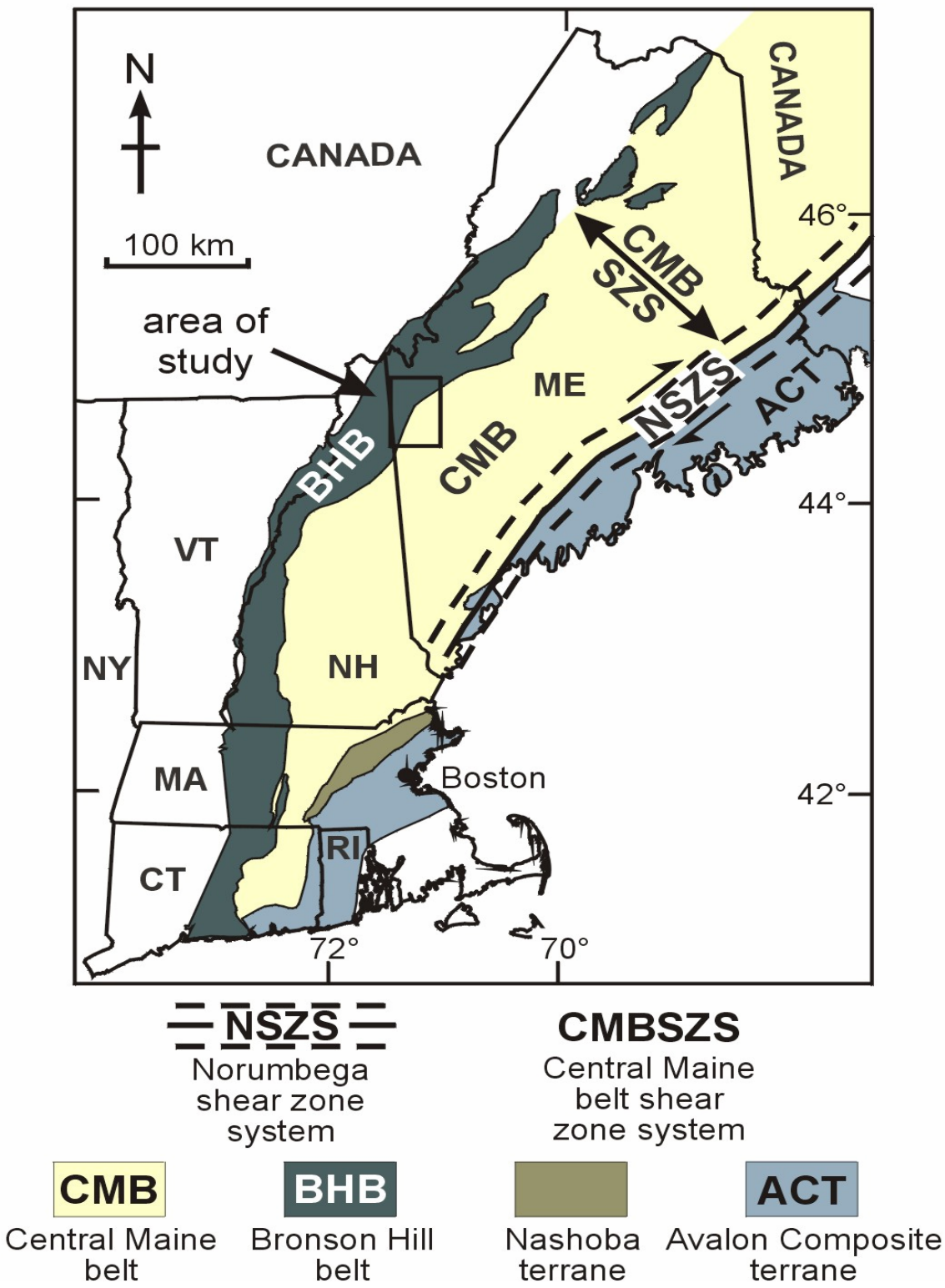


Figure 1: Northern Appalachian region adapted from Tian (2000).

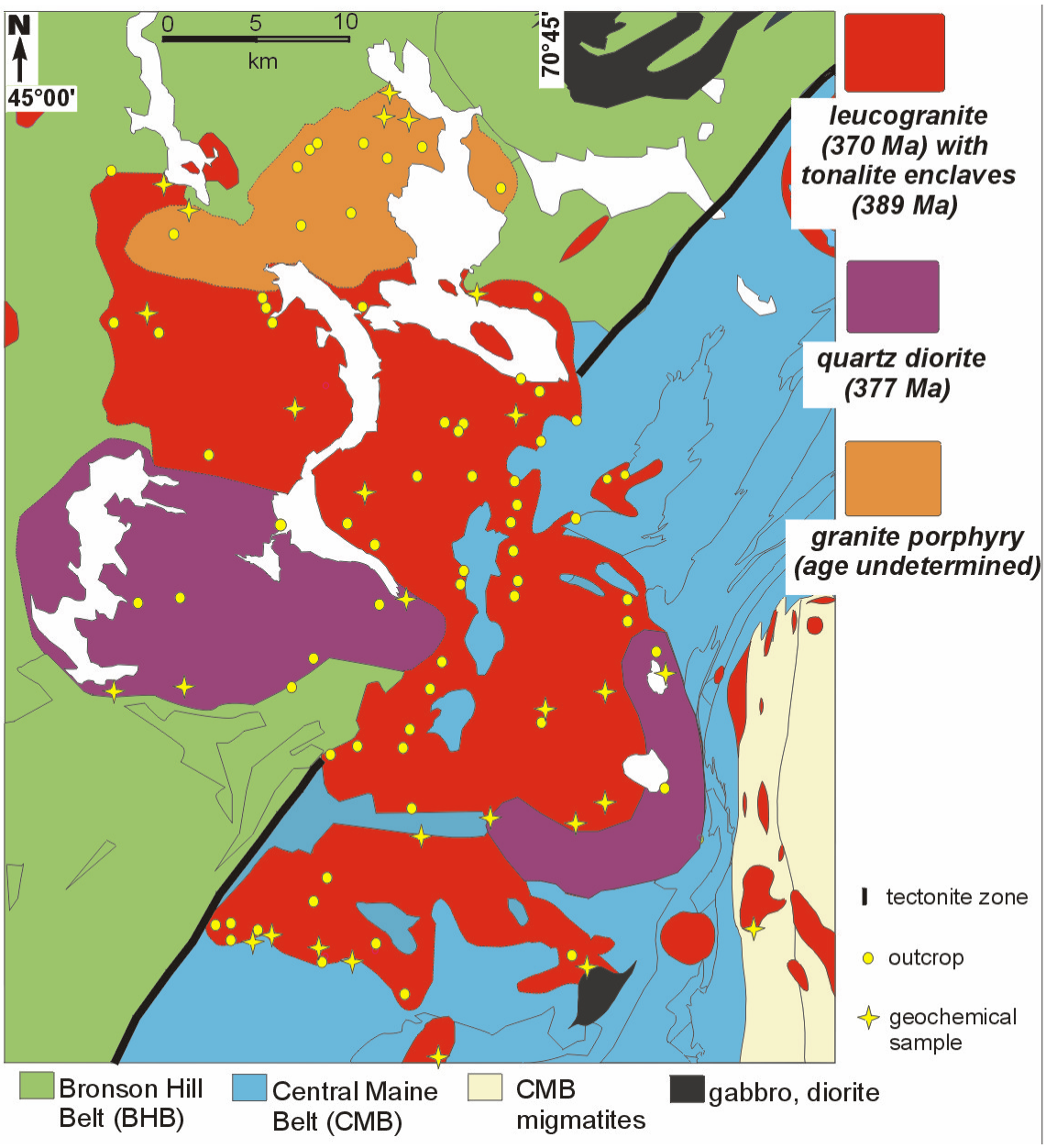


Figure 2: Map of the Mooselookmeguntic Igneous Complex adapted from Tian (2000)

