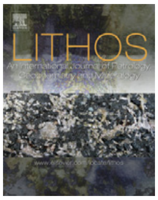
Lithos 202–203 (2014) 317–330

Contents lists available at ScienceDirect

Lithos

journal homepage: www.elsevier.com/locate/lithos



Crystallisation of magmatic topaz and implications for Nb–Ta–W mineralisation in F-rich silicic melts — The Ary-Bulak ongonite massif

Andrea Agangi [a,b,*,1], Vadim S. Kamenetsky [b], Axel Hofmann [a,1], Wojciech Przybyłowicz [c,d], Nikolay V. Vladykin [e]

[a] PaleoProterozoic Mineralisation Group, University of Johannesburg, Auckland Park 2006, South Africa
[b] ARC Centre of Excellence in Ore Deposits and School of Earth Sciences, University of Tasmania, Hobart, TAS 7001, Australia
[c] Materials Research Department, iThemba LABS, National Research Foundation, Somerset West 7129, South Africa
[d] AGH University of Science and Technology, Faculty of Physics & Applied Computer Science, Al. A. Mickiewicza 30, 30-059 Krakow, Poland
[e] Vinogradov Institute of Geochemistry and Analytical Chemistry, SB RAS, Irkutsk, Russia

ARTICLE INFO

Article history:
Received 6 March 2014
Accepted 16 May 2014
Available online 8 June 2014

Keywords:
Topaz
Fluorine
Cryolithionite
Ongonite
Cathodoluminescence

ABSTRACT

Textural, mineralogical and geochemical data on F-rich rhyolite (ongonite) from the Ary-Bulak massif of eastern Transbaikalia help constrain the formation of magmatic topaz. In these rocks, topaz occurs as phenocrysts, thus providing compelling evidence for crystallisation at the orthomagmatic stage. Cathodoluminescence images of topaz and quartz reveal growth textures with multiple truncation events in single grains, indicative of a dynamic system that shifted from saturated to undersaturated conditions with respect to topaz and quartz. Electron microprobe and Raman analyses of topaz indicate near-pure F composition [$Al_2SiO_4F_2$], with very limited OH replacement. Laser ablation ICP-MS traverses revealed the presence of a large number of trace elements present at sub-ppm to hundreds of ppm levels. The chemical zoning of topaz records trace element fluctuations in the coexisting melt. Concentrations of some trace elements (Li, Ga, Nb, Ta and W) are correlated with cathodoluminescence intensity, thus suggesting that some of these elements act as CL activators in topaz. The study of melt inclusions indicates that melts with different F contents were trapped at different stages during formation of quartz and topaz phenocrysts, respectively. Electron microprobe analyses of glass in subhedral quartz-hosted melt inclusions indicate F $\leq$1.2 wt.%, whereas irregular-shaped melt inclusions hosted in both topaz and quartz have F $\leq$9 wt.%. Cryolithionite [$Na_3Li_3Al_2F_{12}$] coexists with glass in irregular inclusions, implying high Li contents in the melt. The very high F contents would have increased the solubility of Nb, Ta and W in the melt, thus allowing progressive concentration of these elements during magma evolution. Crystallisation of Nb–Ta–W-oxides (W-ixiolite and tantalite–columbite) may have been triggered by separation of cryolithionite, which would have caused F and Li depletion and consequent drop in the solubility of these elements.

1. Introduction

Topaz [$Al_2SiO_4(F,OH)_2$] commonly occurs in cavities in F-rich felsic igneous rocks, quartz veins and greisens associated with felsic intrusions (Burt et al., 1982; Kortemeier and Burt, 1988). In many instances, topaz is interpreted as crystallising in the last stages (pneumatolitic stage) of evolution of magmatic-hydrothermal systems (e.g. from gas-filled cavities in volcanic rocks, Christiansen et al., 1983), or as a product of metasomatism and autometamorphism (Haapala, 1977; Lukkari, 2002). In metamorphic rocks, OH-rich varieties of topaz are stable at ultra-high pressure and high temperature (12 GPa, 1100 °C; Alberico et al., 2003; Zhang et al., 2002). However, evidence for topaz formation in the orthomagmatic stage has been presented in some strongly fractionated, F-rich felsic igneous rocks (Haapala and Lukkari, 2005; Naumov et al., 1991; Thomas et al., 2005, 2009; Webster et al., 2004). In some intrusive rocks, such as pegmatite, the magmatic origin of topaz is indicated by the presence of topaz-hosted melt inclusions (e.g. the Kymi granite; Haapala, 1977; Lukkari et al., 2009; or dykes in the Eurajoki Rapakivi Granite Stock; Haapala and Thomas, 2000) and by the simultaneous trapping of topaz and melt in quartz (Thomas et al., 2009). In volcanic rocks, topaz mostly occurs in the groundmass (Burt et al., 1982; Gioncada et al., 2014; Štemprok, 1991), sometimes making the interpretation of its origin difficult, and only rarely as phenocrysts (Kovalenko et al., 1971). Experiments have demonstrated that topaz can crystallise from low-Ca, peraluminous silicate melts containing as little as 1 wt.% F (Christiansen and Lee, 1986), or higher (F $\geq$1.7 wt.%; Dolejš and Baker, 2007, or F $\geq$2–3 wt.%; Lukkari and Holtz, 2007).

