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Principle of Tibetan medicine fluoritum processing by vinegar based on the change of microstructure and chemical composition

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Traditional Chinese medicine (TCM) processing is a cultural treasure of the Chinese nation. The vinegar-quenched processing method of mineral medicine is an important part of traditional Chinese medicine theory. Fluoritum is a commonly used clinical drug in Chinese medicine. Its microstructure and chemical composition will change after vinegar quenching, which will reduce its toxicity and enhance its efficacy. However, the study of chemical composition changes during vinegar quenching is insufficient. The purpose of our study is to compare the chemical composition in differences of fluoritum vinegar processed products from the aspects of microstructure, content of main and trace elements, content of organic elements. The microstructure, content of carbon and nitrogen elements, main and trace elements of fluoritum were observed by thermal field emission scanning, energy spectrum, organic element analyzer, X-ray fluorescence spectrometer and inductively coupled plasma mass spectrometer. The results showed that the particles of vinegar quenched water flying fluoritum processing product became more finer and uniform than other processing product (RSD = 18.9%). The contents of carbon and nitrogen in the vinegar quenched water flying fluoritum processing products are 0.185% and 0.028%, and their contents are increased by nearly 4 and 5 times than fluoritum raw product, respectively. There was no significant change in CaF_2 content in different fluoritum processing products (RSD = 1.61%), but the iron content has nearly doubled. The trace elements in fluoritum show that the contents of different trace elements in fluoritum are very different (RSD = 230%). The elements whose content increased significantly after the vinegar quenched water flying were Li, V, Zn, Ga, Cr (RSD = 80%,RSD = 84.2%,Zn content has never been detected to 11.3 μg.g^{-1}, RSD = 62.3%, RSD = 51.3%). The elements content with decreased are Tl, W (RSD = 25.4%, RSD = 79.5%). The vinegar quenched water flying processing method can be listed as the best processing method for fluoritum because it can make the fluoritum particles smaller and more uniform, increase the content of organic matter and remove toxic and harmful metal elements. The decrease of grain size, the increase of contents of carbon, nitrogen and iron and the decrease of toxic elements Tl, W and U may be the important reasons for the enhancement of efficiency and reduction of toxicity of fluoritum vinegar-quenched processing.

Keywords Chinese crude drug processing, Fluoritum, Microstructure, Traditional Chinese medicine, Trace element

Abbreviations

TCM	Traditional Chinese medicine
SEM	Scanning electron microscopy
XRF	X-ray fluorescence spectrometer
ICP-MS	Inductively coupled plasma mass spectrometer
ZSY	Fluoritum

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DL Detection limit

Fluoritum was first recorded in in the "Shennong Herbal Classics", it taste sweet and warm, live in the valley. It treatment the stomach cough against evil, women wind cold in the womb, no pregnancy for ten years without children. Long-term use will be warm, light body, prolong life[1,2]. Modern studies have shown that fluoritum has the effect of warming kidney and palace, soothing heart and spirit, warming lung and calming asthma, and can be used for kidney yang deficiency, palace cold infertility, palpitation and anxiety, insomnia and dreams, deficiency cold cough and asthma, therefore it is a common medicine in gynecology[3–6]. The main component of fluoritum is CaF_2. The 2020 edition of the Pharmacopoeia of the People's Republic of China stipulates that the content of CaF_2 in fluoritum should be greater than 85%, fluoritum should be washed, calcined and quenched in vinegar, and 100 kg of fluoritum should be quenched in vinegar with 30 kg[7]. However, the detailed parameters of calcining temperature, time, and times of vinegar quench are not specified. In addition, the chemical composition of Chinese medicinal materials is different due to origin reasons[8–11]. These results lead to certain differences in the microstructure and chemical composition of the shot products of fluoritum. .

Traditional Chinese medicine (TCM) processing is a cultural treasure of the Chinese nation. As an important part of the theory of TCM processing, the exploration of the essence of "vinegar into liver" is helpful to standardize the processing production of TCM slices, help to ensure the quality control of TCM slices, and help to guide the scientific and reasonable clinical application of TCM slices[12–14]. TCM processing with vinegar has a very long history of development since it recorded in the first edition of "Fifty-two Disease Prescription", which complements each other with TCM and opens up a broad development space for the clinical application of TCM. As the guiding theory of TCM processing by vinegar, "vinegar into liver" is a typical representative of Chinese medicine processing "enhancing efficacy and reducing toxicity". After vinegar processing, the drug can play the role of introducing medicine into the liver channel, enhancing the soothing of liver and relieving depression, dispersing blood stasis and relieving pain, reducing toxicity and alleviating drug properties[15].

Vinegar is a weak acid, the Chinese medicine processed by vinegar, compared with raw products can improve the solubility of the drug ingredients contained in the body. The difference in solubility will cause the material base amount changes, which in turn produce different pharmacological effects. Acetic acid can combine with free alkaloids to form salt, which makes the acetate of alkaloids easily dissolved by water, increasing the content of active ingredients in aqueous solution. Finally achieving the purpose of detoxification and enhancing the effect of vinegar making drugs[12].Wang Yiwei's research showed that the processed fluoritum had no obvious toxic effect on mice, and could reduce the number of autonomous activities of mice and prolong the sleep time of the pentobarbital sodium model mice[3]. The World Health Organization (WHO) suggests that high concentrations of fluoride in water, above 1.5 mg/L, is considered a known health problem for humans, causing dental and bone fluorosis[16,17]. A large number of studies have shown that the size and chemical composition of fluoritum will be changed after the preparation of vinegar. The temperature and times of calcining had significant effects on mercury content, while the time of calcining and the amount of vinegar had no significant effects on mercury content. The contents of lead, cadmium, arsenic and copper in the fluoritum were reduced from 411.030, 0.315, 8.593, 62.284 mg/kg to 2.491, 0.224, 3.167, 29.593 mg/kg, respectively, while no mercury was detected in the fluoritum product[18]. The chemical composition changes of fluoritum after processing are very important for the rational utilization of the drug.

The change of chemical composition before and after processing is the basis for the optimization of processing technology and the establishment of quality standards, and is also closely related to the analysis and explanation of processing efficiency and toxicity reduction, which is one of the key contents of processing research. Although there were a few studies on the changes of chemical composition before and after the preparation of fluoritum processing by vinegar in the early stage, the study index was single and the systematic research was lacking[19–24]. Previous studies mainly focused on the content of main components of fluoritum, but ignored the changes of microstructure and content of trace elements[25–27]. However, the main medicinal substance of fluoritum is likely to be related to the trace elements it contains. The reduction of toxicity of the fluoritum processing by vinegar may be related to the reduction of toxic element content, and the increase of efficiency may be related to the increase of life element content and the improvement of organic components. Whether the effect of reducing toxicity and enhancing effect of liver channel drugs after vinegar processing is directly from vinegar or TCM after vinegar processing is still needed to be further discussed. The research on the relationship between ingredients and toxicity, effect needs to be further studied, especially the results of the study on the mechanism of toxicity reduction and effect enhancement are insufficient to guide the production process of medicinal vinegar.

In view of the above, this paper through the field sample collection and processing of a mine producing fluoritum in Dachang Town, Qinglong County, Guizhou Province, China. We calcined and vinegarized carefully selected fluoritum minerals. Then, thermal field emission scanning electron microscopy (SEM) were used to analyze the three-dimensional microstructure of fluoritum. Carbon and nitrogen content of organic matter in fluoritum were analyed by organic element analyzer. X-ray fluorescence (XRF) spectrometer and inductively coupled plasma mass spectrometer (ICP-MS) were analyed CaF_2 and trace element content of fluoritum before and after processing with vinegar. This paper attempts to explain the principle of the fluoritum processing by vinegar based on the microstructure and chemical composition changes, and provides experimental basis for the formulation of quality standards of fluoritum.

Materials and methods

Materials

The fluoritum used in this experiment was taken from the Dachang formation of Qinglong antimonia Mine, Dachang Town, Qinglong County, Guizhou Province, China. The sample was identified by researcher Xiao Jiafei and Dr. Li Jinwei of the Institute of Geochemistry of the Chinese Academy of Sciences as the isometric

system fluoride mineral fluorite group fluoritum (CaF_2). Fluoritum minerals are collected by mine workers and us in the formation of fluoritum production, and then determined by our microscopic observation[28]. The remaining samples used in the experiment were kept in the teaching and research department of basic chemistry, college of pharmacy, Guizhou University of Traditional Chinese Medicine. Vinegar was purchased from Qianhe Weiye food limited company, Dongpo District, Meishan City, Sichuan Province, China (batch number: 6928312902413). Acetic acid was purchased from Anhui Zesheng technology limited company (batch number: B020052-OQER5RZK, concentration greater than 99.5%). Hydrogen fluoride (HF) was purchased from Shenzhen noadi chemical technology limited company (batch number: 1.1513.1000, 48%). Nitric acid (HNO_3) was purchased from Shenzhen noadi chemical technology limited company (batch number: 1.00456.2508, 65%). Rhodium (Rh) internal standard solution was purchased from Putian tochuang technology limited company (lot number: BWB2375). Fluoritum standard samples (Samples Number: GBW07250, GBW07251, GBW07252) were purchased from national standard material network, and the recommended value of the standard sample at the website www.ncrm.org.cn. Recommended values for international reference substances OU-6(slate), BCR-1(basalt), GBPG-1 (garnet biotite plagioclase gneiss) can be found at http://georem.mpch-mainz.gwdg.de/.

