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Application of Raman spectroscopy in the nondestructive analyses of ancient Chinese jades

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Jade, as one of the symbols of Chinese material cultures, is the cultural boundary between ancient Chinese and western civilizations. Amphibole, serpentine, turquoise and quartz are the four main kinds of ancient Chinese jades. In this article, the use of Raman spectroscopy in the nondestructive identification of the four kinds of Chinese jades for their phase is discussed. The spectra, in combination with PIXE analysis, help resolve some relevant and further problems. Copyright © 2010 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: nondestructive analysis; Raman spectroscopy; ancient Chinese jades; amphibole jade; serpentine jade; turquoise jade; quartz jade

Introduction

Jade, lacquer, silk and porcelain are well known as the native products of China. Except porcelain, which was invented in the historic period, the other products which first appeared in prehistoric period are called 'the three great prehistoric creations' of China. Among these creations, jade artifacts containing rich cultural meanings are the most ancient. Hence, some Chinese scholars have proposed naming them as 'Jade Culture'. There are more than 20 countries or regions with large numbers of jade deposits all over the world. Jade had been used in the Mayan regions in South and Central America, the Indian regions in North America and the Maoris' regions in New Zealand throughout the ancient times,[1,2] whereas China is the only country with 8000 years of jade culture.[3] As unique treasures of a nation or a clan, jade artifacts had existed throughout the Neolithic and historic periods in China. Chinese jade artifacts are prominent in many aspects, such as materials, carving techniques, styles, decorations and functions. Therefore, Chinese jade culture is regarded as the symbol of Chinese tradition as well as an early divide between ancient Chinese and western civilizations.

In the recent decades, with a great number of ancient jade artifacts unearthed throughout China, jade culture has become an active field, which simultaneously has greatly improved China's status in academia and its social influence. Researchers on Chinese jade are present throughout East Asia because jade is produced and distributed throughout the region. Studies of these researchers include the forms, decorations, styles, functions, carving techniques, replication, appreciation and collection of jade artifacts. Since the 1980s, a number of Chinese scientists, especially geologists, have gradually brought new trends into this field, which started the combination of art and scientific studies on ancient Chinese jade. In general, research on ancient Chinese jade includes three aspects: (1) identification of jade, including its physical properties, mineral and chemical compositions and microstructures; (2) sources of raw materials; and (3) secondary alterations of ancient jade. Identification is the most important part of the basic research on ancient Chinese jade[4] and owing to the precious nature of ancient jade, a nondestructive analytical technique is essential for identification purposes. Raman spectroscopy is now believed to be quite effective for phase analysis of ancient jade but has still not been widely applied in China. It is already known that more than 20 kinds of jade were used in ancient China. The jade artifacts made from tremolite (e.g. the nephrite), serpentine (e.g. Xiuyu), turquoise or quartz are so many that these minerals are regarded as the four main traditional Chinese jades. Some scholars, such as Shurvell *et al.*,[5] Chen *et al.*[6] and Casadio *et al.*,[7] have already researched on the ancient nephrite jades of China by Raman spectroscopy. This paper reports the identification of the four types of Chinese traditional jades with Raman spectroscopy and discusses some relevant and further problems.

Experimental Equipments and Testing Conditions

Because of the rarity of ancient jade artifacts, nondestructive methods are chosen in these experiments: Raman spectroscopy was used for phase analysis, while particle induced X-ray emission (PIXE) was used for chemical composition analysis.

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Raman spectroscopic analysis was carried out at the Laboratory of Advanced Materials, Fudan University. The laser Raman spectrometer used was a Renishaw Invia Reflex instrument. It was equipped with three wavelengths for excitation: 514.5 nm, 20 mW, argon ion laser; 632.8 nm, 17 mW, helium–neon laser; and 785 nm, 300, mW semiconductor laser. A 20× objective lens was commonly used.

