Searching for the earliest use of limestone as a flux in Chinese high-fired ceramic glazes—evidence from Sr isotopic analysis of Chinese northern porcelain

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Abstract

Samples of northern porcelain wares dating to between the 6th and 13th centuries from the three most important northern Chinese ceramic kiln sites, Gongyi, Xing and Ding have been studied in this work. The Sr isotope and chemical compositions of the ceramic glazes of these wares have been determined. Based on the scientific results we have been able to suggest the raw materials used to make the glazes. Using Strontium isotopic analysis we have successfully shown that the earliest use of limestone as a glaze flux so far identified is during the period from the Sui to mid-Tang Dynasties (late 6th- early 9th century) to produce white slip glazed ware in the Xing kilns so it may have been ‘invented’ there.

Keywords: Sr isotopic analysis, North China, porcelain

1. Introduction

Hebei and northern Henan provinces in north China are not only the production centres for many table wares and sanitary ceramics used worldwide nowadays, they are also the birthplace of the first real white porcelain in history. Archaeological excavations have revealed the distribution of the northern ceramic industry during the historical era, and a number of studies have provided insights into how porcelain produced in north China changed over time (Li, 1998, Wood 1999, Kerr and Wood 2004). However these northern ceramic production centres were nearly all devastated during the Mongol invasion in the 14th century and never recovered during the historical era. Moreover, no historical record of the production technology used by them has been found. The understanding of northern ceramic technology we have now is much inferior to what we know about the southern Chinese ceramic technology, which has been preserved in historical records and the uninterrupted passing down of technological knowledge over generations.

One of the key questions regarding northern porcelain is what calcareous flux was used in the glazes. Nearly all Chinese high-fired ceramics have a calcareous glaze, and two calcareous materials, limestone and wood ash, are regarded as the two different fluxes used in Chinese high-fired glaze recipes (Luo 1995). It is certain now that wood ash was a common flux used before limestone glaze was widely adopted in China. However, very specific questions about
when and where limestone was first introduced into glaze-making have not yet been addressed. The key to pinpointing when and where limestone was first used in glaze making is to work out from which varieties of glazes we should look for the answers. It has been repeatedly proven that green stoneware glaze, which was the earliest high-fired ceramic glaze in China, was a wood ash glaze; and southern Qingbai glaze was a limestone based glaze\(^1\) according to historical records and scientific evidences (Huang \textit{et al.} 2020, Ma \textit{et al.} 2014). A recent study suggested that the earliest use of limestone in glaze recipes at Jingdezhen, South China occurred before Qingbai ware was first produced and the early use of limestone at Jingdezhen could have been under the influence of northern porcelain makers (Wu \textit{et al.} 2020). In fact northern porcelain, which was the earliest porcelain in the world according to the original definition of the word ‘porcelain’ (white and high-fired), was basically the only ceramic variety that prevailed in China between green glaze stoneware and Qingbai ware (Kerr and Wood 2004). So it is highly likely that it was among northern porcelain varieties that limestone was first introduced in Chinese glaze making. In this study, varieties of northern porcelain from the three most important northern porcelain production centres between the 6th and 13th centuries, namely Gongyi kilns, Xing kilns and Ding kilns, are studied using Sr isotopic analysis and electron probe microanalysis to address this question.

Another related issue, whether the recipe used for northern porcelain glaze followed the principle of creating high-fired ceramic glaze in South China, namely body material\(^2\) plus calcareous flux, will also be discussed.

2. The development of northern porcelain wares

In terms of visual appearance and chronology, northern porcelain wares can be roughly divided into three phases, namely early porcelain, white slip porcelain and fine porcelain.

The earliest porcelain wares, as defined by archaeologists, first appeared during the late Northern Dynasties (6th century AD) at a few kiln sites in Hebei and northern Henan Provinces along the eastern slope of the Taihang Mountain, where the Chinese Loess Plateau and north Chinese alluvial plain meet (Figure 1). Visually these early porcelain wares look very similar to contemporary northern green glazed stoneware. The two types of ceramics basically have the same shape and they were sometimes fired in the same kiln together. Northern green glaze stoneware was the first high-fired ceramic made in North China, and it is widely regarded as the technological precursor of early northern porcelain, because green glaze stoneware predates northern porcelain by a few decades and the two types of wares have very similar chemical compositions of both their bodies and glazes. However, the early porcelain wares do look slightly paler than contemporary green glazed stoneware, mainly because they have a pale ceramic body.

\(^1\) Wood ash glaze is the glaze made by using calcareous wood ash as the calcareous flux, and limestone based glaze is the glaze made by using pulverized limestone as the main calcareous flux. In this paper wood ash specifically refers to the calcareous ash retrieved from burning wood. This is meant to avoid confusion with the soda-rich ash from burning halophytic plants and silica-rich ash from burning herbaceous plant.

\(^2\) In this paper, body material refers to the processed raw material for ceramic body paste. Body material could have been composed by only one raw material component, such as coal clay, or it could have been composed by several raw material components. Ceramic body is not the main research subject of this work, so to simplify the discussion body material is taken as one single entity in the view of whether it was used in the glaze formula for each porcelain variety.
bodies made with white-firing clay (Wood 1999).

Soon after early porcelain was introduced a new kind of porcelain, which has a white slip layer between the ceramic body and glaze, emerged at the Xing kilns during the Sui dynasty (581-618 AD) (Lu et al. 2012). This was not the first time that a white slip had been used to decorate glazed ceramics in China, but it was the first time this technique had been used on high-fired porcelain wares (Qin 2018). The white slip layer was made by using the finest white-firing clay, a rarity in the carboniferous coal clay in north China. This layer was used to cover the grey and sometimes darkly tinged ceramic bodies made from common coal clay to improve the whiteness of the wares (Tite et al. 2012). During the Tang dynasty (618—907 AD), the production peak of northern porcelain, white slip porcelain were the common wares produced in large quantities by northern kilns. There were a small proportion of non-slipped fine wares produced during the Tang dynasty at the Gongyi and Xing kilns; these wares were regarded as exclusive wares and their glazes were often more alkaline (Wang et al. 2019). These Tang dynasty fine wares are not within the scope of this paper.

