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. Figure 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. Figure 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 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, 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. (1987a) 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 geological studies on quartz as an indicator of earthquake fault movement (Ikeya, 1993). Electron spin resonance-active defects in the silica matrix itself are of primary interest, since they will appear in all chert types. The paramagnetic (containing unpaired electrons) defects in chert, involving impurity ions such as aluminum, germanium, titanium, and carbon-containing compounds, provide a secondary source of information. Variability in composition is known both between different chert types and within samples of the same type.

3. Experimental methods for dating of chert by electron-spin resonance

Figure 2 shows typical chert ESR spectra before and after heating. The ESR spectra of chert are complex and can vary greatly depending on the source of the chert. However, two primary signals are derived from the silica fraction of chert, each of which provides useful information. Both these signals are found in all chert types although the intensity varies. In Figure 2a is a peak labeled E', visible on the high-field (right hand) side of the spectrum. The height of the E' peak, H , is proportional to radiation damage and therefore the basic measurement for calculating ESR ages. This dating peak is used most often since it responds to radiation in a predictable fashion. The so-called “peroxy” signal is visible on the low-field side (note that this name is given for convenience rather than indicating definitive chemical structure

of the radical behind the signal). Figure 2b shows the same chert after heating. Heat destroys the peroxy signal immediately; this can be used to indicate whether a sample has been heated at all. Heating reduces the E' signal, but only at temperatures higher than required to destroy the peroxy signal. For a detailed study of the thermal response of the E' signal, see Toyoda (1993). The optimum temperature range for altering the working properties of flint (350–450°C) corresponds to that producing the most reliable effects on the ESR signal. However, heating in this range does not reduce the signal to zero. If one heats the sample to higher temperatures (>600°C), the E' signal disappears and cannot be regenerated by radiation. Presumably this is associated with a permanent change in the silica structure. In terms of dating, it means that an artifact (or non-artifact such as hearthstone) that had been heated to such high temperatures would have the “clock” not simply reset to zero but broken so that it would never again tell time.

Clearly the signal size in a sample depends on two factors. First is the amount of radiation to which it has been exposed. Some sources of radiation are found within the sample—ions of uranium, thorium and other radioisotopes that have crystallized in the chert. Other sources of radiation are external to the sample, such as radioisotopes in the soil and cosmic radiation. The second factor is the sensitivity of the sample to radiation. Not all chert is equally affected by a given amount of radiation and it is not possible to know in advance what the sensitivity of the sample will be. Therefore, a portion of the sample is powdered and divided into aliquots. One aliquot is left as natural and the others irradiated artificially. The increase in ESR intensity is plotted against the artificial dose. This “growth curve” is then extrapolated to zero intensity, yielding D_e (“extrapolated dose” in Gy), or the amount of radiation (expressed in gamma-equivalent form) needed to produce the observed natural signal. In TL and OSL an identical analysis of glow curve intensities is used to obtain the growth curve, although the curve shapes differ.

A sample of such an extrapolation is found in Figure 3. By dividing D_e by the sum of the known radiation doses both external and internal to the material, the age of the material in years can be found. Equation 1 expresses this relationship mathematically:

$$t = D_e / (D_{ext} + D_{int}). \quad (1)$$

In the equation t is the age in years; D_e is, as defined above, the total dose seen in the sample; D_{ext} is the total dose to the material from external sources in Gy/yr.; and D_{int} is the total dose to the material from internal sources in Gy/yr. Determination of D_{ext} and D_{int} can be very complex.

One common method of determining D_{int} is to use neutron activation analysis to find the concentrations of radioisotopes within the sample. Neutron activation analysis can also be used to find the radioisotope content of the surrounding soil (or other matrix) as a part of determining D_{ext} . Alternatively, one can place a dosimeter on the site and leave it there for 6 months to a year. Which method to use depends on cost and on whether dosimeters can be left on the site for such a long period of time. Of course, either method requires that samples of the matrix in which an artifact was found be available.

