Emanation coefficients for radon (\(^{222}\)Rn) and thoron (\(^{220}\)Rn) were measured from fully metamict samarskite collected from Centennial Cone after 1 h and 24 h annealing in argon from 473 to 1373 K. For the 1 h annealing run, \(^{222}\)Rn emanation coefficients ranged from \(5 \times 10^{-6}\) to \(2.1 \times 10^{-5}\)%, while \(^{220}\)Rn coefficients varied from \(6.3 \times 10^{-3}\) to \(2 \times 10^{-2}\)%.

For the 24 h annealing run, \(^{222}\)Rn coefficients ranged from \(5.8 \times 10^{-6}\) to \(2.3 \times 10^{-5}\)%, while \(^{220}\)Rn coefficients varied from \(4.1 \times 10^{-3}\) to \(1.5 \times 10^{-2}\)%.

The \(^{222}\)Rn and \(^{220}\)Rn emanation coefficients versus annealing temperature data can be described by an exponentially decreasing sinusoidal function. Both \(^{222}\)Rn and \(^{220}\)Rn emanation coefficient values after annealing considerably exceeded those measured from an unheated powder reference sample and from the original samarskite sample.

**Keywords:** samarskite, radon emanations, thoron emanations, recrystallization, Centennial Cone, \(^{222}\)Rn, \(^{220}\)Rn
INTRODUCTION

Samarskite is a complex Nb-Ta-Ti-REE + Y-Ca-U-Th multiple oxide containing uranium, thorium, iron and other elements and has always been found to be completely metamict (Sugitani et al. 1985). Due to its chemical complexity and metamictization, samarskite's chemical formula and crystal structure have not been unambiguously characterized. The proposed structural formulae are: $\text{AB}_2\text{O}_6$, $\text{A}_3\text{B}_5\text{O}_{16}$ and $\text{ABO}_4$ where $\text{A} = \text{REE, U, Th, Ca, Fe and Ti}$, and $\text{B} = \text{Nb, Ta and Ti}$ (Komkov 1965; Graham and Thornber 1974; Ewing 1975; Lumpkin et al. 1988). The recently suggested $\text{ABO}_4$ formula is based on microprobe analysis of 19 samarskite samples after annealing at 800°C under hydrogen and on analysis of samarskite-(Yb) from the Little Patsy pegmatite annealed under a weakly reducing atmosphere at temperatures up to 1100°C (Warner and Ewing 1993; Simmons et al. 2006).

Radon isotopes $^{222}\text{Rn} \ (T_{1/2} = 3.82 \text{ d})$ and $^{220}\text{Rn} \ (T_{1/2} = 55.6 \text{ s})$ belong to the $^{238}\text{U}$ and $^{232}\text{Th}$ decay series and occur as inert gases. As part of the uranium series, $^{226}\text{Ra}$ decays by $\alpha$ emission ($E_\alpha = 4.77 \text{ MeV}$) to form a $^{222}\text{Rn}$ nucleus with an energy of 86 keV. Similarly, $^{224}\text{Ra}$ decays as part of thorium series by $\alpha$ emission ($E_\alpha = 5.67 \text{ MeV}$) with a recoil energy of 103 keV for the daughter $^{220}\text{Rn}$ nucleus. Estimated direct recoil lengths for $^{222}\text{Rn}$ and $^{220}\text{Rn}$ within solids typically range from 20-50 nm (Sakoda et al. 2010; Ishimori et al. 2013). For example, the calculated recoil ranges for $^{222}\text{Rn}$ and $^{220}\text{Rn}$ in quartz and zircon are 34 and 38 nm, and 23 and 26 nm, respectively (Sakoda and Ishimori, 2017). These relatively short ranges mean that without internal defects only radon atoms formed near the mineral surface can be detected as emanations (Krupp et al. 2017 and references therein). Emanation coefficients help characterize retention of radon isotopes within mineral matrices. These ratios (reported as percentages) estimate the number of radon or thoron atoms released
from the mineral relative to the number of radon or thoron atoms produced by the
decay series occurring within the mineral (Semkow 1990; Morawska and Phillips
1993). Emanation coefficients for metamict minerals can be correlated with uranium
and thorium concentrations as well as with their spatial distributions, absorbed \( \alpha \)-
doses, grain size and nuclear track annealing rates. Emanation coefficients may
reflect the extent of structural void space and cracks created by radiation damage
from progressive overlap of recoil nuclei cascades of \(^{238}\text{U}, ^{232}\text{Th} \) and \(^{235}\text{U} \) and their
daughter products.

Few studies have addressed radon emanations from metamict minerals and
only one study has considered radon and thoron emanations from a large sample of
samarskite (Malczewski and Dziurowicz 2015). This study analyzes a fragment of the
same massive, dark brown, fully metamict specimen of samarskite (SCC; Fig. 1)
collected from a granitic pegmatite in Centennial Cone, Jefferson County, Colorado
(USA). Table 1 lists basic characteristics of the SCC specimen. According to
nomenclature proposed for samarskite-group minerals, the SCC sample described
here categorizes as samarskite-(Y) (Hanson et al. 1999; Simmons et al. 2006). As
seen in Table 1, the uranium and thorium concentrations correspond to a calculated
total absorbed \( \alpha \)-dose, \( D_T \), of \( 6.5 \times 10^{17} \alpha \)-decay mg\(^{-1} \). The \( \alpha \)-decays from the \(^{238}\text{U} \)
and \(^{235}\text{U} \) series comprise the dominant contribution to the total \( \alpha \)-dose of samarskite
from Centennial Cone. The ratio of \( \alpha \)-doses from \( D_{238} + D_{235} \) to \( D_{232} \) is about 27.