Ding kilns is regarded as the most important northern porcelain production centre after the Xing and Gongyi kilns declined at the end of Tang dynasty. Ding kilns started production during the late Tang to Five Dynasties period (907—979 AD), and their technological peak was during the northern Song dynasty (960—1127 AD) (Cui et al. 2012). In the earliest phase of Ding kilns’ production, white slip wares were produced, but soon the main products of Ding kilns became fine porcelain without slip. This fine porcelain was praised as one of the five greatest wares made during the Song dynasty, the other four all celadon wares, and it should be regarded as the third phase of northern porcelain production.

3. Samples

Porcelain samples dating to the three production phases from the three most important production centres are included in this study to sustain our knowledge of northern glaze-making and its raw materials. They are:

(1) Early porcelain wares of the Late Northern Dynasties period (c. 6th century AD) from Neiqiu County, the core area of Xing kilns complex (6 samples);
(2) White slip porcelain wares of the Sui to mid-Tang dynasty (c. late 6th—early 9th century AD) from Neiqiu County, Xing kilns (9 samples);
(3) White slip porcelain wares of the Tang dynasty (c. 7th—9th century AD) from Gongyi kilns (8 samples);
(4) White slip porcelain wares of the Five Dynasties period (c. 10th century AD) from Ding kilns (4 samples);
(5) Fine porcelain wares of the Northern Song dynasty (c. late 10th—early 12th century AD) and the Jin dynasty (c. mid-12th—mid-13th century AD) from Ding kilns (6 samples and 5 samples respectively);
(6) Northern green glazed stoneware of Northern Dynasties period (c. late 5th—6th century AD) from Gongyi kilns (8 samples);
(7) Raw materials collected in the area of ancient Ding kilns (6 samples) are also included in this study for reference.
Further detailed sample information is shown in table 1.

4. Analysis

Sr isotopic analysis has been used to study the flux component in ancient western glass since 2000 (Wedepohl and Baumann 2000), and this technique has been introduced into the study of Chinese high-fired ceramic glaze, which is basically a thin layer of glass, in recent years. Previous exploration works have laid the foundation for the application of Sr isotopic analysis in Chinese glazes (Ma et al. 2014, Ma et al. 2016, Li et al. 2019b). A few application works of this newly developed approach and a review paper to generalize our up-to-date understanding of this method have been published (Ma et al. 2019, Shen et al. 2019, Henderson et al. 2020). In this work Sr isotopic compositions of porcelain glazes and bodies determined by thermal ionization mass spectrometry (TIMS) are used as the main data for our investigation, and major and minor elemental compositions of porcelain glazes and bodies determined using electron probe microanalysis (EPMA) provide the basic chemical data.

For Sr isotope analysis, the glaze samples needed to be first separated from the ceramic bodies. Because the glaze layer is very thin (200–400 μm), this separation was achieved by ‘peeling’ the glaze from the body following a series of operations. First, a piece of ceramic shard with glaze was cut off using a flexible diamond-edged rotary dental bit; then the sample was attached to a glass slide with high-purity epoxy resin with the glaze side down for the ease of the following operations. Next the side of the sample originally attached to the ceramic body was mechanically cleaned with a tungsten carbide burr to remove the remaining body and the body-glaze interaction layer attached until only the glaze was left behind. The high-purity epoxy resin and tungsten carbide burr have been tested so that they would not contaminate the samples (Montgomery 2002).

The resulting samples were then taken off the glass slide using boiling Milli-Q water. The boiling water releases the very thin glaze (<200 μm), sometimes in fragments, from the epoxy resin, and the glaze samples drop in the water. Then the glaze samples were collected in clean glass beakers and transferred to a clean (class 100, laminar flow) working area for further preparation. In the clean laboratory, the samples were cleaned ultrasonically in Milli-Q water, dried on a hotplate and then weighed into pre-cleaned Teflon beakers. The samples were spiked with $^{84}$Sr tracer solution and dissolved in Teflon distilled 8M HNO₃ and Ultrapure 29M HF. Samples were converted to chloride form using Teflon distilled 6M HCl. The samples were then taken up in calibrated 2.5MHCl and centrifuged. Strontium was collected using Eichrom AG50 X8 resin columns.

Each sample was then loaded on to a single Re filament with TaF, following the method of Birck (1986). The $^{87}$Sr/$^{86}$Sr and Strontium elemental concentrations were determined by Thermal Ionisation Mass spectroscopy (TIMS) using a Thermo Triton multi-collector mass spectrometer at the National Environmental Isotope Facility at the British Geological Survey. The international standard for $^{87}$Sr/$^{86}$Sr, NBS987, loaded in the same way, gave a value of 0.710260 ± 0.000018 (n=21, 2σ) during the analysis of these samples and sample data was normalized to the accepted value for this standard of 0.710250. Procedural blank values were in the region of 100 pg. The Sr isotopic compositions of samples analysed in this work are reported in table 2.
Electron microprobe analysis was carried out on our glaze samples to determine their chemical compositions. Fragments of each ceramic shard were mounted in cross-section in epoxy resin blocks and polished to a 0.25mm diamond paste finish so as to reveal a flat analytical area. The blocks were carbon coated to prevent surface charging and distortion of the electron beam during analysis. A Shimadzu EPMA-1720 electron microprobe housed in the State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, was used for the chemical analysis of the samples. The system is equipped with four wavelength-dispersive X-ray spectrometers with LIF, TAP, PETJ and LIFH crystals, a single energy-dispersive X-ray spectrometer, and both secondary and backscattered detectors. A defocused electron beam with a diameter of 50 μm was used to prevent volatilization of light elements such as sodium. The probe was run at an accelerating voltage of 20kV and a beam current of 5 nA. The system was calibrated with a natural basalt glass standard for Si, Al, Na, K, Mg, Ca, Ti, Fe and the Corning D glass reference material for P. A ZAF program was used to correct and quantify the results. The Corning D glass reference material was routinely used as a secondary standard to check for accuracy and precision and to monitor any drift in the instrument. The Corning D glass standard was analysed five times during the whole analytical process. The analytical precision and accuracy achieved by using a Corning D standard are listed in Table 3. The chemical compositions of glazes and bodies of the porcelain varieties analysed by EPMA in this work are also reported in table 3. Due to the low totals (90-95 wt%) retrieved from some semi-fused porcelain body analyses, the reported chemical compositions of porcelain bodies have been normalized to 100 wt% and should only be deemed semi-quantitative. The possible reason for the low totals of these ceramic body analyses is that ceramic bodies are multi-phase matrix with cavities created by escaped gas contained in the unfired ceramic paste; they are not ideal analytical subjects for EPMA analysis, which is calibrated by single phase minerals and/or glass, therefore sometimes low totals will be retrieved for semi-fused ceramic bodies. Since ceramic bodies are not the main research subjects of this work, these semi-quantitative data should serve the purpose to provide basic chemical composition profiles of the body materials.

