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THE E_1' CENTER IN NATURAL QUARTZ: ITS FORMATION AND APPLICATIONS TO DATING AND PROVENANCE RESEARCHES

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Abstract: Quartz is one of the minerals useful for electron spin resonance (ESR) dating. The E_1' center is one of well-known paramagnetic defects in crystalline quartz. This center has a unique feature; its intensity increases on heating. An electronic process to explain this increase was found to be controlled not only by the number of oxygen vacancies, which are the precursors, but also by the number of Al hole centers, which depend on the previous radiation dose and on the Al concentration.
The maximum intensity on heating is called the heat treated E_1' center, which has been posited to correspond to the number of oxygen vacancies in quartz and was found to be correlated with the ages of the host granites (Toyoda and Hattori, 2000). The experimental results on spin-spin relaxation times of the E_1' center indicate that external beta and gamma rays create oxygen vacancies in natural quartz rather than alpha or alpha recoil particles (Toyoda *et al*., 2005).
The correlation between the numbers of the oxygen vacancies in quartz and the ages of the host granite made it possible to distinguish the quartz of a sedimentary reservoir from another with different age of crystallization (Toyoda and Naruse, 2002). Quartz fractions extracted from leoss and atmospheric deposition in Japan and from sediments in Japan sea were analyzed by ESR. The temporal change of the contributions from two dust sources in China were discussed in the context of climate change.

Keywords: ESR, dating, quartz, oxygen vacancy, provenance.

1. INTRODUCTION

Quartz is one of the most abundant minerals on the surface of the earth, to which the electron spin resonance (ESR) dating is being applied. ESR dating of quartz has many applications such as in the timing of faulting, sedimentation, volcanic eruption, and artificial heating of stone implements (Ikeya, 1993). Natural quartz shows several ESR signals, E_1', Al, Ti-Li, Ti-H, Ti-Na, and Ge centers. The E_1' center was the signal first used for ESR dating of fault movements (Ikeya *et al*., 1982) and later, for flints (e.g. Porat *et al*., 1994).

The atomic configurations of the paramagnetic E_1' center in quartz has been extensively studied by ESR. It is now thought that the E_1' center is an unpaired electron at an oxygen vacancy (Silsbee, 1961; Feigl *et al*., 1974) as shown in **Fig. 1**. However, there is a debate that it may be a divacancy so as to explain the weak hyperfine splitting of 8 G and 9 G (Jani *et al*., 1983). The strong hyperfine splitting is explained by the one due to ^{29}Si (Silsbee, 1961). Since the early stage of the studies on this center, it is well known that its signal intensity increases on heating (e. g. Weeks and Nelson, 1960). The electronic process for this phenomenon was proposed by Jani *et al*. (1983), who suggested that that the electronic holes at Al hole centers activated by heating are transferred to diamagnetic oxygen vacancies with two electrons (Si-Si

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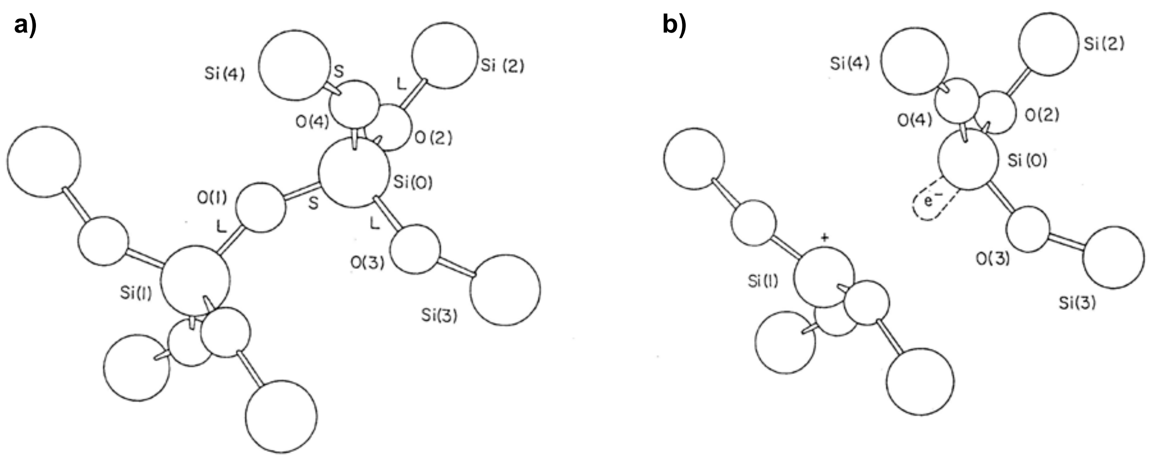

