

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

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12  
13      **Abstract**

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

22  
23      **Keywords:** Sr isotopic analysis, North China, porcelain

24  
25      **1. Introduction**

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

38      One of the key questions regarding northern porcelain is what calcareous flux was used in the  
39      glazes. Nearly all Chinese high-fired ceramics have a calcareous glaze, and two calcareous  
40      materials, limestone and wood ash, are regarded as the two different fluxes used in Chinese  
41      high-fired glaze recipes (Luo 1995). It is certain now that wood ash was a common flux used  
42      before limestone glaze was widely adopted in China. However, very specific questions about

43 when and where limestone was first introduced into glaze-making have not yet been addressed.  
44 The key to pinpointing when and where limestone was first used in glaze making is to work out  
45 from which varieties of glazes we should look for the answers. It has been repeatedly proven that  
46 green stoneware glaze, which was the earliest high-fired ceramic glaze in China, was a wood ash  
47 glaze; and southern Qingbai glaze was a limestone based glaze<sup>1</sup> according to historical records  
48 and scientific evidences (Huang *et al.* 2020, Ma *et al.* 2014). A recent study suggested that the  
49 earliest use of limestone in glaze recipes at Jingdezhen, South China occurred before Qingbai  
50 ware was first produced and the early use of limestone at Jingdezhen could have been under the  
51 influence of northern porcelain makers (Wu *et al.* 2020). In fact northern porcelain, which was  
52 the earliest porcelain in the world according to the original definition of the word ‘porcelain’  
53 (white and high-fired), was basically the only ceramic variety that prevailed in China between  
54 green glaze stoneware and Qingbai ware (Kerr and Wood 2004). So it is highly likely that it was  
55 among northern porcelain varieties that limestone was first introduced in Chinese glaze making.  
56 In this study, varieties of northern porcelain from the three most important northern porcelain  
57 production centres between the 6<sup>th</sup> and 13<sup>th</sup> centuries, namely Gongyi kilns, Xing kilns and Ding  
58 kilns, are studied using Sr isotopic analysis and electron probe microanalysis to address this  
59 question.

60 Another related issue, whether the recipe used for northern porcelain glaze followed the  
61 principle of creating high-fired ceramic glaze in South China, namely body material<sup>2</sup> plus  
62 calcareous flux, will also be discussed.

63

## 64 **2. The development of northern porcelain wares**

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

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

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<sup>1</sup> 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.

<sup>2</sup> 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.

78 bodies made with white-firing clay (Wood 1999).  
79 Soon after early porcelain was introduced a new kind of porcelain, which has a white slip layer  
80 between the ceramic body and glaze, emerged at the Xing kilns during the Sui dynasty (581-618  
81 AD) (Lu *et al.* 2012). This was not the first time that a white slip had been used to decorate glazed  
82 ceramics in China, but it was the first time this technique had been used on high-fired porcelain  
83 wares (Qin 2018). The white slip layer was made by using the finest white-firing clay, a rarity in  
84 the carboniferous coal clay in north China. This layer was used to cover the grey and sometimes  
85 darkly tinged ceramic bodies made from common coal clay to improve the whiteness of the  
86 wares (Tite *et al.* 2012). During the Tang dynasty (618—907 AD), the production peak of northern  
87 porcelain, white slip porcelain were the common wares produced in large quantities by northern  
88 kilns. There were a small proportion of non-slipped fine wares produced during the Tang dynasty  
89 at the Gongyi and Xing kilns; these wares were regarded as exclusive wares and their glazes were  
90 often more alkaline (Wang *et al.* 2019). These Tang dynasty fine wares are not within the scope of  
91 this paper.