Equation 1 also implies that the dose rate has been constant with time so that the total dose is simply the present dose rate multiplied by time. For D_{int} in chert, this latter assumption is generally valid, since uranium and its daughter isotopes are in secular equilibrium. Making the same assumption for D_{ext} is more problematic even over the relatively short period of time that most New World chert artifacts have existed. One must be certain that the object has not moved since it was first buried, since the concentration of isotopes varies with soil types and locations. Even if the isotopic content of the soil has not changed, there are other considerations such as the moisture content of the soil. Water has the ability to absorb radiation and thus prevent it from affecting the sample. Again, one needs either to assume that the present moisture content has been constant or to find a way to evaluate any changes. The effectiveness of cosmic radiation decreases with burial depth, also affecting the dose. The importance of any of these factors can best be shown by preparing a figure such as Figure 4, where the effect on the calculated age of assuming specific external doses is shown. Similar plots can be drawn for individual sediment dose rate factors such as water concentration and/or cosmic radiation.

Several types of New World chert were used in these studies. Fuller descriptions can be found in Table 1. Samples both heated (in antiquity) and unheated were powdered in a vise. The size fraction between 90–250 μm (about the consistency of fine sand) was washed with water and dilute hydrochloric acid to remove surface effects. The powdered sample was then divided and approximately half was heated to 350°C in a tube furnace. For archaeologically heated samples, the samples heated in the laboratory will be referred to as “reheated.” Eight to ten individual portions, approximately 100 mg. each, were prepared from each heated and unheated powder sample. These aliquots were irradiated with a Cs-137 source at a rate of approximately 3 Gy/min in order to produce growth curves of the type seen in Figure 3. The maximum radiation dose was approximately 100 Gy. Studies of other materials and other time

periods have involved maximum doses as high as 30,000 Gy. It is unlikely that laboratory irradiation to extremely high doses truly mimics the effect of thousands of years of natural irradiation (Barabas, *et al.* 1992). Hence there is seldom benefit to extending the growth curve beyond that dose needed to approximately double the natural radiation signal. Post-irradiation treatment varied from none at all, to annealing at room temperature for two weeks, to annealing at 100°C for one week. Annealing eliminates short-lived damage signals that would not be seen in an archaeological sample. It did not significantly affect these preliminary results, but annealing would be essential in an experiment that required minimizing all sources of error.

Table 1. Flint types.

Name	Location
Ocala	Northwest Florida
Fort Hood	Fort Hood Military Reservation, Texas
Crescent	Jefferson/St. Louis Counties, Missouri
Fort Payne	Fort Payne, Alabama
Vanport (Flint Ridge)	Flint Ridge, Ohio
Jasper (Hardyston)	Eastern Pennsylvania
Normanskill	Albany, New York
Briar Creek	Burke County, Georgia

4. Results

For all samples seen so far, heating to 350°C did not reduce the E' signal to zero, in contrast to other reports (Porat and Schwarcz 1991). Careful analysis of Figure 5, where the final intensity is nearly half the original, shows that this is not a kinetic effect that might diminish with further heating. Rather, the value reached after approximately 16 hours is an irreducible minimum, comparable to the “unbleachable signal” sometimes reported in thermoluminescence work. For raw chert the residual signal tends to average about 5% of the original value, which at first glance looks comparable to other sources of error. Unfortunately this is misleading, as in raw chert we are looking at a signal that has taken perhaps many millions of years to develop. An artifact signal, in contrast, has grown over thousands or tens of thousands of years. Thus what is 5% of a large signal is >>5% of the artifact signal. For archaeological samples, the

