Counterclockwise post-emplacement evolution of metatroctolites from Aluminé Igneous-Metamorphic Complex, Neuquén, Argentina.

Ivana Urraza1,3, Sergio Delpino1,2, Laura Grecco2

1 Departamento de Geología, Universidad Nacional del Sur, San Juan 670, Bahía Blanca, Argentina.
iurraza@uns.edu.ar; sdelpino@criba.edu.ar
2 Instituto Geológico del Sur, CONICET-Universidad Nacional del Sur, San Juan 670, Bahía Blanca, Argentina.
mlgrecco@criba.edu.ar
3 Departamento de Geología y Petróleo, Facultad de Ingeniería, Universidad Nacional del Comahue, Buenos Aires 1400, 830 Neuquén, Argentina.

ABSTRACT. Post-crystallization evolution of the metatroctolites of the Ñorquinco lake zone, Aluminé Igneous-Metamorphic Complex, is analyzed. These mafic rocks show coronas around olivine, composed of Opx, Cpx, Spl and Amp (Hbl, and Hbl). The temporal evolution of these rocks was evaluated via petrographic analysis and the construction of a suitable pseudosection based on the whole-rock chemical composition. This analysis was complemented with classic geothermobarometry, from which four stages on the P-T path were established: A. Starting point lies in the stability field of the PI-OL-Opx-Cpx-H2O, with P-T of 936 °C and 2.7 kbar, respectively, indicative of granulite facies conditions; B. Another point in the trajectory is represented by first appearance of amphibole. P-T conditions for Hbl,Pl are 780 °C and 5.9 Kbar, respectively, C. The third point is characterized by the presence of Hbl, and Spl and the disappearance of Ol, leading to the association Pl-Opx-Cpx-Hbl,-Spl-H2O. Equilibrium temperature and pressure for this stage are 780 °C and 5.69 Kbar, respectively; and D. The last point in the path implies the disappearance of Cpx and the retrogression of the phases to Chl with, a concomitant consumption of excess water. Both the equilibrium temperature (694.2 °C) for the stable association Pl-Opx-Hbl,-Spl-Chl, and the narrow stability pressure range (4.5-5.2 Kbar), are constrained by the absence of olivine and garnet. The defined portion of the P-T path indicates cooling from granulite to amphibolite facies with a concomitant pressure increment, defining a counter-clockwise P-T path. U-Pb zircon ages determined for basement xenoliths in metatroctolites and gabbroic inclusions in granodiorites, allows constraining the emplacement of Ñorquinco lake metatroctolites to Upper Paleozoic times.

Keywords: Metatroctolites, Aluminé Igneous-Metamorphic Complex, Reaction coronas, Geothermobarometry, P-T path.

RESUMEN. Evolución antihoraria poscristalización de las metatroctolitas del Complejo Ígneo-Metamórfico Aluminé, Neuquén, Argentina. El objetivo de este trabajo es analizar la evolución poscristalización de cuerpos maficos que afloran en la zona de lago Ñorquinco (sector sur del Complejo Ígneo Metamórfico Aluminé), los cuales han sido clasificados como metatroctolitas. Estas rocas muestran coronas de reacción alrededor del olivino que resultan del reequilibrio posmagmático, compuestas principalmente de Opx, Cpx, Spl y Amp (Hbl, y Hbl). La evolución temporal de las metatroctolitas fue evaluada a partir de relaciones de fase determinadas a partir del análisis petrográfico y de la construcción de una pseudosección adecuada basada en la composición química de la roca total. Este análisis fue complementado con estudios de geothermobarometría clásica, a partir de los cuales se establecieron cuatro estadios sobre una trayectoria P-T: A. El punto de inicio para la retrogresión se ubica en el campo de estabilidad de la asociación PI-OL-Opx-Cpx-H2O, en condiciones de P-T de 936 °C y 2.7 kbar en facies de granulita; B. El segundo estadio sobre la trayectoria está representado por la presencia de anfibol en condiciones de P-T de 780 °C y 5,69 kbar para la estabilidad del par Hbl,Pl; C. El tercer punto en la trayectoria P-T está caracterizado por la aparición de Hbl, y Spl y la desaparición de Ol, lo que conduce a la asociación estable PI-Opx-Cpx-Hbl,-Spl-H2O. Las temperaturas y presiones de equilibrio para este estadio son de 780 °C y 5,69 Kbar; y D. El último punto definido implica la desaparición de Cpx y la retrogradación de las fases a Chl con un consumo concomitante de agua en exceso. Tanto la temperatura de equilibrio (694,2 °C) para la asociación estable PI-Opx-Hbl,-Spl-Chl, como el rango estrecho de la presión de estabilidad (4,5-5,2 Kbar) son limitado por la ausencia de olivino y granate. La trayectoria P-T definida indica enfriamiento a partir de granulita a facies de anfibolita con un incremento concomitante con la presión, definiendo una trayectoria P-T antihoraria. Edades U-Pb en circones determinadas para xenolitos de basement en las metatroctolitas e inclusiones gabroides en granodioritas, permiten delimitar el emplazamiento de las metatroctolitas del lago Ñorquinco al Paleozoico Superior.