The aim of the study is to determine the relationship between \(^{222}\text{Rn} \) and \(^{220}\text{Rn} \)
emanations and annealing temperature for powdered samples of samarskite.
Additionally, this work aims to show that \(^{222}\text{Rn} \) and \(^{220}\text{Rn} \) emanations can be
correlated with the thermally induced transition from the low- to high-temperature
phase of samarskite. Results obtained are compared with emanation values from a
fragment of the original sample, the unannealed powdered reference sample, and
with values from powdered monazite, thorite, uraninite and zircon samples crushed to
comparable small grain size as reported from literature sources (Table 2).

MATERIALS AND METHODS

Concentrations of $^{238}\text{U}$ and $^{232}\text{Th}$ were determined from the intact SCC sample
using $^{214}\text{Pb}$ and $^{214}\text{Bi}$ ($^{238}\text{U}$), and $^{228}\text{Ac}$ ($^{232}\text{Th}$) gamma-ray activities. Activity
concentrations of $^{235}\text{U}$ assumed a natural abundance of $^{238}\text{U}/^{235}\text{U} = 137.88$. Gamma-
ray spectra were recorded using a GX3020 system consisting of a coaxial HPGe
detector (32% efficiency) in a lead and copper shield (60 mm) with a multichannel
buffer (InSpector 2000 DSP). The detector bias voltage was 4000 V and the energy
resolution was 0.8 keV at 122 keV and 1.7 keV at 1.33 MeV. Two software packages
were used for the efficiency calibration and the determination of radionuclides:
LabSOCS (Laboratory Sourceless Calibration Software) and Genie 2000 v.3.4.

After breaking the sample SCC into fragments, 20 pieces of about 2 g were
placed in quartz tubes, sealed under argon, and annealed for 1 h and 24 h in a muffle
furnace. The temperature program ran from 473 K to 1373 K in increments of 100 K.
The furnace stabilized each temperature step within ± 2°C. After annealing, the
samples were quenched and mechanically ground to an average grain size fraction
of 5 μm using an agate ball mill. The original material, crushed to 5 μm grain size but
not annealed, is herein designated SRE. The grain sizes were determined for all
samples using scanning electron microscopy. Six months after annealing, the
powdered samples were placed in copper discs with an outer diameter of 5 cm, an
inner diameter of 2 cm, and a 0.15 cm deep groove. The discs were inserted into a
stainless steel cylinder ($\phi = 8 \text{ cm}$, $h = 3 \text{ cm}$) with two inlets on opposite sides. After
insertion, the lid was firmly tightened and inlets were connected to a desiccant and a
RAD7 inlet (Fig. 2). The RAD7 radon system (Durridge Company, Inc.) was used to measure $^{222}$Rn and $^{220}$Rn emanations. Detailed description of RAD7 electronics and measurement configurations are provided by Durridge Company, Inc. (2000) and in Malczewski and Dziurowicz (2015). The detector operates with a sensitivity of 4 Bq m$^{-3}$, an upper linear detection limit of 800 kBq m$^{-3}$, and a manufacturer’s calibration accuracy of ± 5%. The drying unit remained open to the ambient air (open loop mode). Measurement for a given powdered sample occurred over a 15 min cycle repeated 10 times for a total run time of 150 min. Each measurement was conducted independently using three RAD7 detectors operating within a temperature range of 20 - 23°C and 4 - 8% internal humidity. The final results represent the average of these three runs. Similar to previous reports (Malczewski and Dziurowicz 2015; Malczewski et al. 2018), the total emission rates for $^{222}$Rn ($E_{222}$) and $^{220}$Rn ($E_{220}$) from the samples were calculated in atoms s$^{-1}$ according to the following equations:

$$E_{222} = \frac{C_{222} \cdot v}{6 \cdot 10^4 \cdot \lambda_{222}}$$  \hspace{1cm} (1)

and

$$E_{220} = \frac{1.28 \cdot C_{220} \cdot v}{6 \cdot 10^4 \cdot \lambda_{220}}$$  \hspace{1cm} (2)

where $C_{222}$ and $C_{220}$ are respective $^{222}$Rn and $^{220}$Rn concentrations minus the ambient concentrations (Bq m$^{-3}$) and $v$ is the flow rate of 1 L min$^{-1}$. The terms $\lambda_{222}$ and $\lambda_{220}$ are respective decay constants for $^{222}$Rn and $^{220}$Rn of 2.1 x $10^{-6}$ and 0.012 s$^{-1}$ (Firestone 1996). Our experimental setup (Fig. 2) included a 20 s delay between the emission and measurement by the RAD7 unit. The $C_{220}$ term was therefore multiplied by 1.28.
The $^{222}\text{Rn}$ and $^{220}\text{Rn}$ emanation coefficients ($e_{222}$ and $e_{220}$, respectively) were calculated as the ratio of $^{222}\text{Rn}$ and $^{220}\text{Rn}$ atoms emitted from a samarskite sample ($s^{-1}$) and the total amount of $^{222}\text{Rn}$ and $^{220}\text{Rn}$ produced within the sample. Coefficient equations were as follows:

