



# Article The ESR Signals in Different Minerals and the Bleaching of Feldspar

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Abstract: The use of quartz is critical to the electron spin resonance (ESR) dating of sediments and fault gouges. The germanium center (Ge center) in quartz is a commonly used color center employed in ESR signal measurement. Although Ge center signals in quartz can be detected using an ESR spectrometer, they are weak and sometimes undetectable. Impurities in quartz grains can further aggravate these deficiencies and may even invalidate any attempt to repeat ESR ages due to the deficiencies evident in the processes used in sample preparation. Using sieving, carbonate-organic matter removal, water flotation, magnetic separation, heavy liquid separation, and HF solution etching, we separated quartz, feldspar (plagioclase), mica, and the heavy minerals and measured the ESR signal in each of them to examine the impact of impurities within mineral grains on the ESR signals. From the ESR spectra, we observed intense ESR signals in feldspar and the heavy minerals and weak signals in mica at the same positions as the Ge center in the quartz. The ESR signals in the feldspar proved to be the most intense and overrode the peaks exhibited by the Ge center in the quartz. Feldspar is commonly associated with quartz in sediments, but it is difficult to separate it from quartz as their colors, specific gravities, and magnetic properties are similar. Any ESR signal in quartz containing foreign minerals would therefore be likely to be heavily disturbed by the signals from these foreign minerals, particularly from the feldspar and heavy minerals. ESR signals in the feldspar decreased similarly to those in the quartz when exposed to sunlight, declining by 70%-80% after being exposed for 50 h. Such declination was more obvious in high-altitude areas than in low-altitude areas. Our results indicate that highly pure quartz is required when dating; we would therefore strongly suggest that the procedures for the purification of quartz grains should include floating, heavy liquid separation, and HF solution etching to remove the feldspar, heavy minerals, and any remnant magnetite. Such a procedure would guarantee that the signal that is measured comes from the quartz alone, allowing repeatable measurements using the same spectrometer as well as valid comparisons between the spectrometries derived from different spectrometers.

Keywords: quartz; feldspar; heavy minerals; mica; ESR; Ge center

## 1. Introduction

Quartz was first used in the ESR dating of sediments and fault gouges in the 1980s [1–5] and has continued to be used to date Quaternary eolian, shoreline beach, fluvial, and lacustrine sediments during the last decade [6–18]. The extraction of pure quartz from sediments is required for accurate dating. However, natural, pure quartz is rare in sediments. A complete protocol for processing sediments to isolate pure quartz has already been proposed by Grün [19], but the step whereby heavy liquid separation is used to extract quartz from samples has been omitted during many routine experiments. Other processes that



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). are employed include the use of aqua regia or an HCl solution with a  $H_2O_2$  solution to remove carbonate and organic matter, as well as HF solution etching for the removal of feldspar, heavy minerals, mica, etc. Even then, the resultant quartz is not pure, and its ESR spectrometry overlaps the signals from other minerals. It is not possible at present to separate the ESR signals in quartz from those in remnant minerals if their signals occur at the same position in the magnetic field as the quartz signal. Mineral components and their concentrations in the samples processed using this deficient procedure cannot be repeatedly measured because any differences in temperature and time duration in the etching and the disturbance of the solution during sample processing will not result in the same concentrations of purities of quartz grains. Consequently, different ESR signals and/or ESR dates can be produced for the same sample collected in the same layer of the same moraine and dated by the same technician using the same parameters in the same ESR spectrometer [20,21].

The Ge center (g = 1.997) in quartz is sensitive to sunlight and mechanical friction and can therefore act as a potential color center for sediment dating [22,23]. Sediments are composed of various minerals, and the quartz extracted from them is commonly used for ESR dating. The other minerals can affect the ESR signals of quartz. We therefore separated quartz, feldspar, mica, and the heavy minerals from two glacial tills and analyzed their ESR signal characteristics at g = 1.997 in order to provide a foundation for the purification of quartz grains and consequent ESR dating.

#### 2. Materials and Methods

## 2.1. Sampling

Glacial till and fluvial sediments can be mixed with several or many mineral components. Sample 1 and Sample 2 (corresponding to sampling points 15H3 and 15H4 in the field) were collected from the lower and upper parts of an exposed moraine, respectively, in the Hongliutan Valley in the western Kunlun Mountains (35°51′58.14″ N, 79°23′15.25″ E; 4708 m above sea level (asl)). Sample 3 (corresponding to sampling point SMX18 in the field) was collected from fluvial core sediment extracted from a site in the Sanmenxia Gorge, in the middle reaches of the Yellow River. The samples were collected without direct exposure to sunlight and packed in black plastic bags to avoid any exposure to light during their transportation to the laboratory. All experiments were conducted under ambient lighting and room temperature conditions.