residual signal can be as much as 50% of the archaeological value. This is particularly true of samples from the New World whose regrowth signal will be very small due to their relatively recent manufacture. This in itself does not prevent one from dating chert artifacts. The residual signal, by definition, can be found by heating the artifact overnight at 350°C. If the artifact was heated sufficiently at the time of manufacture, the regrowth signal can be found by subtracting the residual signal from the observed value. In practice it seems better to artificially irradiate both the original (artifact) and the reheated samples and to compare the growth curves. Skinner and Rudolph (1996a) have shown that the growth of the ESR signal is the same in material that has been heated once (i.e., an artifact) as in material that has been heated twice (i.e., a laboratory reheated sample) (Figure 6). The displacement between the growth curve of the artifact and the growth curve of the reheated material yields the value of D_e , corresponding to the growth of the signal since the original heating incident. Figure 7 shows that signal growth of a reheated sample follows the same rule as for the original sample. The primary difficulty lies in the clause “[i]f the artifact was heated sufficiently at the time of manufacture.” While we know in principle that the means of heating (pits under campfires) *could* be sufficient, we do not know in any particular case if this was true. In a series of Ocala cherts from Northwest Florida, the ages obtained varied from 10,000 years (reasonable for the site) to 128,000 years with uncertainties due to environmental factors of about $\pm 20\%$ (Skinner and Rudolph 1996b). This variability is most likely attributable to variability in heating history. The conclusion best drawn from this is that if one has a series of ages from the same site, the youngest is most likely to be correct but that even the youngest age could be significantly greater than the true age of the site if the flint had not been heated sufficiently.

5. Sample screening

An explanation for the “irreducible minimum” signal would be very important. One suggestion is that it relates to the presence of two phases of silica, one amorphous and the other microcrystalline. There is evidence from X-ray crystallography that both phases exist, although such techniques as thin-section microscopy cannot always detect an amorphous phase. But where both phases exist, a quantitative or even qualitative relationship to the residual signal intensity is lacking. Even if the E' signal did go to zero after 16 hours of heating, the uncertainty in the

heating history would be a problem. Dating a site would require examining a number of artifacts in order to have some confidence that the apparent age is reasonable.

Given that many “heated” samples are not suitable for dating, a rapid screening test has been developed to identify the most promising candidates, based on Toyoda (1993). A portion of the sample is heated in the laboratory overnight at 350°C and the reheated spectrum is compared with the original. The greater change observed, the better the sample is as a candidate for full analysis. Testing this hypothesis by completing full irradiation schedules for multiple samples showed significant correlation with more probable ages. Figure 8 is a flowchart illustrating this test. This screening test is clearly better suited to Old World artifacts, which could have a very considerable regrowth signal due to greater archaeological age, than to New World ones. Even with Old World material, however, the samples that gave the most change on heating would be preferable.

At the Middle Paleolithic site of Sajóbáony-Méhéztető, Hungary, flint artifacts were found in a fire pit and judged to have been burnt expediently, not to improve flaking quality. They could nonetheless, in principle, be dated. Examination of the ESR spectra screened samples for heating temperature to find ones that were promising (Skinner *et al.* 2001). Some had been heated to such high temperatures that no radiation signal could be generated. Others had contaminants such as iron that even at low levels masked the radiation-induced signal. However, the relatively rapid screening process did discover several flints that could be dated provided some of the original source material could be found so that the nature of the residual signal could be studied.

Alternatively, one can use the existence of a radiation-sensitive signal associated with the presence of aluminum as an impurity in the silica matrix. This signal appears to be more sensitive to temperature and therefore might more easily be reset by the kind of heating used in antiquity. While one cannot assume that aluminum will always be present in chert, nor that the concentration will be high enough to be detected, most chert does seem to contain this ion. However, the aluminum signal can only be measured at liquid nitrogen temperatures, and also requires subtracting a background spectrum. The results of the two-step process are sufficiently imprecise that they have not been any more useful for New World cherts than the room-temperature method already described. They could be promising for Old World material that is heated but not burnt. A caveat here is that the aluminum signal is slightly light-sensitive so the

samples also need to have about 2 mm of outside material removed before preparing the powder for ESR, and the powdered material must be handled in red light. The powders are kept in light-tight containers when not being studied.

6. Thermoluminescence dating of chert

Thermoluminescence (TL) has been applied to dating flints with considerable success. As noted earlier, the first claims for overlap between Neanderthals and modern *Homo sapiens* in the Near East are based on TL dating of flint (Valladas, *et al.*, 1999). More recently there are other examples from European Middle Pleistocene sites (Martini, *et al.*, 2001) and from North Africa (Dibble, *et al.*, 2012). As with samples studied in this paper, the first task is to determine the degree of heating. Godfrey-Smith, *et al.* (2005) covered methods that can be used. Once that is known, the primary difficulties with TL dating are the same uncertainties in dosimetry found with ESR. An excellent recent summary can be found in Richter (2007).

