

Luminescence properties and compositions of contaminating inorganic minerals separated from gamma-irradiated fresh and white ginsengs from different areas

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Gamma-irradiation (0-7 kGy) of ginseng is permitted in Korea for the purpose of microbial decontamination; with strict labeling, traceability and monitoring requirements. An identification study was conducted to determine the photostimulated-luminescence (PSL) and thermoluminescence (TL) properties of gamma-irradiated fresh and white ginsengs cultivated in different areas. Dose-dependent PSL-based screening was possible for white ginseng samples; however, inappropriate results from non-irradiated fresh ginseng samples were obtained, showing intermediate (700 to 5,000) or positive ($T_2 > 5,000$, irradiated) PSL counts due to the abundance of minerals on the surfaces of the samples. TL analysis of separated minerals from all non-irradiated samples gave TL glow curves of low intensity with a maximum peak after 300°C. However, well-defined irradiation-specific (high intensity with a maximum peak at about 200°C) glow curves were observed for all the irradiated samples, regardless of their type and origins. TL ratios (first glow curve /second glow curve) were also determined to confirm the irradiated (>0.1) and non-irradiated (<0.1) results. SEM-EDX (scanning electron microscope-energy dispersive X-ray) and XRD (X-ray diffraction) spectroscopic analyses showed that feldspar and quartz minerals were the main source for the typical radiation-specific luminescence properties.

Keywords: Ginseng, Gamma-irradiation, Photostimulated-luminescence, Thermoluminescence, SEM-EDX analysis

INTRODUCTION

Medicinal plants, enriched with different functional compounds, could enhance human health with their potent therapeutic benefits. Among them, Korean ginseng (*Panax ginseng* Meyer) is widely used in Asia, especially as an ingredient in traditional Chinese medicine and has also gained world-wide popularity, mainly in the United States and Europe, due to its immune system enhancing and antioxidant activities [1].

Ginseng is harvested as fresh roots, which, like other agricultural commodities, could be contaminated by spoilage or pathogenic microorganisms during harvest-

ing, processing, transportation, storage, or post-harvest treatment. This is a serious threat especially for the medicinal use of ginseng in which the conventional techniques to address microbial contamination, such as fumigation with gaseous ethylene oxide or methyl bromide, are prohibited or restricted for different health safety concerns [1,2]. Food irradiation could be used as an effective approach to cope with microbial safety issues, where different scientists have reported the improved hygienic quality [3,4] and shelf life [5,6] of ginseng and its products without any major compromise to key quality attri-

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butes. Korean ginseng products have emerged on global markets; especially, Hong Kong, Japan, North America, and different European countries are major buyers. Better access to international markets with improved quality is possible using irradiation technology [7].

Different national and international regulations regarding proper monitoring and traceability of irradiation processes and products are being enforced which require proper labeling and reliable identification about irradiated products [8]. Among others, radiation-specific luminescence properties could be used effectively to characterize the irradiation status of samples. Photostimulated-luminescence (PSL) analysis is a quick approach without any complicated sample pretreatment [9]. However, the results could vary greatly depending upon the quantity and quality of the contaminating minerals on the surfaces of the samples [10]. The European standard EN 13751 [9] has recommended PSL analysis as a screening approach, requiring reliable confirmation through a reference method. In order to confirm the PSL results, thermoluminescence (TL) analysis could be used for any food material from which enough (about 0.2 mg) of a silicate enriched mineral fraction can be separated. The radiation-specific properties of the TL glow curve could provide conclusive information on the irradiation history of samples [11,12]. The quality and quantity of silicate minerals (quartz, feldspar, etc.) have a prime role in the key TL properties. Because contaminating (from the environment) silicate minerals are used, the origin of the product describing the composition of the minerals available for the analysis is very important [12].

In this study, the PSL technique was used as a screening approach for the irradiated ginseng samples while TL analysis was conducted for the subsequent confirmation of irradiation status of the samples. The effect the cultivation areas had on the contaminating minerals that were separated from the samples was also investigated with X-ray diffraction (XRD) and scanning electron microscope-energy dispersive X-ray (SEM/EDX) spectroscopy for a better understanding of the radiation-specific luminescence properties.