The meanings of the fluoritum sample numbers involved in this paper are as follows: ZSY-1, fluoritum mineral sample; ZSY-2, fluoritum acetic acid quenched product; ZSY-3, fluoritum to vinegar mass ratio 10:3 vinegar quenched product; ZSY-4, fluoritum vinegar quenched product; ZSY-5, fluoritum water quenched water flying product; ZSY-6, fluoritum acetic acid quenched water flying product; ZSY-7, fluoritum to vinegar mass ratio 10:3 vinegar quenched water flying product; ZSY-8, fluoritum vinegar quenched water flying product.

Instrument

SX-5–12 box-type resistance furnace (Lunan electric furnace oven factory, Shaoxing City, Zhejiang Province, China); XRFuse 6 electric heating melting furnace (XRF scientific, Australia); JSM-7800F thermal field emission scanning electron microscopy (Nippon electronics corporation, Japan); LS 13320 laser diffraction particle size analyzer (Beckman coulter, USA); Team apollo XL energy spectrometer (British company EDAX, Britain); MACRO cube type organic element analyzer vario (Almonta, Germany); ARL perform X4200 X-ray fluorescence spectrometer (Thermo fisher, USA); Plasmaquant-MS elite inductively coupled plasma Mass spectrometer (Analytical instruments jena AG, Germany).

Fluoritum ore sample treatment

Taken the fluoritum ore sample, knocked it with a hammer until it is about 2 cm in a block size, washed the impurities with water, and then grind it with an agate mortar until the powder has passed 200 mesh sieve for use.

Fluoritum processing

Weigh 150 g of uniform fluoritum raw products with a diameter of about 2 cm. Put fluoritum in a ceramic crucible, calcined in a box resistance furnace under stable conditions of 600 ℃ for 10 min. Then take them out and quench them in cold water, so that they are quenched three times, collect the small particles of fluoritum that fall during quenching and dry. Grind fluoritum into fine powder with agate mortar to obtained fluoritum water quench products.

Taken 10 g of the above fluoritum powder, add 5 mL of water, grind with an agate mortar for 5 min until paste, add 400 mL of water, stir for 1 min, let stand for 2 min, pour out the water suspension. Continue grinding the residue, repeat the above operations for 10 times, combine the suspension, let stand overnight, discard the supernate, leave the bottom fluoritum powder. Dry overnight in an incubator at 40 ℃, and grind the fluoritum water quenched water flying product.

Quenching fluoritum with acetic acid in accordance with fluoritum water quench operation process to obtain fluoritum acetic acid quenching product. The fluoritum acetic acid quenched product was prepared by treating the powder according to the water flying operation process of water quenched water flying.

Fluoritum vinegar quenched product preparation according to fluoritum water quench operation procedure. The powder of the fluoritum vinegar quenched product will be processed according to the water flying operation process to produce the fluoritum vinegar quenched product. Weigh 150 g fluoritum, quench with 45 g vinegar, repeatedly quench the fluoritum to completely absorbed the vinegar, dry and ground into powder, obtained the quality ratio of fluoritum and vinegar 10:3 vinegar quench powder. After the fluoritum powder is treated in accordance with water flying process, the mass ratio of fluorite to vinegar 10:3 vinegar quenched water flying powder is obtained.

Microstructure observation of fluoritum

The fluoritum powder was uniformly placed on the glass plate, and the glass plate was placed in the sample chamber of thermal field emission SEM to observed the microstructure of the fluoritum. The operating voltage of the instrument is 20 kV, the current is 10 nA, and the beam spot is 1 μm.

Particle size test of fluoritum and its products

The fluoritum mineral powder samples were dispersed with anhydrous ethanol. The background value was tested before operation, and then the suspension of anhydrous ethanol and fluoritum samples was added to the test cylinder for testing. The particle size measurement range is 17 nm–2000 μm, and the laser contains 132 independent physical angle detectors and 124 analysis channels. The main light source is a solid laser with a power of 5 mW. The maximum detection angle of the instrument is 1500. The accuracy error and reproducibility error of the instrument are less than ± 5%.

Measurement of organic matter content of fluoritum and its products

Weigh 100 mg of fluoritum powder sample and placed it in tin cup, heated the sample in combustion tube to 1000 ℃, and tested the content of carbon and nitrogen in organic element analyzer. The carrier gas used in the experiment was helium and oxygen, and the test pressure was 0.12 MPa and 0.20 MPa, respectively.

Content test of major elements in fluoritum

Accurately weighed 1 g fluoritum powder sample and placed it in a drying oven at 105 ℃ for at least 2 h to removed the adsorbed water in the sample. The sample was added with 20 g lithium tetraborate and lithium metaborate compound flux (mass ratio 66:34) in an alloy crucible with a mass ratio of Pt-Au is 95:5, and then added 0.5 mL saturated ammonium iodide solution was heated at 1050 ℃ for 20 min to melt. The ARL perform'X 4200 X-ray fluorescence spectrometer has a test voltage of 60 kV and a test current of 140 mA. The standard samples used in the experiment were fluoritum standard mineral GBW07250, GBW07251 and GBW07252.

Fluoritum trace elements content test

Prepared of 50 mg fluoritum powder sample into the polytetrafluoroethylene crucible, and added 1 mL hydrogen fluoride (HF) and 1 mL nitric acid (HNO_3) to the cruible. The crucible was sealed in the steel sleeve and heated in the oven at 185 ℃ for more than 24 h to digest the sample. After cooling, taken out the crucible, placed it on a low temperature electric heating plate to steam dry, added 1 mL HNO_3 and continue to dry completely. Accurately added 200 ng/mL rhodium (Rh) internal standard solution 1 mL, 2 mL HNO_3, 3 mL deionized water into the crucible, re-placed in the steel sleeve, and heated at 140 ℃ for 5 h. After cooling, taken out the crucible, shaken well, and then taken 0.4 mL of the above solution into the centrifugal tube. The solution volume is fixed to 8 mL, and then determined by ICP-MS.

Test method of ICP-MS was used argon as the carrier gas, generated plasma at nearly 7000 ℃ through high-frequency oscillation, and used Rh as the internal standard element to monitored the test drift. In the experiment, 1 set of standard samples were added to monitored the drift of instruments for every 5 samples tested. The standard samples used in the experiment were slate (OU-6), basalt (BCR-1) and garnet biotite plagioclase gneiss (GBPG-1). Use the solution method to test the counting rate of each element in the liquid to be tested, and then test the counting rate of the known sample (reference material). Use the counting rate of the known sample content to convert the element content of the sample to be measured. The instrument parameters are shown in Table 1.

Results

Appearance shape characteristics of fluoritum and its products

The common color of the medicinal mineral fluoritum is colorless, green, purple or white, pure fluoritum is colorless, and the green color of fluoritum is caused by the different contents of impurity elements[29]. Peng Jiantang systematically studied the rare earth elements of fluoritum in Qinglong antimony deposit, and the results showed that the Tb/La (lanthanum) and Sm/Nd of green and light green fluoritum in Qinglong antimony deposit were relatively low, and the light rare earth elements were relatively high. Green, light green, light blue, purple, white fluoritum Ce, Sm, Nd content gradually increased[30]. Our experimental results showed that the appearance and morphology of the fluoritum raw product and different processing products were different. The fluoritum used in this experiment is light green (Fig. 1A), and the raw product is milky white after grinding into powder (Fig. 1B). The color of the fluoritum acetate quenched powder (Fig. 1C) is dimmer than that of the raw powder (Fig. 1B). The mass ratio of fluorite to vinegar 10:3 quenched product in Fig. 1D is looser and dimmer than that of the fluoritum in Fig. 1E. There is no obvious difference in appearance between fluoritum water quenched water flying product powder (Fig. 1F) and fluoritum acetic acid quenched water flying product powder (Fig. 1G), both of which are milky white. The mass ratio of fluoritum to vinegar 10:3 vinegar quenched flying powder (Fig. 1H) and fluoritum vinegar quenched flying powder (Fig. 1I) showed no significant difference in appearance, both showing dark gray. The remaining mass of massive fluoritum after vinegar quenching (Fig. 1J) is dark gray, while the small particles dropped by vinegar quenching (Fig. 1K) are dark gray and transparent. Figure 1L is fluoritum acetate quenched granulated product, and mainly colorless transparent particles.

Microstructure characteristics of fluoritum and its processing products

The microstructure and particle size of fluoritum after processing have obvious changes (Fig. 2, Table 2, Particle diameter RSD = 45.5%). SEM results of fluoritum showed that the raw product (Fig. 2A) and the acetic acid

Carrier gas	Argon
Plasma flow velocity	11L/min
Auxiliary gas flow	1.8L/min
Atomizing gas flow	0.87L/min
Sampling depth	5.5 mm
Plasma RF power	1kw
Peristaltic pump speed	24 rpm
Analysis time	1 min

Table 1. ICP-MS instrument parameters.