7. Chert provenance by electron-spin resonance

There is a general consideration discussing provenance, regardless of material or technique. Agreement between artifact and source is useful but not definitive since there could be another identical (for the method) source. More commonly, one can say that a particular source was not used for the artifact in question. With that caveat, ESR may be useful to source chert in addition to dating it, given the different environments in which chert is formed. Differences in ESR spectra have been used to source other materials of archaeological interest (Lloyd *et al.* 1985). For sourcing cherts, one normally looks at the spectrum of the raw material. Heating can also help identify chert types. As seen in Figure 2, heated chert can have peaks attributable to various organic compounds. As the carbon content of chert can be quite variable, these peaks are not always found. Therefore, they can serve as one identification marker for chert sources.

Previous proveniencing studies on chert have centered on geochemical variation, normally detected by trace element analysis (e.g. Julig, this volume; Markham and Floyd, 1998; Cackler *et al.*, 1999). Luedtke (1992) has summarized analytical results for a number of chert types. One would expect that variables such as rare earth element distribution and the presence of detrital components would be a function of both the location of the formation and of the specific

conditions under which it formed. Given local variation in sea bottoms and the potential for diagenetic change after initial precipitation, cases exist in which there is as much variability within a chert type as there is between types. For instance, there are 17 types of Fort Hood chert in a range of 5 km. The techniques of this type of analysis rely heavily on statistical assumptions that can be challenged, although steadily improving. As with dating, applying more than one technique to an artifact increases confidence in the result. Adding another analytical method may also increase the possibility of identifying exotic artifacts in an assemblage.

Griffiths and Woodman (1987b) used variability in components of the peroxy signal to try to identify sources in the British Isles. While certain differences between sources could be identified, there was significant overlap among sources, and numerous samples that did not fit any source. In looking at North American chert types, the components used by Griffiths and Woodman (1987b) could not always be recognized. However, less subtle distinctions that prove useful do exist.

8. Preliminary provenance testing of some North American chert types

Geological samples of eight North American chert types, recovered from sources and known to have been used for artifacts, have been studied for variability in their ESR spectra. These particular types were chosen partly because they are known to have been heated in antiquity (John Holland, pers. comm.; Purdy and Brooks 1971; Anne S. Dowd, pers. comm.), and thus are more likely to provide applicable samples for dating. No effort was made to account for the variability in ESR results by simultaneously examining the detailed geochemistry of the samples. It should be noted that as this study is intended as proof of concept, rather than a definitive method of identifying sample origin for these types, the precise location is not significant. Careful choice of instrumental parameters ensures that the results are not an artifact of signal to noise ratio.

In the unheated spectra, the first discriminator would be the presence or absence of manganese, which has a very distinctive ESR spectrum (e.g., Fort Hood, Figure 9a). This peak is a function of concentration, so the comparison with an artifact would apply only to the specific source. The shape of the peroxy signal can also be compared (e.g., Crescent and Fort Payne, Figures 10a and 11a). The peroxy signal may even be vanishingly small (e.g., Vanport, Figure

12a). If the peroxy signals are similar, the E' signal may vary (e.g., compare Crescent, Figure 10a, and Jasper, Figure 13a).

Variability also appears in the heated spectra. The most distinctive feature in the spectrum of heated chert is the presence or absence of peaks attributable to detrital organic compounds (compare heated Fort Hood which has such peaks, Figure 9b, with heated Crescent, Figure 10b, which does not). Differences in the E' peak can also be seen (compare heated Vanport, Figure 12b, with heated Jasper, Figure 13b). Normanskill unheated chert (Figure 14a) has a peak to the low-field side of the E' peak and a small peroxy peak, similar to that seen in Vanport, but the heated Normanskill type has no carbon-related peaks and a new lowfield peak (Figure 15a).