MATERIALS AND METHODS

Samples and irradiation

Fresh and white (dried) ginseng roots, cultivated in the Punggi, Geumsan, Gimpo, and Gangwon areas of Korea and harvested at the after of 6 years of growth, were obtained from a local market in Korea. The samples were irradiated (0, 1, 4, and 7 kGy) using a Co-60 gamma-ray

source (dose rate 1.5 kGy/h; AECL, IR-79; MDS Nordion International, Ottawa, ON, Canada) at the Korean Atomic Energy Research Institute, in Jeongeup, Korea. The applied doses were calibrated using alanine dosimeters with a 5 mm diameter (Bruker Instruments, Rheinstetten, Germany), and the free-radical signals were determined using a Bruker EMS 104 EPR analyzer (Bruker Instruments).

Photostimulated-luminescence measurements

The PSL measurements were done with a pulsed photo-stimulated luminescence system (serial 0021; Scottish Universities Research and Reactor Center, Glasgow, UK). The samples were cut into small pieces to fill in 50 mm diameter disposable petri dishes (Bibby sterilin type 122), and the photon counts (PCs)/ 60 s were measured in the sample chamber as described in the European standard EN 13751 [9]. The samples with PCs less than 700 were considered as negative (non-irradiated) and more than 5,000 were considered as positive (irradiated), whereas the values between these two limits were classified as intermediate requiring further investigation to confirm the results. All samples were measured in triplicate ($n=3$) under the same laboratory and instrumental conditions.

Thermoluminescence measurements

The PSL screening results were confirmed by the TL analysis, which was done as described in the European standard EN 1788 [12]. A sample was washed with distilled water on a nylon sieve (150 μ m) and contaminating minerals were obtained thorough the density separation technique. The separated minerals (about 0.2 mg) were loaded onto TL discs and the analysis was performed with a thermoluminescence dosimeter system reader (Harshaw 4500; Thermo Fisher Scientific, Waltham, MA, USA) under a pure N₂ gas (99.999%) flush. The first TL glow curve (TL₁) was obtained at a temperature increase rate of 5°C/s from 50 to 400°C. To normalize the TL₁ results, the tested minerals were re-irradiated (1 kGy), and the second TL glow curve (TL₂) was measured. Finally, the TL ratio (integrated area of TL₁/TL₂ between 150 and 250°C) was calculated. The TL glow curve shape, intensity, and TL ratio were used to interpret the identification results [12].

X-ray diffraction measurements

The inorganic mineral dust (0.5 g) separated from the ginseng sample by washing was characterized using a multipurpose X-ray diffractometer (X'Pert Pro; PANalytical, Almelo, The Netherlands) at the Korea Basic Sci-

ence Institute, Daegu. Silicon powder (corundum) was used as a standard reference material to calibrate the X-ray diffractometer. The analysis was performed under the following measurement conditions: X' Celerator (ultra-fast) detector; 0 to 60 degrees of scan angle; 11.9 deg/s of scan rate, Gonio of scan axis; continuous scan mode; and radiations of Cu K α with a wavelength of 1.540598 Å. The XRD spectral measurements were done between 0 and 60° 2θ at a 2° 2θ scan, where the each peak was identified using with reference data.

Scanning electron microscopy-energy dispersive X-ray measurements

SEM/EDX analysis was done to determine the poly-mineral composition of the isolated minerals from the ginseng samples. A field emission scanning electron microscope (model S4300; Hitachi, Tokyo, Japan) equipped with an EDX spectrometer was used at accelerating voltage of 15 kV.

Statistical analysis

All measurements were done in triplicate ($n=3$) and the mean \pm standard deviation values are presented. Origin ver. 6.0 software (Microcal Software, Northampton, MA, USA) was used for the data analysis and presentation.

RESULTS AND DISCUSSION

Photostimulated-luminescence characteristics

PSL analysis is a time-efficient technique which results in easy screening of irradiated samples according to their irradiation history [9]. Table 1 presents the PSL results for the control and irradiated fresh and white ginseng samples, cultivated and harvested in different areas of Korea. All non-irradiated white ginseng samples had

negative PSL counts (<700 PCs) with negligible differences. However, non-irradiated fresh ginseng samples were intermediate (700 to 5,000 PCs), except for one that was positive (>5,000 PCs). The excessive amount of contaminating minerals could be the cause of these false intermediate and positive results [9]. Different scientists studying the irradiation status of onions [13,14] and tea [15] also reported similar results. In this case, an in-house re-irradiation and calibration of the PSL results provided conclusive information. The large differences between the PSL counts of the non-irradiated and 1 kGy-irradiated samples represented the possibility of the absence of irradiation treatment, even if the results from the non-irradiated samples were false positives [9].