Fig. 1. *Atomic configuration models for a) quartz lattice and b) the E_1' center (partially modified after Rudra and Fowler, 1987).*

bond). This makes the vacancies paramagnetic (with one electron). The present paper summarizes the use of the E_1' center for dating, for provenance studies, and for studies on the formation processes of the E_1' center and its precursor (the oxygen vacancy), in nature.

2. THE E_1' CENTER FOR DATING OF QUARTZ

The ESR spectrum of the E_1' center has orthorhombic symmetry with three g factors, 2.00179, 200053, and 2.00030 (Jani *et al.*, 1983). As the second and the third g factors are so close to each other, their powder spectrum is similar with that of axial symmetry as shown in **Fig. 2a** under normally used conditions of ESR measurements of a microwave power of 0.01 mW and the modulation amplitude of 0.1 mT (e. g., Toyoda and Ikeya, 1991). It is also well known that the signal saturates at a low microwave powers of < 0.01 mW (e.g., Ikeya and Ishii, 1989).

This signal has been used for dating of faulting events (e.g., Lee and Schwarcz, 1994) and for heated flints (Porat *et al.*, 1994). Other impurity centers viz. Al and Ti centers have been used for dating of tephra (e.g., Toyoda *et al.*, 1995; 2006). In the use of the E_1' center signal for dating, a caution for the "counterfeit" signal is needed. This is created by gamma ray irradiation as the case for granitic quartz shown in **Fig. 2** (Toyoda and Schwarcz, 1997a). This signal has the g factor and the microwave power dependence similar to that of the "real" E_1' center, its signal shape is isotropic and it decays at 170ºC. This signal was also found in fault gouge (Toyoda and Schwarcz, 1997b), but in some studies, heating did not affect the signal (e.g., Lee and Yanga, 2007).

A correlation between the natural intensities of the E_1' center in granitic quartz and the ages of the host rocks was seen, (Shimoyama, 1986; Odom and Rink, 1989), however, the hydrothermal quartz did not exhibit such a correlation. This result implied that the ESR dating of

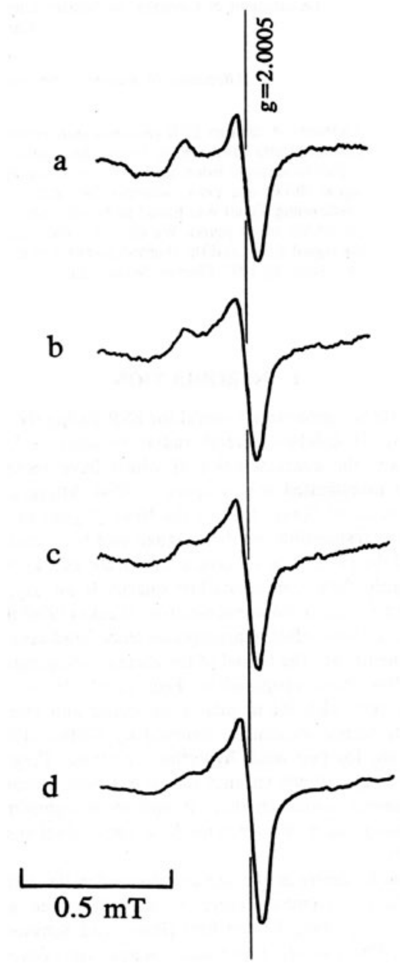

Fig. 2. *Change of the ESR signal of the "E_1' center" in granitic quartz on irradiation (Toyoda and Schwarcz, 1997a). a) no irradiation, b) 3 kGy, c) 6 kGy, and d) 15 kGy. The signal shape turns isotropic due to formation of overlapping "counterfeit" signal. The signals were obtained with a microwave power of 0.01 mW and a modulation amplitude of 0.1 mT.*

quartz may be applicable for the whole history of the earth (Grün, 1989). This correlation is one of the main topics of the present paper. As described in later sections, our later works revealed that the number of oxygen vacancies in a measure more essential than superficial “natural” (no treatment) intensity of the E_1’ center. The above correlation is most probably due to the correlation between the number of oxygen vacancies, which is the precursor of the E_1’ center, and the age.