The MIC is discordant to the regional fabrics and crosscuts regional structure (Solar et al. 1998). Its bulk composition is calc-alkaline with petrographic and geochronologic distinctions within the complex requiring that it was not constructed in a single discrete magmatic event. The MIC crops out on the surface approximately 35 kilometers east to west along strike by 45

kilometers across strike. The complex consists of a main body composed of leucogranite (Mooselookmeguntic Pluton) monazite dated at 370±1Ma. The main body contains tonalitic enclaves, which have been zircon dated 389±2 Ma. A body of quartz diorite (Umbagog Pluton) and a southeastern rim of tonalite have been zircon dated at 377±2 Ma (Tian 2000). Age constraints have allowed for the quartz diorite pluton and the southeastern rim to be related despite petrographic differences as well as prohibiting the tonalitic enclaves and southeastern rim to be directly related. A porphyritic body (Adamstown Pluton) is located in the northeastern portion of the complex but has not been dated and therefore we opt not to dwell on it until and age constraint is available. The extent of the MIC allows for a fair representative sampling of these geochronologically and petrographically distinct regions of the complex.

Lead isotopes may give us an indirect method to map the character of unexposed crust in this region that generated this complex (Ayuso and Bevier 1991). Lead isotopes in Maine have strongly contrasting signatures between granites derived from North American and non-North American sources that can provide a robust tool for discriminating between potential sources. Changes in $^{207}Pb/^{204}Pb$ derive from changes in $^{235}U/Pb$ owing to the difference in half-life ($^{238}U >> ^{235}U$). Significant vertical separations in $^{207}Pb/^{204}Pb$ on a given $^{206}Pb/^{204}Pb$ can therefore only have been produced by ancient (>2Ga) changes in U/Pb. Thus, the Pb-Pb systematics can show the imprint of events in a far greater time in the past than the isochron age (Pegram 1990).

Granites of the northern group in Maine, as defined by Ayuso (1986), have the lowest $^{207}Pb/^{204}Pb$ whereas granites of the coastal lithotectonic block have the highest $^{207}Pb/^{204}Pb$ owing to the influence of an ancient crustal component (Fig. 3). The southern group of Ayuso and

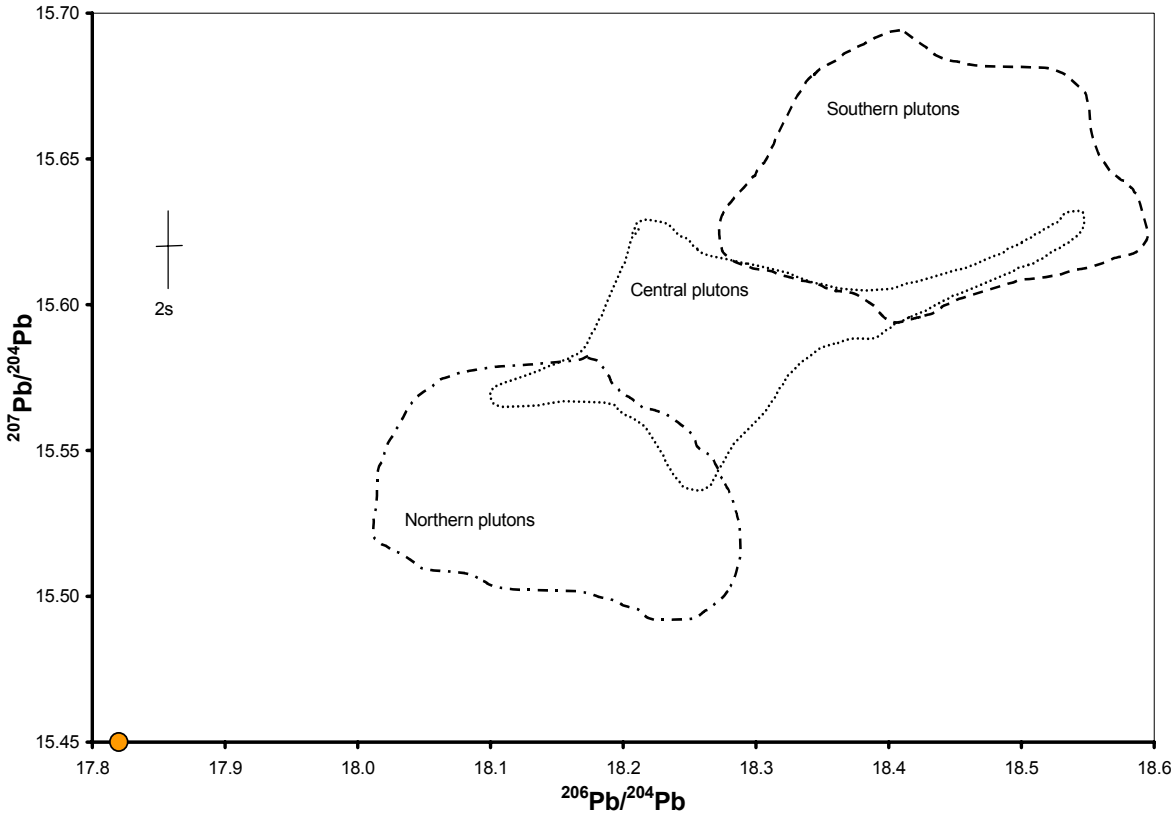


Figure 3: leached feldspar and corrected whole rock data from: Ayuso (1986); Ayuso and Bevier (1991); Devonian mantle estimate of Doe et al. (1985)

Bevier (1991) is interpreted to represent non-North American crustal sources, whereas the northern group has Pb isotopes consistent with Grenville values. From a Pb isotope standpoint, plutons in the Central Maine Belt appear to be a mixture of Grenville and Avalon sources but there is no gradient relating these groups from north to south, thus making a simple mixing interpretation equivocal (Ayuso 1986).

In order to assess the initial Pb isotope composition of a rock, we ideally would like to examine a mineral that contains Pb but no U, since any U present will have decayed to an 'excess' radiogenic component. Feldspars are particularly suited to lead isotope studies because they have low U/Pb. Alkali feldspars contain distinct radiogenic and non-radiogenic Pb isotope reservoirs. Progressive leaching of feldspar grains shows a decrease in the amount of radiogenic

Pb that may indicate the preferential leaching of the more radiogenic reservoirs (Housh and Bowring 1991, McCulloch and Woodhead 1993). Indigenous Pb versus Pb introduced after crystallization may be evaluated partially using leach/residue pairs (Hemming et al. 1996). A general agreement has been found between the least radiogenic isotope composition of feldspars and the Pb isotope composition of associated sulfides (Sinha 1969), suggesting that this method of severe leaching will give us a good estimate of initial Pb.

METHOD OF ANALYSIS

Physical preparation methods:

The following steps were performed in the Geology Department's rock crushing and mineral separation labs under the guidance of Dr. Paul Tomascak. Dr. Harry Becker advised on the proper operation and settings of the Frantz isodynamic magnetic separator.

1) Samples had already been crushed and sufficient material was available for most samples. It was unnecessary to produce additional material. Three samples did not yield sufficient sample volume so they were disaggregated manually with a steel mortar and pestle.
2) To obtain a more homogeneous grain size distribution for later separation steps, samples were sieved to 180 μm < x < 350 μm using stainless steel and plastic sieves.
3) Samples were put into centrifuge tubes for cleaning. Distilled H_2O was added and the tube was agitated. The wash water was decanted taking care not to lose sample. This process was repeated several times. Samples that were not reasonably clean were placed in an ultrasonic bath for five minutes and then the wash water was decanted. Grains were transferred to an aluminum foil tray, rinsed with ethanol, and dried in an oven. Cleaned samples were returned to their cleaned centrifuge tubes.