Palabras clave: Metatroctolitas, Complejo Ígneo-Metamórfico Aluminé, Coronas de reacción, Geotermobarometría, Trayectoria P-T.
1. Introduction

In the southern region of the Aluminé Igneous-Metamorphic Complex (AIMC) (Urraza et al., 2008a and b, 2009, 2011; Urraza, 2014), mafic bodies of variable dimensions are emplaced in a metapelitic sequence composed by schists, gneisses and amphibolites. This sequence of pre-Andean rocks constitutes an accretionary prism related to the subduction of the oceanic plate, bellow the southwestern Gondwana margin during the Paleozoic (Urraza, 2014). Mafic bodies represented by metanorites and metatroctolites, are distributed along the Ñorquinco and Pulmarí lakes (Fig. 1A). The Ñorquinco metatroctolites constitute the northernmost outcrops of metamafic rocks, and are characterized by the presence of coronas developed around relict-magmatic olivine crystals and different replacement textures involving amphiboles. The formation of coronas, reaction rims and symplectites indicates changes in chemical and/or physical factors. These changes can take place either during a prograde or a retrograde metamorphic event, and are sometimes associated with cooling from igneous temperatures (e.g., Griffin and Heier, 1973; Mongkoltip and Ashworth 1983). Kelyphytic corona textures and different types of symplectites are common in gabbros, also in metatroctolites regarding to reactions between olivine and plagioclase (Claeson, 1998; Lang et al., 2004). These microstructures always present great interest as they provide invaluable information in the reconstruction of the metamorphic evolution and P-T conditions of the rocks (Cruciani et al., 2008).

There are many examples in literature of reaction textures, coronas and symplectites; some of them were given in: cumulates in NE Sardinia, Italia (Franceschelli et al., 2002); in metatroctolites from Buchcreek, North Carolina Blue Ridge (Lang et al., 2004); in Rymmen gabbro from Southern Sweden (Claeson, 1998); in gabbros from Black Hill, South Australia (Turner and Stüwe, 1992); in troctolitic gabbros in Norway (Ashworth, 1986), among others. In Argentina, there are some examples in mafic rocks from Sierras de San Luis (Cruciani et al., 2008, 2011, 2012; Brogioni et al., 2007) and in Sierras del Valle Fértil and La Huerta (Otamendi et al., 2010; Gallien et al., 2012). This contribution constitutes the first mention of mafic coronitic rocks outside the Sierras Pampeanas context.

This study was focused on metatroctolites that exhibit coronas between olivine and plagioclase, and involve the analysis of mineral assemblages, textures, microstructures, whole-rock/mineral geochemistry, geochronology and metamorphic reactions, in order to define the P-T trajectory of the metatroctolites of Ñorquinco lake.

2. Geological Setting

The metatroctolites, previously denominated troctolitic metagabbros (Urraza et al., 2012, 2013; Urraza, 2014) form part of the Aluminé Igneous-Metamorphic Complex (AIMC), which has been defined as a set of intrusive-igneous pre-Andean and Andean rocks and its metamorphic country-rocks. The AIMC is located between the Aluminé, Moquehue, Ñorquinco and Pulmarí lakes, in the Neuquén province of Argentina (Urraza et al., 2008a, 2011). The AIMC forms the northern sector of the zone limited by the Pino Hachado-Picún Leufú (PH-PL) and Nahuel Huapi (NH) megalineaments, defined by Ramos (1978) as Aluminé Batholithic Belt (Fig. 1A).

The pre-Andean tectonic context for the AIMC, is represented in figure 1B. The AIMC is located within a complex tectonic framework. According to Vaughan and Pankhurst (2008), the sector between 38° and 40°S presents a high grade of complexity due to the scarcity of detailed information, from what they marked this area with a question mark. This zone limits to the north with the Chilean and Cuyanean terranes, whereas towards the south it is in contact with the North Patagonian Massif and Patagonia. The tectonic Andean frame also presents a high grade of complexity due to the successive emplacement of igneous bodies forming different batholiths. The Patagonian Batholith (PB), located between 38°30’S and 56°S, records the Andean subduction initiation at around 150 Ma ago, in the Jurassic period (Hervé et al., 2007). The northern portion of the PB is named North Patagonian Batholith (NPB). Previously, Gordon and Ort (1993), had called Subcordilleran Patagonian Batholith (SCB) to the cretaceous granitic rocks arranged in a NNE trend. Same authors named Cordilleran Patagonian Batholith (CPB) to the cretaceous granitic rocks distributed along the N-S direction (Fig. 1C).

The locations of the Central Patagonian Batholith (CPB) and the Somuncurá Batholith (SB), are showed in figure 1C. In spite of in figure 1C outcrops of the PB and SCB are only showed to occur to the south of 40°S, rocks corresponding to these batholiths can be recognized up to the 38°30’S (Urraza et al., 2011).
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Paleozoic and Mesozoic granitoids
Middle Paleozoic metasediments
Late Paleozoic andesites
Cenozoic andesites
Metatroctolites
Glacial moraine
Modern basalts
Tertiary basalts
Lineaments

References:

1. L. Aluminé
2. L. Moquehue
3. L. Ñorquinco
4. L. Polcahué
5. L. Pulmarí

FIG. 1. Location and geologic setting for the AIMC. A. Geologic map of the AIMC showing the locations of the metatroctolites (modified after Urraza et al., 2011); B. Geologic pre-Andean frame (modified after Vaughan and Pankhurst, 2008). Note the locations of the study area in a key zone of convergence of several terranes, and which counts up to the present with very scarce geologic information; C. Modified scheme of Gordon and Ort (1993), showing the locus, dimensions and orientation of the bodies that conform the SCB and the PB south of the 40°S. The locations of the CPB and SB, are also showed.
3. Country rocks

The metamorphic basement of the AIMC is represented by small isolated outcrops of quartzofeldeslastic metapelites and amphibolites. Most of the outcrops are constituted by gneisses intensely foliated, with injections of granitic material of the ‘lit par lit’ type and frequently showing isoclinal, intrafoliar and/or pytgmatic folding. With less representation, finely foliated amphibolites have been recognized (Fig. 2). These rocks also show thin injections of the ‘lit par lit’ type along the foliation planes and irregular granitic veins, usually of greater thicknesses, which cut the foliation.