All irradiated samples were positive, regardless of the type and origins of the samples; however, there were considerable differences among the samples for the same type and irradiation dose. This variability in the PSL results might be due to variations in the quantity and quality of the contaminating minerals on the surfaces of the samples [9]. Other scientists have also reported great variability in PSL results, even in the case of different replications from the same sample [10,16] and suggested that PSL technique could only be used to screen large sample lots; however, the results should be confirmed with a reliable identification technique [9].

Thermoluminescence characteristics

The TL analysis was done as a confirmatory or reference technique to identify the irradiation status of fresh and white ginsengs. Different studies have established that TL analysis results are not dependent on the kind of food, but on the quantity and quality of the separated silicate minerals [12]. All non-irradiated ginseng samples had a low-intensity TL glow curve with a maximum peak

Table 1. Photostimulated-luminescence results from non-irradiated and irradiated fresh and white ginsengs cultivated in different areas

Sample	Producing area	Irradiation dose (kGy)			
		0	1	4	7
Fresh ginseng	Punggi	4,029 \pm 1,398 (M) ¹⁾	91,005 \pm 3,686 (+)	1,003,948 \pm 23,434 (+)	557,332 \pm 34,384 (+)
	Geumsan	1,694 \pm 1,227 (M)	304,958 \pm 117,349 (+)	594,029 \pm 98,588 (+)	738,401 \pm 23,783 (+)
	Gimpo	7,095 \pm 3,429 (+)	398,402 \pm 55,661 (+)	1,212,465 \pm 70,932 (+)	3,304,958 \pm 10,838 (+)
	Gangwon	3,948 \pm 1,221 (M)	248,396 \pm 67,224 (+)	475,061 \pm 54,791 (+)	1,004,856 \pm 47,695 (+)
White ginseng	Punggi	318 \pm 98 (-)	22,756 \pm 2,586 (+)	44,129 \pm 434 (+)	75,048 \pm 384 (+)
	Geumsan	307 \pm 17 (-)	50,980 \pm 1,529 (+)	77,392 \pm 988 (+)	94,037 \pm 283 (+)
	Gimpo	335 \pm 9 (-)	33,486 \pm 3,561 (+)	100,294 \pm 7,092 (+)	77,496 \pm 10,838 (+)
	Gangwon	314 \pm 21 (-)	9,047 \pm 3,724 (+)	13,744 \pm 5,479 (+)	68,039 \pm 7,496 (+)

Values are presented as mean \pm standard deviation ($n=3$)

