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ESR signals in quartz: Applications to provenance research – A review

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ABSTRACT

The oxygen vacancies in quartz, measured by electron spin resonance (ESR) as the E'_1 center, and crystallinity index (CI) of quartz by X-ray diffraction have been found to be useful tracers for provenance of sediments. This paper will review the principles of the methods and summarize typical examples of the applications. The differences in sources of loess in Japan were found between MIS 1 and 2 by examining the numbers of the oxygen vacancies, measured as the E'_1 center. Together with CI, the contributions from the Taklimakan and Gobi deserts to marine sediments in Japan Sea were quantitatively investigated. The contribution from Taklimakan correlates with the warmer proxy for the period up to 150 ka. The temporal change in the numbers of oxygen vacancies in quartz of atmospheric depositions in two Japanese cities correlate with the frequencies of "Kosa events", while the temporal change in another city does not correlate but shows gradual decrease, indicating that the route of the transportation of aeolian dust would be different for locations within Japan. Impurity centers in quartz would also be useful indicators for provenance of river sediments, but the current results indicate that the mixture of the river sediments is not simple.

1. Introduction

Quartz is one of the most abundant minerals on the surface of Earth, and has been used for dating by electron spin resonance (ESR) (Ikeya, 1993) and by luminescence (Aitken, 1998). Those dating methods, based on quantum physics, detect the electrons trapped at lattice defects in quartz, which have been created by natural radiation and accumulated in the mineral through geological time scale. These lattice defects in quartz have been found recently to be useful not only for age determination but also for fingerprinting the sources of the sediments. Such provenance studies are important to reconstruct the past atmospheric circulation and aridification by examining the aeolian dust, and also to investigate the temporal change of erosion and regional rain fall by examining the river sediments. As quartz is generally one of the major minerals in sediment, examining the provenance of quartz has the advantage that it directly indicates the provenance of the sediment itself.

The oxygen isotopic ratio of quartz has a long history of studies on provenance since an early comprehensive work by Clayton et al. (1972). The isotopic ratio depends on the temperature of quartz formation (Kita et al., 1985), hence, the type of the original rock. The discussions on provenance of quartz have been made by using this feature (e.g. Palmer et al., 2004). The oxygen isotopic ratio may indicate specific sources or reservoirs (e.g. Mizota et al., 1996). The oxygen isotopic ratios in quartz of sediments in Hawaii were explained by aeolian dust from the arid area of East Asia (Jackson et al., 1971). However, more precise identification of the source regions within East Asia has not yet been possible. Mizota and Inoue (1988) pointed out the increase of the ratio from west to east in deep sea sediments in the Pacific Ocean, but possible additional components influencing the trend are not known.

Among the paramagnetic defects observed in natural quartz, the E'_1 center, an unpaired electron at an oxygen vacancy, has been most successfully applied to the provenance studies together with the crystallinity index of quartz. The possible sources of aeolian dust brought to North Asia, Chinese deserts, are well defined with these two proxies (Sun et al., 2007). The present paper will review the basics of these provenance studies using the ESR signals and crystallinity index and will give several examples of successful results. Then, preliminary studies using other impurity centers, which are related to impurities within quartz lattice, will also be summarized.

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2. Method

2.1. E_1' center and the oxygen vacancy in quartz

The E_1' center is one of the fundamental and major paramagnetic lattice defects in crystalline quartz, which is an unpaired electron at an oxygen vacancy (Feigl et al., 1974). Although there is still debate, the most accepted model (Feigl et al., 1974) is an unpaired electron at a single silicon sp^3 orbital oriented along a bond direction into the vacancy where that silicon relaxes toward the vacancy, while the other silicon on the opposite side with a positive charge, relaxes away from the basal plane of its three oxygen neighbors (Fig. 1).

Unlike impurity centers, it is known that the intensity of the E_1' center increases on heating (Weeks and Nelson, 1960). This is due to an electronic process in quartz that electronic holes are transferred on heating to neutral oxygen vacancies with two electrons (Si–Si bond), so that they recombine one of the two electrons to form the E_1' center (Jani et al., 1983). Based on this electronic process, Toyoda and Ikeya (1991) proposed a protocol to estimate the total number of the oxygen vacancies, to measure the ESR intensity of the E_1' center after gamma ray irradiation to more than 200 Gy followed by heating at 300 °C for 15 min (the heat-treated E_1' center). Toyoda and Hattori (2000) supported this idea by studying the dose responses of the heat treated E_1' center and of the Al center. First, a granitic quartz sample was heated at 450 °C to erase both the E_1' and the Al centers. In that sample, they observed that the intensity of the heat treated E_1' center saturates above 200 Gy while that of the Al center still increases with dose (Fig. 2). They attributed the increase below 200 Gy of the heat treated E_1' center with dose to the increase of the number of the transferred holes from the Al center, while the heat treated E_1' center saturates in the higher dose region because of the limited number of oxygen vacancies in quartz.