FIG. 2. The field characteristics of the different lithological types conforming country-rocks, are showed on the left side of the figure, whereas a microphotography corresponding to each of them are presented on the right. A. Injected gneisses: are composed of the association Qz+Pl+Ms+And+Zrn+Ap. Garnet, biotite and the fibrolitic sillimanite (this last one not observed in the microphotography due to the scale), form the anastomosed mylonitic foliation corresponding to the ductile deformation event that led to the intense recrystallization of quartz and moderate recrystallization of plagioclase; B. Muscovitic schists: present similar deformation to gneisses, showing development of polycrystalline quartz aggregates forming 120° triple junctions, surrounded by folia composed mainly of muscovite; C. Injected amphibolites: composed by hornblende and intensely recrystallized plagioclase.
with different angles (Urraza et al., 2009; Urraza, 2014). The varieties of basement described above correspond to in situ exposures, but they have been also observed as variable sized inclusions in gabbros and tonalites. Rarely and in thin strips, the gneissic basement loses partly its pyctgmatic appearance and acquires a very well defined and very regularly oriented foliation. In this case, the foliation is marked by granitic thin injections, the stretching and boudinage of the thickest veins and by the distribution of abundant micas along the foliation planes. The loss of the intensely folded gneissic structure and the increase of phyllosilicates in these bands, led to the rock to acquire a schistose appearance (Fig. 2B). The original metamorphic paragenesis of the injected gneisses is constituted by Qz+Pl+Ms+And±Bt±Grt+Zrn+Ap (Fig. 2A) (abbreviations after Withney and Evans, 2010). This association is stable at moderated to low temperatures (<620 °C at X$_{H_2O}$=1, or still lower at lower X$_{H_2O}$) and pressures below 3.8 Kb. This early association is overprinted by a ductile deformation event that led to the intense recrystallization of quartz, moderate recrystallization of plagioclase and the development of an anastomosed mylonitic foliation (Fig. 2A). The geothermobarometry of the association stable during this deformation event (Bt+Grt+Sil(Fib)+opaque minerals), gave pressures and temperatures in the ranges 6.2-6.7 Kb and 605-620 °C, respectively. The presence of sillimanite in these rocks require of minimum temperatures of 615 °C at 6.2 Kb and 640 °C at 6.7 Kb (Urraza et al., 2009). The injected amphibolites are composed of Qz+Pl+Hbl±Bt, plus accessories and opaque minerals. Amphibolites also show ductile deformation evidenced by intense recrystallization of plagioclase and amphibole, which underwent significant reduction of the grain size and development of pseudo-polygonal new grains meeting at 120° triple junctions. These fine aggregates arrange in folia, which together with the preferential orientation of relict crystals define the mylonitic foliation (Fig. 2C).

4. Field description of the metatroctolites

The studied metatroctolites show (at outcrop scale) a fine granular texture in the borders of the body that increases progressively in size towards the center, where it develops a coarse to very coarse granular texture (Fig. 3). This rocks show an anas-
tomosed penetrative foliation with a general SSW trend (mean: 200°/80° DD/D) (Fig. 3D).

However, these rocks show a widespread retrogression, the magmatic mineralogical association can be still recognized in some thin sections. The intrusive body contains inclusions of the surrounding metamorphic basement, whose mineral associations and textures have been strongly obliterated (Figs. 3B and C). Regarding mineralogy of these basement inclusions, only quartz and intensely altered plagioclase and biotite are preserved, and the primitive foliation is only marked by the preferred orientation of quartz ribbons. The body of metatroctolites is cut by aplitic dikes of up to 60 cm thickness oriented 130°/66° (dip direction/dip) and coarse pegmatitic dikes in which stand out pericthitic K-feldspar crystals of up to 10 cm and tourmaline (Figs. 3A and E).

5. Geochemistry and classification

A detailed sampling traversing the whole gabbroic body including 11 samples were carried out, in order to asses the structural, textural and compositional variations. Geochemical analysis including major and trace elements, were performed in the Actlabs laboratory, Canada, using ICP-MS. For the classification of the original magmatic rock and the geothermobarometric analysis, samples of the center of the body which better preserve the magmatic (texture and mineralogical composition) and metamorphic characteristics (post-crystallization textures and minerals), were selected.