5. Results

5.1 The Sr isotopic composition data interpretation method applied in this work

Nearly all Chinese high-fired ceramic glazes are calcareous, and this feature makes Sr isotopic analysis a highly suitable technique to study their calcareous fluxes, because common natural calcium sources, namely seashells, limestone and wood ash, all have their characteristic $^{87}\text{Sr}/^{86}\text{Sr}$. Although there are some overlaps between the $^{87}\text{Sr}/^{86}\text{Sr}$ signatures of the three calcium sources, by considering their Sr concentrations, Sr/Ca and bio-available $^{87}\text{Sr}/^{86}\text{Sr}$ in the immediate landscape from which the wood ash originated, we should be able to, in most of the cases, identify which calcium source was used as the calcareous flux in a specific glaze recipe (Henderson et al. 2020). However, unlike the situation in ancient western glass where the Sr in the glass produced was mostly contributed from one source (Sr contributions for low Sr content materials in high amounts or high Sr content materials in low amounts have also been considered in recent works), in Chinese high fired ceramic glazes the Sr was normally contributed from two sources, the calcareous flux and the siliceous material or materials (Ma et al. 2014, Li et al. 2019b).
Theoretically speaking for any material made by fusing two or more raw materials with different Sr isotopic compositions ($^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentration), its Sr isotopic composition should be a mixture of Sr isotopic compositions of the two or more raw material components according to the equation below.

$$\frac{a^{7}\text{Sr}}{m^{7}\text{Sr}_{M}} = \frac{a^{7}\text{Sr}_{A} - m^{7}\text{Sr}_{B}}{m^{7}\text{Sr}_{M}(m^{7}\text{Sr}_{A} - m^{7}\text{Sr}_{B})}A + \frac{a^{7}\text{Sr}_{A} - m^{7}\text{Sr}_{B}}{m^{7}\text{Sr}_{A} - m^{7}\text{Sr}_{B}}B$$  \hspace{1cm} (Equation 1)

Where $a^{7}\text{Sr}_{m}/m^{7}\text{Sr}_{M}$ and $m^{7}\text{Sr}_{M}$ are Sr isotopic ratio and Sr concentration of the mixture, and $a^{7}\text{Sr}_{A,B}$ and $m^{7}\text{Sr}_{A,B}$ are Sr isotopic ratio and Sr concentration of the two mixing components.

Because the Sr isotopic ratio and Sr concentration ($a^{7}\text{Sr}_{m}/m^{7}\text{Sr}_{A,B}$) for the mixing components are constant, the equation could be simplified as

$$\frac{a^{7}\text{Sr}}{m^{7}\text{Sr}_{M}} = \frac{a}{m^{7}\text{Sr}_{M}} + b$$  \hspace{1cm} (Equation 2)

Equation 2 shows that $a^{7}\text{Sr}_{m}/m^{7}\text{Sr}_{M}$ and $m^{7}\text{Sr}_{M}$ of mixtures combined in different proportions of the components should form a hyperbola with the Sr isotopic compositions of the mixing component being the two ends of the mixing line (Faure 1986). When taking $1/m^{7}\text{Sr}_{M}$ as abscissa, we can switch the hyperbola into a straight line, which will show the mixing effect more clearly, but the downside is the X axis would not be linear but distributed according to $m^{7}\text{Sr}_{M}^{-1}$ (Henderson et al. 2020).

Mixing lines are suggested for nearly all Sr isotopic compositions of the glaze varieties we have studied; mixing lines are demonstrated by plotting $a^{7}\text{Sr}/m^{7}\text{Sr}$ against 1000/(Sr ppm) and thereby to suggest what raw materials were used to make the glazes. It has to be borne in mind that a mixing line can only suggest the presence of the main strontium contributors in the glaze formula, but not every component. Therefore the presence of a raw material with a very low absolute strontium contribution will not reflect in a mixing line. For example, when a very pure form of silica was used in a glaze recipe, even a large amount of it may have been used, its presence may not reflect in the mixing line due to its very low absolute Sr contribution to the resultant glaze.

5.2 The chemical and Sr isotopic compositions of Gongyi northern Dynasties green stoneware and Tang dynasty porcelain glazes

Green glazed stoneware was the first high-fired ceramic made in North China and the technological precursor of early northern porcelain. It has been suggested that the northern green stoneware glaze was created following the original southern recipe: wood ash plus body material (Huang et al. 2020). The Sr isotopic compositions of our Gongyi green stoneware glaze samples are very consistent at 0.715-0.718 for $a^{7}\text{Sr}/m^{7}\text{Sr}$ and 300-350 ppm for Sr concentration (Figure 1). The high Sr concentrations and high P$_2$O$_5$ contents average at 0.74 wt% are typical for a wood ash glaze (Henderson et al. 2020), and the high TiO$_2$ contents agree with the suggestion that body material was used in the recipe (Wood 1999).
The early porcelain made at Gongyi kilns was one of the earliest porcelain wares made in China. Due to the rarity of these early porcelain wares, we did not manage to sample them for destructive analysis. However, Gongyi Tang dynasty white slip porcelain, a mature porcelain ware which developed from early porcelain, has been analysed for its chemical and Sr isotopic compositions. A mixing line is clearly suggested by the Sr isotopic compositions of individual Gongyi early porcelain glaze samples, and the high $P_2O_5$ content and high $TiO_2$ content also suggest the presence of wood ash and body material in the recipe.

By plotting the Sr isotopic compositions of the Gongyi white slip porcelain glaze and green stoneware glaze along with that of Gongyi ceramic bodies published by Li et al. (2008) and wood ashes originated from the Loess landscape, we can see quite clearly the connections between them (Figure 2). The Sr isotopic compositions of Gongyi ceramic bodies and wood ashes originated from the Loess landscape approximately occupy the two ends of the mixing line formed by Sr isotopic compositions of Gongyi white slip porcelain glaze, and the Sr isotopic compositions of Gongyi white slip porcelain glaze towards that of wood ash originated from the loess landscape. This pattern suggests wood ash and body material were also the two main raw materials used in Gongyi white slip porcelain glaze, same as green stoneware glaze; but the white slip porcelain glaze clearly used lower proportion of wood ash in the recipe, and this was probably to avoid the dark tinge caused by the impurities from the ash. The lower $CaO/SiO_2$ in Gongyi white slip porcelain glaze also suggests lower wood ash to body material ratio in the glaze recipe.

