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ESR dating of glacial moraine deposits: Some insights about the resetting of the germanium (Ge) signal measured in quartz

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ABSTRACT

The electron spin resonance (ESR) dating of tills using germanium-doped (Ge) paramagnetic centers in quartz has advantages over other dating techniques, as quartz is common, processing is easy, and the technique has the potential for dating features several hundreds of thousands years old. ESR dating of moraines is based on the supposition that either subglacial comminution or exposure to sunlight resets the signal. However, actual dating suggests that a signal that is initially present cannot be bleached to zero by grinding alone. We found that grinding coarse samples (0.5–1 mm in diameter) to the mean grain size of fine sand (0.125–0.193 mm) reduced the signal intensity to 53–69% of its original value. From the value of the signal difference, one can devise a correction factor for ESR ages of subglacial sediment. Polymineralic grains are commonly present in till. Exposure of them to sunlight for several days can reduce the signal intensity to 7–8% of its original value within 1–2 mm thick of the sediment surface. However, within 5–8 mm of the sediment surface, exposure to sunlight for over one week only reduced the signal intensity to mean plateau values of 42–50% of the initial value. Mixing upper and lower layers of the samples during exposure to sunlight changed the signal intensity. This suggests that the amount of bleaching varies spatially. Sediments initially deposited at the margins of ice caps or ice sheets and subsequently overridden may have been sufficiently exposed to sunlight to allow ESR dating of moraines. The purity of the quartz and the grain size have significant impacts on signal intensity; intensive purification and the use of a uniform fine sand fraction are thus recommended.

1. Introduction

When excited by radiation, certain trace elements in the crystalline structure of quartz form paramagnetic (weakly magnetic) centers (point defects). The amount of radiation from the surrounding sediment received by these defects is a function of time, and can be determined using ESR spectroscopy. ESR dating makes use of this time dependence of radiation accumulated by germanium (Ge) paramagnetic centers in quartz grains (Grün, 1989; Rink, 1997). The technique has been used to date both glacial till (Wang et al., 2013; Wu et al., 2001; Zhao et al., 2006; 2012) and fault gouge (Buhay et al., 1988). It is generally assumed that the ESR clock is reset to zero by grinding in faults (Lee and Schwarcz, 1993), and by sunshine in coastal quartz sands (Ye et al., 1993) and moraines (Zhou et al., 2002), and that abrasion partially resets the clock in debris flows (Ye et al., 1998) and subglacial environments (Yi et al., 2002). However, the potential for incomplete resetting limits the use of ESR dating of these geological features.

ESR dating has advantages over radiocarbon (^{14}C) and optically stimulated luminescence (OSL) dating because it can be used to date features that are several hundreds of thousands of years old, and, in contrast to ^{14}C, samples are readily available. Although surface exposure dating using terrestrial cosmogenic nuclides can, in principle, also be used to date very old glacial events, the availability of boulders, their surface weathering, and landform denudation commonly limit the range of this technique.

In 2001 we collected samples of till from road cuts in the Urumqi River valley in the central Tianshan Mountains. We conducted some preliminary experiments on one of these samples (Sample A series). We found that the Ge signal did not decrease as much as

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expected upon grinding and exposure, so we could not assume that these "clocks" had been reset when the till was deposited. This was disappointing, so we set the samples aside. In 2012, encouraged by Liping Zhou and Jon Harbor, who asked what evidence there was for a resetting of the ESR signal during glacial transport, we continued the experiment. The remaining samples, and one new sample collected in 2013, were ground and exposed to sunlight, and examined quantitatively. Herein, we present the results of these laboratory bleaching experiments.

2. Study area and sample collection

The study area, in the Urumqi River drainage basin, is located on the northern slope of Tiager Peak (43°47′N, 86°49′E), in the central Tianshan Mountains (Fig. 1A). The structures, textures and lithology of the Upper Wangfeng (UWF) and Lower Wangfeng (LWF) moraines in the valley have been described by Cui (1981), Li et al. (1981) and Derbyshire (1984), and the fabric and microfabric of the till has been studied quantitatively by Li et al. (2006) and Yi and Cui (2001). The UWF and LWF moraines have been dated to the Last Glacial Maximum (LGM) by cosmogenic surface exposure dating (Kong et al., 2009; Li et al., 2014) and ^{14}C dating (Yi et al., 2004). Samples A was collected from basal till in the lower layer of the UWF moraine (Fig. 1B); Sample B was taken from supraglacial till from the upper layer of the same exposure (Fig. 1C). Sample C was collected from basal till in the LWF moraine (Fig. 1D). Sample D was collected from another valley on the southern slopes of Tiager Peak (Fig. 1E). Because this latter sample contained a lot of fine sand (0.125–0.25 mm), it was used for an analysis of the relation between ESR signal intensity and quartz content. Sample BC is quartz with grain sizes of 0.3–0.45 mm extracted from Samples B and C, subject to irradiation, but without grinding and exposure to sunlight.

During collection, we first dug 0.2–0.3 m back into the exposures. Samples were then excavated under shaded conditions and placed immediately in black bags to avoid direct sunlight.