The representative geochemical composition of metatroctolites is presented in Table 1. According to its SiO$_2$ content (43.1%), this rock is located close to the limit between basic and ultrabasic rocks following the Le Maitre (1989) silica content classification. Taking into account that the mineral proportions of ferromagnesian minerals in the studied metatroctolites are significantly lower than 90%, these rocks are considered to be mafic. The alkalis sum (Na$_2$O+K$_2$O=0.71) and calcium content (11.62%), point to a sub-alkaline signature. In addition, this magnesian-rock presents an X$_{Mg}$=0.73 (in atomic proportions) and very low TiO$_2$ (0.068%). Considering its chemical and mineralogical composition, these metatroctolites can be compared with gabbronorites and gabbroic inclusions in granodiorites found in the same sector of the AIMC. The above mentioned rocks with SiO$_2$ contents in the range 48.38-51.65% and
total alkalis of up 4.44% would correspond to more evolved facies. Compared with the metatroctolites, these rocks are richer in iron ($X_{Mg} = 0.41-0.47$) and TiO$_2$ (1.22-2.55%).

The REE plot in figure 4C, shows a relatively high concentration of LREE and depletion in HREE. The metatroctolites show a strong positive europium anomaly, suggesting the accumulation of plagioclase segregated from the melt. The enrichment of LREE can be explained as the result of contamination from the metasedimentary xenoliths incorporated by the mafic magma. In figure 4C, this rock pattern is
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compared with the REE diagrams corresponding to gabbrorrites and gabbroic inclusions in cretaceous granodiorites (see section 8). The pattern is almost parallel to that of gabbrorrites, although this last one shows a major enrichment in total REE. On the other hand, gabbroic xenoliths in granodiorites show total REE similar to gabbrorrites, but differ from them by the presence of a slight negative europium anomaly (Fig. 4C).

On the base of the modal composition mafic rocks can be classified as troctolites (Fig. 4A), whereas according to its chemical composition as perido-gabbros (Fig. 4B).

### TABLE 1. REPRESENTATIVE MAJOR (WT %) AND REE (PPM) WHOLE-ROCK ANALYSES.

<table>
<thead>
<tr>
<th></th>
<th>Metatroctolite</th>
<th>Gabbroid inclusion</th>
<th>Gabbrorrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>43.1</td>
<td>48.4</td>
<td>51.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>19.7</td>
<td>18.5</td>
<td>19.8</td>
</tr>
<tr>
<td>FeO</td>
<td>10.6</td>
<td>12.0</td>
<td>8.3</td>
</tr>
<tr>
<td>MnO</td>
<td>0.14</td>
<td>0.24</td>
<td>0.17</td>
</tr>
<tr>
<td>MgO</td>
<td>14.7</td>
<td>4.7</td>
<td>4.1</td>
</tr>
<tr>
<td>CaO</td>
<td>11.6</td>
<td>8.1</td>
<td>8.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.61</td>
<td>3.91</td>
<td>4.04</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.10</td>
<td>0.23</td>
<td>0.40</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.07</td>
<td>2.55</td>
<td>1.22</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.01</td>
<td>0.78</td>
<td>0.37</td>
</tr>
<tr>
<td>LOI</td>
<td>0.33</td>
<td>0.85</td>
<td>0.06</td>
</tr>
<tr>
<td>Total</td>
<td>101</td>
<td>100.2</td>
<td>99.67</td>
</tr>
<tr>
<td>La (ppm)</td>
<td>1.27</td>
<td>17.80</td>
<td>14.80</td>
</tr>
<tr>
<td>Ce</td>
<td>2.49</td>
<td>44.00</td>
<td>33.60</td>
</tr>
<tr>
<td>Pr</td>
<td>0.29</td>
<td>6.44</td>
<td>4.60</td>
</tr>
<tr>
<td>Nd</td>
<td>1.18</td>
<td>32.50</td>
<td>19.20</td>
</tr>
<tr>
<td>Sm</td>
<td>0.30</td>
<td>8.82</td>
<td>4.80</td>
</tr>
<tr>
<td>Eu</td>
<td>0.17</td>
<td>1.95</td>
<td>1.78</td>
</tr>
<tr>
<td>Gd</td>
<td>0.33</td>
<td>9.94</td>
<td>4.63</td>
</tr>
<tr>
<td>Tb</td>
<td>0.06</td>
<td>1.65</td>
<td>0.65</td>
</tr>
<tr>
<td>Dy</td>
<td>0.34</td>
<td>9.41</td>
<td>3.65</td>
</tr>
<tr>
<td>Ho</td>
<td>0.07</td>
<td>1.85</td>
<td>0.73</td>
</tr>
<tr>
<td>Er</td>
<td>0.21</td>
<td>5.18</td>
<td>2.25</td>
</tr>
<tr>
<td>Tm</td>
<td>0.03</td>
<td>0.75</td>
<td>0.32</td>
</tr>
<tr>
<td>Yb</td>
<td>0.21</td>
<td>4.59</td>
<td>1.94</td>
</tr>
<tr>
<td>Lu</td>
<td>0.03</td>
<td>0.72</td>
<td>0.30</td>
</tr>
</tbody>
</table>

6. Petrography

The Ñorquinco metatroctolites show a coarse granular texture (Figs. 5A and B), and variable proportions of preserved igneous and late magmatic/subsolidus metamorphic minerals. Relict magmatic olivine crystals are usually fractured and normally exceed 500 µm in size. Magnetite appears filling internal microfractures and in the crystals rims. The most conspicuous characteristic showed by relict olivine crystals is the formation of reaction coronas around it, which are composed mainly of pyroxene, amphibole and spinel.

