Neoproterozoic amorphous "ekanite" (Ca$_2$Th$_{0.9}$U$_{0.1}$Si$_8$O$_{20}$) from Okkampitiya, Sri Lanka: A metamict gemstone with excellent lead-retention performance

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ABSTRACT

A rare gemstone form of "ekanite" from Okkampitiya, eastern Sri Lanka, has a chemical composition of Ca$_2$Th$_{0.9}$U$_{0.1}$Si$_8$O$_{20}$, corresponding to that of the tetragonal mineral ekanite. The Okkampitiya material, however, has undergone amorphization and is found in a fully metamict state, which is ascribed to the long-term accumulation of high levels of self-irradiation damage (1.38×10^{20} alpha decay events per gram). The "ekanite" nevertheless does not show any post-growth chemical alteration, and the radiogenic Pb has been retained. The Okkampitiya "ekanite" yielded a Neoproterozoic ^{207}Pb/^{206}Pb age of 562.1 ± 0.8 Ma (uncertainty quoted at the 95% confidence level) that is concordant within the uncertainties of decay constants. The remarkable Pb-retention performance of "ekanite" contradicts the common hypothesis that metamictization in minerals results in U-Pb discordance. The exceptional chemical durability of the heavily radiation-damaged geological material described here has also implications for materials-science research. High radiation resistance, a key criterion in the search for advanced nuclear waste forms, may not be a prerequisite for high aqueous durability of a solid.

INTRODUCTION

Minerals that incorporate the unstable actinides U and Th in their crystal lattices are subject to corpuscular self-irradiation that, over geologic periods of time, may cause a crystalline to amorphous transition that is referred to as metamictization (Ewing, 1994). The study of radiation-damaged minerals is in particular driven by the need to understand their generally decreased chemical durability (Lumpkin, 2001; Nasdala et al., 2010; Pignatelli et al., 2016). This property change is crucial in the Earth sciences (interpretation of geochronology results, understanding of secondary alteration processes) and materials sciences (assessment of the immobilization performance of potential nuclear waste forms).

It is well known that structural radiation damage enhances the susceptibility of minerals to secondary loss of radiogenic Pb (Krogh and Davis, 1975; Nasdala et al., 1998; Horie et al., 2006; Smye et al., 2014). The U-Pb discordance of actinide-containing minerals therefore

is commonly ascribed to, or even equated to, the radiation-damaged state of samples (Davis and Krogh, 2001; Corfu, 2013, and references therein). Accordingly, geochronologists have undertaken tremendous efforts to remove metamict fractions of samples prior to the isotope analysis (Krogh, 1973, 1982; Mattinson, 2005), in order to obtain less discordant and therefore less biased U-Pb ages. However, we emphasize that there is no absolute link between U-Pb discordance and radiation-damage accumulation. Radiation damage alone does not cause Pb loss or other chemical alteration, as has been shown by the discovery of fully metamict, but nevertheless concordant, zircon (Nasdala et al., 2002).

This feature is also relevant for the immobilization of radioactive waste. Because irradiation-amorphized geological materials may well resist chemical alteration, the same may be true for irradiation-amorphized host ceramics. It is therefore crucial for both geochronologists and materials scientists to understand which solids have high chemical durability (under both dry and wet conditions) even after having become radiation damaged. Here we contribute to this understanding by presenting results of the characterization

of a rather extreme example, the recently found "ekanite" from Okkampitiya, southeastern Sri Lanka (quotes are used herein to indicate that this is not strictly ekanite, because it is an amorphous form of the tetragonal mineral ekanite). This mineral was first discovered in the Ratnapura district, western Sri Lanka (Anderson et al., 1961), and has been found in several other locations worldwide. In spite of being highly radioactive, it has been, and still is, traded as a rare gem material, especially in the Sri Lankan market.

