Journal of Archaeological Science xxx (2013) 1–8

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

The exploration of Sr isotopic analysis applied to Chinese glazes: part one☆

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A R T I C L E I N F O

Article history:
Received 4 March 2013
Received in revised form
26 July 2013
Accepted 12 August 2013

Keywords:
Chinese glaze
Raw materials
Strontium isotopes
TIMS

A B S T R A C T

Ash glaze and limestone glaze are two major glaze types in southern Chinese ceramic technology. In this study strontium isotope compositions were determined in ash glaze samples from the Yue kiln dated to between the 10th and 12th centuries AD, limestone glaze samples from Jingdezhen dated to between the 15th and 18th centuries AD and ceramic raw materials from Jingdezhen. The Sr isotopic characteristics of limestone glaze and ash glaze are completely different. The Sr isotope characteristics of limestone glaze is characterised by low Sr concentrations, large $^{87}Sr/^{86}Sr$ variation, and a two component mixing line. On the other hand the strontium isotope characteristic of ash glaze samples is characterised by a consistent $^{87}Sr/^{86}Sr$ signature and high Sr concentrations with a large variation. The different Sr isotope compositions for the two types of glazes are a reflection of the various raw materials involved in making them. The Sr isotopic composition has been altered by the refinement process that the raw material was subjected to. It was found that the mineralogical changes caused by the alteration are reflected in the Sr isotope results. The potential of Sr isotopic analysis of Chinese glazes is evaluated according to the results produced by this, the first such study.

1. Introduction

Glaze is a functional and decorative layer of glass that seals the surface of ceramics. The high quality glaze of Chinese ceramics was one of the key features that made it so popular around the world and led to it becoming part of a global trade system. To understand the ancient production processes that created this substance, many scientific analytical investigations have been carried out. In this study Sr isotope analysis is used to investigate Chinese high fired glazes, from the time when this technology was at its pinnacle of development in order to understand the technology of the raw materials used and their provenance. Sr isotopic analysis is a long established technique in geology, but only in the last decade has it been applied to the investigation of ancient glass. The present study serves the purpose of exploring this technique's applicability in the context of Chinese high fired glaze.

Like many other things, the development of high fired ceramics in China was divided into a northern zone and a southern zone by the *Qin'ling* Mountain range. The South led the way most of the time, due to easier accessibility of refractory ceramic raw materials in the southern geology. Two types of high fired glaze were most important in the history of southern Chinese ceramics: limestone glaze and ash glaze.[1] Ash glaze was the dominant high fired ceramic coating from 3rd century AD until 14th century AD, and then limestone glaze became the commonest from the mid-14th century AD onwards (Kerr and Wood, 2004). Limestone glaze and ash glaze are both thin layers of opaque to translucent glass, and porcelain stone (weathered acid igneous rock) was the common raw material used to make both glaze types. The difference in the two types of glaze was the flux component. Botanic ash was the flux used in ash glaze, and glaze ash (a mixture of a major component of calcium carbonate powder and botanic ash) in limestone glaze. In the present study, limestone glaze from Jingdezhen, ash glaze from the Yue

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[1] Limestone glaze and ash glaze are frequently described as porcelain glaze and lime glaze. However the present research context to prevent the term 'lime' and 'porcelain' from causing confusions, the fluxes involved for making these glazes—limestone and botanic ash are used.

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http://dx.doi.org/10.1016/j.jas.2013.08.015

kiln and porcelain raw materials from Jingdezhen were chosen as isotopic samples to address the research questions.

2. Background to Sr isotope analysis on vitreous materials

The pioneering work of applying Sr isotopic analysis to glass was done by Wedepohl and Baumann (2000). In this work they demonstrated how the $^{87}Sr/^{86}Sr$ signature and the elemental concentration of Sr should be interpreted in terms of raw materials used for making the glass. They stated that the bulk of the Sr content in glass derived from the lime-bearing portion of the raw material. They also stated that the Sr isotopic composition of imperial period Roman natron glass, which is typical of 350–500 ppm Sr concentration and $^{87}Sr/^{86}Sr$ signature of around that of modern seawater (0.70918), can be attributed to the use of marine molluscan in beach sand; limestone would be expected to introduce a much lower Sr concentration in the glass of c. 100–200 ppm. Wedepohl and Baumann's pioneering work is more scientific speculation than a final statement because they only provided the Sr compositions of 5 samples for one type of glass to back up their theory. But their speculation caught the attention of scientists of ancient glass, and a number of studies investigating strontium isotopes in ancient glass soon followed.

Freestone et al. (2003) studied the Sr isotopic signatures of three types of glass from four sites, for which the source of raw materials was basically known from previous compositional researches. In this study, the authors demonstrated in more detail how the isotopic compositions of glass should be interpreted in terms of the raw materials used. From the glasses from *Bet She'an* and *Bet Eli'ezer* in Israel, which are believed to have been made from natron and coastal sand, they retrieved a similar result to the samples tested by Wedepohl and Baumann. All the samples contain a high Sr concentration and a $^{87}Sr/^{86}Sr$ signature of around that of modern seawater. From the natron glass samples from Ashmunein, Egypt, which are believed to have been made from natron and limestone-bearing sand, they found the Sr contents to fall between 100 and 200 ppm just as Wedepohl and Baumann had speculated. From the plant ash glass samples from Banias, Israel, a high content of Sr (c. 400 ppm) and a $^{87}Sr/^{86}Sr$ signature of between 0.707723 and 0.707797 were found. This Sr composition was interpreted as being determined by plant ash, which is capable of introducing high Sr concentrations and a $^{87}Sr/^{86}Sr$ signature derived from the underlying geology on which the plant grew.

