Radiation Measurements 47 (2012) 195–200

Contents lists available at SciVerse ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

Radiation-induced cathodoluminescent signatures in calcite

Danielle K. Silletti [a], Sarah A. Brokus [a], Elly B. Earlywine [a], Joshua D. Borycz [a], Graham F. Peaslee [a,*], Paul A. DeYoung [b], Nickie J. Peters [c], J. David Robertson [c], JoAnn Buscaglia [d]

[a] Chemistry Department, Hope College, 35 E. 12th St, Holland, MI 49423, USA
[b] Physics Department, Hope College, 27 Graves Pl., Holland, MI 49423, USA
[c] Chemistry Department and Research Reactor Center, University of Missouri, Columbia, MO 65211, USA
[d] Federal Bureau of Investigation, Laboratory Division, Counterterrorism and Forensic Science Research Unit, Quantico, VA 22135, USA

ARTICLE INFO

Article history:
Received 15 July 2011
Received in revised form
10 December 2011
Accepted 21 December 2011

Keywords:
Cathodoluminescence
Calcite
Neutron irradiation
Nuclear forensics

ABSTRACT

At ambient temperatures, a permanent change due to neutron irradiation has been identified in the luminescent properties of the common mineral calcite. Calcite is one of many ubiquitous minerals that are known to exhibit luminescence under electron bombardment, a process known as cathodoluminescence (CL). The UV–Visible spectra of individual calcite grains were measured with CL spectroscopy before and after neutron irradiation. Exposure to neutrons causes additional crystal lattice defects (beyond those naturally-occurring) that leave a permanent, readily-measurable CL signature in the 515 nm region of the spectrum. Dose response results following irradiation have been measured and a spectroscopic signature is described that increases proportionately to neutron dose. The CL measurements are complicated by a dependence on the orientation relative to direction of excitation. When taken into account, the total dose to the crystal can be estimated, and possibly even the direction of the neutron source can be determined. This signature could potentially be developed into a nuclear forensics tool to help identify locations where special nuclear materials have been stored.

1. Introduction

Nuclear proliferation and the potential threat to national security from special nuclear materials (SNM) outside of regulatory control have renewed interest in not only detecting the presence of these substances, but also in the forensic detection of materials' distribution pathways. Typically, the only way to identify where fissile materials have been stored is the measurement of induced radioactivity of adjacent objects by neutrons, due to (n, γ) or neutron capture reactions, since the most intensely ionizing α, β, and γ-radiation from SNM is typically shielded. For most radioisotopes associated with SNM, the induced radioactivity from neutron irradiation can be easily observed for only a few days unless pieces of the radioactive source remain in the area. Thus, there is a pressing need to find new ways to determine where fissile material has been stored. Since neutrons have a long penetration depth, they have the potential to be detected by the changes they induce in the geological constituents of their surroundings.

Calcite, a common carbonate mineral, is found in many different geological formations. Calcite occurs as the primary constituent in limestones and marbles, is a very common cement in clastic sedimentary rocks, and is a main component of hydrothermal deposits. One of the most prevalent minerals in the earth's crust, calcite is also commonly incorporated into conventional building materials such as concrete and plasters. Calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) are two main groups of minerals within the carbonates. Calcite and dolomite have the same isostructure; however, geologically they are distinct from one another. Samples studied for this paper are from dune sand grains.

Minerals such as calcite have been measured by cathodoluminescence (CL) spectroscopy for many years, since the technique was originally developed for use in material science and the geological communities (Palenik and Buscaglia, 2007). CL spectroscopy uses an electron beam to induce fluorescence in certain minerals. The emission of visible light can be observed when the specimen is bombarded with electrons from a cold-cathode tube in a millitorr-range vacuum. Chemical composition and structural defects within each mineral change this emission spectrum and produce a distinct signature for each mineral. To date, CL spectroscopy has only limited use in quantitatively characterizing geological trace materials due to variations in the observed emissions.

---

* Corresponding author. Tel.: +1 616 395 7117; fax: +1 616 395 7118.
E-mail addresses: peaslee@hope.edu (G.F. Peaslee), joann.buscaglia@ic.fbi.gov (J. Buscaglia).

1350-4487/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.radmeas.2011.12.005

Limitations due to differing mineral composition, varying concentration of emitter ions within the mineral lattice, angle of mineral and beam orientations, fluctuating beam intensity and light detection efficiency, and electron channeling are the main problems common in quantitative CL spectroscopy (Habermann, 2002).

In this paper, the quantitative use of CL is proposed as a novel detection method for induced neutron irradiation signatures in calcite. Single naturally-occurring sand grains or geological materials are shown to be reliable passive "dosimeters" for neutron irradiation. This study suggests that the technique could be developed into a nuclear forensic method for the detection of locations where special nuclear materials have been stored. Although thermoluminescence (TL) has been traditionally used with many materials to measure radiation dose (Krbetschek et al., 1997) and the TL signature of calcite has been reported as a measure of natural irradiation (Johnson and Blanchard, 1967; Graves and Roberts, 1972) and has been proposed as a dating method for calcite, the TL measurement is completely destructive. Thus, the capability to repeatedly measure an absorbed radiation dose in calcite with CL has potential applications for a nuclear forensics situation.