An eighth type, Briar Creek, is notable primarily for the extraordinarily small ESR signal even before heating. The resulting ratio of signal to noise makes it difficult to tell in what way it resembles or differs from the other types, but should other samples of Briar Creek chert show the same low ESR intensity, that in itself would be a distinguishing characteristic.

Using both heated and unheated spectra provides more information than relying on either one alone. In a test examining an “exotic” artifact found with a Normanskill assemblage, the unheated spectra differed only subtly while there were major differences in the heated ones (Figures 14 and 15). The exotic sample was expected to be Jasper, on the basis of color and texture, and in fact the ESR spectrum resembles that of Jasper in both heated and unheated states. Rink and Smith (*pers. comm.*) were able to separate local and exotic jasper sources for a microlith blade with ESR, obtaining results similar to those cited in this work.

As with trace element analysis, it remains to be seen whether the broad features outlined above will continue to be helpful when more samples of the same chert type and/or more types of chert are tested. The chemical composition of a chert nodule can depend on whether it formed at one end of a basin or at the other. Given that the ESR spectrum is a function of precise chemical structure, it is reasonable to suppose that ESR properties might vary with basin location as well. However, the presence or absence of carbon radical peaks, as opposed to variations in the size of such peaks, is likely to be a constant factor in a given formation. Furthermore, the range of potential chert types in a given assemblage is unlikely to be unlimited. Importation of Ocala chert from Florida into Michigan, for example, is improbable (although not impossible) when there are so many other usable chert types regionally available. Thus an ability to

distinguish *some* chert types may still be useful. Moreover, ESR testing is rapid and relatively non-destructive; adequate information can be obtained with a sample less than 100 mg. Of course, many artifacts are too valuable for any physical interference, and those would rely on other methods.

9. Conclusions

Applying electron spin resonance techniques to chert—especially New World chert—for the purpose of dating and provenance, is still largely in the proof-of-concept stage.. The theoretical grounding is secure, but practical details need to be refined. What has been established so far regarding ESR as a dating method is that those chert types known to have been heated in antiquity have radiation-related features in common. The effect of heating, once or repeatedly within the known working range, does not alter the material's response to radiation. And chert is sufficiently sensitive to radiation that artifacts only a few thousand years old show a signal sufficient to allow them to be dated, although in practice the experimental uncertainty is too large to be truly useful. Most of these experiments used debitage from workshops rather than artifacts that should not be destroyed. It should be noted, however, that by working in the L-band of ESR (rather than the X-band of most spectrometers, including the one here), whole artifacts can be inserted into the spectrometer and studied without powdering. This deserves attention in future studies.

Applications to source determination are less well developed. It would, however, be reasonably easy to set up an analytical program that would establish whether the information gained from ESR is comprehensive or limited in scope. An example that can perhaps be extended to chert is proveniencing studies on marble. ESR spectra were shown to discriminate between marble quarries in the Eastern Mediterranean (Polikreti and Maniatis, 2002). This has been expanded and quantified by Attanasio *et al.* (2008).

The tendency in scholarly research has been towards increased specialization, but this volume, with contributions from archaeologists, chemists, physicists, and geologists is a clear demonstration of the value of multifaceted collaboration. Advances in all these fields depend on continued contacts across the imaginary boundaries of disciplines.

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References

Aitken, M.J. 1990. *Science-based Dating in Archaeology*. Longman Archaeology Series. London and New York.

Attanasio, D., Brilli, M., Bruno, M. 2008. The Properties and Identification of Marble from Proconnesos (Marmara Island, Turkey): A New Database Including Isotopic, EPR and Petrographic Data. *Archaeometry* 50 747-774.

Barabas, M., Mudelsee, M., Wlather, R., Mangini, A. 1992. Dose-response and Thermal Behaviour of the ESR Signal at $g=2.0006$ in Carbonates. *Quaternary Science Reviews* 11 173-179.

Bartoli, J., Ikeya, M. 1997. ESR dating of pottery: a trial. *Applied Radiation and Isotopes* 48 981-984.

