Lithium enrichment in anatectic pegmatites: new insights from the thermometamorphic aureole of the Adamello batholith

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INTRODUCTION

Lithium is the least dense alkali metal, it is electrochemically active, featuring the highest redox potential value of all metals, and has the highest specific heat capacity of any solid element. These characteristics make it one of the most important commodity for modern life and a key element for modern electric vehicle revolution (e.g. Swain et al., 2017). Newly mined lithium to supply the estimated demand will come largely from pegmatite and related magmatic deposits, evaporative brines, and a growing group of unusual deposits including both rocks and brines (Kesler et al., 2012). Pegmatites are of interest due to their wider geographic distribution, lesser susceptibility to supply disruptions and environmental impact and they are the types of Li deposits on which the research effort has mostly focused on in the last years. Although several works addressing the genesis of Li-enriched pegmatites have been published (e.g. Černý, 1991; Černý & Ercit, 2005; Simmons et al., 1995, 1996, 2008, 2016, 2018), the processes that lead to the formation of these rocks are still not well understood. New research on these economically strategic resources is needed to expand our knowledge on the geological constraints that determine their formation and produce the metal endowment of pegmatites-hosted Li resources. The presented Ph.D. project, in particular, tries to provide tighter constraints on the evolution of Li-pegmatites by studying small Li-enriched bodies emplaced in the thermometamorphic aureole of the Adamello pluton (Northern Italy).

MATERIALS AND METHODS

This study is based on a set of forty samples from low-grade metamorphosed to migmatitic rocks of the Verrucano Lombardo formation as well as barren and Li-rich pegmatites collected in the Forcel Rosso area. In addition, five unmetamorphosed samples of Verrucano Lombardo pelites were also collected. Extensive and detailed field mapping was carried out to identify small-scale lithological variations and map the distribution of pegmatitic dykes. The mineralogy and texture of the collected samples were characterized in fifty-five thin sections by optical microscopy while mineral chemical data were obtained by electron microprobe. The whole rock major elements composition of the samples was determined at the department of Earth Sciences of the University of Milan (Italy) using an iCAP ICP-MS quadrupole coupled with a 193 nm Ar-F excimer laser on pressed powder pellets following the procedure of Peters and Pettke (2016). Data treatment was performed on SILLS (Guillong et al., 2008). The whole rock composition of the zoned LCT pegmatites has not been determined directly due to its extreme textural heterogeneity and large crystal dimensions which have hindered the collection of a single representative sample. To overcome this limitation the average composition of the pegmatites was calculated as the weighted average of the composition of each zone multiplied for their volumetric abundance. Radiogenic Sr and Nd isotopic analyses of 10 selected samples were performed using a Thermo Fisher Neptune Plus MC-ICP-MS at the Istituto di Geoscienze e Georisorse - CNR in Pisa (Italy) in 2% HNO_3 solution containing 20-200 ng*g^{-1} of analyte. The in-situ B isotope composition of tourmaline crystals was measured by LA-MC-ICP-MS technique at the Geochemistry, Geochronology and Isotope Geology Laboratory at the Earth Science Department "A. Desio", University of Milan (Italy) by coupling the laser system used for the trace element determination to a Neptune XT MC-ICP-MS (Thermo Fisher Scientific).

GEOLOGICAL SETTING

The Adamello batholith is the largest of the Tertiary Periadriatic plutons and was emplaced at 6-10 km depth (Broderick et al., 2015) in the central Southern Alps during the Eocene-Oligocene. The rocks of the Adamello massif show a distinct compositional similarity to volcanic rocks of equivalent SiO_2 content from calc-alkaline suites of continental margins (Dupuy et al., 1982). Variation trends of major and trace elements generally resemble trends generated by fractional crystallization

dominated by plagioclase and to a smaller degree by amphibole and pyroxene. Overall, the Adamello plutons show a sequential emplacement from the oldest units in the south (Re di Castello pluton, RdC, ~43 Ma) to the youngest in the north (Avio pluton, ~30 Ma; Del Moro et al., 1985; Schaltegger et al., 2019). Strontium isotope ratios ($^{87}Sr/^{86}Sr$) indicate a mantle origin and tend increase from 0.7036 in the south to 0.7120 in the north (Del Moro et al, 1983; Blundy, 1989) indicating that contamination by radiogenic upper-crustal strontium increased with time, becoming most significant in the youngest, northernmost plutons. Most of the country rocks (ca. 90%) surrounding the Adamello batholith exhibit evidence of contact metamorphism within the ca. 1 km to 4 km thick thermal aureole (Callegari & Brack, 2002), inside which the studied LCT pegmatites are intruded. Two families of pegmatites are present: one Li-enriched related to the migmatites and one Li-poor intruded into the Adamello pluton magmatic mass.

