

# From Mantle Source to an Unusual Late-stage Mineral Wealth in Highest Crustal Levels: A Case Study from the Alkaline-peralkaline Mont Saint-hilaire Complex, Quebec, Canada

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## Summary

We present details of a field-based study on the evolution of alkaline to peralkaline rocks from the Mont Saint-Hilaire complex, Quebec, Canada. The progressive magmatic evolution of the complex is represented by three melt batches: (1) primitive gabbroic rocks ( $X_{\text{Fe}^{\text{cpX}}} = 0.17-0.27$ , where  $X_{\text{Fe}^{\text{cpX}}} = \text{molar Fe}_{\text{tot}}/(\text{Fe}_{\text{tot}}+\text{Mg})$ ), (2) a dioritic/monzonitic rock suite ( $X_{\text{Fe}^{\text{cpX}}} = 0.17-0.41$ ) and (3) highly evolved peralkaline foid syenites ( $X_{\text{Fe}^{\text{cpX}}} = 0.28-1$ ). Nd and oxygen isotope data as well as major and trace element analyses of mineral separates indicate that all rock units derive from a single mantle source presumably by fractional crystallization processes from one parental melt. Solidification in the orthomagmatic stage probably occurred under closed-system conditions.

In the highly evolved peralkaline foid syenites, a wealth of minerals is found in the Poudrette quarry, which made Mont Saint-Hilaire a world-famous mineral locality. The late-stage evolution and formation of these partly exotic and rare minerals was reconstructed using a combination of stable isotopes of late-stage carbonates and comprehensive fluid inclusion studies. To explain the wealth of different minerals, at least two sources are necessary: (1) a mantle-derived and fractionated melt of alkaline character. Such magmas are strongly enriched in incompatible elements such as HFSE and LILE. (2) External fluids, probably in equilibrium with surrounding sedimentary rocks. The influence of this external fluid source is detected by the late-stage carbonate minerals' O and C stable isotope composition, which displays a mixing trend between typical mantle values and sedimentary host rock limestone. Therefore, mixing of these external fluids with the restitic magma and/or its exsolved fluids caused dissolution and re-precipitation processes, resulting in the formation of a large number of rare and exotic minerals.

## Introduction

The Cretaceous Monteregian Hill intrusions form an East-West-trending magmatic alkaline province in South Quebec, Canada. Several intrusive bodies are accompanied by numerous dikes, all emplaced at shallow crustal levels. Mont Saint-Hilaire is one of the intrusive complexes roughly 40 km east of Montreal. It consists of a three-phase progression from (1)

gabbros and (2) diorites/monzonites to (3) peralkaline foid syenites. In the most evolved peralkaline foid syenites the world-famous mineral collecting site of Poudrette Quarry is located. To date, nearly 400 minerals are described from Mont Saint-Hilaire, amongst them more than 40 type minerals. Most of the minerals Mont Saint Hilaire became famous for formed during late-magmatic to hydrothermal conditions. Silicates and carbonates, at least partially characterized by remarkably high contents of HFSE, LILE, halogens and alkalis, make up the major part of them.

It is the aim of the present contribution to reconstruct the magmatic evolution of the complex, to clarify the petrogenetic relationships between the various alkaline to peralkaline rock units and to understand the basics of the formation of the rare minerals using a combination of trace element geochemistry, fluid inclusion studies, Nd, O and C isotope data of mineral separates.

## Methods

Major element compositions of rock-forming minerals allow for reconstructing the crystallization history of the magma and the estimation of intensive parameters. Rock-forming minerals were analyzed using a JEOL 8900 electron microprobe with natural and synthetic standards.

Major element characteristics are complemented by trace element data, which allow for deciphering fractionation processes. Trace elements were analyzed by LA-ICP MS using an Agilent 7500ce quadrupole ICP Ms linked to a New Wave UP 213 Laser ablation system. Petrogenetic relationships between the different melt batches and characteristics of the source of the various rock types were addressed using the Sm-Nd system.  $^{143}\text{Nd}/^{144}\text{Nd}$  isotope ratios from hand-separated mafic silicates were analyzed as described by Marks et al. (2003) and the  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio was calculated from the Sm and Nd concentrations analyzed by LA-ICP MS.

Contamination and alteration processes were investigated by using stable oxygen isotopes. Therefore, the isotopic O composition of mafic mineral separates was determined using the laser fluorination method (Sharp, 1990; Rumble and Hoering, 1994) on a Finnigan MAT 252 isotope ratio mass spectrometer.