3. Experiments

Fine grain sizes are produced by comminution in the subglacial

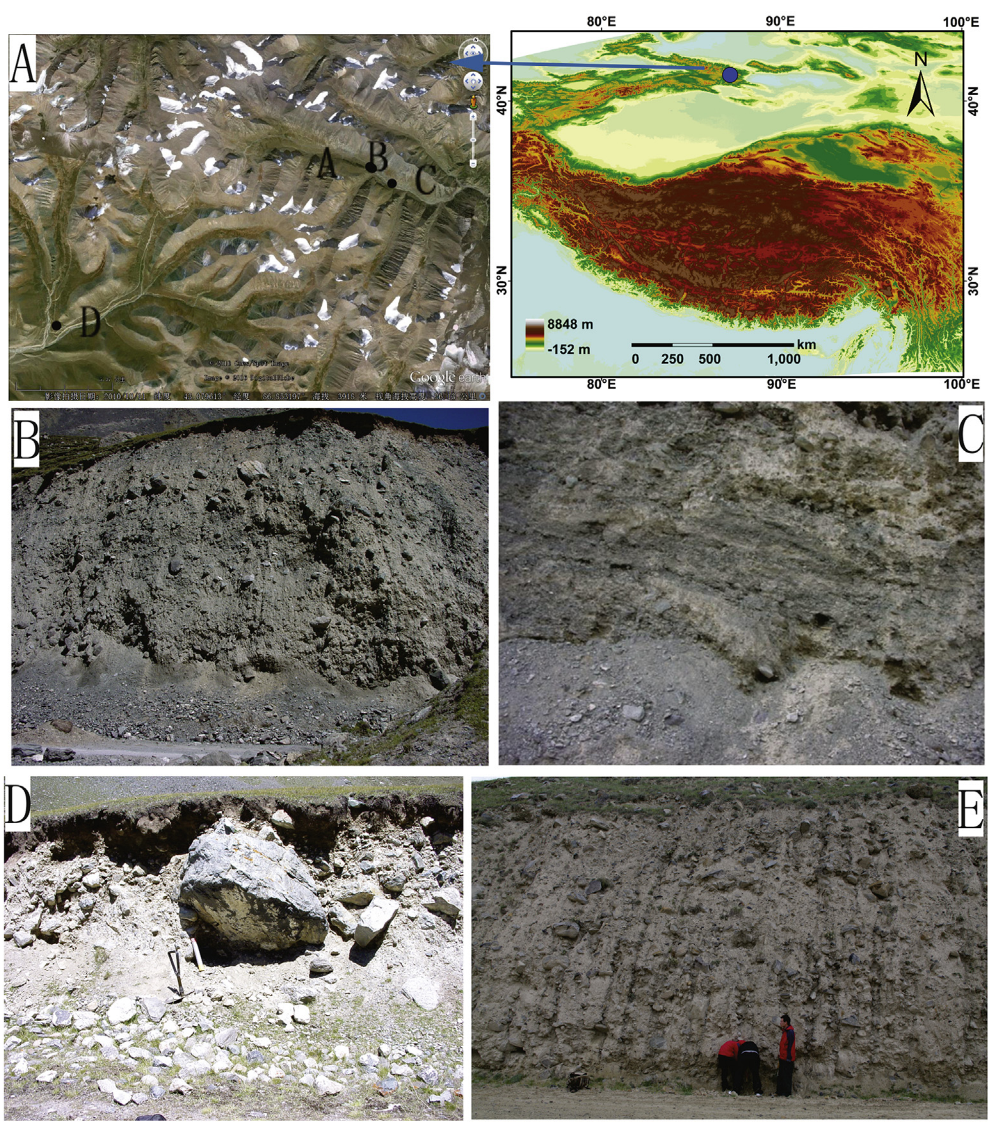

Fig. 1. Location of Tiager Peak in the central Tianshan Mountains. (A) Sampling sites; (B) basal till in the lower layers of the UWF moraine where Sample A was collected; (C) supraglacial till in the upper layers of the UWF moraine where Sample B was collected; (D) basal till in the LWF moraine where Sample C was collected; (E) basal till where Sample E was collected in the moraine on the southern slope.

environment and transported to glacier margins, where they are deposited in ground moraine and in lateral and terminal moraines. The sands in the moraines may occasionally have been exposed to sunlight during deposition. Therefore, we designed the laboratory experiments to first simulate subglacial abrasion and crushing, and then exposure to sunlight. Previous studies have shown that the Ge signal intensity in pure quartz sand can be easily bleached to zero in sunlight (Grün, 1991; Ye et al., 1993) and reduced to two thirds of its original intensity by 1 min of grinding by hand (Ye et al., 1998). Since pure quartz grains are rarely concentrated in moraines, we used both polymineralic samples and pure quartz for our experiments. The processes used during the grinding and exposure experiments are summarized in Fig. 2.

We used three principal samples (A, B and C) and one supplementary sample (D). Grinding and exposure to sunlight were the two standard bleaching processes in our experiments. We use combinations of two sequential subscripts to express the combinations of bleaching methods and material types. The first subscript is a number which represents grinding minutes, and the second subscript, P or Q, represents the material used for sunlight exposure. Numerals, not subscripted, are also used to represent different subsamples. For example, $A_{5P}1$ means that a sample was ground for 5 min (first subscript), polymineralic grains were used for sunlight exposure (second subscript), and that subsample is number one.

Previous studies have shown that the Ge signal intensity in quartz exposed under diffuse natural room light does not decrease (Rink, 1997; Walther and Zilles, 1994). Therefore, the work was done in an indoor laboratory, taking care to ensure that samples were not exposed to direct sunlight during preparation, irradiation, grinding, chemical processing or measurement.

3.1. Irradiation

Because the Ge signal is weak (Walther and Zilles, 1994), we had to amplify it using gamma (γ) irradiation in order to examine any changes in it. First, the 0.5–1 mm size fraction was obtained from

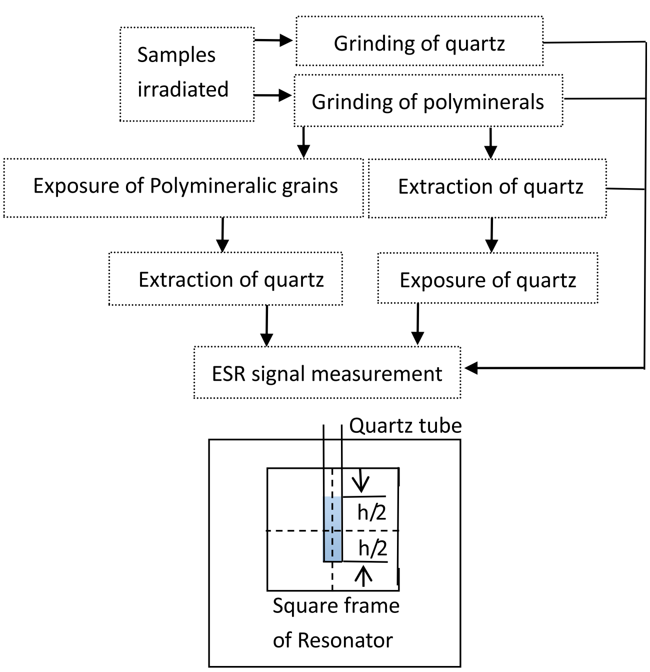

Fig. 2. Upper: Chart of principal experimental procedures. Lower: Position of a sample in resonator during ESR signal measurement. Inner square frame is the central area of the resonator; gray area is the sample in the tube; h is the height of the sample.