4) Some biotite-rich samples benefited from having the biotite separated from the more felsic minerals using a Frantz isodynamic magnetic separator. This eased difficulties encountered in the heavy liquid separation flask caused by the platy nature of biotite. The magnetic separator was at a standard setting for all samples of: 20˚ tilt (away from the magnet), 25˚ inclination, 0.70V, and approximately 0.48 amps. The magnetic fraction was returned to the centrifuge tube and the non-magnetic fraction was used in the next step.
5) K-feldspar or albite grains were separated from the bulk sample by flotation with $Na_6(H_2W_{12}O_{40})\cdot H_2O$ a soluble, non-toxic, high-density liquid. The proper solution density (~2.57 g/cm^3) was calibrated using chips of K-feldspar and albite. Mineral chips were added to the separation flask containing the Na-polytungstate. Initially, both chips floated. Distilled H_2O was added incrementally until the albite chip sank to the bottom of the flask while the K-feldspar remained at the top. A portion of the sample was added to the flask and the solution and grains were agitated with a Teflon stirring rod. Grains of higher specific gravity sank to the bottom of the flask and were periodically removed to a funnel lined with #2 filter paper. These grains were rinsed thoroughly to retrieve as much of the Na-polytungstate from grain surfaces and the filter paper as possible. Additional portions of the bulk sample were added after these heavier minerals were removed and repeated until all sample had been added. When most of the heavier minerals had been removed, a new funnel and #2 filter paper were used to decant and rinse the floating K-feldspar grains. These grains were air-dried overnight and transferred to clean weighing paper containers. For samples with an insufficient amount of K-feldspar, albite was substituted. To obtain albite, the separation process was the same except that a chip of albite was floated and a quartz chip sank to the bottom. Dilute Na-

polytungstate was evaporated on a hot plate until its density was 2.89 g/cm^3, filtered using #1 filter paper, and reused for other samples.

6) A single analysis by thermal ionization mass spectrometry (TIMS) requires 50 – 100ng of Pb. Based on the expected concentration of Pb in the feldspars, we calculated that 10 – 20mg of feldspar is needed (Tomascak 1995). Grains were picked under an optical microscope. A qualitative selection was made for grain clarity, lack of inclusions, and a minimum of cracks. A black background was useful for selecting grains based on clarity and minimal cracks. These grains were then rechecked against a pastel background to remove those with inclusions and variations in color. At least 20 mg of samples with a higher abundance of suitable grains were picked while samples that had a lower abundance of suitable grains tended towards 10 mg. These grains were transferred to plastic sample vials.

Chemical preparation methods:

The following steps were performed in a clean lab environment. Reagents were stored in a sealed container and chemistry steps were performed in class 100 laminar flow hoods to mitigate the addition of environmental Pb. All processes were initially performed under the guidance of Dr. Paul Tomascak.

1) Grains were transferred into clean 7-ml Teflon (FEP) vials and re-weighed. A cleaning solution of ~0.5 ml 6M HCl and ~0.5 ml 7M HNO_3 was added using quartz distilled acids. Vials were capped and transferred to a hot plate (80-90°C) for at least an hour to remove surface contaminants and labile lead. This step was to help ensure that any lead that had been introduced after crystallization, either from the environment or through the actions of fluids moving through the pluton, was removed before leaching. The grains were then rinsed with Milli-Q water three times.

2) Milli-Q water was added to just cover the grains. An equal volume of 29M (wt. %) HF was added and the vials were capped and placed in an ultrasonic bath. The grains were continuously monitored and removed from the ultrasonic bath when approximately 50% (visual estimate) of the grains had dissolved. The approximate extent of dissolution was noted and the grains were rinsed with Milli-Q water to remove the digested material.
3) Grains were completely dissolved by adding 10 drops 29M HF, capping the vial tightly, and transferring them to an 80˚ – 90˚C hotplate until no grains remain. The vial was then uncapped and dried on the hotplate. When dry, several drops of 6M HCl were added and the solution was dried again. Approximately 0.5ml 0.7M HBr was then added to complete dissolution.
4) Each sample solution was processed through anion exchange column chemistry to isolate lead. Columns made of heat-shrink Teflon tubing were filled with Milli-Q water and loaded with 300µl Bio-Rad AG 1-X8 resin. This amount is referenced as 1 resin bed volume (RBV). The resin was cleaned by adding 10 RBV 6M HCl, followed by a rinse of 10 RBV Milli-Q water. 5 RBV 0.7M HBr was then added to condition the resin. The sample solution was added to the column in 5 RBV 0.7M HBr taking care to avoid disturbing the resin. Twenty drops of 2M HCL were added to refine the removal of cations and bromide anion complexes of the large alkalis. The elution to this point was then discarded. 6 RBV of 6M HCl were then added and a clean vial was used to collect the resultant solution. One drop of 7M HNO_3 was added to the vial and the solution was dried. A yield test performed on a k-feldspar sample unrelated to this study was found to yield >90% of Pb.
5) The sample could now be loaded onto a filament for TIMS analysis.

ANALYSIS OF UNCERTAINTY

Procedural blanks are processed using the same chemical preparation techniques as were used for the grains after complete dissolution. Lead blanks assess the ambient amount of lead introduced during sample processing. Blank contents are determined using an isotopically enriched tracer ('spike'), and are calculated by isotope dilution. Given unfavorable sample/blank (<~100), a correction would be necessary, but since these samples have Pb concentrations 10-50ppm (10 ppm x 10 mg = 100 ng Pb; typical blanks <1 ng), this has not been necessary. A table of blanks is included in Appendix I.

All isotope ratio measurements were conducted in the Isotope Geochemistry Laboratory at the University of Maryland. Measurements were made using the Bobcat II, a VG Sector 54 mass spectrometer with 7 faraday collectors and a Daly knob-photomultiplier system (Tomascak 1995). Thermal ionization mass spectrometer (TIMS) data are collected as ratios ($^{204}Pb/^{206}Pb$, $^{207}Pb/^{206}$ Pb, ^{208} Pb $/^{206}$ Pb). A standard solution with known isotopic composition (SRM-981) was analyzed periodically during the analytical period, and the offset in terms of %/a.m.u. (Appendix I) was determined from these measurements. The intensity ratios of unknown samples were converted to the commonly used representations ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}$ Pb, ^{208}Pb $/^{204}$ Pb) and are corrected for instrumental mass fractionation, based on the standard analyses (Table 1).

MASS FRACTIONATION CORRECTION

	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$
Avg standard	16.9125	15.4622	36.6037	2.1643	0.9142
Pb SRM-981	16.9417	15.4996	36.7240	2.1677	0.9149
correction value	0.0862	0.0803	0.0819	0.0783	0.0712
%/ a.m.u.	0.0796				

