Improved detection of EPR signals used in quartz dating

W. Jack Rink† and Yuhei Shimoyama‡
†Subdepartment of Quaternary Research, University of Cambridge, Free School Lane, Cambridge, CB2 3RS, England.
‡Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, England.

Vector electron paramagnetic resonance spectroscopy has been successfully applied to the quartz phase of granites and rhyolites. The E' centre signal has been selectively detected by complete suppression of the OHC signal, thereby resulting in a well defined isolated spectrum for spin concentration determination. This is achieved by variation of the phase of the magnetic field modulation, and takes advantage of saturation transfer which occurs during the relaxation process of the E' centre.

Introduction

EPR dating (usually referred to as ESR dating) has found wide application in Quaternary geochronology and archaeometry (Grün, 1989) and more recently has shown potential for dating back to the Precambrian using quartz (Odom et al, 1989). EPR dating of quartz is presently in a development stage, with efforts underway to date volcanic, plutonic and hydrothermal crystallization of quartz as well as to date faults, cementation in sandstone and ancient heating of flint. The physical basis of EPR dating has been reviewed by Grün (Grün, 1989).

Two types of radiation-induced defect centres which are important to dating quartz are the E' centre (Grün, 1989) and the so called OHC (peroxy radical) centre (Rink and Odom, 1991). The E' centre signal has primarily been used in efforts to date faults (Fukuchi et al, 1986; Ikeya et al, 1982). The E' centre signal, which may be due to one or more types of similar defects, involves oxygen vacancies containing unpaired electrons (Yip and Fowler, 1975; Weil, 1984). In fused silica, two different types of OHC centres are attributed to trapped holes on non-bridging peroxy sites (Friebele et al, 1979). Similar paramagnetic defects apparently occur in crystalline quartz, evidenced by the similarity of the OHC signals in fused quartz to certain signals in crystalline quartz. The precise nature of the OHC centres in quartz is still a source of controversy (Rink and Odom, 1991).

The E' centre in quartz is usually detected by using a microwave power level between 0.01 and 0.1 (mW) (Odom et al, 1989). However, this procedure may only partially suppress the OHC signal. Complete suppression of the OHC signal is important to dating quartz with EPR because in some cases it interferes with determination of the signal intensity of the E' centre. The primary aim of this paper is to describe how improved selective detection of the E' signal can be achieved by the Vector EPR Method.

The Vector EPR Method has been developed firstly in the systems of nitroxide radicals in solution (Shimoyama and Watari, 1986) and later applied to other paramagnetic species (Shimoyama et al, 1990,Watari et al, 1989). The non-linear response of electron spins under saturating conditions is found to be useful, because it promotes a drastic phase change. This phase change then allows the detection of a signal component whose phase shift away from the in-phase position depends upon the relaxation rate of the electron spins (Shimoyama and Watari, 1985).

Experimental Methods

The quartz was separated from the granites using standard methods described elsewhere (Rink and Odom, 1991), and from the rhyolite using H_2SiF_6 acid treatment of the <50 μm fraction to remove feldspars. EPR measurements have been made using a JEOL X-band spectrometer (RE-1X). All spectra were observed with the first harmonic absorption mode (first derivative display), and modulated/demodulated at 100 kHz/100kHz frequencies. The sample was placed at the centre of the cylindrical cavity (TE_{011} mode) in an unsealed fused quartz sample tube.

The phase of magnetic field modulation was varied over the entire available 360° range at intervals of 30°. Two important phase positions of field modulation were identified in the present study: the null phase (also termed out-of-phase or quadrature) and the in-phase of filed modulation. In order to determine these specific values of field modulation, first the OHC signal was observed using 10 mW microwave power and arbitrary phase of field modulation. Then the phase was adjusted to obtain zero intensity of the OHC signal, which is defined as the null phase (Shimoyama and Watari, 1989). At the null phase position, only the E' centre signal was obtained. Then the in-phase value was obtained by simply adjusting the phase of field modulation to a position 90° away from the null phase position.

Results

Figure 1 shows the results of variation between the null phase and the in-phase of field modulation on the spectrum of quartz from the Libyan Addaba Mohamed Salah granite (El-Makhrouf, 1988). fig. 1A shows the in-phase OHC signal, extending from $g \approx 2.010$ to 2.003. In contrast, the spectrum when measured under null phase conditions (fig. 1B) shows only the E' centre at $g \approx 2.001$. Importantly, note also that the OHC signal is completely suppressed. Selective detection of the E' signal has therefore been achieved. Less complete suppression of the OHC signal can be achieved using a microwave power level ca. 0.1 mW or less, as shown in fig. 1C. Selective detection of the E' centre was also achieved using quartz from the Overflow Pond Granite (Dallmeyer et al, 1983) from Newfoundland. Figs. 1D and 1E show similar results obtained for quartz from the Castell Grug Intrusive Rhyolite (Fitch, 1967) from North Wales.