Ongonites are a special type of extremely F-rich rhyolites (F up to 1.5–2 wt.% in whole-rock analyses) with Na/K > 1, which contain phenocrysts of feldspar, quartz, minor mica and, in some cases, topaz (Kovalenko and Kovalenko, 1976; Peretyazhko et al., 2011). These rocks are considered to be the volcanic equivalent of topaz-bearing

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* Corresponding author at: PaleoProterozoic Mineralisation Group, University of Johannesburg, APK Campus, Auckland Park 2006, South Africa.

[1] Tel.: +27 11 559 4087.

http://dx.doi.org/10.1016/j.lithos.2014.05.032
0024-4937/

granites (Letnikov, 2008). Ongonites have first been described in Mongolia and Russia (Kovalenko et al., 1971), and similar rocks of Cenozoic age have been described in the American Cordillera of the USA and Mexico (Burt et al., 1982; Christiansen et al., 1984; Congdon and Nash, 1988; Kortemeier and Burt, 1988), and they are in some cases associated with topazite (quartz-topaz rock) dykes. These rocks typically occur in extensional, intraplate/post-collisional settings (Burt et al., 1982; Kovalenko et al., 2007; Taylor, 1992). Ongonites and other strongly fractionated, topaz-bearing rocks are known to be enriched in Li, B, Sn, Zn, W, Mo and U, other than Nb–Ta, to concentrations that can amount to ore deposits (Antipin et al., 2006; Burt et al., 1982; Christiansen and Lee, 1986; Haapala, 1997; Moghazi et al., 2011; Syritso et al., 2012; Taylor, 1992). Niobium–Ta oxides, such as the columbite–tantalite solid solution series and ixiolite, deposited as magmatic accessory phases and in alteration zones around F-rich intrusions, account for most of the current production of these elements worldwide (Melcher et al., 2014).

This study is focussed on a single ongonite sample from the Ary-Bulak massif, Transbaikalia, Russia (Naumov et al., 1971) containing topaz as euhedral phenocrysts, up to 1–2 mm in size, and as elongate microlites (up to 100 μm in length) in the groundmass. The close association of Nb–Ta–(W) oxide with topaz observed in the Ary-Bulak massif (Kovalenko et al., 1975; Peretyazhko et al., 2011) suggests a link between concentrations of these elements and the formation of topaz. Both topaz and quartz phenocrysts host melt inclusions, which can record the evolution of the melt through different stages of crystallisation, and provide evidence of the nature and composition of melt(s) present at the moment of topaz crystallisation. We use detailed textural and microchemical data to gain insight into the formation of topaz in felsic magmatic systems. We show that the CL and chemical zoning of topaz reflect complex processes, and can be used as a proxy for the trace element composition of the parent melt. Our findings have implications on the origin of Nb–Ta–(W) ore deposits associated with F-rich magmas.