## 2.2. Separation of Minerals

Referring to previous sampling processes [15,24], we established a revised procedure in order to separate the different minerals and purify the quartz (Table A1). The 0.25–0.063 mm fraction was separated using dry sieving and put into a 3000 mL plastic beaker made of high-density polyethylene. The separation of minerals followed the basic methodology used in previous procedures. Carbonates were removed using an HCl solution and organic matter using an  $H_2O_2$  solution. The sample was then rinsed in distilled water to remove the remnant HCl. We employed a water flotation procedure to separate flaky minerals from the sample. The sample was placed in a 3000 mL plastic beaker, to which water was added in order to produce a suspended solution. The sample was left undisturbed for 60 s, and any suspended flaky minerals were poured into another beaker. This process was repeated until the mica sample was sufficient to allow ESR signal measurement. Further tap water was added to the sample to produce a suspended solution. Once again, the sample was left undisturbed for 30-60 s, and any suspended flakes were removed. This process was repeated until the water was clear. The flaky mineral sample was cleaned. The remaining sample was rinsed twice with distilled water and then dried in an oven at a temperature of 40 °C. Magnetite was separated from the remainder of the sample using a strong, permanent magnetic field. Heavy minerals, such as feldspar and quartz, were separated using heavy liquid separation. For the separation of quartz and feldspar, the specific gravity of the heavy liquid was 2.65. When the heavy mineral was separated, the specific gravity of the heavy liquid was 2.75. The separated heavy minerals, feldspar and quartz, were put into a 250 mL glass beaker and rinsed with distilled water three to four times to remove any remaining heavy liquid. This was subsequently dried in an oven at a temperature of 40  $^{\circ}$ C. The sample was then sieved into two fractions with grain sizes of 0.25–0.125 mm and 0.125–0.063 mm. Each quartz sample was placed into a plastic beaker, and a concentrated HF (40%) solution was added to etch the quartz for approximately 60-80 min (for the 0.25-0.125 mm fraction) or no more than 60 min (for the 0.125–0.063 mm fraction) in order to remove the alpha-irradiated outer part of quartz and any remnant feldspar, mica, and mineral inclusions. The sample was then rinsed with distilled water twice before  $HNO_3$  (20%) was added to remove the remnant fluorite on the granular surfaces. The sample was then cleaned twice with distilled water and dried in an oven at a temperature of 40 °C. Each quartz sample was checked with both the naked eye and a polarized microscope, and a repeat etching procedure was conducted if the quartz was not pure enough (Figure A1). All separated minerals were checked under a polarized microscope, and no foreign minerals were found. Thus, the monominerals of quartz, feldspar, and mica, and one heavy polymineral, were successfully separated using sieving, water flotation, magnetic separation, heavy liquid separation, and HF etching (Figure A2). The feldspar was classified as plagioclase due to its gray/white color and the occluded angle of its two crossed cleavages identified under the polarizing microscope.

In order to compare the differences in ESR signal intensities between coarse and fine grain sizes, the quartz, feldspar, and mica samples extracted from Samples 1 and 2 were separated into two fractions (i.e., 0.25–0.125 mm and 0.125–0.063 mm) using mechanical dry sieving (Table A2), with the exception of the 0.125–0.063 mm mica fraction, which did not produce a sufficient mineral quantity for ESR signal measurement.

Quartz, feldspar, heavy polyminerals, and mica were separated from portions of both Samples 1 and 2 without the use of artificial irradiation for ESR signal measurements (Table A2). The 0.125–0.25 mm and 0.63–0.125 mm feldspar grain fractions extracted from the remaining portions of Sample 1 were F-1600 with the irradiation dose of 1600 Gy. They were subdivided into between eight and ten parts, with equal weights of 0.25 g, for sunlight bleaching experiments. In addition, a portion of feldspar was extracted from Sample 3 without artificial irradiation, and was classified into two subsamples, Sample F-L and F-B, in preparation for sunlight bleaching at high-altitudes (Lhasa) and low-altitudes (Beijing), respectively (Table A3).

