DETERMINING THE MAGMATIC EVOLUTION AND DEGREES OF CONTAMINATION IN PEGGY'S COVE MONZOGRANITE, HALIFAX PLUTON, NOVA SCOTIA

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INTRODUCTION

In dirty peraluminous granites such as the South Mountain batholith (SMB; Lackey et al., this volume, Fig. 1), distinguishing between magmatic and post-magmatic processes presents a critical challenge to understanding their contamination history. Oxygen isotope ratios are useful for understanding the complex record of magmatic, hydrologic, and thermal alteration in the Earth's crust (Taylor and Sheppard, 1986). These isotope data can fingerprint supracrustal contributions to magmas; rocks that have interacted with the Earth's surface at some stage in their evolution become enriched in ^{18}O (Taylor, 1968). The refractory mineral zircon retains magmatic $\delta^{18}O$ values due to slow oxygen diffusion (Valley, 2003), and thus analysis of oxygen isotopes in whole zircons is a valuable tool for differentiating magmatic chemical evolution from post-crystallization processes.

Previous oxygen isotope studies of the SMB report high whole rock (WR) $\delta^{18}O$ values. Longstaffe et al. (1980) find that $\delta^{18}O$(WR) across the SMB varies from 10.1-12.0‰. The authors also analyze $\delta^{18}O$(WR) of the Meguma Group clastic metasedimentary rocks, and report values between 10.0-12.9‰. Other more recent isotope studies (Chatterjee et al., 1985; Kontak et al., 1991; Clarke et al., 1993) confirm trends observed by Longstaffe et al. (1980). By using geochemistry and $\delta^{18}O$ of zircon to examine variation of magmatic $^{18}O/^{16}O$ in the Peggy's Cove monzogranite unit of the Halifax pluton, we apply a new geochemical tool in order to parse out crustal differentiation documented in the SMB.

GEOLOGIC SETTING

The Halifax pluton (HP) is located at the southeastern edge of the SMB (Lackey et al., this volume, Fig. 1). This 1060 km^2 body (MacDonald, 2001) has relatively discrete boundaries and crops out in the Halifax metro area and in coastal exposures along the Atlantic Ocean between Halifax Harbor and St. Margaret's Bay. The mapped units of the HP (Fig. 1) are differentiated by Canadian workers using mafic mineral and mica content, as well as the presence of megacrystic textures (MacDonald and Horne, 1988; MacDonald, 2001).

The Peggy's Cove monzogranite is a 1-3 km wide band along the Atlantic Coast, and is probably the outermost southern unit of the HP (Fig. 1; MacDonald, 2001). Variably megacrystic with occasional swarms of pegmatite and aplite dikes, the Peggy's Cove unit is rich in metasedimentary xenoliths and enclaves of diverse compositions and sizes. The unit varies regionally in xenolith type and abundance, megacryst presence and orientation, accessory mineral assemblage, and prevalence of magmatic and mafic enclaves. The Cranberry Head locality, in the western part of the unit, contains a spectacular exposure of swirling