PIXE is a complementary experiment that was carried out using the external beam PIXE technique on the tandem accelerator NEC9SDH-2 at the Modern Physics Institute, Fudan University. The samples exposed in air can be tested directly for determination of chemical compositions as well as the types and contents of microelements without any limits on the size or shape of the samples. The proton beam spot is about 1 mm in diameter. The beam intensity is adjusted to 0.05 nA for measuring the major elements. But when microelements are tested, the intensity of the beam is increased to 0.5 nA in order to improve the yield of X-rays.

Analysis and Discussion

Amphibole jade (tremolite–actinolite series)

Analysis of modern samples

The tremolite–actinolite series is a member of the amphibole group of silicate minerals with a double-chain structure composed of SiO_4 tetrahedra. Its chemical formula is $Ca_2(Fe,Mg)_5Si_8O_{22}(OH)_2$, and Mg and Fe show isomorphism in nature. One can distinguish tremolite from actinolite on the basis of the ratio of Mg/(Mg + Fe). For example, tremolite is characterized by an Mg/(Mg + Fe) ratio $\geq$0.90, while actinolite is characterized by a ratio in the range 0.50–0.90. Tremolite or actinolite with a fibrous interlaced microstructure is known as 'amphibole' jade[8] or by other names such as 'nephrite' or 'Hetian jade'. Nephrite has been the most important material used for jade artifacts in both ancient and modern China. Nephrite artifacts unearthed in high quantity and quality constitute the major part of ancient Chinese jade culture. In this research, two selected modern samples were analyzed by Raman spectroscopy. The white sample came from the Heishan mining area at Hetian County in Xinjiang Province, and the dark green sample was from the Huangtaizi mining area at Manasi County in Xinjiang Province. Figures S1 and 1 show the morphologies and test results of the two samples, respectively. The minimum scale is 1 mm.

In Figs. S1 and 1, the curves show the vibrations of the silicon–oxygen bond, metal–oxygen bond and lattice in the 100–1100 cm^{-1} range. Specifically, the bands at 1030 and 1059 cm^{-1} reveal the antisymmetric stretching vibrations of the $Si–O_b–Si$; the band at 930 cm^{-1} is due to the symmetric stretching mode of the O–SiO-linkages, that at 674 cm^{-1} corresponds to the symmetric stretching vibrations of $Si-O_b–Si$ bridges and that at 223 cm^{-1} indicates the vibrations of the O–H–O groups. In the <650 cm^{-1} spectral region, except for 223 cm^{-1}, the assignment of the observed bands is problematic because of the coupling of the vibrations of the MO_6 and MO_8 polyhedra (M: cations in octahedral or cubic sites) to the deformation modes of the $(Si_4O_{11})_\infty$ ribbons and to the F–O bonds.[9,10] The 3600–3700 cm^{-1} range reflects the stretching vibration of OH^-. Fe^{2+} and Mg^{2+} linked to OH^- occupy three positions at M1, M2 and M3 in the sequence as A(Mg, Mg, Mg), B(Mg, Mg, Fe), C(Mg, Fe, Fe) and D(Fe, Fe, Fe). Generally speaking, the band due to the OH stretching vibration presents one peak when the Fe^{2+} content is very small, whereas two to four peaks will appear with increasing Fe^{2+} content. Huang[11] has claimed that when $Mg/(Mg + Fe^{2+}) \times 100\% > 95.8\%$, there is only one vibration mode (at 3675 cm^{-1}, corresponding to A, expressed as 3675 cm^{-1} – A), two vibrational modes appear when the ratio is 92.3–93.8% (3675 cm^{-1} – A, 3662 cm^{-1} – B) and three vibration modes are present when $Mg/(Mg + Fe^{2+}) \times 100\% < 92.3\%$ (3675 cm^{-1} – A, 3662 cm^{-1} – B, 3645 cm^{-1} – C). As Fig. 1 shows, the Raman spectrum of the white amphibole sample has a single peak at 3675 cm^{-1}, while that of the dark green sample has three peaks at 3675, 3662 and 3645 cm^{-1}. The PIXE results of the two samples are shown in Table 1. On the basis of the 23 oxygen atoms, the occupying ratio of Fe and Mg in the white amphibole is $Mg/(Mg + Fe^{2+}) \times 100\% = 4.745/(4.745 + 0.025) \times 100\% = 99.5\%$ (The result is from the calculations using the crystal chemical formula; according to the PIXE results, the total number of oxygen atoms in the sample is 2.911, so that the cation number of Mg is $(24.02/40) \times 23/2.911 = 4.745$, and that of Fe is $(0.23/72) \times 23/2.911 = 0.025$.) with one vibration peak, which indicates that it is a kind of tremolite. The cation ratio of the dark green amphibole is $Mg/(Mg + Fe^{2+}) \times 100\% = 4.278/(4.278 + 0.701) \times 100\% = 85.9\%$ with three vibration peaks, which implies that it belongs to the actinolite type. The results are consistent with those of previous studies. A black jade dagger axe tested by Chen *et al*.[6] shows $Mg/(Mg + Fe^{2+}) \times 100\% = 72.4\%$ with four vibration peaks (3675, 3662, 3645, and 3626 cm^{-1} – D) in the range between 3600 and 3700 cm^{-1}. To sum up, important information can be acquired from the Raman spectrum to distinguish tremolite from actinolite, according to the number and location of vibrational peaks in the 3600–3700 cm^{-1} range.

