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RESEARCH ARTICLE

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Analytical comparison between unprepared and calcined magnetitum (Cishi)

Abstract The phases, chemical composition, surface appearance, crystal size, specific surface and thermal behavior of the unprepared and calcined forms of the mineral Magnetitum (Cishi), used as Chinese traditional medicine, were characterized by using X-ray powder diffraction, scan electron microscopy, inductively coupled plasma-atomic emission spectometry (ICP) and thermogravimetric (TG). The results indicated that after calcination the main phase Fe_3O_4 of the calcined Magnetitum (Duan Cishi) remained, while the Fe_2O_3 phase disappeared. The contents of the harmful chemical elements Cd and Pb were obviously reduced, while the crystal size increased from 24.5 to 35.7 nm and surface loosened. There were different TG curves for unprepared and calcined Magnetitum (Cishi) samples on heating. The former showed two weight-losing steps (at 367.9–422.1°C and 568.8–594.1°C), and the latter only one. These results might serve as a base for quality evaluation of Magnetitum (Cishi).

Keywords Chinese traditional medicine, magnetitum, Cishi, X-ray powder diffraction, scan electron microscopy, trace elements

1 Introduction

Traditional Chinese medicine, because of the uncertainty of its identification, could not be marketed worldwide. Past research relied on mainly macroscopical examinations of Magnetitum (Cishi) [1]. With the development of modern techniques, X-ray powder diffraction (XRD), thermogravimetric (TG), scan electron microscopy (SEM), etc. are used in the characterization of Chinese medicines gradually [2,3].

Magnetitum (Cishi) is a commonly used mineral in TCM [4], and it was first recorded in Shen Nong Ben Cao Jing. Magnetitum (Cishi) is also called as Xuan Shi, Xi Tie Shi, etc. It is essentially an oxide mineral Magnetite (Fe_3O_4) belonging to spinel group. Salty in flavour, cold in nature, Magnetitum is attributed to liver, heart and kidney channels. From ancient times until present, the material medica Magnetitum (Cishi) was used in two different preparations, raw and calcined. The unprepared Magnetitum (Sheng Cishi) recorded in Chinese Pharmacopoeia [4] is mainly used to calm the liver, benefit yin and suppress the sthenic yang. It calms and sedates the spirit, is used for treatment of restlessness, tremors, convulsions, irritability, dizziness, vertigo and blurred eyesight, and calcined Magnetitum (Duan Cishi) is mainly used to improve auditory and visual acuity, often used for treatment of insufficiency of the liver and kidney manifested as tinnitus, deafness, blurring of vision and cataractcure, dyspnea, spermatorrhea, etc. In this article, analytical comparison between raw and calcined Magnetitum (Cishi) were carried on using XRD, SEM, ICP-AES, TG. The results may serve as a base for the quality evaluation of the medicine.

2 Experiments

2.1 Reagents

Unprepared and calcined Magnetitum (Cishi) samples are obtained from the Nanjing University of Traditional Chinese Medicine. HCl (G.R), HNO_3 (G.R) and H_2O (distilled twice) are used as ICP experiment reagents. The concentrations of standard solution of Zn, Cd, Pb, Co, Ni, Mn, Cr, Cu, Mo are 1.0×10^{-5} g·mL^{-1}, respectively, and Fe standard solution is 1.0×10^{-4} g·mL^{-1}. All the test solution is prepared in accordance with GB/T602.

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2.2 Instruments

Superficial appearance of the unprepared and calcined Magnetitum (Cishi) was observed through the JSM-5610LV scanning electron microscope. The experimental accelerating voltage was 20 kV.

The phase and crystal size of the unprepared and calcined Magnetitum (Cishi) were determined by Rigaku D/max-rC type rotating anode X-ray diffractometer, operated at 40 kV and 50 mA and equipped with a graphite crystal monochrometer (DS = SS = 1°, RS = 0.15 mm, scanning speed was 3°/min). $CuK_{\alpha 1}$ radiation was used for data collection. The 2θ scanning range was 5°–85°. X-ray diffraction line broadening and the Scherrer equation were used to calculate the crystal size of the unprepared and calcined Magnetitum (Cishi) [5].