$$e_{222} = \frac{E_{222}}{N_{222}}$$  \hspace{1cm} (3)$$

and

$$e_{220} = \frac{E_{220}}{N_{220}}$$  \hspace{1cm} (4)$$

where $N_{222}$ and $N_{220}$ represent respective estimates of $^{222}\text{Rn}$ and $^{220}\text{Rn}$ nuclei in the sample. Since $\gamma$-emitters in both uranium series ($^{234m}\text{Pa} \rightarrow ^{226}\text{Ra} \rightarrow ^{214}\text{Pb} \rightarrow ^{214}\text{Bi}$) and thorium series ($^{228}\text{Ac} \rightarrow ^{224}\text{Ra} \rightarrow ^{212}\text{Pb} \rightarrow ^{212}\text{Bi} \rightarrow ^{208}\text{Th}$) were in radioactive equilibrium within the sample analyzed, we assumed that $^{222}\text{Rn}$ and $^{220}\text{Rn}$ values equaled corresponding $^{238}\text{U}$ and $^{232}\text{Th}$ activity concentrations.

Powdered and annealed samarskite samples were also analyzed for their X-ray diffraction (XRD) patterns using a Philips X’Pert diffractometer measuring CuK$\alpha$ radiation from the $\Theta-\Theta$ system in scan mode with a 0.02° step size. Figures 3 and 4 show XRD patterns. These figures indicate recrystallization of the fully metamict samarskite SCC begins at 673 K and 573 K for samples subjected to 1 h and 24 h annealing, respectively. The positions of the main diffraction peaks are the same as those reported by Sugitani et al. (1984) for a Kawabe samarskite (Japan) obtained after annealing at 550, 650 and 950° C in a reducing H$_2$ atmosphere. Sugitani et al. (1984) suggested that the original samarskite phase is formed only under reducing...
conditions, whereas our results suggest that heating in an inert argon atmosphere also restores metamict samarskite to its original crystalline state.

RESULTS

Table 3 lists the total emission rates and calculated $^{222}$Rn and $^{220}$Rn emanation coefficients for the unannealed reference sample and samples of samarskite after annealing in argon for 1h ($e_{1h222}$ and $e_{1h220}$). Table 4 lists the total emission rates and $^{222}$Rn and $^{220}$Rn emanation coefficients ($e_{24h222}$ and $e_{24h220}$) calculated for samples after 24 h annealing in argon.

$^{222}$Rn emanation coefficients versus temperature after 1 h annealing

As shown in Table 3 and Fig. 5, the unheated reference sample (SRE) gave the lowest $^{222}$Rn emanation value of $4.9 \times 10^{-6}$ %. For annealed samples, emanation coefficients varied from $5 \times 10^{-6}$ % to $2.1 \times 10^{-5}$ % with an average (arithmetic mean) value of $1.51 \times 10^{-5}$ %. Among annealed samples, those annealed at 973 K (S7) and 1073 K (S8) gave the lowest $e_{1h222}$ values of $5 \times 10^{-6}$ % and $9.6 \times 10^{-6}$ %, whereas those annealed at 673 K (S4) and 573 K (S3) gave the highest values of $2.1 \times 10^{-5}$ % and $2 \times 10^{-5}$ %. Figure 5 shows $e_{1h222}$ initially increasing from 473 K to 673 K. At annealing temperatures of 773-873 K, $e_{1h222}$ significantly decreases to a minimum value observed at 973 K (S7). After this point, $e_{1h222}$ values gradually increase up to 1373 K (S11).

$^{220}$Rn emanation coefficients versus temperature after 1h annealing

Similar to the $^{222}$Rn emanation data, the unheated reference sample (SRE) gave the lowest observed $^{220}$Rn emanation value of $3.8 \times 10^{-3}$ % (Tab. 3 and Fig. 6). For annealed samples, $^{220}$Rn emanation coefficients ($e_{1h220}$) ranged from $6.3 \times 10^{-3}$ % to $\sim 2 \times 10^{-2}$ % with an average value of $1.27 \times 10^{-2}$ %. Samples annealed at 973 K
(S7) and 1173 K (S9) gave the lowest $e_{1h220}$ values of $6.3 \times 10^{-3}$ % and $8.4 \times 10^{-3}$ %, whereas those annealed at 1373 K (S11) and 773 K (S5) gave the highest $e_{1h220}$ values of $2 \times 10^{-2}$ % and $1.8 \times 10^{-2}$ %, respectively. As seen in Fig. 6, $^{220}$Rn emanation coefficients increase from 473 K to 773 K and then, similar to $^{222}$Rn emanation coefficients, rapidly decrease to a minimum at 973 K (S7). At higher temperatures, $^{220}$Rn emanation coefficients increase up to a maximum value observed at 1373 K (S11). Variation in $^{220}$Rn emanation coefficients with temperature resemble those observed for $^{222}$Rn emanation coefficients except for sample S11, which gave the highest $e_{1h220}$ value observed.