Blackwell, B. A. B., Leung, H. Y., Skinner, A. R., Schwarcz, H. P., Lebel, S., Valladas, H., Blickstein, J. I. B., Divjak, M. N.. 2000. External Dose Rate Determinations of ESR Dating at Bau de l'Aubesier, Provence, France. *Quaternary International*, 68–71, 345–361.

Cackler, P.R., Gascock, M.D., Neff, H., Iceland, H., Pyburn, K.A., Hudler, D., Hester, T.R. and Chiarulli, B.M. 1999. Chipped stone artefacts, source areas, and provenance studies of the northern Belize chert-bearing zone. *Journal of Archaeological Science* 26, 389–397

Dibble, H.L., Aldeias, V., Alvarez-Fernández, E., Blackwell, B. A. B., Hallett-Desquez, E., Jacobs, Z., Goldberg, P., Lin, S.C., Morala, A., Meyer, M.C., Olszewski, D.I., Reed, K., Reed,

D., Rezek, A., Richter, D., Roberts, R.G., Sandgathe, D., Schurmans, U., Skinner, A. R., Steele, T.E., el-Hajraoui, M. 2012. New Excavations at the Site of Contrebandiers Cave, Morocco. *PaleoAnthropology* 2012, 145-201.

Domanski, M., Webb, J. A., Boland, J. 1994. Mechanical Properties of Stone Artefact Materials and the Effect of Heat Treatment. *Archaeometry* 36, 177–208.

Godfrey-Smith, D.I., Bouchet, L., von Bitter, P.H., Storck, P.L. 2005. Thermal Activation Characteristics and Thermoluminescence of Chert from the Red Wing, Ontario Region, and its Putative Heat Treatment in Prehistory. *Geochromometria* 24. 13-20.

Griffiths, D. R., Bergman, C.A., Clayton, C.J., Ohnuma, K., Robins, G.V., Seeley, N.J. 1987a. Experimental Investigation of the Heat Treatment of Flint. In: Sieveking, G.G., Newcomer, M.H., (Eds.), *The Human Uses of Flint and Chert*, pp. 43–52. Cambridge University Press, Cambridge.

Griffiths, D. R., Woodman, P.C. 1987b. Cretaceous Chert Sourcing in North East Ireland: Preliminary Results. In: Sieveking, G.G., Newcomer, M.H., (Eds.), *The Human Uses of Flint and Chert*, pp. 249–252. Cambridge University Press, Cambridge.

Ikeya, M. 1975. Dating a Stalactite by Electron Paramagnetic Resonance. *Nature*, 255, 48–50.

Ikeya, M. 1993. *New Applications of Electron Spin Resonance: Dating, Dosimetry and Microscopy*. World Scientific, Singapore.

Luedtke, B. E. 1992. *An Archaeologist's Guide to Flint and Chert*. Archaeological Research Tools No. 7. Institute of Archaeology, University of California, Los Angeles.

.

Lloyd, R. V., Smith, P. W., Haskell, H.W. 1985. Evaluation of the Manganese ESR Method of Marble Characterization. *Archaeometry* 27, 108–116.

Markham, M. and Floyd, P.A. 1998. Geochemical fingerprinting of West Cornish greenstones as an aid to provenancing Neolithic axes. *Geoscience in southwest England* 9, 218–223.

Martini, M., Sibilis, E., Croci, S., Cremaschi, M. 2001. Thermoluminescence (TL) Dating of Burnt Flints: Problems, Perspectives and Some Examples of Application. *Journal of Cultural Heritage* 2, 179–190.

Polikreti, K., Maniatis, Y. 2002. A new methodology for the provenance of marble based on EPR spectroscopy. *Archaeometry* 44. 1-22.

Porat, N., Schwarcz, H.P. 1991. Use of Signal Subtraction Methods in ESR Dating of Burnt Flint. *Nuclear Tracks and Radiation Measurements*. 18, 203–212.

Purdy, B. A., Brooks, H.K. 1971. Thermal Alteration of Silica Minerals: An Archaeological Approach. *Science* 173, 322–325.