The content of trace elements, which exist in the unprepared and calcined Magnetitum (Cishi), was measured with Leeman PS-I type ICP-AES. Three parallel samples of the unprepared and calcined Magnetitum (Cishi) were put into beakers of 25 mL. The samples were digested with concentrated HCl and HNO_3 by heating to near boiling point until the color of residue became white, and then cooled, filtered and washed. The last filtrate is used for experiment.

The TG spectrum of the unprepared and calcined Magnetitum (Cishi) was obtained by using American PE Corporation TGA-7 in an argon atmosphere. The rate of heating was 20°C min^{-1}, over the temperature range from room temperature to 650°C.

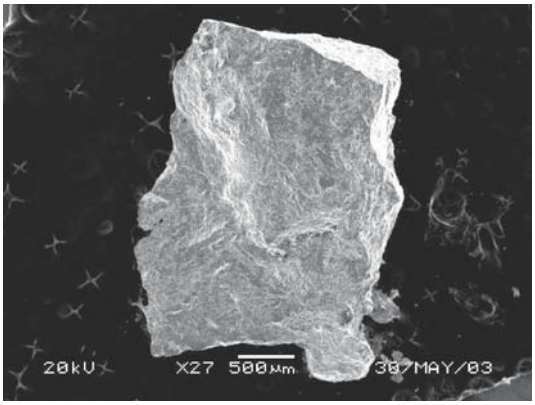

Fig. 1 SEM images of unprepared Cishi

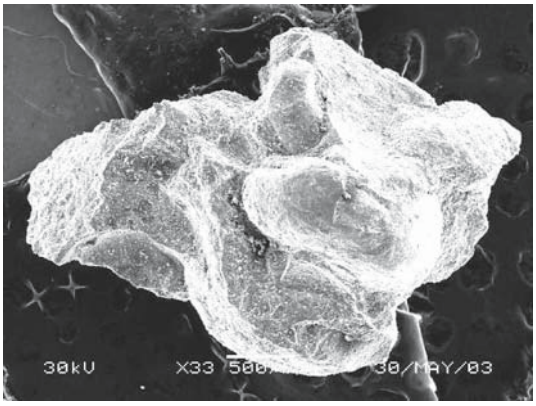

Fig. 2 SEM images of Duan Cishi

3 Results and discussion

3.1 The appearance of unprepared and calcined Magnetitum (Cishi)

Observed from the surface, the edges and corners of the unprepared Magnetitum (Sheng Cishi) are clear and assume irregular mass. The unprepared Magnetitum varies in size, its cross section is comparatively neat, its surface is tight and hard, and it assumes a brownish colour. In powdered form, unprepared Magnetitum assumes dark brown colour with weak magnetism, but the calcined Magnetitum (Duan Cishi) assumes a dark brown colour and its powder form assumes black colour with stronger magnetism. The edges and corners almost disappear, with smooth and loosened appearance. In Figs. 1 and 2 the SEM of the unprepared and calcined Magnetitum (Cishi) respectively are shown. The surface structure of the calcined Magnetitum (Duan Cishi) is very obviously suitable for contact with other medicinal materials in the solution when processed in water and can cause the elemental composition of the medicine easier to dissolve.

3.2 Determination of the phase, crystal size and specific surface area of unprepared and calcined Magnetitum (Cishi)

The standard data processing program was used for the calculations and then search–match program was used to make comparison between the measured data and standard file [6] so as to choose the best fit of the patterns. The main results of qualitative analysis are given in Table 1. X-ray powder diffraction patterns of the unprepared and calcined Magnetitum (Cishi) are shown in Figs. 3 and 4. We can see clearly that there are differences between the unprepared and calcined Magnetitum (Cishi). Apart from the Fe_3O_4 and α-SiO_2, the unprepared Magnetitum (Sheng Cishi) also contains Fe_2O_3. We assume that this is because of the exposure of the unprepared Magnetitum (Sheng Cishi) to open air for a long time, resulting in the gradual oxidation of the surface. After