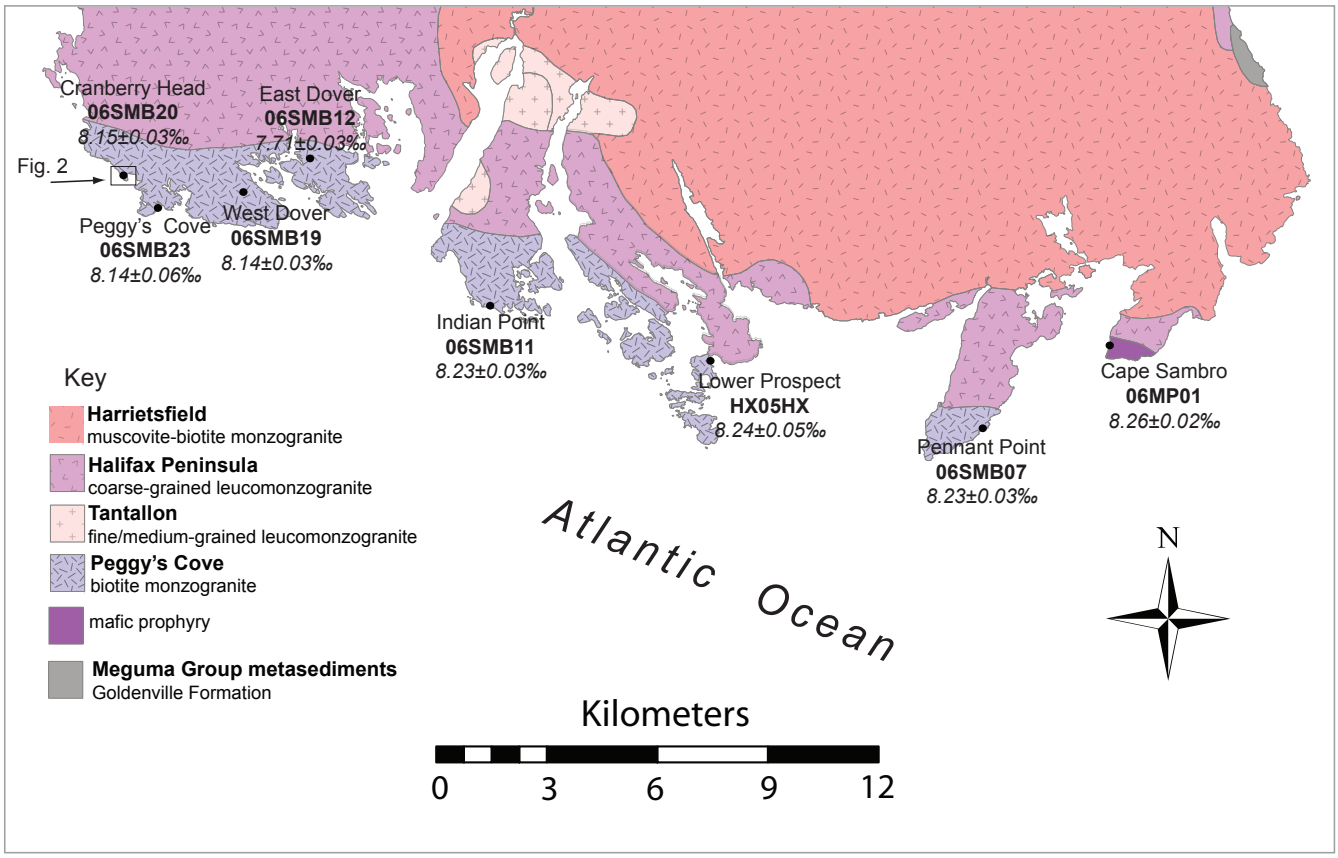

Figure 1. Sampling sites along the Atlantic coast of the Halifax pluton. Sample numbers are in bold and the results of zircon oxygen isotope analysis are included in italics. Sampling sites in the east have lower $\delta^{18}O$(zrc) values than those in the west, and the outlying $\delta^{18}O$(zrc) value from East Dover is close to the mapped contact between the Peggy's Cove monzogranite and the Halifax Peninsla leucomonzogranite. The Cranberry Head locality is shown in detail in Figure 2.

biotite schlieren and thirteen meter-scale "intermediate enclaves" rimmed with a diverse xenolith community and megacrystic feldspars (Fig. 2).

ANALYTICAL METHODS

We sampled nine different sites along the Atlantic Coast of the Halifax pluton (Fig. 1), taking 10-15 lb samples for zircon extraction. In addition to samples from the Peggy's Cove monzogranite, two intermediate enclaves at Cranberry Head were sampled (Fig. 2), as well as the mafic porphyry that crops out at the tip of Cape Sambro. An additional monzogranite sample, collected by J.S. Lackey in spring of 2005 at Lower Prospect and processed separately, was integrated into this study, bringing the total number of samples prepared for $\delta^{18}O$(zrc) analysis to ten.