Richter, D. 2007. Advantages and Limitations of Thermoluminescence Dating of Heated Flint from Paleolithic Sites. *Geoarchaeology*, 22, 671-683.

Rink, W.J., Bartoli, J., Schwarcz, H.P., Shane, P., Bar-Yosef, O. (2007). Testing the reliability of ESR dating of optically exposed buried quartz sediments. *Radiation Measurements* 42, 1618-1626.

Schwarcz, H. P. 2002. Chronometric Dating in Archaeology: A review. *Accounts of Chemical Research*, 35, 637-643.

Schwarcz, H.P., Buhay, W.M., Grün, R., Valladas, H., Tchernov, E., Bar-Yosef, O., Vandermeersch, B. 1989. ESR Dating of the Neanderthal site, Kebara Cave, Israel. *Journal of Archaeological Science*, 16, 653-659.

Skinner, A.R. 2006. An Introduction to Electron Spin Resonance (ESR) Dating in Archaeology and Paleontology. *The Review of Archaeology*, 27, 87-97.

Skinner, A. R. 2014. Electron Spin Resonance, General Principles. *In*: Rink, W.J. Thompson, J. W (Eds.), *The Encyclopedia of Scientific Dating Methods*. Springer-Verlag, Berlin-Heidelberg.

Skinner, A.R., Blackwell, B.A.B., Adams. B. 2001. Electron Spin Resonance and Lithic Technology. Society for American Archaeology Abstracts of the 66th Annual Meeting, p. 346.

Skinner, A. F., Rudolph, M.N. 1996a. The Use of the E' Signal in Flint for ESR Dating. *Applied Radiation and Isotopes* 47, 1399–1404.

Skinner, A. F., Rudolph, M.N. 1996b. Dating Flint Artifacts with Electron-Spin Resonance: Problems and Prospects. *In*: Orna, M.V., (Ed.) *Archaeological Chemistry: Organic, Inorganic and Biochemical Analysis*. Symposium Series 625. American Chemical Society, Washington, D.C. 37–46.

Speer, C. 2010. Understanding the Effects of Heat Treatment on Edwards Plateau Chert. *Ethnoarchaeology* 2 153-172.

Toyoda, S., Ikeya, M., Dunnell, R.C., McCutcheon, P.T. 1993. The Use of Electron Spin Resonance (ESR) for the Determination of Prehistoric Lithic Heat Treatment. *Applied Radiation and Isotopes*, 44, 227-231.

Valladas, H., Mercier, N., Froget, L., Hovers, E., Joron, J. L., Kimbel, W. H., Y. Rak, Y. 1999. TL Dates for the Neanderthal Site of the Amud Cave, Israel. *Journal of Archaeological Science* 26. 259-268.

Appendix A: Theoretical basis of electron-spin resonance

All spectrometric methods require the absorption of resonant energy in order to change a chemical system from one well-defined state to another. Electron spin resonance detects energy absorbed by unpaired electrons. The most stable chemical bond consists of electrons that are paired, one spinning in one direction, the other in the other. Radiation can remove one electron. In theory this creates two unpaired electrons, the one that is removed and the one that remains. In practice the latter is much easier to detect since its chemical environment is reproducible. “Chemical environment” means the precise relationship of the unpaired electron to all the other atoms in its neighborhood. The ESR signal is very sensitive to the chemical composition; if one or more of the neighboring atoms is changed, the signal will shift position and/or change shape. In ESR spectrometry, the absorption of energy causes the unpaired electron to reverse the direction of its spin.

