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In situ production of alpha particles and alpha recoil particles in quartz applied to ESR studies of oxygen vacancies☆

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Abstract

The intensity of an ESR signal associated with oxygen vacancies in quartz (E_1' center and heat-treated E_1' center) are correlated with the radiometric age of their host rocks. Two natural processes are responsible for the production of oxygen vacancies (1) lattice damage along alpha recoil and alpha particle tracks and (2) randomly distributed ionization damage from energetic electrons (beta particles) and gamma photons. The aim of this paper was to determine whether the track damage process is dominant relative to the ionization processes. Heat-treated E_1' centers are considered a proxy measure of the oxygen vacancy concentration. In situ alpha irradiation of quartz was accomplished by neutron irradiation of lithium and boron-bearing quartz. We found that the oxygen vacancy population measured by ESR was a factor of 2 higher than estimated from calculations of the damage using Ziegler's TRIM software. Considering the uncertainties in absolute determinations of spin concentration from ESR signals, the agreement is very good and supports the theory that alpha particle damage is largely responsible for oxygen vacancy production during natural irradiation of quartz over intervals of hundreds of millions of years. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

The ESR dating method has been applied to quartz in order to obtain ages of fault movements, volcanic eruptions, sedimentation and heating of flint. The application of the ESR method was previously limited to Quaternary time until Odom and Rink (1989) found a correlation between the ESR intensities of the E'_1 center (and the peroxy radical signals) and the crystallization age of their host rocks.

The E_1' center is a lattice defect in quartz, an oxygen vacancy having an unpaired electron (Feigl et al., 1974). The E_1' center increases on heating while other impurity centers decrease. In granitic quartz the intensity of the E_1' center first increases by up to a factor of five during heating to 300°C, and then decreases at higher temperatures if the heating time is 15 min in a stepwise heating experiment (Toyoda and Ikeya, 1991). According to Jani et al. (1983), this increase of the intensity is due to recombinations of electronic holes supplied by hole centers, such as an Al center ($[AlO_4]^0$), with one of the electrons in neutral oxygen vacancies (Si–Si bond). On heating, a hole is released from a hole center and moves to a neutral oxygen vacancy with two electrons and recombines with one of the electrons thus forming an E_1' center.

Using this characteristic of the E_1' center, a method was proposed to evaluate the concentration of its host lattice site, the oxygen vacancies (Toyoda and Ikeya, 1991; Toyoda et al., 1992). Gamma-ray irradiation to more than 200 Gy forms hole centers in quartz, then heating at 300°C transfers the electronic holes. The resulting E_1' center intensity is called the heat-treated E_1' center. The gamma-ray irradiation above 200 Gy gives the constant heat-treated E_1' center intensity (Toyoda and Ikeya, 1991; Toyoda et al., 1992). It was proposed that the intensity of the heat-treated E_1' center is a proxy measurement of the total oxygen vacancy population, based on the assumption that the transfer of holes is complete, converting all oxygen vacancies to E_1' centers that are paramagnetic. A correlation was also found between the ages of granitic rocks and the intensities of the heat-treated E_1' center in quartz extracted from the granites (Toyoda, 1992, 1998), though the

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correlation was not as good as that found using the unheated E_1' signal (Odom and Rink, 1989).

Rink and Odom (1991) proposed that the alpha recoil nuclei emitted from uranium and thorium contained in quartz are the primary source of the oxygen vacancy accumulation in nature. They obtained the concentrations of U and Th in quartz to be 30–90 and 50–180 ppb, respectively. Based on equations derived by Seitz (1949) and the TRIM software of Ziegler (1985), they estimated the amount of oxygen vacancies that should have been created due to U and Th quartz over the time interval since crystallization. They found that the spin concentrations (1 per vacancy) associated with measured E_1' centers were between 0.02 and 20% of the amount of oxygen vacancies calculated. As a result of the study described below, however, the claim was made that the deficit of measured E_1' centers was due to the fact that only part of them were measured without the use of the hole transfer technique (heating induced).