Analysis and discussion of ancient Chinese jade

As seen in Fig. S2, 82QXM117 : 7 and 97WHT2503③:2, which are two incomplete jade rings unearthed from the Huangjiayan site at Wangjiang County, Anhui Province, are the jade artifacts of the Xuejiagang Culture (3500–2600 B.C.). Comparing Fig. 2 to Fig. 1, it can be concluded that both rings are made from tremolite because there is a single vibration peak in the 3600–3700 cm^{-1} region. The result of PIXE analysis is shown in Table 2; based on the 23 oxygen atoms, the cation ratio of 82QXM117 : 7 is $Mg/(Mg + Fe^{2+}) \times 100\% = 4.666/(4.666 + 0.184) \times 100\% = 96.2\%$, that of the outer layer of 97WHT2503③:2 is $Mg/(Mg + Fe^{2+}) \times 100\% = 4.833/(4.833 + 0.170) \times 100\% = 96.6\%$ and that of the inner layer of 97WHT2503③:2 is $Mg/(Mg + Fe^{2+}) \times 100\% = 4.723/(4.723 + 0.182) \times 100\% = 96.3\%$. This result is quite comparable to the curves in Fig. 2. In addition, 97WHT2503③:2 had been weathered during burial for such a long time that it shows a white color with very loose structure. Raman spectroscopy and PIXE analysis of the inner layer indicate that this sample is still made of tremolite, with no phase change. It can be concluded that the weathering process had little impact on the phase of the ancient jade.

Serpentine jade

Analysis of modern sample

Serpentine is a kind of silicate mineral with a layer structure constituted by SiO_4 tetrahedra and MgO octahedra. Its chemical formula is $Mg_6(Si_4O_{10})(OH)_8$. Serpentine is thought to be one of the earliest jades recognized and utilized by humans. In China, a great number of serpentine jade artifacts have been excavated from Neolithic sites that are 7000 years old. Xiuyan

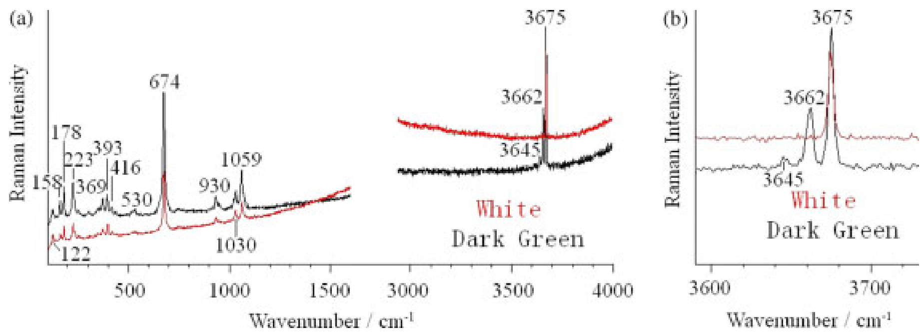

Figure 1. (a) Raman spectra of the two samples; (b) enlargement of the 3600–3700 cm^{-1} region.