¹⁾Threshold value: T₁=700, T₂=5000, (-)<T₁, T₁<(M)<T₂, (+)>T₂

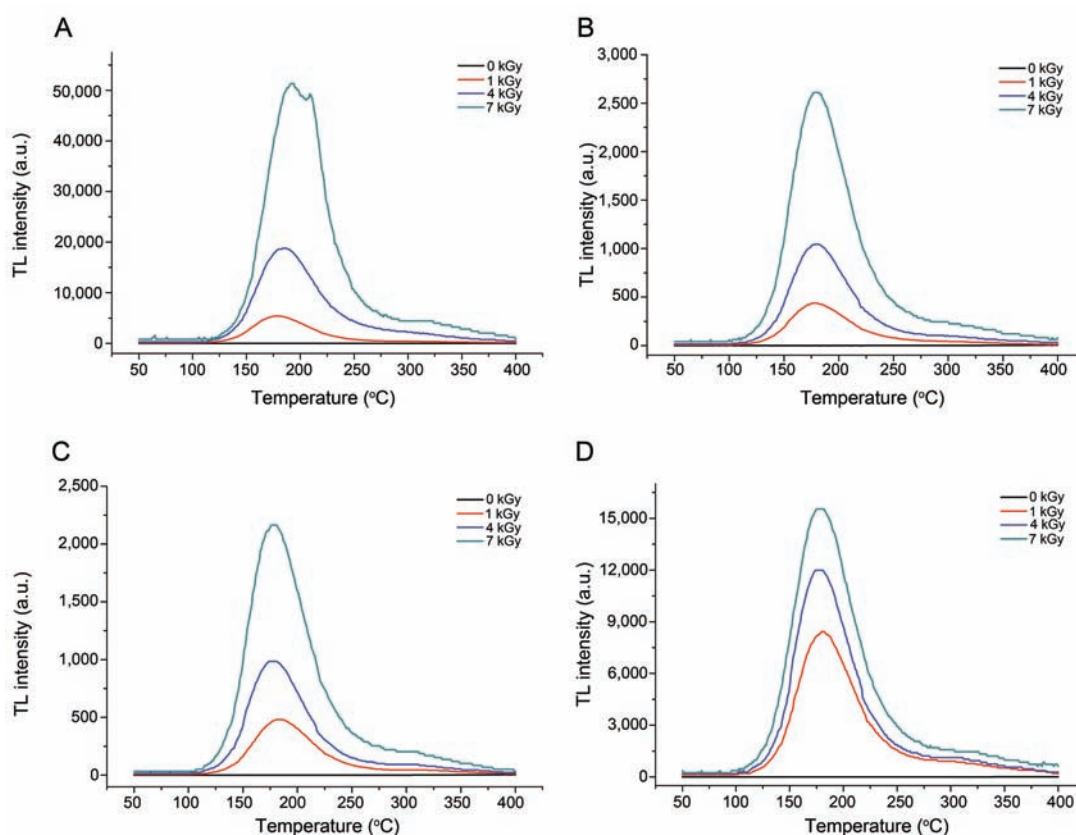


Fig. 1. Thermoluminescence (TL) glow curves of contaminating inorganic minerals separated from gamma-irradiated fresh ginsengs cultivated in different areas. (A) Punggi region, (B) Geumsan region, (C) Gangwon region, and (D) Gimpo region.

Table 2. Thermoluminescence (TL) ratio (TL_1/TL_2) of contaminating inorganic minerals separated from non-irradiated and irradiated fresh and white ginsengs cultivated in different areas

Sample	Cultivated area	Irradiation dose (kGy)			
		0	1	4	7
Fresh ginseng	Punggi	0.001±0.000	0.241±0.048	0.311±0.074	0.617±0.152
	Geumsan	0.026±0.583	0.814±0.354	1.469±0.873	4.354±1.008
	Gangwon	0.035±0.006	0.462±0.039	2.545±1.595	1.565±0.336
	Gimpo	0.011±0.005	0.288±0.004	0.422±0.039	0.608±0.125
White ginseng	Punggi	0.005±0.001	0.256±0.056	0.336±0.162	0.415±0.137
	Geumsan	0.004±0.007	0.325±0.158	1.102±0.374	2.287±0.386
	Gangwon	0.013±0.007	0.125±0.057	0.333±0.096	0.549±0.155
	Gimpo	0.058±0.007	0.389±0.107	0.251±0.039	0.472±0.134

Values are presented as mean±standard deviation ($n=3$).

after 300°C (Figs. 1 and 2). The TL peak after 300°C was due to a natural geological signal; however there was no peak in the radiation-specific temperature range (150°C to 250°C) of the TL glow curve, showing the absence of any irradiation history [12]. All irradiated ginseng samples revealed typical radiation-specific TL glow curves with maximum peaks of high intensities at about 200°C. A clear discrimination of non-irradiated and irradiated

samples was possible. The dose-dependency of the TL glow curve intensity was most prominent in samples from the Punggi region, whereas the same was comparatively less obvious in the sample from the Gimpo region. The composition of the minerals and their relative sensitivity to irradiation treatment might be the cause for this variation [13].