$^{222}$Rn emanation coefficients versus temperature after 24 h annealing

As shown in Table 4 and Fig. 7, and similar to the $^{222}$Rn emanation coefficients after 1h annealing, all samarskite samples annealed for 24 h gave higher $e_{24h222}$ values than those of the unannealed reference sample ($e_{SRE222}$; Tab. 3). The $^{222}$Rn emanation coefficients for samples annealed for 24 h ranged from $5.8 \times 10^{-6}$ % to $2.3 \times 10^{-5}$ % with an average value of $1.34 \times 10^{-5}$ %. Samples annealed at 473 K (S12) and 1373 K (S21) gave the lowest $e_{24h222}$ values of $5.8 \times 10^{-6}$ % and $9 \times 10^{-6}$ %, whereas those annealed at 573 K (S13), 673 K (S14) and 773 K (S15) gave the highest values of $2.3 \times 10^{-5}$ % and $2 \times 10^{-5}$ % (respectively). Figure 7 shows that the $e_{24h222}$ emanation coefficient increases fourfold from sample S12 (473 K) to sample S13 (573 K) and noticeably decreases to a local minimum for sample S17 (973 K). In contrast to the 1h annealing data, $e_{24h222}$ values for samples annealed at the highest temperatures decrease with increasing temperature.

$^{220}$Rn emanation coefficients versus temperature after 24 h annealing
Similar to the $^{220}\text{Rn}$ emanation coefficients after 1 h annealing, the unheated reference sample (SRE) also gave the lowest $^{220}\text{Rn}$ emanation value after 24 h (Tables 3 and 4 and Fig. 8). For samarskite samples annealed for 24 h, $^{220}\text{Rn}$ emanation coefficients ($e_{24h220}$) ranged from $4.1 \times 10^{-3}\%$ to $1.5 \times 10^{-2}\%$ with an average value of $9.87 \times 10^{-3}\%$. Samples annealed at 473 K (S12) and 1073 K (S18) gave the lowest $e_{24h220}$ values of $4.1 \times 10^{-3}\%$ and $5.7 \times 10^{-3}\%$, whereas samples annealed at 773 K (S15) and 673 K (S14) gave the highest values of $\sim1.5 \times 10^{-2}\%$ (for both). The $^{220}\text{Rn}$ emanation coefficients increase from 473 K to 773 K and then significantly decrease to a second minimum at 1073 K (S18). The $e_{24h220}$ values increase for samples annealed at 1173 K (S19) and 1273 K (S20), but the $e_{24h220}$ value for sample S21 annealed at 1373 K decrease to $7.4 \times 10^{-3}\%$. Variation in $^{220}\text{Rn}$ emanation coefficients ($e_{24h220}$) with temperature resembles those observed for $^{222}\text{Rn}$ emanation coefficients ($e_{24h222}$; Fig. 7) except in the case of sample S18 (1073 K), which exhibited a distinct minimum (Fig. 8).

**DISCUSSION**

Samples of samarskite annealed for both 1 h and 24 h gave maximum $^{222}\text{Rn}$ emanation coefficients ($e_{1h222}$ and $e_{24h222}$) within a 573 K to 773 K temperature range. Both datasets also showed a clear minimum at 973 K (Figs. 5 and 7). Samples annealed for 1 h above 973 K gave $e_{1h222}$ values that increase up to 1373 K whereas those annealed for 24 h gave $e_{24h222}$ values that decrease at 1273 K and 1373 K.

Using the analogy of a damped sinusoidal vibration, the variation in all $e_{1h222}$, $e_{24h222}$, $e_{1h220}$, and $e_{24h220}$ emanation coefficients with temperature, after annealing for 1 h and 24 h in argon, can be relatively well fitted using an exponentially decreasing sinusoidal function of the form:

\[(5)\]
\[ e_i(\%) = e_{0i} + A_i \cdot \exp(-b_i \cdot T) \cdot \sin(c_i \cdot (T - T_{0i})) \]

where \( e_{0i} \) is the weighted average of \( e_i \), \( A_i \) is the initial amplitude of the envelope, \( b_i \) is the damping factor of emanation, and \( T_{0i} \) is the temperature at which \( e_i \) equals \( e_{0i} \). The term \( c_i = \pi / \Delta T_i \), where \( \Delta T_i \) is the periodicity of \( e_{0i} \) and \( T_{0i} \). The index \( i \) (\( i = 1, 2, 3, \) and \( 4 \)) refers to \( e_{1h222}, e_{24h222}, e_{1h220}, \) and \( e_{24h220} \), respectively. The parameters are explained in Fig. 9, the values of the fitted parameters are listed in Table 5, and the fitted curves are shown in Fig. 10.

The function graphs exhibit two temperature ranges, from 473 K to about 1000 K and from 1000 K to 1373 K, which generally coincide with the recrystallization path proposed by Sugitani et al. (1984). Their research suggested that the low-temperature orthorhombic samarskite phase formed after 16 h annealing in \( \text{H}_2 \) at 550°C (823 K) and then on heating up to 950°C (1273 K), at which point a high-temperature monoclinic phase is formed. A splitting of the most intense diffraction peak \( (2\Theta \approx 30^\circ) \) into a doublet accompanies the transition from the low- to high-temperature phase. For the Kawabe samarkite, it occurred after heating at 650°C (923 K), whereas in our study the same main diffraction peak \( (2\Theta \approx 30^\circ) \) began splitting at 973 K (Figs. 3 and 4). Warner and Ewing (1993) annealed samarskite samples at 800°C (1073 K) in an \( \text{H}_2 \) atmosphere for 4 h. Those annealed samples were not completely crystalline, which agreed well with our results. Tomašić et al. (2010) analysed a fully metamict samarskite from Beinmyr pegmatite (Norway) annealed in air and \( \text{Ar}/\text{H}_2 \) atmosphere. The high-temperature samarskite phase was not observed at temperatures lower than 800°C (1073 K). The TGA-DTA data for samarskite from Beinmyr recorded from RT (298 K) to 1000°C (1273 K) showed a strong endothermic peak occurring at about 300°C (573 K). This result coincides well
with the observation of the highest emanations of $^{222}$Rn in a narrow temperature range of 573 to 673 K (Figs. 5 and 7).

