PIXE AND IXX ANALYSIS OF MUSEUM PAPER–LIKE OBJECTS

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ABSTRACT

The study of paper damage under bombardments of protons and X–rays is reported. An on–demand beam pulsing system is useful for the PIXE analysis of delicate objects. IXX (or PIXE–induced XRF) is more suitable than PIXE in terms of damage to the sample. Some new PIXE and IXX applications of archaeological paper–like samples in recent years are given.

Keywords PIXE, IXX, Paper–like object, Ancient Chinese painting, Ancient paper money

1 INTRODUCTION

In 1988, a 6SDH–2 tandem accelerator was employed in the laboratory of Palais du Louvre to study antiquities and art works with ion beam analysis (IBA) techniques, an important tool for art and archaeological investigations. Particle induced X–ray emission (PIXE), as an important IBA technique, has been widely applied by scientists and archaeologists to analyze museum objects with its advantages of high sensitivity, rapidity, nondestructiveness, simultaneous multielement analysis[1]. Since the early PIXE study of the famous ancient swords of Goujian (~ 600 B.C.) in 1978[2], archaeological application has become an important subject of research programmes in the Accelerator Laboratory of Fudan.

Oberviously, nondestructiveness is of vital importance to PIXE analysis of art and archaeological objects. Usually, much of these objects is made of ceramics, metals, siliceous materials or gemstones[3], to which almost no damage can occur during PIXE analysis due to the firmness of their atomic structure. For delicate objects, *e.g.* documents, stamps, paintings and other paper–like or organic samples, there is hardly guarantee of nondestructiveness. The possible damage effects *e.g.* visible color changes, obvious fragility must be treated with great care in the analysis of precious

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paper-like objects. Thanks to the earliest study and some successful applications by Cahill's group at Davis[4-9], PIXE analysis of museum paper-like objects has attracted more and more attention in many laboratories.

Based on previous work of archaeological applications[2,10], the analysis of paper-like sample has been performed by the PIXE group at Fudan. An improved on-demand beam pulsing system was built in 1986[11,12] on which many types of paper, paintings, and printed materials were analysed. The heat and radiation damage to paper have been systematically studied, especially on the latter[13]. It was found that both low beam current density and low total beam fluence are essential to PIXE analysis of precious irreplaceable paper-like objects[13].

In addition, X-rays were used as exciting source which causes less damage than MeV protons by orders of magnitude. A new IXX (or PIXE-induced XRF) system was built in 1989, and improved on a 2× 3MV tandem in 1990[14]. Both in principle and practice, IXX is more suitable for heat-sensitive and delicate specimens, and it can be used as a complementary technique of PIXE in many aspects. By using external PIXE with on-demand pulsing and the IXX system, many museum paper-like samples have been analyzed in recent years, such as ancient documents, Chinese paintings and paper money. Some examples are reported here.

2 DAMAGE OF PAPER-LIKE OBJECTS UNDER IRRADIATION

2.1 Heat and radiation damage

During X-ray fluorescence analysis (XRF), it is inescapable to cause certain damage to the sample no matter what kind of exciting projectiles is adopted, such as electrons, ions or photons. In general, there are two mechanisms of damage, *i.e.* the heat and radiation damage.

The heat damage is due to the temperature rise of samples which is determined by the energy balance between the energy deposit of incident projectiles and the heat removal. Obviously low irradiation intensity and cooling can reduce the temperature rise and the heat damage may be negligible under certain conditions. According to C J Sparks[15], the ratio between energy deposits in a sample by protons and X-rays is about 10^2—10^7 with regard to same minimum detection limit. The more heat-sensitive specimens is the greater ratio will be.