Aliquots of each sample were sent to the Geoanalytical Laboratory at Washington State University for X-ray fluorescence analysis of 28 major and trace elements, following the methods of Johnson (1999). Zircon was separated from the remaining sample by standard crushing, density, and magnetic separation techniques (Valley et al., 1994; Lackey et al., 2002; Lackey et al., 2005) at Macalester College. Leeching of the zircon separates with nitric acid to remove non-magnetic phosphate and sulfide minerals was followed by treatment with hydrofluoric acid, which dissolves regions in zircon crystals that have been subject to radiation damage and are susceptible to oxygen isotope diffusion after crystallization (Valley, 2003). Powdering of acid-treated separates with a boron-carbide

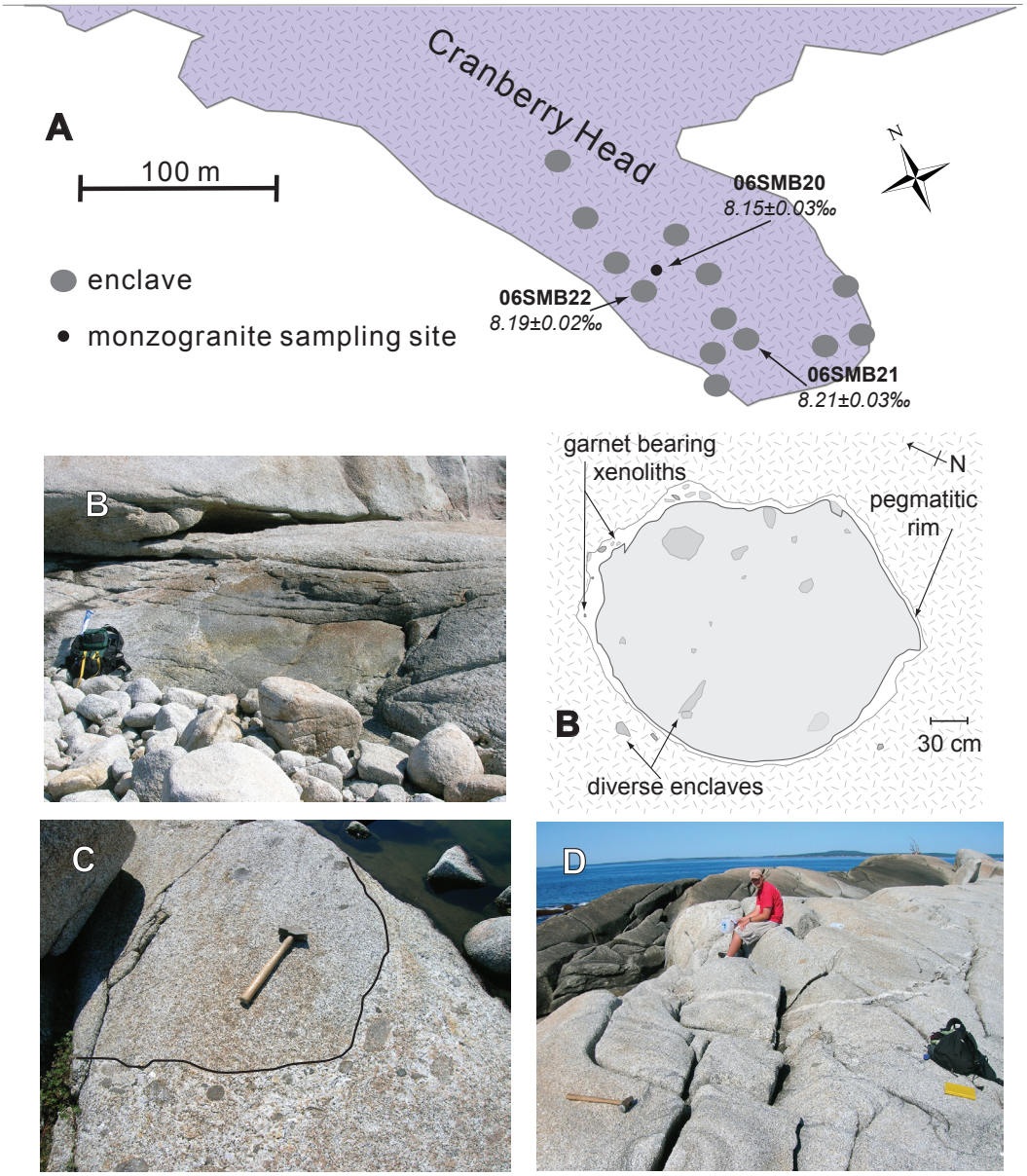

Figure 2. Features of the Cranberry Head locality. (A) The distribution of meter-scale enclaves in this coastal monzogranite exposure; two were sampled for $\delta^{18}O$(zrc) analysis. (B) Field photo and sketch of one sampled enclave (SMB21) showing the association with smaller enclaves and pegmatitic "rim" of feldspars containing metasedimentary xenoliths that are often garnet bearing. (C) Enclave with a wider rim (delineated in photo) containing diverse community of xenoliths and small enclaves. Hammer length 70cm. (D) An individual sitting in the midst of a large enclave for scale. The rim arcs across the center of the photo, continuing over the edge of the cliff towards the ocean.

mortar and pestle limited grain-size effects and maximized the efficiency of laser fluorination.

