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Seeing Snails in a New Light

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ABSTRACT

Luminescence is exhibited by many common minerals, some of which have been exploited for dating. Calcite has the potential to date events that occurred over millions of years, but a series of challenges has hindered its use in dating limestone building stones, speleothems, and mollusk shells. Now, however, calcite from an unexpected source is giving promising results: the opercula grown by certain species of snail. Coupled with innovations in luminescence imaging systems, snail opercula offer an exciting new approach that may finally unlock calcite's potential for dating.

KEYWORDS: thermoluminescence, *Bithynia, opercula*, human evolution, Quaternary

INTRODUCTION

Farrington Daniels, a former professor at the University of Wisconsin (Figure 1), is acknowledged as one of the pioneers in the use of luminescence from minerals for dating geological and archaeological events (Daniels et al. 1953). What is less frequently recognized is that much of his work in the 1950s, and the work in the subsequent decade, focused not just on quartz and feldspar (the subject of all of the other articles in this issue of *Elements*), but on limestones and other materials where the principal emission of luminescence was from carbonates. Calcium carbonate ($CaCO_3$) exists in nature as three chemically identical but structurally different polymorphs: calcite, aragonite and vaterite. Johnson (1960) showed that the most stable polymorph, calcite, emitted an intense thermoluminescence (TL) signal, but that aragonite did not. By the end of the 1960s it appeared that luminescence from calcite, either inorganic (e.g. limestones, speleothem) or biogenic (e.g. gastropod shells), offered an age range covering many millions of years. Yet, if you search the literature today you will find only

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a tiny number of papers using calcite for luminescence dating, and an absolute explosion of applications using quartz and the feldspars. As is demonstrated in this issue of *Elements*, these latter two minerals provide geochronological techniques that have been successful at answering an extraordinary diversity of questions in archaeology, geomorphology and Quaternary geology. But these quartz- and feldspar-based methods are limited to the last few hundred thousand years and require that the sample was exposed to daylight at deposition or that it was heated to temperatures in excess of 300 °C. In contrast, calcite can be used to date the time of precipitation of the mineral and offers a geochronometer that can date back several millions of years. So why has calcite not been used more widely in luminescence dating, particularly given the extended timespan it can cover? This article tries to answer this question, and explains the enormous potential for the use of calcite that has now been unlocked by recent innovations, most notably by the choice of snail opercula made of calcite as the target material for dating.

FIGURE 1 *Farrington Daniels (1889–1972) spent the majority of his career at the University of Wisconsin (USA) and was a pioneer in the use of luminescence for geological dating.*

HOW HAS CALCITE BEEN USED IN THE PAST FOR LUMINESCENCE DATING?

Calcite that has previously been exposed to ionizing radiation (e.g. alpha, beta or gamma radiation) emits a thermoluminescence signal dominated by emission in the yellow to orange part of the spectrum. In common with other minerals used for luminescence dating, the luminescence in calcite arises from electronic charge trapped within the crystal. When the sample is heated, this charge is liberated, and energy is released as photons of light – this is the luminescence signal that is measured. The intensity of the luminescence emission is related to the amount of energy that has been absorbed from ionizing radiation and then stored in the mineral, and is related to how long a mineral has been exposed to that ionizing radiation.

Quartz and feldspar struggle to date events older than a few hundred thousand years ago because the defects within the minerals where charge can be stored become full (saturated). Once saturation is reached, the mineral is no longer able to store additional charge generated by additional ionizing radiation (Figure 2). A good analogy for this is the rechargeable battery in your mobile phone. When you first start charging an empty battery the amount of energy stored in it increases continuously. However, as the battery approaches being fully charged, the rate of charging decreases, and ultimately you get to a point where you can continue charging the battery but no additional energy is stored because it is full. The same principle occurs with charge trapped in minerals, such as quartz and feldspar. When the defects in the crystal are full, the luminescence signal stops growing and, hence, it is impossible to date older events. The 'battery' in calcite also has a limit, but what makes it different is that it continues to fill for a much longer period of time than for quartz or feldspar. The continued growth of the TL signal from calcite in response to radiation doses of many thousands of gray (1 gray = 1 joule of absorbed radiation dose per kilogram) means that calcite has the potential to date events over the last 2 to 4 million years, or more.

