LETTER: ACTINIDES IN GEOLOGY, ENERGY, AND THE ENVIRONMENT†
Chemistry and radiation effects of davidite

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ABSTRACT

Davidite (A$_2$M$_2$O$_{21}$) samples from five different geological localities contain approximately 0.2 to 9.5 wt% UO$_2$ (0.02 to 0.65 atoms per formula unit) and <0.1 to 1.3 wt% ThO$_2$ (<0.01 to 0.09 atoms per formula unit). Maximum amounts of other notable cations include 3.7 wt% V$_2$O$_5$, 4.1 wt% Cr$_2$O$_3$, 2.5 wt% Y$_2$O$_3$, 5.6 wt% La$_2$O$_3$, 6.0 wt% Ce$_2$O$_3$, 4.0 wt% MnO, 2.4 wt% ZnO, 2.7 wt% SrO, and 4.9 wt% PbO. As a result of the variation in age and Th-U content, the calculated $\alpha$ decay dose ranges from ~0.2 to 44 $\times$ 10$^{16}$ $\alpha$/mg (~0.06 to 14.5 dpa). For samples with ages of 275–295 Ma, the critical dose for amorphization based on electron diffraction is ~0.8 $\times$ 10$^{16}$ $\alpha$/mg. Natural davidite is commonly altered to rutile, ilmenite, titanite, and other minor phases.

Keywords: Davidite, $\alpha$ decay, uranium, thorium, lanthanides, alteration, amorphization

INTRODUCTION

Davidite, a member of the crichtonite mineral group, ideally A$_2$M$_2$O$_{21}$, is an accessory Fe-Ti-oxide mineral in plutonic, metamorphic, and hydrothermal rocks and may be an important carrier of U, Th, Y, and lanthanides. In general, crichtonite group minerals are also important host phases for transition metals (e.g., Sc, V, Cr, Mn, Zn) and other elements such as Sr, Ba, and Pb. Davidite is unusual as it exhibits a v-shaped chondrite-normalized lanthanide element distribution (Campbell and Kelly 1978). The observed chemical complexity is undoubtedly related to the range of metal cation sites available in the structure (e.g., Gatehouse et al. 1979). The observed lanthanide element pattern of davidite is due to the partitioning of light and heavy lanthanides between the large, 12-coordinated A-site and the smaller M1 octahedral site.

Gong et al. (1995) proposed the crichtonite structure type as a candidate host phase for nuclear waste disposal. Previous research on Synroc titanate ceramics (see Vance 2012 for a recent review) has shown that the crichtonite group mineral loveringite may be present as a major phase in Fe-rich formulations (Lumpkin et al. 1995). One clear advantage of this structure type is the potential to capture a range of actinides, fission products, and processing contaminants. However, there remain a number of concerns for crichtonite waste forms, including the waste loading, processing flexibility, aqueous durability, and radiation damage response. One approach to the assessment of waste form phases is the study of natural analogues (e.g., Lumpkin 2006; Lumpkin and Geisler-Wierwille 2012) and this is the basic theme of the present investigation.

SAMPLES AND METHODS

The samples investigated in this study range in age from approximately 275 to 1580 Ma (see Table 1). Davidite samples from Connecticut (D3), Norway (D2), and Australia (D6, D7) have been assigned ages of 275, 295, and 1580 Ma, respectively, based on geological data reported in previous work (e.g., Ludwig and Cooper 1984; Lumpkin and Ewing 1988; Lumpkin et al. 2012). For the sample from Mozambique (D8), we have adopted an estimated age of 600 Ma based on previous geological information and U-Th-Pb dating (Davidson and Bennett 1950; Darnley et al. 1993; Andreoli 1984). The sample from Arizona (D4) appears to have an age of approximately 145–160 Ma based on a description of the geology, mineralogy, and radiometric dating of the associated Jurassic plutonic rocks of the Quijoota Mountains area, south-central Arizona (Pabst and Thomassen 1959; Anderson and Nourse 2005).

In this paper, we use a nominal age of 150 Ma for calculation of $\alpha$ decay dose (D) and displacements per atom (dpa) for sample D4.

Additional literature data are included in Table 1 for desaurite from the Buca della Vena mine, Tuscany, Italy (Orlandi et al. 1997); loveringite from the Jimberlana intrusion, Western Australia (Campbell and Kelly 1978; Gatehouse et al. 1978); davidite-loveringite from Biggejavir, Norway (Olenad 1988); and davidite from Bidjovagge, Norway (Björljykke et al. 1990). The age of desaurite is not well constrained and could be related to Alpine metamorphism and compressive deformation at 27 Ma or extentional deformation at 8–12 Ma (Costagliola et al. 1999; Montomoli et al. 2005). According to published descriptions, desaurite from Italy and loveringite from Australia are partially to heavily damaged by $\alpha$ decay of Th and U, but do not appear to be completely amorphous as the grains can be restored to single crystals by heat treatment. The samples from Biggejavir and Bidjovagge have been described as amorphous and “non-metamict,” respectively.

Electron beam microanalyses, backscattered electron images, and secondary electron images were obtained from polished sections of the samples using a JEOL JSM-6400 SEM operated at 15 kV and equipped with a Noran Voyager energy-dispersive spectrometer (EDX). The instrument was operated in standardless mode; however, the sensitivity factors were calibrated for semi-quantitative analysis using a range of synthetic and natural standard materials. Analytical data were corrected for matrix effects (absorption, fluorescence, atomic number).

TEM was performed on crushed fragments dispersed on holey carbon grids using a JEOL 2000FXII TEM equipped with a Link ISIS energy-dispersive X-ray (EDX) microanalysis system and operated at 200 kV. The chemistry of the davidite...