Effects of thermal annealing on water content and $\delta^{18}$O in zircon

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ABSTRACT

Primary water and oxygen isotope composition are important tools in tracing magma source and evolution. Metamictization of zircon due to U-Th radioactive decay may introduce external secondary water to the crystal, thereby masking the primary water and oxygen isotope signature. Recently, Raman-based screening has been established to select the low-degree metamict zircons. However, such an approach may not be appropriate for ancient samples, in which nearly all zircons are metamict. It was reported that thermal annealing can potentially heal crystals and retrieve primary water content and $\delta^{18}$O information from metamict zircons, given the weaker hydrogen bond of secondary water than that of primary water. Heating experiments at temperatures of 200–1000 °C over a period of 2–10 h reveal that annealing can effectively recover primary water and oxygen isotopes from metamict zircons. Primary water in crystalline and metamict zircons remains intact when heated at <700 °C, while secondary water can be effectively expelled from metamict zircons when heated at 600 °C for >4 h, which represent the optimal annealing treatment condition. Hydrothermally altered zircon is an exception. It only yields the minimum estimate of its primary water contents at 600 °C over a period of >4 h, probably due to partial primary water loss during metamictization for hydrothermal zircons. Moreover, the proportion of low-$\delta^{18}$O (<4.7‰) zircon grains that may be influenced by secondary water dropped from ~21% at <600 °C to ~9% when annealed at >700 °C. This study therefore provides the basis for applying zircon water and $\delta^{18}$O proxies to geologically ancient samples.

Keywords: Metamict zircon, secondary water, primary water, oxygen isotopes, thermal annealing, diffusion

INTRODUCTION

Zircon water content and oxygen-hafnium isotope compositions have been widely used as geochemical tools in constraining igneous processes (Kemp et al. 2007; Liebmann et al. 2021; Meng et al. 2021; Pidgeon et al. 2013, 2017; Valley et al. 1994; Xia et al. 2021; Xu et al. 2021; Yang et al. 2022; Yao et al. 2021). Although zircon is a nominally anhydrous mineral (NAM), it always contains a trace amount of water during its crystallization from magma (hereby termed primary water) (De Hoog et al. 2014; Liebmann et al. 2021; Meng et al. 2021; Wang et al. 2018; Xia et al. 2021; Yang et al. 2022; Yao et al. 2021). Water diffuses slowly in zircon (cf. many other NAMs such as garnet and olivine), indicating that zircon can better retain the primary water content (Ingrin and Zhang 2016; Zhang 2015). It has been reported that primary water in zircon has the potential to be a sensitive magma hygrometer (Xia et al. 2021). Oxygen isotope composition is a powerful tool to trace the source of magma (Valley et al. 1994). For example, Kemp et al. (2007) identified the crust-mantle mixing origin of I-type granites (cf. many other NAMs such as garnet and olivine), indicating that water is present in the form of hydrous mineral inclusions or fluid inclusions (Woodhead et al. 1987; Nasdala et al. 1995, 2001b; Palenik et al. 2003; Woodhead et al. 1991a). Crystal lattice of metamict zircon is expanded and open to infiltration of external secondary water (Nasdala et al. 2001a; Pidgeon et al. 2013), thereby masking the primary water content. For example, the water content in metamict zircon can be up to 16.3 wt% (Aines and Rossman 1986). In metamict zircons, water is present in the form of hydrus mineral inclusions or fluid inclusions (Woodhead et al. 1991b). In addition, some neutral H$_2$O molecules may be present along cracks and grain boundaries (Woodhead et al. 1991b). Since the oxygen isotope composition of secondary water may be different from that of zircon, the measured $\delta^{18}$O of metamict zircon could deviate significantly from its original signature (Gao et al. 2014; Liebmann et al. 2021; Wang et al. 2014; Yang et al. 2022). Moreover, zircon with high-radiation damage has a different matrix effect from that of crystalline zircon (Allen...