RESULTS

P-T conditions and Role of fluids in partial melting

In the contact aureole of the collisional metaluminous Adamello pluton (Italy), pelites reached hornfels facies conditions locally undergoing partial melting, forming Crd-bearing and Crd-absent migmatities. This small-scale migmatitic field is spatially associated with barren and Lithium-Cesium-Tanatalum (LCT) pegmatitic dykes of granitic composition, suggesting a direct link between low-pressure partial melting and generation of Li-enriched felsic melts. Phase equilibria modelling reveals that the Crd-bearing metapelitic migmatites produced around 20 vol.% melt fraction through fluid-assisted melting reactions, while the Crd-absent stromatic metatexites produced ca. 35 vol.% of melt during fluid-rich partial melting. No melting was expected in strictly fluid-absent conditions. Peak P-T metamorphic conditions were calculated at 690-700°C and 300 MPa for both rock types. Because of the steep contact thermal gradient, the underlying and older conglomerates of the Verrucano Formation, of which the pelitic succession is part of, as well as rocks of the Collio Formation experienced comparably lower temperature metamorphism. Their mica-poor mineral compositions prevented them from melting and influencing the local anatectic processes. Crd-bearing migmatites leucosomes are compositionally similar to anatectic melts obtained by phase equilibria modelling, connected to fluid-assisted melting and defined as unfractionated. The leucosomes dominated by Kfs-Bt cumulus mineral composition and extremely enriched in K_2O, Sr and Ba are connected to fluid-rich melting and Crd-absent migmatites.

The first documented case of anatectic LCT pegmatites in italy

Major and trace element modelling suggests that part of the melt formed during fluid-present melting was extracted from the source. The composition of this evolved anatectic magma is compatible with the chemical composition of the migmatites-hosted LCT pegmatites. Whole rock Sr-Nd isotopic data confirm that the Li-rich pegmatites of the Forcel Rosso area are indeed crustally derived (ca. 0.74 $^{87}Sr/^{86}Sr_i$ and ca. -10 εNd) marks them as produced by direct anatexis of metapelites. The isotopic data characterizing the pluton-hosted pegmatites (0.705 $^{87}Sr/^{86}Sr_i$, -3 εNd) marks them as mantle-derived and directly linked to the Adamello batholith, clearly marking the lack of direct relationship existing between this magmatic intrusion and pegmatites featuring Li enrichment in its contact aureole. The data from this study shows that cordierite, or the absence of it, plays a key role in regulating the lithium transfer during partial melting in low pressure migmatites. Zircon U-Pb ages for all pegmatites in the area point to the same age of the Adamello pluton intrusion, from 37.5 to 38.5 Ma, and trace elements compositions outline important differences in the geochemical signature between pluton-derived and metapelite-derived pegmaties. LCT pegmatites zircons are rich in Y while pluton-related pegmatites zircons are enriched in Th. The Ti-in-zircon geothermometer confirms that anatectic pegmatites crystallized at the peak metamorphic temperature calculated through phase equilibria modelling.

Tourmaline as petrogenetic indicator: confirming the hypothesis

Once defined that Li-enriched pegmatites are anatectic, tourmaline was used to study the continous evolution of the metapelitic system from unmetamorphosed up to the conditions of pegmatite crystallization. This mineral is the main boron carrier among the rock forming minerals and it's obiquitous in the studied rocks. Studying the major element composition and boron isotopic signature several changes and trends are identified highlighting how this mineral evolves through the metamorphic history of metapelites, revealing a seemingly more complex picture compared to what is reported in the published literature data. Also, the data show how this mineral records variations during pegmatites crystallization processes making it valuable in the interpretation of their complex internal evolution processes.

IMPLICATIONS AND CONCLUSIONS

This Ph.D. project proved that Li-enriched pegmatites may be anatectic and originate through fluid-present melting of metapelites, even in the thermometamorphic aureole of plutons. This work identifies the mineral cor-

dierite as the main regulator of lithium liberation during low-pressure anatexis of suitably Al-rich pelitic rocks. The results highlight that in-source and en-route melt fractionation play an extremely important role each time magma is extracted from its source and that this process is the one ultimately responsible for the formation of Li-enriched melts. Pegmatitic zircons, although complex, can be used as tracers in order to help define the origin of pegmatitic dykes, particularly in cases in which these bodies are too old for Sr isotopic determination. The studied area shows that small scale variations in the pre-anatectic abundance and presence of aqueous fluids influences melt production and melt composition of different migmatitic areas. Finally, the metamorphic and magmatic history of the studied tourmaline crystals highlights how this mineral may record almost every boron-involving reaction and help unravel the complex history of migmatites, pegmatites and Tur-bearing plutons.

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