As shown in Table 5, the calculated $b_i$ values after 24 h annealing, both for $e_{24hh222}$ and $e_{24h220}$, are about one to two orders of magnitude higher than those for $e_{1h222}$ and $e_{1h220}$ after 1 h annealing. Combined with X-ray patterns, this means that the high-temperature and long-lasting (24 h in this case) annealing lead to the formation of a stable, fully crystalline polymorph of samarskite. As a result, small fluctuations for both $e_{24hh222}$ and $e_{24h220}$ emanation coefficients about their average values are observed (Figs. 10 b and d). After 1 h of annealing, these fluctuations are noticeably higher (Figs. 10 a and c).

As seen in Fig. 11, ratios of $e_{1h222}$ to the $^{222}$Rn emanation coefficient of the unheated sample ($e_{SRE222}$) ranged from 1 to 4 with an average 3.1. Ratios of $e_{1h222}$ to the $^{222}$Rn emanation coefficient reported for original SCC sample ($e_{SCC222}$; $1.28 \times 10^{-6}$) varied from 8 to 16 with an average value of 11.8. Ratios corresponding to $^{222}$Rn emanation coefficients after 24 h annealing gave similar values. As shown in Fig. 12, the ratio of $e_{24h222}$ to the SRE reference sample emanation coefficient ranged from about 1 to 5 with an average value of 2.7. Ratios of $e_{1h222}$ to the SCC $^{222}$Rn emanation coefficient varied from 5 to 18 with an average value of 10.4. Average $^{222}$Rn emanation coefficients for samarskite samples ground to a ~5 μm grain size fraction were about two orders of magnitude lower than those reported by Garver and Baskaran (2004) for samples of monazite, zircon, thorite and uraninite, which were crushed to the grain sizes of less than 63 μm and annealed at 873 K for 6 h (Tab. 2). These samples gave ratios of the coefficients from $^{222}$Rn emanations after annealing at 873 K to the coefficients from unannealed samples from 0.25 to 0.57, with an average value of 0.4. This value differs from the respective $e_{1h222}/e_{SRE222}$ and
e$_{24h222}$/e$_{SRE222}$ values of 3.1 and 2.7 reported here. Our results show that annealed samples of samarskite SCC always result in higher values of $^{222}$Rn emanation than the unannealed reference sample. A similar effect should be observed for other metamict phases.

The 1.27 x $10^{-2}$ average value for $^{220}$Rn emanation coefficients after 1 h annealing (e$_{1h220}$) slightly exceeded the 9.87 x $10^{-3}$ average value calculated for samarskite samples after 24 h annealing (e$_{24h220}$). Generally, $^{220}$Rn emanation coefficients from both 1 h and 24 h annealing exceed $^{222}$Rn emanations (e$_{1h222}$ and e$_{24h222}$) by about three orders of magnitude. Figure 13 shows that ratios of e$_{1h220}$ to the $^{220}$Rn emanation coefficient for the unannealed reference sample (e$_{SRE220}$) range from about 2 to 5 with an average value of 3.3. Ratios of e$_{1h220}$ to the original SCC sample $^{220}$Rn emanation coefficient (e$_{SCC220}$ = 3.8 x $10^{-4}$ %) vary from 17 to 51 with an average value of 33. After 24 h annealing (Fig. 14), ratios of e$_{24h220}$ to the emanation coefficient of the SRE reference sample range from about 1 to 4 with an average value of 2.6. Ratios of e$_{24h220}$ to SCC sample $^{220}$Rn emanation coefficients vary from 11 to 40 with an average value of 26. From Figs. 11-14, it appears that the emanation coefficients for both the $^{222}$Rn and $^{220}$Rn, annealed at temperatures from 473 K to 1373 K, are 3 times higher on average than these observed for the unannealed sample. These figures also show that the emanation coefficients for both $^{222}$Rn and $^{220}$Rn from samarskite SRE, crushed to 5 µm grain size, exceeded by only one order of magnitude those observed for the intact 4 cm fragment, SCC. A similar effect with reference to granite was reported by Amin and Rama (1986). There was no observed significant difference between radon emanation coefficients from a granite cube with a 30 cm edge and 1-2 mm granite grains.

**IMPLICATIONS**
The observed variations in the $^{222}$Rn and $^{220}$Rn emanation coefficients with temperature for samples of fully metamict samarskite-(Y) ground to a 5 $\mu$m grain size and annealed from 473 K to 1373 K coincide well with the structural conversion from a low- to high-temperature samarskite phase reported in previous studies. The same mineral species showed noticeably different emanation coefficients of radon and thoron depending on the crystallographic system induced by annealing in an argon atmosphere. The $^{222}$Rn emanation coefficients obtained both for 1 h and 24 h annealing were significantly lower than the values reported in the literature for comparable metamict minerals. The results reported here indicate that samarskite-(Y) behaves as a closed system for radon retention across a very broad temperature range, from an untreated sample to a sample annealed at 1373 K, despite the high concentration of uranium and unusual structural complexity.