SAMPLES AND EXPERIMENTAL METHODS

The "ekanite" specimens studied originate from Okkampitiya, Moneragala district, Uva province, southeastern Sri Lanka (for details, see the GSA Data Repository[1]). The structural state of samples was investigated by electron diffraction, X-ray diffraction, and Raman and laser-induced photoluminescence (PL) spectroscopy. Electron diffraction patterns were obtained by means of an FEI Tecnai G2 F20 X-Twin thermal emission microscope (TEM). The system was operated at 200 kV and 0.5 nA beam current. Powder X-ray diffraction was done by means of a Philips X'Pert system, using Cu-Kα radiation. Raman and PL were obtained using a Horiba LabRAM HR Evolution system, using 473 nm (8 mW; Raman) and 532 nm laser excitation (12 mW; PL), respectively. The chemical compositions of samples were determined by wavelength-dispersive X-ray analysis, using a CAMECA SX100 electron probe microanalyzer (EPMA) operated at 15 kV acceleration voltage and 40

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nA beam current. The U-Pb age was determined for two "ekanite" fragments by means of solution isotope dilution–thermal ionization mass spectrometry (ID-TIMS) analysis (Krogh, 1973). The two fragments were cleaned with HNO_3, H_2O, and acetone, weighed on a microbalance, transferred to Savillex vials and dissolved in HF after adding a ^{202}Pb-^{205}Pb-^{235}U spike. One of the solutions was then split onto two columns with ion-exchange resin to allow for aliquot analyses. Then Pb and U isotope compositions were measured in a MAT262 mass spectrometer. The spike composition was calibrated against the synthetic ET100 solution (Condon et al., 2008), which is provided by the EARTHTIME initiative (http://www.earthtime.org). Details of the sample solution and isotope measurement procedures were described elsewhere (Corfu, 2004). More experimental and data-reduction details are provided in the Data Repository.

RESULTS

General Description and Characterization

The Okkampitiya "ekanite" mostly shows different shades of green in daylight and vitreous luster, indistinguishable from samples from the western Ratnapura area (Figs. 1A–1F; study and discussion of the color causes are in the Data Repository). Both dark solid and fluid inclusions are prevalent (Fig. 1B), whereas inclusion-free stones (Fig. 1F) are rare. Solid inclusions observed in this study include an apatite-group mineral, thorium silicate, and silica. Whether these inclusions are primary in nature, or have formed following recrystallization within the radiation-damaged "ekanite" host, is unclear. The refraction of the Okkampitiya material was found to vary between 1.575 and 1.594, and its specific gravity is 3.27–3.29 g/cm^3. There is virtually no luminescence under ultraviolet illumination.

The "ekanite" specimens studied here were recovered from gravels in an alluvial gem pit near Okkampitya. The rough stones (Mohs hardness ~6) do not show rounded shapes, as would be expected for a fluviatile gravel material. Rather, some of the material is reminiscent of moldavite-type tektite due to the uneven surface, with a multitude of grooves, bumps, hollows, and cavities (Figs. 1D and 1E). This indicates that the "ekanite" gravel pieces are eluvial or colluvial, deposited near their primary source, which, however, remains unknown.