Odom and Rink (1989) first reported that the correlation between the natural intensity of the E_1' center in natural quartz and the ages. Toyoda (1992) and Toyoda and Hattori (2000) showed that the number of the oxygen vacancies in quartz, obtained by using the above technique, correlates with age of the host granite in the age range of 10 Ma–1 Ga (Fig. 3). Although Rink and Odom (1991) proposed that the oxygen vacancies are created by the alpha recoil nuclei from U and Th in the quartz matrix, Toyoda et al. (2005) obtained the conclusive results that the oxygen vacancies are formed by beta and gamma rays. They examined the spin–spin relaxation times of the heat treated E_1' center by pulsed ESR technique to indicate that the oxygen vacancies in granitic quartz have been created by low linear energy transfer (LET) radiation such as beta particles (electron beam) but not by high LET radiation such as alpha or alpha recoil particles. These results are also supported by the experiments of high dose irradiation by gamma rays given to quartz (Toyoda et al., 1996): the numbers of oxygen vacancies created by gamma ray irradiation were consistent with the number of those created by beta and gamma rays of natural radiation.

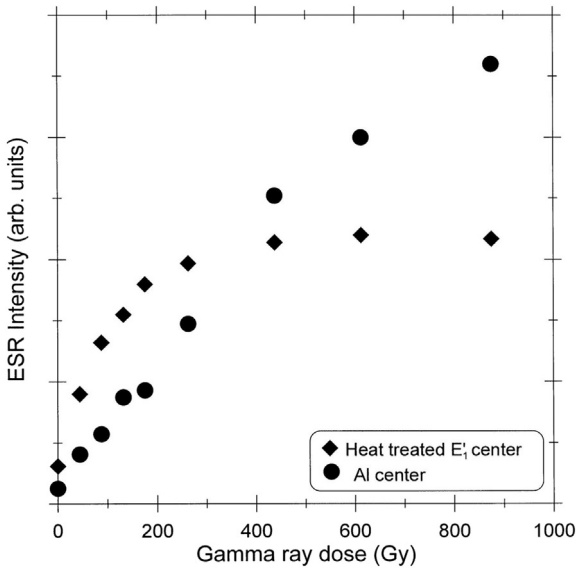

Fig. 2. Dose response of the Al center and the heat treated E_1' center in granitic quartz after heating at 450 °C (Toyoda and Hattori, 2000). The intensity of the Al center increases with dose while that of the heat treated (regenerated) E_1' center saturates above 200 Gy.

2.2. Impurity centers

In natural quartz, ESR signals of impurity centers are observed, as well as that of the E_1' center. The observed intensities of the impurity centers are a function of the concentration of the impurities in quartz and the radiation doses given, as shown for the Al center in the following. The concentrations of impurities in quartz, which are in ppm order, would be affected by the concentrations of those elements in the hydrothermal fluid from which quartz has been crystallized, and therefore would be a parameter to characterize quartz in the aspect of determining its origin.

An aluminum atom replacing a silicon atom in quartz, having an extra electron, accompanies an alkali ion for charge compensation. When irradiated, it traps an electronic hole at one of its p-orbitals, releasing the alkali ion, and forms an aluminum hole center, $[AlO_4]^0$ (Nuttal and Weil, 1981; Hitt and Martin, 1983). Usami et al. (2009)

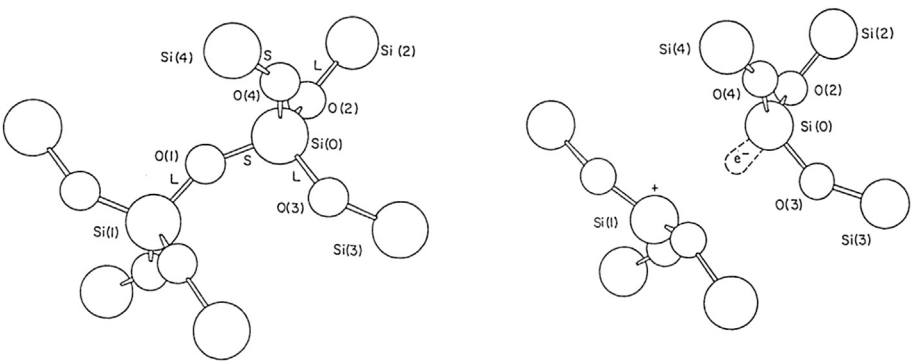

Fig. 1. Atomic configuration models for quartz lattice (left) and the E_1' center (right) (partially modified after Rudra and Fowler, 1987).

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