Samples A, B and C through sieving, washed in tap water, and rinsed in distilled water. In order to test whether signal intensity decreases at the same rate in the samples with different initial values, Samples A, B and C were then irradiated in the Department of Technical Physics of Peking University, using 1200 Gy, 1600 Gy, and 2800 Gy from ^{60}Co, respectively. The irradiated samples were kept under normal room conditions for ten years and the signals in them ensure stable. A 0.125–0.25 mm fraction was extracted from Sample D by sieving, irradiated by 1600 Gy from ^{60}Co and then chemically processed. This is the fraction commonly used for ESR dating. We used it for an analysis of the relation between signal intensity and mass of quartz. For this analysis, we prepared subsamples, at 0.05 g intervals, from 0.1 to 0.6 g.

3.2. Grinding

Samples A, B and C were ground by hand in 125 mm and 300 mm ceramic mortars for up to 5 min. As part of our control management, about 10 g were extracted from each of the irradiated polymineralic subsamples, and ESR signal intensities in these quartz subsamples (A_0, B_0 and C_0) were subsequently measured directly without exposure to sunlight and grinding. The rest of each sample was then ground for 1 min and 5 min to produce subsamples with different grain sizes, and the ESR signal intensity in quartz extracted from subsamples was measured. Signal intensity in Subsamples A_0 and A_1 were measured at the Marine Geological Institute in Qingdao, Shandong province. They were used only for qualitative analysis and were subsequently discarded fourteen years ago because of disappointing results.

Similarly, the pure quartz sample BC was ground for 0, 1, 5 and 9 min to produce subsamples BC_0, BC_1, BC_5 and BC_9.

Because the strength and speed of grinding varied from person to person, and because the sample amount affects the final ground product even if strength and speed are similar for all grinding episodes, the effect of any grinding was evaluated quantitatively as a function of grinding time and/or grain size.

3.3. Exposure

Subsample A_5, ground for 5 min, was separated into nine aliquots which were exposed to sunlight for 0, 1, 2, 4, 6, 16, 26, 60 and 108 h. Each aliquot weighed 7 g. Similarly, the B_5 series was separated into four aliquots, which were exposed to sunlight for 0, 1, 2 and 4 h. Each aliquot weighed 1.2 g. The C_5 series was separated into seven aliquots which were exposed to sunlight for 0, 1, 2, 4, 6, 16 and 26 h. Each aliquot weighed 2 g.

In order to evaluate the penetrative effect of sunlight, we used sediment layer 5–8 mm thick for the A_5 series and 1–2 mm thick for the B_5 and C_5 series during exposure.

In order to compare the bleachability of polymineralic samples, as apposed to pure quartz, during exposure, we extracted pure quartz subsamples A_{5Q}, B_{1Q}, B_{5Q}, C_{0Q}, C_{1Q} and C_{5Q} for exposure to sunlight for 1 and 4 h.

Short wavelengths in sunlight, including ultraviolet light, are most effective in bleaching ESR signals (Walther and Zilles, 1994), and these wavelengths are more common at high altitudes, where glaciation is common. Therefore, the exposure experiments were carried out between August 25 and September 5, 2012 at 3650 m asl on the balcony (29.64530°N, 91.03274°E) of the laboratory office building of the Institute of Tibetan Plateau Research in Lhasa, Tibet (Fig. 3). All exposures started at 12:00 local time (13:00 Beijing time). After 19:00, the samples were taken inside and exposure continued at 09:00 the next day, with the exception of the two samples exposed for the longest time. These two samples were exposed from 09:00 to 21:00 from 31 August until 5 September. If the weather was overcast or wet, the experiment was suspended until the weather improved. All samples were placed in glass beakers to allow sunlight to penetrate, and to minimize sample loss and any wind disturbance.

Normally, each subsample was a mixture containing upper and lower parts of the exposed samples. We periodically took off the surface layer from some samples, then shook the beakers with the remainder and mixed the mineral layer for further exposure in order to simulate sediment disturbance during or after deposition. After 4 and 60 h of exposure, the surface layer was taken from A_{5P} series as subsamples $A_{5P}4$ and $A_{5P}8$, respectively. After 2 h of exposure, surface layer was taken from B_{5P} series as subsample $B_{5P}3$. After 4 and 16 h of exposure, surface samples of $C_{5P}4$ and $C_{5P}6$ were taken, respectively. The remaining material was mixed and exposed continuously.