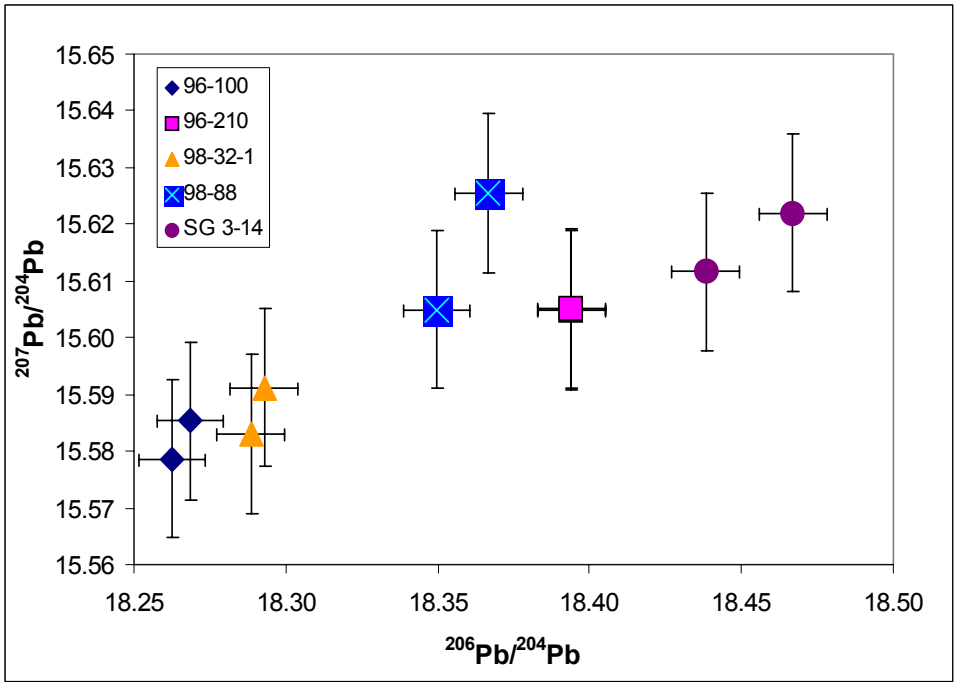
Table 1: Standard analyses fractionation corrected to refererence values of Thirlwall (2002)

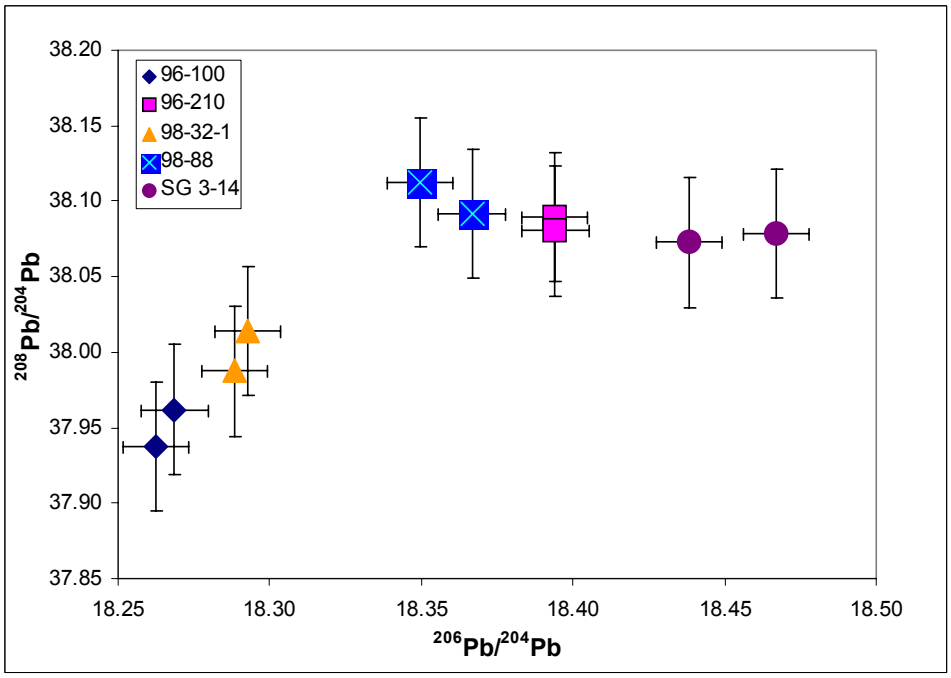
Precision can be assessed mainly through reproducibility of standard measurements, but also by comparison of this uncertainty with the reproducibility of additional preparations of the same sample (replicates) or analysis of multiple batches of the same sample. This study prepared replicates of three types: 1) replicate analysis of a single sample from one chemical preparation loaded on separate filaments (96-210) 2) samples that were picked, chemically processed, and analyzed separately (96-100, 98-32-1, 98-88) 3) for long-term reproducibility of TIMS, a sample from the Sebago batholith (SG 3-14) was picked and chemically processed. A table of replicates is located in Appendix I.

In order to assess the effect of leaching on the resultant isotopic ratios, sample 98-88 and the replicate of 98-32-1 were leached ~75% rather than ~50%. The samples were also picked to ensure that there was a minimum difference in the size of the feldspar grains selected. As observed in the laboratory, smaller grains tended to leach much more quickly than larger grains and therefore the leaching process may have been stopped when the overall volume of the sample had been leached 50% but the individual larger grains may have each been leached less than 50%. This higher degree of leaching and greater grain size selectivity resulted in a marked decrease in 207Pb/204Pb, most dramatically in 98-88, yet did not yield isotopic compositions

distinct beyond statistical error (Fig. 3a & 3b). The inference drawn from these replicates was that although different degrees of leaching can adjust the measured isotopic ratios of a sample somewhat, severe leaching cannot alter the basic character of a sample from Avalon-like to non-Avalon.

Table 4a and 4b: Replicate data with error





Difference in the isotopic composition of the Sebago batholith sample (SG 3-14) from Tomascak (1995) can be attributed to a number of factors. First, grain selection is an inherently qualitative and somewhat subjective process. Grains accepted by one researcher may be rejected by another and therefore affect the overall ratios to some extent. Even replicates picked by the same researcher are rarely identical due to microscopic inclusions in the grain that even the most vigilant visual examination may not identify. It is also likely that the apparent variations in SG 3-14 are due to small changes in the chemical preparation procedures for isolating lead, a new silica gel (not available in 1995) which was used to load the filaments, or updates and changes to the VG Sector 54 mass spectrometer that have occurred in the intervening years.

Results

Nd isotope data from Tian (2000) from these rocks and Pb isotope data for leached K-feldspars are listed in Table 2. Quartz diorite $^{207}Pb/^{204}Pb$ values range from 15.56 to 15.58, spanning from Grenville values to those values typical of central plutons (Fig. 4). $\varepsilon_{Nd(370Ma)}$ are -2.7 to -0.7, a range that is less 'evolved' than typical Grenville compositions but well within typical Avalon crustal ranges (Fig.5). Three of the enclaves have $\varepsilon_{Nd(370Ma)}$ of -2.7 to -2.5, or more Avalon-typical, although one sample $\varepsilon_{Nd(370Ma)}$ = -9.9, a value typical of evolved Grenville crust or some sediments. The $^{207}Pb/^{204}Pb$ of three enclaves ranges from 15.57 to 15.58, or typical of a central pluton, with one sample's $^{207}Pb/^{204}Pb$ = 15.60, which falls within error of a southern pluton. Leucogranite $\varepsilon_{Nd(370Ma)}$ (–6.9 to -0.5) values span the range of typical Avalon and Grenville values as well overlap the values of other portions of the pluton. The $^{207}Pb/^{204}Pb$ range from 15.54 to 15.62, or from Grenville to Avalon values.