Table 1 XRD three strongest lines of unprepared and calcined Magnetitum (Cishi)

Phases		α-SiO_2			Fe_2O_3			Fe_3O_4	
$d_{Std./(nm)}$	0.3343	0.4260	0.1817	0.2690	0.1690	0.2510	0.2532	0.1484	0.2967
$d_{Unprepared/(nm)}$	0.3343	0.4259	0.1817	0.2698	0.1694	0.2528	0.2528	0.1485	0.2967
$d_{Calcined/(nm)}$	0.3348	0.4255	0.1816	ND	ND	ND	0.2531	0.1484	0.2968

being processed in high temperature with vinegar, the unprepared Magnetitum (Sheng Cishi) was converted to calcined Magnetitum (Duan Cishi) and the main phase Fe_3O_4 remained, whereas Fe_2O_3 was dissolved and discarded. So the magnetism of the calcined Magnetitum (Duan Cishi) is stronger and the surface is more loosened. When used as decoction, dissolution of the effective elements is easier, and therefore it is more convenient for the trace elements to be absorbed by human body.

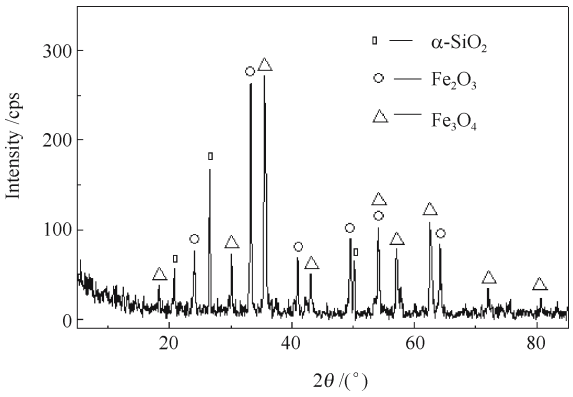

Fig. 3 XRD pattern of unprepared Cishi

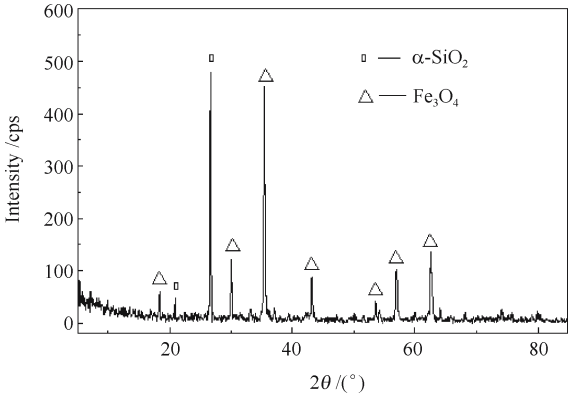

Fig. 4 XRD pattern of Duan Cishi

The mean crystal size of the unprepared and calcined Magnetitum (Cishi) calculated according to Scherrer equation is 24.5 and 35.7 nm, respectively. Obviously the crystal size of calcined Magnetitum (Duan Cishi) is larger. With the size value and density $\rho = 5.18\ g \cdot cm^{-3}$, the corresponding specific surface area of unprepared and calcined Magnetitum (Cishi) are also calculated. They are $4.73 \times 10^5\ cm^2 \cdot g^{-1}$ and $3.24 \times 10^5\ cm^2 \cdot g^{-1}$, respectively.