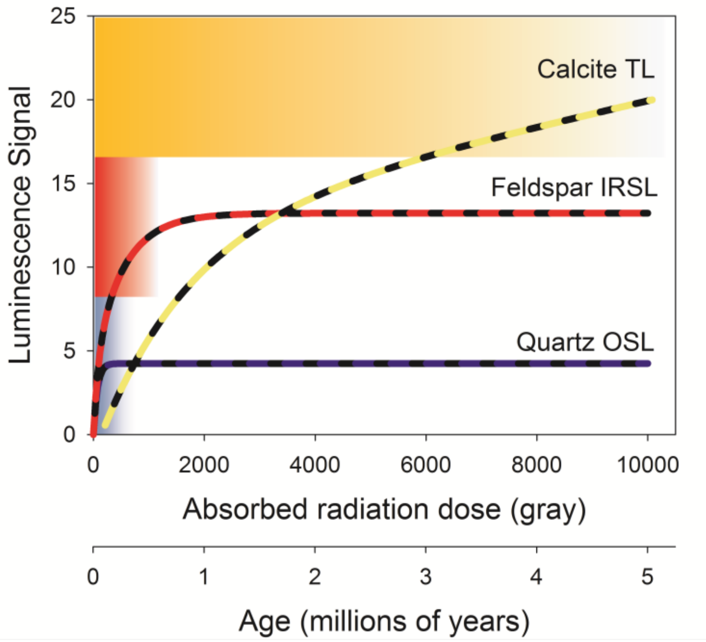

***Figure 2** Growth of different luminescence signals with radiation dose. The quartz optically stimulated luminescence (OSL) signal saturates first, followed by the feldspar infrared stimulated luminescence (IRSL) signal, and then the thermal luminescence (thermoluminescence; TL) signal from calcite. The signals increase in response to absorbed radiation dose (measured in units of gray; SI abbreviation Gy). The effective age ranges over which each material can be used are shown by the shaded horizontal bars and are calculated assuming a typical dose rate of 2 Gy per thousand years.*

The time period that can be recorded by calcite covers the entire geological period in which we are living (called the Quaternary). This period is characterized by repeated large climatic swings: in the high- to mid-latitudes, large regions were periodically covered by ice sheets. Over this same period of time, our genus *homo* appeared and evolved into a diverse range of species, including *Homo erectus* and *Homo sapiens*. Our knowledge of the early evolution of hominins is hampered because few dating methods are available in this time-range. One of the few methods to cover the whole period is argon–argon (Ar/Ar) dating: this type of dating is able to provide precise ages but can only be applied to volcanic materials such as tephra or lava. In volcanically active regions, such as east Africa, Ar/Ar dating has provided the linchpin of our current understanding of human evolution. However, in non-volcanic areas – such as southern Africa, north Africa, the Middle East, much of Asia, and much of Europe – dating the early Quaternary remains difficult. The luminescence signal from calcite would cover this time period and be a valuable addition to the range of dating methods available. What attempts have been made in the past to date different types of calcite?