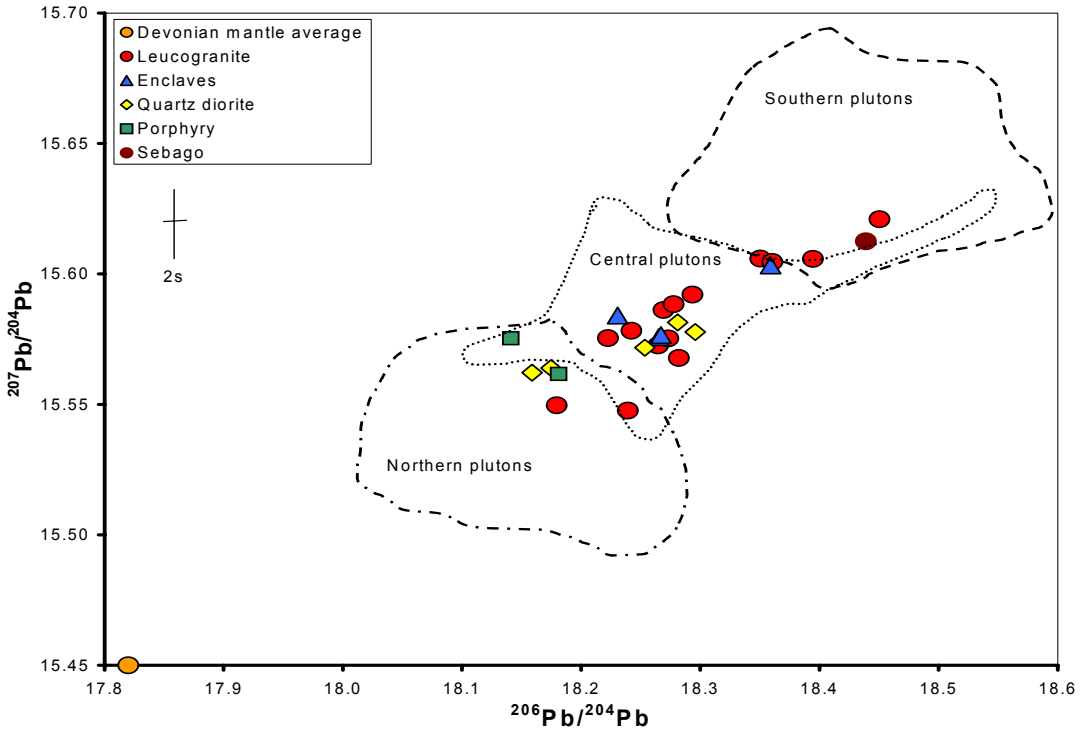
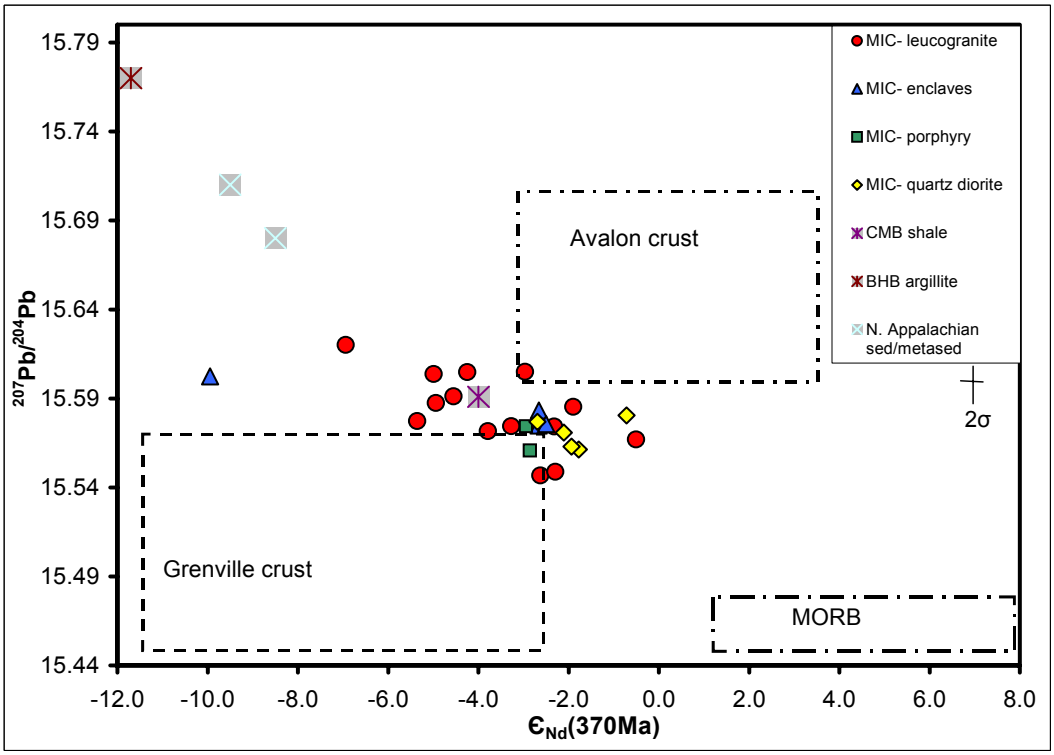


Figure 5 & figure 6: data from Ayuso (1986); Ayuso and Bevier (1991); Devonian mantle estimate of Doe et al. (1985); Pegram (1990); Ayuso and Schulz (in press); Arth and Ayuso (1997)



Discussion

Isotopic constraints

Pb isotopes do not allow for an unequivocal interpretation of possible source components as they mostly fall in the field between the distinctly northern and southern plutons. The data for all rock types within the MIC do not allow their generation to have been from a mix of the estimated Devonian mantle of Doe et al. (1985) and Grenville but does not equivocally exclude other two component mixes.

A previous Nd isotopic study allowed for multiple interpretations of source regions for the MIC (Tian 2000). Two problems in particular were faced. First, it is difficult to discriminate between enriched mantle and Avalon basement because both reservoirs may have identical ranges in $\varepsilon_{Nd\ (370Ma)}$. Second, some Nd data span to negative values of $\varepsilon_{Nd\ (370Ma)}$ which overlap Grenville sources. Mid-crustal metasedimentary rocks such as those exposed throughout the Central Maine Belt have equivalent isotopic compositions and therefore crustal anatexis could not be excluded as a possible source component. In short, Nd isotopes alone cannot separate these components.

Though limited studies exist in the region that pair Nd data with Pb data, those that do allow us to further constrain potential source components, particularly the primitive end-member. Two types of mantle components may be involved in MIC petrogenesis. Lithospheric mantle, which has been indicated as a source of voluminous Mesozoic magmatism (Pegram 1990), shows a strong correlation between Pb and Nd with the most radiogenic $^{207}Pb/^{204}Pb$ having the highest $\varepsilon_{Nd(t).}$ The trend in the data of all rock types of this study of low $^{207}Pb/^{204}Pb$ values at $\varepsilon_{Nd(370Ma)} \sim 0$ does not allow for an enriched continental lithospheric source for the MIC but still allows for a more normal depleted mantle. Moderately depleted (MORB-like) mantle pairs low $^{207}Pb/^{204}Pb$

with very radiogenic Nd (Samson et al. 1995) and therefore can satisfy the requirements of a primitive component in MIC petrogenesis.

The evolved end-member component of MIC petrogenesis does not appear to be satisfied by any of the existing basement rock candidates. Sedimentary rocks that are known in the area and have paired Nd and Pb data appear to satisfy the need for an evolved end-member that possesses both unradiogenic Nd and high $^{207}Pb/^{204}Pb$ (Arth and Ayuso 1997, Ayuso and Schulz in press).

Quartz diorites

The quartz diorite data fall in a restricted $^{207}Pb/^{204}Pb$ range that can be satisfied by a mix of Grenville and Avalon sources yet this mixture of magmas would likely produce a more felsic rock type and therefore a mantle component is indicated for its petrogenesis. The limited range of the quartz diorite data allow for them to have been generated by a homogenous source though it does not definitively illustrate what that source was.

The two least radiogenic samples were obtained from the southeastern rim that is across the tectonite zone from the larger quartz diorite body. The distinction in Pb space makes it unlikely that this rim and the main body of quartz diorite were derived from a common source as these rim samples are distinctly Grenvillian in isotopic composition and do not show the influence of a radiogenic source component.

With constraints on the nature of the primitive component, an Avalon/Grenville mix as well as a mix of MORB and Avalon may satisfy the quartz diorite composition. Given that the Avalon/Grenville mix would likely be too felsic, the inclusion of a MORB component could satisfy the conditions imposed by Nd and Pb data while generating a more mafic melt.