Table 1. PIXE results of amphibole (tremolite, actinolite) jades

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Cr_2O_3	MnO	FeO	CoO	NiO	ZnO	Sum
white	0.48	24.02	1.36	60.51	0.29	0.21	12.80	0.00	0.05	0.02	0.23	0.00	0.02	0.00	99.99
Dark green	0.49	20.89	1.25	57.22	0.32	0.38	12.50	0.03	0.18	0.17	6.16	0.05	0.23	0.04	99.91

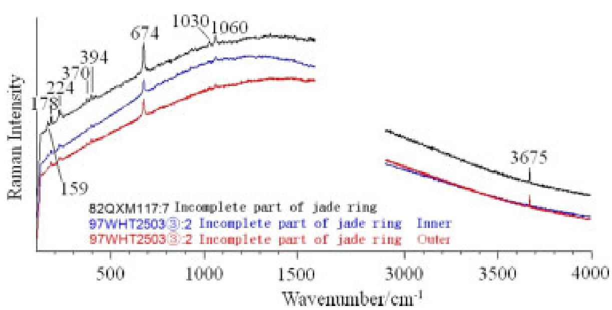

Figure 2. Raman spectra of ancient amphibole (tremolite) jades.

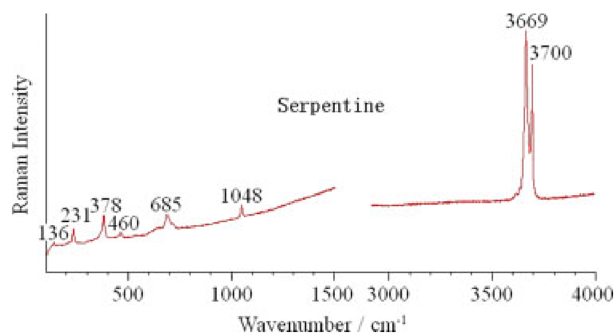

Figure 3. Raman spectrum of a modern serpentine sample.

County in Liaoning Province is not only an important area of tremolite minerals but also a source of serpentine minerals. The sample studied here is from this area. Figures S3 and 3 show the morphology and test results of the sample, respectively.

The peaks in the 3600–3700 cm^{-1} region reveal the stretching vibrations of M–OH; the peak at 3700 cm^{-1} indicates the stretching vibration of Fe–OH (Fe takes the place of Mg) and the peak at 3669 cm^{-1} suggests the stretching vibration of Mg–OH. The peak at 1048 cm^{-1} is attributed to the antisymmetric stretching vibrations of the $Si–O_b–Si$ groups, which also shows that this sample is made from antigorite. The peak at 685 cm^{-1} reflects the symmetric stretching vibrations of $Si–O_b–Si$, while that at 378 cm^{-1} implies the symmetric bending vibrations of the SiO_4 tetrahedra. The peak at 231 cm^{-1} is due to the vibrations of O–H–O groups,[12] and the peak at 460 cm^{-1} is produced by the translational vibrations of Mg–OH and the vibrations of SiO_4.[13]

Analysis and discussion of ancient artifacts

As shown in Fig. S4, M103 : 2-1, M103 : 2-2 and M103 : 2–3 are three jade tubes unearthed from the Xuejiagang site (3500–2600 B.C.) located at Xuejiagang village, Wanghe town, Qianshan County in Anhui Province. These jade artifacts are in ivory white with homogeneous quality and some yellow weathering spots. The researchers often considered them to be of the same type – tremolite jade – because they have similar appearance and color. The Raman spectra of these ancient artifacts are shown in Fig. 4.

The Raman spectra of M103 : 2-1 and M103 : 2–3 display strong consistency, and the peaks at 230, 380 and 686 cm^{-1}, which are the distinguishing peaks of serpentine, so M103 : 2-1 and M103 : 2–3 are determined to be serpentine jades. The peaks of M103 : 2-2 are at 227, 391, 674, 1028 and 1060 cm^{-1}, which are the characteristic peaks of tremolite; thus M103 : 2-2 is identified as a tremolite jade.