In the TL analysis, the same minerals (already mea-

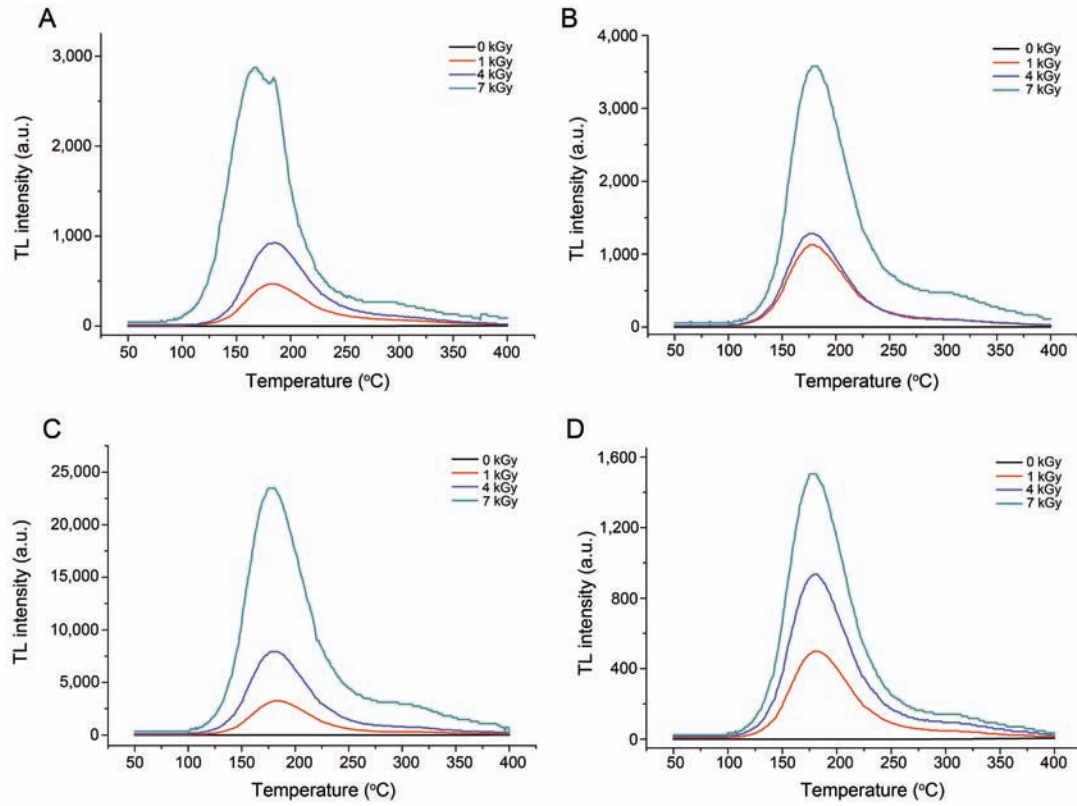


Fig. 2. Thermoluminescence (TL) glow curves of contaminating inorganic minerals separated from gamma-irradiated white ginsengs cultivated in different areas. (A) Punggi region, (B) Geumsan region, (C) Gangwon region, and (D) Gimpo region.