Oxygen isotope analyses were performed at the University of Wisconsin stable isotope laboratory by CO_2 laser fluorination, following techniques described by Valley et al. (1995). A gas source Finnigan MAT 251 mass spectrometer was used to measure isotope ratios. The analyses were standardized against the University of Wisconsin Gore Mountain garnet standard (UWG-2), which has an accepted

$\delta^{18}O$ value of 5.80‰. On the day of analysis, the UWG-2 was measured at 5.74‰ and the correction was 0.06‰.

RESULTS

$\delta^{18}O$(zrc) values in the Peggy's Cove monzogranite vary from 7.71-8.26‰. Monzogranite values cluster between 8.14±0.06‰ and 8.15±0.03‰ in the west and 8.23±0.03‰ and 8.26±0.02‰ in the east, excluding the sample from East Dover (SMB12, $\delta^{18}O = 7.71\pm0.03$‰). The intermediate enclave samples SMB21 and SMB22 from Cranberry Head have values within a standard deviation of each other, 8.21±0.02‰ and 8.19±0.03‰. The mafic porphyry (MP01) has the highest $\delta^{18}O$(zrc) value, 8.26±0.02‰. Two trends appear in $\delta^{18}O$ values plotted against major element weight percent data that reflect an east to west variation within the Peggy's Cove unit, exemplified by the plot of $\delta^{18}O$(zrc) versus weight percent silica in Figure 3. Eastern samples and intermediate enclaves (located in the west) are enriched in ^{18}O relative to the western samples with similar weight percent silica.

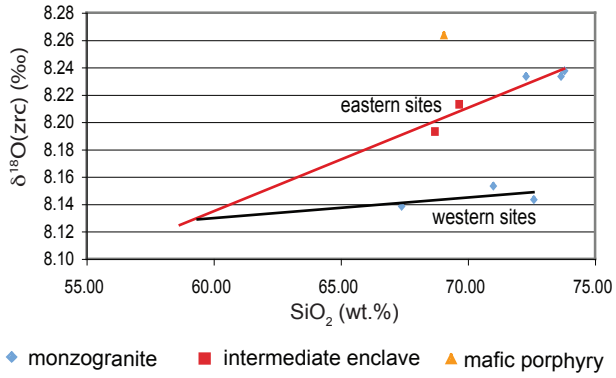

Figure 3. A plot of $\delta^{18}O$(zrc) versus weight percent silica reveals two trends in the regional variation of $\delta^{18}O$(zrc) values. The eastern monzogranite and intermediate enclaves (located in the west) are more enriched in $^{18}O/^{16}O$ than the monzogranite sampled in the west. The mafic porphyry lies outside both trends.

Given these values of $\delta^{18}O$(zrc), we calculate equilibrium $\delta^{18}O$ values for whole rock (Lackey et al., 2007) and phases such as quartz (Valley et al., 2003). Valley et al. (2003) report the following experimental relationship between different phases A and B:

$$\delta^{18}O_A - \delta^{18}O_B = A_{A\text{-}B}10^6/T^2 \text{ (T in Kelvin)} \qquad (1)$$

By choosing magmatic temperatures, we use published coefficients to predict what the $\delta^{18}O$ value should be for one phase based on data from another. At 800°C quartz in equilibrium with this study's zircons would have a δ18O value from 10.24-10.56‰, while at 600°C the values would be from 11.18-11.73‰ (Fig. 4). Similarly, Lackey et al. (2007) use the following linear relationship between silica content and $\delta^{18}O$(WR):

$$\text{Calculated } \delta^{18}O(WR) = (\text{wt. \% } SiO_2)(0.0612) - 2.4982 + \delta^{18}O(zrc) \qquad (2)$$

Given values for $\delta^{18}O$(zrc) and weight percent silica for a sample, we can calculate what the $\delta^{18}O$(WR) should be if the zircons are in isotopic equilibrium with the rock. These values vary between 9.71-10.26‰ (Fig. 4).