## 2.3. Sunlight Bleaching of Feldspar

Feldspar is one of the most abundant minerals in sediment samples and is not easily separated from quartz owing to their similar physicochemical properties [25]. The density of the quartz is from 2.65 to 2.51 g/cm<sup>3</sup> [26], and the feldspars have a density range of 2.54–2.76 g/cm<sup>3</sup> [27]. The signal in the Ge center in quartz has been observed to decrease markedly after direct exposure to sunlight [28]. We therefore conducted experiments on feldspar to determine whether or not it behaved similarly to quartz during sunlight bleaching. Each subsample was put on a piece of sulfate paper in a layer < 1 mm thick before being covered by a glass slide to avoid mass loss brought about by wind (Figure A3).

The samples selected for the sunlight bleaching experiments were subdivided into between eight and ten subsamples. Samples F-1600 and F-L were exposed to sunlight at a high-altitude in Lhasa (3650 m asl; 29.64530° N, 91.03274° E); Sample F-B was exposed to sunlight at a low-altitude in Beijing (43.5 m asl; 29.64530° N, 91.03274° E). The degrees to which the different subsamples were bleached by sunlight were then compared. These exposure experiments were carried out between July and September of 2019. In Lhasa, the first windows of sunlight exposure were from 13:00 to 16:30 everyday, and the next windows of exposure were from 10:30 to 18:30 every day. If the weather was overcast or cloudy, the experiments were suspended until the weather was good. The bleaching periods lasted between 0.5 and 63.3 h. In Beijing, the samples were exposed to sunlight from July to September of 2019 and from 10:00 to 16:30 every day. The bleaching period lasted between 0.5 and 51 h (Table A3).

## 2.4. Measurement of ESR Signals

Monomineral samples were weighed (Table A2) and placed into pure quartz tubes. ESR spectra were produced using a JES-FA200 ESR spectrometer set to the following parameters: room temperature; X-band; microwave power = 1.0 mW; central magnetic field = 323.142 mT; sweep width =  $\pm 5 \text{ mT}$ ; modulation frequency = 100.00 kHz; and time constant = 0.03 s. A manganese marker was put into the resonator for each measurement. For the Ge center in the quartz, ESR intensities were measured using signals set at g = 1.997 (Figure A4). ESR signal intensities in the feldspar, mica, and heavy polyminerals were measured at the same position in the magnetic field as those of the Ge center in the quartz. All measured signal intensities were normalized by the intensity of the Mn marker placed inside the cavity. The relative values of the ESR signal intensities measured at different times and for different minerals could therefore be compared with each other.

#### 3. Results

3.1. Comparison of the ESR Signal Intensities of Feldspar, Mica, and the Heavy Polyminerals with Those of Quartz

The ESR signals of the feldspar, mica, and heavy polyminerals observed at the same positions as the Ge center in the quartz are summarized in Table 1.

**Table 1.** Occurrence of ESR signals of feldspar, mica, and heavy polyminerals at the position of the Ge center in quartz.

Sample Number	Grain Size/mm	Feldspar	Heavy Minerals	Mica	
Sample 1	0.25-0.125	Y	Y	Y	
	0.125-0.063	Y	Y	Ν	
Sample 2	0.25-0.125	Y	Y	Y	-
	0.125-0.063	Y	Y	Ν	

 $\overline{Y}$  = have a signal; N = no sample.

The results show that the Ge center signals of quartz were present in the samples. More than one signal peak occurred in the scanning magnetic field range for the feldspar, heavy polyminerals, and mica, with particularly intense signals being displayed at the same positions as the Ge center of the quartz (Figures 1–4). The shapes of the ESR spectra and the signal intensities of the minerals were different between the 0.25-0.125 mm and 0.125–0.063 mm fractions. The ESR signals in the feldspar for these two fractions, without artificial irradiation, displayed clear peaks on the spectra at the same position as the Ge center in the quartz and were the most intense compared with the signals of other minerals such as quartz, mica, and heavy polyminerals (Figures 1 and 2). Clear peaks in the heavy polyminerals were detected on the spectra at the same positions as the Ge center of the quartz, but the signal intensity for the 0.125–0.063 mm fraction was more intense than that for the 0.25–0.125 mm fraction. Weak peaks occurred on the mica spectrum for the 0.25–0.125 mm fraction. The base line of its spectrum was straight and similar to the background noise level. The quantity of mica in the 0.125–0.063 mm fraction was insufficient to produce a spectrum. The ESR signals were strong at the same positions as the Ge center in the quartz.