Limestone

Limestone is a sedimentary rock comprised primarily of calcium carbonate in the form of calcite. Limestones have been used in a number of different ways to date events in the past. Where limestones were burnt in antiquity, for instance as hearth stones (Rogue et al. 2001) or in cave walls (Guibert et al. 2015), this heating will have removed any charge trapped in the mineral, and charge will then have built up steadily, recording the time elapsed since the heating event. Limestone is also a common building material, especially for high-status buildings in great civilizations such as those of Ancient Egypt and Ancient Greece. During the quarrying and dressing of limestone, the surface is exposed to daylight leading to a reduction in the trapped charge. After construction, a number of faces of the block will be shielded from daylight and so the trapped charge will build up as time passes. This concept has been used to date ancient pyramids in Greece such as the pyramid of Hellenikon (Figure 3) (Theocaris et al. 1997). However, in this application two main challenges occur. The first is the mineralogical purity of the limestone and whether the luminescence signal that is detected arises from calcite or from other mineralogical impurities. The second is that the method relies upon the TL signal from calcite being reduced by exposure to sunlight when the limestone was prepared. Unfortunately, the TL signal from limestone is only reduced over periods of many hours or days by sunlight, and is not completely removed. The result is that additional measurements have to be made to estimate the TL signal remaining in the limestone when the building was constructed. As a consequence of these problems, recent efforts to date such structures have focused on using the luminescence signal from quartz impurities found within the limestones, rather than the limestone calcite itself (Liritzis 2011). The optically stimulated luminescence (OSL) signal from these quartz impurities can be used, and is bleached much more quickly than the TL signal, being reset to a low level within only tens of seconds or minutes of exposure to sunlight. In this case, where the samples are comparatively young, and where the event being dated is the last exposure to daylight, quartz appears to be a better mineral than calcite.

FIGURE 3 *The Hellenikon pyramid is constructed from limestone in the region of Argolis (Greece). This pyramid's construction was dated to 2,730 ± 720 years ago using thermoluminescence measurements on its limestone walls (Theocaris et al. 1997). Photo: Panos Karas/Shutterstock.com.*

Speleothems

A speleothem is a general term for any of the multitude of structures formed from precipitated $CaCO_3$ within caves. Examples of speleothems include stalagmites and stalactites which, when sliced in half, may show growth bands rather like tree-rings. In the 1970s and 1980s, a number of attempts were made to use thermoluminescence to date speleothems. The event being dated, in this instance, is the precipitation of the carbonate (normally calcite, but sometimes aragonite or dolomite. Uranium-series disequilibrium methods of dating are ideal for dating most speleothems, but the U–Th method is only applicable to a maximum of ~350–500 thousand years ago (ka) when the two isotopes ^{234}U and ^{230}Th return to isotopic equilibrium.

Early TL studies of calcite showed that the thermoluminescence method could potentially date well beyond the 500 ka upper limit of U-Th dating. A series of speleothem dating studies through the 1970s and 1980s produced mixed results. Some studies showed significant differences between thermoluminescence ages and ages determined by uranium-series methods (e.g. Wintle 1978); other studies showed much closer agreement (e.g. Debenham and Aitken 1984). Franklin et al. (1988) demonstrated the potential of this TL approach by applying it not to speleothems but to two samples from a calcite vein in a lower Eocene chalk. They generated ages of 5.5 million years (Ma) and 4.1 Ma. Unfortunately, only limited independent age control was available for this material – the sample was known to be younger than 55 Ma and older than the limit of U-series methods at the time of that study, i.e. ~350 ka – so the accuracy of these ages is unclear. However, even after 30 years of subsequent work, these remain the oldest ages generated by luminescence methods known to the present authors.

One of the challenges of applying luminescence to speleothems was the difficulty of calculating the annual radiation dose the samples were exposed to since crystallization. The fact that speleothems are ideal for uranium-series disequilibrium methods makes them challenging for luminescence dating: as radioactive equilibrium is restored, the ionizing radiation dose emitted by the speleothem will change through time. Furthermore, uranium may not be evenly distributed in speleothems, causing additional challenges in obtaining dose-rate measurements that are correct for the material used for thermoluminescence measurements (Wintle 1978). A second problem was the apparent inclusion within speleothems of specks of limestone, or silicates that had retained charge that had accumulated prior to the formation of the speleothem (Debenham et al. 1982). Finally, a series of problems were encountered during sample preparation prior to thermoluminescence analysis. Sample preparation normally involves cutting and/or crushing to produce a powder with a grain size of a few tens or hundreds of micrometres in diameter. It appears that for some samples, crushing calcite can induce a series of changes in the thermoluminescence signal (e.g. Wintle 1978; Khanlary and Townsend 1991). The combination of these challenges, and the rapid improvement in the precision available with uranium-series methods, soon led to luminescence methods on speleothems being discontinued.