The clear discrepancies in the $Al_2O_3$ and $SiO_2$ contents and $SiO_2/Al_2O_3$ between the Gongyi white slip porcelain glaze and ceramic body suggests body material was not the only siliceous material used in the formula and some extra $SiO_2$ should have been introduced in the glaze by a third raw material component. The presence of this third raw material in the glaze formula is not very clearly shown by the mixing line; but the high $^{87}Sr/^{86}Sr$ end of the extrapolation of the mixing line goes slightly above the Sr isotopic compositions of the ceramic bodies (Figure 2B), and this should hint the presence of this third raw material. The Sr contribution introduced by this third raw material to the glaze should have been quite small, possibly due to only a small amount of this third material was added in the formula or it was a rather pure form of silica, which contains very low content of Sr, and that is the reason why it is not clearly suggested by the mixing line.

5.3 The chemical and Sr isotopic compositions of early porcelain glaze from Xing kilns

Late northern Dynasties period early porcelain made in Xing kilns is one of the earliest porcelain wares made in China. The six individual Sr isotopic compositions of Xing early porcelain glaze form a clear mixing line; the high Sr concentration end of the mixing line points to the Sr isotopic composition of wood ash carrying typical $^{87}Sr/^{86}Sr$ from the loess landscape (Figure 3). The low Sr concentration end of the mixing line, however, does not point directly to the Sr isotopic composition of the body material (Figure 3B). This suggests that the body material was not used as the sole siliceous raw material in the glaze formula. Chemical compositions of Xing early porcelain bodies and glazes also support this suggestion; as Xing early porcelain glazes have a rather high $Na_2O$ content averaging 3.05 wt%, which is not seen in the porcelain body. This $Na_2O$ content is unlikely to have been introduced in the wood ash, because it is well known that
sodium is toxic for most land plants (Horie and Schroeder 2004), and the ash of those plants would normally contain less than 3.0 wt% Na₂O (Vassilev et al. 2010). Halophytic plant species are tolerant to alkalies including Na⁺ and are therefore exceptions to this rule; their ash can contain over 10 wt% Na₂O. The non-halophytic plant ashes originating from the loess landscape have low Na₂O contents of less than 1 wt% as many data show (Kerr and Wood 2004, Li et al. 2019b), and this is also confirmed by many chemical compositions of wood ash glazes made at production sites located in the loess dominated area (Shen et al. 2019, Huang et al. 2020). Therefore the Na₂O content in the glaze must have derived from a material other than the body and wood ash. Although the body material should not be the only siliceous raw material used to make glaze, the high TiO₂ contents of Xing early porcelain glaze do suggest that the body material was still used as one component in the recipe (Wood 1999, Wood 2009).

5.4 The chemical and Sr isotopic compositions of white slip porcelain glazes from Xing and Ding kilns

The pattern of Sr isotopic compositions of Xing Sui to mid-Tang white slip porcelain glazes changes completely from that of Xing early porcelain (Figure 4A). The Sr isotopic compositions of Xing white slip porcelain glaze also display a straight mixing line (Figure 4B), but for this glaze the low Sr concentration end of the mixing line has a low 87Sr/86Sr and the high Sr concentration end a high 87Sr/86Sr, which is just the opposite to the mixing lines displayed by Sr isotopic compositions of Gongyi white slip porcelain glaze and Xing early porcelain glaze. This change of Sr isotopic composition pattern suggests a major shift of glaze recipe at Xing kilns.

The Sr isotopic compositions of Ding Five Dynasty white slip porcelain glaze share the same pattern with Xing white slip porcelain glaze, and their chemical compositions are also very similar (Figure 4, Table 3). This suggests Xing and Ding white slip glaze were made using a similar formula, which agrees with the well accepted suggestion that the establishment of early Ding kilns was largely influenced by Xing technology and it could have been due to the relocation of some Xing potters at Ding kilns during the late Tang to Five Dynasty period (Li 1983).

Regarding this completely new recipe of white slip porcelain glaze reflected by Sr isotopic compositions, firstly the calcareous raw material in the formula has changed. The ends of the mixing lines for Xing and Ding white slip porcelain glazes do not point to the Sr isotopic compositional range of wood ash originating from the loess landscape like that of Xing early porcelain glaze and Gongyi glazes, but instead they both point at a Sr isotopic composition of around 0.7080 for 87Sr/86Sr and 200 ppm for Sr concentration (Figure 4B, 4D, 4F), a characteristic isotopic composition of Ordovician limestone occurred in the North China Platform, which have distinctly lower Sr concentration than that of worldwide limestone average 460 ppm (Figure 4). According to the geological map of north China, the eastern slope of Taihang Mountain, on which the Xing and Ding kilns are located, is among the areas in which limestone abundantly outcrops (Figure 1). The limestone in this area is of an Ordovician date. The area of the North China Platform, which is a geological label encompassing most of central North China, was a sea during the Ordovician period, and the limestone was formed in the marine environment of the time (Zhang et al. 2018). A key feature of this Ordovician limestone is that commonly it had experienced various degrees of dolomitization. Therefore a large proportion of limestone in this area had been turned into dolomitized limestone or dolomite. According to Zhang et al. (2018),
limestone, dolomitized limestone and dolomite of this area have Sr concentrations of between 296 ppm and 79 ppm, which are far below the worldwide limestone average 460 ppm, and the $^{87}\text{Sr}/^{86}\text{Sr}$ of between 0.7086 and 0.7118. The Sr isotopic compositions of Ordovician limestone and dolomite sampled from the eastern Taihang Mountain in this study are (154 ppm, 0.708400) and (18 ppm, 0.70792), which agrees with the data reported by Zhang et al. (2018), and they are also plotted in Figure 4.