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

100

### 101 **3. Samples**

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

- 105 (1) Early porcelain wares of the Late Northern Dynasties period (c. 6<sup>th</sup> century AD) from  
106 Neiqiu County, the core area of Xing kilns complex (6 samples);
- 107 (2) White slip porcelain wares of the Sui to mid-Tang dynasty (c. late 6<sup>th</sup>— early 9<sup>th</sup> century  
108 AD) from Neiqiu County, Xing kilns (9 samples),
- 109 (3) White slip porcelain wares of the Tang dynasty (c. 7<sup>th</sup> —9<sup>th</sup> century AD) from Gongyi kilns  
110 (8 samples)
- 111 (4) White slip porcelain wares of the Five Dynasties period (c. 10<sup>th</sup> century AD) from Ding  
112 kilns (4 samples);
- 113 (5) Fine porcelain wares of the Northern Song dynasty (c. late 10<sup>th</sup>—early 12<sup>th</sup> century AD)  
114 and the Jin dynasty (c. mid-12<sup>th</sup>—mid-13<sup>th</sup> century AD) from Ding kilns (6 samples and 5  
115 samples respectively);
- 116 (6) Northern green glazed stoneware of Northern Dynasties period (c. late 5<sup>th</sup>—6<sup>th</sup> century  
117 AD) from Gongyi kilns (8 samples)
- 118 (7) Raw materials collected in the area of ancient Ding kilns (6 samples) are also included in  
119 this study for reference.

120 Further detailed sample information is shown in table 1.

121

#### 122 **4. Analysis**

123 Sr isotopic analysis has been used to study the flux component in ancient western glass since  
124 2000 (Wedepohl and Baumann 2000), and this technique has been introduced into the study of  
125 Chinese high-fired ceramic glaze, which is basically a thin layer of glass, in recent years. Previous  
126 exploration works have laid the foundation for the application of Sr isotopic analysis in Chinese  
127 glazes (Ma *et al.* 2014, Ma *et al.* 2016, Li *et al.* 2019b). A few application works of this newly  
128 developed approach and a review paper to generalize our up-to-date understanding of this  
129 method have been published (Ma *et al.* 2019, Shen *et al.* 2019, Henderson *et al.* 2020). In this  
130 work Sr isotopic compositions of porcelain glazes and bodies determined by thermal ionization  
131 mass spectrometry (TIMS) are used as the main data for our investigation, and major and minor  
132 elemental compositions of porcelain glazes and bodies determined using electron probe  
133 microanalysis (EPMA) provide the basic chemical data.

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

144 The resulting samples were then taken off the glass slide using boiling Milli-Q water. The boiling  
145 water releases the very thin glaze ( $<200 \mu\text{m}$ ), sometimes in fragments, from the epoxy resin, and  
146 the glaze samples drop in the water. Then the glaze samples were collected in clean glass beakers  
147 and transferred to a clean (class 100, laminar flow) working area for further preparation. In the  
148 clean laboratory, the samples were cleaned ultrasonically in Milli-Q water, dried on a hotplate  
149 and then weighed into pre-cleaned Teflon beakers. The samples were spiked with  $^{84}\text{Sr}$  tracer  
150 solution and dissolved in Teflon distilled 8M  $\text{HNO}_3$  and Ultrapure 29M HF. Samples were  
151 converted to chloride form using Teflon distilled 6M HCl. The samples were then taken up in  
152 calibrated 2.5M HCl and centrifuged. Strontium was collected using Eichrom AG50 X8 resin  
153 columns.

154 Each sample was then loaded on to a single Re filament with TaF, following the method of Birck  
155 (1986). The  $^{87}\text{Sr}/^{86}\text{Sr}$  and Strontium elemental concentrations were determined by Thermal  
156 Ionisation Mass spectroscopy (TIMS) using a Thermo Triton multi-collector mass spectrometer at  
157 the National Environmental Isotope Facility at the British Geological Survey. The international  
158 standard for  $^{87}\text{Sr}/^{86}\text{Sr}$ , NBS987, loaded in the same way, gave a value of  $0.710260 \pm 0.000018$   
159 ( $n=21, 2\sigma$ ) during the analysis of these samples and sample data was normalized to the accepted  
160 value for this standard of 0.710250. Procedural blank values were in the region of 100 pg. The Sr  
161 isotopic compositions of samples analysed in this work are reported in table 2.