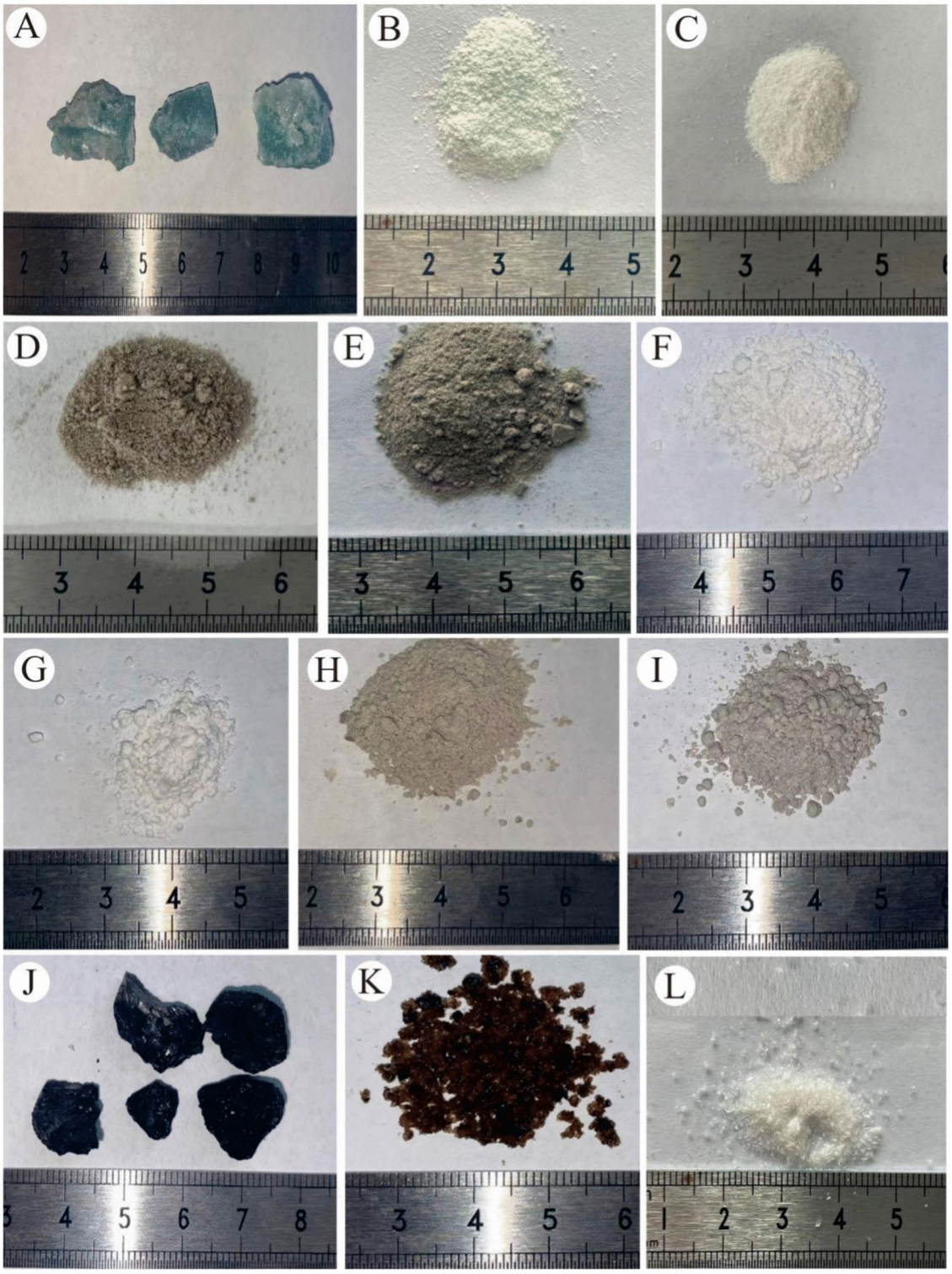

Fig. 1. Photos of fluorite and its processing products. (**A**). Fluoritum raw product; (**B**) Fluoritum mineral powder; (**C**) Fluoritum acetic acid quenched powder; (**D**) The mass ratio of fluoritum to vinegar 10:3 vinegar quenched powder; (**E**) Fluoritum vinegar quenched powder; (**F**) Fluoritum water quenched water flying processing product powder; (**G**) Fluoritum acetic acid quenched water flying processing product powder; (**H**) Mass ratio of fluoritum to vinegar 10:3 vinegar quenched water flying processing product powder; (**I**) Fluoritum vinegar quenched water flying processing product powder; (**J**) Mass ratio of fluoritum to vinegar 10:3 vinegar quenched block products; (**K**) The mass ratio of fluoritum to vinegar 10:3 vinegar quenched processing products; (**L**) Fluoritum acetate quenched granulated product.

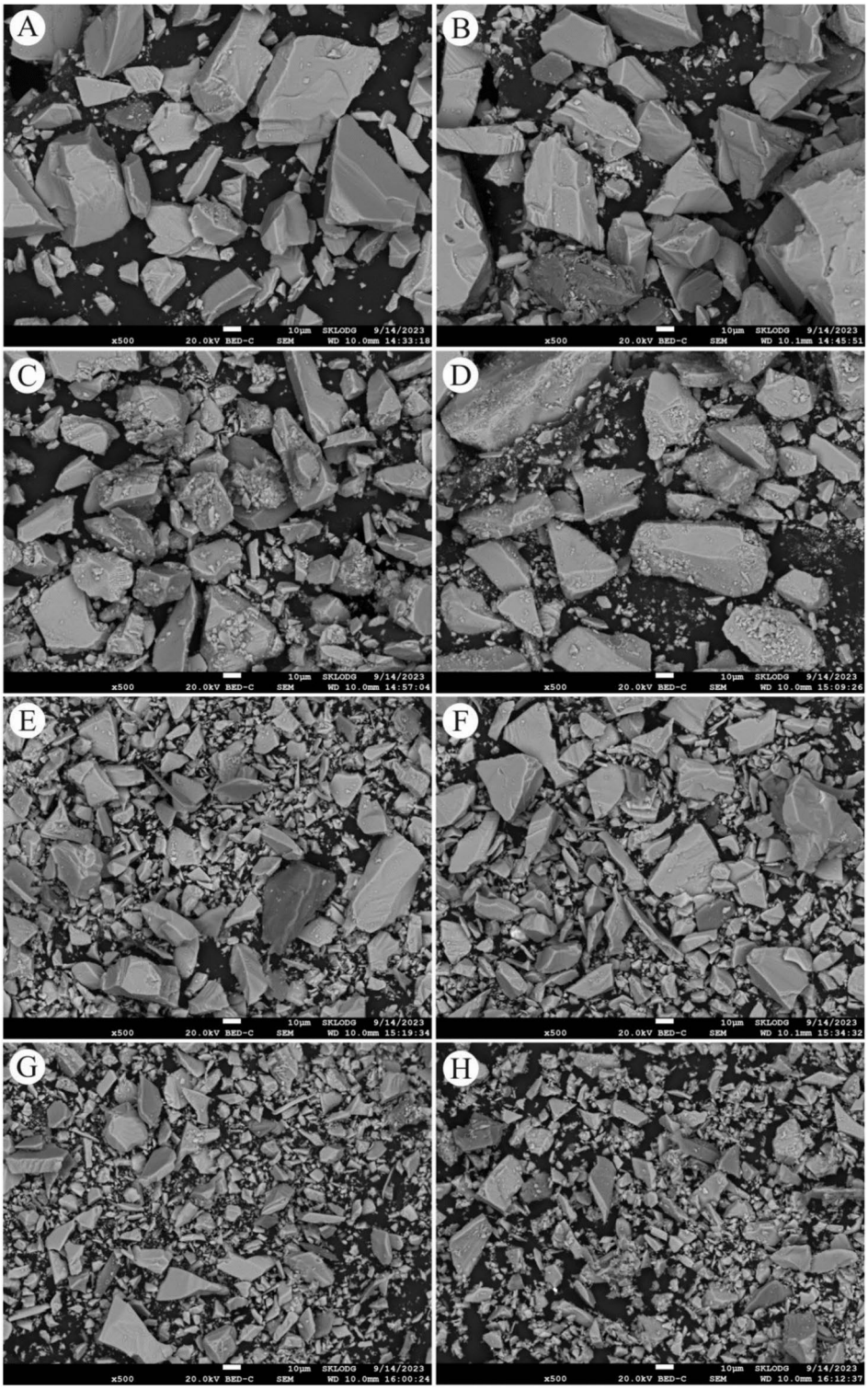

Fig. 2. SEM photos of fluorite and its processing products. (**A**) SEM photo of fluoritum mineral sample; (**B**) SEM photo of fluoritum acetic acid quenched product; (**C**) SEM photo of fluoritum to vinegar mass ratio 10:3 vinegar quenched product; (**D**) SEM photo of fluoritum vinegar quenched product; (**E**) SEM photo of fluoritum water quenched water flying product; (**F**) SEM photo of fluoritum acetic acid quenched water flying product; (**G**) SEM photo of fluoritum to vinegar mass ratio 10:3 vinegar quenched water flying product; (**H**) SEM photo of fluoritum vinegar quenched water flying product.

Particle diameter (um)	ZSY-1	ZSY-2	ZSY-3	ZSY-4	ZSY-5	ZSY-6	ZSY-7	ZSY-8	RSD
Mean	122.1	95.18	105.4	98.28	51.58	40.79	35.51	48.61	45.5%

Table 2. Results of fluoritum particle size.

quenching product (Fig. 2B) had similar microstructure. The difference is that the particle size of fluoritum after acetic acid quenching is more uniform (Fig. 3B), and the particle size of fluoritum before vinegar quenching is disorganized (Fig. 3A). Compared with other fluoritum processing products, the grain size of fluoritum was larger, the particle size was hundreds of microns (mean particle diameter is 122.1 μm). The particle size was uneven (Fig. 3A), and the particle roundness was poor and the edges were sharp (Fig. 2A). The mass ratio of fluoritum to vinegar 10:3 vinegar quenched product (Fig. 2C) and fluoritum vinegar quenched product (Fig. 2D) have similar microscopic structure, and their particle size is similar to that of fluoritum acetic acid quenched product (Fig. 3C,D similar with Fig. 3B), with uneven particle size and poor roundness. However, there are many fluoritum particles with a diameter of about 1 micron attached to the surface of the fluoritum particles, which may be related to the quenching with vinegar after the stage burning (Fig. 2C,D). Figure 2E,F,G,H are all fluoritum water flying processing products potos, so their particle size is significantly smaller than that of fluoritum that has not been processed by water flying, and some particle size is generally less than 10 microns, and their diameter size distribution histogram appears to have two peaks, one peak at about 10 microns, and the other peak at about 100 microns. The particle size of vinegar-quenched water flying products (Figs. 2G,H, 3G, 35.51 μm and Fig. 3H, 48.61 μm) is smaller(RSD = 18.9%) than that of water-quenched fluoritum (Figs. 2E, 3E, 51.58 μm) and acetic acid (Figs. 2F, 3F) quenched water flying processing products. The experimental results show that water flying and vinegar quenching can make the particles of fluoritum finer and more uniform.