Results of chemical analyses by means of an EPMA are presented in the Data Repository. The elements U, Pb, and Fe were detected as minor constituents, with fairly uniform concentrations within and among samples. Other elements analyzed were found to be below the respective EPMA detection limit in all, or at least in most, analyses. No indication was found of any fluid-driven or other post-growth
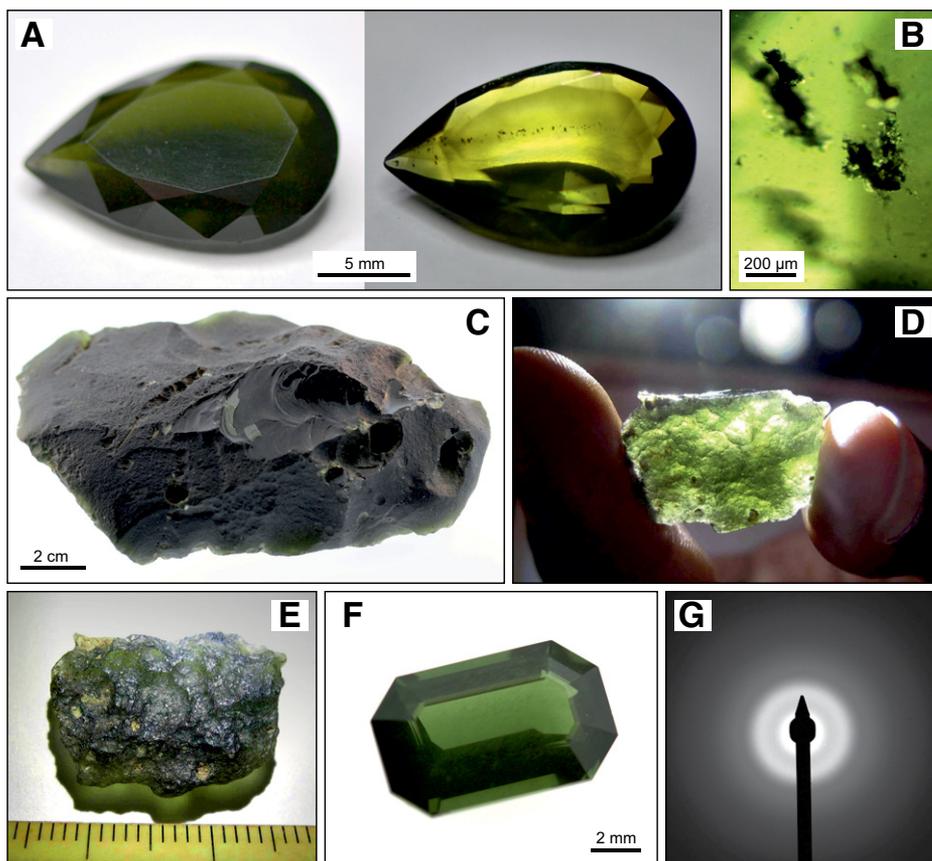

Figure 1. Images of "ekanite" (i.e., amorphous forms of the tetragonal mineral ekanite) samples. A: Photographs of a 7.05 ct stone from Sri Lanka (collection of G. Giester, Vienna, Austria). The typical yellowish bottle-green color is seen under front illumination (left), whereas illumination from behind reveals numerous predominantly xenomorphic inclusions (right). B: Photomicrograph of multiphase inclusions of irregular shape. C: A giant (3211 ct) rough "ekanite" from Eheliyagoda, Ratnapura district, Sri Lanka (collection of the Natural History Museum, Vienna, Austria; M5816). D: A transparent rough stone (11.23 ct) from Okkampitiya. E: Specimen in D in reflected light, showing a moldavite-like (tektite like) appearance. F: Sri Lankan gem "ekanite" (2.34 ct) of exceptional quality (collection of the Natural History Museum, Vienna; M4911). G: Photograph of the electron diffraction pattern of an "ekanite" specimen as observed in the transmission electron microscope.

chemical alteration, such as the presence of elevated levels of non-formula elements or notably deficient EPMA analytical totals (Nasdala et al., 2009). Backscattered electron images (not shown) appeared fairly uniform and did not reveal any alteration textures. The general chemical formula calculated from the EPMA results is $Ca_2Th_{0.9}U_{0.1}Si_8O_{20}$. The chemical composition of the material investigated therefore corresponds well to that of the Ca-Th-silicate mineral ekanite.

Structural State and Radiation Damage

The Okkampitiya samples studied here are not exactly ekanite because they are amorphous, whereas the mineral ekanite, per definition, has a tetragonal crystal structure (space group $I422$; Szymański et al., 1982). As stated above, we therefore refer to the Okkampitiya material as "ekanite" with quotation marks. The amorphous state of the "ekanite" was first revealed by electron diffraction in the TEM. There are no diffraction maxima, merely blurred rings typical of

amorphous solid matter are observed (Fig. 1G). X-ray powder diffraction patterns do not show any distinct Bragg peaks (Fig. 2A) and Raman spectra do not yield distinct vibrational bands (Fig. 2B). Low-intensity emissions related to rare earth elements (REEs) in laser-induced PL spectra are broad, have low intensity, and do not show any crystal field–related fine structure (Fig. 2C).