162 Electron microprobe analysis was carried out on our glaze samples to determine their chemical  
163 compositions. Fragments of each ceramic shard were mounted in cross-section in epoxy resin  
164 blocks and polished to a 0.25mm diamond paste finish so as to reveal a flat analytical area. The  
165 blocks were carbon coated to prevent surface charging and distortion of the electron beam  
166 during analysis. A Shimadzu EPMA-1720 electron microprobe housed in the State Key Laboratory  
167 of Advanced Metallurgy, University of Science and Technology Beijing, was used for the chemical  
168 analysis of the samples. The system is equipped with four wavelength-dispersive X-ray  
169 spectrometers with LIF, TAP, PETJ and LIFH crystals, a single energy-dispersive X-ray spectrometer,  
170 and both secondary and backscattered detectors. A defocused electron beam with a diameter of  
171 50  $\mu\text{m}$  was used to prevent volatilization of light elements such as sodium. The probe was run at  
172 an accelerating voltage of 20kV and a beam current of 5 nA. The system was calibrated with a  
173 natural basalt glass standard for Si, Al, Na, K, Mg, Ca, Ti, Fe and the Corning D glass reference  
174 material for P. A ZAF program was used to correct and quantify the results. The Corning D glass  
175 reference material was routinely used as a secondary standard to check for accuracy and  
176 precision and to monitor any drift in the instrument. The Corning D glass standard was analysed  
177 five times during the whole analytical process. The analytical precision and accuracy achieved by  
178 using a Corning D standard are listed in Table 3. The chemical compositions of glazes and bodies  
179 of the porcelain varieties analysed by EPMA in this work are also reported in table 3. Due to the  
180 low totals (90-95 wt%) retrieved from some semi-fused porcelain body analyses, the reported  
181 chemical compositions of porcelain bodies have been normalized to 100 wt% and should only be  
182 deemed semi-quantitative. The possible reason for the low totals of these ceramic body analyses  
183 is that ceramic bodies are multi-phase matrix with cavities created by escaped gas contained in  
184 the unfired ceramic paste; they are not ideal analytical subjects for EPMA analysis, which is  
185 calibrated by single phase minerals and/or glass, therefore sometimes low totals will be retrieved  
186 for semi-fused ceramic bodies. Since ceramic bodies are not the main research subjects of this  
187 work, these semi-quantitative data should serve the purpose to provide basic chemical  
188 composition profiles of the body materials

189

## 190 **5. Results**

### 191 ***5.1 the Sr isotopic composition data interpretation method applied in this work***

192 Nearly all Chinese high-fired ceramic glazes are calcareous, and this feature makes Sr isotopic  
193 analysis a highly suitable technique to study their calcareous fluxes, because common natural  
194 calcium sources, namely seashells, limestone and wood ash, all have their characteristic  $^{87}\text{Sr}/^{86}\text{Sr}$ .  
195 Although there are some overlaps between the  $^{87}\text{Sr}/^{86}\text{Sr}$  signatures of the three calcium sources,  
196 by considering their Sr concentrations, Sr/Ca and bio-available  $^{87}\text{Sr}/^{86}\text{Sr}$  in the immediate  
197 landscape from which the wood ash originated, we should be able to, in most of the cases,  
198 identify which calcium source was used as the calcareous flux in a specific glaze recipe  
199 (Henderson *et al.* 2020). However, unlike the situation in ancient western glass where the Sr in  
200 the glass produced was mostly contributed from one source (Sr contributions for low Sr content  
201 materials in high amounts or high Sr content materials in low amounts have also been considered  
202 in recent works), in Chinese high fired ceramic glazes the Sr was normally contributed from two  
203 sources, the calcareous flux and the siliceous material or materials (Ma *et al.* 2014, Li *et al.*  
204 2019b).

205 Theoretically speaking for any material made by fusing two or more raw materials with different  
 206 Sr isotopic compositions ( $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr concentration), its Sr isotopic composition should be a  
 207 mixture of Sr isotopic compositions of the two or more raw material components according to  
 208 the equation below.

$$209 \quad \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_M = \frac{Sr_A Sr_B \left( \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_B - \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_A \right)}{Sr_M (Sr_A - Sr_B)} + \frac{Sr_A \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_A - Sr_B \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_B}{Sr_A - Sr_B} \quad (\text{Equation 1})$$

210 Where  $\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_M$  and  $Sr_M$  are Sr isotopic ratio and Sr concentration of the mixture, and  $\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_{A,B}$   
 211  $Sr_{A,B}$  are Sr isotopic ratio and Sr concentration of the two mixing components.