**Figure 1.** Comparison of the ESR spectra of quartz with those of feldspar, heavy minerals, and mica with 0.25–0.125 mm grain size in Sample 1.



**Figure 2.** Comparison of the ESR spectra of quartz with those of feldspar and heavy minerals with 0.125–0.063 mm grain size in Sample 1.



**Figure 3.** Comparison of ESR spectra of quartz with those of feldspar, heavy minerals, and mica with 0.25–0.125 mm grain size in Sample 2.



**Figure 4.** Comparison of the ESR spectra of quartz with those of feldspar and heavy minerals with 0.125–0.063 mm grain sizes in Sample 2.

The spectra of the minerals in Sample 2, without artificial irradiation, were approximately similar to those of Sample 1, though with some minor differences. The ESR signal of the feldspar present in the 0.25–0.125 mm fraction was very strong (Figure 3), but relatively weak in the 0.125–0.063 mm fraction (Figure 4). The heavy polyminerals in each of the two fractions displayed a clear peak at the same position as the Ge center in the quartz. The ESR signal of the mica present in the 0.25–0.125 mm fraction was clearly detectable (Figure 3). The quantities of mica and magnetite present in the 0.125–0.063 mm fraction were insufficient to detect their signals.

## 3.2. Characteristics of the ESR Signals of Feldspar Exposed to Sunlight

The ESR spectra of the feldspar changed significantly when they were exposed to sunlight (Figure 5). The ESR signal intensity of the feldspar located at the same position as the Ge center in the quartz of Sample F-1600 displayed a general tendency to decrease after being exposed to sunlight in Lhasa for between 34 and 62.5 h. The ESR signal intensity of the 0.25–0.125 mm fraction decreased sharply for the first half hour of exposure. It increased for the next 4.17 h but did not override its initial value. It subsequently decreased continuously by 60.8% of its original value after 34 h of exposure and by 86.3% of its original value after 62.5 h (Figure 6 and Table A3). The ESR intensity of the 0.125–0.063 mm fraction increased for the first two h before decreasing for the next 2–18 h of exposure to sunlight. From 18 h to 34 h, the ESR signals increased again. After 34 h of exposure, the signal intensity decreased by 41.5% (Figure 6 and Table A3).



**Figure 5.** ESR spectra of feldspar from Sample F-1600 with artificial irradiation exposed to sunlight in hours. (**a**) 0.25–0.125 mm fraction; (**b**) 0.125–0.063 mm fraction.



**Figure 6.** Changes in ESR signal intensities of feldspar (same position—g factor—as Ge center in quartz) from Sample F-1600 versus exposure to sunlight. The black is a 0.25–0.125 mm fraction, and the red is a 0.125–0.063 mm fraction.

## 3.3. Feldspar Bleaching at Two Different Altitudes

With the increase in the number of hours during which the subsamples were exposed to sunlight at a high-altitude (Lhasa), the ESR signal intensity of the feldspar showed significant decreases and increases. The ESR signal intensity of Sample F-L (Lhasa) decreased by 52.2% after 15.3 h of exposure to sunlight. When feldspar was exposed to sunlight at a low-altitude (Beijing), the ESR signal intensity of Sample F-B (Beijing) also decreased and increased markedly during the first 18.5 h of exposure. After 18.5 h of exposure, the ESR signal intensity decreased by 14.7%. With continued exposure, the ESR signal intensity appeared to plateau before decreasing by 19.3% after 51 h of exposure (Figure 7 and Table A3).



**Figure 7.** Changes in ESR signals of feldspar in Sample F-L (Lhasa) and Sample F-B (Beijing) versus exposure hours to sunlight.

## 4. Discussion

4.1. Impact of the Feldspar, Mica, and Heavy Polyminerals on the Signals in the Ge Center of Quartz

The ESR signals of the feldspar and the heavy polyminerals are clearly evident at the same positions of the Ge center in the quartz (Figures 1–4). This would appear to indicate that the mixture of feldspar and/or heavy polyminerals with quartz increases the intensities of the signals at the same positions as the Ge center in the quartz.

Although the signal of the mica in Sample 1 at the same position as the Ge center in the quartz was weak, the signal for the 0.25–0.125 mm fraction of Sample 2 remained strong. This would suggest that mica mixed with quartz might also have caused interference with the quartz signal.