Enclaves

The enclave data trends from distinctly Grenville in composition to within error of an Avalon composition in Pb isotopic space. Again, a mix between Grenville and Avalon components or between Avalon and MORB components can satisfy this data. A spatial analysis of the sample locations, however, may allow for some interpretations of this range. As the enclaves are the oldest portions of the pluton, their isotopic compositions may have been perturbed when later batches of magma intruded adjacent to the enclaves. Differences in isotopic compositions may be due to the sample location relative to the adjacent leucogranite and the extent within the enclave of interactions with these later intrusions. The three enclaves that fall into the central pluton field are perhaps more susceptible to the homogenizing effects of later intrusions. Their overlap in Pb space with many of the leucogranite and quartz diorite samples may be a reflection of this homogenization.

Most of the enclaves are consistent with generation from a mix of Grenville and Avalon or MORB and Avalon except for one sample (98-32-2). It exhibits the most evolved $\varepsilon_{Nd(370Ma)}$, the most radiogenic Pb signature, and it is from the only enclave that was sampled north of the tectonite zone. The spatial characteristics of this sample relative to the other enclaves allow for the possibility of a different source region, isolation from overprinting events, or differing petrogenetic systematics.

Leucogranites

The leucogranites show a correlation between Nd and $^{207}Pb/^{204}Pb$ with the most radiogenic Pb samples exhibiting the lowest $\varepsilon_{Nd(370Ma)}$. The leucogranites, however, pose many of

the same challenges to interpretation as the enclaves. They trend from rather non-radiogenic or Grenville-like to radiogenic Avalon-like values though most samples again fall in the equivocal central region. This array allows for generation from a mixed Grenville/Avalon source or a mixed Avalon/MORB source while continuing to preclude the possibility of a Grenville/MORB mix. The least radiogenic samples are not spatially related in that they are located to the extreme north and south of the pluton. Samples in the central zone all have $^{207}Pb/^{204}Pb$ ratios of approximately 15.7 on a limited $^{206}Pb/^{204}Pb$ and overlap with a number of the enclaves and quartz diorites. This overlap allows for the possibility that a single process relates different rock types or that a homogenizing process overprinted existing isotopic compositions.

The most radiogenic samples (Avalon-like) are all located to the south of the tectonite zone, although all of the samples in this southern portion of the MIC are not Avalon-like. The systematics that allow for this distinction are unclear at this time. There also exists the possibility that the portions of the pluton north and south across the tectonite zone are different ages because only one monazite age from the southern portion was obtained by Tian (2000) and therefore the two portions may sample isotopically distinct sources.

The structural setting and subsurface structure of the pluton itself allow for the possibility of differing rates of ascent and emplacement that would likely be reflected in the isotopic characteristics. The pluton is thicker to the south of the tectonite zone and therefore shallower structural portions of the body are exposed (Solar et al. 1998). Magma in this thicker region may have been farther from wallrock contacts and therefore less likely to have been affected by later overprinting events or contact with the country rock.

A visual examination of the feldspar grains of the more radiogenic samples showed that they tended to be larger, clearer, and contain fewer cracks and apparent alteration than less

radiogenic leucogranite samples. The physical quality of the grains suggests that these samples were not subjected to post-crystallization processes that demonstrably altered the feldspars therefore it is likely to have been petrogenetic or emplacement processes that account for the isotopic distinctions. The larger grain size of these feldspars (an average modal distribution of grains after physical processing closer to .5 mm for radiogenic samples; average modal distribution closer to .25 mm for less radiogenic samples) does allow for the possibility that the higher radiogenic Pb contents are, at least in part, a laboratory relic of the leaching process. The decrease in $^{207}Pb/^{204}Pb$ of the sample replicates allows for the possibility that the larger grains have a smaller common lead core relative to their size and that 50% leaching is not sufficient to remove this more radiogenic reservoir to the same degree as samples with smaller grains. It is unclear, however, if this laboratory relic can fully account for the distinction of these samples from those falling within the central pluton region of Ayuso and Bevier (1991) as they retain their more radiogenic signatures after higher degrees of leaching. It is, perhaps, an area for further investigation in the future.

There is considerable overlap of the isotopic compositions of the leucogranites with other portions of the MIC yet the leucogranites span a broader range in both Nd and Pb. In addition to the possibility of a Grenville/ Avalon mix, a best-fit line through the array allows for a mix between MORB and a radiogenic sediment component. Paired Nd and Pb data for sediments (Arth and Ayuso 1997, Ayuso and Schulz in press) trend toward unradiogenic Nd and high $^{207}Pb/^{204}Pb$ thus, these sediments provide the best 'evolved' end member for the mixing suggested by the leucogranites.

Implications for petrogenesis and emplacement

Tectonic models and previous studies of plutons in Maine have suggested a connection between rates of ascent and emplacement of magmas within plutons (Pressley and Brown 1999, Solar et al. 1998, Tomascak 1995, Miller et al. 1988, Zorpi et al. 1989). An existing geochemical heterogeneity of a source may be preserved or erased depending on the rate of ascent and solidification of individual melt batches (Pressley and Brown 1999). Individual melt batches may ascend and pond at shallower levels which allows them to be spatially related but not share common sources or to not share the same proportions of similar source materials (Samson et al. 1995). A slower cooling portion of a plutonic body is more likely to have a chance to mix before crystallization and homogenize its isotopic signature to some extent.

In the MIC, the quartz diorites north of the tectonite zone exhibit the most homogeneous compositions in Nd, Pb, trace and major element composition suggesting that its necessary source components (MORB-like mantle and evolved crust) were homogenized during ascent and emplacement. The southeast rim is distinct in terms of Pb despite overlapping ranges of $\varepsilon_{Nd(t)}$. The data do not allow for the quartz diorite pluton and southeast rim to be derived from a homogenous source but the location of the two areas on either side of the tectonite zone suggests that they were derived from a source with inherent heterogeneity, two distinct sources, or different mechanisms of ascent and emplacement resulted in differing isotopic compositions.

The enclaves exhibit spatial and isotopic characteristics that suggest they also reflect a heterogeneous source, distinct source regions, or differing systematics north and south of the tectonite zone. The possibility also exists within this rock type that the seemingly anomalous northern enclave is of a different age, which could account for the isotopic distinctions.

The leucogranites, although very well correlated in terms of Pb and Nd compositions, are more problematic. They appear to exhibit distinct source regions in Pb space and yet when combined with Nd isotopes, they suggest a mixture of source components of differing proportions.

The isotope data from the MIC indicate that the surficial boundary between the BHB and CMB may be a more profound localized geochemical and geophysical boundary than previously recognized. The leucogranites exhibit this feature in that no samples with $^{207}Pb/^{204}Pb$ >15.6 have been identified north of the tectonite zone. The only enclave sampled north of the tectonite zone has a Nd and Pb isotopic signature unequivocally distinct from its southern counterparts. The quartz diorites have both geochemical and petrographic differences on either side of the tectonite zone all leading to the conclusion that the tectonite zone represents a regional feature of some importance.

Mixing Models

In order to assess the possibility of two-component mixing, modeling of different source components was adapted from Langmuir et al. (1978). Samples of different mixing pairs are listed in Appendix II. Source component isotopic ratios and concentrations were adapted from Pegram (1990), Ayuso and Schulz (in press), Arth and Ayuso (1997), and Ayuso and Bevier (1991).

A MORB/Avalon mix is possible for the quartz diorites that requires an input of less than 10% of the MORB-like component. It cannot account for the full range of data of the leucogranites or enclaves but this mixture does satisfy the requirement for a mantle component to explain the intermediate composition of the quartz diorites.

A Grenville/Avalon mix also allows for the quartz diorite compositions with an input of 40 - 50% Grenville. This possibility can generate the requisite Nd and Pb isotopic composition of the quartz diorites but it has been discounted on the grounds that it would produce a more felsic melt than is necessary. It cannot account for the full range of leucogranite or enclave data without having a Grenville source that spanned the full range of possible Nd while mixing with a much more limited Avalon crust range. It is difficult to model the very limited and specific parameters for this mix and therefore it is not a likely explanation for the MIC.

