entire delignification kinetic process (5). Furthermore, the activation energy obtained for the cleavable aryl ether bonds, 132 kJ/mole, is in good agreement with the value of 123 ± 9 kJ/mole obtained from model compound kinetics (6). The agreement value of the 134 kJ/mole (32 kcal/mole) obtained by the empirical power law technique (5) is considered fortuitous because this technique lacks a molecular basis (1). Values of $k$ in Table 1 are of the same order of magnitude as those obtained for model dimers (6).

There is no experimental value to compare with the calculated activation energy for the cross-linking reaction. This reaction is also known as a recondensation in which the cross-links formed may no longer involve phenolic hydroxyl groups in the kraft medium (1).

I conclude that the treelike model can be used to elucidate the structure and reactions of lignin both qualitatively and quantitatively. Specifically, the model is capable of interpreting the following properties of lignin: (i) classification and identification of cleavable linkages, (ii) change of molecular weight averages and distribution of the lignin sol with delignification (1, 7), and (iii) kinetics of delignification.

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## Dating of a Fault by Electron Spin Resonance on Intrafault Materials

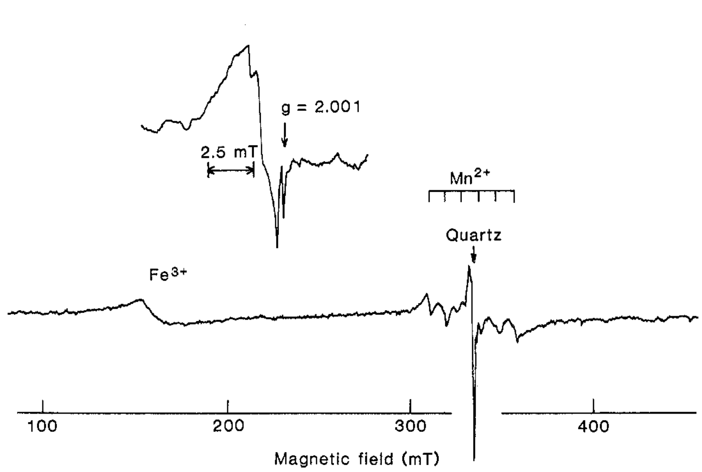
Abstract. *The total dose of natural radiation and the age were determined from paramagnetic defects in quartz grains at a fractured fault zone. Young age at the fault indicates that the accumulated defects in rocks were destroyed by high stress or high temperature at the time of the last fault movement, setting the clock time to zero. The technique was applied to quartz grains crushed by uniaxial compression in the laboratory to verify this interpretation.*

The time of formation or movement of an active fault is important for tracing the history of large earthquakes and assessing the safety of construction sites for nuclear power stations or large buildings from a geological point of view. Fault and fault movement have been studied extensively in geology and geography (1, 2). Generally, faults are accompanied by fracture zones composed of the breccia and gouge called intrafault material. Fault movement has been dated by applying the potassium-argon method to an illite in intrafault materials (3) and by fission track dating of epidotes formed along the fault plane (4). We have developed a method of estimating the time of fault formation or last movement by dating quartz grains from intrafault materials by an electron spin resonance (ESR) method.

Electron spin resonance is useful for the study of natural radiation damage in geological materials (5–7) and for dating such biological materials (8) as shells, corals (9), and fossil bones and teeth (10). Its use for dating fault movement is based on the premise that the lattice defects produced by natural radiation in quartz grains are annihilated by high shearing stress and temperature rise around the fault plane at the time of fault formation or movement. It is assumed that the clock time was set to zero when the movement occurred. This is similar to the assumption made in thermoluminescence dating of ceramics that the firing of clays by ancient humans set the clock time to zero (11). Natural radiation after that time then produces additional lattice defects.

Quartz and feldspar were separated with a magnetic separator from intrafault gouge (clay) and breccia from the Atotsugawa fault, a typical active fault in central Japan (12). Fine grains 74 to 250 μm in diameter were sieved and immersed in HCl for 8 hours. Measurements were made at room temperature with an X-band ESR spectrometer (Japan Electron Optics FE) with 100-kHz field modulation. Artificial gamma irradiation was carried out with a $^{60}Co$ source.

Figure 1 shows an ESR derivative absorption spectrum of such grains taken from the intrafault material. A signal associated with radiation-induced de-



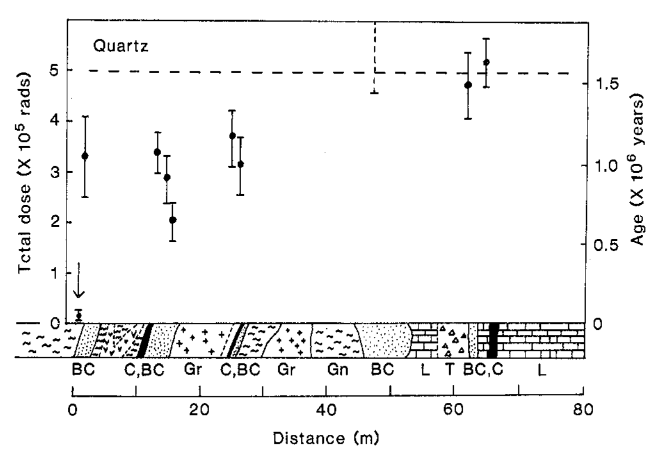




Fig. 1 (left). Electron spin resonance derivative absorption spectrum of quartz grains separated from gouge from Atotsugawa fault. An expanded spectrum of the signal associated with radiation damage in quartz is shown at the top. Fig. 2 (right). Total dose of natural radiation of quartz grains at several sites in the Atotsugawa fault zone. The smallest TD at the age of the fault zone is indicated by the arrow. The age based on the TD and an annual dose rate of 310 mrad is shown on the right ordinate. The abbreviations *BC*, *C*, *Gr*, *Gn*, *L*, and *T* indicate brecciated clay, clay, granite, gneiss, limestone, and talus, respectively.

fects in quartz was detected at a value of the $g$ factor of 2.001, along with signals for paramagnetic $Mn^{2+}$ and $Fe^{3+}$. The lattice model of the defect produced by natural radiation in quartz has been discussed in detail (*7, 13*). The present defects are identified as the E′ center. Thermal annealing studies showed that these defects are removed by annealing at about 360°C, accompanied by thermoluminescence. The stability of the defects or the fading time at 20°C, roughly estimated from the peak temperature of thermoluminescence, is a few million years (*8*).