212 Because the Sr isotopic ratio and Sr concentration ( $\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_{A,B}$  and  $Sr_{A,B}$ ) for the mixing components  
 213 are constant, the equation could be simplified as

$$214 \quad \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_M = \frac{a}{Sr_M} + b \quad (\text{Equation 2})$$

215 Equation 2 shows that  $\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}_M$  and  $Sr_M$  of mixtures combined in different proportions of the  
 216 components should form a hyperbola with the Sr isotopic compositions of the mixing component  
 217 being the two ends of the mixing line (Faure 1986). When taking  $\frac{1}{Sr_M}$  as abscissa, we can switch  
 218 the hyperbola into a straight line, which will show the mixing effect more clearly, but the down  
 219 side is the X axis would not be linear but distributed according to  $Sr_M^{-1}$  (Henderson *et al.* 2020).

220 Mixing lines are suggested for nearly all Sr isotopic compositions of the glaze varieties we have  
 221 studied; mixing lines are demonstrated by plotting  $^{87}\text{Sr}/^{86}\text{Sr}$  against  $1000/(\text{Sr ppm})$  and thereby to  
 222 suggest what raw materials were used to make the glazes. It has to be borne in mind that a  
 223 mixing line can only suggest the presence of the main strontium contributors in the glaze formula,  
 224 but not every component. Therefore the presence of a raw material with a very low absolute  
 225 strontium contribution will not reflect in a mixing line. For example, when a very pure form of  
 226 silica was used in a glaze recipe, even a large amount of it may have been used, its presence may  
 227 not reflect in the mixing line due to its very low absolute Sr contribution to the resultant glaze.

228

## 229 **5.2 The chemical and Sr isotopic compositions of Gongyi northern Dynasties green stoneware** 230 **and Tang dynasty porcelain glazes**

231 Green glazed stoneware was the first high-fired ceramic made in North China and the  
 232 technological precursor of early northern porcelain. It has been suggested that the northern  
 233 green stoneware glaze was created following the original southern recipe: wood ash plus body  
 234 material (Huang *et al.* 2020). The Sr isotopic compositions of our Gongyi green stoneware glaze  
 235 samples are very consistent at 0.715-0.718 for  $^{87}\text{Sr}/^{86}\text{Sr}$  and 300-350 ppm for Sr concentration  
 236 (Figure 1). The high Sr concentrations and high  $\text{P}_2\text{O}_5$  contents average at 0.74 wt% are typical for  
 237 a wood ash glaze (Henderson *et al.* 2020), and the high  $\text{TiO}_2$  contents agree with the suggestion  
 238 that body material was used in the recipe (Wood 1999).

239 The early porcelain made at Gongyi kilns was one the earliest porcelain wares made in China.  
240 Due to the rarity of these early porcelain wares, we did not manage to sample them for  
241 destructive analysis. However, Gongyi Tang dynasty white slip porcelain, a mature porcelain ware  
242 which developed from early porcelain, has been analysed for its chemical and Sr isotopic  
243 compositions. A mixing line is clearly suggested by the Sr isotopic compositions of individual  
244 Gongyi early porcelain glaze samples, and the high P<sub>2</sub>O<sub>5</sub> content and high TiO<sub>2</sub> content also  
245 suggest the presence of wood ash and body material in the recipe.

246 By plotting the Sr isotopic compositions of the Gongyi white slip porcelain glaze and green  
247 stoneware glaze along with that of Gongyi ceramic bodies published by Li *et al.* (2008) and wood  
248 ashes originated from the Loess landscape, we can see quite clearly the connections between  
249 them (Figure 2). The Sr isotopic compositions of Gongyi ceramic bodies and wood ashes  
250 originated from the Loess landscape approximately occupy the two ends of the mixing line  
251 formed by Sr isotopic compositions of Gongyi white slip porcelain glaze, and the Sr isotopic  
252 compositions of Gongyi green stoneware glaze are on the extrapolation of that of Gongyi white  
253 slip porcelain glaze towards that of wood ash originated from the loess landscape. This pattern  
254 suggests wood ash and body material were also the two main raw materials used in Gongyi white  
255 slip porcelain glaze, same as green stoneware glaze; but the white slip porcelain glaze clearly  
256 used lower proportion of wood ash in the recipe, and this was probably to avoid the dark tinge  
257 caused by the impurities from the ash. The lower CaO/SiO<sub>2</sub> in Gongyi white slip porcelain glaze  
258 also suggests lower wood ash to body material ratio in the glaze recipe.