2. Geological setting

The 142 ± 0.7 Ma old (Kostitsyn et al., 1996) Ary-Bulak massif forms a laccolith, 700 × 1500 m in size, intruding Late Jurassic–Early Createaceous shales and limestones of the Ust'–Boryza Formation and basalt (Antipin et al., 2009; Kovalenko and Kovalenko, 1976; Peretyazhko and Savina, 2010b). The centre of the Ary-Bulak massif consists of porphyritic ongonite with up to 20 vol.% phenocrysts of sanidine, albite, quartz, Li-mica (zinnwaldite) and occasional topaz. The fine-grained groundmass mostly contains quartz, feldspar and topaz. These rocks contain up to 1.5 wt.% F (Kovalenko et al., 1975; Peretyazhko et al., 2011). To the southwest, the porphyritic rocks grade into an aphanitic variety of ongonite, which forms a quenched contact zone up to 100 m wide (Peretyazhko et al., 2011). These rocks contain rare phenocrysts of quartz and sanidine, and prosopite [$CaAl_2F_4(OH)_4$] (Peretyazhko et al., 2011). Whole-rock analyses indicate strong enrichment in Nb, Ta, W, Sn, Li and Rb in comparison with average continental crust (e.g. up to 73 ppm Nb, 48 ppm Ta, 30 ppm W, respectively), and typically flat or concave upwards primitive-mantle normalised rare earth element (REE) patterns with pronounced negative Eu anomalies (e.g. Syritso et al., 2012). Even higher concentrations of these elements have been measured in melt inclusions (Nb up to 180 ppm, Li up to 698 ppm; Peretyazhko and Savina, 2010b). The massif was emplaced at the same time as other shallow intrusions of similar composition in Eastern Transbaikalia (Khrangilay complex, Badanina et al., 2006). Evidence for the presence of different immiscible saline fluids, brines and melts, including silicate, Ca-fluoride, Mg-fluoride (MgF_2) and aluminofluoride melts in the Ary-Bulak massif, has been provided by inclusion studies (Peretyazhko and Savina, 2010a,2010b; Peretyazhko et al., 2007b). Further, anomalous Cs and As concentrations (up to 17 wt.% Cs) were reported in some quartz-hosted silicate melt inclusions (Peretyazhko and Savina, 2010a; Peretyazhko et al., 2007a). A glass derived by quenching of the CaF melt is also abundant in the groundmass of aphanitic and some porphyritic samples, and results in a positive Ca–F correlation and locally extremely high F contents (up to ~19 wt.%; Peretyazhko et al., 2011). Small (up to 5 μm) quartz-hosted silicate melt inclusions homogenise at 650–750 °C (Peretyazhko et al., 2011), although larger inclusions either homogenise at much higher temperatures (around 1000 °C) or do not homogenise, possibly due to decrepitation.

3. Sample preparation and analytical techniques

A sample of topaz-phyric ongonite from the central part of the Ary-Bulak massif (sample AB1) has been studied in thin section by optical microscopy, back-scattered mode (BSE) and cathodoluminescence (CL) mode of scanning electron microscope (SEM). The trace element variation in topaz phenocrysts was studied in situ by electron probe microanalyser (EPMA) and laser ablation ICP-MS. Part of the sample has been crushed in a steel mortar and sieved. Quartz and topaz grains were hand-picked from the fraction 0.2–1 mm, mounted in epoxy and polished for inspection. Grains selected for melt inclusion studies were extracted from the epoxy using a hot needle and mounted individually. Previous studies have shown the high volatile content of quartz-hosted melt inclusions in these rocks (up to 12 wt.% H_2O; Naumov et al., 1984). During heating experiments, high water contents make quenching to homogeneous glass difficult, and boiling effects are commonly observed upon cooling (Naumov et al., 1971). Thus, we decided to study unheated melt inclusions. Unexposed and exposed melt inclusions were studied by laser Raman spectroscopy, EPMA, energy dispersion spectroscopy (SEM-EDS), and proton-induced X-ray emission microprobe (micro-PIXE).

3.1. EPMA and EDS

EPMA analyses of topaz phenocrysts, feldspar, mica and melt inclusion glass were carried out with a four WDS spectrometer-equipped Cameca SX100 electron microprobe at the Spectrum Centre of the University of Johannesburg. Beam intensity of 10 nA, acceleration of 10 kV and defocused beam (10 μm spot size) were used in order to prevent element diffusion. A set of natural minerals, including fluorite, Na-pyroxene, olivine, almandine, diopside, K-feldspar, wollastonite, halite, apatite, hematite and rutile, were used as reference materials. Elements were analysed for 10 to 30 s on-peak and off-peak. Detection limit, estimated from counting statistics, was between 200 and 500 ppm for most elements, except Fe (800 ppm) and F (1000 ppm). Additional analyses of glass and mineral phases were performed by EDS using a Tescan Vega 3 electron microscope equipped with a (Li)Si X-ray detector at the Spectrum Centre. Element calibration was made on a series of minerals and native elements. Spot size was 2–10 μm, acceleration 20 kV.

3.2. LA-ICP-MS

Trace element compositions of topaz phenocrysts have been investigated using laser ablation inductively-coupled mass spectrometry (LA-ICP-MS) at the University of Tasmania. A Coherent CompEX solid state 193 nm laser, and an Agilent 7500 quadrupole mass spectrometer were used. Analyses were performed along lines placed across growth textures identified by CL images, and into the groundmass. During the analyses, 20 s of background acquisition were followed by 100 s ablation at 3 μm/s speed, corresponding to traverses ~300 μm long. Ablation was performed at 10 Hz repetition rate, 30 μm spot size and 3.5 J/cm^2 fluence. Quantification of element concentrations was obtained using glass NIST 612 as primary standard and assuming stoichiometric abundance of Al, which was used as the internal standard. Glasses GSD1g and BCR were used as secondary standards.

3.3. Raman

In situ, non-destructive Raman analyses of multi-phase melt inclusions and various minerals were performed with a confocal laser