Plagioclase appears either as relict magmatic crystals of the original mineralogy (Pl₁), or filling fractures (Pl₂). Its presents deformation twins and rounded rims when it is in contact with amphibole. The orthopyroxene is mainly present in the reaction coronas, although a few magmatic big interstitial crystals were recognized in some thin sections. Magmatic clinopyroxene (Cpx₁) appears as small relict crystals surrounded by other phases (Fig. 6B and D). Cpx₂ forms part of the coronas around olivine and plagioclase crystals, sometimes forming symplectitic intergrowths with spinel. The presence of orthopyroxene and Cpx₂+Spl symplectites developed around olivine crystals can be attributed to the typical reaction: Pl₁+Ol+Cpx₁+Hbl₁+H₂O⇔Opx+Cpx₂+Hbl₂+Pl₂+Spl. Excess of H₂O needed for the reaction, can be either attributed to a late magmatic origin, or to an external incorporation. The metatroctolites are carriers of an important sulfide mineralization, represented principally by pyrotnite, pentlandite and chalcopyrite. These ore minerals were also found filling fractures in the adjacent country rocks.
FIG. 4. A. Modal classification based on the proportions of plagioclase, pyroxene and olivine; B. TAS Diagram (whole alkalis versus silica) of Cox et al. (1979), adapted by Wilson (1989) and Middlemost (1994) for plutonic rocks. The studied samples lie inside the subalkaline area, and within the perido-gabbros field; C. REE composition of metatroctolites, gabbronorites and gabbroic inclusions in granodiorites normalized to Boynton (1984).
7. Mineral Chemistry

The chemical compositions of the metagabbro mineral phases present in the metatroctolite were analyzed using a microprobe JEOL 8200 from the Earth and Atmospheric Sciences laboratory of the Alberta University, Canada. The analytical conditions were 15kV accelerating voltage, beam current of 15nA and 3-5 µm spot size. Analyses representative of the different mineral phases and their structural formulas, are presented in Table 2.

7.1. Olivine

It appears as a primary magmatic mineral bordered by reaction coronas composed of pyroxenes and amphiboles. The composition of olivine varies from Fo$_{69}$ to Fo$_{73}$. Olivine shows only negligible compositional variations between crystals cores and rims.

7.2. Plagioclase

Plagioclase forms part of the original magmatic association of the metatroctolites. It is characterized by high An contents, which varies between 89.2% and 95.6% (Table 2) and lies in the Anorthite field when plotted on the ternary diagram Ab-An-Or (Fig. 7B). Both petrographically and geochemically is possible to recognize two generation of plagioclase: as phenocrystals (Pl$_1$) and interstitially (Pl$_2$). The composition of Pl$_1$ is fairly uniform, varies between An$_{89}$-An$_{90}$ while Pl$_2$ is substantially more calcium -rich (An$_{96}$).

7.3. Orthopyroxene

This phase appears in the reaction coronas developed between olivine and plagioclase. Classification of orthopyroxene was carried out using
the triangular diagram En-Fs-Wo (Fig. 7C). The proportion of enstatite (En) and ferrosilite (Fs) varies between 69% and 73% (Xₐ₋₇₇), whereas the wollastonite component does not overcome 5% for any crystal (Table 2). Orthopyroxene crystals in the metatroctolites have predominantly magnesian compositions, and lie in field of broncite.

7.4. Clinopyroxene

Chemical composition of clinopyroxene crystals (Fig. 7D), can be expressed in terms of the relative proportion of the clinoenstatite-clinoferrosilite-wollastonite components. The analyzed grains indicate that clinopyroxenes are calcium-magnesium
### Table 2. Representative Chemical Compositions of the Original-Magmatic Minerals and Phases Produced by Different Post-Emplacement Reactions Recognized in the Metatroctolites from Norquinc Lake.

<table>
<thead>
<tr>
<th>Mineral Sample</th>
<th>OX 152</th>
<th>OX 156</th>
<th>OX 188</th>
<th>OX 191</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>38.49</td>
<td>38.67</td>
<td>37.53</td>
<td>38.01</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.01</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>FeO</td>
<td>25.99</td>
<td>25.03</td>
<td>30.31</td>
<td>27.88</td>
</tr>
<tr>
<td>MnO</td>
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<td>0.00</td>
<td>0.02</td>
<td>0.01</td>
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<tr>
<td>MgO</td>
<td>37.16</td>
<td>38.01</td>
<td>33.04</td>
<td>35.34</td>
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<td>CaO</td>
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<td>Na₂O</td>
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<td>K₂O</td>
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<td>101.63</td>
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Numbers of ions on the basis of 4 Oxigens

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<th>OX 188</th>
<th>OX 191</th>
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<td>SiO₂</td>
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<tr>
<td>Ti</td>
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</tr>
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</tr>
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<td>Fe/Fe+Mg</td>
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<td>0.27</td>
<td>0.34</td>
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<td>0.73</td>
<td>0.66</td>
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</tbody>
</table>

Numbers of ions on the basis of 32 Oxigens

---

Chemical mineral analyses expressed as oxide weight %.

---

Mineral formula calculated with the program Minpet, v2.02 (Richard, 1995).

---

Mineral compositions expressed as oxide weight %.

