Dry annealing of metamict zircon: A differential scanning calorimetry study

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ABSTRACT

We report the results of a differential scanning calorimeter (DSC) study of the annealing of a metamict Sri Lankan zircon. Raman measurements on most chips of the powdered zircon starting material, Sri Lankan zircon (WZ19), showed no evidence of a crystalline structure, whereas a few chips retained residual Raman bands typical of highly radiation damaged zircon. DSC runs on aliquots of the powdered sample were heated to 850 and 1000 °C at rates of 2 and 10 °C/min and to 1500 °C at a rate of 10 °C/min. Raman spectroscopy was used to investigate the crystallinity of grains at selected temperature stages. Exothermal peaks were observed at about 910 and 1260 °C during the DSC run to 1500 °C. The 910 °C peak was demonstrated by Raman spectroscopy to mark the crystallization of tetragonal zirconia and the exothermic peak at about 1260 °C was demonstrated to represent the reaction of zirconia and amorphous silica to form crystalline zircon. The degree of crystallinity of these grains was almost identical to that of highly crystalline zircons from recent gem gravels from New South Wales. A small number of experimental chips from DSC analyses under 1000 °C were found to have zircon Raman bands that indicated they had undergone partial annealing. The present experimental results suggest that reconstitution of amorphous zircon to the crystalline state by dry annealing will rarely occur in terrestrial geological settings, even under extreme metamorphic conditions.

Keywords: Radiation damage, metamict zircon, radiation damage annealing, differential scanning calorimeter, zircon Raman spectra

INTRODUCTION

The breakdown of the zircon structure by the radioactive decay of minor components U and Th and their radioactive daughters has been the subject of research for over 50 years (e.g., Holland and Gottfried 1955; Pabst 1952; Weber 1990; Ewing et al. 2003; Zhang et al. 2000; Nasdala et al. 2001; Geisler et al. 2001, and others). Understanding the damage processes and the structural changes of zircon as it evolves to the metamict state is important in explaining discordant results in zircon U-Pb dating, anomalous zircon (U-Th)/He ages (e.g., Guenthner et al. 2013), and in estimating the integrity of zircon as a host for the disposal of actinide nuclear waste and predicting the properties of zircon in ceramic applications. The annealing of radiation damaged zircon is equally important in the above fields as well as fission track dating (e.g., Hasebe et al. 2003) and has applications in geochronology in its own right (e.g., Pidgeon 2014).

Early investigations of zircon radiation damage and annealing used optical (e.g., Vance and Anderson 1972), X-ray diffraction (XRD) techniques (e.g., Holland and Gottfried 1955) and various density and electron microscope (TEM) techniques (e.g., Weber 1990; McLaren et al. 1994; Capitani et al. 2000). Differential thermal analysis has also been applied (Lipova et al. 1965; Kulp et al. 1952) and more recently Raman spectroscopy has proved to be extremely effective in monitoring changes in radiation damage in zircons (Nasdala et al. 1995; Geisler et al. 2001; Zhang et al. 2000). Several researchers concluded that annealing of metamict zircon takes place in two stages involving first, the formation of zirconia and second, full recrystallization back to the original zircon structure. Weber (1990) reported that annealing of a Pu doped amorphous zircon involved two steps, initial crystallization of pseudo-cubic zirconia at about 1050 °C and full density recovery at about 1450 °C where the zircons transforms back to its original zircon structure. Colombo and Chrosch (1998) also reported that the recovery of thermally treated metamict Sri Lankan zircon involved two phases, zircon and pseudo-cubic ZrO2. Váczi et al. (2009) reported that dry annealing of fully metamict zircon involved initial formation of ZrO2, between 800 and 1000 °C prior to the formation of crystalline zircon above 1150 °C. McLaren et al. (1994) also reported the formation of zirconia on dry heating a high-U Sri Lankan zircon to 900 °C. In the present research our objective was to investigate the progressive annealing and phase changes in metamict zircon during isochronal dry annealing, as determined by a differential scanning calorimeter (DSC) study using Raman spectroscopy to monitor the evolving zircon crystal structure.

THE ZIRCON SAMPLE

The zircon sample used in the study, WZ19, was a black, translucent pebble from the Sri Lankan alluvial deposits. The U and Th concentrations of the pebble, determined on an aliquot of the powdered sample, are 9902 and 2296 ppm, respectively, by isotope dilution ICP-MS. The α-dose experienced by the zircon was 13.2 × 1015 α/µg, determined from the U and Th concentrations and a “radiation damage age” for Sri Lankan zircons of 375 Ma (Palenik...