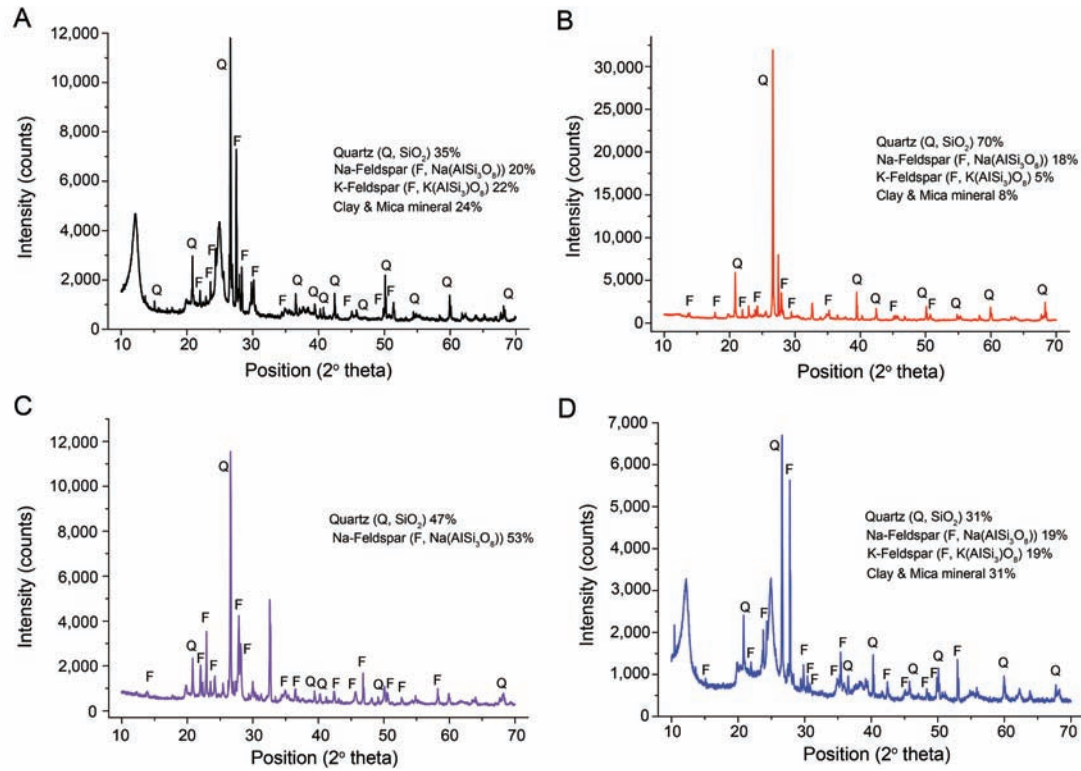


Fig. 3. XRD (X-ray diffraction) spectra of contaminating inorganic minerals separated from fresh ginsengs cultivated in different areas. (A) Punggi region, (B) Geumsan region, (C) Gangwon region, and (D) Gimpo region.

sured for TL₁) were used as a reference material after re-irradiation (1 kGy) to confirm the reliability of the TL results [12]. The TL ratios (Table 2) for all non-irradiated

samples were <0.1 and all irradiated samples >0.1, confirming the quality of the minerals on the TL discs to obtain valid identification results. The results of this study