Characteristics of organic matter content of fluoritum and its products

The results showed that the contents of carbon and nitrogen in fluoritum and its processed products were significantly different (carbon RSD = 63.3%, nitrogen RSD = 65.3%) (Table 3). The contents of carbon and nitrogen in fluoritum raw product were 0.048 and 0.006%, respectively. After quenching with vinegar, the contents of carbon and nitrogen increased to 0.150% and 0.020%, which increased by 3 times. The contents of carbon and nitrogen in the vinegar quenched water flying processing products are 0.185 and 0.028%, respectively, and their contents are increased by nearly 4 and 5 times, respectively, indicating that the content of organic elements in the vinegar water flying product is higher. However, the ZSY-3 sample contains 9.3% more carbon than the ZSY-4 sample, and the ZSY-3 sample contained 25% more nitrogen than the ZSY-4 sample. The ZSY-7 sample contains 24.8% more carbon than the ZSY-8 sample, and the ZSY-7 sample contained 14% more nitrogen than the ZSY-8 sample. There was no significant difference in the content of carbon and nitrogen between samples ZSY-3 and ZSY-4, and between samples ZSY-7 and ZSY-8, indicating that the amount of vinegar had no significant difference in changing the content of organic elements. In addition, it was found that the contents of carbon and nitrogen elements of ZSY-2 and ZSY-6 were not significantly different from those of raw products. The ZSY-2 sample contains 13% more carbon than the ZSY-6 sample, and the ZSY-2 sample contained 16% more nitrogen than the ZSY-6 sample. This indicating that organic elements carbon and nitrogen could not enter the mineral crystals after acetic acid quenched the fluoritum.

Characteristics of main element content of fluoritum and its processing products

The results of the content of major elements of fluoritum showed that the raw and processed products in this experiment all met the requirements of Pharmacopoeia of the People's Republic of China (2020 edition) that the content of CaF_2 should be higher than 85% (Table 4), indicating that the samples were qualified[7]. The lowest content of CaF_2 is the fluoritum water quenched flying processing product (ZSY-5), its content is 88.29%, the highest content of CaF_2 is the fluoritum to vinegar mass ratio 10:3 vinegar quenched processing product (ZSY-3), its content is 92.41%. The results showed that there was no significant change in CaF_2 content of fluoritum before and after processed (RSD = 1.47%). The content of CaF_2 measured in all samples in this experiment is not significantly different from that of standard samples (RSD = 1.61%). However, the contents of SiO_2, Al_2O_3 and Fe_2O_3 in different fluoritum are different (Table 2), which indicates that processing has a great influence on the contents of these three elements. The experimental results also show that the fluoritum and its processing products in this experiment all contain a certain amount of Si and Al element (Fig. 4), which may be related to the geological environment where the fluoritum is located. The fluoritum in this experiment was taken from Qinglong antimony ore area, where the formation contains a large amount of silica (SiO_2) and kaolinite ($Al_2Si2O_5(OH)_4$) minerals[31,32]. Si rich mineral fluid will unconsciously enter the fluoritum mineral lattice, resulting in the fluoritum containing Si. The Fe_2O_3 content of ZSY-7 and ZSY-8 samples are 0.11 and 0.10 respectively, Fe_2O_3 content of ZSY-1 sample is 0.06. After the vinegar was quenched, the Fe_2O_3 content was about doubled, but the amount of vinegar was not correlated with the increase of Fe_2O_3 content. Because vinegar generally contains abundant organic elements and trace metal elements[14], the increase in iron content in vinegar-processed fluoritum may be related to the introduce of iron elements in vinegar.

Content characteristics of trace elements in fluorite and its products

The international standard sample OU-6 mineral powder is diluted with distilled water and prepared into a standard solution[9,10,33]. The concentration of elements in the standard solution is shown in Table 5. The standard sample OU-6, BCR-1 and GBPG-1 were tested with the test condition of 2.9, and the standard sample value and the blank value of the instrument background were used to make the standard curve. With the signal strength

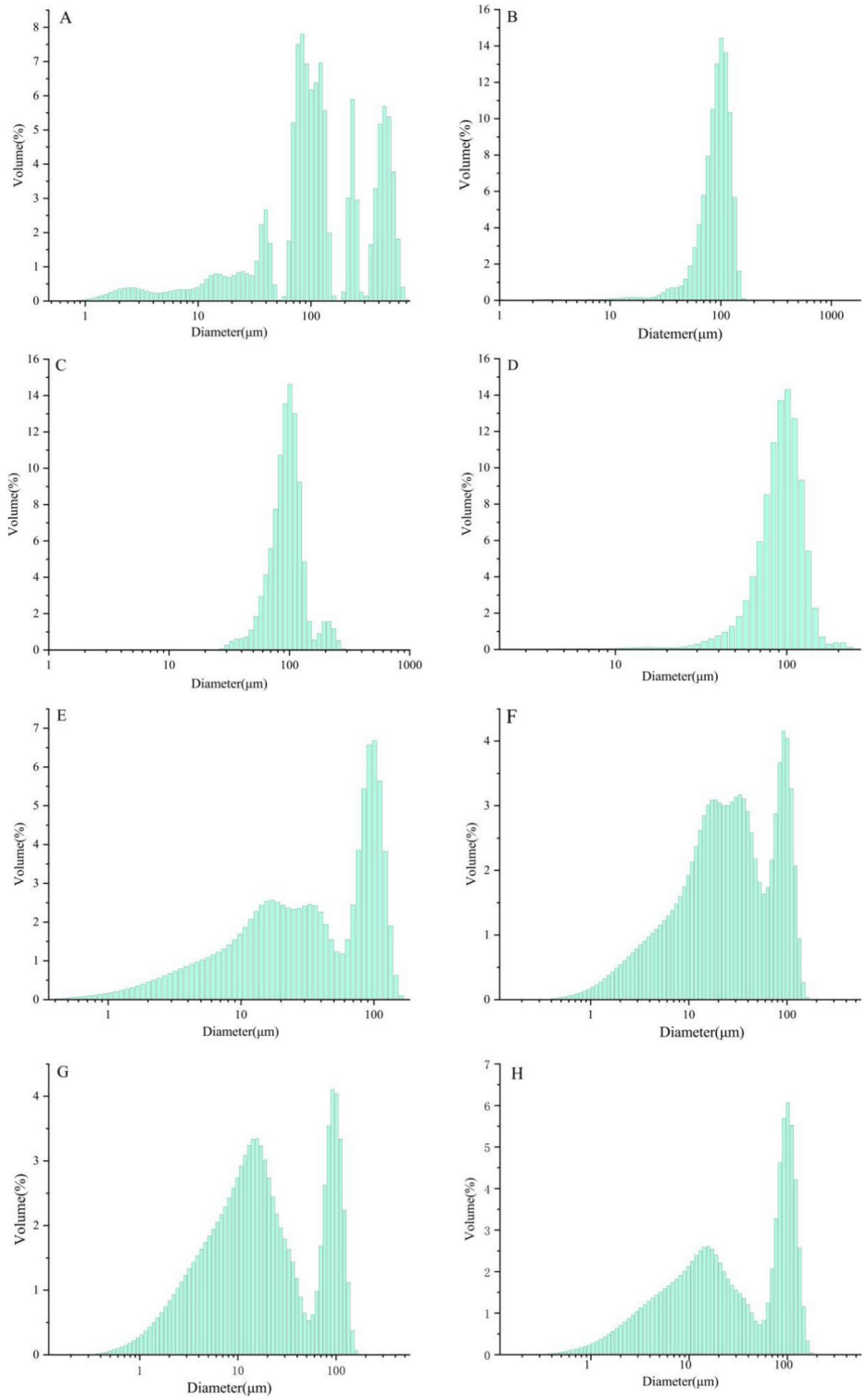

Fig. 3. Histogram of particle size distribution of fluoritum. (**A**). Histogram particle size of fluoritum mineral sample; (**B**) Histogram particle size of fluoritum acetic acid quenched product; (**C**) Histogram particle size of fluoritum to vinegar mass ratio 10:3 vinegar quenched product; (**D**) Histogram particle size of fluoritum vinegar quenched product; (**E**) Histogram particle size of fluoritum water quenched water flying product; (**F**) Histogram particle size of fluoritum acetic acid quenched water flying product; (**G**) Histogram particle size of fluoritum to vinegar mass ratio 10:3 vinegar quenched water flying product; (**H**) Histogram particle size of fluoritum vinegar quenched water flying product.

Samples number	ZSY-1	ZSY-2	ZSY-3	ZSY-4	ZSY-5	ZSY-6	ZSY-7	ZSY-8	RSD (%)
C (%)	0.048	0.043	0.164	0.150	0.081	0.038	0.231	0.185	63.3
N (%)	0.006	0.007	0.025	0.020	0.009	0.006	0.032	0.028	65.3

Table 3. Content of carbon and nitrogen in fluoritum and its processing products (n = 1).