259

260 The clear discrepancies in the Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> contents and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> between the Gongyi white  
261 slip porcelain glaze and ceramic body suggests body material was not the only siliceous material  
262 used in the formula and some extra SiO<sub>2</sub> should have been introduced in the glaze by a third raw  
263 material component. The presence of this third raw material in the glaze formula is not very  
264 clearly shown by the mixing line; but the high <sup>87</sup>Sr/<sup>86</sup>Sr end of the extrapolation of the mixing line  
265 goes slightly above the Sr isotopic compositions of the ceramic bodies (Figure 2B), and this  
266 should hint the presence of this third raw material. The Sr contribution introduced by this third  
267 raw material to the glaze should have been quite small, possibly due to only a small amount of  
268 this third material was added in the formula or it was a rather pure form of silica, which contains  
269 very low content of Sr, and that is the reason why it is not clearly suggested by the mixing line.

270

### 271 **5.3 The chemical and Sr isotopic compositions of early porcelain glaze from Xing kilns**

272 Late northern Dynasties period early porcelain made in Xing kilns is one of the earliest porcelain  
273 wares made in China. The six individual Sr isotopic compositions of Xing early porcelain glaze  
274 form a clear mixing line; the high Sr concentration end of the mixing line points to the Sr isotopic  
275 composition of wood ash carrying typical <sup>87</sup>Sr/<sup>86</sup>Sr from the loess landscape (Figure 3). The low Sr  
276 concentration end of the mixing line, however, does not point directly to the Sr isotopic  
277 composition of the body material (Figure 3B). This suggests that the body material was not used  
278 as the sole siliceous raw material in the glaze formula. Chemical compositions of Xing early  
279 porcelain bodies and glazes also support this suggestion; as Xing early porcelain glazes have a  
280 rather high Na<sub>2</sub>O content averaging 3.05 wt%, which is not seen in the porcelain body. This Na<sub>2</sub>O  
281 content is unlikely to have been introduced in the wood ash, because it is well known that

282 sodium is toxic for most land plants (Horie and Schroeder 2004), and the ash of those plants  
283 would normally contain less than 3.0 wt% Na<sub>2</sub>O (Vassilev *et al.* 2010). Halophytic plant species  
284 are tolerant to alkalis including Na<sup>+</sup> and are therefore exceptions to this rule; their ash can  
285 contain over 10 wt% Na<sub>2</sub>O. The non-halophytic plant ashes originating from the loess landscape  
286 have low Na<sub>2</sub>O contents of less than 1 wt% as many data show (Kerr and Wood 2004, Li *et al.*  
287 2019b), and this is also confirmed by many chemical compositions of wood ash glazes made at  
288 production sites located in the loess dominated area (Shen *et al.* 2019, Huang *et al.* 2020).  
289 Therefore the Na<sub>2</sub>O content in the glaze must have derived from a material other than the body  
290 and wood ash. Although the body material should not be the only siliceous raw material used to  
291 make glaze, the high TiO<sub>2</sub> contents of Xing early porcelain glaze do suggest that the body material  
292 was still used as one component in the recipe (Wood 1999, Wood 2009).

293

#### 294 **5.4 The chemical and Sr isotopic compositions of white slip porcelain glazes from Xing and Ding** 295 **kilns**

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

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

309 Regarding this completely new recipe of white slip porcelain glaze reflected by Sr isotopic  
310 compositions, firstly the calcareous raw material in the formula has changed. The ends of the  
311 mixing lines for Xing and Ding white slip porcelain glazes do not point to the Sr isotopic  
312 compositional range of wood ash originating from the loess landscape like that of Xing early  
313 porcelain glaze and Gongyi glazes, but instead they both point at a Sr isotopic composition of  
314 around 0.7080 for <sup>87</sup>Sr/<sup>86</sup>Sr and 200 ppm for Sr concentration (Figure 4B, 4D, 4F), a characteristic  
315 isotopic composition of Ordovician limestone occurred in the North China Platform, which have  
316 distinctively lower Sr concentration than that of worldwide limestone average 460 ppm (Figure 4).  
317 According to the geological map of north China, the eastern slope of Taihang Mountain, on which  
318 the Xing and Ding kilns are located, is among the areas in which limestone abundantly outcrops  
319 (Figure 1). The limestone in this area is of an Ordovician date. The area of the North China  
320 Platform, which is a geological label encompassing most of central North China, was a sea during  
321 the Ordovician period, and the limestone was formed in the marine environment of the time  
322 (Zhang *et al.* 2018). A key feature of this Ordovician limestone is that commonly it had  
323 experienced various degrees of dolomitization. Therefore a large proportion of limestone in this  
324 area had been turned into dolomitized limestone or dolomite. According to Zhang *et al.* (2018),