3.4. Quartz extraction

Preliminary testing showed that any chemical reaction during the removal of carbonate and organic matter was not sufficiently strong to produce enough heat to weaken the signal in the Ge center. We therefore added *aqua regia* to the samples in plastic beakers, in a ratio of 1 ml:1 g or >1 mm:1 g, and left the admixture for 8 h to remove organics and carbonates. We then poured out the solution, rinsed the samples in distilled water three times, and dried them in an oven at 50 °C. The magnetic minerals were then removed with a permanent magnet. Other heavy minerals and most of the feldspar were removed by heavy liquid separation (using silicotungstic acid solution). Next, a concentrated HF solution was added to the samples and left for 80 min to dissolve the remainder of the feldspar and other light minerals. After pouring off the HF solution, the samples were twice rinsed in distilled water. Then, distilled water was added to the samples and the mixture was stirred using a glass bar to allow any mica and chlorite flakes in series A, B and C to float. We then waited for several seconds before pouring out the surface water containing the suspended minerals. We repeated this process several times until no suspended flakes were present in the water. The samples were then dried and weighed. After etching, the quartz concentrations in the ground samples were >99% pure. Because this simple flotation process consumed multiple fine quartz grains, Sample D was not treated by flotation, so that there would be a sufficient amount of quartz for signal measurement. Instead, this sample was treated with diluted H_2NO_3 solution to remove any possible post-etching calcium fluoride residue. The sample was then rinsed three times to remove any residual chemical solution, and dried in an oven at 50 °C. It was checked visually and by polarizing and/or stereoscopic microscope. Few chlorite particles were removed by hand, and the remainder was etched for a further 20–40 min until we estimated that the quartz concentration was 95% or higher.

3.5. Grain size analysis

Grain size analyses were carried out on ground polymineralic and quartz subsamples. Pretreatment followed common procedures. The organic matter and carbonate in a weighed fraction from the polymineralic samples were removed using H_2O_2 and HCl solutions, respectively. The samples were then rinsed several times with distilled water. The treated samples were then dispersed in a solution of sodium hexametaphosphate and 0.1–0.5 g of each sample, dependent on grain sizes of the samples, were measured using a Melvin laser particle sizer. The ground quartz subsamples were measured directly, without any other chemical pretreatment. The grain size distributions of samples A, B and C were obtained by sieving. The grain size distribution of Sample BC series was obtained using both laser particle analysis and sieving. We used Folk mean size and frequency distribution to describe grain size characteristics.

3.6. Measurement of ESR signals

The Ge signal intensity was measured at room temperature using a Bruker EMX 6/1 ESR spectrometer at the Institute of Geology, China Earthquake Administration. Samples were put in the central area of the resonator. To avoid any impact on the signal from anisotropy of quartz grains, each sample was measured three or four times, with the test tube rotated 120° or 90° between measurements, respectively; the same spectrometer parameters were used, and the mean measured values were taken as denoting signal intensity. For all samples, the ESR peak-to-peak intensity measurements were carried out using signals at g = 1.9970 for the Ge center, an X-band, microwave power = 2.0 mW, central magnetic field = 3525 G, sweep width = 50 G, frequency = 9.852 GHz, modulation frequency = 100 kHz, modulation amplitude = 1 G (1 G = 10^{-4} T), time constant = 40.96 ms and sweep time = 10.486 s. Since signal intensity was strong in some samples and weak in others, we used a high reserved gain value (RG) for weak signals and a low RG for strong signals. Signal intensities were normalized by comparing RG 3.17 and weight 0.3 g.

In order to evaluate the effect of grain size on signal intensity, coarse (0.3–0.45 mm), medium (0.125–0.3 mm) and fine (0.063–0.125 mm) subsamples were separated from subsamples A_{5P} series, and coarse and medium subsamples were separated from C_{5P} series, for ESR signal measurement.

Fig. 3. Photo showing samples being exposed to sunlight at 3650 m asl in Lhasa, Tibet.

Because of the loss of weight of some samples during quartz purification, we could not keep each aliquot at the desired weight of 0.3 g, and had to make weight corrections. We measured signal intensities of the D series ranging from 0.1 to 0.6 g at 0.05 g intervals. The D series subsamples were measured five times, with the tube rotated ~72° between each measurement, and half of each test tube subsample (calculated from subsample height) was passed through the center of the resonator in order to ensure similar resonance conditions in the ESR resonator for quantitative analysis of the relation between signal intensity and mass of quartz (Fig. 2). The other test conditions are the same as described above.

4. Results

The Ge center ESR signals of both the polymineralic and the pure quartz subsamples were clear in the studied samples. Typical ESR spectra of the samples, both original samples and those processed by grinding and exposure to sunlight, are shown in Fig. 4. Grain size distributions display mono-modal peaks in ground polymineralic samples of Series A, B and C (Fig. 5A), and bimodal peaks in ground quartz samples (Fig. 5B), where the BC series was a combination of two populations. As grinding progressed, the grain sizes of both populations decreased simultaneously. As the grinding time increased, the Folk-Ward mean size decreased from coarse sand to fine sand or silt for all sample series (Fig. 5).

The signal intensity in quartz with grain sizes of 0.125–0.25 mm was linearly correlated with mass of quartz, with a significance level of 0.01 and the r^2 value of 0.989 (Fig. 6). We used the regression equation $y = 0.991x + 0.099$ (Fig. 6) to normalize the weight difference.

As the grinding time increased and grain size decreased, the Ge signal intensity in quartz extracted from polymineralic samples decreased monotonically with grain size (Fig. 7) After particles were ground to fine sand, the signal intensity had decreased by 31%–47%.