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**Figure captions**

**FIGURE 1.**
Photo of fully metamict samarskite (SCC) from Centennial Cone, Colorado, USA. The specimen is 4 cm in length. About half of the specimen was used in this study.

**FIGURE 2.**
Experimental setup for measuring $^{222}$Rn and $^{220}$Rn emanations from powdered samarskite samples.

**FIGURE 3.**
X-ray diffraction (XRD) patterns for the unheated SRE samarkite sample and samples after 1 h annealing under argon from 473 K (S2) to 1373 K (S11).

**FIGURE 4.**
X-ray diffraction (XRD) patterns for samarskite samples after 24 h annealing under argon from 473 K (S12) to 1373 K (S21).

FIGURE 5.

$^{222}$Rn emanation coefficients for unheated SRE samarskite sample ($e_{\text{SRE}222}$) and for samples after 1 h annealing in argon ($e_{1h222}$) from 473 K to 1373 K.

FIGURE 6.

$^{220}$Rn emanation coefficients for unheated SRE samarskite sample ($e_{\text{SRE}220}$) and for samples after 1 h annealing in argon ($e_{1h220}$) from 473 K to 1373 K.

FIGURE 7.

$^{222}$Rn emanation coefficients for unheated SRE samarskite sample ($e_{\text{SRE}222}$) and for samples after 24 h annealing in argon ($e_{24h222}$) from 473 K to 1373 K.

FIGURE 8.

$^{220}$Rn emanation coefficients for unheated SRE samarskite sample ($e_{\text{SRE}220}$) and for samples after 24 h annealing in argon ($e_{24h220}$) from 473 K to 1373 K.

FIGURE 9.

The parameters used in this work to describe variations in the $^{222}$Rn and $^{220}$Rn emanation coefficients with temperature, based on Eq. (5).

FIGURE 10.

Plots of (a) $e_{1h222}$, (b) $e_{24h222}$, (c) $e_{1h220}$, and (d) $e_{24h220}$ versus temperature. The solid lines show the fit to the experimental data based on Eq. (5). Thin horizontal lines represent the fitted values of $e_{0i}$.

FIGURE 11.
Plot of ratios of $^{222}$Rn emanations from samarskite samples after 1 h annealing $(e_{1h222})$ to $^{222}$Rn emanation from unheated reference sample $(e_{SRE222})$ (circles) and ratios of $e_{1h222}$ to $^{222}$Rn emanation from original sample $(e_{SCC222})$ (triangles) versus temperature. Thin solid line shows average $e_{1h222} / e_{SRE222}$ ratio and thick solid line shows average $e_{1h222} / e_{SCC222}$ ratio.

FIGURE 12.

Plot of ratios of $^{222}$Rn emanations from samarskite samples after 24 h annealing $(e_{24h222})$ to $^{222}$Rn emanation from unheated reference sample $(e_{SRE222})$ (circles), and ratios of $e_{24h222}$ to $^{222}$Rn emanation from original large sample $e_{SCC222}$ (triangles) versus temperature. Thin solid line shows average $e_{24h222} / e_{SRE222}$ ratio and thick solid line shows average $e_{24h222} / e_{SCC222}$ ratio.

FIGURE 13.

Plot of ratios of $^{220}$Rn emanations from samarskite samples after 1 h annealing $(e_{1h220})$ to $^{220}$Rn emanation from unheated reference sample $(e_{SRE220})$ (squares) and ratios of $e_{1h220}$ to $^{220}$Rn emanation from original sample $(e_{SCC220})$ (inverted triangles) versus temperature. Thin solid line shows average $e_{1h220} / e_{SRE220}$ ratio and thick solid line shows average $e_{1h220} / e_{SCC220}$ ratio.

FIGURE 14.

Plot of ratios of $^{220}$Rn emanations from samarskite samples after 24 h annealing $(e_{24h220})$ to $^{220}$Rn emanation from unheated reference sample $(e_{SRE220})$ (squares) and ratios of $e_{24h220}$ to $^{220}$Rn emanation from original sample $(e_{SCC220})$ (inverted triangles) versus temperature. Thin solid line shows average $e_{24h220} / e_{SRE220}$ ratio and thick solid line shows average $e_{24h220} / e_{SCC220}$ ratio.
### Table 1

Age, basic chemical composition (wt.%), calculated absorbed $\alpha$-doses and $^{222}$Rn and $^{220}$Rn emanation coefficients for the original intact samarskite sample (SCC).

<table>
<thead>
<tr>
<th>Element</th>
<th>wt.%</th>
<th>Calculated Absorbed $\alpha$-Doses</th>
<th>$e_{^ {222} \text{Rn}}$</th>
<th>$e_{^ {220} \text{Rn}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>20.12(81)</td>
<td>6.5 x $10^{17}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>2.39(10)</td>
<td>2.3 x $10^{16}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>2.0(1)</td>
<td>5.77 x $10^{17}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>1.78(10)</td>
<td>4.97 x $10^{16}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>2.83(15)</td>
<td>1.28 x $10^{-6}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>7.17(32)</td>
<td>3.8 x $10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>29.05(64)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>5.19(54)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>2.69(56)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Th</td>
<td>1.82(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>10.54(40)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$a$ Bryant et al (1981). $b$ Doses were calculated as: $D_{238} = 8 \times N_{238}(e^{1.238} - 1)$, $D_{235} = 7 \times N_{235}(e^{0.235} - 1)$, $D_{232} = 6 \times N_{232}(e^{1.232} - 1)$ and $D_T = D_{238} + D_{235} + D_{232}$. $N_{238}$, $N_{235}$ and $N_{232}$ are the present number of atoms of $^{238}$U, $^{235}$U and $^{232}$Th per milligram, $\lambda_{238}$, $\lambda_{235}$ and $\lambda_{232}$ are the decay constants of $^{238}$U, $^{235}$U and $^{232}$Th (respectively), and $t$ is the geologic age. The absorbed $^{238}$U $\alpha$-doses were calculated assuming a natural atomic abundance of $^{238}$U/$^{235}$U = 137.88. $c$ $^{222}$Rn emanation coefficient ($e_{222}$) and $^{220}$Rn emanation coefficient ($e_{220}$).
Table 2

