

The method to represent the ESR signal intensity of the aluminum hole center in quartz for the purpose of dating

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Abstract

The aluminum hole center (Al center, $[AlO_4]^0$) in quartz is one of the signals useful for ESR dating of tephra, sediments, faults, and flints. The best peak position in the spectrum was investigated to measure the intensity of the Al center signal which has a complex structure of the powder spectrum. The peak height from the top of the first peak ($g=2.0185$) to the bottom of the 16th peak ($g=1.9928$) of the main part of the signal is recommended to be taken as the signal intensity of the Al center, where the best reproducibility was obtained of the peak heights examined with avoiding the interference from the peroxy signal. The reproducibility of the peak intensities improved with reducing the size of the quartz grains, to be less than 6% (one sigma error) for grain size fractions less than 250 μm when the signal intensity is measured by the method recommended above.

Keywords

ESR, quartz, Aluminum center, peroxy center

1. Introduction

Quartz has been used to obtain ages of faults (e.g. Fukuchi, 1986, Lee and Schwarcz, 1994), tephra (e.g. Imai et al., 1985, Toyoda et al., 1995), sediments (Yokoyama et al., 1985), and flints (Porat et al., 1994) by electron spin resonance (ESR) dating method. The ESR signal due to aluminum hole center, $[AlO_4]^0$, an aluminum impurity replacing a silicon trapping an electronic hole, is one of the useful signals for this method. The ESR signal shows a complex structure due to hyperfine splitting, nuclear Zeeman, and quadrupole terms due to ^{27}Al ($I=5/2$) (Nuttall and Weil, 1981). As powder samples are measured for the purpose of dating, we usually see averaged powder spectrum where each term has its anisotropy as well as its g factor.

It is not trivial which peak height to take as the intensity of the signal. Each research group who studies ESR dating of quartz has had their own way of measuring the intensity. Yokoyama et al. (1985) observed 16 peaks in the main part of complex spectrum and examined equivalent doses from those peaks. They found that the D_{ES} (equivalent doses) obtained for 16 peaks and for the peak height from top of the first to the bottom of the 16th peak were consistent except for two after extrapolating the dose response curves. They decided to take the peak height from the top of the first to the bottom of the 16th.

On the other hand, Imai and Shimokawa (1988) took a peak height from the maximum to minimum of the main part of this signal with an modulation amplitude of 0.5 mT. By using a large modulation amplitude, they obtained a good reproducibility of the signal. Toyoda and Ikeya (1991) took a peak to peak intensity of the first peak with a nominal g factor of 2.018 of this signal. They took an average of six measurements rotating the sample tube in the cavity in order to reduce the variability due to angular dependence of the signal. They used grain size fractions of 75-250 μm and obtained reproducibility of about 5%. In the present work, the best way of these three methods was searched to evaluate the intensity of the Al center by comparing the reproducibility of the intensity with respect to the grain size of the sample and by examining possible interference from other signals.

2. Samples

Two quartz samples were prepared for the present experiment. One is named "ECH" from a quartz vein, France, and the other is from a sediments, named "C260", near a site shocked by a meteorite in Chad. ECH was crushed gently in a mortar with a pestle and sieved to 50-100, 100-200, 200-400, 400-800, and 63-250 μm fractions after being irradiated by ^{60}Co gamma rays to 2 kGy. The other sample, C260, was crushed and sieved to

extract a 100-200 μm grain size fraction where no gamma rays were given.

3. ESR measurements I

ESR signals in C260 were observed with a Bruker ESR spectrometer, ESP-300 to compare the spectrum at room temperature with that at 77K. We used microwave power of 1 mW for the measurements at room temperature or of 5 mW for those at liquid nitrogen temperature, a modulation frequency of 100 kHz and an amplitude of 0.1 mT, and a scan range of 10 mT, a sweep time of 83 seconds. The measurements at liquid nitrogen temperature (77K) were done with a finger dewar filled with liquid nitrogen while the measurements at room temperature were also done with a finger dewar without filling liquid nitrogen in order to make the frequency of the resonant microwave as close as possible with the measurements at liquid nitrogen temperature. Precise g factors were determined from the magnetic fields measured at two end points of the spectrum by using a NMR gaussmeter, and from the microwave frequency measured by using a frequency counter.