How dolomitization occurred exactly is part of a heated debate in geology (Wang et al. 2016). However, it has been confirmed that dolomitization would reduce the Sr concentration in limestone and increase the whole rock $^{87}\text{Sr}/^{86}\text{Sr}$ at the same time. The Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ of limestone that went through different degrees of dolomitization in the North China Platform also fits this trend (Figure 4). This is the reason why the Sr concentrations of Ordovician limestone in this area fall below the worldwide average limestone Sr concentration of 460 ppm (Wedepohl and Baumann 2000), and the limestone used in Xing and Ding white slip porcelain glaze suggested by the mixing line is only at Sr concentration around 200 ppm: the limestone used for these glazes should have been local low degree dolomitized limestone. The elevated MgO contents (MgO $\geq$ 2.5 wt%) and lower CaO/MgO ($\approx$ 5.4) of Xing and Ding white slip porcelain glazes compared to that of Jingdezhen ordinary limestone based glaze (MgO $< 0.5$ wt%, CaO/MgO $\approx$ 20.4) is another suggestion of low degree dolomitized limestone had been used as the flux for these glazes.

Despite the Sr isotopic compositions suggest Xing and Ding white slip porcelain glazes were fluxed by local Ordovician limestone, we also noticed that the P$_2$O$_5$ contents of Xing and Ding white porcelain glazes are rather high, higher than most limestone glazes we studied before (Ma et al. 2014, Ma et al. 2016), and that the P$_2$O$_5$ level in Xing white porcelain glaze is only slightly lower than that of the wood ash based Xing early porcelain glaze. As P$_2$O$_5$ content is often taken as an indicator of whether limestone or wood was used as the flux for a certain glaze, people may argue that this discordant $^{87}\text{Sr}/^{86}\text{Sr}$ signature and high P$_2$O$_5$ combination should suggest wood ash originating from trees growing on limestone soil rather than loessic soil was used as the flux, because such wood ash could bear a limestone $^{87}\text{Sr}/^{86}\text{Sr}$ signature and high P$_2$O$_5$ contents. However, considering loess cover the entire landscape of central North China, and that the wood ash used for Xing early porcelain glaze, and every other wood ash based glazes made in central North China all came from the loess landscape; it is rather unlikely that wood ash originating from limestone soil was used only for Xing and Ding white slip porcelain glazes. Besides, this flux with a limestone signature and a high P$_2$O$_5$ content not only occurred at the Sui-Tang Xing kiln and the Five Dynasties Ding kilns, it also occurs in South China at Jingdezhen for northern style porcelain production during the Five Dynasties period (Wu et al. 2020). It would have been too much of a coincidence if the three production sites all happened to use wood ash originating from limestone soils at the same time for the same type of ware.

As it has been found that P$_2$O$_5$ content is a rather vague index to indicate whether limestone or wood ash was the flux used in a certain glaze (Henderson et al. 2020), and Sr isotopic composition should be a much stronger index to rely on when it comes to the matter. The Sr isotopic compositions should overrule P$_2$O$_5$ content here as the main glaze flux indicator for Xing

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Data used for comparison are quoted from Ma et al. (2014), the analytical technique and condition applied in the two study are very similar, so the data should be comparable.
and Ding white slip porcelain glaze. As for the reason why the limestone based flux used for Xing and Ding white slip glaze also bore rather high P$_2$O$_5$ content, we may have to consider factors such as how the limestone based flux was processed at this early stage. This issue is addressed in detail in the section 6.1.

Moreover, based on the Sr isotopic data we can also suggest that the body material was not used as the siliceous raw material in the Xing and Ding white slip porcelain glaze, as the Sr isotopic compositions of ceramic bodies of Xing and Ding white porcelain plot far off the extrapolation of the mixing lines formed by the Sr isotopic compositions of their glazes (Figure 4). The very low TiO$_2$ content of Xing and Ding white slip glazes also suggest body material, which contains much higher TiO$_2$ (Table 3) would not have been added in the recipe, at least not as a main component. According to the mixing line the siliceous raw material for Xing and Ding white slip glaze should have been a material with high $^{87}$Sr/$^{86}$Sr ($\geq 0.720$) and high Sr concentration (c. 400 ppm). The possible nature of this material is tentatively discussed in the section 6.3.

5.5 The chemical and Sr isotopic compositions of Ding northern Song and Jin fine porcelain glazes

The Sr isotopic compositions of Ding northern Song and Jin fine porcelain glazes are again different from the earlier white slip porcelain glaze. The individual Sr concentration of each glaze sample in fine glazes is much lower, basically between 100 ppm and 200 ppm while other glazes studied here have Sr concentrations between 200 ppm and 450 ppm (Figure 5A). Mixing lines are formed by individual Sr isotopic compositions of the two fine glazes; however the raw materials suggested by the mixing lines are quite different. As shown in Figure 5B, it appears that limestone was the flux used in Ding northern Song fine porcelain glaze and wood ash was the flux used in Ding Jin fine porcelain glaze. This change is also supported by the obvious elevated P$_2$O$_5$ contents and lower CaO/P$_2$O$_5$ in Jin fine porcelain glaze than Northern Song fine glaze, and this was also noted by Cui et al. (2012).

As shown in Figure 5B, the siliceous raw materials used in Ding Northern Song fine glaze and Ding Jin fine glaze are also different. The body material falls on the extrapolation of the Ding Jin fine porcelain glaze mixing line, suggesting it was the siliceous raw material used in this glaze; the high TiO$_2$ content averaging at 0.8 wt% in this glaze also agree with this suggestion. On the other hand, the Sr isotopic compositions of Ding Northern Song fine porcelain bodies do not fall exactly on the extrapolation of the mixing line from the glazes, but to the right-hand side of it. This suggests that the body material was not the only siliceous raw material used in this glaze. Moreover the siliceous material used in the glaze was also different from the one used for Ding Five Dynasties period white slip porcelain glaze, which contains high Sr concentrations and high $^{87}$Sr/$^{86}$Sr. The siliceous material used in the Northern Song fine porcelain glaze recipe should have a rather low Sr content and high $^{87}$Sr/$^{86}$Sr.

6. Discussion

6.1 The earliest use of limestone in Chinese high-fired glazes

The primary aim of this study is to search for the earliest use of limestone in Chinese high-fired glazes. Previous studies have allowed us to narrow down the range to be investigated to
Northern porcelain varieties dating to between the 6th and 10th centuries AD.