The radiation damage, including sputtering, element migration and atomic displacement, is directly caused by the bombardments of projectiles. The atomic displacement, which is the major contributor to the damage and is also called Frenkel pair radiation damage, takes place when an atom gains enough recoil energy to free from the binding of surrounding atoms[16,17]. Photons do not have enough momentum to cause such a damage. Electrons of greater than 100keV cause Frenkel damage in carbon matrix. Therefore, the radiation damage caused by photons is negligible, compared with damage by ions. For hard solid or crystalline objects the displacement damage is not complete until the proton fluence reaches about $10^{20}cm^{-2}$. So the maximum limitation of incident proton fluence for nondestructive PIXE analysis is generally 10^{17}—$10^{18}cm^{-2}$, *i.e.* 0.016—0.16 C/cm^2, which is more than enough for routine analysis. For delicate objects, however, especially organic matter including paper-like objects, the limitation will drop many orders of magnitude because of their unstable chemical property.

To summarize, the nondestructiveness of XRF using an ion or X-ray exciting source is true only under certain conditions, especially for the delicate objects. Not only for heat but also for radiation damage, the deterioration of sample property caused by ions is much more serious than that by X-rays.

2.2 Damage of paper

Paper is one of the four great inventions in ancient China and has been used for about two thousand years. Innumerable ancient and modern paper-like objects including documents, books and paintings have been recording the history of human civilizations[18].

Paper is usually made of plants such as wood, bamboo, hemp and bark. Its essential component is cellulose, $(C_6H_{10}O_5)_n$[18]. This structure of glucose radical determines the instability of chemical properties and fragility of paper. Under irradiation the molecular chains will easily be broken, leading to color changes and mechanical performance degradation of paper.

Several types of modern paper were bombarded by protons or X-rays to observe the damages of the paper specimens, the following three are of typical interest, Xuan paper (~28 g/m^2), which is composed mainly of pure natural cellulose and has been used for traditional Chinese painting and calligraphy since the Tang Dynasty (618—907 A.D.); art paper (90—105 g/m^2) which contains a large amount of chemical additives and is normally used for pictures and magazines in modern times; and white tissue (~ 11g/m^2), which contains both natural cellulose and a small amount of chemical additives.

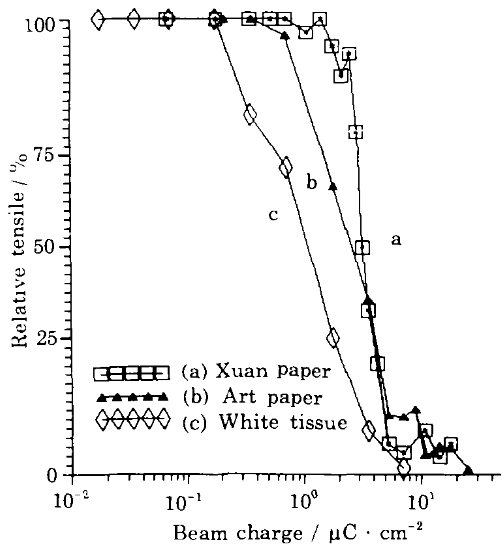

Fig.1 Change of paper tensile strength with beam fluence

Paper discoloration and tensile strength degradation under 2.1MeV proton bombardment of low beam current density ($< 10nA/cm^2$) were tested as a function of the proton numbers. The target temperature rise which was measured by a digital infrared thermometer was less than 5°C, so that the heat damage was negligible. The experimental results show that the paper deterioration depends only on the total beam fluence. Fig.1 shows the degradation of paper tensile strength of the three types of paper versus the beam fluence.

Each type of the paper samples has maximum limit of beam fluence. For Xuan paper, the limit is 0.4—0.6 $\mu C/cm^2$, which is orders of magnitude lower than the common value ($\sim 0.1\ C/cm^2$) for crystalline objects. It was found that purer natural cellulose was less likely to be damaged, as the chemical additives were much more easily destroyed than cellulose[13].

However, there was no visible damage of Xuan paper after being irradiated by 4.5keV X-rays on the IXX system with a dose of up to 10^{16} photons/cm^2, which was more than enough for obtaining the minimum detection limit of 0.1ppm. X-rays are consequently more suitable for the analysis of paper-like samples as well as other organic biological samples.

