Data repository: Neoproterozoic "ekanite" ($Ca_2Th_{0.9}U_{0.1}Si_8O_{20}$) from Okkampitiya, Sri Lanka: A metamict gemstone with excellent lead-retention performance

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1. Background information

The discovery of the Ca-Th-phyllosilicate ekanite (ideal chemical formula Ca₂Th[Si₄O₁₀]₂) began in 1953, when Mr. F.L.D. Ekanayake of Colombo, a Sri Lankan customs officer and Fellow of the Gemmological Association, came across two unusual gemstones in the local Colombo gem market. These dark green, cabochon-cut stones originated from a gem pit near Eheliyagoda, located northwest of Ratnapura, in Sri Lanka's Sabaragamuwa province (Gübelin, 1961, 1962). Initially, the stones were suspected to be a devitrified antique glass (Mitchell, 1954). However, Mr. Ekanayake – who was described as "good and painstaking gemologist with a flair for the unusual" by Mitchell (1961) – was still convinced the material represented a new gem variety and mineral species. Its natural formation was, among others, indicated by the observation of inclusions that, in spite of being inside a glassy host, showed apparent crystallographic orientation. It took, however, eight years until the appearance of the first description of the mineral ekanite (Anderson et al., 1961), which was named in honor of its discoverer F.L.D. Ekanayake. More detailed delineations of the course of discovery are found elsewhere (Gübelin, 1961, 1962; De Silva, 2008; Tennakone, 2011).

In the first publication, ekanite was described as a metamict mineral (Anderson et al., 1961). The tetragonal structure of ekanite, space group *I*422, was first determined by Szymański et al. (1982) from non-metamict sample material from the Thombstone Mountains, Yukon Territory, Canada. Earlier findings of "crystalline ekanite" (Ginzburg et al., 1965; Mokeyeva and Golovastikov, 1966; Richard and Perrault, 1972; Perrault and Richard, 1973) are

to be assigned to alkali-bearing analogs of this mineral, such as turkestanite (Pautov et al., 1997) and steacyite (Perrault and Szymański, 1982). In the meantime, several more occurrences of ekanite have been discovered, including other Sri Lankan gem fields (Dissanayake et al., 2000), Tulare County, California (Walstrom and Dunning, 2003), Pitigliano, Grosseto Province (Demartin et al., 1982) and Monte Somma, Naples Province (Russo et al., 2013) in Italy, and Siberia, Russia.

We have studied "ekanite" specimens that originate from a new location: Okkampitiya, Moneragala district, Uva province, eastern Sri Lanka. Here, the Buttala klippe derived from the Highland Complex is located within rocks of the Vijayan Complex (Mathavan and Fernando, 2001; see also Munasinghe and Dissanayake, 1982; Zoysa, 2014). The area is characterized by Proterozoic rocks that have experienced high-grade metamorphism during the Pan-African event at ca. 610–520 Ma (Kröner et al., 2013). The Okkampitiya-Buttala field hosts many small placer deposits of gem-bearing sediments, many of them being located within karstic potholes and chasms in marble. The majority of heavy gemstones in these sediments are believed to be derived from rocks of the Highland Complex in the northwest, transported over tens of kilometers into the area by the Kumbukkan Oya river (Mathavan et al., 2000).



Supplementary Figure DR1: Simplified geological map of the southern part of Sri Lanka (modified from Mathavan and Fernando, 2001; Kröner et al., 2013). O = Okkampitiya (location of the new "ekanite" find). E = Ellawalla near Eheliyagoda (location of first discovery that has produced gem "ekanite" for many years). KC = Kadugannawa Complex. MQ = Miocene to Quaternary.

2. Analytical details

For X-ray powder diffraction analysis, the range 5–95° 20 was scanned with a step size of 0.02° 20 and an effective scan speed of 12 s per step. Structure refinement of the annealed sample was done using Rietveld refinement (e.g., Rietveld, 1969) using Bruker's Topas software. For Raman and PL analysis, the Horiba Evolution spectrometer was calibrated using the Rayleigh line and Kr-lamp emissions. Further experimental details are described in Lenz et al. (2015).