Mixing between MORB and regional sediments seems to be the most likely two-component mixing model that is viable. An input of less than 10% of MORB is able to account for the isotopic composition of all but the most radiogenic leucogranite sample. All the quartz diorite samples can be derived with approximately the same level of MORB mixing. All but the most radiogenic enclave can also be modeled with less than 10% MORB input. The limited amount of paired Nd and Pb data allows for the possibility that there is a regional sediment that satisfies the isotopic composition necessary to produce even the radiogenic enclave signature in a mixture with MORB.

Suggestions for future work

At the Isotope Geochemistry Laboratory, University of Maryland, we have recently obtained a preparation of Pb double spike. Double spike can increase the precision of TIMS analyses by decreasing the error associated with the measurements. The error generated by TIMS measurements is partially a function of the size of the signal from the sample or standard. There is a much higher natural abundance of ^{208}Pb relative to ^{204}Pb and therefore the measured signal of

^{204}Pb is much smaller and less precise. A double spike preparation can be added to allow $^{207}Pb/^{204}Pb$ ratios to be measured at ~2 and $^{206}Pb/^{204}Pb$ at ~ 4, therefore with higher precision.

Future work could also include generating paired Nd and Pb data on more possible source components including sediments. One of the limitations imposed on this study has been the lack of paired Nd/Pb data for many of the formations of different rocks that may have played a role in MIC petrogenesis. As evidenced by this study, pairing these two systems can provide more robust constraints on source components than either system can provide independently.

In the course of this study, an observation of the apparent displacement of the MIC along the tectonite zone was made. As we have recognized the possibility of this tectonite zone as a geochemical and geophysical boundary within the body of the pluton, a further investigation of the effect this tectonite zone and its impact on magma ascent pathways may warrant further investigation. A refinement of the importance of the surficial boundary between BHB and CMB in the regional model may be necessary.

Conclusions

The data support a petrogenetic model involving three principal parts.

1) Magma was generated by melting of pelitic sediments or their metamorphic equivalents and mixed with less than 10% bulk volume of a mantle component.
2) Magma that formed the MIC was derived primarily from a heterogeneous source that is reflected in the isotopic ratios or from a homogeneous source that then differentiated during ascent and emplacement.

3) The surficial boundary between the BHB and CMB represents a profound very localized geochemical and geophysical boundary capable of producing distinct isotopic ratios within geochronologically and petrographically similar rocks of the MIC.

This study indicates that chemical and isotopic data from evolved granites can allow for a detailed characterization of source materials. The combination of Nd and Pb isotopic systems can be a robust analytic tool to discriminate between complex petrogenetic systems in the Northern Appalachians.

Acknowledgements

This project would not have been possible without the patience and contstant support of my advisor Paul Tomascak. Thank you for challenging me and always being willing to answer my seemingly endless questions. To Mike Brown for affording me the opportunity to work on your project and go to GSA. It was a great experience. To Harry Becker for his help with the Frantz and to Dazhi Jiang for his insights that he was kind enough to share with me. To Bill Minarik for the many conversations about all things geologic. Most of all, I would like to thank my children and my husband. Without their constant good cheer and distraction, I would be incomplete.

Appendix I

BLANK, STANDARD, AND REPLICATE ANALYSES

BLANKS

reagent blanks	Pb
Milli-Q H2O	6 pg/g
1x 0.8M HBr	4 pg/g
1x 6M HCl	5 pg/g
1x 29M HF	10 pg/g
TAB (Kfs)	99 pg

TAB = total analytical blank, including loading blank;
Kfs= K-feldspar chemistry;
"1x" refers to single distilled reagent

REPLICATE ANALYSES

sample	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
96-210#	18.3940	15.6049	38.0896
	18.3940	15.6051	38.0803
96-100+	18.2685	15.5853	37.9620
	18.2625	15.5787	37.9374
98-32-1+	18.2928	15.5912	38.0141
*	18.2885	15.5831	37.9875
98-88*+	18.3496	15.6050	38.1125
	18.3667	15.6255	38.0916
SG 3-14+	18.4670	15.6220	38.0787
	18.4382	15.6116	38.0726

#= two filaments of the same chemical preparation
+= separately processed batches of the same sample
*= samples that were leached ~75%

STANDARD ANALYSES

Pb isotopic composition: SRM-981

Date	$^{206}Pb/^{204}Pb$	% std. error	$^{207}Pb/^{204}Pb$	% std. error	$^{208}Pb/^{204}Pb$	% std. error	$^{208}Pb/^{206}Pb$	% std. error	$^{207}Pb/^{206}Pb$	% std. error
4/28/02	16.9211	0.0028	15.4715	0.0026	36.6367	0.0025	2.1651	0.0005	0.9143	0.0006
4/28/02	16.9201	0.0040	15.4715	0.0039	36.6387	0.0042	2.1654	0.0016	0.9144	0.0010
9/26/02	16.9179	0.0036	15.4694	0.0035	36.6286	0.0036	2.1651	0.0011	0.9144	0.0011
9/26/02	16.9105	0.0041	15.4564	0.0043	36.5931	0.0041	2.1639	0.0008	0.9141	0.0009
9/26/02	16.9082	0.0038	15.4548	0.0036	36.5824	0.0031	2.1636	0.0008	0.9140	0.0009
9/26/02	16.9183	0.0033	15.4687	0.0033	36.6273	0.0032	2.1649	0.0007	0.9143	0.0008
9/26/02	16.9152	0.0043	15.4651	0.0043	36.6148	0.0042	2.1647	0.0007	0.9143	0.0008
10/8/02	16.9117	0.0033	15.4687	0.0031	36.5981	0.0033	2.1641	0.0011	0.9142	0.0008
10/8/02	16.9126	0.0040	15.4622	0.0039	36.6032	0.0041	2.1643	0.0010	0.9142	0.0008
10/9/02	16.9039	0.0041	15.4545	0.0043	36.5810	0.0049	2.1641	0.0012	0.9143	0.0007
10/14/02	16.9112	0.0032	15.4589	0.0034	36.5946	0.0033	2.1639	0.0007	0.9141	0.0008
10/14/02	16.9045	0.0050	15.4508	0.0050	36.5699	0.0051	2.1633	0.0008	0.9140	0.0009
10/19/02	16.9171	0.0028	15.4667	0.0028	36.6183	0.0029	2.1646	0.0010	0.9143	0.0009
10/19/02	16.9137	0.0029	15.4652	0.0027	36.6150	0.0028	2.1648	0.0006	0.9144	0.0007
11/16/02	16.9034	0.0029	15.45319	0.003	36.56453	0.0028	2.163151	0.0006	0.914208	0.0009
11/16/02	16.9102	0.0068	15.45832	0.0071	36.59329	0.0067	2.163935	0.0008	0.914146	0.0009