Artificial gamma irradiation enhances the signal representing defects in quartz grains. The total dose (TD) of natural radiation was obtained from the initial signal intensity, $I_0$, and the signal intensity after gamma irradiation of $Q$ rads, $I(Q)$, by fitting the linear enhancement with the equation

$$I(Q) = I_0(1 + Q/\mathrm{TD}) \qquad (1)$$

Figure 2 shows the TD's of quartz grains at several points in an outcrop of the Atotsugawa fault which cut a Paleozoic Hida gneiss group consisting of granites, gneiss, limestone, and Mesozoic rock. The fault zone is about 30 m wide at the outcrop, consisting of five fractured zones a few meters wide. The TD's at central points in the fault zone are roughly 200 to 500 krad. The defect production shows a tendency to saturate, which gives a large ambiguity in TD obtained from Eq. 1. However, the growth in defect concentration is linear with radiation dose for quartz grains along the fault plane, and the production efficiency is high. A TD of about 20 krad was obtained from Eq. 1. The TD's for quartz grains in parent rocks could not be obtained accurately since the signal intensity of E′ centers was not clearly enhanced by gamma irradiation. These results indicate that the defects in quartz in intrafault materials were annihilated at some time and the defect production rate was increased.

It was noted that the intrafault materials contained laminar, fibrous, and spherical particles, which suggested that localized melting had occurred on the fault plane (*14*). Theoretical calculations indicate a temperature rise of about 1000°C in some cases (*15*). Such melting or recrystallization would occur due to the high shearing stress responsible for the fault movement. Defects may be annihilated far below 360°C, before recrystallization occurs.

We applied uniaxial stress to quartz grains and crushed them by compression. The ESR signal intensity of the E′ center was decreased by one-half as the stress was increased to about 100 MPa. It has been reported that plastic deformation destroyed color centers, like F centers and F aggregate centers, in alkali halides by the movement of dislocations (*16, 17*). We therefore conclude that radiation-induced defects or trapped electrons in quartz grains were annealed out by local frictional heating or by plastic deformation and that this occurred at the time of fault formation. We also observed intrafault materials at another outcrop of the Atotsugawa fault with a small TD of about 10 krad due to recent fault movement.

The annual gamma radiation at several points in the fault zone 50 cm below the ground surface was measured with a sensitive $CaSO_4$(Tm) thermoluminescence dosimeter (Panasonic TLD, UD-110S) to be about 130 mrad per year. The uranium, thorium, and potassium contents of the intrafault material were determined by gamma-ray spectroscopy with a Ge(Li) detector and found to be $\sim 1.5 \pm 0.1$ ppm, $7.9 \pm 0.4$ ppm, and $1.8 \pm 0.1$ percent, respectively. The calculated annual doses of alpha, beta, and gamma radiation ($D_\alpha$, $D_\beta$, and $D_\gamma$) based on the contents of radioactive elements are 980, 192, and 116 mrad per year, assuming secular equilibrium of the disintegration series (*11*). The result obtained with the thermoluminescence dosimeter agrees well with the value of $D_\gamma$, considering the contribution of half of the cosmic rays (about 15 mrad per year) 50 cm below the ground (*11*).

The dose from alpha radiation, $D_\alpha$, should not be fully taken into account for quartz grains since the content of radioactive elements in quartz is negligible. The surface region damaged by external alpha radiation constitutes about 30 percent of the volume of the grains. The efficiency of defect production by alpha radiation ($k$ value) is generally taken to be 0.1 to 0.2. Considering the volume damaged, the effective dose from alpha radiation would be about 0.03 to 0.06 $D_\alpha$. However, the damaged surface region is removed appreciably by etching with HCl or $H_2SiF_6$ during sample preparation, and we confirmed that further etching with HCl or HF did not affect the signal intensity of E′ centers appreciably. Thus we tentatively neglect the contribution from alpha radiation, which is 30 to 60 mrad per year at most, and use the calculated values of $D_\beta$ and $D_\gamma$ of 310 mrad per year. A tentative age estimated from TD is shown on the right ordinate in Fig. 2. It is known that radon and its daughters accumulate at fault zones. The contribution of radioactive elements after radon in its disintegration series is generally small if the effect of alpha radiation can be neglected.

The age of quartz grains along the fault plane is about $6.5 \times 10^4$ years; the last fault movement at the site would have occurred at that time. This age should be multiplied by the factor 0.95 if the fault was not deep at that time and the contribution from cosmic rays, 15 mrad per year, is taken into account. The contribution from alpha radiation, if any, would be about 10 percent in the age estimation.

This study indicates that ESR can be used to estimate the time of last fault movement in the Quaternary by dating the quartz grains in intrafault materials. Systematic studies involving ESR dating of intrafault materials together with more accurate estimates of radiation might clarify the history of fault movements and earthquakes in the vicinity.

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