Henderson et al. (2005) is another exploratory work that contributed to the early understanding of how Sr concentrations and the $^{87}Sr/^{86}Sr$ signatures reflect the raw materials used in ancient glass production. This work was the first to compare the Sr isotopic compositions of raw materials with raw glass from the primary glass-making factory site at al-Raqqa, Syria. In this study 4 natron glass samples and 7 plant ash glass samples along with 2 quartz pebble samples and 2 plant samples from the vicinity of the site were subjected to Sr isotopic analysis. The Sr compositions of the 4 natron glass showed that feldspar could be another end member in the natron glass Sr balance. The Sr isotopic compositions of the quartz pebbles verified the suggestion made by Wedepohl and Baumann that they would contribute in a negligible way to the Sr isotopic composition in glass. The 2 plant samples analysed in the study were *Alhagi maurorum medik*; these were harvested close to the glass factory site and their $^{87}Sr/^{86}Sr$ ratios are about the same as found in the plant ash factory raw glasses, so it confirmed the assumption that plant ash glass inherited its Sr isotopic composition from the ashed plant (the lime-bearing component).

Degryse et al. (2010) is another work that concerns the basics of Sr isotopic application to glass. This work showed that in a (Scottish) temperate climate the Sr composition of botanic ash could be affected not only by the underlying geology but sometimes also by the hydrology of the immediate area where the plants grew. Although there were other Sr isotope analyses on ancient glass, the aforementioned four works provide the basic knowledge in this area.

Although this study is probably the first application of Sr isotopes to Chinese glazes, it is not the first use of Sr isotopic analysis in the investigation of Chinese ceramics. Li et al. (2006) studied the trace elements and Sr–Nd isotopic compositions of 13 visually indistinguishable Tang dynasty Sancai ceramic body samples to provenance them according to their geochemical characteristics. 11 of these samples were from the two most important Sancai production sites (5 from Gongxian kiln and 6 from Yaozhou kiln), and 2 were modern fakes. The results showed that Sr–Nd isotopic compositions not only provide a better distinction between ancient Sancai wares from different production sites than trace element analysis, but also clearly distinguished the genuine ceramics from the fakes. The geochemical separations between ancient and fake ceramics indicate that different raw materials were used in their production.

3. Description of samples and relevant background

Two types of glaze are involved in the present study—limestone glaze and ash glaze from South China. In terms of the limestone glaze, no other site is more representative than Jingdezhen, because arguably Jingdezhen is the place where the limestone glaze was first developed in South China and where it was applied for the longest time. Blue-and-white ware was the commonest Jingdezhen porcelain type which was covered with limestone glaze. Twelve blue-and-white shards from Jingdezhen were selected for this study, ten of them are Ming and Qing dynasty official kiln products from different reigns: XD1, XD3 (Xuande period: 1425–1435 AD), CH2, CH5 (Chenghua period: 1464–1487 AD), ZD5, ZD11 (Zhengde period: 1505–1521 AD), JJ1, JJ10 (Jiajing period: 1521–1567 AD), QL3, QL7 (Qianlong period: 1735–1795 AD), and the other two are high quality traditional 'folk kiln' export porcelain wares from the Ming dynasty Wanli period (1572–1620 AD): EP1, EP2.

Ash glaze was the dominant type of glaze used before limestone glaze was introduced. Arguably the Yue kiln produced one of the highest quality ash glazed ceramics of all time. At the peak of its production Yue kiln high quality products were used as court tribute and the colour of these wares was praised in poems as being mysterious. Eight samples from the Silongkou Yue kiln site near the Shanglin lake kiln complex, Cixi, Zhejiang Province, four dated to the Five Dynasties and Ten Kingdoms period (907–960 AD): Ya-1, Ya-2, Ya-3, Ya-5, and four dated to early Southern Song dynasty (1127–c.1150 AD): Yb-1, Yb-2, Yb-3, Yb-5, are included in our study.

Ancient Chinese glaze recipes are made up of two components—the flux and the siliceous portion. The siliceous materials for southern Chinese high fired ceramics were commonly weathered acid igneous rock, and they are commonly referred to as porcelain stone in many publications (Guo, 1987). Porcelain stone forms the major part of the glaze slip[2] as well as the body paste. The refinement process is crucial to porcelain stone, for it not only reduces the impurities in the original rock, but also turns porcelain stone from rock into a useable material. The refined porcelain stone in Jingdezhen is made in the form of *Petuntse*白不 (little white brick). Seven porcelain stone samples from Jingdezhen are included in our study, and two of them from *Yao'li* (YL A, YL B) belong to a sub-

[2] Glaze slip is a suspension which is applied to the surface of ceramic biscuit. This layer turns into the glaze after being fired.

Please cite this article in press as: Ma, H., et al., The exploration of Sr isotopic analysis applied to Chinese glazes: part one, Journal of Archaeological Science (2013), http://dx.doi.org/10.1016/j.jas.2013.08.015