For EPMA (electron probe micro-analyzer) analysis, slabs were coated with carbon. The following lines were analyzed (the respective calibrant materials, which included synthetic standards and natural references, and the peak/background counting times are quoted in brackets): Na–K α (albite; 20/10 s), Si–K α (sanidine; 20/10 s), P–K α (fluorapatite; 20/10 s), K– K α (sanidine; 20/20 s), Ca–K α (wollastonite; 20/10 s), Ti–K α (TiO; 40/20 s), Mn–K α (spessartine; 20/10 s), Fe–K α (almandine; 20/10 s), Sr–L α (SrSO₄; 40/20 s), Y–L α (YPO₄; 40/20 s), Zr–L α (zircon; 20/10 s), La–L α (LaPO₄; 40/20 s), Ce–L α (CePO₄; 40/20 s), Nd–L β (NdPO₄; 20/10 s), Sm–L β (SmPO₄; 30/15 s), Gd–L β (GdPO₄; 30/15 s), Pb–M α (vanadinite; 120/60 s), Th–M α (CaTh[PO₄]₂; 20/10 s), and U–M β (U metal; 80/40 s). Detection limits for individual elements were calculated using Cameca's Peaksight software, which is based on the method of Ziebold (1967). The modified $\phi(\rho z)$ routine of Merlet (1994) was used for matrix correction and data reduction. More EPMA experimental details are described elsewhere (Breiter et al., 2009; Škoda et al., 2015).

Oxide	Content [*] (wt%)	Detection limit [†] (wt%)	
SiO ₂	55.7 ± 0.5	0.02	
CaO	13.3 ± 0.1	0.03	
FeO	0.14 ± 0.01	0.04	
PbO	$\textbf{0.79}\pm\textbf{0.03}$	0.03	
ThO ₂	$\textbf{26.9} \pm \textbf{0.3}$	0.07	
UO ₂	$\textbf{2.76} \pm \textbf{0.18}$	0.05	
Total	99.8 ± 0.6		

Supplementary Table DR1: Chemical composition of Okkampitiya "ekanite".

Note: The elements Na, P, K, Ti, Mn, Sr, Y, Zr, La, Ce, Nd, Sm, and Gd have also been analyzed. Data are not reported here because concentrations were in most cases below the detection limit of our EPMA.

* Means of 33 individual analyses.

⁺ Calculated using the Peaksight software, following Ziebold (1967).

3. U-Pb geochronology data

For converting isotopic ratios into ages, and for plotting the results, a 238 U decay constant of 1.55125×10^{-10} a⁻¹ and a 235 U decay constant of 9.84850×10^{-10} a⁻¹ (Jaffey et al., 1971) were used. The Isoplot program (Ludwig, 2003) was used for the calculation of ages and for the preparation of the Concordia plot.

Nr.	Weight (μg)	U (ppr	T n) (pr	'n [*] om)	Th/U [*]	²⁰⁶ Pb/ ²⁰⁴ Pb [†]	Pb _{total} (ppm)	Pb _{com} § (ppm)
1	28	202	00 226	600	11.2	48189	7315	2.3
2	15	244	00 262	2700	10.8	49283	8656	2.7
3	57	192	00 206	6900	10.8	58430	6821	1.8
4	57	191	00 206	500	10.8	59680	6810	1.8
Nr.	²⁰⁶ Pb/ ²³⁸ U [#]		²⁰⁶ Pb/ ²³⁸ U	207 r	7 הר <i>ו</i> 235, ו#	207 pr /206 pr #	²⁰⁷ Pb/ ²⁰⁶ Pb	Disc.**
			age [#] (Ma)	U ^{ar} (de			age [#] (Ma)	(%)
1	0.09042±0.0	00042	558.0±2.5	0.733	36±0.0037	0.05884±0.0006	561.2±2.2	0.6
2	0.09103±0.0	00038	561.6±2.3	0.739	92±0.0034	0.05889±0.0006	563.0±2.2	0.3
3	0.09107±0.0	00043	561.9±2.5	0.739	90±0.0037	0.05886±0.0006	561.8±2.2	0.0
4	0.09114±0.0	00046	562.3±2.7	0.739	99±0.0040	0.05888±0.0006	562.5±2.2	0.0
Mea	n ages:		561.0±2.0				562.1±0.8	0.2

Supplementary Table DR2: Results of ID-TIMS U-Pb isotopic analyses.

Notes: Isotopic ratios are corrected for common Pb (204 Pb method). Isotopic ratios and ages are quoted with 2σ uncertainties.

^{*} Th abundance and model Th/U ratio were calculated from ²⁰⁸Pb/²⁰⁶Pb and sample age.

[†] Measured ratio.

§ Fraction of initial common lead (i.e. Pb of non-radiogenic origin).

[#] Corrected for fractionation, spike, blank and initial common Pb.

^{**} U-Pb discordance (i.e. 1 minus the quotient of the ²⁰⁴Pb-corrected ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²⁰⁶Pb ages).