4. ESR measurements II

The Al center signals in series of ECH samples were recorded with a Varian ESR spectrometer and with a variable temperature apparatus which kept the sample

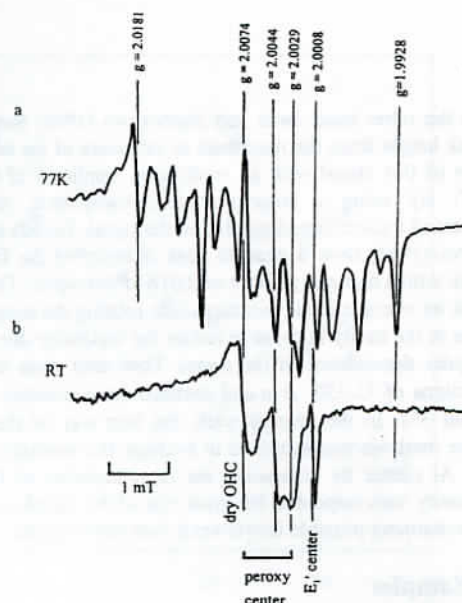


Fig. 1 ESR spectra observed in a sedimentary quartz sample (C260) a) at 77K and b) at room temperature. The main part of Al center signal was observed at 77K while peroxy radical and the E_1' center signals are observed at room temperature.

at 90K. We used a microwave power of 5 mW, a modulation frequency of 100 kHz and an amplitude of 0.1 mT, a scan range of 10 mT and a time constant of 0.3 seconds. The mass of each sample was 100 mg where grain size varies sample to sample. The peak to peak height at nominal g factor of 2.0181 (Method 1, following the method used by Toyoda and Ikeya, 1991) and the height from the top of the first ($g=2.0185$) to the bottom of the 16th ($g=1.9928$) peaks of the main part of the Al center (Method 2, following the method used by Yokoyama et al., 1985) were taken as the intensities. The measurements were repeated six times with rotating the sample tube within the cavity. The average and the standard deviation of the six measurements were calculated for each method.

5. Results

5.1 Signals interfering with that of the Al center

Figure 1 shows the spectra observed in C260 at room temperature and at 77K. The microwave frequencies were 9.41253 GHz at room temperature and 9.41045 GHz at 77K. The two spectra were placed in the figure so that the g factors in each spectrum coincide with each other where precise g factors were calculated from the magnetic fields and the microwave frequencies.

The spectrum observed at room temperature (Fig. 1b) shows the signal of the E_1' center ($g=2.0008$ at center) together with those of the peroxy radical. The identification of the latter signal was done by Odom and Rink (1989) and more precisely discussed by Ikeya (1993). The spectrum observed in the present study shown in Fig. 1b is essentially consistent with those observed in the above studies. The authors of those papers insisted that the g factors of this signal coincide with those of peroxy radical found in quartz glass studied by Stapelbroek et al. (1979). The anisotropic g factors of the peroxy radical (dry OHC) in quartz glass are 2.0014, 2.0074, and 2.067. If we assume that we observe right half of this signal in Fig. 1b, $g=2.0074$ is indeed consistent with one of the g factors of peroxy radical in quartz glass but there is no signal showing the bottom at $g=2.0014$ while the g factor at the bottom of observed signal is 2.0029, instead. In addition, in Fig. 9.5 of Ikeya (1993), he showed a peak corresponding to $g=2.067$, but the position for this g factor in the spectrum is wrong, the g factor at the position he indicated is actually 2.039, instead. The position for $g=2.067$ must be at 3.82 cm left from the position indicated in that figure. Although the signal identification of peroxy radical in quartz is still doubtful, we could tentatively call this signal "peroxy radical" according to the previous papers.

In the spectrum observed at 77K (Fig. 1a), 16 peaks were observed as Yokoyama et al. (1985) reported. It is clear from Fig. 1 that the signals of "peroxy" and the E_1' center can overlap the region between the 6th to the 12th peaks of the Al center signal.

5.2 Signal reproducibility according to grain size

The standard deviations (1σ) of the intensities for

six measurements were calculated as

$$\sigma = \sqrt{\frac{\sum_{i=1}^6 (x_i - x_m)^2}{5}}$$

where x_i denotes the intensity in each measurement and x_m the average of six measurements. These standard deviations were then divided by the averages to obtain the relative variabilities (σ/x_m) in the signal intensity which are shown in Fig. 2 for Methods 1 and 2 as a function of grain size of the sample. The variabilities are smaller for smaller grain size fractions for both methods where those in Method 2 are systematically smaller than those in Method 1. The variability was 3% in both method for the 50-100 μm fraction but increase up to 42% for Method 1 of the 400-800 μm fraction. It seems that there is a general belief that crushing reduces the ESR signal intensities probably based on the results obtained for the experiments simulating faulting (e. g. Miki and Ikeya, 1982). However, in the present experiment, we did not observe any systematic decrease in signal intensity with decreasing the grain size of the sample although there was variation beyond the measurement reproducibility possibly because of sample inhomogeneity between aliquots. The effect of crushing on radiation sensitivity in dose response would be another important issue to affect dating results, which we do not discuss in the present paper.