DISCUSSION

Oxygen Isotopes

Variations in $\delta^{18}O$(zrc) data from the Peggy's Cove monzogranite and mafic porphyry are small but systematic and range from 8.14-8.26‰, excluding the outlier 7.71‰ (SMB12, discussed below). The values exhibit a geographic trend, where the western sites have lower $\delta^{18}O$(zrc) values (8.14-8.15‰) than those in the east (8.19-8.26‰) for equivalent weight percent silica values (Fig. 3).

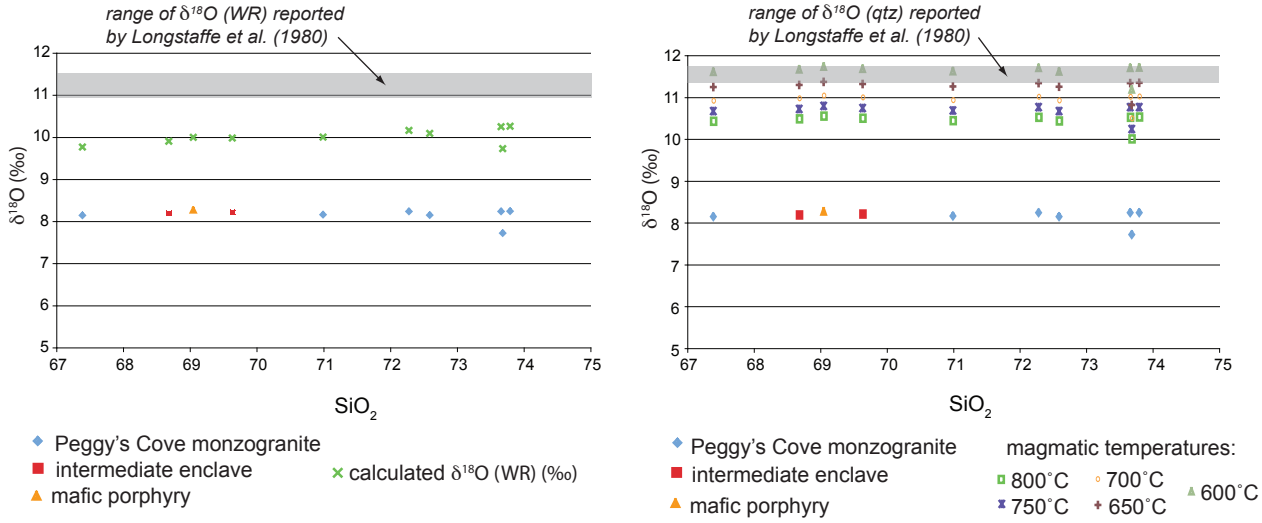

Figure 4. Plots of the equilibrium $\delta^{18}O$ (‰) of whole rock and quartz calculated from our $\delta^{18}O$ (zrc) values in the Peggy's Cove monzogranite and mafic porphyry. When those calculated values are compared to published oxygen isotope data for the Halifax pluton (the shaded regions; Longstaffe et al., 1980), the reported values are higher than those predicted by $\delta^{18}O$ (zrc) data. Both calculations indicate that the rock is not in isotopic equilibrium with zircon. For example, crystallization temperatures below 650˚C are necessary for the quartz and zircon phases to be in equilibrium, but that temperature is unlikely for a peraluminous granite (Huang et al., 1981).

It is qualitatively clear from this small sampling that the intermediate enclaves, located in the west, are more chemically similar to the monzogranite and mafic porphyry in the east than their host monzogranite at Cranberry Head. Surprisingly, the mafic porphyry has the highest $\delta^{18}O$(zrc) value at 8.26±0.02‰; $\delta^{18}O$(WR) typically increases with weight percent silica because more felsic magmas have a greater percentage of high-$\delta^{18}O$ minerals such as quartz and feldspar (Valley, 2003).