The electronic process to form E_1’ centers from oxygen vacancies

Since the early stage of the studies on this center, it is well known that its signal intensity increases on heating (e.g. Weeks and Nelson, 1960). Jani *et al*. (1983) attributed this increase to an electronic process. Al hole centers in quartz, which is an Al atom replacing a Si and trapping an electronic hole, is activated by heating to release the holes which are then transferred to diamagnetic oxygen vacancies with two electrons (Si-Si bond). This diamagnetic oxygen vacancy that exists at the lowest energy level as shown by numerical simulation (Rudra and Fowler, 1987), turns into a quasi-stable paramagnetic state, an E_1’ center, by trapping an electronic hole that recombines with one of the two electrons.

Based on this electronic process, Toyoda and Ikeya (1991) proposed a protocol to estimate the total number of the oxygen vacancies, obtained by measuring 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 minutes (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. In granitic quartz heated to 450ºC, at which the E_1’ center is erased, 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. 3**). They attributed this increase of the heat treated E_1’ center with dose below 200 Gy to the increase of the number of the transferred holes. In the higher dose region the saturation occurs due to limited number of oxygen vacancies in quartz.

Recently, Usami *et al*. (2009) observed that the Al concentration also controls the formation of the E_1’ center. When the Al concentration is low, the number of Al center created by irradiation is also low to result in a smaller number of the heat treated E_1’ center, as the number of holes to be transferred is smaller. Usami *et al.*’s work contests the premise of Toyoda and Ikeya (1991) that the heat treated E_1’ center represents the true number of oxygen vacancies, in the case of the samples with low Al concentration such as hydrothermal quartz. However, this would still be true for other types of natural quartz with higher Al concentrations.

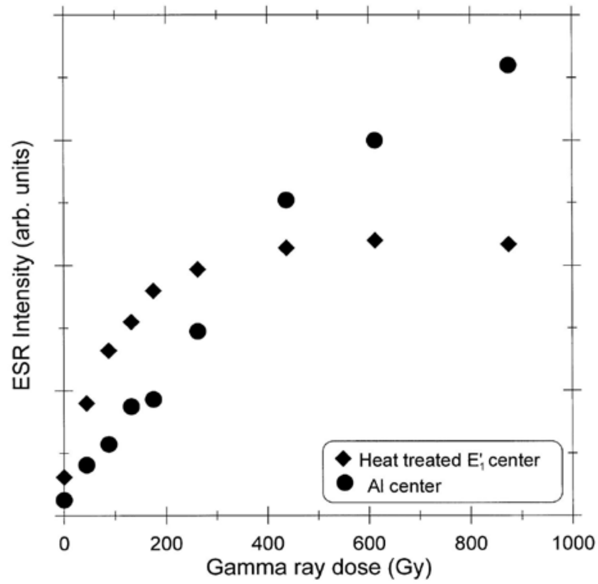

Fig. 3. *Dose response of the Al center and the heat treated E_1’ center in granitic quartz (Toyoda and Hattori, 2000). The intensity of the Al center increases with dose while that of the heat treated (regenerated) E_1’ center saturates above 200 Gy.*

The natural processes to create oxygen vacancies in quartz

Based on the idea that the number of the heat treated E_1’ center indicates the number of oxygen vacancies, Toyoda (1992) and Toyoda and Hattori (2000) showed that the number of the oxygen vacancies in quartz correlates with age of the host granite in the age range of 10 Ma to 1 Ga (**Fig. 4**). This was similar to that obtained by Odom and Rink (1989) for natural intensity of the E_1’ center.