6. Discussion

Fig. 1 indicates that the peroxy signal overlaps part of the Al center signal. It will interfere with the intensity of the Al center if the top or the bottom used for the peak height evaluation is in this region and if the peroxy radical is observed at 77K. The method used by Shimokawa and Imai (1987) would be the case. The bottom in one of their figures is at $g=2.002$ which the bottom of the peroxy signal is at. The signal shapes observed at 77K in sedimentary quartz are sometimes different from those observed in quartz from tephra. The former case was observed by Tanaka et al. (1997). It is probably because a large peroxy signal overlaps the Al signal making the signal shape different. Yokoyama et al. (1985) reported that the 9th and 10th Al center lines give inconsistent D_E s. It might also be because of the interference from the peroxy signal and / or from the E_1' center signal.

Therefore, the signal intensity of the Al center signal should not be taken so that top or bottom is between $g=2.000$ and $g=2.008$ unless no peroxy signal is observed such as in volcanic quartz samples. Imai and Shimokawa (1988) obtained consistent D_E s for volcanic tephra by using several different methods of measuring the Al center, even in one of which the bottom of the peak height is within this g factor region. It is probably because their sample did not include any peroxy signal.

Odom and Rink (1989) reported that the intensities of the peroxy radical are correlated with the

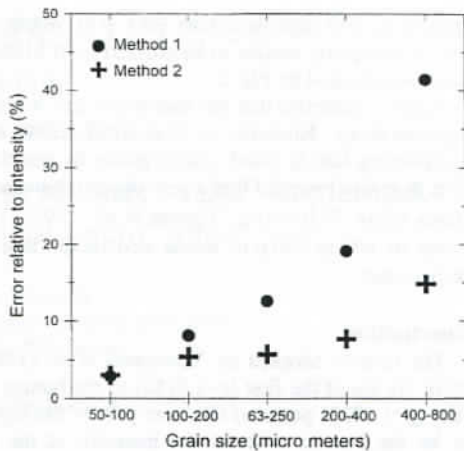


Fig. 2 Relative statistical errors in repeating measurements with rotating the sample tube in the cavity. Solid circles denote the results by Method 1, peak to peak intensity of the first peak of the main part ($g=2.0181$) and solid squares by Method 2, from the top of the first peak ($g=2.0185$) to the bottom of the 16th peak ($g=1.9928$). Method 2 gives systematically smaller error than Method 1.

ages of their host rocks. This is consistent with the discussion above. Young volcanic quartz samples do not show any peroxy radical without giving interference while originally old quartz samples such as sediments, metamorphic rocks, and fault gouge show the peroxy radical signal which interfere the Al center signal.

The two methods described here are both free from interference with the peroxy and/or E_1' center signal as shown in the Fig. 1. None of those peaks are overlapped at and around nominal $g=2.0181$ and 1.9928 .

The intensity of the Al center signal varies significantly when the sample tube is rotated in the cavity especially when the quartz grains are coarse. It is because the Al center signal has very sensitive angular dependence. For coarser grain size samples, the signals are not averaged enough even with 100 mg. As shown in Fig. 2, Method 2 gives results systematically better than Method 1. As for Method 2, we first suspected that the peak height might be interfered by peroxy radical signal, but it is actually safe as indicated by Fig. 1. The peroxy signal is between the two points from which the signal peak height is taken, but there is no interference at both points. The baseline is also at the same level as shown in Fig. 1b.

In the present study, there was no systematic decrease in the Al center signal intensity by crushing. Therefore, the more the sample is crushed, the better reproducibility of the measurements, hence, the better data one obtains. However, the typical statistical error in D_E is 10% when it is obtained by extrapolating the dose response curve to zero ordinate. Therefore, it would be enough for the signal intensities to be obtained within

this precision. For this, less than 250 μm would be enough for the quartz sample to be crushed to, if Method 2 is used, as indicated by Fig. 2.

Figure 2 indicates that the finer grain size is better for reproducibility. However, it is so much effort and time consuming task to crush quartz grains to less than 100 μm . It is also reported that a new signal is produced for grains below 75 μm (e.g. Toyoda et al., 1993). The grain size of 100 to 250 μm would also be the best in this respect, too.

7. Conclusion

The method adopted by Yokoyama et al. (1985) that from the top of the first ($g=2.0185$) to the bottom of the 16th ($g=1.9928$) peaks of the main part of the signal would be the best to evaluate the intensity of the Al center in quartz of the two methods discussed in the present study. The method gives a good reproducibility when the grain size of the quartz is less than 250 μm . The intensity is also free from the interference from the peroxy radical signal even in sedimentary quartz and in fault gouge which usually show large peroxy signals. One should note that the present conclusion applies quartz samples which show peroxy and E_1' centers, such as granitic or sedimentary origin. It is also necessary to pay attention to any possible interference of other signals, such as broad background.

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