The ESR signal intensity also decreased as the time of exposure

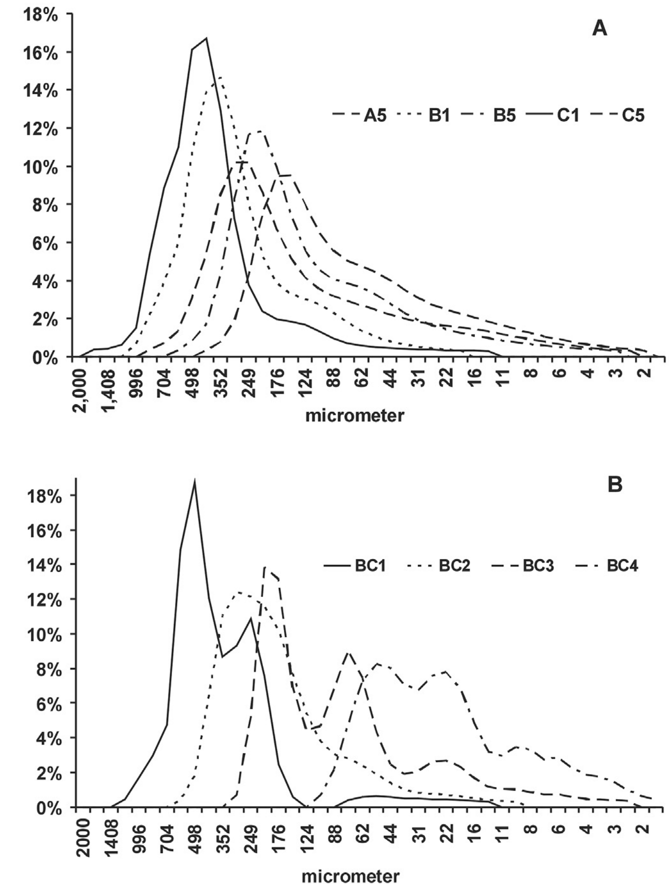

Fig. 5. Grain size distributions. (A) polymineralic samples of Series A, B and C, ground for 1 min and 5 min; (B) pure quartz ground over 0, 1, 5 and 9 min. Note: Subsample A_1 was thrown away 15 years ago and cannot be shown here.

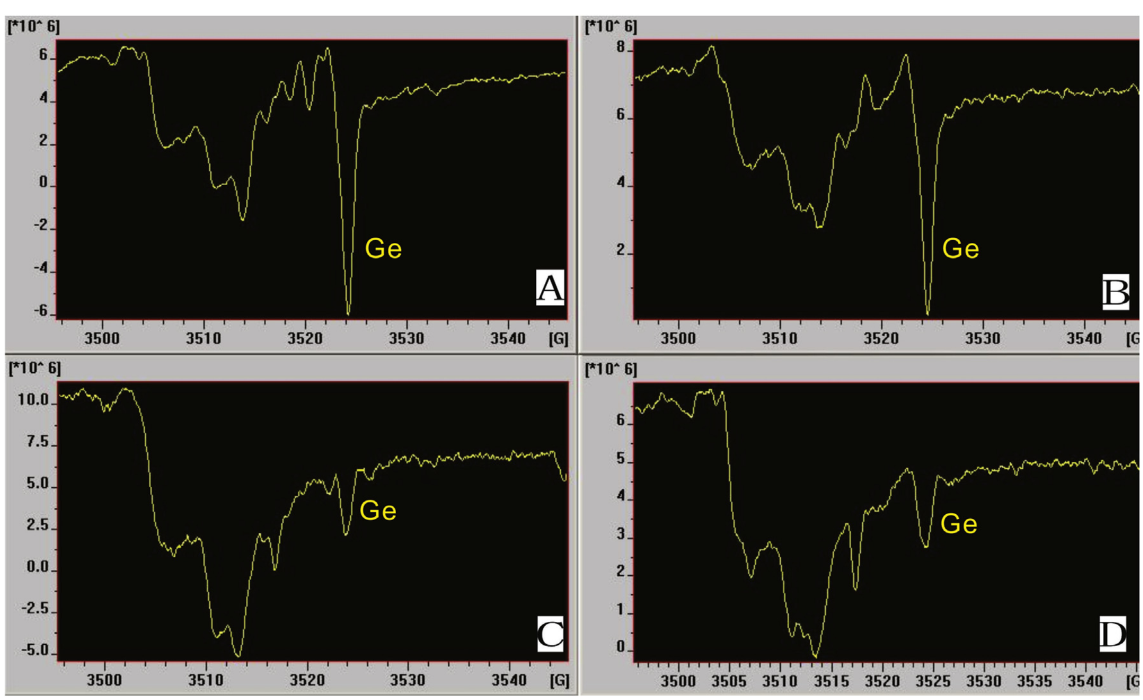

Fig. 4. Selected ESR spectra of the Ge centers in quartz extracted from Series C. (A) original polymineralic sample; (B) polymineralic sample ground for 5 min; (C) quartz sample exposed to sunlight for 4 h; and (D) polymineralic sample ground for 5 min and exposed for 1 h.

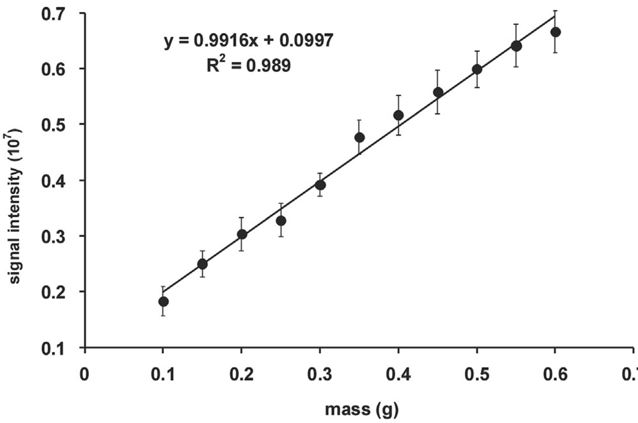

Fig. 6. Relation between signal intensity in Ge center and mass of quartz.

to sunlight increased. After 4 h of exposure, the signal intensity decreased to two thirds of the initial value for the A_{5P} series and to one quarter for the B_{5P} and C_{5P} series (Fig. 8). Then it decreased to 7–8% of the initial value after a further 22 h for the C_{5P} series, but remained roughly constant at 42–50% after a further 104 h for the A_{5P} series.

Regarding the signal intensity in samples which were disturbed during exposure to sunlight, there were one or two instances in the A_{5P}, B_{5P} and C_{5P} series in which it increased more after disturbance than in the samples which were exposed to sunlight for shorter hours, but were not disturbed (Fig. 8).