---

Numbers of ions on the basis of 4 Oxigens

---

Numbers of ions on the basis of 32 Oxigens

---

Numbers of ions on the basis of 6 Oxigens
Symbols for different minerals:

- ▲ Olivine
- ■ Plagioclase
- ○ Orthopyroxene
- ▼ Clinopyroxene
- ● Spinel + Chlories
- □ Hbl-1
- ● Hbl-2
- ★ Tremolite

FIG. 7. A. Olivine classification diagram (isomorphic binary series forsterite-fayalite, based on the Mg/(Mg+Fe)2+ and Fe2+/Fe2++Mg proportions; B. Ab-An-Or ternary diagram; C. Ternary diagram for orthopyroxene classification. Observe the intermediate compositions of the isomorphic series between the end-members enstatite (En) and ferrosilite (Fs); D. Ternary diagram for classification of clinopyroxene. Note the intermediate compositions of the isomorphic series between the extremes clinoenstatite (Cen) and clinoferrosilite (Cfs); E. Prism of Johnston for classification of spinel group minerals; F. Triangular diagram of trivalent cations (Fe3+-Cr3+-Al3+); G. Diagram of spinel classification according to the relative proportions of bivalent and trivalent ions; H. Classification of calcic amphiboles [(Na+K)<0.5, Ti<0.5] according to Leake et al. (1997); I. Classification of calcic amphiboles [(Na+K)>0.5, Ti<0.5] according to Leake et al. (1997); J. Chlorite classification diagram (taken from Deer et al., 1992).
diopsides, with a wollastonitic component varying between is 46.16%-48.19%, and X_Mg 83-85 (Table 2). Cpx₁ is the relict phases, although scarce Cpx₂ is found only in coronas.

7.5. Spinel

Pure end-members of the spinel group are rarely found in nature. They can be subdivided on the base of their dominant divalent and trivalent cations. The compositions of the multicomponent system of the spinel group, can be plotted on the prism of Johnston (Fig. 7E), whose extremes are given by magnetite, magnesiowüstite, spinel, magnesiochromite and chromite (Deer et al., 1992). Gargiulo et al. (2013) propose classification diagrams based on the faces of the Johnston’s prism. Figure 5F, shows a classification of the spinel group based on the exchange of the trivalent cations on the Y position. This classification allows separating the fields of Fe³⁺-rich spinels representing the magnetite end-member, from the Cr³⁺- and Al³⁺-rich fields corresponding to chromite and hercynite end-members, respectively. Figure 5G, shows that the analyses individuals have intermediate compositions between spinel and hercynite, with most of them being located within the pleonaste field. Only one analysis lies on the spinel field, which corresponds to aSpl-Hbl symplectite developed in the contact between olivine and plagioclase crystals (Fig. 6 A-C).

7.6. Amphiboles

Three generations of amphiboles were recognized in the metatroctolites. The first two classify as hornblendes (Hbl₁, Hbl₂) and the third as tremolite (Tr). According to Leake et al. (1997), Hbl₁ classifies as magnesium-hornblende, although most of them lie on the limit with the tchermarkitic-hornblende field as shown in figure 4G. The petrographic analysis shows that Hbl₁ is replaced by Hbl₂, whose composition corresponds to an edenite-hornblende (Fig. 7H). The tremolitic amphibole, replaces the olivine crystals and the minerals forming the reactions coronas, and clearly corresponds to a very late-low temperature retrogression.

7.7. Chlorite

Chlorites are magnesian and classify as chlinochlores in the Si versus (Fe³⁺+Fe²⁺) diagram (Deer, 1992) (Fig. 7I). Like tremolites, chlorites correspond to a late-low temperature alteration event.

8. Mineral re-equilibration

The sequence of mineral re-equilibriations in metatroctolites from Norquinco lake is shown in Table 3. The original igneous association is constituted by Ol+Pl₁+Cpx₁. First replacement textures are represented by the growth of Opx on Cpx₁ crystals (stage A in Table 3). The appearance of Hbl₁ due to hydration of the previous phases form the association corresponding to stage B. Spl, Hbl₂ and Pl₂ formed during stage C. Stage D is characterized by the late formation of Tr and Chl.

8.1. Stage A formation of Orthopyroxene

Orthopyroxene is the first mineral representing replacement textures in the metatroctolites. It clearly replace the igneous minerals Ol-Cpx₁. Convex grain boundaries towards olivine in Ol-Opx contacts, indicate growth of orthopyroxene at the expense of olivine crystals.

8.2. Stage B formation of Mg-Hornblende (Hbl₁)

The development of amphibole (Hbl₁) is the result of the reaction between Ol-Cpx₁ and Pl₁ with the progressive increase in H₂O concentration. The widespread occurrence of Hbl₁ generates lobed edges

<table>
<thead>
<tr>
<th>Stage</th>
<th>relict igneous association</th>
<th>Post-emplacement evolution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td>Ol</td>
<td>Ol₁</td>
</tr>
<tr>
<td></td>
<td>Pl₁ (An₉₀-₉₅)</td>
<td>Pl₁2 (An₉₅)</td>
</tr>
<tr>
<td></td>
<td>Cpx₁</td>
<td>Cpx₂</td>
</tr>
<tr>
<td></td>
<td>Spl</td>
<td>Spl</td>
</tr>
<tr>
<td></td>
<td>Opx</td>
<td>Opx</td>
</tr>
<tr>
<td></td>
<td>Hbl₁</td>
<td>Hbl₁</td>
</tr>
<tr>
<td></td>
<td>Hbl₂</td>
<td>Hbl₂</td>
</tr>
<tr>
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<td>Tr</td>
<td>Tr</td>
</tr>
<tr>
<td></td>
<td>Chl</td>
<td>Chl</td>
</tr>
</tbody>
</table>
around Pl, and sometimes full replacement of Ol, although some small remnants of Ol with irregular borders were found. It is not possible to recognize close contacts between Ol and Pl because Hbl is always present between these original phases.