Toyoda et al. (1996) suggested that beta and gamma rays from outside the quartz could account for the majority of oxygen vacancy production in natural quartz. Their study was stimulated by the results from Wieser and Regulla (1989), who showed that the heated E_1' signal in quartz could be used as a gamma radiation dosimeter useful to doses as high as 10^7 Gy, which are similar to doses experienced by natural quartz from beta and gamma rays over hundreds of millions of years. In order to test this theory, Toyoda et al. (1996) irradiated the quartz samples with gamma ray doses equivalent to those calculated to be given by natural radiation based on the ages and concentrations of radioactive elements of the host rocks. They found rough agreement between the calculations and experiment, which supported the idea that oxygen vacancies are created by external beta and gamma rays. However, in this approach a heat treatment step was required to make the E_1' intensity increase, whereas no significant increases occur after gamma radiation without the many heating steps to 300°C. Since the latter corresponds much more closely to the natural radiation environment of the quartz, the question of the process involved in the natural accumulation of oxygen vacancies remained an open one.

2. Methods and materials

A ^{10}B with a cross section of 3837 b reacts with a thermal neutron to emit a ^{7}Li and an alpha with energies of 0.841 and 1.473 MeV, respectively. A ^{6}Li with a cross section of 942 b reacts with a thermal neutron to emit a tritium and an alpha with energies of 2.731 and 2.049 MeV, respectively. When a quartz sample bearing boron and/or lithium is irradiated by thermal neutrons, energetic alpha particles and alpha recoil nuclei are produced in the quartz matrix. These charged particles bombard the lattice creating lattice defects such as oxygen and silicon vacancies along their trajectories until they stop in the quartz matrix.

Six synthetic and two natural quartz samples were prepared for the present experiment as listed in Table 1. The boron concentrations in the samples were obtained by thermal neutron prompt gamma ray analysis using nuclear reactor JRR-3 at the Japan Atomic Energy Research Institute. The lithium concentrations were obtained by ICP mass spectroscopic analysis after

Table 1
Sample descriptions, concentrations of boron and lithium, oxygen vacancies calculated based on TRIM, and the concentrations of the heat-treated E_1' center observed[a]

Sample no.	Description	B (ppm)	Li (ppm)	Neutron fluence (cm^{-2})	Calculated[a] (g^{-1})	Observed[b] (g^{-1})
0	B-doped synthetic	1.5	nm[c]	1.2×10^{17}	1.2×10^{15}	4.5×10^{15}
				1.0×10^{16}	1.0×10^{14}	1.6×10^{14}
1	B-doped synthetic	1.4	3.5	1.1×10^{17}	1.2×10^{15}	1.7×10^{16}
2	B-doped synthetic	3.5	2.4	1.1×10^{17}	2.6×10^{15}	7.4×10^{15}
3	Li-doped synthetic	0.14	25.0	1.1×10^{17}	1.3×10^{15}	3.1×10^{15}
				2.3×10^{16}	2.8×10^{14}	2.1×10^{14}
4	Li-doped synthetic	0.14	16.9	1.1×10^{17}	9.2×10^{14}	8.1×10^{15}
				2.3×10^{16}	1.9×10^{14}	9.2×10^{14}
5	Li-rich natural hydrothermal	0.26	3.5	1.1×10^{17}	3.5×10^{14}	2.6×10^{15}
				2.3×10^{16}	7.4×10^{13}	9.4×10^{14}
6	Quartz vein	0.43	0.041	1.1×10^{17}	3.1×10^{14}	2.0×10^{15}
7	Synthetic (no dope)	0.28	0.19	1.2×10^{17}	2.3×10^{14}	3.1×10^{15}
				1.0×10^{16}	2.0×10^{13}	1.2×10^{14}
8	Hydrothermal	0.59	nm[c]	1.2×10^{17}	4.6×10^{14}	2.5×10^{15}
				1.0×10^{16}	3.9×10^{13}	1.5×10^{14}

[a]Calculated: oxygen vacancies calculated based on the results by TRIM.
[b]Observed: number of heat-treated E_1' centers observed. For the samples whose Li concentrations are not measured, the concentration was tentatively assumed to be zero in this preliminary experiment when the numbers of oxygen vacancies are calculated.
[c]nm: not measured.

dissolution in hydrofluoric acid. Neutron irradiations were also made using a reactor JRR-3. We made two types of irradiations, one with a flux of 1.9×10^{13} n cm^{-2} s^{-1} for 10 or 20 min with a cadmium ratio (the ratio of the total neutron to the fast neutron fluxes) of 300 yielding the fluences shown in Table 1. The other irradiation had a flux of 6.0×10^{13} n cm^{-2} s^{-1} for 30 min with a cadmium ratio of 26. The latter irradiations gave higher thermal neutron doses but together with relatively higher fast neutron fluences. Unfortunately, the fast neutron doses were unavoidable, as it would have been ideal to irradiate only with thermal neutrons.