In the A_{5P} series which were covered by 5–8 mm of sample during exposure (Fig. 8A), signal intensity is higher in 0.3–0.45 mm grain sizes than in 0.125–0.3 mm sizes; in turn, the latter values were very slightly higher than in 0.063–0.125 mm grain sizes. In the C_{5P} series, signal intensities in the 0.3–0.45 mm grain size decreased by approximately the same amount as in the 0.125–0.3 mm grain size; this series was covered by a thin layer (1–2 mm thick) of sample during exposure (Fig. 8B).

The signal intensity of pure quartz subsamples exposed directly to sunlight decreased to 20–59% of the initial value after 1 h, and to 8–10% after 4 h (Fig. 9).

5. Discussion

5.1. Effect of grinding on the Ge signal

Ye et al. (1998) found that 1 min of laboratory grinding decreased the Ge center's ESR intensity in quartz subsamples by 38%. Our results support this result and show that the signal intensity in quartz extracted from grinding polymineralic samples decreased by 47% for the B series when the mean size was reduced from coarse sand (mean size: 0.75 mm) to fine sand (mean size: 0.143 mm); for the C series it decreased by 31% when the mean grain size was reduced from coarse sand to fine sand (mean size: 0.084 mm) (Fig. 7). Grinding of pure quartz grains to silt (mean size: 0.024 mm) in the BC series decreased signal intensity by ~37%. The final signal intensity tends to be the same value of ~2.0–2.2 × 10^7 regardless of the initial value was (Fig. 7). It would seem, therefore,

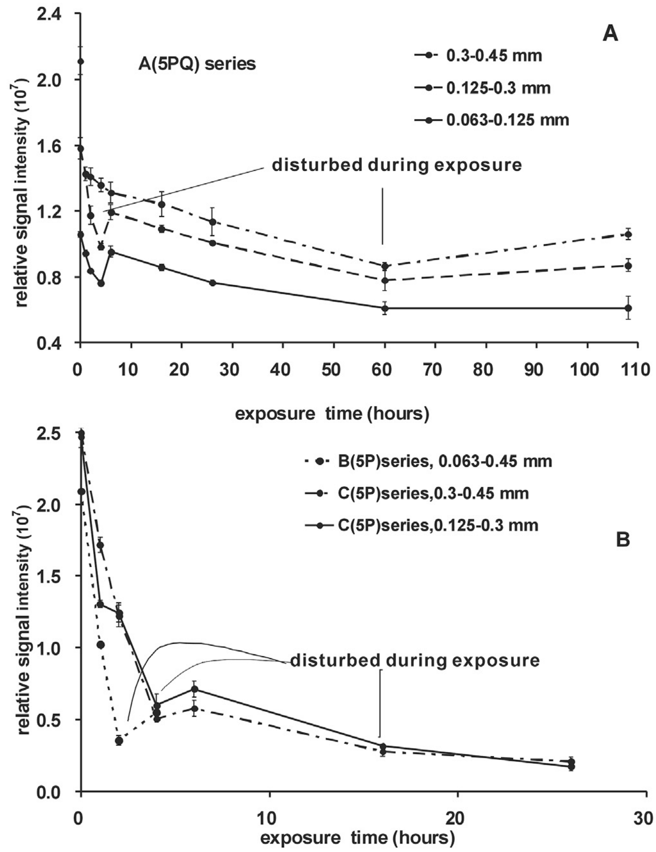

Fig. 8. The Ge signal intensity in quartz extracted from polymineralic samples as a function of hours of exposure to sunlight.

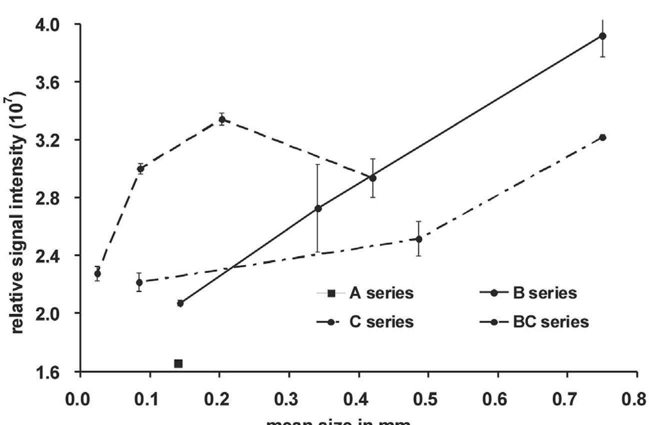

Fig. 7. Changes in Ge signal intensity in quartz extracted from polymineral subsamples (B and C series) and quartz subsamples extracted from directly-ground pure quartz (BC series) as a function of grain size or grinding time.

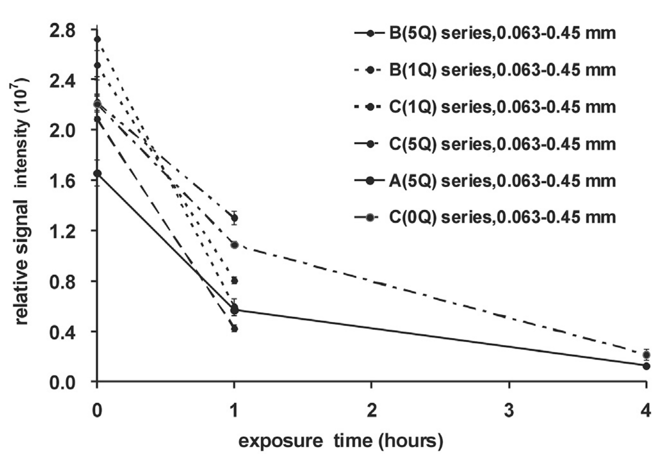

Fig. 9. The Ge signal intensity in pure quartz as a function of hours of direct exposure to sunlight.

that the ESR signal intensity cannot be decreased further with simple manual grinding.