Previously reported $^{222}\text{Rn}$ emanation coefficients for metamict minerals crushed to grain size of less than 63 $\mu$m and heated for 6 h (Garver and Baskaran 2004).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating temperature (K)</th>
<th>$e_{222}$ (%)</th>
<th>$e_{600/RT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monazite</td>
<td>RT</td>
<td>2.05</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>873</td>
<td>0.66</td>
<td>0.32</td>
</tr>
<tr>
<td>Zircon</td>
<td>RT</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>873</td>
<td>0.47</td>
<td>0.45</td>
</tr>
<tr>
<td>Uraninite</td>
<td>RT</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td></td>
<td>873</td>
<td>0.30</td>
<td>0.57</td>
</tr>
<tr>
<td>Thorite</td>
<td>RT</td>
<td>5.38</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>873</td>
<td>1.34</td>
<td>0.25</td>
</tr>
</tbody>
</table>

| Average | 0.40       |
Table 3
Total emission rates and $^{222}$Rn and $^{220}$Rn emanation coefficients for the samarskite samples after 1 h annealing and for unheated reference sample (SRE).

<table>
<thead>
<tr>
<th>Annealing temperature (K)</th>
<th>Sample</th>
<th>$N_{^{222}}$ (10$^8$ atoms)</th>
<th>$E_{^{222}}$ (atom s$^{-1}$)</th>
<th>$e_{1h^{222}}$ (%)$^a$</th>
<th>$N_{^{220}}$ (10$^3$ atoms)</th>
<th>$E_{^{220}}$ (atom s$^{-1}$)</th>
<th>$e_{1h^{220}}$ (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>SRE</td>
<td>7.26</td>
<td>35.6</td>
<td>4.90 x 10$^6$</td>
<td>7.23</td>
<td>0.27</td>
<td>3.76 x 10$^{-3}$</td>
</tr>
<tr>
<td>473</td>
<td>S2</td>
<td>4.91</td>
<td>56.1</td>
<td>1.14 x 10$^5$</td>
<td>4.89</td>
<td>0.46</td>
<td>9.46 x 10$^{-3}$</td>
</tr>
<tr>
<td>573</td>
<td>S3</td>
<td>2.93</td>
<td>58.9</td>
<td>2.01 x 10$^5$</td>
<td>2.92</td>
<td>0.30</td>
<td>1.02 x 10$^{-2}$</td>
</tr>
<tr>
<td>673</td>
<td>S4</td>
<td>4.95</td>
<td>102</td>
<td>2.07 x 10$^5$</td>
<td>4.93</td>
<td>0.83</td>
<td>1.69 x 10$^{-2}$</td>
</tr>
<tr>
<td>773</td>
<td>S5</td>
<td>4.91</td>
<td>93.3</td>
<td>1.90 x 10$^5$</td>
<td>4.89</td>
<td>0.88</td>
<td>1.79 x 10$^{-2}$</td>
</tr>
<tr>
<td>873</td>
<td>S6</td>
<td>6.04</td>
<td>112</td>
<td>1.86 x 10$^5$</td>
<td>6.02</td>
<td>0.82</td>
<td>1.36 x 10$^{-2}$</td>
</tr>
<tr>
<td>973</td>
<td>S7</td>
<td>6.96</td>
<td>35</td>
<td>5.04 x 10$^6$</td>
<td>6.94</td>
<td>0.44</td>
<td>6.34 x 10$^{-3}$</td>
</tr>
<tr>
<td>1073</td>
<td>S8</td>
<td>5.69</td>
<td>54.9</td>
<td>9.65 x 10$^6$</td>
<td>5.67</td>
<td>0.53</td>
<td>9.34 x 10$^{-3}$</td>
</tr>
<tr>
<td>1173</td>
<td>S9</td>
<td>4.75</td>
<td>65</td>
<td>1.37 x 10$^5$</td>
<td>4.74</td>
<td>0.37</td>
<td>8.36 x 10$^{-3}$</td>
</tr>
<tr>
<td>1273</td>
<td>S10</td>
<td>5.29</td>
<td>83.5</td>
<td>1.58 x 10$^5$</td>
<td>5.27</td>
<td>0.79</td>
<td>1.49 x 10$^{-2}$</td>
</tr>
<tr>
<td>1373</td>
<td>S11</td>
<td>4.98</td>
<td>87.2</td>
<td>1.75 x 10$^5$</td>
<td>4.97</td>
<td>0.98</td>
<td>1.97 x 10$^{-2}$</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td>1.51 x 10$^{-3}$</td>
<td></td>
<td>1.27 x 10$^{-3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Estimated uncertainties $\Delta e_{^{222}}/e_{^{222}} < 14\%$. $^b$ Estimated uncertainties $\Delta e_{^{220}}/e_{^{220}} < 10\%$. 
Table 4

Total emission rates and $^{222}$Rn and $^{220}$Rn emanation coefficients for samarskite samples after 24 h annealing.