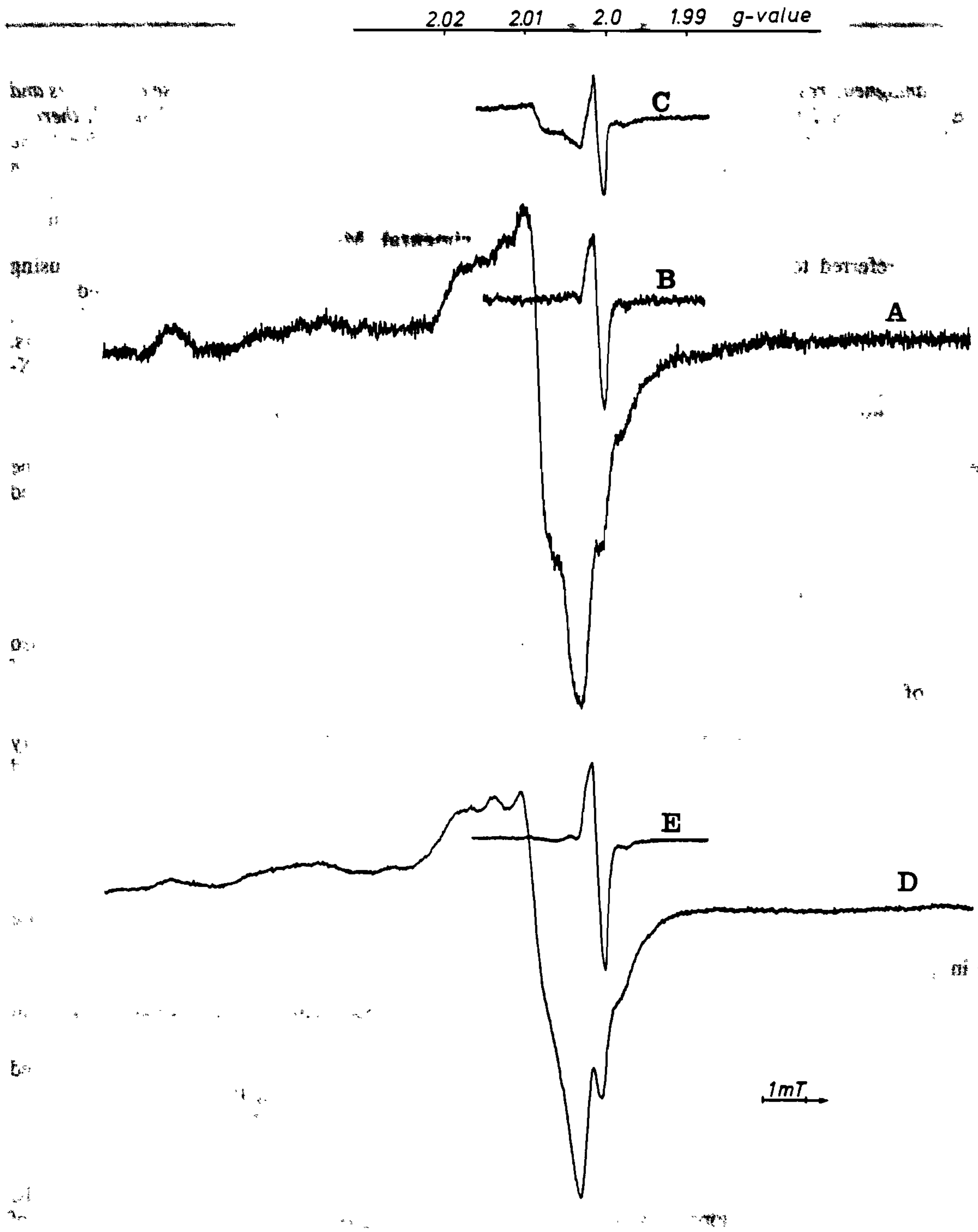

Figure 1. EPR spectrum of quartz isolated from the Addaba Mohamed Salah granite (A, B, C) and Castell Crug intrusive rhyolite (D,E) under various experimental conditions. A and D) in-phase spectrum showing OHC signal between g ≈ 2.010 and 2.003 obtained at 10 mW microwave power. B and E) null phase spectrum showing only E' centre signal obtained at 10 mW power. C) in-phase spectrum showing E' signal and OHC signal obtained at 0.1 mW power. All spectra obtained using 0.2 mT modulation amplitude.