The next issue was the process in nature, that creates the oxygen vacancies and/or the E_1’ centers in quartz. Rink and Odom (1991) proposed alpha recoil nuclei from U and Th contained in quartz matrix in ppb order as the possible process on the premise that LET (linear energy transfer) has to be high enough to move an oxygen atom. Wieser and Regulla (1989) showed that gamma ray irradiation creates the heat treated E_1’ center in synthetic quartz, however they did not describe their results in the context of oxygen vacancies. Toyoda *et al*. (1996) observed that the oxygen vacancies (heat treated E_1’ center) are created in natural quartz by gamma ray irradiation in the range of 1×10^4 to 5×10^6 Gy (**Fig. 5**). The number of oxygen vacancies is consistent with the number of the oxygen vacancies in natural granitic quartz samples for the external beta and gamma ray doses calculated from the ages of the granites and its U, Th, and K concentrations. They concluded that it is possible that the oxygen vacancies in granitic quartz were created by external

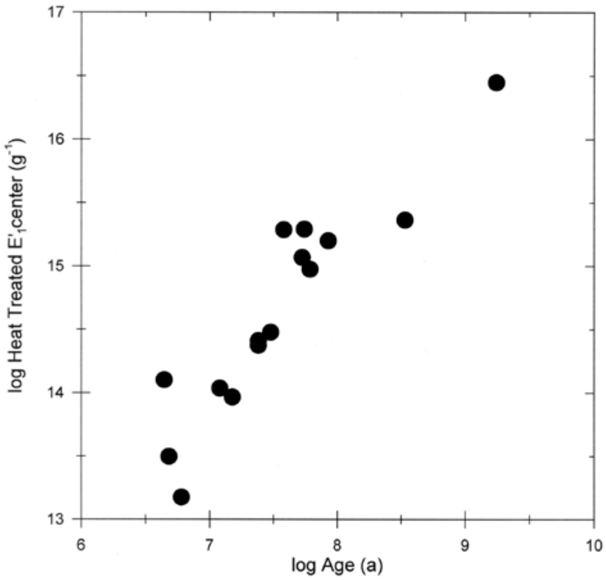

Fig. 4. *The numbers of oxygen vacancies (heat treated E_1' center) per gram in quartz are plotted against the ages of the host granites to find the correlation between them (Toyoda, 1992).*

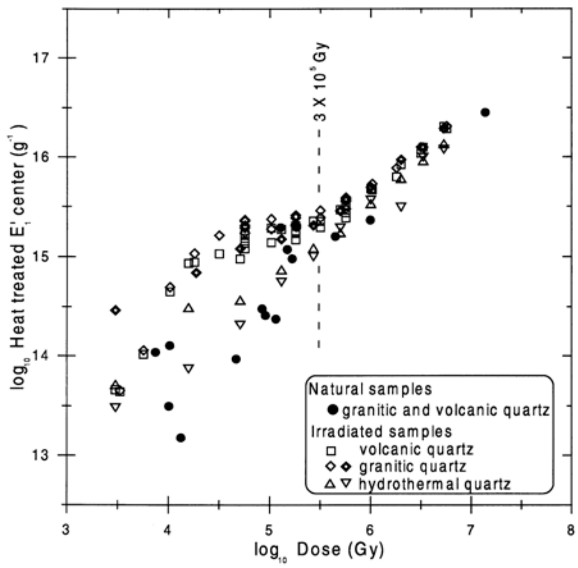

Fig. 5. *The number of oxygen vacancies per gram in quartz plotted against the irradiated gamma ray doses together with those observed in natural quartz (Toyoda* et al.*, 1996). The horizontal axis for the natural quartz (closed circles) denotes the beta and gamma ray doses calculated from the ages of host granites and the dose rates obtained from U, Th and K concentrations. Irradiated samples consist of five volcanic, granitic, and hydrothermal quartz samples, individually indicated by different symbols. The samples were heated at 600°C first to erase out the oxygen vacancies. Subsequently, the samples were given the gamma ray doses indicated by the horizontal axis.*

natural beta and gamma rays. Toyoda *et al*. (2001) examined the formation efficiency of oxygen vacancies by internal particles by looking at neutron irradiated boron doped quartz where internal alpha particles are created by a nuclear reaction. The number of the oxygen vacancies created by internal alpha and alpha recoil particles were roughly in agreement with those calculated. This result supports the suggestion that the alpha and alpha recoil particles from U and Th contained in quartz matrix of ppb order can also create the observed number of oxygen vacancies.