8.3. Stage C: formation of Mg-Hornblende (Hbl), Spinel and Cpx

As a result of the progressive changes in the physical conditions, a new amphibole (Hbl) replacing the pre-existing phases is formed. Spl generates symplectites with Hbl, around Ol and Pl. Hbl replaces Hbl and forms reaction rims around Cpx-Hbl, and Opx-Hbl. Cpx was recognized in some coronas associated with Spl. Hbl and Spl form symplectites around relict phases.

8.4. Stage D: formation of Chl-Tr

The formation of Chl and Tr in very low proportions is attributed to the last stage of retrogression. Chl is mainly replacing the different phases of the corona and surrounding olivine. Magnetite filling fractures inside olivine crystals, is also assigned to this stage.

9. Phase relations, geothermobarometry and P-T path

In order to evaluate the stability of the observed mineral associations, a suitable P-T pseudosection was constructed with the program Perplex_X (Connolly, 1990, version 2013). The diagram was calculated using the whole-rock chemistry of the metatroctolites (Fig. 8), considering the chemical system Na$_2$O-CaO-FeO-MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O and including the following phases: plagioclase, olivine, orthopyroxene, clinopyroxene, spinel, amphibole, garnet, chlorite and water. The solid solution models for olivine, clinopyroxene, orthopyroxene garnet, spinel and chlorite correspond to Holland and Powell (1998, and updated versions); for plagioclase and amphibole were used the formulations of Newton et al. (1980) and Dale et al. (2005), respectively.

Pseudosection analysis was complemented with the application of classical geothermobarometry to selected mineral pairs. Using the Opx-Cpx geothermometer of Wood and Banno (1973) and the Cpx-Pl geobarometer of Kretz and Jen (1978), a temperature of 936 °C and a pressure of 2.7 Kb were obtained (Table 4). This point, when plotted on the pseudosection (A) of figure 8, locates within the stability field of the association Opx+Pl+Cpx+Hbl+H$_2$O. Possibly, there was not available free water during this first stage, but the incorporation of this fluid component is necessary in order to generate the hydrated phases observed. This free water might have been originated during late magmatic crystallization, supplied by an external source, or by a combination of both provenances. Point A is considered to be the nearest condition to the reached metamorphic peak by the metatroctolites, and it is established as the starting point for the post-emplacement trajectory.

The conditions of the point B in figure 8, were calculated through the geothermometer TB of Holland and Blundy (1994), using the mineral pair Pl$_2$-Hbl$_1$ and the Al-in-Hbl geobarometer of Johnson and Rutherford (1989) for Hbl$_1$, obtaining a temperature of 851 °C and a pressure of 4.26 Kb. Point B lies in the stability field of the association Ol+Pl+Cpx+Opx+Hbl$_1$+H$_2$O, and differs from the previous one for the first appearance of the amphibole (Hbl$_1$). The trajectory between points A and B implies increasing pressures and decreasing temperatures, and requires of the availability of free water to form amphibole. The P-T condition of stage B is well constrained by the compositional isopleths of X$_{Ms}$ in Opx (0.77), as well as in Cpx X$_{Ms}$ =0.85 (Fig. 9A, B). Anorthite proportions in Pl for the stage B is around (X$_{Ca}$ =0.96), whose composition is the same as that obtained for Pl$_2$ with microprobe analysis. X$_{Si}$ in amphibole varies between 6.5 and 6.6 (a.p.f.u) (Fig. 9 C and D). The estimated isopleths are fully coincident with the P-T conditions obtained for stage B using classical geothermobarometry.

Textural relationships indicate that Hbl$_1$ is replaced by the Hbl$_2$, which indicates a new stage of mineralogical re-equilibrium. Applying the same thermometer and geobarometer to Pl$_2$-Hbl$_2$ pair, a temperature of 780 °C and a pressure of 5.69 Kb were obtained. This point represented in figure 8 with the letter C, corresponds to the stability field of the mineral association Pl+Cpx+Opx+Amph+Spl+H$_2$O. The transition from the previous to this stability field carries with it the disappearance of Ol and the appearance of the Hbl$_2$+Spl pair. Petrography shows that this later phases are always spatially and texturally associated. The appearance of spinel is consistent with petrographic
CounterClockwise post-emplacement evolution of metatroctolites from Aluminé Igneous-Metamorphic Complex...

observations, which indicates the development of the reaction Ol+Pl=Opx+Cpx+Spl, typical of these rock types. Given that reaction Spl+Px=Grt+Ol, which fixes the upper pressures limit for the stability of the association listed above, did not take place considering the total absence of garnet in the studied rocks, point C establishes an approximated maximum for pressures reached by these rocks. The X$_{Si}$ composition in Hbl$_2$ is around 6.6-6.7 (a.p.f.u), though the stage C calculated using conventional geothermobarometry corresponds to a little high composition X$_{Si}$ 6.9-7.0 for the isopleths (Fig. 9D).

Finally, the presence of chlorite allows estimation of a temperature of 694 °C, calculated with the formulation Al-in-Chl of Cathelineau (1988). According to pseudosection of figure 8, the formation of chlorite is associated to the total consumption of water and clinopyroxene present in the previous paragenesis, giving place to the new stable association Pl+Opx+Amp+Spl+Chl. Considering the calculated temperature for chlorite, a range of pressures can be estimated considering the absence of olivine in the above listed association which fix a minimum pressure at ~4.5 Kb, and the entire absence...
TABLE 4. GEOTHERMOBAROMETRIC RESULTS OBTAINED FROM THE APPLICATION OF THE DIFFERENT FORMULATIONS INDICATED, TO SEVERAL MINERAL PHASES.