Dry annealing of the sample material at 1450 °C led to structural reconstitution of (tetragonal) ekanite (Fig. 2). A Rietveld analysis of the X-ray diffraction pattern of the annealed sample (Fig. 2A) yielded unit-cell parameters of $a_0 = 7.461(1)$ Å; $c_0 = 15.011(1)$ Å; $V_0 = 835.6(3)$ Å^3 (space group $I422$). These values correspond well with the ekanite unit-cell parameters of Szymański et al. (1982), who reported $a_0 = 7.448(3)$ Å; $c_0 = 14.893(6)$ Å; $V_0 = 833.9(10)$ Å^3. The Raman spectrum of the annealed sample (Fig. 2B) is assigned to crystalline ekanite, based on its distinct similarity to the Raman spectrum of synthetic $Ca_{0.5}Na_{1.5}ThSi_8O_{20}$ (which, however,
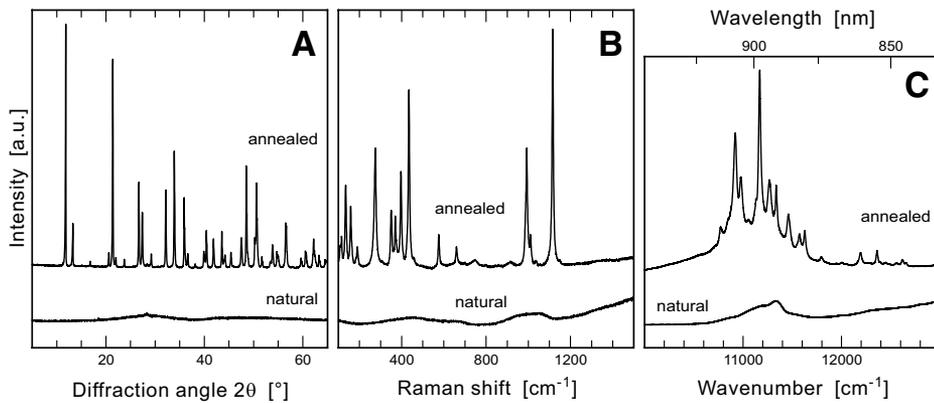
Figure 2. Analytical results before and after dry annealing of "ekanite" (i.e., amorphous forms of the tetragonal mineral ekanite) at 1450 °C. A: X-ray powder diffraction patterns obtained using Cu-Kα radiation. B: Raman spectra (473 nm excitation). C: Photoluminescence spectra (532 nm excitation) showing the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ electronic transition of Nd^{3+} in the near-infrared range.

is tetragonal, space group *P4/mmc*; Jin and Soderholm, 2015). Reconstitution of the crystalline state is indicated also by REE^{3+}-related PL emissions showing crystal field splitting after annealing (for the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ electronic transition of Nd^{3+} shown in Fig. 2C).

U-Pb Geochronology

Results of four single ID-TIMS analyses (two fragments, including replicate analyses on aliquots) are presented in a Concordia plot (Fig. 3); data are available in the Data Repository (Table DR2). The vast majority of the lead present is radiogenic in nature and only ~2–3 ppm is initial Pb (Table DR2); this indicates that Pb was widely excluded in primary growth. The ID-TIMS measurements gave the following means: $^{206}Pb/^{238}U$ age 561.0 ± 2.0 Ma; $^{207}Pb/^{235}U$ age 561.2 ± 1.7 Ma; $^{207}Pb/^{206}Pb$ age 562.1 ± 0.8 Ma (uncertainties quoted at the 95% confidence level). This age seems to agree well with granulite facies metamorphism in southern Sri Lanka during the Pan-African event (Kröner and Williams, 1993). In conclusion, the "ekanite" yielded a concordant Neoproterozoic
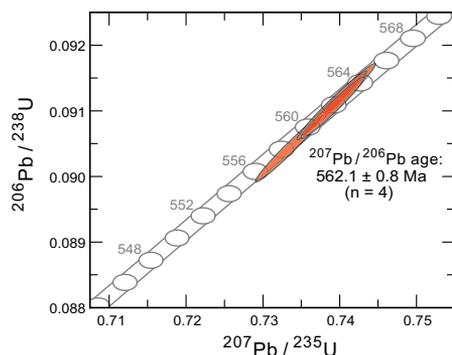

Figure 3. Concordia plot of U-Pb data as obtained by solution isotope dilution–thermal ionization mass spectrometry. Error ellipses represent 2σ uncertainties.

age, without having undergone any noticeable continuous or episodic secondary loss of the radiogenic Pb.