Late-stage processes were reconstructed applying different methods: As carbonates are among the most abundant late-stage minerals, we analyzed their C and O isotope compositions. The O and C isotope compositions were determined as described by Spötl and Vennemann (2003). For interpretation, fractionation factors of Das Sharma et al. (2002) were applied.

Fluids involved in late-stage processes are preserved in fluid inclusions, which were analyzed microthermometrically on a Leica DMLP microscope combined with a Linkam THMS 600 heating/freezing station. Qualitative detection of Raman-active species was performed on a Dilor Jobin Yvor Raman spectroscope and a blue Ar laser (488nm).

## Examples

Major element EMPA data of clinopyroxene and feldspar show continuous evolutionary trends from calcic to sodic through all three stages. Trace element data of amphiboles (Fig.1, left) confirm a continuous fractionation trend from gabbroic, dioritic/monzonitic to foid-syenitic melt batches. An enrichment of all REE and a parallel shift to higher contents of the whole REE pattern is observed as well as the formation of a slightly negative Eu anomaly (due to fractionation of plagioclase) from the (1) gabbros to the (2) diorites/monzonites. In the most evolved rocks, crystallographic effects of Na- and  $\text{Fe}^{3+}$ -rich minerals fundamentally change the shape of the REE-pattern (Fig.1, left; Marks et al., 2004b). In the last stage of foid syenite (3) crystallization, further REE-bearing phases (e.g. eudialytes<sub>si</sub>) compete with amphiboles for REE and lower the level of REE-concentration in amphiboles.

$\epsilon\text{Nd}(T=125\text{ Ma})$  vary between 3.4 and 5.7 (Fig.1, right). Within the specific error of the method, most samples from all three rock units overlap, implying a single mantle source for all melt batches.  $\delta^{18}\text{O}$  for separates of cpx, amph, ol and bt scatter from 3.9 to 6.3‰ (relative to VSMOW). Therefore, the O isotope composition for most samples lies in the range of typical mantle values (e.g. Eiler, 2001) and significant contamination can be ruled out.

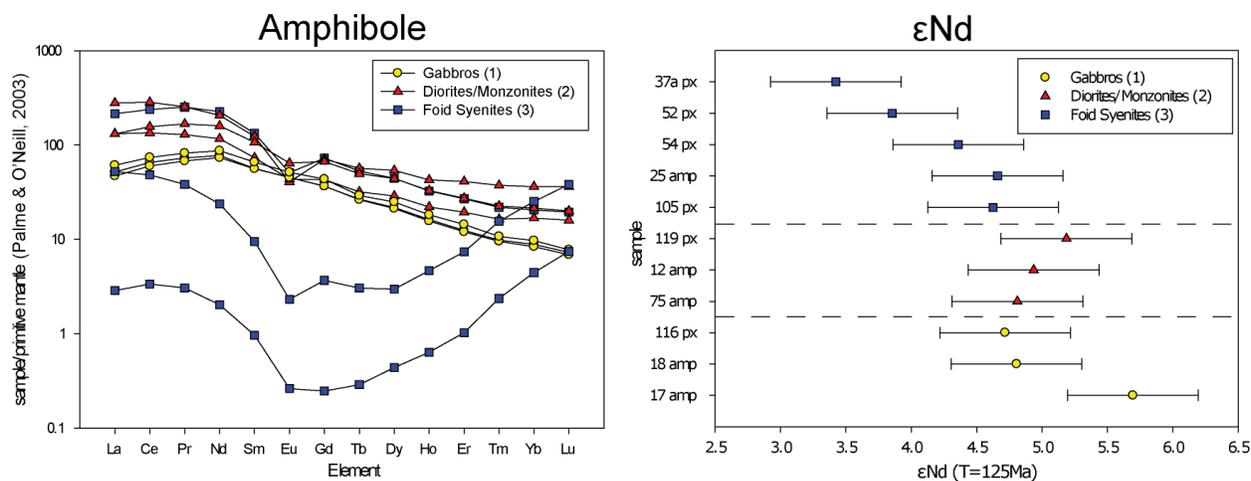


Fig.1: Trace element characteristics of amphibole (left). Data show the whole range of REE in amphiboles for a given suite. Right: age-corrected  $\epsilon_{Nd}$  values from mafic mineral separates.

Late-stage carbonate minerals from cavities, vugs and replacement reactions were analyzed for their C and O isotope compositions. All carbonates fall in an array linking the mantle box with a meter-sized, coarse-grained marble xenolith (representing former sediment) sampled in the Poudrette quarry (Fig.2, left). Therefore, we infer that the late-stage carbonates have precipitated from a mixed fluid of magmatic and meteoric origin.