Studies of the grain sizes (Boulton, 1978; Haldorsen, 1981; Hooke and Iverson, 1995) and microfabrics (Mahaney et al., 1988; Yi, 1997; Yi and Cui, 2001) of glacial till have demonstrated that fine sand and silt are produced by subglacial comminution. At present, we cannot simulate the strength and length of grinding that occurs in the subglacial environment. However, the mean grain sizes of fine sand produced in our grinding experiments are similar to those produced by glacial comminution. These grain sizes are commonly used for ESR dating (Fig. 7). Therefore, based on grain size, subglacial comminution could bleach one third to one half of the Ge center's ESR signal intensity for 0.063–0.45 mm grain sizes. In other words, two thirds to one half of the ESR signal in quartz would be inherited if the till were not exposed to sunlight.

5.2. Effect of exposure to sunlight on the Ge signal

Grün (1989, 1991) and Ye et al. (1993) found that the Ge signal in quartz grains in coastal beach sand was reset to zero after 1 h of exposure to sunlight. Our experimental results show that the signal intensity in quartz subsamples decreased by 41–80% after 1 h, and by 90–92% after 4 h (Fig. 9). The Ge signal was thus not zeroed as rapidly as in previous studies, probably because of dependence of sample properties (Toyoda et al., 2000).

However, pure quartz rarely exists in till, and our results show that the signal in quartz extracted from a polymineralic sample was not bleached to zero after 108 h of exposure to natural sunlight. Instead, the signal intensity decreased, then stabilized, with values ranging between 42% and 50% of the original value (Fig. 8A). When the exposed samples were 1–2 mm thick, the signal intensity decreased by three quarters after 4 h of exposure, and by 92–93% after 26 h of exposure (Fig. 8B). Mixing a sample during exposure may decrease the average signal intensity somewhat further (Fig. 8). These result would suggest that bleaching of till in sunlight varies with sedimentary characteristics. The Ge center's signal might be reset prior to/during deposition in quartz-rich interlayers of mountain glacier moraines, or on the margins of ice caps or ice sheets; along margins, concentrations of till within the ice can be much lower, and comminuted fine particles can become exposed at the glacier's surface, thus experiencing greater exposure to sunlight. If the residual dose cannot be evaluated, the ages derived from the Ge center must be treated as estimated maxima.

5.3. Effect of grain size on the Ge signal

The Ge center's ESR signal intensity was higher in the coarse (0.3–0.45 mm) than in the medium (0.125–0.3 mm) grain size fraction, and higher in the medium fraction than in the fine one (0.063–0.125 mm) (Fig. 8A). This would suggest that smaller grains are more easily mechanically bleached than larger ones. Grain sizes of 0.063–0.25 mm are commonly used for ESR dating of till (Shi et al., 2001; Wang et al., 2011; Yi et al., 2002; Zhao et al., 2010, 2012). Finer grains (0.06–0.125 mm) would be better for dating, as they exhibit less anisotropy, and any subglacial grinding would have reset the clock closer to zero. However, purification of fine quartz grains is difficult. Calcium fluoride would precipitate on the surface of finer grains during sample preparation, decreasing the signal intensity. Removal of feldspar and the outer layer of quartz grains damaged by α-radiation and grinding would consume large quantities of quartz. We would suggest, therefore, that fine sand (0.125–0.25 mm) would be better for dating, as other minerals within these grains can be easily and simply separated from quartz, and any removal of the outer layer by etching using HF solution will not consume many quartz grains.

5.4. Effect of irradiation on the Ge signal

ESR signal was amplified by irradiation. Initial values were different for each ground sample series, but the final signal intensity tends to be the same value of ~2.0–2.2 $\times$ 10^7 (Fig. 7). In contrast, it seems that signal intensity decreases in parts of the samples exposed to sunlight (Fig. 8). This implies that geological processes mainly control mechanical or optical bleaching. Since geological processes vary in spatial and temporal patterns, we suggest that correction for the residual dose should be carried out in each sample.

6. Conclusion

Laboratory grinding reduced signal intensities in the Ge centers of 0.063–0.45 mm quartz by one third to one-half of their initial values. Additional grinding to silt did not further reduce the signal intensity. This could be used to estimate the residual signal, and thus to correct paleo-doses. However, this should be cross-checked using independent dating methods or the residual dose from a modern till so as to determine the strength or pressure to be used in laboratory grinding. Signal intensity varied across experimental samples collected from the same moraine. This would suggest that bleaching may vary spatially; it was thus impossible to obtain an absolute signal intensity that could be used for correction of residual signals in all samples.

Signal intensity in the Ge centers of 0.125–0.45 mm quartz grains may be zeroed when exposed at the surface of polymineralic sediments for several days. Sediments may be sufficiently exposed to sunlight at the margins of ice caps and/or ice sheets, where the ice is clean and subglacially-crushed particles can become exposed at the ice surface.

Quartz purity and grain size are important controls on signal intensity and intensive purification and use of a uniform fine sand fraction are thus recommended.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.quageo.2016.06.003.

References

Boulton, G.S., 1978. Boulder shapes and grain-size distributions of debris as indicators of transport paths through a glacier and till genesis. Sedimentology 25, 773–799.
Buhay, W.M., Schwarcz, H.P., Grün, R., 1988. ESR dating of fault gouge—the effect of grain-size. Quat. Sci. Rev. 7, 515–522.
Cui, Z.J., 1981. Kinds and features of glacial moraine and till at the head of Urumqi river, Tianshan. J. Glaciol. Geocryol. 3, 36–48 (Chinese with English summary).
Derbyshire, E., 1984. Till properties and glacier regime in parts of high Asia: Karakoram and Tian Shan. In: White, R.O. (Ed.), The Evolution of the East Asian Environment. Hong Kong University Press, Hong Kong, pp. 84–110.
Grün, R., 1989. Present status of ESR-dating. Appl. Radiat. Isotopes 40, 1045–1055.

Grün, R., 1991. Potential and problems ESR dating. Nucl. Tracks Radiat. Meas. 18, 143–153.