Biogenic Calcite

Many organisms secrete calcite, or its polymorph aragonite, to form a protective shell or some other hard structure. Johnson (1960) looked at calcium carbonate from a wide variety of organisms to see which gave luminescence signals, and he discovered that specimens composed primarily of calcite gave a TL signal, while those that were aragonitic did not. Johnson and Blanchard (1967) looked at shells of the marine bivalve molluscs *Ostrea* and *Pecten* from the Holocene back to the Cretaceous and found that the

TL signal increased with age over this period. A challenge for measuring TL from such bivalves is the intimate intergrowth of calcite with the biological framework used by the organism (Carmichael et al. 1994). The presence of organic residues in the sample led to the generation of spurious TL (a TL signal that is not related to radiation dose), and this was compounded by the problems associated with crushing of samples during sample preparation, something that had been discovered from the work on speleothems. Ninagawa et al. (1992) tried a number of approaches to reduce these spurious signals and used TL to date calcite shells of the Pectinidae family. In their comparison with other methods (including fission track ages), Ninagawa et al. (1992) were able to date back to ~600 ka. However, once again, this approach has not been adopted widely, and another attempt to use luminescence of calcite for dating came to little.

SNAIL OPERCULA – THE PERFECT MATERIAL FOR DATING?

So, is there a future for luminescence dating of calcite? We would argue strongly that there is. The answer to many of the challenges posed by the TL dating of calcite is to choose your target material carefully. Kirsty Penkman and colleagues at the University of York (UK) have spent the last decade or more improving the reproducibility and reliability of amino-acid racemization measurements of Quaternary materials (Penkman et al. 2013). A particular focus of this work has been upon the opercula of the freshwater snail *Bithynia tentaculata* (Figure 4). This snail is unusual because it secretes its operculum as the more stable polymorph calcite instead of aragonite. The operculum of a snail serves as a trapdoor attached to the upper-part of the snail's muscular foot, effectively closing the shell once the snail retreats inside, which can prevent the snail from drying out and/or provide protection from predators. In addition to being ideal for amino-acid racemization measurements, the calcitic opercula of the species *Bithynia tentaculata* are ideal for luminescence. The samples are small enough (typically 3–4 mm in length, and a few hundred micrometres in thickness) that they do not require crushing, but can be analyzed whole. Furthermore, the organic content of the opercula is extremely low, and a simple treatment with chemical bleach is sufficient to remove any organics at the surface. The problems of dosimetry posed by the high concentrations of uranium in speleothems are much less important in these biologically secreted calcites where uranium concentrations are much lower. Finally, unlike dating limestones, when analysing snail opercula it is the crystallization of the mineral that is the event dated, and so there is no concern about whether the luminescence signal was reset or not.