<table>
<thead>
<tr>
<th>Annealing temperature (K)</th>
<th>Sample</th>
<th>$N_{222}$ (10$^8$ atoms)</th>
<th>$E_{222}$ (atom s$^{-1}$)</th>
<th>$e_{24h222}$ (%)$^a$</th>
<th>$N_{220}$ (10$^3$ atoms)</th>
<th>$E_{220}$ (atom s$^{-1}$)</th>
<th>$e_{24h220}$ (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>473</td>
<td>S12</td>
<td>6.81</td>
<td>39.7</td>
<td>5.82 x 10$^{-5}$</td>
<td>6.79</td>
<td>0.28</td>
<td>4.14 x 10$^{-5}$</td>
</tr>
<tr>
<td>573</td>
<td>S13</td>
<td>3.29</td>
<td>75.3</td>
<td>2.29 x 10$^{-5}$</td>
<td>3.28</td>
<td>0.45</td>
<td>1.37 x 10$^{-5}$</td>
</tr>
<tr>
<td>673</td>
<td>S14</td>
<td>3.49</td>
<td>69.2</td>
<td>1.98 x 10$^{-5}$</td>
<td>3.48</td>
<td>0.51</td>
<td>1.46 x 10$^{-5}$</td>
</tr>
<tr>
<td>773</td>
<td>S15</td>
<td>4.91</td>
<td>96.1</td>
<td>1.96 x 10$^{-5}$</td>
<td>4.89</td>
<td>0.74</td>
<td>1.52 x 10$^{-5}$</td>
</tr>
<tr>
<td>873</td>
<td>S16</td>
<td>5.21</td>
<td>60.1</td>
<td>1.16 x 10$^{-5}$</td>
<td>5.19</td>
<td>0.65</td>
<td>1.04 x 10$^{-5}$</td>
</tr>
<tr>
<td>973</td>
<td>S17</td>
<td>5.69</td>
<td>54.5</td>
<td>9.56 x 10$^{-6}$</td>
<td>5.67</td>
<td>0.50</td>
<td>8.83 x 10$^{-6}$</td>
</tr>
<tr>
<td>1073</td>
<td>S18</td>
<td>7.57</td>
<td>93.2</td>
<td>1.23 x 10$^{-5}$</td>
<td>7.54</td>
<td>0.43</td>
<td>5.74 x 10$^{-5}$</td>
</tr>
<tr>
<td>1173</td>
<td>S19</td>
<td>3.98</td>
<td>49.4</td>
<td>1.24 x 10$^{-5}$</td>
<td>3.96</td>
<td>0.37</td>
<td>9.20 x 10$^{-5}$</td>
</tr>
<tr>
<td>1273</td>
<td>S20</td>
<td>4.70</td>
<td>50.4</td>
<td>1.07 x 10$^{-5}$</td>
<td>4.68</td>
<td>0.45</td>
<td>9.51 x 10$^{-5}$</td>
</tr>
<tr>
<td>1373</td>
<td>S21</td>
<td>6.48</td>
<td>58.6</td>
<td>9.02 x 10$^{-6}$</td>
<td>6.46</td>
<td>0.48</td>
<td>7.40 x 10$^{-5}$</td>
</tr>
</tbody>
</table>

Average 1.34 x 10$^{-5}$ 9.87 x 10$^{-4}$

$^a$ Estimated uncertainties $\Delta e_{222}/e_{222} \leq 14\%$.

$^b$ Estimated uncertainties $\Delta e_{220}/e_{220} \leq 10\%$. 
Table 5

Fitted parameters for the function given by Eq. (5).

<table>
<thead>
<tr>
<th>i</th>
<th>Parameter</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$e_0$ (%)</td>
<td>$1.37 \times 10^{-5}$</td>
<td>$1.17 \times 10^{-5}$</td>
<td>$1.24 \times 10^{-2}$</td>
<td>$9.1 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$A_i$ (K$^{-1}$)</td>
<td>$1.48 \times 10^{-5}$</td>
<td>$3.27 \times 10^{-4}$</td>
<td>$6.1 \times 10^{-3}$</td>
<td>$6.9 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$b_i$ (K$^{-1}$)</td>
<td>$6.8 \times 10^{-4}$</td>
<td>$5.3 \times 10^{-3}$</td>
<td>$9.8 \times 10^{-5}$</td>
<td>$3.9 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$T_0$ (K)</td>
<td>506</td>
<td>504</td>
<td>547</td>
<td>520</td>
</tr>
<tr>
<td></td>
<td>$\Delta T_i$ (K)</td>
<td>339</td>
<td>346</td>
<td>342</td>
<td>415</td>
</tr>
<tr>
<td></td>
<td>Adj. $R^2$</td>
<td>0.82</td>
<td>0.81</td>
<td>0.78</td>
<td>0.76</td>
</tr>
</tbody>
</table>

* Individual uncertainties estimated for parameters are $\leq 20\%$
FIGURE 3
FIGURE 8
FIGURE 12