Haldorsen, S., 1981. Grain-size distribution of subglacial till and its relation to glacial crushing and abrasion. Boreas 10, 91–105.

Hooke, R.L., Iverson, N.R., 1995. Grain-size distribution in deforming subglacial tills–role of grain fractures. Geology 23, 57–60.

Kong, P., Fink, D., Na, C., Huang, F., 2009. Late quaternary glaciation of the Tianshan, central Asia, using cosmogenic ^{10}Be surface exposure dating. Quat. Res. 72, 229–233.

Lee, H.K., Schwarcz, E.P., 1993. An experimental study of shear-induced zeroing of ESR signals in quartz. Appl. Radiat. Isotopes 44, 191–195.

Li, D., Yi, C., Ma, B., Wang, P., Ma, C., Cheng, G., 2006. Fabric analysis of till clasts in the upper Urumqi river, Tian Shan, China. Quat. Int. 154, 19–25.

Li, S., Cui, Z., Wang, J., Zhang, Z., 1981. Lithology and morphological characters of till, glacial fluvial alluvial deposits at the head of Urumqi river, Tianshan. J. Glaciol. Geocryol. 3, 78–91 (Chinese with English summary).

Li, Y., Liu, G., Chen, Y., Li, Y., Harbor, J., Stroeven, A.P., Caffee, M., Zhang, M., Li, C., Cui, Z., 2014. Timing and extent of Quaternary glaciations in the Tianger Range, eastern Tianshan, China, investigated using Be-10 surface exposure dating. Quat. Sci. Rev. 98, 7–23.

Mahaney, W.C., Vortisch, W., Julig, P., 1988. Relative differences between glacially crushed quartz transported by mountain and continental ice–some examples from North America and East Africa. Am. J. Sci. 288, 810–826.

Rink, W.J., 1997. Electron spin resonance (ESR) dating and ESR applications in quaternary science and archaeometry. Radiat. Meas. 27, 975–1025.

Shi, Z.T., Ye, Y.G., Zhao, Z.J., Fang, X.M., Li, J.J., 2001. ESR dating of late Cenozoic molassic deposits in the Jiuxi basin. Sci. China Ser. D. 44, 203–209.

Toyoda, S., Voinchet, P., Falguères, C., Dolo, J.M., Laurent, M., 2000. Bleaching of ESR signals by the sunlight: a laboratory experiment for establishing the ESR dating of sediments. Appl. Radiat. Isotopes 52 (5), 1357–1362.

Walther, R., Zilles, D., 1994. ESR studies on bleached sedimentary quartz. Quat. Sci. Rev. 13, 611–614.

Wang, J., Pan, B., Zhang, G., Cui, H., Cao, B., Geng, H., 2013. Late quaternary glacial chronology on the eastern slope of Gongga mountain, eastern Tibetan plateau, China. Sci. China-Earth Sci. 56, 354–365.

Wang, J., Zhou, S., Zhao, J., Zheng, J., Guo, X., 2011. Quaternary glacial geomorpholo Gy and glaciations of Kongur mountain, eastern Pamir, China. Sci. China-Earth Sci. 54, 591–602.

Wu, Y.Q., Cui, Z.J., Liu, G.N., Ge, D.K., Yin, J.R., Xu, Q.H., Pang, Q.Q., 2001. Quaternary geomorphological evolution of the Kunlun pass area and uplift of the Qinghai-Xizang (Tibet) plateau. Geomorphology 36, 203–216.

Ye, Y.G., Diao, S.B., He, J., Gao, J.C., Lei, X.Y., 1998. ESR dating studies of palaeo-debris-flow deposits in Dongchuan, Yunnan Province, China. Quat. Sci. Rev. 17, 1073–1076.

Ye, Y.G., He, J., Diao, S.B., 1993. Study on ESR ages of late Pleistocene coastal aeolian sands. Mar. Geol. Quat. Geol. 13, 85–90.

Yi, C.L., 1997. Subglacial comminution in till–evidence from microfabric studies and grain-size distributions. J. Glaciol. 43, 473–479.

Yi, C.L., Cui, Z.J., 2001. Subglacial deformation: evidence from microfabric studies of particles and voids in till from the upper Urumqi river valley, Tianshan, China. J. Glaciol. 47, 607–612.

Yi, C.L., Jiao, K.Q., Liu, K.X., He, Y.Q., Ye, Y.G., 2002. ESR dating of the sediments of the Last glaciation at the source area of the Urumqi river, Tianshan mountains, China. Quat. Int. 97–8, 141–146.

Yi, C.L., Liu, K.X., Cui, Z.J., Jiao, K.Q., Yao, T.D., He, Y.Q., 2004. AMS radiocarbon dating of late Quaternary glacial landforms, source of the Urumqi river, Tianshan–a pilot study of C-14 dating on inorganic carbon. Quat. Int. 121, 99–107.

Zhao, J., Song, Y., King, J.W., Liu, S., Wang, J., Wu, M., 2010. Glacial geomorphology and glacial history of the Muzart river valley, Tianshan range, China. Quat. Sci. Rev. 29, 1453–1463.

Zhao, J.D., Lai, Z.P., Liu, S.Y., Song, Y.G., Li, Z.Q., Yin, X.F., 2012. OSL and ESR dating of glacial deposits and its implications for glacial landform evolution in the Bogeda Peak area, Tianshan Range, China. Quat. Geochronol. 10, 237–243.

Zhao, J.D., Zhou, S.Z., He, Y.Q., Ye, Y.G., Liu, S.Y., 2006. ESR dating of glacial tills and glaciations in the Urumqi river headwaters, Tianshan mountains, China. Quat. Int. 144, 61–67.

Zhou, S.Z., Li, J.J., Zhang, S.Q., 2002. Quaternary glaciation of the Bailang river valley, Qilian shan. Quat. Int. 97–8, 103–110.