It is not that limestone has never been suggested as the flux for certain northern porcelain glazes during this period. Quite a few studies have done so based on the P$_2$O$_5$ contents of some northern porcelain glazes (Li 1998, Lu et al. 2012), but some studies have challenged such a suggestion, and the argument is also mainly based on the P$_2$O$_5$ contents of certain varieties of northern porcelain glazes (Kerr and Wood, 2009, Cui et al. 2012). This confusing situation is also considered in this study: some glazes identified as having limestone fluxes based on their Sr isotopic compositions, such as Ding Five Dynasties white slip glaze and Ding northern Song fine glaze have similar or even higher P$_2$O$_5$ contents than the glazes identified as wood ash glazes. This is a long standing issue in the area of northern porcelain study, and it has prevented scholars from gaining a clear understanding of the technological developments of northern porcelain glaze and when the use of limestone as a glaze flux emerged.

This study sets out to investigate whether limestone was indeed used for making northern porcelain glazes by using Sr isotope analysis and to pinpoint the time when limestone started to be used. This study also hopes to clarify why P$_2$O$_5$ contents in northern glazes has created confusion and cannot give us a clear clue about the matter.

Xing Sui to mid‐Tang white slip porcelain glaze is the earliest limestone based glaze identified by Sr isotopic composition in both North China and South China so far. The glaze made at the Xing kilns before white slip porcelain glaze was wood ash based early porcelain glaze and green stoneware glaze. However, Xing white slip porcelain glaze still has a comparatively high P$_2$O$_5$ content, despite its Sr isotopic composition mixing line suggesting that limestone was used as the flux in the recipe. We have ruled out the possibility that wood ash originating from plants growing on limestone soil was used as the flux for this glaze, which would otherwise be a good interpretation for a material with a limestone 87Sr/86Sr signature and high P$_2$O$_5$ contents. We ruled it out because we noticed this flux with a limestone signature and high P$_2$O$_5$ contents also occurred at Five Dynasties Ding kilns and Five Dynasties Jingdezhen. It would be too much of a coincidence if the three production sites all happened to use wood ash originating from a limestone soil at the same time for the same type of ware. The more sensible interpretation for this flux with limestone 87Sr/86Sr and comparatively high P$_2$O$_5$ content should have something to do with the way how limestone was prepared for glaze making at this stage. This issue was also discussed by Wu et al. (2020).

To allow limestone to be used as flux in a glaze suspension, it has to be first pulverised into very fine powder, the grain size of which should be in the same range as wood ash and clay particles to allow them to be mixed thoroughly in suspension. Given the hardness of limestone, this would have been very difficult to achieve by a physical method, so limestone was burnt to powder in the historical period and the recorded fuel for the task was herbaceous plants such as straw, rice husk and bracken. According to the multiple historical records describing the process of turning rocky limestone into fine powder at Jingdezhen, the earliest of which was made in the late Southern Song dynasty (c. 1214-1234), limestone had to be burnt multiple times during the process, because not only did the limestone have to be turned into fine powder, it also had to be re-carbonated from quicklime (CaO) or slaked lime (Ca(OH)$_2$) back into calcium carbonate (CaCO$_3$) to avoid the drastic chemical reactions with water and causticity. Therefore, the resultant powder
would actually be a mixture of limestone and botanic ash. Such powder is still being produced at Jingdezhen, and it is locally called *youhui* (glaze ash). Analyses of modern glaze ash showed that limestone accounts for the vast majority of its content, and the chemical composition of glaze ash probably has not changed much since the late Northern Song dynasty (Ma *et al*. 2014, Wu *et al*. 2020). But when limestone based glaze first appeared at Jingdezhen during the Five Dynasties period and early Northern Song dynasty (c. 10th century), the limestone-based flux used then also contained more \(P_2O_5\) than later times (Wu *et al*. 2020). This suggests that the processing method used then may have been different from that of later times, described in historical texts, and a higher proportion of botanic ash should have included in the powder. However this higher content of botanic ash residue in the burnt limestone powder would have had little influence to the Sr isotopic composition of the burnt limestone powder because botanic ash resulted from burning Herbaceous plants like bracken and rice husk content very low Sr content (Ma *et al*. 2014, Ma *et al*. 2016). This should be the reason why we find high \(P_2O_5\) contents in glazes that have limestone Sr signatures from the Sui to the early northern Song dynasties, and why \(P_2O_5\) contents cannot be used as a clear indicator for whether limestone or wood ash was used as the main flux.

In any case the period of Sui to mid-Tang dynasty (late 6th-early 9th century) should therefore have been a transition period when limestone started to replace wood ash as the main calcareous flux in glaze making in China before the recorded method of preparing limestone powder was established.

White slip porcelain first appeared at Xing kilns in the Sui dynasty (581-619) and were the main products there during the Tang dynasty (618-907). Unfortunately, our Xing white slip porcelain samples cannot specifically date to the short span of the Sui dynasty like that of Lu *et al*. (2014), but we should be able to conclude that the earliest use of limestone as a glaze flux identified so far should have occurred when white slip porcelain were produced at Xing kilns during the Sui to mid-Tang dynasty (late 6th to early 9th century).

6.2 The siliceous raw material used for glazes in Xing kiln products

The principle for glaze making in South China had been body material plus calcareous flux for most production centres, no matter whether the calcareous flux was wood ash or limestone (Wood 1999). Due to the very different geologies of North China and South China, the chemical and mineralogical composition of the materials for the ceramic bodies in North China and South China are quite different, especially for the \(SiO_2\) and \(Al_2O_3\) contents and \(SiO_2/Al_2O_3\) (Guo 1987). The body material used in the south was porcelain stone which generally has a comparatively high \(SiO_2\) content, low \(Al_2O_3\) content and high \(SiO_2/Al_2O_3\) (Rehren and Yin 2012). On the other hand the northern body material, which was mainly composed of coal clay, has a lower \(SiO_2\) content, higher \(Al_2O_3\) and lower \(SiO_2/Al_2O_3\) (Tite *et al*. 2012). However the chemical compositions of high fired ceramic glazes made in North China and South China were less different, whether it was a wood ash based glaze or a limestone based glaze, as the \(SiO_2/Al_2O_3\) of the formulae should be higher than 3.6-3.0 and ideally at 4-5 to allow an amorphous glass matrix to form effectively in

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* The word ‘botanic’ is used here to emphasize its compositional difference from wood ash, which is calcareous. The vegetation used for burning limestone in practice and in historical literature is not wood but herbaceous plants like straw, rice husk and bracken, and the ash of these plants is very low in calcium and strontium but high in silica. Therefore the residual botanic ash in the powder would result elevated \(SiO_2\) and \(P_2O_5\) content, but it hardly introduces any Sr.
the SiO₂-Al₂O₃-CaO-MgO-Na₂O-K₂O system (Partyka et al. 2015). These factors forced northern potters to seek other siliceous raw materials for their glaze recipe, and not just to rely on such body materials. From our chemical and Sr isotopic results of Xing glazes, we can see this quite clearly.