Content (%)	CaF_2	SiO_2	Al_2O_3	Fe_2O_3	Loss on ignition
GBW07250	93.59	5.74	0.15	0.16	/
GBW07251	89.73	9.68	0.08	0.18	/
GBW07252	91.53	7.89	0.19	0.11	/
ZSY-1	92.15	4.51	0.29	0.06	2.82
ZSY-2	91.33	3.50	0.42	0.05	4.35
ZSY-3	92.41	2.95	0.71	0.07	3.46
ZSY-4	90.81	4.22	0.84	0.1	3.83
ZSY-5	88.29	6.24	0.86	0.07	4.48
ZSY-6	91.28	3.78	0.52	0.08	3.98
ZSY-7	89.97	3.69	1.07	0.11	5.03
ZSY-8	90.01	4.14	1.07	0.10	4.58
RSD	1.61%	40.7%	65%	40%	17.2%

Table 4. Content of main elements of fluoritum and its processing products (n = 1). *LOI* loss on ignition.

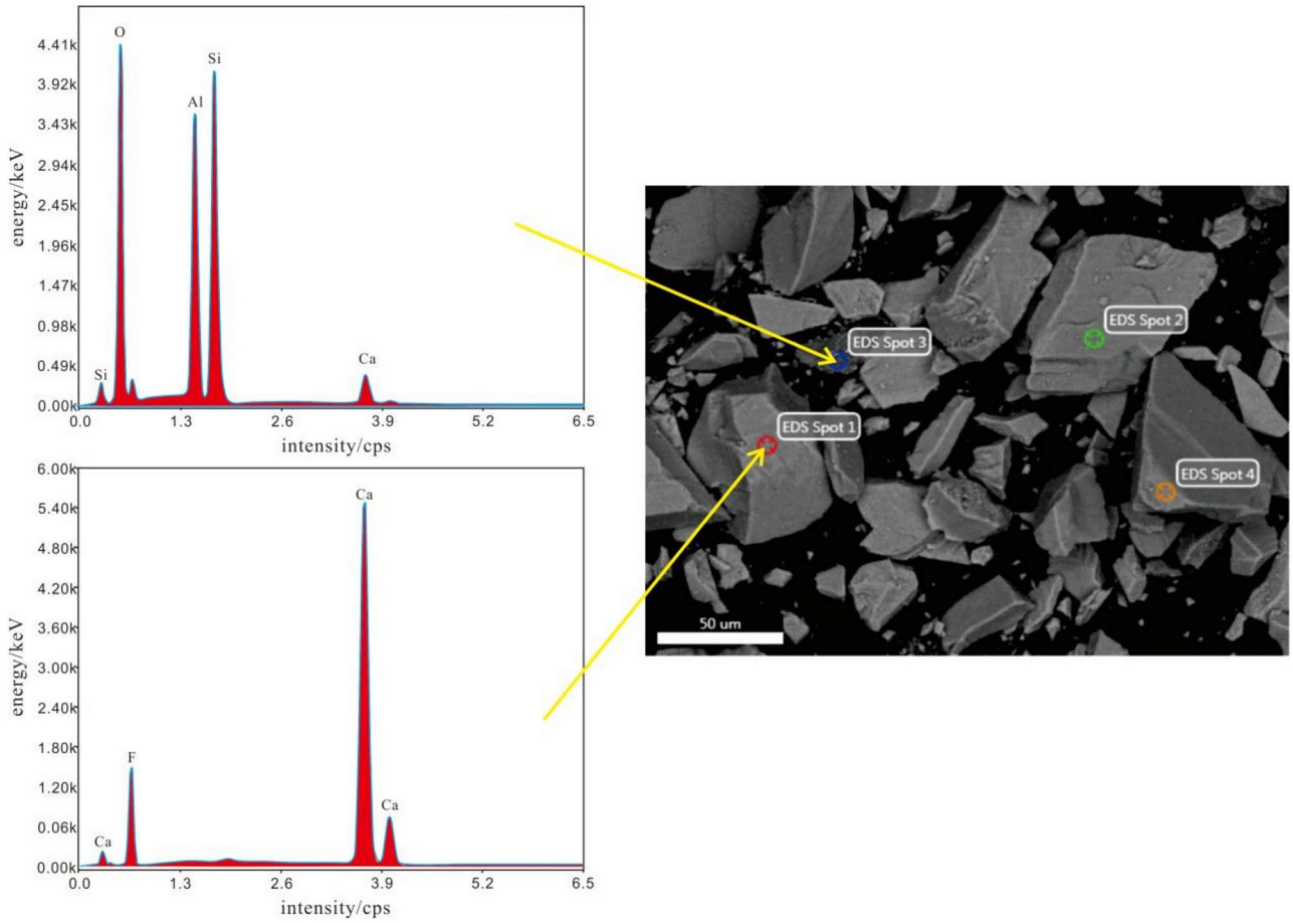

Fig. 4. EDS spectra of fluoritum particles.

Element	Concentration (ng/mL)	Blank	Slope	Detection limit (ug/g)
Li^{7}	101	0	0.078280	0.0054
Be^{9}	10.7	0	0.026871	0.0162
Sc^{45}	31.1	0	0.044147	0.0184
V^{51}	137	0	0.224921	0.0092
Cr^{52}	78.8	0	0.243896	0.0436
Co^{59}	37.1	0	0.225781	0.0054
Ni^{60}	248	0	0.054200	0.0493
Cu^{65}	248	0	0.053473	0.0306
Zn^{66}	319	0	0.022926	0.0291
Ga^{71}	32.3	0	0.104862	0.0007
Ge^{72}	8	0	0.118377	0.0021
As^{75}	21	0	0.027077	0.0076
Rb^{85}	128	0	0.231116	0.0024
Sr^{86}	139	0	0.035169	0.0276
Y^{89}	35.3	0	0.336170	0.0004
Zr^{91}	182	0	0.040686	0.0040
Nb^{93}	22.8	0	0.257406	0.0050
Mo^{100}	8	0	0.037527	0.0025
Ag^{109}	8	0	0.112656	0.0024
Cd^{114}	8	0	0.055127	0.0024
In^{115}	8	0	0.257754	0.0008
Sn^{120}	10.7	0	0.213465	0.0141
Sb^{123}	8.55	0	0.055973	0.0048
Cs^{133}	16	0	0.279137	0.0005
Ba^{135}	485	0	0.018800	0.0616
La^{139}	41	0	0.280842	0.0008
Ce^{140}	82.4	0	0.265471	0.0036
Pr^{141}	15.8	0	0.315088	0.0005
Nd^{146}	37	0	0.054344	0.0014
Sm^{147}	13.9	0	0.044332	0.0005
Eu^{151}	9.36	0	0.144787	0.0002
Gd^{157}	13.3	0	0.053553	0.0007
Tb^{159}	8.85	0	0.293333	0.0001
Dy^{163}	13	0	0.066762	0.0004
Ho^{165}	9.01	0	0.254679	0.0001
Er^{166}	11	0	0.085378	0.0004
Tm^{169}	8.44	0	0.246604	0.0001
Yb^{174}	11	0	0.072472	0.0004
Lu^{175}	8.45	0	0.217043	0.0001
Hf^{179}	12.7	0	0.029414	0.0008
Ta^{181}	9.06	0	0.120908	0.0015
W^{184}	8	0	0.034725	0.0074
Tl^{205}	8	0	0.117081	0.0016
Pb^{206}	236	0	0.036508	0.0100
Bi^{209}	8	0	0.109890	0.0003
Th^{232}	19.5	0	0.156129	0.0003
U^{238}	9.96	0	0.161902	0.0003

Table 5. Results of linear relationship investigation in standard solution.

as the ordinate f(x) and the sample concentration as the abscissa x, the standard curve was drawn and linear regression was performed. The working curve is shown in (Supplementary information 1). The test results of the standard sample and the RSD values between the test results and the recommended values of the standard sample are shown in Table 6. Except that the RSD between the test values of Ge, Ag,Cd and Bi elements and the recommended values of the standard sample is greater than 10%, the RSD values between the test values of the remaining 43 elements and the recommended values of the standard sample are all less than 10%, indicating that the instrument is stable and the test results are reliable. The results show that the standard curve has a good

