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Studying chert with electron-spin resonance

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ABSTRACT

Archaeologists generally want to know how old their artifacts are and from where they came. Electron-spin resonance (ESR) is a tool for studying chert using radiation-induced signals analogous to those used for thermoluminescence (TL) and optically stimulated luminescence (OSL) dating. As a dating technique, it is well established for tooth enamel and shells, and initial studies suggest it may be possible to date quartz sediments. For this study, however, it is presently applicable only to heated chert. Work on samples from numerous sources has confirmed that heating chert is a complex process, and both the duration and temperature of heating must fall within certain ranges in order to obtain datable samples. Both Old World and New World material has been dated. Looking at these samples has also shown that variability among sources may permit proveniencing.

1. Introduction

Over the last half-century, one of the important developments in archaeology has been the growing use of the methods of physical science to answer crucial questions about the age, origin, and technological implications of material remains. Almost always, the first issue to be studied is the age. No single method has been universally helpful—dating methods are limited in their time frame and materials—and all techniques have sensitivity problems. As a result, an archaeologist often has, frustratingly, no choice in selection of a dating method.

Consider five specific dating methods in common use by archaeologists and paleontologists. Two of them, radiocarbon and potassium/argon (or argon/argon) dating, use the decay of radioisotopes and are therefore 'absolute' methods, independent of the sample environment. They are relevant in different time periods because the radioactive atoms decay at different rates – ^{14}C (carbon-14) has the (comparatively) short half-life of around 5700 years, while ^{40}K (potassium-40) decays much more slowly with a half-life of 1.25 billion years. The other three methods are commonly called 'trapped charge methods' and are important in filling the gap between the numerical methods. Electron spin resonance (ESR), thermoluminescence (TL) and optically stimulated luminescence (OSL) measure the accumulation of radiation damage in a sample from radioactive substances in the soil and in the sample itself. These methods, conventionally called 'chronometric', therefore depend on environment and uncertainties about environmental change over time affect the calculated ages. TL detects the radiation damage by heating the sample and annealing (removing) the damage. During this process, light is emitted and the intensity of the light is proportional to the amount of damage. OSL stimulates light emission with light of a different frequency. ESR, as will be discussed in more detail later, measures the damage directly at room temperature. Fig. 1 shows generally accepted age ranges for these techniques. Between the five, one can obtain in principle information about all stages of human physical and cultural evolution. Fig. 1, however, is only part of the story. Argon/argon dating is only possible where volcanic eruptions have created suitable samples, for example. OSL, TL and ESR are not interchangeable, either in time range or sample selection. OSL dates the last exposure of quartz grains in sediment to light. Naturally this means samples are very often available. However, the date of the sediment may not be the same as that of human occupation. The samples may not have been exposed to light sufficiently to zero the geological signal. Both TL and ESR date material directly attributable to human occupation, but in numerous cases sites showing occupation (such as hearths or unheated tools) have only small samples (or none) suitable for these techniques. Sample collection for OSL must be done without exposing the sample to light; collection for the other methods is not affected. Sample preparation is generally easier for electron spin resonance than for luminescence, but TL and OSL often show greater sensitivity, which is why they can be used for younger materials than can ESR. Not all materials that can be dated by thermoluminescence can be dated by electron spin resonance, and vice versa. TL is commonly used to date pottery; efforts to find a suitable ESR signal in pottery have

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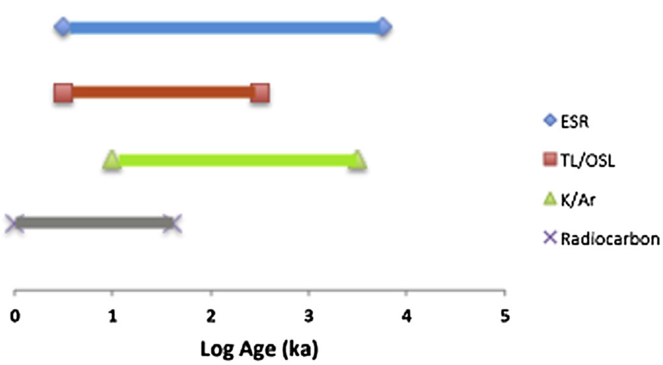

Fig. 1. Generally accepted age ranges for commonly used dating methods.

been largely unsuccessful (Bartoli and Ikeya, 1997). Tooth enamel, one of the best ESR dating materials (e.g., Skinner, 2014), cannot be dated by TL because heating changes the enamel itself and thus the regeneration signal in TL is not comparable to the initial spectrum. Signal measurement with electron spin resonance has an advantage over that of TL and OSL. Because the signal is not destroyed during the measurement, measurements can be repeated on the same sample, rather than using duplicate samples and consuming more of the archaeological material. Familiarity with these types of promises and the limitations of any method is prerequisite to a successful outcome.