The results of Sr isotope and chemical analysis of our early porcelain samples from Xing kilns show that body material was not the sole siliceous material in the glaze formula. Although green stoneware glaze from Xing kilns is not studied in this work, from its chemical composition reported in Huang et al. (2020), we can see that it has a very similar chemical composition to Xing early porcelain, and there is also a Na₂O content discrepancy between Xing green stoneware body and glaze which suggests that another raw material, apart from body material and wood ash, was included in the glaze recipe.

When white slip porcelain came along, Xing potters not only used a new calcareous flux in its recipe, they also gave up using body material in the glaze completely. Five Dynasty Ding potter also inherited this approach. It was first noticed by Wood (1999) that the TiO₂ and Fe₂O₃ contents of Xing white slip porcelain glaze are too low for the body material to be the main siliceous material in the recipe and our Sr isotopic results also suggest the same.

A consideration of why potters gave up using body material for this glaze should be quite straightforward: they did not want the impure grey-firing body material to reduce the whiteness of wares created by the white slip. The nature of clay found in northern China is coal clay; the majority of coal clay is not the white-firing type and only a small proportion of coal clay can produce a white colour after being fired (Tite et al. 2012). The purpose of using white slip in porcelain production in the first place would have been to increase the visual whiteness of the wares while not using too much of the precious white-firing clay. Therefore it was only sensible that Xing potters gave up using body material in the glazes to avoid the whiteness of the wares being compromised.

6.3 The porcelain glaze recipes of the Ding kilns

Previous studies of Ding kilns porcelain glazes have reached quite different conclusions about the raw materials used in Ding glazes, especially for the flux. According to the high MgO contents in Ding glazes and the rich dolomite resources in the vicinities of the Ding kiln complex, Li and Guo (1983) suggested that the flux for Ding glazes was either dolomite or dolomitized limestone. According to the low CaO/P₂O₅ ratio of Ding glaze, Kerr and Wood (2004) suggested wood ash could still be the flux in the Ding glaze recipe. Based on the negative correlation of MgO and CaO and the relatively high P₂O₅ content, Cui and et al. (2012) suggested that two raw materials were involved: one was wood ash but the other was unknown. By analysing some possible glaze raw materials unearthed by excavation, Kang and et al. (2014) suggested a limestone based powder, which is made by firing limestone using wood as fuel, was the flux for Ding glazes.

The four quite different interpretations of Ding glaze chemistries all have sound reasoning but lead to rather different conclusions about the raw materials used. What should we take from them?

Our Sr isotopic results suggest that the three glazes studied in this work, which were made in
different parts of Ding kilns complex during different historical periods, were made by three
different recipes. Is this the reason why we get contradictory interpretations from the previous
studies? These studies were trying to simplify a singular approach for the entire duration of Ding
glaze production. But the real situation for glaze making at the Ding kilns may have kept changing
throughout its production and perhaps even between different workshops at the same time.

Our Sr isotopic compositions of Ding Five dynasties white slip glaze produced at Beizhen village
do suggest dolomitized limestone was used as the flux for this glaze, and we have explained why
it has comparatively high P₂O₅ content.

The possible glaze making raw materials analysed by Kang et al. (2014) were unearthed from a
Northern Song dynasty workshop located at Jianci village and the analytical results suggest that a
fairly pure (not highly dolomitized) limestone was the flux used at the site. This limestone powder
was pulverized by burning cypress wood because cypress ash has been identified in the powder.
This suggestion is also consistent with our Sr isotopic results for Ding Northern Song fine
porcelain glaze produced at Jianci village.

The low CaO/P₂O₅ in Ding glaze was noted by Kerr and Wood (2004) and by Cui et al. (2012). They
suggested that wood ash was the flux used: we have observed this but only in Jin dynasty fine
porcelain glaze from Jianxi village. The CaO/P₂O₅ of this glaze is actually the lowest value among
all the glazes studied in this work. It is even lower than the confirmed wood ash green stoneware
glaze from Gongyi kilns. Our results agree with those published by Cui et al. (2012) who found
that the lowest CaO/P₂O₅ was in samples made at Jin dynasty Jianxi village. This low CaO/P₂O₅
also coincides with our Sr isotopic results for the glaze which suggest that the flux used may have
switched back to wood ash.

Technologically reverting back from a limestone based glaze to wood ash based one is
retrogressive. Limestone is a far superior calcareous raw material than wood ash: pulverized
limestone is much easier to produce in large quantities than wood ash given the abundance of
limestone in the area, and pulverized limestone is much purer with lower levels of e.g. P₂O₅ and
MnO for making colourless porcelain glaze than wood ash. When pottery production progresses
and develops in a normal way, this technological regression should not have happened.

However, the Ding kilns did get devastated at the end of the northern Song dynasty when Jurchen
invaded and took Heibei province where the Ding kilns were located. According to historical
records and archaeological excavations, after the devastation the production of Ding kilns did not
recover for another 30 years when the Jurchen Jin had stabilized the governance in the area (Li
and Bi 1987). Many skilled Ding potters fled from Quyang during the turmoil, and some of them
got to Jingdezhen, which is southern Song territory, to carry on their practice. The Ding type
wares made at Jingdezhen during this period were called southern Ding wares (Liu 1974). At the
end of 30 years of this disruption when Ding kilns resumed their production, it seems that the
technology used (in the Jin dynasty), at least for production in Jianxi village, was not the same as
northern Song Ding technology. A comparatively less developed technology was used instead.
Ding kilns did recover to mass production during the Jin dynasty, but to what extent the old

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5 Our Northern Song dynasty fine porcelain samples and the samples studied in Kang et al. (2014) were from the
same excavation
6 Our Ding kiln samples and samples studied in Cui et al. (2012) are also from the same excavations.
fashioned glaze recipe replaced the northern Song Ding glaze recipe should be addressed by further studies.