Element	OU-6	BCR-1	GBPG-1	ZSY-1	ZSY-2	ZSY-3	ZSY-4	ZSY-5	ZSY-6	ZSY-7	ZSY-8
Li	91.8	12.4	19.6	1.01	0.757	0.914	1.02	3.31	2.11	2.66	3.82
RSD	0.65	2.79	4.78	1.94	2.30	2.02	4.61	3.84	11.05	6.99	1.75
Be	2.51	1.53	0.872	0.038	0.029	0.028	0.037	0.104	0.082	0.093	0.106
RSD	4.10	3.16	2.23	4.94	8.88	8.64	13.44	69.66	200.0	142.9	66.67
Sc	23.1	33.9	14.2	1.03	1.33	2.96	2.43	1.45	1.08	2.76	2.03
RSD	3.13	2.76	1.36	7.38	7.20	8.59	7.80	23.11	20.30	16.20	17.32
V	131	431	101	4.36	4.86	12.3	13.0	5.76	6.47	17.2	16.2
RSD	0,90	4.05	3.22	2.09	3.96	2.25	1.73	2.21	0.62	2.35	2.66
Cr	74.8	16.5	177	5.24	7.04	7.70	9.53	6.48	9.83	11.2	13.0
RSD	3.91	2.18	1.74	7.69	2.82	1.62	3.16	1.79	2.13	2.85	3.01
Co	29.5	38.0	20.3	3.44	3.61	3.58	3.80	3.81	3.45	3.84	4.43
RSD	0.94	1.89	2.84	2.66	1.85	0.94	4.22	1.31	1.65	2.18	1.72
Ni	38.9	13.5	56.3	52.4	53.3	52.0	52.5	52.6	54.2	52.4	55.8
RSD	1.67	2.67	4.03	8.20	4.91	1.13	2.99	7.71	6.02	4.44	6.82
Cu	41.4	20.1	29.3	1.23	1.10	1.31	1.49	1.21	1.59	1.88	2.16
RSD	3.11	3.98	1.67	0.48	1.81	1.23	4.35	4.79	5.35	1.71	5.82
Zn	114	134	82.3	/	/	/	1.68	/	/	/	11.3
RSD	1.77	2.42	1.74	/	4.27	2.67	2.37	4.73	11.10	1.95	10.78
Ga	24.3	22.0	19.2	0.443	0.470	0.757	0.784	0.681	0.694	1.14	1.14
RSD	0.09	0.00	2.24	2.16	11.83	4.71	6.27	5.09	17.23	13.71	14.01
Ge	5.49	7.58	3.69	0.140	0.158	0.150	0.149	0.146	0.162	0.169	0.169
RSD	/	94.70	91/03	2.05	4.47	1.89	5.41	4.09	5.56	3.62	4.90
As	13.1	0.705	0.749	1.28	2.41	2.64	1.45	6.78	3.62	20.4	37.5
RSD	0.54	5.74	/	1.98	1.89	2.85	2.05	2.07	6.02	2.26	8.19
Rb	121	49.0	58.3	0.714	0.482	0.767	0.595	1.17	1.05	1.18	1.65
RSD	0.47	2.65	2.54	1.47	1.68	3.5	5.42	1.87	1.02	2.23	4.53
Sr	131	331	355	43.1	44.0	47.9	46.7	43.5	44.0	50.1	48.2
RSD	0.06	0.21	1.67	4.45	1.73	3.19	4.06	3.14	10.65	6.22	8.06
Y	27.1	34.9	18.5	69.1	75.4	127	123	70.0	75.5	130	129
RSD	0.65	6.01	1.94	1.46	4.06	6.62	5.51	10.38	34.31	7.20	26.72
Zr	175	188	224	0.310	0.193	0.323	0.246	1.44	1.16	1.33	2.00
RSD	0.34	0.75	2.42	1.58	8.88	6.44	4.53	8.56	29.59	32.36	34.63
Nb	15.1	14.5	10.7	0.447	0.300	0.232	0.195	0.333	0.277	0.264	0.341
RSD	1.47	2.48	5.28	10.61	29.12	15.79	36.27	5.33	46.98	34.27	33.43
Mo	0.730	1.65	1.75	0.253	0.175	0.374	0.401	0.101	0.144	0.343	0.365
RSD	/	2.18	2.05	4.87	7.27	5.23	5.65	4.98	14.39	9.43	11.94
Ag	0.303	0.252	0.243	0.026	0.029	0.054	0.041	0.030	0.021	0.064	0.152
RSD	/	114.05	74.71	2.09	5.79	4.23	1.08	2.36	20.70	17.98	15.64
Cd	0.165	0.226	0.181	0.018	0.059	0.081	0.115	0.063	0.103	0.107	0.216
RSD	34.69	38.14	74.59	2.66	2.68	1.63	0.88	3.44	54.54	19.75	11.36
In	0.127	0.096	0.060	/	/	/	0.001	/	0.020	0.007	0.005
RSD	/	3.01	/	6.93	4.71	13.05	7.80	8.95	50.19	63.18	30.00
Sn	3.13	2.96	3.58	/	/	/	/	0.042	/	/	0.029
RSD	9.91	6.50	/	6.89	10.39	8.28	10.41	6.19	20.90	14.74	8.92
Sb	0.607	0.650	0.228	14.9	13.3	15.6	17.7	19.9	20.6	25.4	26.6
RSD	6.97	3.34	/	9.78	12.15	24.37	7.51	4.17	18.48	9.06	11.33
Cs	7.76	0.944	0.315	0.123	0.091	0.077	0.075	0.357	0.256	0.273	0.397
RSD	2.33	1.19	1.11	1.03	8.02	5.22	1.21	6.23	5.92	14.89	5.70
Ba	471	675	883	3.07	/	0.336	0.275	0.988	1.42	1.84	2.36
RSD	0.93	0.63	1.97	1.17	1.78	3.95	1.48	2.87	8.33	11.65	9.42
La	32.4	25.1	50.4	4.87	5.14	4.80	4.93	5.13	5.05	5.19	5.24
RSD	1.30	0.57	3.49	6.06	11.93	14.95	5.34	6.77	19.61	5.26	37.40
Ce	75.5	52.4	99.2	9.20	10.0	7.27	7.35	9.70	9.45	7.78	7.97
RSD	1.02	1.73	2.79	1.84	2.69	6.52	4.76	8.79	24.08	8.98	23.09
Pr	7.72	6.50	11.0	1.84	1.93	1.61	1.62	1.91	1.91	1.71	1.73
RSD	0.73	3.19	2.83	2.63	13.10	15.47	8.05	12.82	23.81	55.10	85.71

Continued

Element	OU-6	BCR-1	GBPG-1	ZSY-1	ZSY-2	ZSY-3	ZSY-4	ZSY-5	ZSY-6	ZSY-7	ZSY-8
Nd	29.3	27.6	42.4	9.86	10.4	8.91	8.75	10.1	10.1	9.15	9.07
RSD	0.70	3.01	1.49	5.82	21.56	18.43	9.29	14.82	150.1	125.2	115.5
Sm	5.88	6.34	6.75	2.38	2.53	2.56	2.55	2.50	2.49	2.80	2.66
RSD	0.48	2.73	0.42	11.01	18.76	28.02	10.63	26.82	110.2	62.81	152.5
Eu	1.32	1.88	1.71	0.806	0.849	1.03	1.01	0.821	0.841	1.07	1.02
RSD	2.11	2.58	3.23	6.20	4.47	14.29	2.77	8.00	42.51	28.41	38.49
Gd	5.34	6.62	4.56	3.76	4.06	5.26	5.12	3.69	3.99	5.36	5.26
RSD	0.93	0.64	2.74	12.00	3.91	9.30	9.47	14.91	13.49	7.11	6.04
Tb	0.854	1.04	0.633	0.619	0.662	0.951	0.894	0.616	0.654	0.948	0.908
RSD	0.33	0.68	3.78	14.99	15.66	7.34	14.5	28.22	129.6	115.5	56.45
Dy	4.99	6.36	3.28	3.70	4.04	6.22	5.91	3.70	3.99	6.45	6.08
RSD	0.00	0.22	0.43	11.07	22.40	12.22	26.12	14.61	24.75	29.28	32.20
Ho	1.04	1.31	0.686	0.757	0.819	1.33	1.31	0.748	0.822	1.38	1.33
RSD	2.07	2.75	0.41	4.71	25.19	8.70	25.17	17.73	59.48	86.78	72.22
Er	3.01	3.56	2.02	1.91	2.06	3.42	3.47	1.89	2.16	3.63	3.42
RSD	0.71	1.38	0.35	3.68	20.20	9.81	7,95	14.03	102.7	55.49	84.20
Tm	0.447	0.533	0.304	0.214	0.235	0.411	0.405	0.217	0.263	0.417	0.406
RSD	1.12	3.49	0.94	10.10	33.21	15.02	31.58	46.98	91.06	100.7	67.13
Yb	2.95	3.32	1.98	1.09	1.18	2.09	1.99	1.09	1.28	2.22	2.06
RSD	1.19	1.27	1.76	3.36	18.87	21.63	15.71	39.04	43.19	84.20	84.20
Lu	0.444	0.489	0.302	0.146	0.157	0.268	0.264	0.134	0.171	0.284	0.267
RSD	0.95	2.97	1.85	15.90	44.91	28.59	11.76	23.78	56.45	56.45	69.10
Hf	4.57	4.65	5.89	0.078	0.070	0.116	0.110	0.085	0.112	0.137	0.164
RSD	1.98	4.42	2.13	26.41	15.67	23.50	20.31	28.87	21.99	72.22	71.45
Ta	1.16	0.901	0.434	1.03	0.672	0.508	0.413	0.433	0.350	0.351	0.403
RSD	6.37	7.52	5.77	21.15	19.31	19.75	17.03	21.61	5,69	25.45	21.42
W	1.53	0.482	0.320	1.18	0.851	0.751	0.618	0.572	0.607	0.507	0.547
RSD	6.27	6.44	6.96	5.03	16.25	9.08	15.83	9.55	18.37	11.38	8.63
Tl	0.511	0.285	0.262	0.001	/	0.005	0.005	0.003	0.023	0.010	0.011
RSD	2.58	3.63	/	7.03	3.35	1.93	1.42	5.01	8.31	10.34	14.80
Pb	29.6	14.0	13.9	0.273	0.213	0.812	0.709	0.428	0.814	1.11	2.05
RSD	3.38	2.05	1.01	0.96	2.00	1.07	2.16	1.13	2.70	14.21	17.42
Bi	0.661	0.220	0.121	0.293	0.167	0.137	0.119	0.102	0.261	0.213	0.200
RSD	/	91.63	123.88	11.17	12.02	13.65	5.54	11.56	22.10	28.18	21.48
Th	10.9	5.80	11.0	0.218	0.197	0.118	0.099	0.272	0.296	0.205	0.231
RSD	3.85	2.16	1.46	2.48	22.87	6.91	4.21	8.44	42.70	45.42	53.50
U	1.91	1.69	0.876	0.063	0.059	0.118	0.112	0.077	0.088	0.163	0.147
RSD	1.83	2.47	1.91	5.56	3.19	4.74	2.03	2.73	53.37	72.37	80.45

Table 6. Contents of trace elements in fluoritum and its products ($\mu g.g^{-1}$) (n = 4). / Indicates that it is not detected.

linear relationship and the instrument is stable. The standard parameters of each element are shown in Table 5. The measurements were repeated four times for each sample to be tested, and the results showed that the relative standard deviation (RSD) of most samples to be tested was less than 10.00%, indicating good reproducibility of sample data. The RSD values of each element of the sample to be tested are shown in Table 6 and (Supplementary information 2). After random single element test, it was found that except the RSD of very low content of elements is greater than 10%, the RSD of other elements to be measured were all less than 5.00%, indicating good precision of the instrument (Table 6).