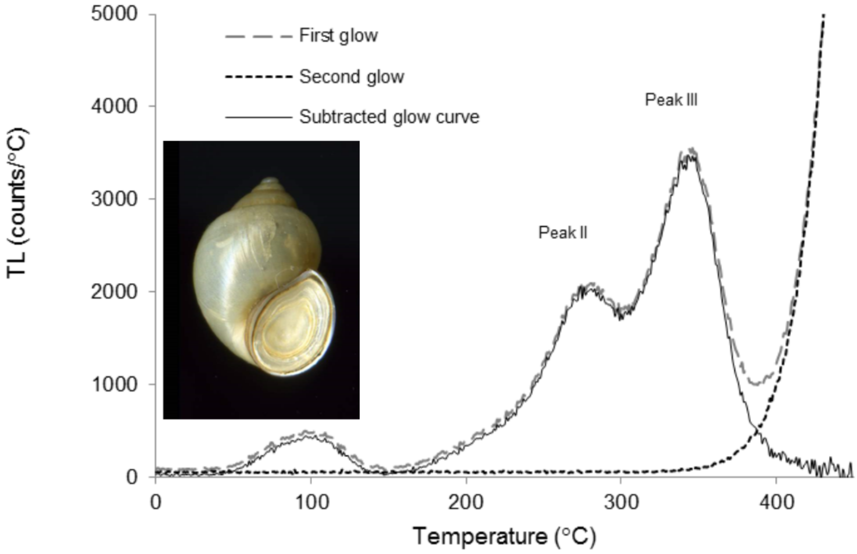

FIGURE 4 *Luminescence signals from the opercula of the snail Bithynia tentaculata. The snail shell is approximately 8 mm tall, and the operculum is about 4 mm in length. The operculum was heated from room temperature to 400 °C at 0.5 °C per second. After subtracting the incandescent signal ("second glow") from the first measurement, the subtracted signal shows three peaks in the thermoluminescence (TL) glow curve. MODIFIED FROM STIRLING ET AL. (2012).*

Thermoluminescence from Snail Opercula

After irradiation in the laboratory, the TL signal from *Bithynia tentaculata* opercula has three peaks (Figure 4), one each at ~100°C, 275°C and 335°C (heating at 0.5°C/s). However, samples which have received a radiation dose during burial over geological time only show the two higher temperature peaks. Each TL peak is associated with a specific defect in the calcite lattice, and the stability of the charge in these defects varies. The lifetime of charge tends to be longer for TL peaks occurring at higher temperatures. The lowest temperature TL peak in calcite can be seen to decrease in size during storage in the laboratory over a matter of hours, but the current estimates for the lifetime of charge in the two higher temperature peaks are ~70 Ma and ~140 Ga, respectively

(Stirling et al. 2012). This means that signal stability would only become a problem for samples much older than ~10 Ma.

In fact, saturation of the TL signal is likely to mean that the maximum age that can be dated is less than 10 Ma. Measurements on snail opercula have shown that the two high temperature TL peaks continue to grow at doses of 8,000 Gy or more (Stirling et al. 2012). In typical environments where the dose rate would be 2 Gy per thousand years or less, this would mean that it would be possible to obtain ages of 4 Ma or more (FIGURE 2).

Imaging Luminescence from the Opercula

Luminescence from geological materials used for dating is normally measured using a photomultiplier tube, with most systems being optimized to detect emissions in the blue part of the spectrum where quartz and feldspar emit strongly. Such systems can be used to measure the TL signal from opercula, but are not optimal because the primary emission from calcite is in the yellow, at about 580 nm. An additional disadvantage of using photomultiplier tubes is that the light from different parts of a sample are integrated, which means that it is not possible to see any spatial variations within a sample. Recent developments in charge-coupled devices (CCDs), especially electron-multiplied charge-coupled devices (EMCCDs) mean that these now not only approach the sensitivity of photomultiplier tubes but also bring two advantages for the analysis of calcitic opercula. The first advantage is that EMCCD devices are more sensitive than photomultiplier tubes in the yellow–orange part of the spectrum; the second advantage is that EMCCDs give spatially resolved measurements (Duller et al. 2015), allowing the intensity of the luminescence signal to be mapped across a sample. By combining a number of images of the TL signal from each operculum, an age for each part of the operculum can be calculated (Figure 5). This could reveal whether any part of the operculum has undergone recent recrystallization – any areas affected by recrystallisation would be expected to give much younger ages. In the samples analyzed so far this does not appear to be an issue.