<table>
<thead>
<tr>
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<th>P (Kbar)</th>
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<td>Opx-Cpx1</td>
<td>933</td>
<td>Cpx1-Pl1</td>
<td>2.7</td>
</tr>
<tr>
<td>Wood and Banno (1973) P=2.7</td>
<td></td>
<td>Ellis (1980) T=933 ºC</td>
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<tr>
<td>Average</td>
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<td>Average</td>
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</tr>
<tr>
<td>Cpx1-Pl1</td>
<td>839</td>
<td>Mg-Hbl (Hbl-1)</td>
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<tr>
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<td>Ed-Hbl (Hbl-2)</td>
<td>5.69</td>
</tr>
<tr>
<td>Average Pl-Hbl 1 and Cpx1-Hbl 1</td>
<td>851.5</td>
<td>Average Al in Hbl</td>
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<tr>
<td>Al in Chl</td>
<td>694.2</td>
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<td>4.26</td>
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<td>Putirka (2008) Eqn 36</td>
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<td>Ed-Hbl (Hbl-2)</td>
<td>5.69</td>
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</table>

FIG. 9. Compositional isopleths. A. \(X_{Mg}\) in Orthopyroxene; B. \(X_{Mg}\) in Clynopyroxene; C. An in plagioclase; D. \(X_{Al}\) in amphiboles. The post-emplacement stages B, C and D (showed with stars) are the P-T values calculated with conventional geothermobarometry.
of garnet in these rocks establishing a maximum pressure of ~5.2 Kb (Fig. 8). Letter D in figure 8, is located in the middle of these values and at the calculated temperature. Taking into account that the continuity of the trajectory is limited by the last stability field, the trajectory must continue along a path characterized by the decrease of temperatures and pressures (Fig 8).

10. Estimation of the metatroctolites relative age

The presence of abundant metasedimentary xenoliths from the country-rocks fixes a maximum Late Devonian age (360 Ma, Urraza et al., 2009). On the other hand, xenoliths of strongly deformed metagabbros composed of Opx+Pl+Hbl+Bt+Ilm, were found included in granodiorites. In spite of these xenoliths are strongly affected by deformation, they preserve a mineralogical and geochemical composition similar to the studied metatroctolites. In the present contribution, a U-Pb zircon age of 309±31 Ma has been determined for the metagabbroic xenoliths, whereas for the host granodioritic rocks a U-Pb zircon age of 82±1.6 Ma was established (Fig. 10 A and B). Isotopic data were acquired using a Nu Plasma MC-ICP-MS coupled to a laser ablation system. The well-calibrated zircon standard LH-9415 was used as the standard for the normalization of the Pb/U values in the University of Alberta. Simonetti et al. (2006) show the advantages of using U-Pb laser ablation for zircon, monazite and titanite grains in standard petrographic thin section and demonstrate the effectiveness of the in situ technique in providing accurate and relatively precise age information. A laser beam spot of 40 µm was used; considering it is the appropriate size for Paleozoic rocks. Simonetti et al. (2006) mention that it should prove particularly valuable for obtaining U-Pb ages in reconnaissance-type studies, such as preliminary geological studies of regions that contain little or no prior geochronological age information. Therefore, it is an appropriate technique for preliminary information in the AIMC.

The ages found for the country-rock xenoliths and gabbroic inclusions in granodiorites, constrain the metatroctolites formation to Upper Paleozoic times, which allows linking its intrusion to the early stages of gondwanian magmatism.

11. Conclusions

1. Mafic rocks from the north of Ñorquinco lake were classified based on the primary modal composition as metatroctolites, and on the base of the alkalis content as perido-gabbros.

2. The primary-magmatic association composed mainly of Pl₁+Ol₁+Cpx₁+Hbl₁, was re-equilibrated during the post-emplacement thermal descent giving place to the formation of coronas around olivine crystals, with successive formation of orthopyroxene, clinopyroxene (Cpx₂), amphibole (Hbl₂) and spinel.

FIG. 10. A. Tera-Wasserburg concordia representation of the data obtained from analyzed zircons, using thin section in situ LA-ICP-MS with a 40 µm bundle. U-Pb age for gabbroic inclusions in granodiorites; B. Wetherill concordia U-Pb age for host granodiorites.
3. The presence of water, either late-magmatic or externally incorporated, gave place to the appearance of high temperature amphiboles ($Hbl_1$, $Hbl_2$) and the late lower-temperature phases, chlorite, magnetite and tremolite. These phases formed by the hydration of the primitive anhydrous phases, and crystallized at different stages of the evolution of these rocks.

4. Considered together, textural relationships established via petrographic studies, pseudosection analysis and geothermobarometry, allow us to reconstruct a counterclockwise P-T path for the post-emplacement evolution of the metatroctolite. This trajectory is consistent with the evolution determined for the adjacent country-rocks previously studied by the authors (Urraza et al., 2009).

5. Based on the established ages for basement xenoliths in metatroctolites and gabbroic inclusions in granodiorites, the emplacement of the Norquinco lake metatroctolites can be constrained to the Upper Paleozoic.

Acknowledgements

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