Table 2. PIXE results of ancient amphibole (tremolite) jades

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO	CoO	ZnO	Sum
82QXM117:7	1.31	23.30	1.95	58.49	0.01	0.02	13.08	0.06	0.07	1.65	0.04	0.03	100.01
97WHT2503③:2-outer	2.79	24.05	2.36	57.25	0.28	0.10	11.40	0.00	0.07	1.52	0.03	0.03	99.88
97WHT2503③:2-inner	1.42	23.77	2.50	59.37	0.12	0.13	10.82	0.05	0.02	1.65	0.04	0.04	99.93

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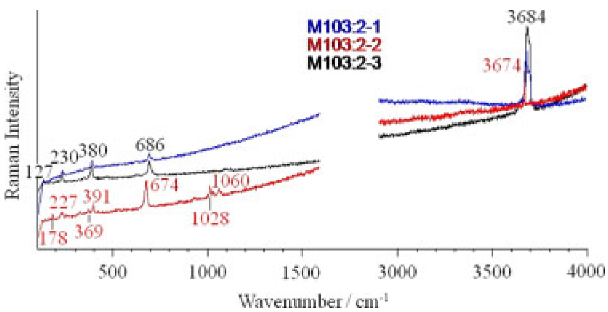

Figure 4. Raman spectra of the ancient artifacts.

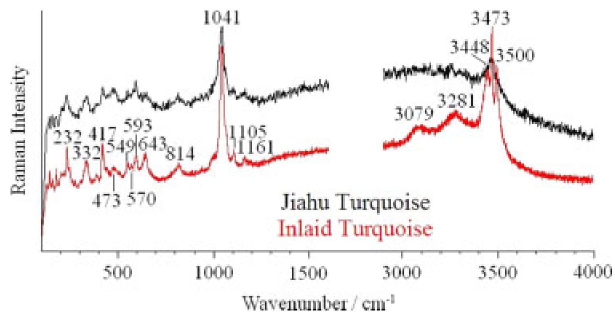

Figure 5. Raman spectra of ancient turquoise jades.

Because of the obvious differences in color, transparency and density between fresh tremolite and serpentine, it is quite easy to distinguish them by visual examination. However, owing to the long burial process, the two kinds of jade from the Neolithic sites in southern China present similar appearances. Thus, visual examination tends to be unreliable when recording the number and types of the jade artifacts from archaeological sites.

Turquoise jade

Turquoise is a kind of hydrated copper-aluminum phosphate mineral. Its chemical formula is $CuAl_6[PO_4]_4[OH]_8 \cdot 5H_2O$. The major turquoise-producing countries include China, Iran, Egypt, the United States and Chile. Some provinces in China have turquoise mines, such as Hubei, Shannxi, Henan, Anhui, Yunnan and Xinjiang. Hubei is known as 'the town of oriental turquoise', where turquoise of very high quality is produced. As the mines of turquoise are distributed widely, this mineral was used as jade by the ancient people in the Neolithic age. According to the current archaeological findings, the earliest turquoise artifacts were found in the Peiligang site at Xinzheng County in Henan Province dated back 7500 to 8200 years, including a square-shaped pendant and two beads.[14] A large number of ancient turquoise artifacts have been unearthed all over China. Thus, turquoise is regarded as the traditional and famous jade and deeply cherished by Chinese people. Nowadays, turquoise is still one of the favorite precious stones in the Middle East, Europe, western United States, Tibet, etc.

A number of turquoise jades were excavated from the Jiahu site (7000–5800 B.C.), Wuyang County, Henan Province. For these valuable and ancient samples, nondestructive analytical techniques such as X-ray diffraction (XRD) and Raman spectroscopy are preferable. Under the microscope, it is observed that some dark gray inclusions are present in the turquoise jades.[15] Therefore, the micro-technique of Raman spectroscopy is quite suitable for avoiding those inclusions and identifying the turquoise. One piece of turquoise artifact was chosen to be tested using Raman spectroscopy and PIXE analysis. Its morphology, Raman spectrum and PIXE result are shown in Figs. S5 and 5 and Table 3, respectively.