In summary, the ESR signals of non-quartz minerals appear in the magnetic field at locations similar to the Ge center in quartz. If these non-quartz minerals are present in a quartz sample, it is most likely that their signals interfere with the signal of the Ge center in the quartz. It is even possible that the presence of such non-quartz minerals may preclude the Ge center's signal from being measured, resulting in different signal values in multiple measurements of the Ge center in the same sample. It is therefore a vital prerequisite

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that purified quartz samples be obtained in order to increase the reproducibility of signal measurements and the accuracy of ESR dating.

#### 4.2. Impact of Mineral Grain Sizes on the Signals in the Ge Center in Quartz

When comparing the ESR signal intensities of the two grain size fractions of the feldspar and heavy polyminerals, we can see that the signal in the 0.125–0.063 mm fraction was stronger than that in the 0.25–0.125 mm fraction (Figures 1–4). We would therefore posit that fine-grained minerals are more likely to exert a greater impact on ESR signals than coarse-grained ones.

Some quartz particles contain inclusions, potentially leading to the ESR signals in purified quartz being affected by mineral signals. The selection of fine-grained size components could therefore reduce the possible content of any inclusions, reducing the potential interference caused by impurity signals on the Ge center signals in quartz. However, the content of particles < 0.06 mm in size is often low, and it can be difficult to separate minerals of this grain size. We would therefore recommend that the 0.25–0.125 mm and 0.125–0.063 mm fractions be used to extract quartz samples for ESR dating. The results of the two components can be checked against each other.

#### 4.3. Bleaching of Feldspar in Sunlight

The Ge center in quartz is sensitive to exposure to sunlight [28]. In our study, the ESR signals in feldspar also showed a certain response to sunlight (Figures 5–7). Exposure to sunlight appeared to cause the ESR signal in feldspar to decline, but this signal did not completely return to zero after 60 h of exposure, regardless of whether the sample was artificially irradiated or not. At room temperature, the ESR signal in feldspar remained relatively strong.

When sunlight exposure times were the same, feldspar at a high-altitude (Lhasa) lost 97.4% of its ESR signal, while feldspar at a low-altitude (Beijing) only lost 19.3% of its ESR signal (Figure 7). Even if the exposure time was increased, the ESR signal in feldspar in Beijing did not decline significantly. The original signal intensity of F-B was 0.641. After 2 h of exposure, the signal attenuation was the highest, losing 46.0%, and then the signal was enhanced. Until 18.5 h, the signal tended to a flat value and lost 19.3%. The initial signal of F-L was 0.824, and the signal also showed an increasing trend after 2 h. With the increase in exposure time, the signal gradually decreased, and at 63.3 h, it lost 97.4% of its initial signal. Short-wave radiation from sunlight, including ultraviolet (UV) light, is effective in reducing ESR signals [29]. These wavelengths are more common at high-altitudes and could cause the ESR signal to decline more dramatically than at low-altitudes.

The most widely distributed centers in feldspars are  $O^-$  and  $Ti^{3+}$ , as well as  $Fe^{3+}$  impurity [30]. The  $O^-$  center developed in all feldspars when the samples were irradiated. The center was designated as  $O^-$  -Al in quartz. As distinct from quartz, in feldspars, the Al- $O^-$  -Al center is formed with two Al atoms. Previous studies had given ESR spectra of orthoclase and microcline, and their ESR results showed two prominent signals with g values of about 1.95–2.05 and 3.6–4.0 [31]. In our research, the signal near g = 1.997 was most likely the Al- $O^-$  -Al center. We speculated that the free electrons escaped or the Al- $O^-$  -Al was broken when exposed to the solar radiation, so the signal intensity of the Al center gradually decreased with increasing sunlight exposure. However, from the variation of the data (Figures 6 and 7), the signals came to fluctuate within the 5 h of bleaching, and that showed the downward trend after that. These signals were measured at room temperature whether there was a change at low temperature, or whether more signals were observed. Perhaps it was related to conversion with low temperature signals, and these problems need more data to be solved.

A short period of exposure to sunlight did not completely bleach the ESR signals of the Ge center in feldspar. The results of this study would therefore suggest that feldspar is not a suitable mineral for the ESR dating of moraines. Since the Ge center signal in feldspar is

strong at the same position as the Ge center in quartz, any feldspar associated with quartz should be completely removed.

