

In Situ Monitoring of Hydrothermal Leaching from Metamict Zircon by Using Synchrotron X-ray Fluorescence

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Introduction

Studies of fluid-induced trace element mobility in alpha-decay-damaged minerals have important application to U-Pb geochronology [1, 2]. Zircon is commonly used in U-Pb age dating and is a potential host phase for the disposal of weapons plutonium [3]. Experiments conducted on zircon-aqueous fluid interaction [1, 4] show that Pb, U, and Th are mobile in metamict zircon under hydrothermal conditions. However, modeling the hydrothermal leaching of Pb and other elements in metamict minerals is complicated by uncertainties in the structural state of the mineral, nanoscale heterogeneities, and changes in the structure and chemistry of the zircon caused by the interaction with hydrothermal fluids. This modeling problem is addressed by *in situ* x-ray fluorescence analysis of the aqueous fluid during interaction with a zircon grain at elevated temperatures and pressures.

Methods and Materials

Experiments were performed by using a modified hydrothermal diamond anvil cell (Fig. 1). The absorption of the incident and secondary x-rays by the surrounding diamond was reduced by laser drilling

grooves into the diamond to within 80 μm of the fluid sample chamber. A fragment of a metamict zircon from the Georgeville granite, Nova Scotia, was loaded into the cell, together with either dilute HCl or a KF aqueous solution. A Br spike (1000 ppm) was added to the solution for calibration purposes. The zircon was placed at the bottom of the sample chamber such that the incident x-ray beam was blocked by the rhenium gasket. The beam was precisely positioned above the gasket in order to analyze only the solution part of the sample.

The Georgeville zircon is chemically and structurally heterogeneous and contains numerous thorium silicate (thorogummite) inclusions. Figure 2 shows a backscatter electron image of a region within a polished wafer of the zircon used in this study.

Measurements were performed by using an incident x-ray energy of 17.5 keV and a spot size of approximately 20 μm . Spectra were collected continuously in 5-minute intervals by using a 13-element Ge detector. Data analyses involved the measurement of peak areas after fitting and subtraction of the background. X-ray yields were corrected for matrix effects, and the concentration of Pb in solution was quantified by using the Br spike as an internal standard.

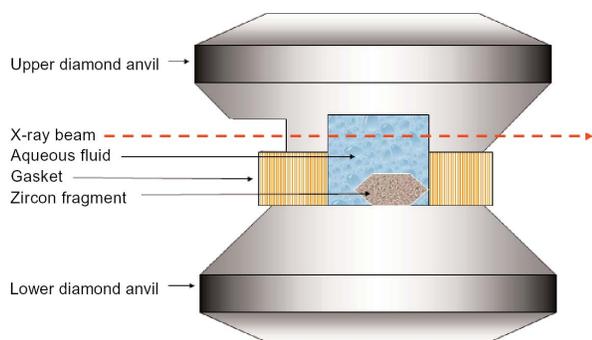


FIG. 1. Modified hydrothermal diamond anvil cell. A sample chamber was milled in the center of the upper anvil, and the diamond was removed to facilitate the transmission of incident and secondary x-rays.

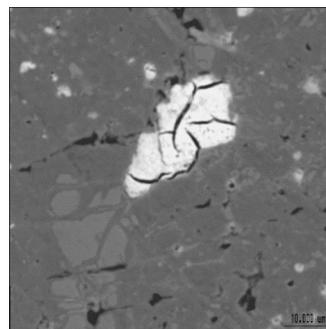


FIG. 2. Backscatter electron image of a region within the Georgeville zircon. The bright inclusions are thorogummite. The zircon host displays nanometer-scale variations in Ca, Y, U, Th, and Yb concentrations due to alteration.

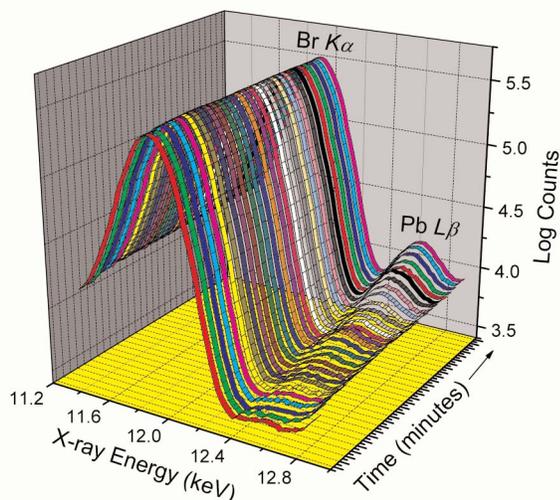


FIG. 3. X-ray fluorescence spectra measured at 300°C from a 5-wt% KF aqueous solution during interaction with a zircon fragment. Spectra were collected in 5-minute intervals for a period of 150 minutes.

Results

The x-ray fluorescence spectra in Fig. 3 show an increase in Pb counts relative to Br as a function of time, measured at 300°C and 110 MPa. The concentration of Br in the solution remained constant at 1000 ppm during the run. The concentration of Pb in the aqueous fluids increased from 0 to 37 ppm over a period of 150 minutes. During the run, the Pb concentration of the aqueous fluid increased at a rate 0.15 ppm/min for first hour, then the rate increased to 0.42 ppm/min.

Discussion

During the experiment, initial leaching of Pb occurred at 300°C in the KF solution and at 400°C in the dilute HCl solution. The variation in the rate of Pb leaching was most likely due to the dissolution of nanometer-size inclusions of galena (PbS) that were encountered by the fluid as it penetrated the nearly amorphous zircon grain. Galena inclusions were also found in zirconolite; they are believed to be the product of precipitated radiogenic Pb [5]. The results demonstrate the potential for using synchrotron x-ray fluorescence and the hydrothermal diamond anvil cell to monitor leaching rates in structurally and chemically complex solids at elevated temperatures and pressures.

Acknowledgments

This work was funded by grants from the Natural Sciences and Engineering Research Council (NSERC) of Canada for research and equipment to A.J. Anderson and by a Research Corporation grant to R.A. Mayanovic. Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contracts W-31-109-ENG-38.

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