The process of embedding the point-like or sheet of jade into the same or different materials to decorate or to enhance the aesthetic value is called jade inlaying. Turquoise has been used as inlay material for a long time in China. For example, a caved bone cup inlaid with a round turquoise unearthed from one site of Dawenkou Culture (4300–2600 B.C.) at Taian County, Shandong Province, is one of the earliest evidence of turquoise inlaying.[16] Since then, turquoise was widely used as inlaying material on bone, bronze and iron artifacts. The turquoise inlaid in a bronze sword guard of the Warring States period (475–221 B.C.) was chosen for Raman spectroscopy and PIXE analysis. The morphology and Raman spectrum are shown in Figs S5 and 5, and the result of the PIXE analysis is listed in Table 3.

The three bands observed at 3500, 3473, and 3448 cm^{-1} indicate the OH stretching vibrations of the hydroxyl units, and those at 3500 and 3448 cm^{-1} are the secondary peaks of 3473 cm^{-1}. The broad peaks at 3281 and 3079 cm^{-1} are attributed to OH stretching vibrations of H_2O. Antisymmetric stretching vibrations of PO_4 result in the strong peak at 1041 cm^{-1} and two small peaks at 1161 and 1105 cm^{-1}. The peak at 814 cm^{-1} is attributed to the vibrations of H_2O. Antisymmetric bending vibrations of PO_4 result in the peaks at 643, 593, 570 and 549 cm^{-1}. Symmetric bending vibrations of PO_4 are at 473 and 417 cm^{-1}. The peaks at 332 and 232 cm^{-1} may be assigned to the stretching vibrations of Cu–O.[17]

As shown in the Table 3, the result of PIXE analysis of the inlaid turquoise in the bronze sword is quite close to the theoretical value, which indicates that the tested area is little disturbed by the surrounding rock wall. While Jiahu turquoise has a relatively high value of SiO_2, it can be explained by the fact that its PIXE analysis could not avoid the region of the rock wall, which is mainly composed of quartz.

Cryptocrystalline quartz jade

In the Paleolithic age, the ancestors preferred stones with relatively high hardness and toughness as the raw materials for artifacts, with Mohs hardness of more than 6 and that did not easily crack. Because of the wide distribution and large quantity of the quartz and quartzite in China, most ancestors would have preferred this kind of materials. According to the size of the particles, the quartz jades are divided into two types: (1) phanerocrystalline quartz jade, such as the crystals and (2) cryptocrystalline quartz jade, including agate, chalcedony, jasperite, and so on. These materials have similar luster and color, which makes them 'beautiful stones'. In terms of the archaeological findings, both these types have been widely used for a long time. In the early Neolithic Age, quartz was usually used for ornaments. Since then, quartz has been made less into stone tools. Indeed, it was more often categorized as a kind of jade in the early period. Particularly, agate (including chalcedony), also attributed to quartz, is one of the four traditional kinds of Chinese jades.

Analysis of modern samples

A number of modern samples were selected for the examination: Item 33, quartz, from Changhua City, Zhejiang Province; Item 35, crystal, from Donghai County, Jiangsu Province; Item 38, chalcedony, from Huzhou City, Zhejiang Province; Item 39, agate, from Lingyuan County, Liaoning Province; Item 42, jasperite, from

Table 3. PIXE results of ancient turquoise jades

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Cr_2O_3	Fe_2O_3	CoO	NiO	CuO	ZnO
Jiahu turquoise	1.42	1.54	37.46	23.01	21.11	0.11	0.32	0.05	0.13	6.04	0.02	0.00	7.82	0.74
Jiahu turquoise (Wall rock)	0.89	1.30	40.69	53.38	1.25	0.19	0.25	0.32	0.35	0.00	1.22	0.00	0.03	0.09
Inlaid turquoise	1.96	0.35	46.27	0.66	37.44	0.10	0.02	0.01	0.00	0.93	0.02	0.01	9.03	3.19

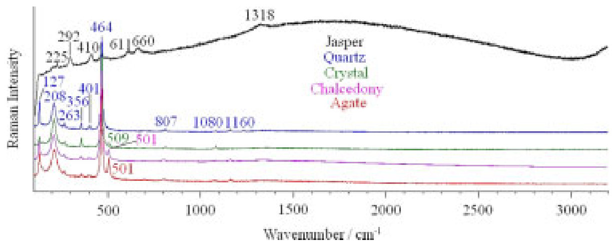

Figure 6. Raman spectra of modern quartz samples.