#### 5. Conclusions

Measurements of the ESR signals of five separated minerals revealed that the signals in feldspar and the heavy polymineral were strong and those in the mica weak, at the same positions as the Ge center in the quartz. In addition, the signals in the feldspar at the same position as the Ge center in the quartz displayed similar responses to quartz when exposed to sunlight. The presence of these minerals in the quartz samples would have interfered with the signal measurements used for ESR dating. We would therefore strongly suggest that any feldspar and heavy polyminerals be removed using heavy liquid separation. Water flotation should also be used to remove any mica. Sunlight could degrade the ESR signal of feldspar in the moraine. Over 60 h of sunlight, the ESR signal in feldspar could not completely disappear. In the irradiated feldspar, the rate of large particle size was faster than that of small particle size. The bleaching of feldspar was more obvious at highaltitudes, and the same sample decayed faster at higher altitudes. Therefore, improving the purity of quartz samples, especially to remove feldspar, was an important prerequisite to obtaining accurate dating signals. It was recommended to increase the percentage of quartz composition to 99% or above so that non-quartz single mineral grains could not be seen under the microscope to ensure the accuracy and stability of the signal intensity used in ESR dating.

**Author Contributions:** Conceptualization, W.B.; methodology, W.B. and C.Y.; software, W.B. and H.Y.; validation, W.B., X.X. and G.H.; formal analysis, W.B. and C.Y.; investigation, W.B. and C.Y.; resources, W.B., C.Y. and H.Y.; data curation, W.B.; writing—original draft preparation, W.B.; writing—review and editing, W.B. and C.Y.; visualization, W.B.; supervision, W.B.; project administration, W.B.; funding acquisition, W.B. and C.Y. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** All data needed to evaluate the conclusions in the paper are present in the paper and that are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

## Appendix A



**Figure A1.** (a) Separation of minerals using heavy liquid separation in a funnel. Feldspar grains are floating on the upper surface, quartz grains are suspended in the middle, and heavy polymineral grains are deposited at the bottom. In the figure, the heavy polyminerals have dropped in the Brinell funnel and the quartz grains have dropped to the lower part of the heavy liquid; (b) samples before heavy liquid separation treatment; (c) samples after heavy liquid separation, and the purity of quartz is significantly improved.



**Figure A2.** Separated minerals from Sample 1 as observed under a polarizing microscope: (**a**) quartz; (**b**) feldspar; (**c**) the heavy polyminerals; and (**d**) mica.





**Figure A3.** The bleaching of feldspar exposed to sunlight in Lhasa as Sample F-1600 and Sample F-L (**a**) and in Beijing as Sample F-B (**b**).



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Figure A4. ESR spectrum of quartz [32].

Voinchet et al., 2007 [15]	Ye et al., 1993 [32]	This Article
1. A fraction of 0.1–0.2 mm was extracted by water sieving.	1. A fraction of 0.25–0.06 mm was extracted by water sieving.	1. A fraction of 0.25–0.063 mm was extracted.
2. Soaked in $H_2O_2$ for 12 h.	2. Treated with $H_2O_2$ to remove organic material.	2. Treated with $H_2O_2$ to remove organic material.
3. In HCl for 12 h.	3. Soaked in 6 M HCl to dissolve carbonate.	3. Soaked in HCl to dissolve carbonate.
4. In 40% HF for 45 min to eliminate feldspars and etch the grain quartz.	<ol> <li>Subsequently etched with concentrated HF for about 1 h to remove the outer layers of the quartz grains.</li> </ol>	4. Rinsed in distilled water to remove the remnant HCl.
5. Fluorides and heavy minerals were then removed using HCl and bromoform, respectively.	5. Washed in water and dried at 40 $^{\circ}\text{C}.$	5. Employed a water flotation procedure to separate flaky minerals from the sample. The flaky mineral sample was cleaned.
	6. Magnetic minerals are removed by a magnetic separator.	6. Washed in water and dried in an oven at a temperature of 40 °C.
		<ol> <li>Magnetite was separated using a strong, permanent magnetic field.</li> </ol>
		<ol><li>Heavy minerals, feldspar, and quartz were separated using heavy liquid separation.</li></ol>
		9. Sieved into two fractions with grain sizes of 0.25–0.125 mm and 0.125–0.063 mm.
		10. The concentrated HF solution was added to etch the quartz for 60–80 min for the 0.25–0.125 mm fraction and no more than 60 min for the 0.125–0.063 mm fraction.
		<ol> <li>Rinsed with distilled water twice, a diluted HNO<sub>3</sub> solution was added to remove the remnant fluorite on the granular surfaces.</li> </ol>
		12. Cleaned with distilled water twice and dried in an oven at a temperature of 40 $^\circ\mathrm{C}.$
		13. Each quartz sample was checked with both the naked eye and a polarized microscope, and a repeat etching procedure was conducted if the quartz was not pure enough.