3 EXPERIMENTAL SYSTEMS

3.1 External PIXE and on-demand pulsing system

The on-demand beam pulsing system was built on the external beam PIXE system at Fudan[11]. The technique not only alleviates pulse pile-up to a great extent, but also minimizes irradiation induced target damage. By introducing a fast pile-up rejection path with a fast pile-up inspector (FPI), the pulse pile-up interval of the on-demand system was improved to about 90ns, which is one third of its previous value[12]. The block diagram of this improved system is shown in Fig.2. The other improvements include better monitoring of the external proton beam by RBS and the availability of the beam spot size on targets using a diffusing foil and variable collimators. These help a lot in our archaeological applications.

3.2 IXX system

As a small-accelerator-based X-ray fluorescence technique, IXX has been gradually used to make up the drawbacks of PIXE since the first experiment was done in 1978[19—23]. It eliminates the spectral interferences from major matrix elements and significantly suppresses the background by selecting the proper primary target. Because of its nondestructiveness, it is more suitable for the analysis of heat-sensitive and delicate specimens.

On the basis of our previous work, an improved IXX system was built on a 2× 3MV tandem accelerator in 1990. The experimental arrangement is shown in Fig.3. The transmission geometry, rather than a reflection one, is more compact and gives a large solid angle of irradiation and detection. The primary targets are pure metal foil (tens of microns thick) stuck on the exit window with strong vacuum glue. In addition to protons, some light ions have been employed, such as helium, lithium and silicon ions. By repeated improvement of experimental conditions, such as increasing the solid angle of irradiation and detection as well as choosing the optimum ion species and energy, minimum detection limit of sub-ppm level has been achieved for either thin or thick target when an X-ray fluence of the order of 10^{11}—10^{13} was obtained.

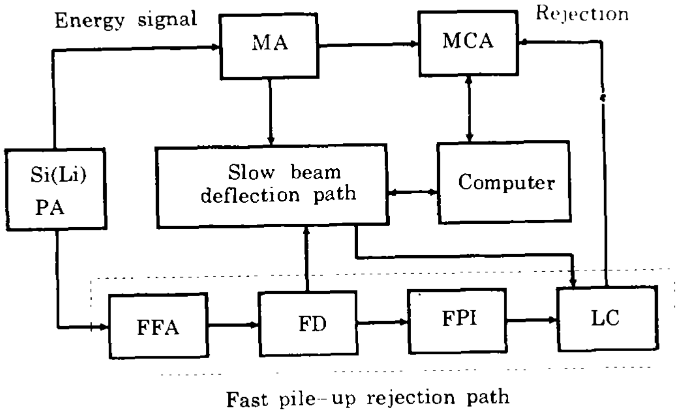

Fig.2 Block diagram of the on—demand beam pulsing system with a fast pile—up rejection path

PA— Preamplifier, MA— Main amplifier, MCA— Multichannel analyser, FFA— Fast filter amplifier, FD— fast discriminator, FPI—Fast pile-up inspector, LC—Logic circuits

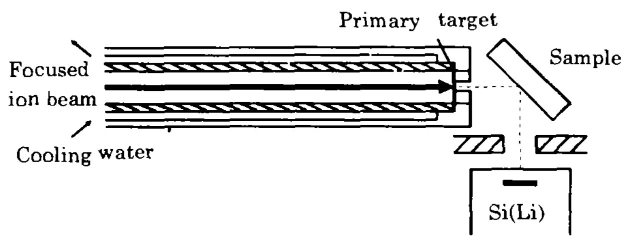

Fig.3 The arrangement of IXX analysis

It is indicated that IXX is complementary to PIXE in many aspects. Details of the IXX system was reported elsewhere[24].

4 APPLICATIONS

4.1 Analysis of ancient Chinese paintings

In almost all Chinese history and art museums the traditional experience is usually the major analytical method for the study and authentication of ancient Chinese paintings. The PIXE analysis of ancient traditional Chinese paintings at

Fudan began in 1987.