IMPLICATIONS

The amorphous state of the samples studied is interpreted as the result of extensive radioactive self-irradiation. From the present mean concentrations of Th (~225,000 ppm) and U (~20,700 ppm) and the U-Pb age (ca. 561 Ma), a time-integrated self-irradiation dose of 1.38 × 10^{20} alpha (α) events per gram is calculated. Note that this dose is more than one order of magnitude higher than the alpha dose of ~1 × 10^{19} α/g (Zhang et al., 2000; Nasdala et al., 2002) that is needed to cause irradiation-induced amorphization of Sri Lankan zircon. It therefore seems reasonable to interpret the Okkampitiya material studied as a chemically unaltered product of initially tetragonal ekanite, transformed to the present metamict (i.e., amorphous) state because it underwent the impact of a huge alpha event dose over geological periods of time. This is supported also by the observation that dry annealing has resulted in the formation of crystalline ekanite, which we interpret as reconstitution of the initial structural state.

The observed absence of any significant loss of the radiogenic Pb was decidedly against our expectation, given the complete metamictization of the "ekanite" samples studied. In addition, the fresh appearance of the "ekanite," i.e., not showing any indication of post-growth chemical alteration in spite of having been exposed to near-surface weathering, was rather surprising. Similar observations have, however, been made for another mineral: high-U zircon samples may in some cases show no chemical alteration, and, in particular, concordance of the U-Pb isotope system, despite having undergone complete amorphization (Nasdala et al., 2002, 2014; Kostrovitsky et al., 2016). However, significant Pb loss causing strong U-Pb discordance has

been observed from non-metamict zircon (Flowers et al., 2010). These previous results and ours contradict the general assumption that radiation damage directly causes Pb loss (Mezger and Krogstad, 1997; Breeding et al., 2004), chemical alteration (Hoskin, 2005; Hay and Dempster, 2009; Xu et al., 2012), and even complete dissolution and/or destruction of minerals and other solids (Matzke, 1992; Malusà et al., 2013).

We do not deny the well-established fact that radiation damage is in strong control of Pb-loss processes, but we do not agree with the reverse: strong radiation damage can be, but must not necessarily be, associated with Pb loss. The example of Okkampitiya "ekanite" verifies that even irradiation-induced amorphization of a solid may well accompany excellent long-term alteration resistance and lead-retention performance. We may speculate that the variable milieu conditions undergone by a radiation-damaged mineral or material, possibly including weathering and other chemical attacks and/or Pb mobilization in a thermal event, are in control of whether leaching or alteration processes take place. In addition, the accessibility of alteration fluids to radiation-damaged interiors, i.e., to interiors that are particularly susceptible to Pb loss, may be a significant factor (Nasdala et al., 2010; Ault et al., 2012). In contrast, susceptibility of a mineral to radiation-damage accumulation alone cannot be the only control of the occurrence of post-growth chemical changes. Note that zircon (i.e., a mineral that undergoes metamictization) facilitates determination of Eoarchean and even Hadean ages.

The preceding may provide valuable information for the immobilization of radionuclides. One of the quality requirements for advanced nuclear waste forms is their irradiation resistance, and so the search for potential host materials involves, among other studies, irradiation-resistance studies (Wang et al., 1999; Sickafus et al., 2000). We are not proposing that the mineral ekanite be used for immobilizing radionuclides because this would require extensive experimental performance assessment. However, the rather extreme case of metamict but nevertheless unaltered and concordant "ekanite" may stimulate some reconsideration whether materials considered for advanced nuclear-waste immobilization need necessarily to be irradiation resistant. Rather, future searches for potential host forms for nuclear waste should address the immobilization performance (chemical durability and aqueous leachability) of minerals and related materials after being irradiation damaged or even amorphized.

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