After neutron irradiation, the samples were heated at 300°C for 15 min to observe the heat-treated E_1' center. ESR measurements were done with a microwave power of 0.01 mW, a scan range of 5 mT, a scan time of 8 min, and a time constant of 0.3 s using a JEOL, RE-3X ESR spectrometer.

3. Results

By using a computer program named TRIM (Ziegler, 1985), formation of the oxygen vacancies in quartz were simulated in each calculation using 500 incident charged particles. On average, a ^{7}Li with an energy of 0.841 MeV produced 102 oxygen vacancies, an alpha with 1.473 MeV produced 47, a tritium with 2.731 MeV produced 23, and an alpha with 2.049 MeV produced 48. The total number of oxygen vacancies created was calculated by multiplying the number of vacancies per energetic particle with the relevant lithium or boron concentration, Avogadro's number, the isotope ratio, the cross section, and neutron fluence. The concentrations ranged from 0.1 to 3 ppm for boron and from 1 to 30 ppm for lithium. The results of the calculations, the measured spin concentrations and the chemical analysis are given in Table 1.

Fig. 1 shows the spin concentrations of the heat-treated E_1' centers as a function of the calculated amount based on TRIM. For the lower neutron fluences shown by solid squares, no clear correlation was found. The higher fluences (solid circles) do show a strong correlation with the calculated oxygen vacancy concentration. When a line is fit to these points by the least-squares method, the slope was obtained to be 2.0 and the intercept was found to be 1.8×10^{15} g^{-1}.

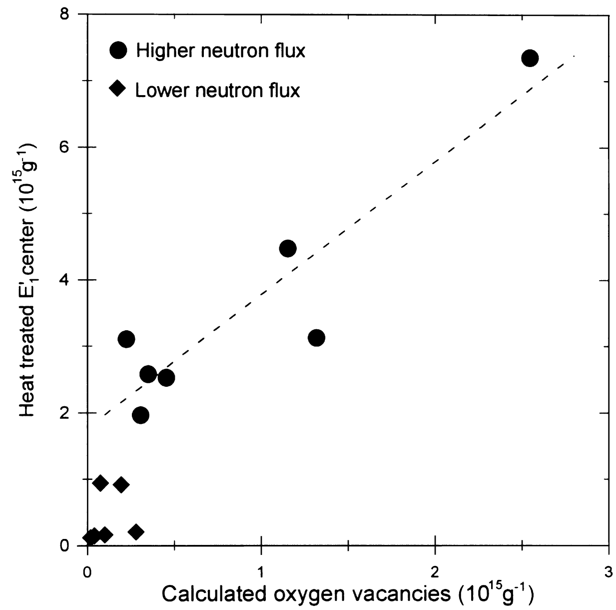

Fig. 1. The intensity of the heat-treated E_1' center observed in B- and Li-bearting quartz samples after irradiation by thermal neutrons as a function of theoretically calculated number of oxygen vacancies based on TRIM calculation. Solid circles denote the samples irradiated with a neutron flux of 6.0×10^{13} n cm^{-2} s^{-1} for 30 min (a total fluence of 1.1×10^{17} n cm^{-2}) and solid squares denote those with 1.9×10^{13} n cm^{-2} s^{-1} for 10 or 20 min (1.1×10^{16} or 2.3×10^{16} n cm^{-2}). There was no correlation among points of lower flux while a line was fit to points of higher flux to obtain an intercept of 1.8×10^{15} g^{-1} and a slope of 2.0.