4. Coloration analysis (optical absorption spectroscopy) details

Optical absorption spectra were measured at room temperature in the spectral range 28600–2000 cm⁻¹ (350–5000 nm wavelength) by means of a Bruker IFS66v/S FTIR spectrometer equipped with a mirror-optics IR-scope II microscope. Appropriate combinations of light sources, beam splitters and detectors were used: Xe lamp, quartz beam splitter and GaP detector for the range 28600–20000 cm⁻¹ (1024 scans; 40 cm⁻¹ spectral resolution); W lamp, quartz beam splitter and Si detector for the range 20000–10000 cm⁻¹ (1024 scans; 20 cm⁻¹ spectral resolution); W lamp, quartz beam splitter and Si detector for the range 20000–10000 cm⁻¹ (1024 scans; 20 cm⁻¹ spectral resolution); W lamp, quartz beam splitter and Ge detector for the range 10000–5200 cm⁻¹ (512 scans; 10 cm⁻¹ spectral resolution); globar, KBr beam splitter and liquid-nitrogen cooled MCT (mercury cadmium telluride) detector for the range 5200–2000 cm⁻¹ (512 scans; 10 cm⁻¹ spectral resolution). The final optical absorption spectrum hence consists of a combination of four sub-spectra, which were aligned to match in absorbance if necessary. Circular areas 200 µm in diameter were analyzed in transmission geometry.





Cut "ekanite" gems typically appear dark green in reflected light but may show much lighter colors in transmitted light, in some cases the highly valuated banana-leaf yellowish green (Fig. 1A). There are two main spectral features in the visible range of the electromagnetic spectrum that are in virtual control of the coloration. First, an absorption continuum increases gradually in the blue range toward the ultraviolet. Second, a broad absorption band lies in the orange to red range (maximum near 15700 cm⁻¹, or 637 nm wavelength). The two features bracket an "optical transmission window" in the green to yellowish green range, at around 17900 cm⁻¹. "Ekanite" is also well transmitting in the red range below 15000 cm⁻¹; this however contributes only to a much lesser extent to the mineral color, due to the comparably poor sensitivity of the human eye in this spectral range. The 15700 cm⁻¹ band is assigned to absorption related to an irradiation-induced defect, perhaps the oxygen-site vacancy. This

absorption band is hence considered, with appropriate restraint, as some kind of analog of the irradiation-induced defect absorption in diamond (GR1: neutral C-site vacancy; Clark and Walker, 1973). Our assignment to a defect-related (rather than a trace-element-related) center is supported by the disappearance of this band after defect healing and structural reconstitution through dry annealing. Outside the visible range and hence without contribution to the coloration, the absorption spectrum is characterized by two near-infrared bands (near 7000 and 9750 cm⁻¹) that are assigned to uranium (compare Vance, 1973; Zhang et al., 2003). A broad, asymmetric band in the mid-infrared range (near 3530 cm⁻¹) might be due to the presence of small amounts of molecular H₂O. Based on the calibration of Libowitzky and Rossmann (1997), the band integral observed corresponds to hypothetical water content on the order of 0.02 wt%.

5. Additional discussion

The accumulation of radiation damage in minerals is controlled by two competing processes, namely, self-irradiation causing atomic displacements, and thermal annealing (Meldrum et al., 1998; Nasdala et al., 2001). Any information on the post-formation thermal history of the "ekanite" hence would be most valuable in evaluating the present radiation damage.

The absence of any water-worn surface features of the "ekanite" indicates short transportation-pathway lengths, indicating eluvial or colluvial gravels. However, no country rock was found exposed in the Okkampitiya gem pit, and no possible host rock has been discovered thus far whose weathering may have released the "ekanite". In conclusion, the primary source of the "ekanite" remains fully unknown.

There is the striking observation that virtually all zircon specimens from Ratnapura gem gravels seem to have experienced the same uniform (low-temperature) thermal history which has resulted in incomplete retention of the radiation damage (Nasdala et al., 2004). It seems reasonable to consider that the "ekanite" must have experienced a similar thermal history and also may have retained a fraction of the total damage sustained. Very obviously, even this partial damage accumulation was sufficient to cause complete amorphization.

Davis and Krogh (2000) have discussed that Pb leachability from zircon depends strongly on the irradiation dose, with annealed zircon being virtually not leachable at all. These authors concluded that the effectiveness of any nuclear-waste-disposal medium should be improved if it is kept at a temperature above the level for spontaneous annealing of α -event damage. Based on our and other recent results, we hold to a different opinion. Keeping solids at elevated temperatures may indeed prevent accumulation of the radiation damage through continuous annealing. The drawbacks are that (i) diffusion rates and chemical reactivity are increased at elevated temperatures, and (ii) numerous annealings following ballistic displacements involve numerous atomic movements that contradict the immobility requirement.

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