As a general principle, in any case, a site should be dated by more than one independent method. Note that although all trapped charge methods rely on radiation damage, they measure different materials and different defects, so dates from one can be used to confirm results from another. Schwarcz et al. (1989) dated Kebara Cave with both ESR and TL. Recently all three methods were applied to a site in Morocco (Dibble et al., 2012) and within experimental error the results agreed.

There are, of course, numerous methods other than those noted above. Aitken (1990) is an excellent reference accessible to the general reader as well as to the archaeologist. Further, archaeometrists are continually refining methods to extend them to new materials and new time periods. New methods arise as well. Schwarcz (2002) summarized ‘Trapped Charge Dating’ including newer variations such as infrared stimulated luminescence (IRSL), where the principles of TL and OSL are extended to other regions of the electromagnetic spectrum. Collaboration between archaeologists and the ‘hard’ sciences is both exciting and productive.

Archaeological applications using ESR are relatively new, although ESR has been a scientific technique for over 50 years. Ikeya (1975) was among the first to utilize ESR for geological dating problems such as movement of earthquake faults and variations in sea level due to climate change. The extension to archaeology and paleoanthropology followed logically when researchers turned to objects older than the carbon-14 limit. Electron spin resonance dating has been most successful with tooth enamel (e.g., Skinner, 2006) but also carbonates including calcite from stalagmites and mollusk shells. Additionally, ESR dating of light-bleached quartz has been suggested (Rink et al., 2007). Bones are another datable material of interest to archaeologists; unfortunately there is not yet a reliable protocol for dating them. Chert is an obvious additional choice for investigation since many sites in North America and elsewhere contain primarily chert artifacts. Burnt chert has been studied, for example, in the dating of Bau de l'Aubesier, France (Blackwell et al., 2000) and Paleolithic sites in Italy (Martini et al., 2001). It was a key component in determining ages for Neanderthal cave sites in the Middle East (Valladas et al., 1999), demonstrating potential overlap between *Homo sapiens* and *Homo neanderthalis*.

This article will outline the main points involved in using ESR as a dating technique: the selection of appropriate samples, their preparation and examination, and the types of supporting information needed for a complete analysis of a given material. While the emphasis is on chert, the approach may be useful with other materials of archaeological interest including other lithics and certain types of sediment. In addition, preliminary results suggest ESR may be useful for the other major question before archaeologists, the origin of their samples. ESR is a sensitive tool for distinguishing trace paramagnetic materials. Thus its potential for proveniencing will also be discussed.

2. Electron-spin resonance signals in chert

A full understanding of ESR theory is not needed to apply the method to archaeological materials. For those interested, theoretical details are discussed in Appendix A. It may be useful for those interested in finding suitable samples other than chert.

Dating archaeological artifacts requires that the “clock” be zero at the time humans made or used the artifact. In the case of chert, heating at the time of manufacture can in principle remove any “geological signal” that was created by radiation damage between the time of chert formation and the time of artifact manufacture. Thus to obtain samples suitable for dating, one looks for heated chert rather than the raw material.

Ancient peoples heated at least some of their chert material purposefully. Heating makes some chert types easier to work (e.g., Purdy, 1971; Domanski, 1994) and produces sharper edges. The color change that usually accompanies heating may also make a more attractive product. Not all chert types can be heated—for many, heating explodes the nodules. The effects of heating on workability depend on the maximum temperature reached, the duration of heating, and the rate of heating. Physical examination (color, luster) does not always reveal whether a given artifact has been heated; even if one knows that it has been heated, the degree of heating may not be sufficient for technological change. It is possible to heat enough to change color without affecting the mechanical properties, and it is possible to overheat the material so that it becomes brittle and fractures, rather than flakes (Luedtke, 1992). While there is no direct evidence that ancient peoples used any particular heating technology, modern experiments have shown that the optimum maximum temperature for improving chert workability is usually around 350–450 °C, and heating times of at least several hours are needed. This is not always true (Speer, 2010) Griffiths et al. (1987) showed that these conditions could easily be obtained by burying the chert under a campfire. Heating is not invariably a desirable technology, since the sharp edges of heated chert can dull quickly. Dull edges make, for example, poor choppers.

Exposure to heat other than burial under a fire produces different results. Simply throwing nodules of chert into a hot fire, causing them to shatter, may be a purposeful effort to obtain smaller workable pieces. However, this neither improves working qualities nor does it by itself reset the geologically acquired radiation damage signal. Chert artifacts may also fall into the fire accidentally after manufacture and/or use, or may be heated by natural fires.

The geochemistry of chert has been more than adequately addressed by other contributors to this volume. Chemically, chert is essentially silica, as are sand and quartz. Therefore to date chert by ESR, one needs to demonstrate that radiation can cause ESR-detectable damage in silica, then to investigate the effect of heat on the signals that result. ESR effects in silica were first noted in