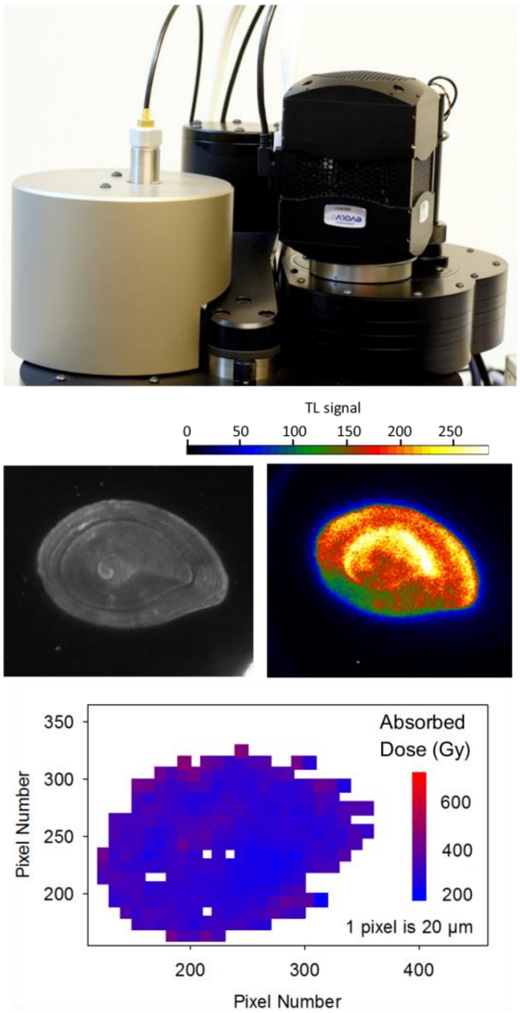

***Figure 5** (**Upper**) Electron multiplying charge-coupled device (EMCCD), developed by Kook et al. (2015) used to obtain spatially resolved thermoluminescence (TL) data from snail opercula. (**Middle**) On the left is a visible image of an operculum; on the right is the TL signal from each part of the operculum. (**Lower**) The estimated absorbed dose (equivalent dose; in units of gray) received during burial for each part of the operculum. This data has been processed to look at regions 200 $\times$ 200 micrometers (μm) in size, although the EMCCD has a pixel size of 20 μm.*

Testing the Method

Developing a robust method of dating calcitic opercula is still at an early stage. Nevertheless, preliminary data from a site in Purfleet (Essex, UK) are encouraging. Purfleet is part of a stepped series of river terraces along the lower course of the River Thames that have been mapped and studied for well over one hundred years (Bridgland et al. 2013). Each terrace is associated with a warm interglacial phase. Purfleet preserves a series of freshwater beds, including a shell bed rich in *Bithynia tentaculata*

(Figure 6). The specific *Bithynia* bed is thought to date to marine isotope stage (MIS) 9, which corresponds to sometime in the period 277–338 ka) on the basis of the position of the terrace in the sequence, amino-acid racemization, biostratigraphy, and luminescence ages on quartz from the site. Analysis of opercula from this site gives a preliminary age of 316 ± 22 ka, well within the age range obtained from other methods.

FIGURE 6 *Sampling for snail opercula at Purfleet (Essex, UK), a site with sediments deposited during an interglacial period dating to 278–318 ka (marine isotope stage 9).*

A GLIMPSE INTO THE FUTURE

What does the future hold for luminescence dating of calcite? With the right choice of target material, the possibility of providing numerical age estimates for geological and archaeological events over the last four million years using calcitic opercula preserved within archaeological and geological records appears to be within sight. As well as *Bithynia* opercula, a number of other biogenic calcites also hold potential. Some slugs secrete an internal plate of calcite, and these plates give TL signals as good as calcitic opercula (Duller et al. 2009). Other potential targets are earthworm calcite granules (e.g. those produced by *Lumbricus terrestris*; Canti et al. 2015) or the calcite of the valves produced by some of the larger species of ostracods.

Almost 65 years on since the pioneering work of Farrington Daniels, dating of biogenic calcite finally seems set to revolutionize the capability of luminescence dating, significantly enhancing the age range over which this family of techniques can be applied, and, hence, opening a new chapter in the study of archaeological and geological events.

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