To print painter's or collector's seals on a painting is peculiar for traditional Chinese painting in the world; they are normally red or orange marks. Seal is the designation or fingerprint of a painting, which is very important for the study and authentication of ancient paintings. The seal ink is a kind of paste usually made of cinnabar (HgS), moxa, castor oil, *etc*. The analysis of its elemental composition by PIXE and IXX can provide some new information and evidence to the authentication of the painting. Sometimes it can distinguish directly whether a painting is fake or real.

Besed on the analysis of various papers, seal ink pastes and pigments, a lot of traditional Chinese paintings of Ming and Qing Dynasties have been analysed by PIXE or IXX, including the paintings of Badashanren and Qian Zai. Major target of the analysis is the seal ink, the finger-print of which may well be the concentrational ratios between its elemental compositions.

Fig.4 "Taoshi Shuangqin" of Badashanren's painting analysed (a) and two red seals on this painting (b)

Table 1

The comparison of the peak area ratio Hg/Zn of two seals: "Kedeshengxian" and "Badashanren", on two paintings A and B of Badashanren

Painting		Hg (*L*)/ Zn (*K*) A	B
Seal	Ke.	33	46
	Ba.	32	38

4.1.1 Paintings of Ming Dynasty

Badashanren (1626—1705 A.D.), one of the most famous Chinese painters, is addressed respectfully the great master of painting not only in China but also in the international painting world. His innovation and development on freehand brushwork of traditional Chinese painting carried forward the cause and forged ahead into the future, more and more being studied by and influencing the international painting world[25—29]. As an inevitable consequence, there have been many fake paintings since this painter became famous, like all other famous painters in the world. The PIXE or IXX analysis may help the authentication of his numerous works.

Fig.4 shows one of Badashanren's paintings, "Taoshi Shuangqin", and two seals on it, which were analysed by using our improved on-demand system. The proton beam fluence is about 0.05—0.1 $\mu C/cm^2$ while the beam current density is 0.2—0.6nA/cm^2.

The elemental area ratio Hg/Zn of seal ink paste acts as a designation for helping distinguish between real and fake, when the experimental geometry and other conditions are the same. The comparison of two Badashanren's paintings is listed in Table 1, among which painting A is exactly real and B may be fake according to traditional experience method. The analyses of two pairs of seals respectively with almost same shape, size and color give different ratios of Hg/Zn. The results provide new scientific information for the study of Badashanren's paintings.

4.1.2 Paintings of Qing Dynasty

Qian Zai (1708—1793 A.D.) was a famous painter in the Qing Dynasty. He was good at painting flowers and plants. One of his paintings analysed is "Peach Blossom", drawn in 1792. Many golden spots can be clearly seen on the paper. This kind of paper is called Sprinkling-gold paper, a kind of pretty and precious paper used in traditional Chinese painting and calligraphy[18]. There are several red seals on it. The paper and seals were analysed by IXX with a Mo primary target. An IXX spectrum of seal ink paste is shown in Fig.5. The results show that the composition of these golden spots is true gold, and the seal ink paste of all seals is made of cinnabar (HgS) with the same elemental composition. Definite information has been provided to help archaeologists reveal the manufacture craft of ancient Sprinkling-gold paper.