Fluid inclusion petrography shows fluid inclusions in early-crystallized liquidus phases to be of secondary origin whereas late-stage minerals commonly bear primary inclusions. In samples from all suites, two groups of fluid inclusions can be distinguished (Fig.2, right): In primitive rocks,  $CO_2$  inclusions dominate over aqueous inclusions of variable salinity. In minerals from highly evolved rocks and late-stage environments, aqueous inclusions of variable salinities dominate over  $CO_2$  inclusions. Therefore, the formation of all fluid inclusions can be attributed to one event, which we interpret to be contemporary to the precipitation of numerous late-stage minerals. Preliminary stable isotope studies of the  $CO_2$  trapped in secondary fluid inclusions in primitive samples as well as  $CO_2$  released from primary inclusions from late-stage minerals overlap in  $\delta^{18}O$  compositions with the late-stage carbonate minerals at values of around 24‰ (VSMOW) which is much higher than one would expect for a mantle value (Fig.2, left).

## Conclusions

Magmatic rocks of the three melt batches present at Mont Saint-Hilaire differ strongly in whole rock chemistry, degree of fractionation and mineralogy. Nd and O isotopes, however, argue for one source region and a common parental melt for all rock suites with only minor degrees of contamination. All melt batches are petrogenetically linked by fractional crystallization in the course of a closed-system process. Such closed-system crystallization is known from other alkaline - peralkaline complexes, such as the Ilímaussaq intrusion (Marks et al., 2004a). Only in the very late-stage evolution of the complex at temperatures close to or even below the solidus, open-system behaviour is detected: in melt pots and aggregations of magmatic fluids, where volatile-rich, most fractionated melt with extremely low solidus temperatures or magmatic fluids collected, the influx of external fluids locally changed conditions and intensive parameters. In the course of this mixing processes, dissolution, transport and re-precipitation of elements lead to the formation of the famous rare and exotic minerals.

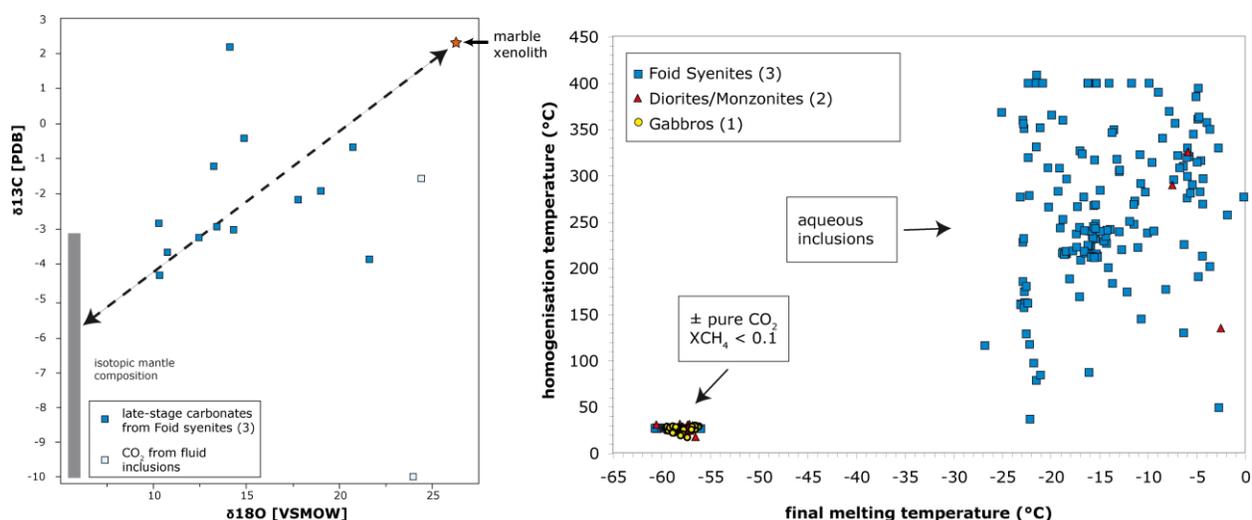


Fig.2: O and C stable isotopes of late-stage carbonates and CO<sub>2</sub> from fluid inclusions (left); Fluid inclusion results, displayed as final melting temperature vs. homogenisation temperature (right).

## Acknowledgements

Gabi Stoschek, Bernd Steinhilber and Elmar Reitter are thanked for their help with the isotope analyses. Peter Tarassoff and Laszlo Horvath kindly provided sample material. Benjamin Walter helped with the mineral separating. McGill University is thanked for the sampling permission and co-operation at the McGill Nature Reserve. Financial support by the DFG is highly acknowledged (grant number MA 2135/12-1).

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