Any substance that contains unpaired electrons is called “paramagnetic” because the electrons can interact with a magnetic field. In the presence of a magnetic field the two spin directions have different energies (one is parallel to the magnetic field; the other is anti-parallel). The sample to be studied is placed in a magnetic field, which is varied until the resonant value, the value that corresponds to the difference in energy between the two spin directions, is reached. At that value, the unpaired electron absorbs energy and produces a signal. When the field energy is any value greater or less than the resonant value, the electron remains in its original spin direction. While the direction of the spin may change, the electron remains unpaired at all times during the ESR measurement, allowing the same sample to be measured repeatedly. Therefore the experimenter can investigate the effect of different experimental conditions, and also check anomalous results. In contrast, with TL the input of thermal energy causes unpaired electrons to recombine, destroying the dating information. To repeat a TL dating experiment requires a new sample. Equation 2 describes the resonant phenomenon, where H is the value of the magnetic field, β is a constant, and g is a factor that characterizes a given unpaired electronic state:

$$\text{Energy} = g\beta H. \quad (2)$$

The value of g is a function of the environment of the electron as described above. Therefore each type of unpaired electron will have a different g -value and will absorb energy in a different part of the magnetic spectrum. The size of the absorption peak will be a function of the number of unpaired electrons of that particular type.

For those accustomed to looking at absorbance spectra, ESR spectra will look quite different. ESR spectrometers are designed to show the first derivative of the absorption spectrum because presenting data in this fashion makes it easier to detect the changes in peak position that most researchers seek. However, the original peak size can be found from the “height” of the ESR peak if the shape of the original peak is known. Figure 16 shows this relationship. Naturally formed materials such as chert seldom have as simple an ESR spectrum as implied by Figure 16. Nonetheless it can usually be demonstrated that the ESR peak height is sufficiently proportional to the amount of radiation damage to allow one to plot intensity directly from the spectrum.

Figure Captions

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

Figure 2. ESR spectra of a) unheated and b) heated chert from the Ocala formation, Florida. The unheated spectrum shows peroxy and E' peaks; H represents the height of the signal used for dating.

Figure 3. Typical growth curve for ESR intensity as a function of radiation dose. The shape of the curve is a saturating exponential; once saturation intensity is reached, the age appears to be infinite.

Figure 4. The effect of varying D_{ext} on the calculated object age. The central point is the age as calculated with modern dose rate parameters. The error bars represent 1σ errors. In this case, the external dose rate can vary from about 200 $\mu\text{Gy/a}$ to about 400 $\mu\text{Gy/a}$ without changing the calculated age by more than 2σ . Other examples may provide larger or smaller ranges.

Figure 5. Effect of heating at 350C on the E' signal. Prolonged heating yields an irreducible minimum signal.

Figure 6. Growth of the ESR signal in an archaeologically heated artifact before and after reheating to find the minimum signal.

Figure 7. The ESR intensities for the unheated artifact have been shifted by 21 Gy. The two curves now lie on a single line. Thus the D_e for this artifact is 21 Gy.

Figure 8. Suggested protocol for rapid screening to detect promising artifacts for dating.

Figure 9. ESR spectra of a) raw and b) heated Fort Hood chert. Note the presence of manganese in the raw spectrum, and organic radical peaks in the heated. The peroxy peak in the raw spectrum also shows some small complexity.

Figure 10. ESR spectra of a) raw and b) heated Crescent chert. Note the complex E' peak in the raw sample and the absence of organic radicals in the heated spectrum.

Figure 11. ESR spectra of a) raw and b) heated Fort Payne chert. Note the complex shapes of the peroxy and E' peaks in the raw spectrum.

Figure 12. ESR spectra of a) raw and b) heated Vanport chert. Note that the peroxy peak is vanishingly small compared to the E'. The E' peak shows complexity in both the raw and heated samples.

Figure 13. ESR spectra of a) raw and b) heated Hardyston (Jasper) chert. The unheated spectrum resembles Crescent, but the E' is broad rather than showing a distinct complex element.

Figure 14. ESR spectra of a) Normanskill and b) suspected exotic cherts, unheated. Only minor differences can be seen.

Figure 15. ESR spectra of a) Normanskill and b) suspected exotic cherts, heated. The two are now clearly distinguishable.

Figure 16. The relationship between intensity and the first derivative of intensity. The ESR “peak height,” H , corresponds to the width of the original peak at half-maximum value. The mathematical relationship between peak width and area allows values of H to be used to measure absorption.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

POTENTIAL SCREENING PROTOCOL FOR ESR DATING OF FLINTS

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

First Derivative of Absorption