



INVESTIGATION OF THE TEMPORAL CHANGE OF THE SOURCES OF AEOLIAN DUST DELIVERED TO EAST ASIA USING ELECTRON SPIN RESONANCE SIGNALS IN QUARTZ

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Abstract: The temporal change in the number of oxygen vacancies in quartz was investigated by observing the E₁' center in the atmospheric depositions collected at two cities in Japan in the recent past. The depositions collected at Fukuoka in March show the ESR intensities being correlated with the sum of the number of the days, in the month, on which Kosa was observed while no such correlation was found in the deposition those collected at Akita but a trend of decrease with time. The present results suggest that the number of oxygen vacancies in quartz might be useful to estimate quantitatively the contribution of the dust originated from China to the atmospheric deposition in Japan.

Keywords: ESR, Kosa.

1. INTRODUCTION

The E₁' center is one of the major paramagnetic lattice defects in crystalline quartz, which is an unpaired electron at an oxygen vacancy (Feigl *et al.*, 1974). Unlike other impurity centers, it is known that the intensity of the E₁' center increases on heating (Weeks and Nelson, 1960), due to an electronic process in quartz that electronic holes are transferred on heating to neutral oxygen vacancies with two electrons (Si-Si bond) to recombine one of the two electrons to form the E₁' center (Jani *et al.*, 1983). Based on this nature of the E₁' center, it was proposed that the relative number of oxygen vacancies is obtained by measuring the signal intensity of the E₁' center after gamma ray irradiation to more than 200 Gy

followed by heating at 300°C for 15 minutes (Toyoda and Ikeya, 1991; Toyoda and Hattori, 2000).

For granitic quartz, this heat treated E₁' center, indicative of the number of oxygen vacancies in quartz, was found to be correlated with the ages of the host granites (Toyoda and Hattori, 2000). This observation implies that oxygen vacancies are created in natural quartz by some natural radiation. Toyoda (2005) showed that external gamma and beta rays from the minerals surrounding quartz creates the oxygen vacancies.

The number of oxygen vacancies in quartz was further found to be useful in investigating the source of aeolian dust in the past. Toyoda and Naruse (2002) showed that the numbers of oxygen vacancies in quartz in aeolian dust accumulated in loess sequences formed in northern Japan in MIS 2 are systematically larger than those in southern Japan in MIS 2 and in both regions in MIS 1, latter values

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being consistent with those in Chinese loess plateau. They argued that there was significant contribution of dust to northern Japan in MIS 2 from a source with ages older than the source which contributes to Chinese loess plateau, most probably those from north eastern Siberia where basement rocks are Precambrian.

Nagashima *et al.* (2007) further investigated the dust contributions to sediments in core samples taken in Sea of Japan using the E_1' center signal intensities (number of oxygen vacancies) and crystallinity indexes of quartz, based on the difference in those values, where the number of oxygen vacancies ranges from 4.5 to 9.6 for fine grain sediments in Taklimakan desert and from 12.3 to 16.6 for Mongolian Gobi desert (Sun *et al.*, 2007). They found that the contribution from Taklimakan desert had been higher in warmer period and that from Mongolian Gobi desert in colder period during the last 150 ka.

At the beginning of spring, originated in dust storms in arid areas of China, fine grain air borne dust particles are brought to Japan by the westerly wind, which are observable by the eye. The sky turns yellowish brown due to the dust particles, being called Kosa (yellow sand). Observable amount of dust particles is sometimes deposited in living areas. It is known that many of the dust particles originated in the Mongolian Gobi desert as shown by the back trajectory analysis (Sugimoto *et al.* 2002). However, quantitative analysis for the temporal variation of transportation of the dust from China to Japan has not been done to date. In the present study, the temporal change in the number of oxygen vacancies in quartz was investigated in atmospheric depositions collected at two cities in Japan in the recent past of 50 years. It is shown that the ESR (electron spin resonance) intensity of the heat treated E_1' center in quartz would be a useful proxy in discussing quantitatively the contribution of Chinese dust component in the atmospheric depositions.