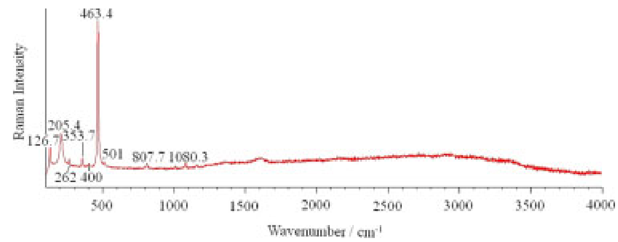

Figure 7. Raman spectrum of 97WHT2603 M51:1.

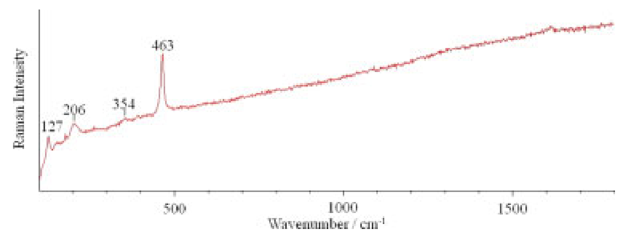

Figure 8. Raman spectrum of M264S1.

Huzhou City, Zhejiang Province. Figures S6 and 6 and Table 4 present the morphologies, Raman spectra and the PIXE results of these samples, respectively.

Figure 6 and Table 4 indicate that the main composition of these quartz jade artifacts is SiO_2. In the Raman spectrum of jasperite, the peaks at 127 and 464 cm^{-1} are the characteristic of quartz, while the other peaks at 225, 292, 410, 611, 660 and 1318 cm^{-1} are characteristic of hematite,[18,19] which indicates that jasperite is composed of quartz and hematite. On the basis of the peak at 410 cm^{-1}, it can be estimated that a small number of Fe atoms in hematite may be substituted by Al atoms, as seen from the peak shift from 410 to 405 cm^{-1} with increasing Al content of hematite from 0 to 20%.[20] The Raman spectrums of quartz, quartz crystal, agate and chalcedony are fairly comparable, except that the crystal, agate and chalcedony present one Raman peak within the range of 500–510 cm^{-1} while the quartz does not show any. The peak of the crystal is around 509 cm^{-1}, while the peak of agate or chalcedony is around 501 cm^{-1}. It is known that the agate and chalcedony have the same mineral and chemical composition, except that agate has some ribbon figures. The peaks at 1080 and 1160 cm^{-1} in the 1000–1200 cm^{-1} range are attributed to the antisymmetric stretching vibrations of Si–O, the peak at 807 cm^{-1} in the 600–900 cm^{-1} region indicates the symmetric stretching vibrations of Si–O, the peaks at 464, 401 and 356 cm^{-1} in the 300–600 cm^{-1} range are due to the bending vibrations of Si–O and the peaks at 208 and 263 cm^{-1} in the region between 200 and 300 cm^{-1} can be attributed to the rotary vibrations or the translational vibrations of SiO_4. It is worth noting that the peaks at 501 cm^{-1} of agate and chalcedony are not due to the bending vibrations of Si–O in α-quartz but to the symmetric bending vibrations of Si–O in 'moganite' quartz, which belongs to the monoclinic polycrystalline quartz group. Moganite quartz often exists in agate and chalcedony.[21] The 509 cm^{-1} peak of crystal belongs to a kind of quartz variant, which might be generated during the transformation from α-quartz to certain low symmetry variants.[22]

Analysis and discussion of ancient artifacts

As shown in Fig. S7, 97WHT2603 M51 : 1, an incomplete jade ring, was unearthed from the Huangjiayan site (3500–2600 B.C.) at Wangjiang County, Anhui Province, dated to *ca* 5000 B.P. The PIXE results in Table 5 suggest that its main composition is SiO_2, while the Raman spectrum (Fig. 7) further establishes the material as quartz. The peak at 501 cm^{-1} and the absence of ribbon structure also show that 97WHT2603 M51 : 1 is made of chalcedony.