Appendix II

Mixing Data

MIXING DATA

Pb	mantle+avalon		mantle+grenville		grenville+avalon		mantle + sediment
A	15.45		15.45		15.51		15.45
B	15.65		15.51		15.65		15.77
a, ppm	0.5		0.5		29		0.5
b, ppm	30		30		31		10
c	C	c	C	c	C	c	C
30.00	15.65000	30	15.51000	31	15.65000	1	15.591
29.97	15.65000	29.9705	15.51000	30.998	15.64987	0.9995	15.590992
29.71	15.64997	29.705	15.50999	30.98	15.64869	0.995	15.590921
24.10	15.64917	24.1	15.50975	30.6	15.62346	0.9	15.589068
21.15	15.64858	21.15	15.50957	30.4	15.60993	0.85	15.587721
18.20	15.64780	18.2	15.50934	30.2	15.59623	0.8	15.585964
15.25	15.64672	15.25	15.50902	30	15.58233	0.75	15.583579
12.3	15.64512	12.3	15.50854	29.8	15.56826	0.7	15.580154
9.35	15.64251	9.35	15.50775	29.6	15.55399	0.65	15.57482
6.4	15.63750	6.4	15.50625	29.4	15.53952	0.6	15.565364
3.45	15.62391	3.45	15.50217	29.2	15.52486	0.55	15.544
0.5	15.45000	0.5	15.45000	29	15.51000	0.5	15.45

eNd	mantle +avalon		mantle +grenville		grenville + avalon		mantle + sediment
A	5		5		-5		5
B	0.1		-5		0.1		-12
a, ppm	17		17		40		17
b, ppm	30		40		30		20
c	C	c	C	c	C	c	C
30	0.10000	40	-5.00000	30	0.10000	20	-4.00000
29.987	0.10278	39.977	-4.99575	30.01	0.09320	19.997	-3.99975
29.87	0.12789	39.77	-4.95725	30.1	0.03223	19.97	-3.99748
27.4	0.70803	35.4	-4.03955	32	-1.17500	19.4	-3.93827
26.1	1.05747	33.1	-3.45921	33	-1.75455	19.1	-3.89510
24.8	1.44355	30.8	-2.79221	34	-2.30000	18.8	-3.83871
23.5	1.8723404	28.5	-2.01754	35	-2.81429	18.5	-3.76190
22.2	2.35135	26.2	-1.10687	36	-3.30000	18.2	-3.65116
20.9	2.88995	23.9	-0.02092	37	-3.75946	17.9	-3.47761
19.6	3.50000	21.6	1.29630	38	-4.19474	17.6	-3.16667
18.3	4.19672	19.3	2.92746	39	-4.60769	17.3	-2.44828
17	5.00000	17	5.00000	40	-5.00000	17	1.00000

Bibliography

Arth, JG and Ayuso, RA (1997) The Northeast Kingdom batholith, Vermont: Geochronology and Nd, O, Pb, and Sr isotopic constraints on the origin of Acadian granitic rocks. *Geological Society of America Memoir* 191, 1-18.

Ayuso, RA (1986) Lead-isotopic evidence for distinct sources of granite and for distinct basements in the northern Appalachians, Maine. *Geology* 14322, 322-325.

Ayuso, RA and Bevier, ML (1991) Regional differences in Pb isotopic compositions of feldspars from plutonic rocks of the northern Appalachian Mountains, U. S. A, and Canada: a geochemical method of terrane correlation. *Tectonics* 10, 191-212.

Ayuso, RA and Arth, JG (1992) The Northeast Kingdom batholith, Vermont: magmatic evolution and geochemical constraints on the origin of Acadian granitic rocks. *Contributions to Mineralogy and Petrology* 111, 1-23.

Ayuso, RA and Schulz (in press) Nd-Pb-Sr isotope geochemistry and origin of the Ordovician Bald Mountain and Mount Chase massive sulfide deposits, northern Maine. *Economic Geology Monograph on Massive Sulfide Deposits of northern New Brunswick and Maine*

Brown, M and Solar, GS (1999) The mechanism of ascent and emplacement of granite magma during transpression: a syntectonic granite paradigm. *Tectonophysics* 312, 1-33.

Doe, BR Delevaux, MH Algers, JP (1985) The plumbotectonics of the West Shasta mining district, Eastern Klamath Mountains, California. *Economic Geology* 80, 2136-2148.

Hanson, GN (1978) The application of trace elements to the petrogenesis of igneous rocks of granitic composition. *Earth and Planetary Science Letters* 38, 26-43.

Hemming, SR McLennan, SM and Hanson, GN (1994) Lead isotopes as a provenance tool for quartz: Examples from plutons and quartzite, northeastern Minnesota, USA. *Geochim. Cosmochim. Acta* 58, 4455-4464.

Hemming, SR McDaniel, DK McLennan, SM and Hanson, GN (1996) Pb isotope constraints on the provenance and diagenesis of detrital feldspars from the Sudbury Basin, Canada. *Earth and Planetary Science Letters* 142, 501-512.

Housh, T and Bowring, SA (1991) Lead isotopic heterogeneities within alkali feldspars: Implications for the determination of initial lead isotopic compositions. *Geochim. Cosmochim. Acta* 55, 2309-2316.

Huppert, HE and Sparks, RSJ (1988) The generation of granitic magmas by intrusion of basalt into continental crust. *Journal of Petrology* 29, 599-624.

Langmuir, CH Vocke, RD Jr. Hanson, GN and Hart, SR (1978) A general mixing equation with applications to Icelandic basalts. *Earth and Planetary Science Letters* 37, 380-392.

McCulloch, MT and Woodhead, JD (1993) Lead isotopic evidence for deep crustal-scale fluid transport during granite petrogenesis. *Geochim. Cosmochim. Acta* 57, 659-674.

Miller, CF Watson, EB and Harrison, TM (1988) Perspectives on the source, segregation and transport of granitoid magmas. *Transactions of the Royal Society of Edinburgh: Earth Sciences* 79, 135-156.

Pegram, WJ (1990) Development of continental lithospheric mantle as reflected in the chemistry of the Mesozoic Appalachian Tholeiites, U.S.A. *Earth and Planetary Science Letters* 97, 316-331.

Pressley, RA and Brown, M (1999) The Phillips pluton, Maine, USA: evidence of heterogeneous crustal sources and implications for granite ascent and emplacement mechanisms in convergent orogens. *Lithos* 46, 335-366.

Samson, SD Coler, DG Speer, JA (1995) Geochemical and Nd-Sr-Pb isotopic composition of Alleghanian granites of the southern Appalachians: Origin, tectonic setting, and source characterization. *Earth and Planetary Science Letters* 134, 359-376.

Sinha, AK (1969) Removal of radiogenic lead from potassium feldspars by volatilization. *Earth and Planetary Science Letters* 7, 109-115.

Solar, GS Pressley, RA Brown, M and Tucker, RD (1998) Granite ascent in convergent orogenic belts: Testing a model. *Geology* 26, 711-714.

Stacey, JS and Kramers, JD (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth and Planetary Science Letters* 26, 207-221.

Stewart, DB (1989) Crustal Processes in Maine. *American Mineralogist* 74, 698-714.

Tian, J (2000) A geological and geochemical study of the Mooselookmeguntic composite pluton, west-central Maine and east-central New Hampshire. MS Thesis, University of Maryland, College Park, MD.

Todt, W Cliff, RA Hanser, A and Hofmann, AW (1996) Evaluation of a 202Pb-205Pb double spike for high-precision lead isotope analysis. In: Hart Sr. and Basu A. (Eds), Earth Processes: Reading the Isotopic Code, AGU Monograph 95, 429-437.

Tomascak, PB (1995) The petrogenesis of granitic rocks in southwestern Maine. PhD Dissertation, University of Maryland, College Park, MD.

Tomascak PB, Krogstad EJ and Walker RJ (1996) Nature of the crust in Maine, USA: evidence from the Sebago batholith. *Contributions to Mineralogy and Petrology* 125, 45-59.

Thirlwall, MF (2002) Multicollector ICP-MS analysis of Pb isotopes using a 207Pb-204Pb double spike demonstrates up to 400 ppm/amu systematic errors in Tl-normalization. *Chemical Geology* 184, 255-279.

Zen, E (1983) Exotic terranes in North Eastern Appalachians- Limits, candidates, and ages: A speculative essay. *Geologic Society of America Memoir* 158, 55-81.

Zorpi, MJ Coulon, C Orsini, JB and Cocirta, C (1989) Magma mingling, zoning, and emplacement in calc-alkaline granitoid plutons. *Tectonophysics* 157, 315-329.