Toyoda *et al*. (2005) examined the spin-spin relaxation times of the heat treated E_1' center by pulsed ESR technique. The spin-spin relaxation time T_2, obtained by Hahn's spin echo method, corresponds to the local concentration of the spins; i. e. the T_2 is shorter when the distances between local spins are smaller (indicating the defects created by high LET radiation such as alpha particles) while it is longer when the distance is larger (indicating low LET). T_2 values for granitic quartz and for the ones from uranium ore are similar to those of electron irradiated quartz and are larger than the samples with helium ions implantation which simulated alpha particles. These results indicate that the oxygen vacancies in granitic quartz as also in quartz of uranium ore were created by low LET radiation such as beta particles (electron beam) but not by high LET radiation such as alpha or alpha recoil particles. These results supported the idea that the oxygen vacancies in natural quartz are created by external beta and gamma rays. The next issue will be to find a protocol to obtain ages of granites using the heat treated E_1' center with additive dose and/or regenerative dose methods.

Thermal stability of the oxygen vacancies

The thermal stability of the oxygen vacancies were studied by Toyoda and Ikeya (1991) by observing the intensities of the heat treated E_1' center after heating above 450°C. With increasing temperature, the intensities of the regenerated E_1' center (after gamma ray irradiation to 1 kGy and heating at 300°C) decreased. Assuming that the decay kinetics was second order, the authors found that the oxygen vacancies are stable up to 1 Ga, more than any other paramagnetic defects in natural quartz. This result supported the idea that ESR could be used in dating of the early history of the earth (Grün, 1989).

3. APPLICATIONS TO PROVENANCE RESEARCH

The provenance of surface sediments is a subject of interest as it indicates the history of transportation of the sediments, which is directly related with climatic/tectonic changes of that region. Thus for example, large amounts of aeolian dust are transported from dried areas in Eurasian continent to the Japan Sea and the Japanese islands through the westerly jet. The history of the provenance of aeolian dust should indicate the history of the variation of the westerly jet and the climate in the source regions.

Quartz is one of the major minerals in sediments; therefore, the provenance of quartz indicates that of sediments. The oxygen isotopic ratio of quartz has a long history of such studies on provenance since the 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 discussion on provenance of quartz may be made in such contexts (e.g. Palmer *et al*., 2004). The oxygen isotopic ratio may also indicate specific sources or reservoirs (e.g. Mizota *et al*., 1996). The oxygen isotopic ratios in quartz of sediments in Hawaii was explained by aeolian dust from 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 isotopic ratio from west to east in deep sea sediments in Pacific Ocean, which could be explained by addition of another source of sediments with a higher isotopic ratio. However, the possible source of adding a component is not known.

Thermoluminescence (TL) color of quartz grains is another possible marker for provenance of quartz. Hashimoto *et al*. (1986) found that the red and blue TL emissions from quartz grains, depend on the type of their source rock. Although the mechanism causing the various TL colors is more complex (e.g. Hashimoto *et al*., 2001), TL color was seen as a useful tool to identify a rock type of the source (Yawata and Hashimoto, 2004). Shimada (2008) examined TL color of quartz grains to estimate the sources of river sediments in Nara Basin, Japan, but only qualitative inference could be drawn.

It was found that the number of oxygen vacancies, measured as the ESR intensity of the heat treated E_1' center, is a useful indicator for provenance studies. This is based on the correlation between the number of oxygen vacancies in quartz and the age of the host granites (**Fig. 4**, Toyoda, 1992; Toyoda and Hattori, 2000). This premise works when the number of the oxygen vacancies in quartz of one dust reservoir differs significantly from that of another. This in turn depends on the original crystallization age of the basement rocks from which dust is generated by weathering. When the ages of the basement rocks that supply dust are different from location to location, it is possible to distinguish their origins by measuring the number of oxygen vacancies. Thus, it is reasonable to expect that the number of oxygen vacancies in quartz can inform on the provenance of quartz.

Based on the above premise, the numbers of the oxygen vacancies in quartz of loess samples in Japanese Islands were systematically measured. It was shown that their number in Japanese loess is about the same with that in Chinese loess plateau in MIS 1. In MIS 2, loess samples in southern Japan shows the similar value as in MIS 1. However, the number of oxygen vacancies in northern Japan is systematically larger in those in southern Japan, implying that in the north, the aeolian dust came from sources comprising from older basement rocks, possibly Precambrian rocks in Siberia, having contributed to the loess deposited in northern Japan in MIS 2 (Naruse *et al*., 1997; Ono *et al*., 1998; Toyoda and Naruse, 2002).