3.3 The comparison of the trace element between unprepared and calcined Magnetitum (Cishi)

From the results of ICP (Table 2), we can see that both unprepared and calcined Magnetitum (Cishi) contain the same trace elements beneficial for human health such as Zn, Co, Ni, Mn, Cr, Cu, Mo, but the content of harmful elements Cd and Pb are lower in the calcined Magnetitum (Duan Cishi) obviously and this result agrees with that of Chen and Zhen [7]. This is because some elements turn volatile compounds when processed at high temperature and on reaction with vinegar. In recent years, the studies [8,9] of trace elements involved in physiological mechanisms indicated that Fe can facilitate the formation of hematin and red blood cells in the human body, and can improve the function of central nervous system, sedation of activity and cessation of bleeding. Cu can accelerate absorbance and use of iron in body. Fe, Cu and Co cooperate in forming the plasma cell of the body. When unprepared Magnetitum (Sheng Cishi) was calcined, the content of Cd and Pb reduces as well as that of Cu and Co. Therefore the unprepared Magnetitum (Sheng Cishi)'s anti-anxious, grume is superior to the calcined Magnetitum (Duan Cishi). Zn is an important trace element in the human body involved in various physiological functions. It is the ingredient and the activating agent of many kinds of enzymes and directly participates in the synthesis of nucleic acids and the proteins and the organization metabolism, affects cell division and its regeneration; therefore Zn can accelerate the healing of the wound, skin inflammation etc. Fe, Cu and Mn are also involved in the above metabolism process, and they can more or less influence wound healing. These functions of these beneficial elements agree with the records of some Chinese drug books, such as Ben Cao Gang Mu and Yu Qiu Yao Jie [4,10].

Table 2 The contents of the nine trace elements of specimens

Trace elements	Zn	Cd	Pb	Co	Ni	Mn	Cr	Cu	Mo
Content / ($\mu g \cdot g^{-1}$) (Unprepared)	194	21.4	775	173	122	388	162	800	186
Content / ($\mu g \cdot g^{-1}$) (Calcined)	101	16.7	296	81.5	90.2	783	92.0	538	138

3.4 The TG curve difference of unprepared and calcined Magnetitum (Cishi)

Figure 5 shows the TG curves of unprepared and calcined Magnetitum (Cishi) in heating process. Obviously, the shape of their TG curves are different; unprepared Magnetitum

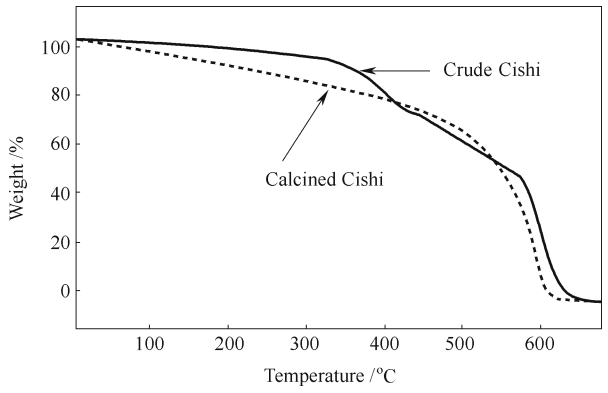

Fig. 5 TG curves of unprepared and calcined Magnetitum (Cishi)

(Sheng Cishi) in heating process has two reducing weight steps which are between 367.9–422.1°C and 568.8–594.1°C, but calcined Magnetitum (Duan Cishi) has only one. This indicates that the unprepared Magnetitum (Sheng Cishi) possibly contains impurity or volatile matter.

4 Conclusions

From the results above we conclude that both unprepared and calcined Magnetitum (Cishi) have Fe_3O_4, but the unprepared Magnetitum (Sheng Cishi) also contains Fe_2O_3. The crystal size of calcined Magnetitum (Duan Cishi) is larger and the specific surface area smaller. The surface of the unprepared Magnetitum (Sheng Cishi) is tight and hard, but the calcined Magnetitum (Duan Cishi) is smooth and loosened. The magnetism of the unprepared Magnetitum (Sheng Cishi) is weaker, while that of the calcined Magnetitum (Duan Cishi) is stronger. Both unprepared and calcined Magnetitum (Cishi) have the same trace elements beneficial to human health such as Zn, Co, Ni, Mn, Cr, Cu, Mo, but content of harmful elements Cd and Pb are lower obviously in the calcined Magnetitum (Duan Cishi). Their TG curves are different and the unprepared Magnetitum (Sheng Cishi) in heating process has two weight reducing steps, but calcined Magnetitum (Duan Cishi) has only one.

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