325 limestone, dolomitized limestone and dolomite of this area have Sr concentrations of between  
326 296 ppm and 79ppm, which are far below the worldwide limestone average 460 ppm, and  
327  $^{87}\text{Sr}/^{86}\text{Sr}$  of between 0.7086 and 0.7118. The Sr isotopic compositions of Ordovician limestone  
328 and dolomite sampled from the eastern Taihang Mountain in this study are (154 ppm, 0.708400)  
329 and (18 ppm, 0.70792), which agrees with the data reported by Zhang *et al.* (2018), and they are  
330 also plotted in Figure 4.

331 How dolomitization occurred exactly is part of a heated debate in geology (Wang *et al.* 2016).  
332 However, it has been confirmed that dolomitization would reduce the Sr concentration in  
333 limestone and increase the whole rock  $^{87}\text{Sr}/^{86}\text{Sr}$  at the same time. The Sr concentration and  
334  $^{87}\text{Sr}/^{86}\text{Sr}$  of limestone that went through different degrees of dolomitization in the North China  
335 Platform also fits this trend (Figure 4). This is the reason why the Sr concentrations of Ordovician  
336 limestone in this area fall below the worldwide average limestone Sr concentration of 460 ppm  
337 (Wedepohl and Baumann 2000), and the limestone used in Xing and Ding white slip porcelain  
338 glaze suggested by the mixing line is only at Sr concentration around 200 ppm: the limestone  
339 used for these glazes should have been local low degree dolomitized limestone. The elevated  
340 MgO contents ( $\text{MgO} \geq 2.5$  wt% ) and lower CaO/MgO ( $\approx 5.4$ ) of Xing and Ding white slip  
341 porcelain glazes compared to that of Jingdezhen ordinary limestone based glaze<sup>3</sup> ( $\text{MgO} < 0.5$  wt%,  
342  $\text{CaO}/\text{MgO} \approx 20.4$ ) is another suggestion of low degree dolomitized limestone had been used as  
343 the flux for these glazes.

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

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

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<sup>3</sup> 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.

366 and Ding white slip porcelain glaze. As for the reason why the limestone based flux used for Xing  
367 and Ding white slip glaze also bore rather high P<sub>2</sub>O<sub>5</sub> content, we may have to consider factors  
368 such as how the limestone based flux was processed at this early stage. This issue is addressed in  
369 detail in the section 6.1.

370 Moreover, based on the Sr isotopic data we can also suggest that the body material was not used  
371 as the siliceous raw material in the Xing and Ding white slip porcelain glaze, as the Sr isotopic  
372 compositions of ceramic bodies of Xing and Ding white porcelain plot far off the extrapolation of  
373 the mixing lines formed by the Sr isotopic compositions of their glazes (Figure 4). The very low  
374 TiO<sub>2</sub> content of Xing and Ding white slip glazes also suggest body material, which contains much  
375 higher TiO<sub>2</sub> (Table 3) would not have been added in the recipe, at least not as a main component.  
376 According to the mixing line the siliceous raw material for Xing and Ding white slip glaze should  
377 have been a material with high <sup>87</sup>Sr/<sup>86</sup>Sr (≥0.720) and high Sr concentration (c. 400 ppm). The  
378 possible nature of this material is tentatively discussed in the section 6.3.

### 379 ***5.5 The chemical and Sr isotopic compositions of Ding northern Song and Jin fine porcelain*** 380 ***glazes***

381 The Sr isotopic compositions of Ding northern Song and Jin fine porcelain glazes are again  
382 different from the earlier white slip porcelain glaze. The individual Sr concentration of each glaze  
383 sample in fine glazes is much lower, basically between 100 ppm and 200 ppm while other glazes  
384 studied here have Sr concentrations between 200 ppm and 450 ppm (Figure 5A). Mixing lines are  
385 formed by individual Sr isotopic compositions of the two fine glazes; however the raw materials  
386 suggested by the mixing lines are quite different. As shown in Figure 5B, it appears that limestone  
387 was the flux used in Ding northern Song fine porcelain glaze and wood ash was the flux used in  
388 Ding Jin fine porcelain glaze. This change is also supported by the obvious elevated P<sub>2</sub>O<sub>5</sub> contents  
389 and lower CaO/P<sub>2</sub>O<sub>5</sub> in Jin fine porcelain glaze than Northern Song fine glaze, and this was also  
390 noted by Cui *et al.* (2012).