Nagashima *et al*. (2007a) proposed that the Crystallinity Index (CI) measured using X ray diffraction is another proxy to reveal the source of the aeolian dust. From the number of oxygen vacancies and the crystallinity index, Nagashima *et al*. (2007b) calculated the ratios of the contributions from three sources, Taklamakan, Siberia, and Japanese river, to the sediments taken from a core in Japan Sea down to 150 ka. It was found that the contribution from Taklamakan dominates in warmer period while that from Siberia is larger in colder period (**Fig. 6**), and that the Taklamakan contribution correlates with the isolation at 30ºN in June.

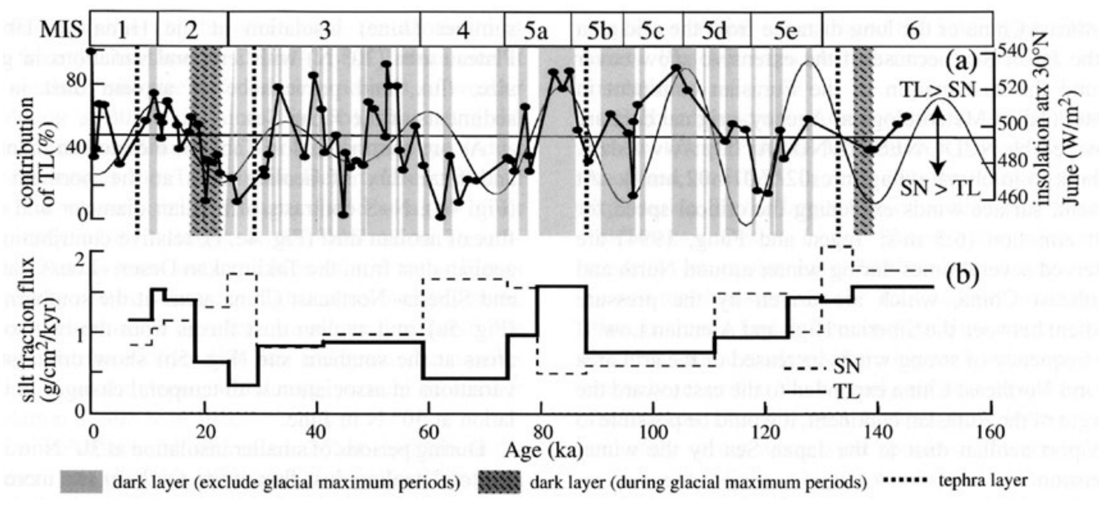

Fig. 6. *The contributions from eolian dusts from Taklamakan desert and Siberia to sediment in Japan sea as a function of the deposition age. The change of the contribution from Taklamakan desert is consistent with insolation at 30ºN in June (solid curve) (Nagashima* et al*., 2007b).*

Yamamoto *et al*. (2010) investigated, the number of oxygen vacancies in quartz of atmospheric deposition to Japanese cities in recent past. They found that the number of oxygen vacancies in quartz is larger in finer fractions, where the highest values in those fractions are consistent with the value of the samples from Taklamakan desert. Comparing with the grain size distributions, they concluded that the number of oxygen vacancies in quartz in the atmospheric depositions varies due to the variation of the value in the source rather than due to the contamination of local components.

Transportation of sediments is a key issue which corresponds to climate change and the development of geomorphology. ESR signals in quartz can be useful fingerprints to identify the sources of the sediments and to indicate the mode of transportation. Shimada (2008) studied the ESR signals of the impurity centers, Al hole and Ti-Li centers as well as the E_1' center in sediments in Nara basin, central Japan. She succeeded to specify one of the rivers which could have brought sediments to an alluvial fan. Isozaki (2009) made a systematic investigation on the E_1' center and the crystallinity index of quartz in the sediments in Takalamakan desert and found that the sediments are imhomogeneus within the desert. Then she discussed the process to form uniform dust which goes out from the desert to become one of the main sources of atmospheric deposition in East Asia and the Pacific Ocean.

4. SUMMARY

The E_1' center in quartz is one of the fundamental paramagnetic lattice defects for which extensive investigations have been made. Its formation process in nature is an interesting topic, where our conclusion is external beta and gamma rays, being related to possible dating method of granite in the age range of 10 Ma to 1 Ga. There are also many potential applications in earth science using this fundamental lattice defects especially on provenance researches where ESR signals can be non destructive fingerprints of sediment transportation on the surface of the earth, like many isotopes, such as noble gases, Sr, Nd, H, O, C, N etc. have been used to identify the source materials.

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