The test results of trace elements in fluoritum show that the contents of different trace elements in fluoritum are very different (RSD = 230%), and the contents of the same trace elements are also different between raw product and different processed products (Table 6). For example, the RSD value of As element content between fluoritum raw products and different products is 136.2%. The content of yttrium in the fluoritum was the highest, and its content varied from 69.1 to 130 $\mu g.g^{-1}$, and the content of yttrium in the fluoritum processed products was increased to different degrees than that in the raw product, and the content of Y was the most obvious increase in the vinegar quenched and vinegar quenched water flying products (ZSY-7, ZSY-8 samples compared with ZSY-1 samples), the RSD values are 43.3 and 42.8% respectively. The content of vanadium (V), nickel (Ni), strontium (Sr), antimony (Sb) and light rare earth elements lanthanum (La), cerium (Ce), prasodmium (Pr), neodymium (Nd), and samarium (Sm) are high in the fluoritum, and their content ranges from 1.61 to

55.8 μg.g^{-1}, and most of the other trace elements are lower than 1 μg.g^{-1}. The elements whose content increased significantly after the vinegar quenched water flying were Li, V, Zn, Ga, Cr(RSD = 80%,RSD = 84.2%,Zn content has never been detected to 11.3 μg.g^{-1}, RSD = 62.3%, RSD = 51.3%). The elements content with decreased are Tl, W (RSD = 25.4%, RSD = 79.5%). Zn is necessary for life, Tl, W, U are toxic and harmful elements. The increase of the content of essential elements and the decrease of the content of toxic and harmful elements may be the mechanism of effect-enhancing and toxicity-reducing in fluoritum by processing. Of course, this inference needs to be confirmed by more stringent pharmacological experiments.

In order to more deeply understand the trace elements content correlation of fluoritum and its different processed products, OriginPro 2018 software was used to do the correlation hotspot map, systematic cluster analysis pedigree map and principal component analysis of trace elements contained in fluoritum and its products. As can be seen from the correlation hotspot map of trace elements, most areas of the graph are red or blue, indicating that most trace elements in fluoritum have good correlation (red and blue areas in the figure indicate good correlation, and white areas indicate poor correlation) (Fig. 5).

From the phylogenetic diagram of systematic cluster analysis of trace elements content in fluoritum, it is found that the distance between ZSY-1 and ZSY-2 is relatively close, the distance between ZSY-5 and ZSY-6 is relatively close, the distance between ZSY-3 and ZSY-4 is relatively close, the distance between ZSY-7 and ZSY-8 is relatively close (Fig. 6). This shows that there is no significant difference between fluoritum raw product and acetic acid quenched product from the point of view of trace elements. In addition, the distance between fluoritum water quenched water flying product and fluoritum acetic acid quenched water flying product is also relatively close, these four products show that there is not much difference between fluoritum water quenched and acetic acid quenched, acetic acid and water quenched effect is almost the same, acetic acid may only play the effect of making fluoritum crisp. The mass ratio of fluoritum to vinegar 10:3 is not significantly different from the fluoritum vinegar quenched product, indicating that the amount of vinegar used in vinegar quenched may be irrelevant from the perspective of the influence of trace element content. The mass ratio of fluoritum to vinegar 10:3 is relatively close to the fluoritum vinegar quenched product, and the result of similar content of trace elements also proves this view.

The principal component analysis diagram of trace elements in fluoritum has a similar rule to the phylogenetic diagram of systematic cluster analysis, that is, ZSY-1 and ZSY-2 samples are located in the negative semi-axis of principal component 1 and principal component 2, and ZSY-3 and ZSY-4 samples are located in the positive

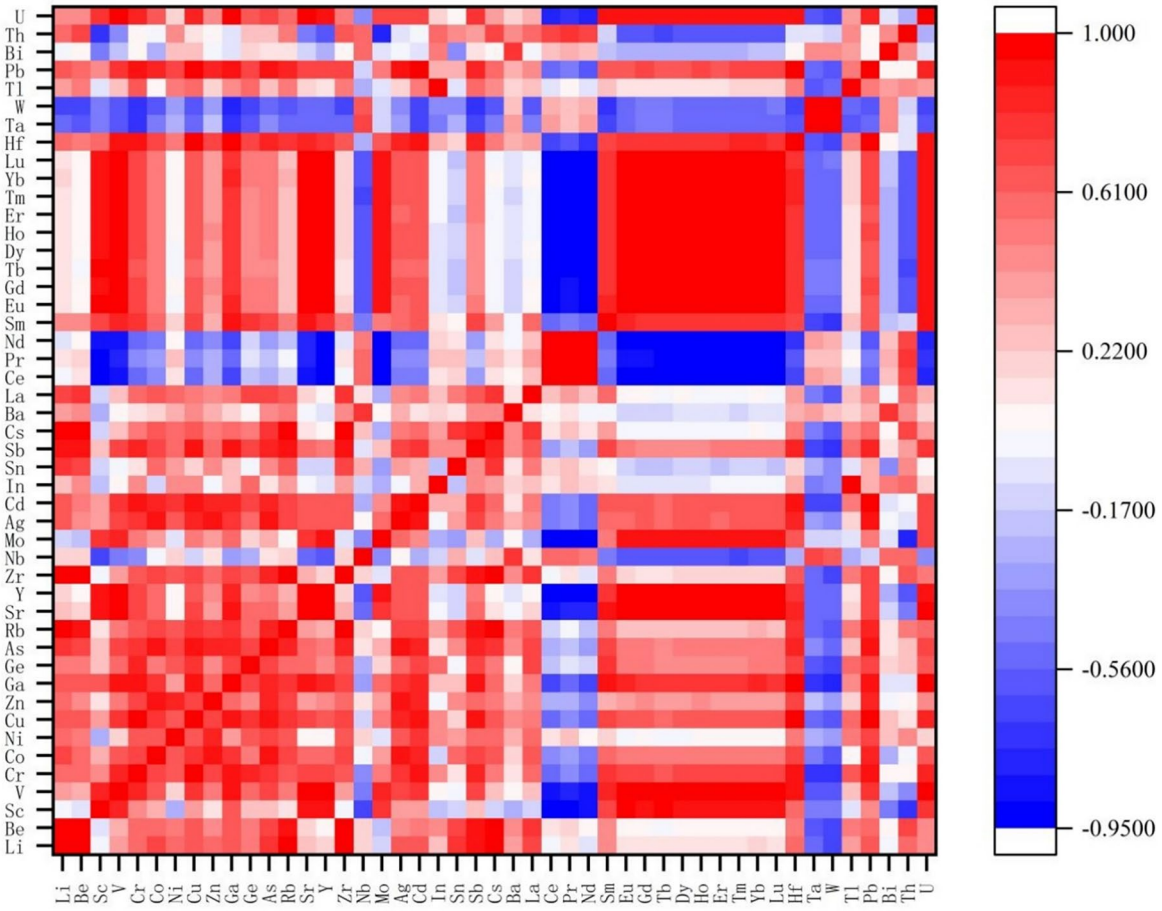

Fig. 5. Elements contents correlation hotspot map of fluoritum and its different processed products.

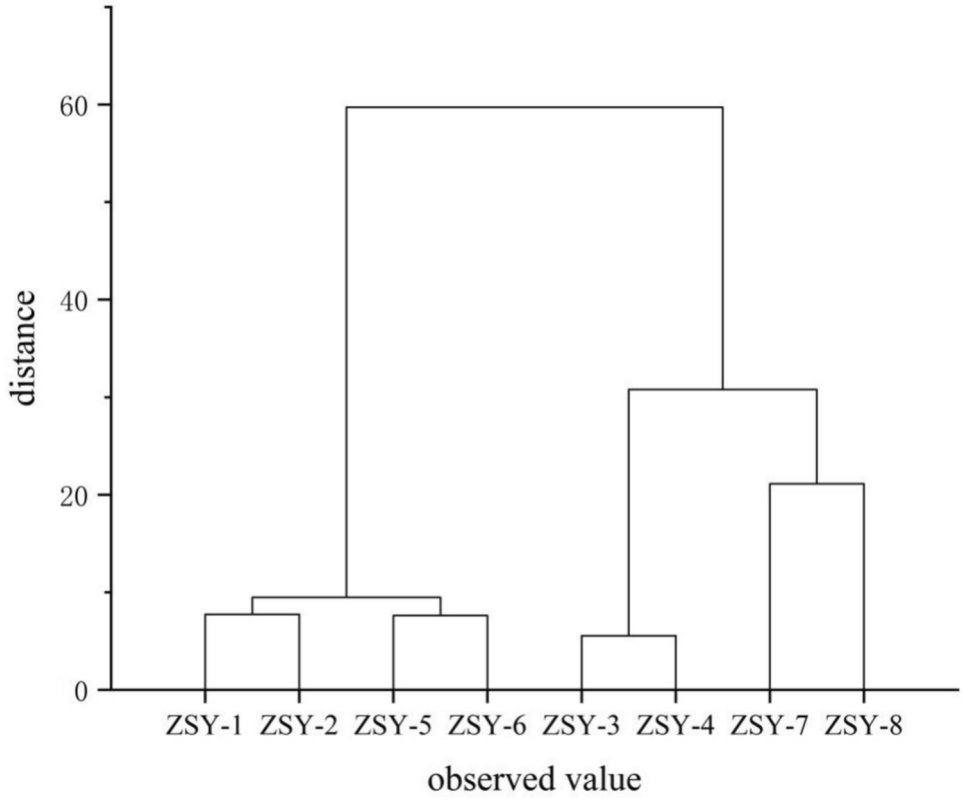

Fig. 6. Phylogenetic diagram of systematic cluster analysis of fluoritum and its different processed products.

semi-axis of principal component 1 and the negative semi-axis of principal component 2 (Fig. 7). The two samples ZSY-5 and ZSY-6 are located in the negative semiaxial part of principal component 1 and the positive semiaxial part of principal component 2. The two samples ZSY-7 and ZSY-8 are located in the positive semiaxial part of principal component 1 and the positive semiaxial part of principal component 2 (ZSY-7 sample is located near axis 0). The phylogenetic and principal component analysis diagrams of trace elements in fluoritum explain the differences and relations between fluoritum and its different processed products.