391 As shown in Figure 5B, the siliceous raw materials used in Ding Northern Song fine glaze and Ding  
392 Jin fine glaze are also different. The body material falls on the extrapolation of the Ding Jin fine  
393 porcelain glaze mixing line, suggesting it was the siliceous raw material used in this glaze; the  
394 high TiO<sub>2</sub> content averaging at 0.8 wt% in this glaze also agree with this suggestion. On the other  
395 hand, the Sr isotopic compositions of Ding Northern Song fine porcelain bodies do not fall exactly  
396 on the extrapolation of the mixing line from the glazes, but to the right-hand side of it. This  
397 suggests that the body material was not the only siliceous raw material used in this glaze.  
398 Moreover the siliceous material used in the glaze was also different from the one used for Ding  
399 Five Dynasties period white slip porcelain glaze, which contains high Sr concentrations and high  
400 <sup>87</sup>Sr/<sup>86</sup>Sr. The siliceous material used in the Northern Song fine porcelain glaze recipe should have  
401 a rather low Sr content and high <sup>87</sup>Sr/<sup>86</sup>Sr.

402

## 403 **6. Discussion**

### 404 ***6.1 The earliest use of limestone in Chinese high-fired glazes***

405 The primary aim of this study is to search for the earliest use of limestone in Chinese high-fired  
406 glazes. Previous studies have allowed us to narrow down the range to be investigated to

407 Northern porcelain varieties dating to between the 6<sup>th</sup> and 10<sup>th</sup> centuries AD.

408 It is not that limestone has never been suggested as the flux for certain northern porcelain glazes  
409 during this period. Quite a few studies have done so based on the P<sub>2</sub>O<sub>5</sub> contents of some  
410 northern porcelain glazes (Li 1998, Lu *et al.* 2012), but some studies have challenged such a  
411 suggestion, and the argument is also mainly based on the P<sub>2</sub>O<sub>5</sub> contents of certain varieties of  
412 northern porcelain glazes (Kerr and Wood, 2009, Cui *et al.* 2012). This confusing situation is also  
413 considered in this study: some glazes identified as having limestone fluxes based on their Sr  
414 isotopic compositions, such as Ding Five Dynasties white slip glaze and Ding northern Song fine  
415 glaze have similar or even higher P<sub>2</sub>O<sub>5</sub> contents than the glazes identified as wood ash glazes. This  
416 is a long standing issue in the area of northern porcelain study, and it has prevented scholars  
417 from gaining a clear understanding of the technological developments of northern porcelain  
418 glaze and when the use of limestone as a glaze flux emerged.

419 This study sets out to investigate whether limestone was indeed used for making northern  
420 porcelain glazes by using Sr isotope analysis and to pinpoint the time when limestone started to  
421 be used. This study also hopes to clarify why P<sub>2</sub>O<sub>5</sub> contents in northern glazes has created  
422 confusion and cannot give us a clear clue about the matter.

423 Xing Sui to mid-Tang white slip porcelain glaze is the earliest limestone based glaze identified by  
424 Sr isotopic composition in both North China and South China so far. The glaze made at the Xing  
425 kilns before white slip porcelain glaze was wood ash based early porcelain glaze and green  
426 stoneware glaze. However, Xing white slip porcelain glaze still has a comparatively high P<sub>2</sub>O<sub>5</sub>  
427 content, despite its Sr isotopic composition mixing line suggesting that limestone was used as the  
428 flux in the recipe. We have ruled out the possibility that wood ash originating from plants  
429 growing on limestone soil was used as the flux for this glaze, which would otherwise be a good  
430 interpretation for a material with a limestone <sup>87</sup>Sr/<sup>86</sup>Sr signature and high P<sub>2</sub>O<sub>5</sub> contents. We ruled  
431 it out because we noticed this flux with a limestone signature and high P<sub>2</sub>O<sub>5</sub> contents also  
432 occurred at Five Dynasties Ding kilns and Five Dynasties Jingdezhen. It would be too much of a  
433 coincidence if the three production sites all happened to use wood ash originating from a  
434 limestone soil at the same time for the same type of ware. The more sensible interpretation for  
435 this flux with limestone <sup>87</sup>Sr/<sup>86</sup>Sr and comparatively high P<sub>2</sub>O<sub>5</sub> content should have something to  
436 do with the way how limestone was prepared for glaze making at this stage. This issue was also  
437 discussed by Wu *et al.* (2020).