2. EXPERIMENTAL PROCEDURE

The samples of atmospheric deposition (total deposition = wet + dry) were collected for a month in a 0.5 m² plastic open surface collector installed in the observation field of the meteoritic observatories at Fukuoka and at Akita (Fig. 1). The collected samples in the container were heated to evaporate out the water. Meteorological Research Institute offered the atmospheric depositions collected in March and in June in 1964 to 2000 for the present study. Samples of fine grain river sediment were also collected at Fukuoka as Fig. 2a and at Akita as Fig. 2b which would represent possible local dust sources.

About 150mg of each sample was treated with 50ml acetic acid of 20% for 8 hours to remove carbonate, and then soaked in a mixed solution of 40ml sodium citrate ($Na_3C_6H_5O_7$) at the concentration of 0.3 mol/l, 5ml $NaHCO_3$ at the concentration of 1 mol/l, and 3 g of hydro-sulfide sodium ($Na_2S_2O_4$) at 80°C for 8 hours to remove iron and magnesium oxides. Subsequently, the sample

was treated with 20% solution of hydrogen peroxide (H_2O_2) heated at 60°C for 8 hours to remove organic matter. Finally, the sample was treated with hexafluoro-silicic acid (H_2SiF_6) for 1 week to remove feldspars. After rinsing, a fine grain size fraction less than 16 μ m was extracted using the Stoke's law.

ESR signals in the samples were observed with an ESR spectrometer, JEOL JES-PX2300 at Okayama University of Science. The signal intensity of the E_1' center was measured after gamma ray irradiation to 2.5Gy and heating at 300°C for 15 min to measure the number of oxygen vacancies (Toyoda and Hattori, 2000). The measurement was performed at room temperature at conditions as follows; a microwave power of 0.01mW, a magnetic field modulation frequency of 100kHz, its amplitude of 0.1 mT, a center field of 336.0mT, a sweep range of 5 mT, a scan time of 30 s, a time constant of 0.03 s. The ESR signal intensity of the E_1' center in quartz is expressed in a spin unit where one spin unit is equivalent to 1.3×10^{15} spin/g (Toyoda and Naruse, 2002) after dividing the value by the sample mass and the quartz content obtained as described below.

The chemical treatment aimed to extract pure quartz from the samples, but it was not possible due to clay minerals in the sample. The quartz content in the sample after the chemical treatment was determined by the XRD analysis using the internal standard method with silicon (Klug and Alexander, 1974) where the content of quartz was obtained from the ratio of XRD peak areas at 20.9° of quartz and the one at 28.4° of silicon in sample with

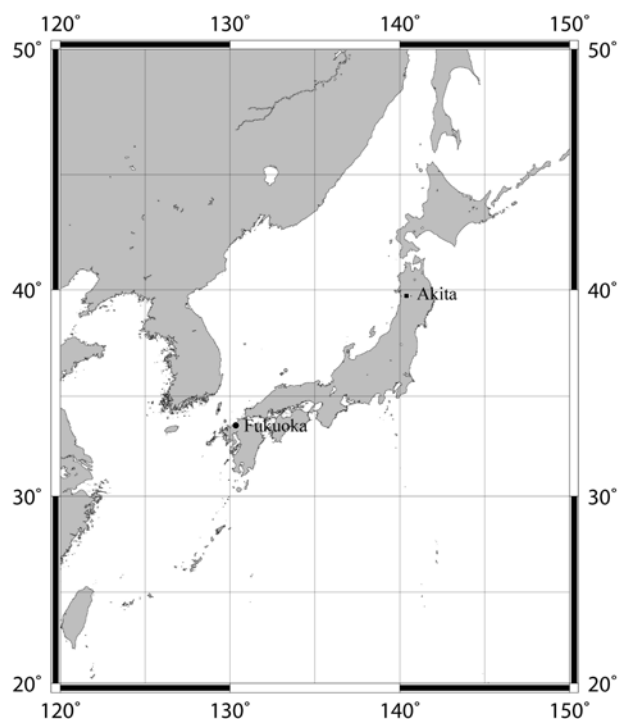


Fig. 1. Locations of Fukuoka and Akita where the sample of atmospheric deposition were collected.

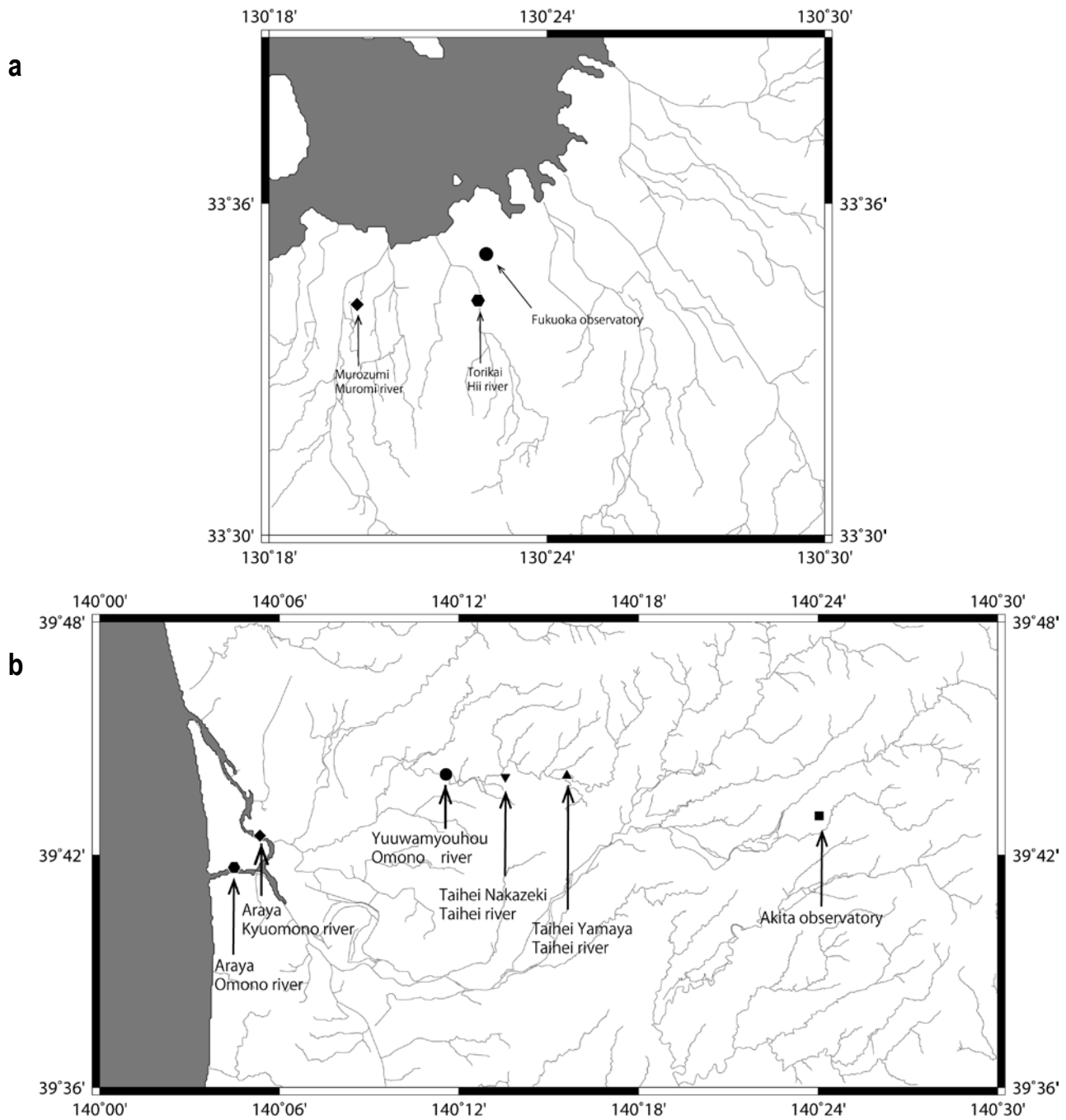


Fig. 2. Sampling locations (a) at Fukuoka and (b) at Akita for river sediments and the locations of observatories where atmospheric deposition were collected.

known amount of silicon, typically 10% of total mass. The XRD analysis was performed by using the PANalytical X' Part Pro X-ray diffractometer with a tube voltage of 45 kV and a tube current of 40mA at the University of Tokyo. The obtained quartz contents were typically 20% to 40%.

3. RESULTS AND DISCUSSIONS

The temporal variation in the number of oxygen vacancies in quartz were obtained as shown in **Figs. 3a** to **3d** for the depositions in March at Fukuoka, in June at Fukuoka, in March at Akita, and in June at Akita, respec

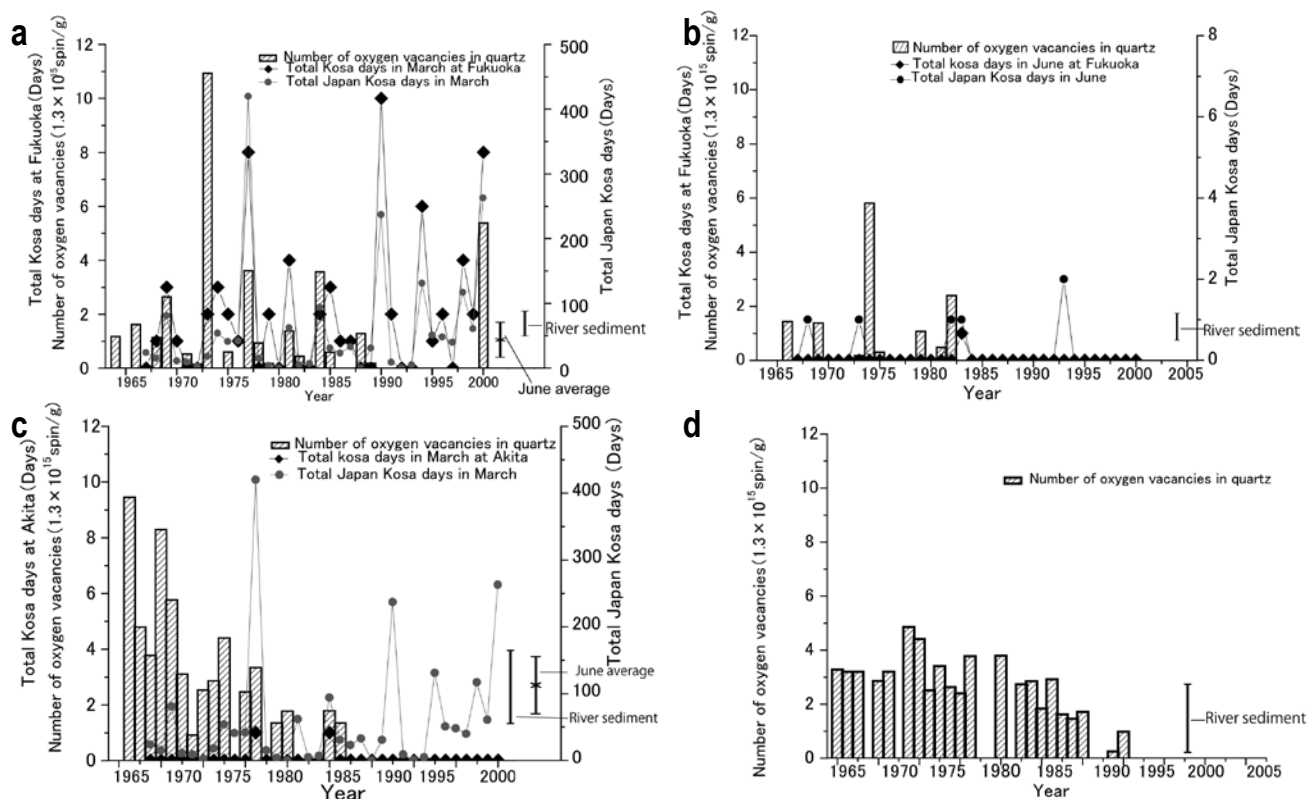


Fig. 3. Temporal change of oxygen vacancies in quartz extracted from atmospheric depositions and the total Kosa days (a) in March at Fukuoka, (b) in June at Fukuoka (c) in March at Akita and (d) in June at Akita.

tively. The numbers of the days on which Kosa was observed in the month, summed for all 123 observatories in Japan (total Japan Kosa days) (Japan Meteorological Agency <http://www.jma.go.jp/jma/indexe.html>) are also shown in **Fig. 3a** to **3d** together with the numbers of the days on which Kosa was observed in the month in the city (total Kosa days). For the years with ESR no data in **Fig. 3**, ESR measurements were not possible because the amount of quartz was not sufficient. The number of oxygen vacancies observed in quartz extracted from river sediments collected at Fukuoka and at Akita are shown in **Table 1**.

The number of oxygen vacancies in quartz of atmospheric deposition collected at Fukuoka in March shows several peaks in the temporal change as in **Fig. 3a**. Most of those peaks match the peaks of the total Japan Kosa days (years 1969, 1973, 1977, 1984, 2000) and also those of the total Kosa days in Fukuoka. The numbers of total Japan Kosa days are almost proportional to that in Fukuoka meaning that the total Japan Kosa days are controlled by the Kosa days in western Japan.

Except for a high value in 1974, the average value for Fukuoka in June (**Fig. 3b**) is 1.04 ± 0.79 , being consistent with the values for the river sediments. Considering that Kosa events were rarely observed in June as shown in **Fig. 3b**, main component of the atmospheric deposition

in June would be originated in local sediment. Where the values observed in June would be considered as the “background”, the values observed in March at Fukuoka, exceeding this “background”, would have contribution from the source with higher oxygen vacancies which is correlated with the peaks in total Kosa days (**Fig. 3a**). As satellite images revealed that Kosa events are originated in dust storms in arid areas in China, this source can most probably be dust originated in China. This interpretation

Table 1. The number of oxygen vacancies observed quartz extracted from river sediment.

Location	The number of oxygen vacancies (spin unit)
Akita	
Yuuwamyohou Omono river	1.32
Araya Omono river	0.36
Araya Kyuomono river	1.03
Taihei Nakazeki Taihei river	3.07
Taihei Yamaya Taihei river	1.89
Average	1.53 ± 1.02
Fukuoka	
Muromi river	2.02
Hii river	1.09

is consistent with the previous observation that the number of oxygen vacancies in quartz in fine grain silt has high values, for example, 12.3 to 16.6 in the Mongolian Gobi desert (Sun *et al.*, 2007).

At Akita, the values in March showed gradual decrease with time (Fig. 3c), having no correlation with total Kosa days. Average value for Akita in June, 2.72 ± 1.09 , is in the range of those of local river sediments, 1.53 ± 1.02 (Table 1), indicating that the dust in June is again mostly originated in local sediment. If this value in June is considered to be the “background”, the values in March exceeding this “background” would indicate the contribution from dust originated in China. However, not like at Fukuoka, those high values do not correlate with Kosa days because Kosa has seldom been observed at Akita, only one day in 1977 and in 1984, none in June.

As shown in Fig. 3c, in March, the number of oxygen vacancies, hence, the contribution of dust originated in China gradually decreased. This might correspond to the gradual temporal decrease of spring dust storm frequency in northern China (Zhu *et al.*, 2008). The difference between Fukuoka and Akita in temporal change of the oxygen vacancies in quartz of atmospheric depositions might indicate that the mode of transportation of the dust from China to Japan is different depending on the location within Japan. At Fukuoka, contribution of the dust originated in China is controlled by episodic Kosa events in the specific years. On the other hand, at Akita, it is controlled by more averaged dust “reservoir”. Transportation from that “reservoir” is not witnessed by eye, maybe because it is much diluted, but is detected by ESR as the number of oxygen vacancies in quartz.

When we assume the end members, the concentrations of oxygen vacancies in quartz, in the dust originated in China and in the local background, quantitative argument in the contribution is possible. If the source of the dust originated in China is assumed to be Mongolian Gobi as estimated by the back trajectory analysis (Sugimoto *et al.*, 2002), the number of oxygen vacancy should be 12.3 to 16.6 (Sun *et al.*, 2007), the present observed value indicate the contribution of the component of Mongolian Gobi in the atmospheric deposition. When the local end member value is assumed to be 3.62, which is average of the deposition in March, the value 4.40 (year 1974) corresponds to the contribution of 22% of Gobi component, and the value 8.29 (year 1968) to 52%.

4. SUMMARY

The temporal changes in the number of oxygen vacancies in quartz of atmospheric depositions collected at Akita and at Fukuoka were investigated. The temporal change of the number in the sample collected at Fukuoka in March is correlated with the total Kosa days, while no correlation was found in Akita but gradual decrease with age. The number of oxygen vacancies in quartz in the atmospheric deposition might be an indicator to estimate quantitatively the contribution of the dust originated from China to the atmospheric deposition. The difference between Fukuoka and Akita would imply possible difference in mode of transportation of the dust to these two cities.

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