Discussion

Vinegar, ancient known as oxalis, acyl, bitter wine, rice vinegar and so on. It is one of the most common liquid excipients in the processing of TCM. According to the theory of the five tastes of TCM, vinegar tastes sour, bitter and warm, and the sour taste is favored by the liver. According to the relationship between the five viscera and the five tastes in "SuWen Xuanming WuQi Chapters", it can be seen that acid enters the liver, and the liver hosts the blood and the drainage, so as to treat various blood syndromes and stagnation of qi[34]. Cuzhi is a method of processing TCM with vinegar as auxiliary material. The chemical composition of vinegar is mainly organic acids, amino acids, alcohols, esters, aldehydes, sugars and other organic matter[13]. The chemical composition of different vinegar varies greatly, and the most important elements of these substances are C and N [14]. The results of this study show that the content of C and N elements in fluoritum processed by vinegar is significantly higher than that of raw and other processed products, and there are some differences between different vinegar products. The content of carbon and nitrogen in fluoritum prepared with vinegar is double that of other prepared products. This part of organic matter may be the pharmacodynamic material basis of fluoritum[12,13]. In addition, it was also found that there was no substantial difference between water quenched product and acetic acid quenched product on the chemical composition of fluoritum, indicating that Chinese medicine scientists processed fluoritum with vinegar instead of acetic acid have some scientific truth, and it was not that the higher the content of acetic acid, the higher the content of organic matter.

The SEM microstructure of the vinegar quenched water flying processing product showed that the particle size of the fluoritum was significantly smaller than that of the fluoritum after direct grinding and immediate quenching after calcination, but the main problem of the fluoritum after processing was uneven particle size, which had a serious impact on drug absorption and bioavailability[35,36]. Therefore, the vinegar quenched water flying product is obviously superior to the direct grinding and calcined product in terms of particle size. In traditional Chinese medicine, mineral drugs are mostly quenched with calcined or post-calcined vinegar, so that they are easy to be crushed and decocted out effective ingredients, so as to improve their efficacy. Studies have shown that mineral drugs often produce acetate after vinegar quenching. The main component of fluoritum is calcium fluoride. Soluble calcium acetate is produced after high-temperature calcination and vinegar quenching,

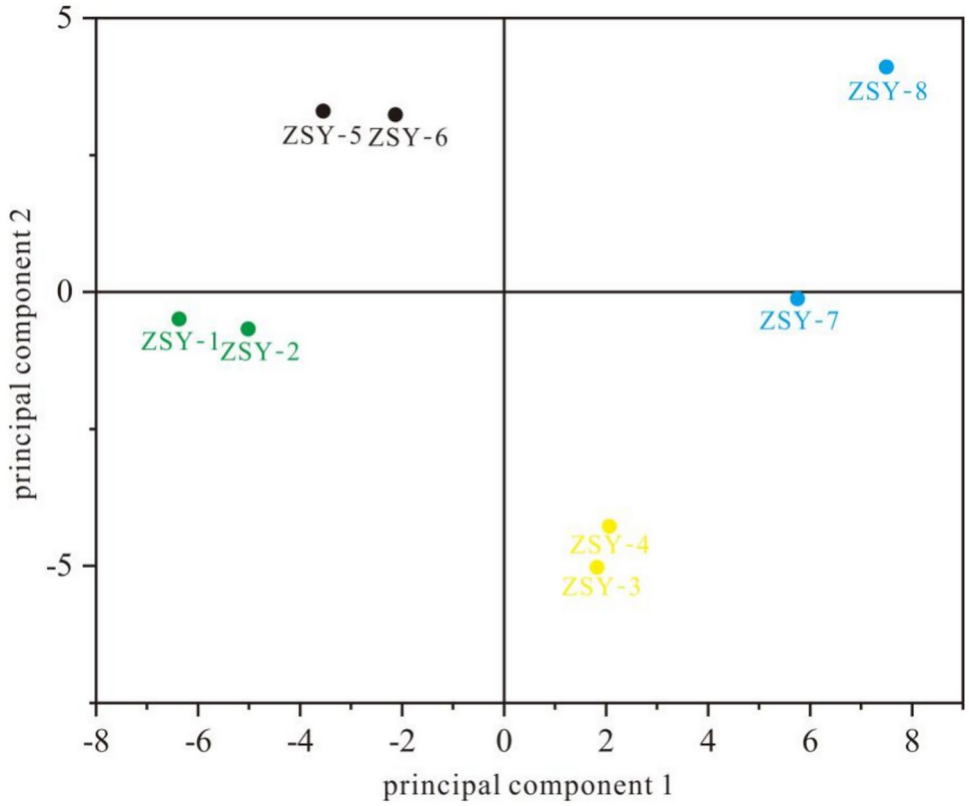

Fig. 7. Principal component analysis of fluoritum and its different processed products.

which is easy to crush, has a high solubility and is easily absorbed by the body, thus giving full play to the drug effect[14].

Although different raw fluoritum products have different colors, some scholars have shown that there is no significant difference in the efficacy of different colors of fluoritum[28]. The color of fluoritum is mainly caused by the difference in the content of trace elements. Whether the difference in the content of trace elements has a difference in drug efficacy needs to be verified by more stringent pharmacodynamic experiments. The content of main and trace elements of fluoritum showed that different processing method had no significant effect on the content of main elements. However, the results of trace element content showed that the Zn content of the fluoritum vinegar quenched product was 1.68 μg/g, but the Zn content increased to 11.3 μg/g after the vinegar quenched with water flying, which increased nearly 7 times. Zinc is an essential element for life[37], and the increase of zinc content in vinegar quenched water flying products may be an important basis for the efficiency improvement of fluoritum vinegar. In addition, the contents of Li, V, Ga and Cr were increased in different degrees after the processing. The elements content with decreased are Tl, W. These three elements all have certain toxicity, and the reduction of their content is conducive to the reduction of the toxicity in fluoritum[38,39]. As, Sb is a toxic and harmful element, and the reason for the high content in the sample in this study is that the formation near the sample contains stibnite, which contains a large amount of As, Sb elements[28,40]. Therefore, the significant effect of water-flying processing of mineral drugs in reducing the content of soluble toxic metal elements and increasing the life elements should be considered. On the one hand, some elements such as arsenic and mercury are volatile at high temperature. On the other hand, it may be that the addition of vinegar in the process of high-temperature quenching can make some harmful elements quickly dissolve and take away with the volatilization of vinegar.

In summary, the grain size of fluoritum is smaller and more uniform after quenching with vinegar. After vinegar quenching, the organic elements carbon and nitrogen in vinegar enter the fluoritum, carbon and nitrogen are important raw materials for the synthesis of some enzymes and nutrients in the human body, so the fluoritum with increased carbon and nitrogen elements after vinegar quenching is more effective[41]. The main element CaF_2 did not change significantly after vinegar quenching and before vinegar quenching, but the iron content increased about twice. Iron is the main element in the blood and often appears in the form of coordination compounds in heme, and the increase of iron content after vinegar helps the synthesis of heme in the human body[42]. Because there are many kinds of trace elements in fluoritum, there is no obvious law in the increase and decrease of the content of life elements and toxic elements in fluoritum after vinegar quenching. The research in this aspect needs to be more in-depth and detailed to elaborate the connotation of vinegar production to enhance efficiency and reduce toxicity.

Conclusions

The microstructure, contents of organic elements and main and trace elements of fluoritum minerals and its vinegar products from Dachang Town, Qinglong County, Guizhou Province were analyzed by means of thermal field emission SEM, organic element analyzer, X-ray fluorescence spectrometer and ICP-MS. The results show that after processed with vinegar, organic elements carbon and nitrogen in vinegar will enter a large number of fluoritum, so vinegar preparation has a certain scientific significance. From the point of view of chemical composition, the mass ratio of fluoritum to vinegar 10:3 is not significantly different from that of vinegar processing, indicating that the amount of vinegar prescribed in the pharmacopoeia of the People's Republic of China may have to be reconsidered. The vinegar quenched water flying processing method can be listed as the best processing method for fluoritum because it can make the fluoritum particles smaller and more uniform, increase the content of organic matter and remove toxic and harmful metal elements. The decrease of grain size, the increase of contents of carbon, nitrogen and iron and the decrease of toxic elements Tl, W may be the important reasons for the enhancement of efficiency and reduction of toxicity of fluoritum vinegar-quenched processing.

Data availability

Data is provided within the manuscript or supplementary information files.

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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