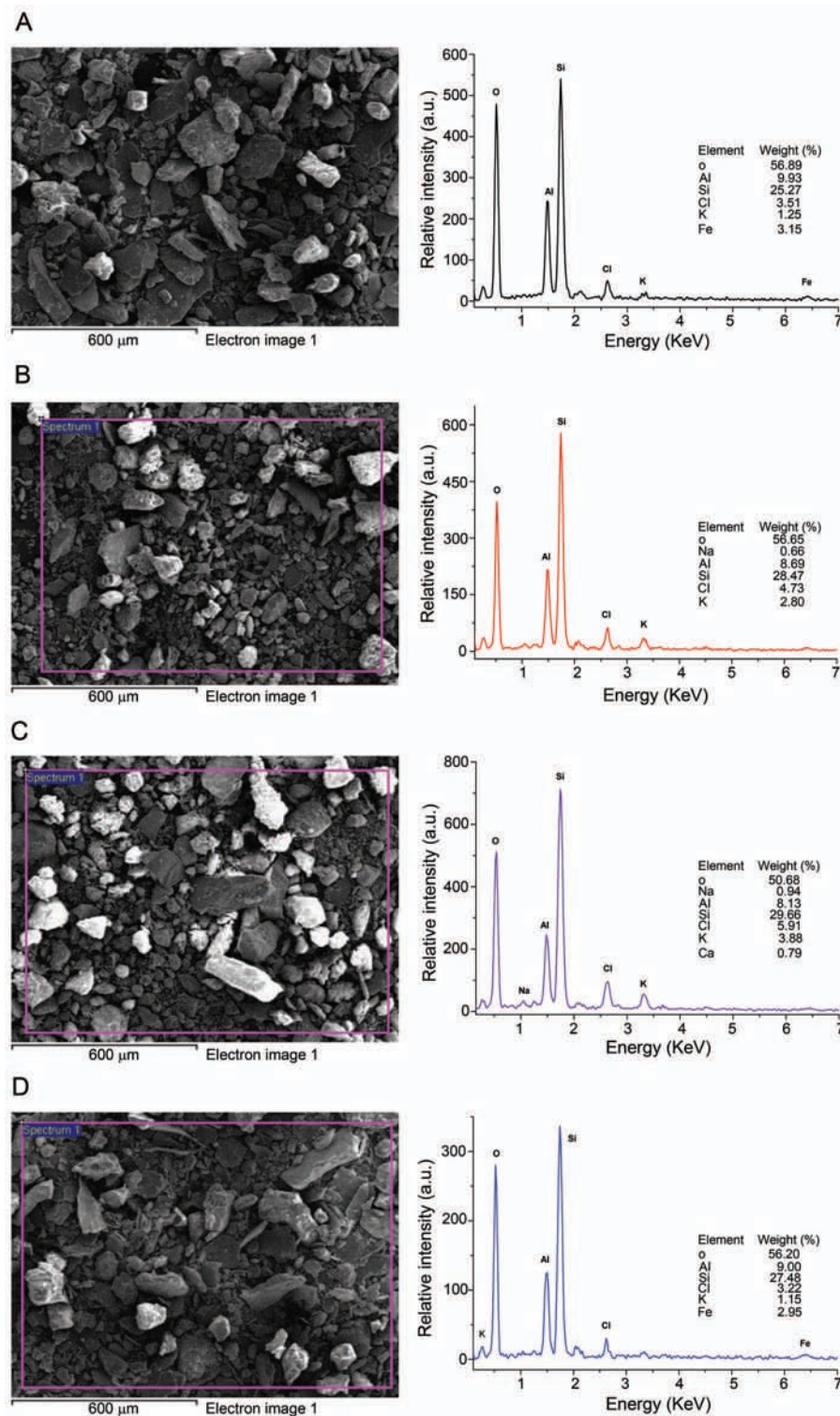


Fig. 4. SEM-EDX (scanning electron microscope-energy dispersive X-ray) spectra of contaminating inorganic minerals separated from fresh ginsengs cultivated in different areas. (A) Punggi region, (B) Geumsan region, (C) Gangwon region, and (D) Gimpo region.

are in good agreement to those reported for irradiated fresh mushrooms [17], onions [13], kiwifruits [18], and sesame seeds [19].

Mineral composition

The radiation-induced luminescence properties are primarily dependent upon the quality and quantity of the inorganic minerals present on the surfaces of samples [12]. These minerals are present as contamination from the environment during cultivation, harvesting, transportation or processing. Hence, the mineral compositions of the separated inorganic dust greatly depend upon the regions where cultivation and processing are done [20,21]. The minerals separated from the fresh ginseng samples (cultivated in different regions) were analyzed by XRD spectroscopy shown in Fig. 3.

XRD spectroscopy requires a relatively large quantity of sample (about 0.5 g), which is not always possible, especially in the case of foodstuffs with relatively small contaminating minerals. Therefore, SEM/EDX analysis was also done which requires a small amount (about 50 mg) of separated minerals (Fig. 4). Both techniques gave comparable results showing that quartz and feldspar minerals were the main source of radiation-specific luminescence properties [21]. SEM/EDX analysis could be used as an alternative to XRD spectroscopy in the case of a small amount of mineral samples being present, which is required to be characterized by its composition. Among silicate minerals, feldspar minerals have very a high sensitivity to irradiation treatment and their TL properties usually define the overall TL glow curve characteristics of irradiated samples, where the effect of quartz and other minerals, even present in large quantities, is usually masked [21]. Feldspar minerals were present in all the samples and were in relative abundance in samples from the Gangwon and Punggi areas. The TL glow curves of the samples from these regions also showed more dose-dependency with well-defined TL peaks (Fig. 1). Clay and mica minerals have poor radiation-induced luminescence properties. Relatively, the less dose-dependent TL results from the samples from the Gimpo region were justifiable considering the high concentrations of clay and mica minerals.

In conclusion, PSL could be effective in screening the samples with respect to their irradiation status. However, false positive results were observed due to the abundance of contaminating minerals on the surfaces of the fresh ginseng samples. A strong TL glow curve with maximum peak at about 200°C was a prominent characteristic of the irradiated samples regardless of their type and cultivation

region. The confirmation of the TL results was possible by determining the TL ratio (TL_1/TL_2). Feldspar and quartz minerals were responsible for the radiation-specific luminescence properties, where the TL glow curve shape and intensity were mainly defined by the feldspar contents of the contaminating inorganic minerals.

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