438 To allow limestone to be used as flux in a glaze suspension, it has to be first pulverised into very  
439 fine powder, the grain size of which should be in the same range as wood ash and clay particles to  
440 allow them to be mixed thoroughly in suspension. Given the hardness of limestone, this would  
441 have been very difficult to achieve by a physical method, so limestone was burnt to powder in  
442 the historical period and the recorded fuel for the task was herbaceous plants such as straw, rice  
443 husk and bracken. According to the multiple historical records describing the process of turning  
444 rocky limestone into fine powder at Jingdezhen, the earliest of which was made in the late  
445 Southern Song dynasty (c. 1214-1234), limestone had to be burnt multiple times during the  
446 process, because not only did the limestone have to be turned into fine powder, it also had to be  
447 re-carbonated from quicklime (CaO) or slaked lime (Ca(OH)<sub>2</sub>) back into calcium carbonate (CaCO<sub>3</sub>)  
448 to avoid the drastic chemical reactions with water and causticity. Therefore, the resultant powder

449 would actually be a mixture of limestone and botanic ash<sup>4</sup>. Such powder is still being produced at  
450 Jingdezhen, and it is locally called *youthui* (glaze ash). Analyses of modern glaze ash showed that  
451 limestone accounts for the vast majority of its content, and the chemical composition of glaze ash  
452 probably has not changed much since the late Northern Song dynasty (Ma *et al.* 2014, Wu *et al.*  
453 2020). But when limestone based glaze first appeared at Jingdezhen during the Five Dynasties  
454 period and early Northern Song dynasty (c. 10<sup>th</sup> century), the limestone-based flux used then also  
455 contained more P<sub>2</sub>O<sub>5</sub> than later times (Wu *et al.* 2020). This suggests that the processing method  
456 used then may have been different from that of later times, described in historical texts, and a  
457 higher proportion of botanic ash should have included in the powder. However this higher  
458 content of botanic ash residue in the burnt limestone powder would have had little influence to  
459 the Sr isotopic composition of the burnt limestone powder because botanic ash resulted from  
460 burning Herbaceous plants like bracken and rice husk content very low Sr content (Ma *et al.* 2014,  
461 Ma *et al.* 2016). This should be the reason why we find high P<sub>2</sub>O<sub>5</sub> contents in glazes that have  
462 limestone Sr signatures from the Sui to the early northern Song dynasties, and why P<sub>2</sub>O<sub>5</sub> contents  
463 cannot be used as a clear indicator for whether limestone or wood ash was used as the main flux.  
464 In any case the period of Sui to mid-Tang dynasty (late 6<sup>th</sup>-early 9<sup>th</sup> century) should therefore  
465 have been a transition period when limestone started to replace wood ash as the main  
466 calcareous flux in glaze making in China before the recorded method of preparing limestone  
467 powder was established.

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

## 474 **6.2 The siliceous raw material used for glazes in Xing kiln products**

475 The principle for glaze making in South China had been body material plus calcareous flux for  
476 most production centres, no matter whether the calcareous flux was wood ash or limestone  
477 (Wood 1999). Due to the very different geologies of North China and South China, the chemical  
478 and mineralogical composition of the materials for the ceramic bodies in North China and South  
479 China are quite different, especially for the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (Guo 1987).  
480 The body material used in the south was porcelain stone which generally has a comparatively  
481 high SiO<sub>2</sub> content, low Al<sub>2</sub>O<sub>3</sub> content and high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (Rehren and Yin 2012). On the other  
482 hand the northern body material, which was mainly composed of coal clay, has a lower SiO<sub>2</sub>  
483 content, higher Al<sub>2</sub>O<sub>3</sub> and lower SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (Tite *et al.* 2012). However the chemical compositions  
484 of high fired ceramic glazes made in North China and South China were less different, whether it  
485 was a wood ash based glaze or a limestone based glaze, as the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> of the formulae should  
486 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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<sup>4</sup> The word 'botanic ash' 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<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> content, but it hardly introduces any Sr.

487 the  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO-