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THE GRAIN SIZE INFLUENCE ON THE E1' CENTRE OBSERVED IN QUARTZ OF ATMOSPHERIC DEPOSITION AT TWO JAPANESE CITIES: A PRELIMINARY STUDY

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Abstract: The grain size influence on the number of oxygen vacancies in quartz was investigated by ESR in atmospheric deposition collected at two Japanese cities, Fukuoka and Akita, in 1969 and 1971. The finer grain size fraction shows the highest value of concentration of oxygen vacancies, most closely resembling dust originating in the Taklamakan desert. Month to month and year to year variation of the dependence was also observed which could possibly be attributed to the variation of the mixture ratio of at least two dust sources in China, A conclusive statement can not be made at this stage.

Keywords: ESR, E'center, Atomospheric deposition, quartz.

1. INTRODUCTION

The change of atmospheric circulation system in the past is an important issue for studies of paleoclimate. Aeolian dust accumulated in the past will be a clue for such studies. In previous studies it was found that its origin was different in the last glacial maximum and in Holocene. This was achieved by measuring the number of oxygen vacancies indicated by the ESR (electron spin resonance) intensity of the E_1'centre in quartz extracted from loess (Naruse *et al*, 1997; Ono *et al*., 1998; Toyoda and Naruse, 2002). That number in Japanese loess is 6-8 units (1 unit = 1.3×10^{15} spin/g) – a values similar to that found in Chinese loess plateau in MIS 1. On the other hand, for MIS 2, this is also observed in loess samples from southern Japan the values being in the range 10-17 units. These values are systematically larger in northern Japan, implying a contribution of aeolian dust from sources originating from older basement rocks. Nagashima *et al*. (2007) investigated the sources of the aeolian dust accumulated in the sediment of the Sea of Japan using the number of oxygen vacancies in quartz together with another proxy - crystallinity index of quartz. A correlation between the dust contribution from Taklamakan desert and the summer insolation index at 30ºN was found.

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In the present study, we investigated the concentration of oxygen vacancies in quartz extracted from atmospheric deposition at two Japanese cities in order to examine if the same methodology with ESR is applicable to recent aeolian dust. Igarashi *et al*. (2009) measured radioactive isotopes ^{137}Cs and ^{90}Sr in atmospheric deposition in Japanese cities and found that the ratio (^{137}Cs / ^{90}Sr) has been increasing with time in the last 50 years. They attributed this trend to aridification of the dust source regions within China. The ESR signals in quartz extracted from atmospheric deposition might be sensitive to such a source change.

2. THE E_1' CENTRE AND THE OXYGEN VACANCY IN QUARTZ

The E_1'centre is a paramagnetic defect associated with an oxygen vacancy in quartz (Silsbee, 1961; Feigl *et al*., 1974). It is well known that its signal intensity increases during heating (e. g. Weeks and Nelson, 1960). Jani *et al*. (1983) attributed this phenomenon to an electronic process in which activated by heating holes at Al hole centres are transferred to diamagnetic oxygen vacancies with two electrons (Si-Si bond). As a result the vacancies become paramagnetic (with one electron). Using this feature, an experimental procedure was proposed to estimate the relative number of oxygen vacancies (Toyoda and Ikeya, 1991; Toyoda and Hattori, 2000). This procedure consists of a gamma ray irradiation to more than 200 Gy followed by heating at 300°C for 15 minutes. They proposed that the intensity of the E_1' centre measured after this procedure (the heat treated E_1' centre) corresponds to the number of oxygen vacancies in quartz.

Using this technique, a correlation between the number of oxygen vacancies in quartz and the ages of the host granites was found (Toyoda, 1992; Toyoda and Hattori, 2000). Toyoda *et al.* (2005) suggested that external gamma and beta rays from the minerals surrounding quartz create the oxygen vacancies.

The studies to differentiate the sources of aeolian dust using the E_1' centre in quartz is based on the correlation between the number of the oxygen vacancies in quartz and the age of the post rocks, i.e., the method is successful when the ages of the sources of quartz, probably basement rocks, differ by an order of magnitude.

3. EXPERIMENTAL PROCEDURE

Dust samples representing atmospheric deposition were collected in a 4 m^2 plastic open surface collector installed in the observation field of observatories at Fukuoka and Akita (**Fig. 1**) for one month. The collected samples in a container were heated to evaporate the water.

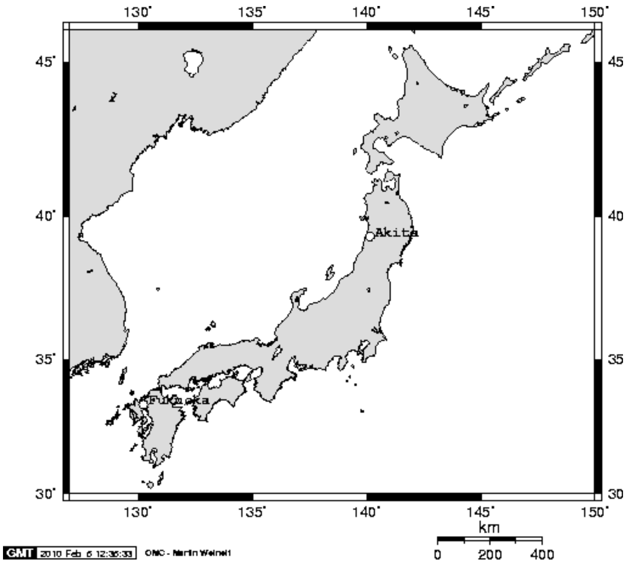

Fig. 1. *The locations of the cities where atmospheric dust samples were collected.*

About 150 mg of a sample was treated with 50 ml of acetic acid of 20% for 8 hours, then soaked in a mixed solution consisting of 40 ml of sodium citrate ($Na_3C_6H_5O_7$) of 0.3 mol/l, 5 ml of $NaHCO_3$ of 1 mol/l, and 3 mg of hydro-sulfide sodium ($Na_2S_2O_4$) at 80°C for 8 hours. Subsequently, the samples were treated with 20% hydrogen peroxide solution (H_2O_2) and heated at 60ºC for 8 hours. The sample was then separated to grain size fractions, >32 μm, 16-32 μm, 8-16 μm, and 4-8 μm with the application of the Stoke's law.

ESR signals in the samples were measured with an ESR spectrometer, JEOL JES-PX2300. The number of oxygen vacancies was measured as the intensity of the E_1' centre after gamma ray irradiation to 1 Gy and heating at 300ºC for 15 min (Toyoda and Ikeya, 1991). The following measurement conditions of the ESR were used: the microwave power of 0.01 mW, the magnetic field modulation frequency of 100 kHz, its amplitude of 0.1 mT, the centre field of 336.0 mT, the sweep range of 5 mT. The measurements were carried out at room temperature.

4. RESULTS

The number of oxygen vacancies measured in quartz of our dust samples are shown in **Figs. 2a** for Fukuoka and **2b** for Akita as a function of grain size. The numbers of the oxygen vacancies are described in a unit of 1.3×10^{15} spins/g as was done in previous studies (Toyoda and Naruse, 2002; Nagashima *et al.*, 2007). It is a common feature that smaller grain size fractions show higher number of oxygen vacancies although there are month to month and year to year variations in the average level. The ESR signal of the E_1'centre was not detected due to a large interfering signal in all samples in February 1969 at Fukuoka. The values are higher for 1969 than for 1971 at both cities. The average level is higher in April than in February at Akita but the opposite is true for Fukuoka in 1971.

A reason for the higher number of oxygen vacancies in finer fractions may be that the signal is related to a surface defect. However, this is not the case as the number is not inversely proportional to the grain size.

5. DISCUSSION

Kosa is a very well-known meteorological phenomenon of aeolian dust storm generated in inland China arriving in Japan. The sky is so hazy that one can see the precipitating dust. The location-days totals are listed in **Table 1**, which is the sum, for the observatories, of the number of days in a month, on which Kosa was observed. The number is larger in 1969 than in 1971, being consistent with our results that the numbers of oxygen vacancies in quartz are larger in 1969 than in 1971. This would indicate that the main part of the precipitated atmospheric dust was brought by Kosa, having higher oxygen vacancy values from inland China. The number of oxygen vacancies in finer fraction, ranging up to 8.5 units is consistent with the values observed by Toyoda and Naruse (2002), for MIS 1 or in southern Japan and in inland China for MIS 2, which is 6-8 units, and that of Taklamakan component reported by Nagashima *et al.* (2007), which is 8.8 units. This is also confirmed by our observation of the local river sediments in the present study. The numbers of oxygen vacancies in quartz from river sediments which are possible local dust components, were 1.23 units in Fukuoka and 1.75 units in Akita, indicating that those high values are not local. **Figs. 3a** and **3b** shows the fraction of the mass of the grain sizes of the total mass of quartz extracted.

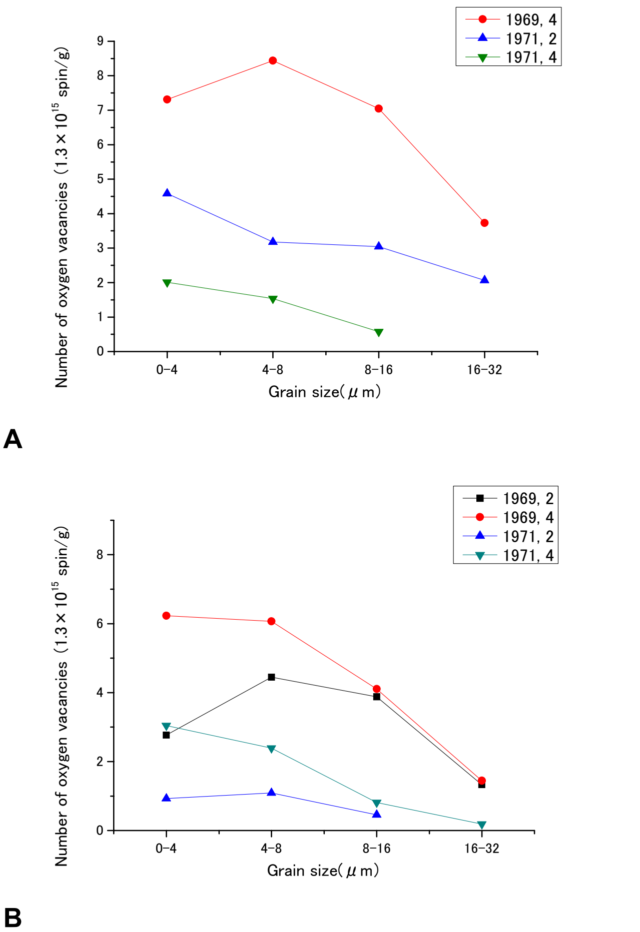

Fig. 2. *Grain size distributions of oxygen vacancies in quartz of atmospheric deposition collected (A) at Fukuoka and (B) at Akita*

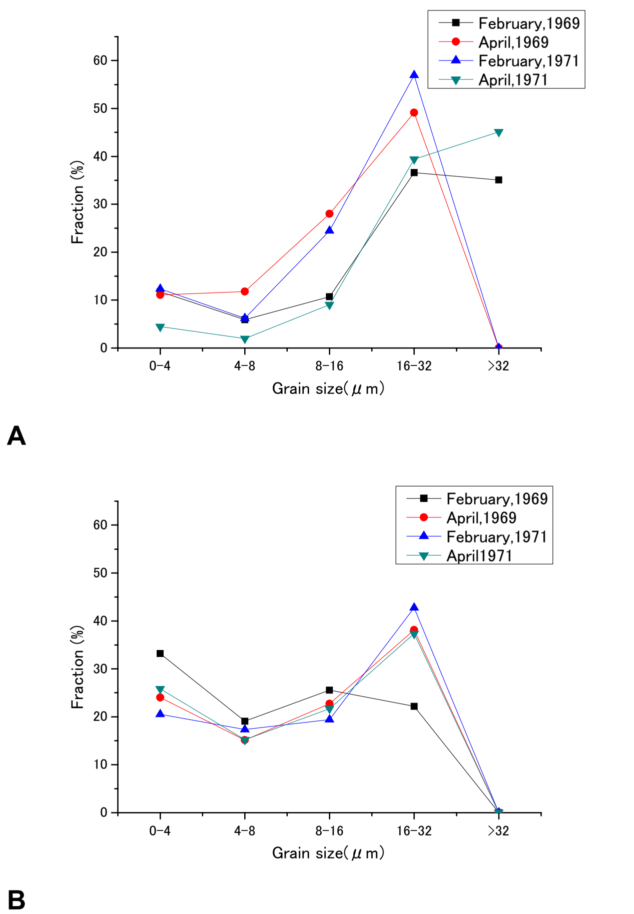

Fig. 3. *Grain size dependence of fractions of mass of quartz extracted for the sample (A) at Fukuoka and (B) at Akita*

All samples show bimodal distribution. It is natural to interpret these two components as aeolian dust peaking at less than 4 micrometers and the coarser local sediment, although the amount in coarser fractions is larger in Fukuoka. This indicates that we should look at grain size fractions less than 8-16 μm to examine aeolian dust in atmospheric deposition. If the fine component corresponds to the aeolian dust from China and coarser component to local, our results on the highest values shown in **Figs. 2a** and **2b** are consistent with the discussions in the previous paragraph. The number of oxygen vacancies in the finest two fractions would represent the values for dust coming from China, while the values for coarser fractions are lower because of the mixture of local quartz with lower oxygen vacancy values.

However, the results for the other finer fractions shown in **Figs. 2a** and **2b** are not so simple. The numbers of oxygen vacancies in finer two fractions for April 1969 are 6.0-8.5 units both at Fukuoka and Akita, being consistent with the values for Taklamakan (Nagashima *et al.*, 2007) while the values are lower in 1971 at both cities and in Feb. 1969 at Akita. We could still adhere to the idea that finer fractions are aeolian dust from China, to explain these lower values. It would be supported by the grain size distribution shown in **Figs. 3a** and **3b**; the grain size distributions are not much different except for April 1971 at Fukuoka where the fraction for the smallest grain size is less than 5%. There is no clear correlation between the oxygen vacancy values and the mass of the atmospheric deposition (**Table 1**), neither. These facts would imply that the number of the oxygen vacancies in dust from China varies from one month to another month and from one year to another year. One could explain this by the dust originating from at least two sources, where one may be the Taklamakan desert and the other should have a lower oxygen vacancy value, and depending on the ratio of the mixture, the oxygen vacancy values vary between months and years. Akita would more clearly show this feature. In February, the dust starts in the second source with a lower oxygen vacancy values, then the first source with higher value, maybe Taklamakan, dominates in April, but the contribution from the second source would have been generally larger in 1971.

However, it is still possible that local dust has contributed to finer fractions, making the oxygen vacancy values lower. As the present study is a preliminary work to examine the oxygen vacancies in atmospheric deposi tion, and examines only one parameter, it is not possible to discuss more than two components. Further studies are necessary to examine other features of quartz, such as crystallinity index, oxygen isotopes, ESR intensities of impurity centres.

Table 1. *The mass of the collected atmospheric deposition and the number the days on which Kosa was observed.*

Year	Month	Mass of the collected atmospheric deposition (g) at Akita	Mass of the collected atmospheric deposition (g) at Fukuoka	Location-days total*
1969	February	7.93	10.67	0
1969	April	14.35	24.08	276
1971	February	10.44	13.28	2
1971	April	18.85	17.25	43

6. SUMMARY

The numbers of oxygen vacancies in quartz of atmospheric depositions were investigated. Finer fractions show higher values where the highest values are consistent with the dust value at Takalamakan desert, while the coarser fraction indicates the local values as is also indicated from the grain size distribution. The grain size distribution indicates that the size fractions less than 8-16 μm should be examined to study the aeolian dust component. The pattern of the oxygen vacancy values versus grain size varies month to month, year to year. No conclusive explanation was obtained in the present study while it is possibly because of variations of mixture ratio of two or more dust sources in China.

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