Geographical variation in the Peggy's Cove monzogranite suggests that the unit heterogeneously incorporated metasedimentary country rock during crystallization and may indicate a trend in which the felsic rocks in the core of the HP have lower $\delta^{18}O$ than those at the pluton's less evolved mafic rim. Emplacement mechanisms for the pluton proposed by Canadian workers suggest that the outer units, including the biotite monzogranite, granodiorite, and mafic porphyry, intruded first, followed by the more felsic leucogranites at the core of the pluton (MacDonald and Horne, 1988). In this model early melts, already enriched in ^{18}O from a sedimentary source rock, would mix with the high $\delta^{18}O$ Meguma metasedimentary rocks during emplacement, driving up $\delta^{18}O$ in zircon and the magma as a whole. The first melts to be emplaced would clear the way for later magmas to intrude without significant contact with country rock. Additionally, MacDonald and Horne (1988) observe that the early, more mafic Halifax Pluton units have abundant xenoliths, while the later leucogranites are xenolith-poor, even when located close to the pluton boundary. Outcrop-scale textures observed at Cranberry Head including the intermediate enclaves with pegmatitic, xenolith-rich rims record a history of local magma mingling and wall rock contamination. Thus, the abundance of metasedimentary xenoliths may correlate to these data and help explain regional variation in $\delta^{18}O$(zrc) not only in the Peggy's Cove

monzogranite, but also on the scale of the larger pluton. The outlying $\delta^{18}O$ value of 7.71±0.03‰ at East Dover (SMB12) is similar to a sample with a $\delta^{18}O$(zrc) value of 7.62±0.03‰ from the interior of the pluton (Harrietsfield unit; Nowak and Lackey, unpublished data). It is possible that geologic mapping in the East Dover area is wrong, and our sample SMB12 is not actually Peggy's Cove monzogranite, but one of the units mapped in the pluton's core. If additional sampling of the various HP units for $\delta^{18}O$(zrc) analysis results in values that continue this trend of low $\delta^{18}O$(zrc) in more "evolved" units, we will be better able to quantify and constrain the relationship between emplacement and magmatic evolution of the Halifax pluton, and contamination by ^{18}O enriched sources.

Implications for Post-magmatic Isotope Exchange

Calculated oxygen isotope values in quartz and whole rock from this study's $\delta^{18}O$(zrc) are not consistent with the values reported by Longstaffe et al. (1980), indicating late-stage oxygen isotope exchange with an enriched $\delta^{18}O$ reservoir has occurred in the Peggy's Cove monzogranite. Longstaffe et al. (1980) find a $\delta^{18}O$(qtz) average value of 11.6±0.2‰ (n=3) from the Halifax pluton, while reasonable crystallization temperatures for peraluminous magmas, such as 750˚C (Huang et al., 1981), predict an average $\delta^{18}O$(qtz) value of 10.7±0.16‰. $\delta^{18}O$(zrc) values from this study predict whole rock oxygen isotope values ranging from 9.72-10.26‰ significantly lower than the average 11.24±0.31‰ observed by Longstaffe et al. (1980; Fig. 4). Thus it appears that the monzogranite is no longer in isotopic equilibrium with zircon, as it presumably was during crystallization (Valley, 2003). There are models for late-stage mobile fluids in the batholith (Kontak et al., 2002; Clarke et al., 2004), and our study strengthens the hypothesis that this hydrothermal activity significantly altered whole rock geochemistry of the SMB.

CONCLUSIONS

East-west variations in $\delta^{18}O$(zrc) values along coastal exposures of the Halifax pluton suggest that the magma heterogeneously mixed with ^{18}O-enriched material during pluton emplacement, crystallization, or both. Field observations, whole rock geochemistry, and $\delta^{18}O$(zrc) values of meter-scale intermediate enclaves at the Cranberry Head locality provide additional evidence for mingling and mixing in the magma chamber. $\delta^{18}O$(zrc) values are in disequilibrium with published whole rock and quartz oxygen isotope values from the pluton, indicating that late stage isotopic exchange enriched the monzogranite in ^{18}O. Enrichment of the outer units of the pluton relative to the more evolved core can be better constrained with ongoing oxygen isotope studies of the HP. $\delta^{18}O$ of zircon provides a particularly useful tool for deciphering the magmatic history of the Halifax pluton, for it can differentiate between magmatic and subsolidus geochemical evolution. For granitoid rocks, this distinction is critical for understanding crustal formation and recycling processes.

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