Different authors agree on the use of siliceous raw materials to make Ding glazes: a body material may have been used in the formula but it was not the main siliceous material used because the TiO₂, Fe₂O₃ and Al₂O₃ contents of the glazes are too low for the body material to be the main siliceous raw material used in the formula (Wood 1999, Cui et al. 2012, Kang et al. 2014). The Sr isotopic composition is not a very suitable index to suggest what specific siliceous raw materials were used in glaze formulae, but we can still see from the mixing lines of the three Ding glazes studied here that their siliceous raw materials were all different: a material with high Sr concentration (c. 400 ppm) and high $^{87}$Sr/$^{86}$Sr ($\geq 0.72$) was used as the main siliceous material for Five Dynasties white slip glaze; a material with a low Sr concentration ($\lesssim 100$ ppm) and high $^{87}$Sr/$^{86}$Sr ($\geq 0.72$) was used in the formula of Northern Song dynasty fine glaze; and body material was used in Jin fine porcelain glaze. Although it is not very sound to infer the nature of the siliceous raw material used in a glaze formula by the Sr isotopic composition suggested by mixing lines, the high $^{87}$Sr/$^{86}$Sr signature and chemical composition of the siliceous materials used in Ding Five Dynasties white slip glaze, Ding northern Song dynasty fine glaze and Xing white slip porcelain glaze do suggest they could have derived from (possibly weathered products of) felsic rocks with very old ages. The Precambrian gneissose granitic complex is the main felsic outcrop on the eastern slope of the Taihang Mountain (Figure 1), and one K-feldspar sample collected from this outcrop near Ding kilns has very high $^{87}$Sr/$^{86}$Sr at 0.762020. Therefore some weathered felsic rocks from the eastern slope of Taihang Mountain, especially the light colour sort with low TiO₂ and Fe₂O₃ contents (Ren et al. 2009), which has the same chemical composition as the rocky materials unearthed in the excavation of Ding kilns in 2009 (Wood 2013), could have been the siliceous material used for relevant Xing and Ding glazes.

The same recipe for Xing Tang dynasty white slip porcelain glaze and Ding Five Dynasties white slip porcelain glaze suggested by our Sr isotopic data (and the very similar chemical compositions of the two porcelain wares) agree with the claim made by other scholars that the establishment of the Ding kilns during late Tang dynasty and early Five Dynasties period may have been the result of direct Xing technology relocation around the time when the Xing kilns declined in late Tang dynasty (Li 1983).

The quality peak of Ding kilns was during the Northern Song dynasty: the Ding wares are regarded as one of the five great wares made during the Song dynasty. From a technological point of view, the occurrence of such a peak in quality should be attributed to Ding potters giving up white slip porcelain production transferred from Xing kilns and starting to produce new delicate fine porcelain wares instead. Our Sr isotope and chemical data also suggest a whole new glaze recipe was developed for these fine new wares.

7. Conclusions

The estimation is based on the growth of radiogenic $^{87}$Sr equation: $\frac{^{87}Sr}{^{86}Sr}$ = $\frac{^{87}Sr}{^{86}Sr}_0 + \frac{^{87}Rb}{^{86}Sr}_0 (e^{\lambda t} - 1)$, $\lambda$ = 1.42 × 10⁻¹¹ yr⁻¹ ($^{87}$Rb decay constant), $\frac{^{87}Sr}{^{86}Sr}_0$ = 0.699 (primordial meteorite value), $\frac{^{87}Rb}{^{86}Sr}_0$ = 0.53 (average concentrations of rubidium in terrestrial rocks) (Faure and Powell 1972).
The profound differences in the raw materials used for northern and southern ceramic glaze production made it very difficult for northern potters to retain the glaze making principles which initially derived from the south, namely the use of body material plus calcareous flux. This is very clear to see in the practice followed by the Xing kilns. Though Xing potters kept the wood ash flux during the early years, they added another material to their glaze formula with high Na$_2$O in the earliest phase of their production. Soon Xing potters came up with a completely new approach to manufacturing porcelain by using white slip to improve the whiteness of the wares and limestone as a glaze flux. At this point during the Sui to mid-Tang dynasty (late 6th-early 9th Century) limestone was, for the first time, used as a glaze flux in Chinese high-fired ceramic making, and it was probably used in a mixture along with wood ash. This approach completely freed porcelain production at the Xing kilns from the limitation imposed by sourcing scarce resources, namely white-firing clay and wood ash. Xing potters also gave up using body material as the main siliceous raw material in the glaze, possibly because they did not want the grey-firing body material to compromise the whiteness of the ware. The white slip was very easy to copy, although the new limestone-based glaze formula may have been kept secret until the Xing technology relocated to Quyang to found the Ding kilns. The new fine porcelain and the new glaze formula associated with the fine porcelain saw the quality peak of Ding kilns during the Northern Song dynasty and before the Jurchen invasion devastated this production site. When production of Ding kilns recovered again some 30 years later, at least at some workshops, an old fashioned glaze recipe based on wood ash and body material was picked up again.

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References


*Figure 1 the simplified location maps and surrounding geologies of Gongyi kilns, Xing kilns and Ding kilns*
Figure 2A (left) and 2B (right) Sr isotopic composition of Gongyi green stoneware glaze (GY-GS), Gongyi Tang white slip porcelain glaze (GY-TP) and some relevant raw materials.

Figure 3A (left) 3B (right) Sr isotopic composition of Xing early porcelain glaze (X-EP) and Body (X-EP Body) and wood ash originated from Loess landscape.

Figure 4A (Top left) 4B (Top right) 4C (middle left) 4D (middle right) 4E (bottom left) 4F (bottom right) Sr isotopic composition of Xing Sui to mid-Tang (X-ST) dynasty white slip porcelain glaze, Ding Five Dynasties (D-FD) white slip porcelain glaze, their ceramic bodies (X-ST-body, D-FD-body) and some possible raw materials from the region (The double arrow is to point out the alteration of the Sr isotopic compositions of the Ordovician limestone rendered by the dolomitization process, from undolomitized limestone with high Sr concentration and low $^{87}\text{Sr}/^{86}\text{Sr}$ to highly dolomitized limestone with low Sr concentration and high $^{87}\text{Sr}/^{86}\text{Sr}$).

Figure 5A (left) 5B (right) Sr isotopic composition of Ding northern Song (D-NS), Jin (D-J) fine porcelain glaze, their ceramic bodies (D-NS-body, D-J-body) and limestone and dolomite from the region and wood ash from Loess landscape.