Figure 2 shows the variation of the peak-to-peak amplitude of the first harmonic absorption of the E' and OHC signals as a function of the phase of field modulation. It is seen in fig. 2B that at 0.05 mW microwave power, where little saturation is involved, both the E' and OHC signals behave similarly. This clearly shows that neither signal can be selectively detected using this approach. On the other hand, fig. 2A shows that at 10 mW microwave power, a phase offset appears, which displaces the E' centre about 90° away from the OHC signal. Trow at 90° in fig. 2A indicates the null phase position used to record the spectrum in fig. 1B, whereas the arrow at 0° indicates the in-phase position for obtaining the spectra of fig. 1A and 1C.

Discussion

Previous attempts at selective detection of the E' signal obtained only the type of spectrum shown in fig. 1C, in which the OHC signal may still be a significant component of the spectrum. Complete suppression of the OHC signal yields the E' signal on a flat baseline (fig. 1B). This is extremely useful when integration of the E' signal is employed in spin concentration determinations. E' centre spin concentration determinations are used in the development of a quartz dating method that involves Schottky-Frenkel radiation defects (Rink and Odom, 1991; Rink, 1990).

The saturation transfer phenomenon that promotes signal suppression during quadrature detection can be induced by two different mechanisms. They are spectral diffusion and saturation recovery (Shimoyama and Watari, 1986). Since the quartz system involves only hindered molecular motion, spectral diffusion is not expected. Therefore, saturation recovery is mainly responsible for saturation transfer in the quartz system. The process of saturation recovery depends upon the relaxation times of the various paramagnetic species in the quartz. The saturation transfer due to the saturation recovery modulates the inherent phase of the resonance line with respect to the reference wave of field modulation. The other words, the passage or velocity of field change associated with 100 kHz field modulation at certain applied fields detects phase differences due to different relaxation times of the OHC and E' centres in the quartz.

It is clear that application of this technique will have considerable value in selective detection of signals embedded within complex spectra of other minerals suitable for EPR dating. This is because microwave power saturation is often used to remove undesirable signals in minerals used for dating.

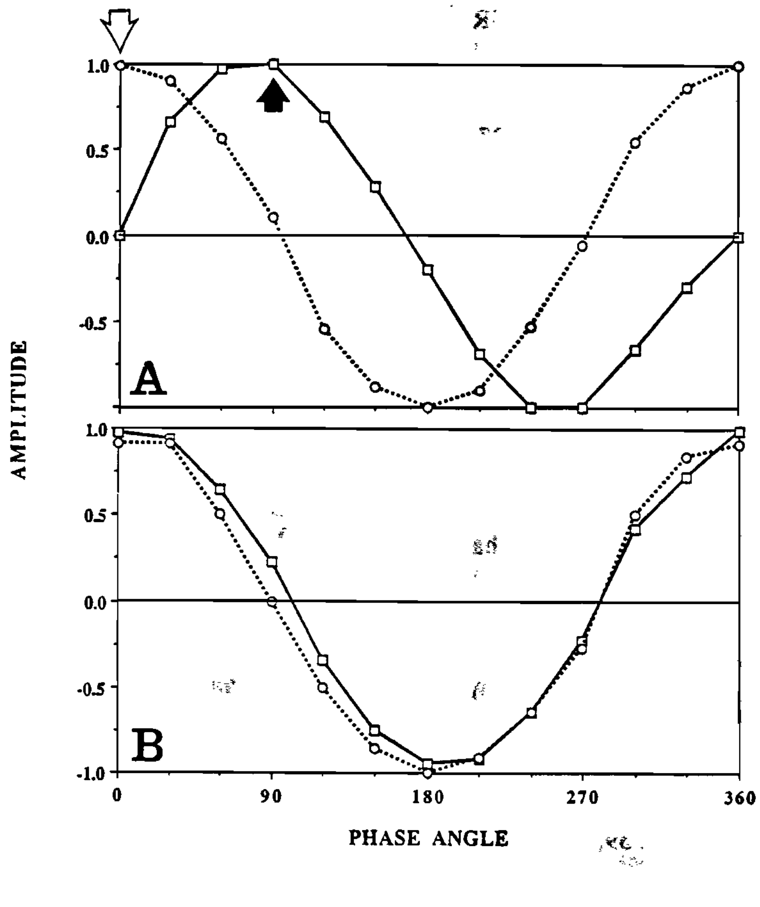

Figure 2. Variation of normalized peak-to-peak amplitudes of the first harmonic absorption of the E' (squares) and OHC (circles) signals versus phase of magnetic field modulation. A) 10 mW microwave power, B) 0.05 mW microwave power. The arrows indicate the null phase position (dark arrow) and the in-phase position (open arrow) used to obtain the spectra of figs. 1B and 1A respectively.

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