M264S1 (Fig. S8), excavated from the cemetery of Ying State in Pingdingshan City, Henan Province, is dated to the Middle and Late Western Zhou Dynasty (*ca* 8th–10th century B.C.). In terms of the shapes inside and outside, M264S1 might be a tube with serious weathering, and it cannot be classified as quartz by visual

Table 4. PIXE results of modern quartz samples

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO	MnO	Fe_2O_3	Sum
33 Quartz	0.00	0.80	1.16	97.99	0.00	0.00	0.00	0.05	0.00	0.00	100
35 Quartz crystal	0.41	0.19	1.10	97.46	0.17	0.15	0.11	0.00	0.00	0.00	99.59
38 Chalcedony	1.92	1.43	1.82	94.48	0.00	0.06	0.00	0.00	0.07	0.21	99.99
39 Agate	1.88	0.40	1.46	95.55	0.32	0.00	0.03	0.00	0.00	0.00	99.64
42 Jasperite	1.32	0.87	2.85	91.16	0.90	0.20	0.18	0.00	0.00	2.40	99.88

Table 5. PIXE result of 97WHT2603 M51 : 1

	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	FeO
97WHT2603 M51 : 1	1.02	1.01	96.85	0.45	0.41	0.13

Table 6. PIXE results of faience of the middle and the late Western Zhou Dynasty

Number	Era	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	Cl	K_2O	CaO	TiO_2	Cr_2O_3	Fe_2O_3	CuO	ZnO
HNWK③-67	Mid-Western Zhou Dynasty	1.38	0.68	1.26	92.98	0.47	0.00	0.51	0.30	0.04	0.02	0.31	2.06	0.00
HNZZ-23	Late Western Zhou Dynasty	0.61	0.14	1.39	92.2	1.24	0.07	1.73	0.39	0.11	0.00	0.12	1.93	0.03

examination. It is observed that there are some brown attachments both inside and outside and some areas in light blue-green. Under a stereomicroscope, it can be found that the grain size is relatively large and the structure is very loose. The Raman spectrum (Fig. 8) reveals that the M264S1 is made of quartz. The quartz is so stable that all the quartz implements in archaeological records are well preserved without any weathering. Gan and Dong[23] claimed that the dozens of artifacts from the cemetery of Ying State are faiences (the predecessor of Chinese ancient glasses), which fired under 700–800 °C. The result of PIXE analysis is shown in Table 6, which indicates that the faience in that period might have been formed by pure quartz and a small quantity of slag of bronze smelting at 700–800 °C. The slag is rich in Cu, so that the faiences display green color as shown in the right panel of Fig. S8.

Conclusions

Nondestructive analysis is one of the basic principles in antiquity or heritage studies. Raman spectroscopy is eminently applicable for analyzing the phase structure of ancient artifacts, since it has a number of advantages such as non-contact implementation, short detection time, and very little sample preparation. As one of the important symbols of Chinese traditional culture, jade is the earliest boundary between Chinese and western cultures. Amphibole, serpentine, turquoise and quartz are four main materials of ancient Chinese jade. Their phase or material can be well identified by Raman spectroscopy, especially for the amphibole jade, in order to differentiate whether it belongs to tremolite jade or actinolite jade by the number and location of vibrational peaks within the range of 3600–3700 cm^{-1}. The peaks in Raman spectra correspond to the stretching or bending vibrations of different chemical bonds. Combined with component analysis methods such as PIXE, some related issues, particularly the special phenomena caused by weathering processes during burial, have been discussed in depth.

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Supporting information

Supporting information may be found in the online version of this article.

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