Peralkalinity in peraluminous granitic pegmatites. I. Evidence from whewellite and hydrogen carbonate in fluid inclusions

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Abstract
Fluid inclusions in pegmatite minerals were studied using Raman spectroscopy to determine the carbon species. Carbon dioxide is very abundant in the aqueous liquid and vapor phases. Occasionally, CH₄ was found in the vapor. In the aqueous liquid, HCO₃⁻ was detected in fluid inclusions in tantalite-(Mn) from the Morrua Mine and in late-stage quartz from the Muiâne pegmatite and the Naipa Mine, all in the Alto Ligonha District, Mozambique. Moreover, we observed a carbonate (calcite group) in fluid inclusions in garnet from the Naipa Mine and in beryl from the Morrua Mine, both in the Alto Ligonha District, Mozambique, and a calcite-group carbonate and whewellite [CaC₂O₄·H₂O] in fluid inclusions in topaz from Khoroshiv, Ukraine. The occurrence of oxalate is interpreted to be due to a reaction of some form of carbon (possibly CO or bitumen) with a peralkaline fluid. Our results support the hypothesis that, although counterintuitive, hydrogen carbonate-rich peralkaline fluids may locally be involved in the evolution of peraluminous granitic pegmatites, in which peralkaline minerals are normally absent or very rare.

Keywords: Whewellite, carbonate, hydrogen carbonate, oxalate, CO₂, fluid inclusion, pegmatite

Introduction
Carbon species are of particular interest in geochemistry and petrology because they can provide information on formation conditions. With the exception of the ubiquitous carbon dioxide, they are rare in peraluminous granitic pegmatites. Fluid inclusions with nahcolite [NaHCO₃] and zabuyelite [Li₂CO₃] crystals in addition to aqueous carbonate/bicarbonate-rich solution and CO₂ have been reported to occur in graphic granite of simple pegmatites from the Klippeløkken granite quarry, east of Rønne, Bornholm Island, Denmark (Thomas et al. 2011) and in pegmatitic granites from the Marcação, Gado Branco, and Piciu quarries, in the Borborema Pegmatite Province, NE-Brazil (Beurlen et al. 2014). Similarly, crystal-rich inclusions containing zabuyelite, calcite, pollucite-analcime, quartz/cristobalite, albite, and cookeite were found in spodumene from the Tanco, Jiajika, Muiâne, Bikita, Kamativi, Lacorne, Zhawulong, and other pegmatites (London 1986; Anderson et al. 2001; Lima et al. 2003; Thomas and Davidson 2010; Li and Chou 2016, 2017; Mulja and Williams-Jones 2018; Xiong et al. 2019). Macrosopic primary carbonates [calcite, rhodochrosite, siderite, cerussite (maybe secondary), calcioanalcite-(Ce), bastnaesite-(Ce), synchisite-(Ce), parisite-(Ce), and even zabuyelite] and carbonate-rich fluorapatite are generally very rare in peraluminous granitic pegmatites, but there are several reports from well-studied localities, e.g., the Bennett, Berry-Havey, Dunton, Emmons, Mount Mica, and other pegmatites in Maine, U.S.A., the Palermo No. 1 and No. 2 Mines, New Hampshire, U.S.A., the Foote Mine, North Carolina, U.S.A., the Tanco Mine, Manitoba, Canada (www.mindat.org), and the Khoroshiv (Volyn) pegmatites, Ukraine (Lyckberg et al. 2009). Vuggy masses of Mn and Fe carbonate occur in the core zone of the Mount Mica pegmatite (Simmons et al. 2016). London (2013) noted the occurrence of carbonates (calcite or rhodochrosite) in “pocket” assemblages of granitic pegmatites. Alkali carbonate/bicarbonate-bearing fluid inclusions in graphitic granite and pegmatitic granite have been interpreted to indicate the existence of peralkaline fluids early in the pegmatite evolution (Thomas et al. 2006a, 2011; Beurlen et al. 2014), although peraluminous phases crystallize until the latest stages. On the other hand, it has been argued that zabuyelite, cristobalite, and cookeite in crystal-rich fluid inclusions in spodumene were formed by a late-stage subsolids reaction of spodumene with the entrapped CO₂-rich aqueous fluid (Anderson et al. 2001; Anderson 2013, 2019). Such a reaction appears to have occurred in the case of quartz-hosted primary fluid inclusion containing spodumene, calcite, and rossmanite [□(LiAl₈)Al₆(Si₆O₁₈)(BO₃)₃(OH)(OH)] from the Lacorne spodumene pegmatite (Mulja and Williams-Jones 2018).

Carbonates in peraluminous granitic pegmatites can be viewed as oddities, and their origin is still unclear. Even stranger appears to be the sporadic occurrence of kerite in “pockets” with beryl and topaz in pegmatites at Khoroshiv (Volodarsk-Volynskii), Ukraine (Lyckberg et al. 2009). Because carbon species can provide information about formation conditions, we studied fluid inclusions with carbon-bearing phases in pegmatite minerals from the Alto Ligonha region, Mozambique (von Knorring and Condliffe 1987; Dias and Wilson 2000), the Khoroshiv District, Ukraine (Lyckberg et al. 2009), and the Erongo region, Namibia (Cairncross and Bahmann 2006) using Raman spectroscopy.

Experimental methods
Doubly polished sections were prepared from quartz, beryl, elbaite, tantalite-(Mn), almandine-spessartine, albite, and K-feldspar from four pegmatites (Muiâne,