Sample Number	Laboratory Number	Sample Number of Tube	Mineral	Grain Size/mm	Weight/g
	15H3	15H3-1	mica	0.25–0.125	0.2504
	15H3	15H3-2	heavy polymineral	0.25-0.125	0.2507
	15H3	15H3-3	feldspar	0.25-0.125	0.2505
Sample 1	15H3	15H3-5	quartz	0.25-0.125	0.2506
	15H3	15H3-6	heavy polymineral	0.125-0.063	0.2505
	15H3	15H3-7	feldspar	0.125-0.063	0.2507
	15H3	15H3-9	quartz	0.125-0.063	0.2506
Sample 2	15H4	15H4-1	mica	0.25-0.125	0.2502
	15H4	15H4-2	heavy polymineral	0.25-0.125	0.2507
	15H4	15H4-3	feldspar	0.25–0.125	0.2508
	15H4	15H4-5	quartz	0.25–0.125	0.2505
	15H4	15H4-6	heavy polymineral	0.125-0.063	0.2502
	15H4	15H4-7	feldspar	0.125-0.063	0.2508
	15H4	15H4-8	quartz	0.125-0.063	0.2508

**Table A2.** Sequential numbers of quartz tubes holding samples with approximately the same weight for Figures 1 and 2.

**Table A3.** ESR signal intensities of Sample F-1600 with 1600 Gy irradiated and Samples F-L and F-B without irradiation as a function of exposure hours to sunlight.

SN	Lab. Number	Grain Size/mm	<b>Exposure Hours</b>	Signal/Marker
	15H3-3 (1)	0.25-0.125	0	15.079
	15H3-3 (2)	0.25-0.125	0.5	9.675978
	15H3-3 (3)	0.25-0.125	1	10.2013
	15H3-3 (4)	0.25-0.125	2	11.88068
	15H3-3 (5)	0.25-0.125	4.17	13.84177
	15H3-3 (7)	0.25-0.125	8	12.77982
Sample F-1600 (1600 Gy irradiated) - - - - - - -	15H3-3 (8)	0.25-0.125	18	5.087605
	15H3-3 (9)	0.25-0.125	34	5.917465
	15H3-3 (10)	0.25-0.125	62.5	2.0696
	15H3-7 (1)	0.125-0.063	0	13.58382
	15H3-7 (2)	0.125-0.063	0.5	15.40268
	15H3-7 (3)	0.125-0.063	1	14
	15H3-7 (4)	0.125-0.063	2	20.3
	15H3-7 (5)	0.125-0.063	4.17	14.144
	15H3-7 (6)	0.125-0.063	8	10.03684
	15H3-7 (7)	0.125-0.063	18	1.892162
	15H3-7 (8)	0.125-0.063	34	7.952491

SN	Lab. Number	Grain Size/mm	Exposure Hours	Signal/Marker
Sample F-L	SMX18-G_1	0.2-0.1	0	0.824
	SMX18-G_2	0.2–0.1	0.5	0.232
	SMX18-G_3	0.2–0.1	1	1.403
	SMX18-G_4	0.2–0.1	2	1.149
	SMX18-G_5	0.2–0.1	4	0.379
	SMX18-G_6	0.2–0.1	7.3	0.837
	SMX18-G_7	0.2–0.1	15.3	0.394
	SMX18-G_8	0.2–0.1	31.3	0.354
	SMX18-G_9	0.2–0.1	63.3	0.021
- Sample F-B -	SMX18-L_1	0.2–0.1	0	0.641
	SMX18-L_1	0.2–0.1	0.5	1.187
	SMX18-L_1	0.2–0.1	1	0.495
	SMX18-L_1	0.2–0.1	2	0.346
	SMX18-L_1	0.2–0.1	4	0.473
	SMX18-L_1	0.2–0.1	8	1.261
	SMX18-L_1	0.2–0.1	18.5	0.547
	SMX18-L_1	0.2–0.1	32	0.526
	SMX18-L_1	0.2–0.1	51	0.517

Table A3. Cont.

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