2. Methodology

2.1. Calcite samples

Kilogram quantities of beach sand were collected from both the shoreline and back dunes of beach complexes near Holland, MI, which is located along the eastern shores of Lake Michigan. The sand samples were mechanically sieved and a total of 166 individual carbonate grains were hand-selected from the 355–420 μm sieve fraction. This technique would work on any size calcite grains, but the hand-selection becomes more difficult with smaller sieved sand fractions. Each grain was subjected to homogeneity testing with CL spectroscopy prior to neutron irradiation. Three dolomitic grains were discovered during the preliminary screening, where the dominant CL spectral peak centroid was red-shifted by approximately 20 nm relative to calcitic grains from the same sample. These three dolomitic grains were removed from subsequent analysis, resulting in 163 total calcite grains for analysis.

2.2. Experimental conditions

Two neutron sources were used for sample irradiation. A Pu(Be) source was used to irradiate test specimens with a low ($\sim 10^6$ neutrons/cm^2) neutron flux. Further work was completed using the University of Missouri Research Reactor (MURR). At MURR, the samples were irradiated in a pneumatic tube facility at the 10 MW reactor for up to 300 s, subjecting the samples to dosages up to 2.46×10^{13} neutrons. Specific neutron fluences were calculated to be: 0 (not irradiated), 2.46×10^{12} (irradiated for 30 s), 4.92×10^{12} (60 s), 9.83×10^{12} (120 s), 1.47×10^{13} (180 s), and 2.46×10^{13} neutrons (300 s). Both sources produce a spectrum of fast neutrons that are capable of producing lattice defects in mineral crystals.

The dose rate calculations for neutrons and gamma rays from MURR were done using a detailed MCNP5 steady-state model (MCNP X-5, 2005) of the reactor core. In particular, dose rates were computed at target position of irradiation channel ROW2, which is located in the graphite reflector region of the core. Targets to be irradiated in ROW2 are always secured within a Rabbit made of high density polyethylene (HDPE). Therefore, it was essential to include the precise geometry of the Rabbit and its components, and their exact material composition as a fixed part of the MURR core model for the computations. Since HDPE is a hydrogenous material, its presence is expected to further thermalize the neutron flux that traverses it. Therefore, appropriate thermal scattering laws (MCNP X-5, 2005; Mattes and Keinert, 2005) for neutrons were added in its material definition so that the correct thermal neutron distribution is obtained within the Rabbit.

For the MCNP5 calculations, a criticality (i.e., kcode) source was defined. To obtain overall reasonable statistics, the kcode parameters were set so that 80 million source (i.e., starting) neutrons were generated. The mode of calculation was set to transport both neutrons and photons. An MCNP F4 tally structure was used to obtain continuous-energy neutron and photon flux distribution within the Rabbit's containment. This tally structure was varied to include documented energy-dependent flux-to-dose rate conversion factors (MCNP X-5, 2005; ANS-6.1.1 Working Group, 1977; ICRP Committee 3 Task Group, 1971) for both neutrons and photons. The tallied dose rates are plotted in Fig. 1 in units of Rem/hr.

CL spectroscopy was performed using a CITL Mk 5-2 cold-cathode system, attached to a Leica S8APO stereomicroscope. Operating conditions included an accelerating voltage of 11.6–12.0 kV and an electron current of 280–400 μA. Light in the UV–Vis–NIR region, emitted by the excited surface atoms of the individual calcite mineral grains, was focused through a leaded-glass window and detected via a fiber optic cable attached to the stereomicroscope. A spectrum with a bandwidth of 350–1100 nm was measured with an Ocean Optics USB 2.0 fiber optic spectrometer with a collection time between 0.5 and 16 s. The optical resolution of this spectrometer is approximately 0.5 nm; this is much smaller than the observed peak widths.

Spectra were processed using commercial software – Peakfit© (SPSS, 2000), with five main Gaussian functions. Dark current background spectra with the same collection times were subtracted from each measured mineral spectrum.

3. Results/discussion

3.1. The CL signal from calcite

The CL signal from each calcite sample was recorded prior to irradiation and, in some cases, replicate spectra were obtained to demonstrate the robustness of the CL measurement over time. The

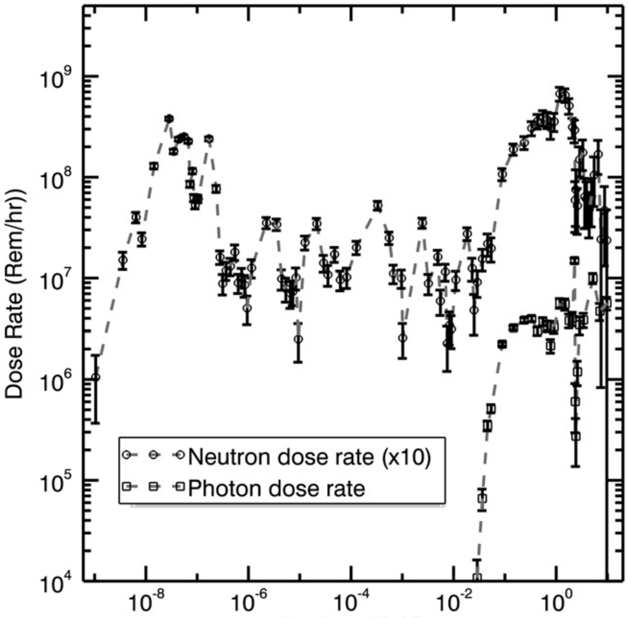

Fig. 1. Predicted neutron (circles) and photon (squares) dose rates as a function of incident energy inside a Rabbit irradiated at MURR.