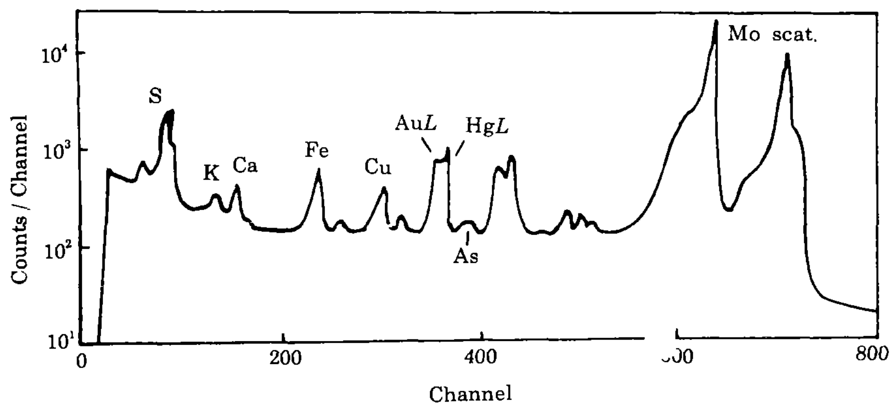

Fig.5 An IXX spectrum of seal ink paste on "Peach Blossom" with a Mo primary target

4.2 IXX analysis of ancient paper money of China

The appearance of paper money is a great advance in the currency history. The earliest paper money in the world began circulation between about 1008—1016 A.D. in the Northern Song Dynasty of China. Up to the Yuan Dynasty (1271—1368 A.D.), the paper money became the major currency. In the Ming Dynasty (1368—1644A.D.), the paper money of Daming Tongxing Baochao began to be issued in 1375 and circulated together with gold, silver and copper coins. The paper money of Daqing Baochao was used only for 10 a after 1853 in Qing Dynasty (1644—1911 A.D.)[18,30,31].

The paper used for Daming Tongxing Baochao is made of mulberry bark. Owing to its age, it is scarce, rare and shabby as well. There are six denominations, among which the one-thousand-cash may be the biggest paper money in size all over the world, ~34cm long, 22cm wide. On its face there are two red seals and one on the back, indicating where it was issued and printed. Daqing Baochao is made of white thick paper. A piece of five-hundred-cash made in Xian Feng 6th year is analysed, only one name seal on it, is as good as new for its age of 139 years only. Several seals on two above-mentioned samples were analysed by using the IXX system with a Mo primary target. Two spectra, shown in Fig.6, tell us that the seal ink paste on Daqing Baochao is made of cinnabar as usual ones on paintings, but the Daming Tongxing Baochao is completely different. The major component of this ink paste is lead and there is no mercury, signifying that it is made of minium (Pb_3O_4) which is often used nowadays to make general seal ink in factories. There is no record in any historical document that the minium seal ink paste was used in the Ming Dynasty. It is supposed that the artificial cheap minium used instead of the natural expensive cinnabar may be due to the economic recession and the depreciation of paper money in the latter part of the Ming Dynasty. Meanwhile, these results show the level of Chinese chemical craft in the Ming Dynasty.

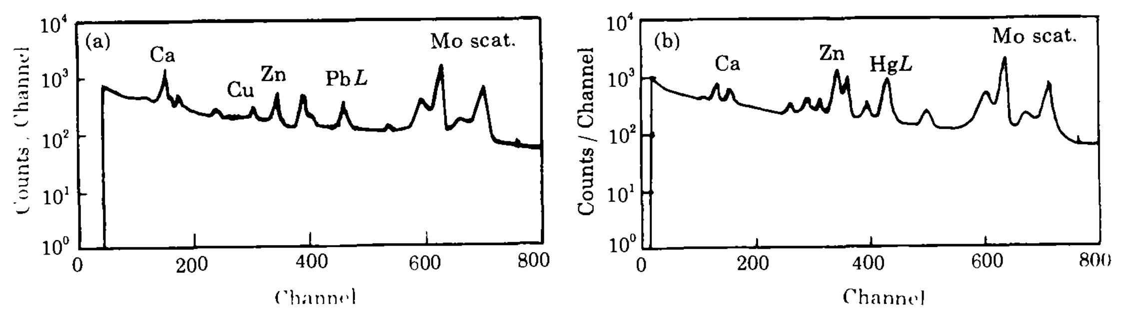

Fig.6 IXX spectrum of seal ink on (a) "Daming Tongxing Baochao" and (b) :Daqing Baochao"

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