4. Discussion

The heat-treated E_1' center was observed even in quartz samples with low Li and B concentration. This amount of the signals was probably created by fast neutrons which accompanied the thermal neutrons in the irradiation. Fig. 1 shows that the signal intensity is larger for samples with higher Li and B concentration, i.e., higher calculated amount of oxygen vacancies. This clearly indicates that the samples have a component created by nuclear reactions of B and Li with thermal neutrons. Thus, the observed heat-treated E_1' center is the sum of the components created by fast neutrons and by the nuclear reactions, the intercept of the line fit to the points in Fig. 1 corresponds to the amount signal created by fast neutron irradiation. The slope of the line would be 1 if the thermal neutrons created the same amount of signal as that predicted by the calculation, however the slope is 2.0, indicating that more signal was present than expected from the calculation. There are a number of factors that might account for this difference.

We determined the spin concentration of unpaired electrons in oxygen vacancies by comparing the signal to another quartz which had its spin concentration determined by comparison with DPPH, an organic compound with only one unpaired spin per molecule. Therefore, the total number of spins per gram of DPPH is easily determined. Then the integral of the DPPH first derivative signal is compared with that of the unknown, and this ratio gives the spin concentration ratio after correcting for mass and spectrometer response. However, this approach suffers in two main respects (1) the integrated lines have very different shapes and (2) the sensitive cavity volume occupied by the DPPH is usually much less than that of the quartz. An error of 50% in the spin concentrations would not be unexpected due to these factors. Thus, agreement to within a factor of two between experiment and calculation is quite good, with the experimental result being only 50% larger than the upper limit associated with the minimum error expected in the measurements. However, the higher values are unexpected considering that many of the alpha particles and recoil particles would have traveled through fluid inclusions in the synthetic quartz, and therefore, have not done any damage while doing so.

Another possibility is that the heated E'_1 center concentration is an overestimate of the number of oxygen vacancies that were actually produced by the irradiation. Indeed, the natural E' center concentration is always smaller than the heated one for both this experiment and for samples irradiated in nature. The heating may actually convert some defects into oxygen vacancies rather than just transferring holes. In this case, the energy imparted by the alpha particles and alpha recoil particles may not be above the threshold needed to produce an oxygen vacancy, but the damage done might be enough to result in an oxygen vacancy after thermal assistance during the heat treatment. Correspondingly, the calculated number of oxygen vacancies would be lower than the observed ones because oxygen vacancies are only "created" during the simulation when the threshold to move the oxygen sufficiently far away is actually exceeded. In any case, this explanation is consistent with the fact that the unheated E'_1 correlation with age (Odom and Rink, 1989) is considerably better than that observed when the heated E'_1 center was used (Toyoda, 1992).

As for the result obtained by Rink and Odom (1991) that the observed E'_1 center intensity was less than 20% of the amount of oxygen vacancies obtained by TRIM, it would probably be partly because only a part of the oxygen vacancies were paramagnetic in their samples. If they had observed the heat-treated E'_1 center, the intensity would have been up to five times larger, as the increase of the E'_1 center by heating was up to five times in granite. Therefore, if heating gives the artifact, their observation coincides with TRIM calculation at the highest value but the rest still cannot be explained. One possibility might be that part of U and Th which they analyzed were in inclusions so that the recoil nuclei did not produce oxygen vacancies in quartz matrix. Even if heating gives some artifact, the present result indicates that the intensity of the heat-treated E'_1 center is a proxy of the amount of the oxygen vacancies within factor 2, according to the present result, implying that the alpha and alpha recoil nuclei possibly create a major part of oxygen vacancies in natural quartz.

As shown in Fig. 1, the lower flux points did not give any correlation while the above discussion is based only on higher flux points. This might possibly indicate that fast neutrons give effects correlating with the horizontal axis, e.g., some nuclear reaction with Li, B, or some other trace elements, while we assumed that the fast neutron gives constant production of oxygen vacancies. Further detailed studies would be needed to clarify this issue.

5. Conclusions

The experimental results showed that in situ alpha irradiation and alpha recoil irradiation produce oxygen vacancies. The reasonably good agreement between calculation and experiment suggests that alpha recoil and alpha particle possibly give a significant contribution in oxygen vacancies in natural quartz. There is also a possibility that the excess production of oxygen vacancies relative to the calculated values might be an artifact of the heating of the sample, and that the natural E'_1 center intensity may be a better geochronometer than the heated one. Further studies on the efficiency of alpha recoil in producing oxygen vacancies are still needed in order to be able to determine the age of crystallization of igneous rocks and quartz veins.

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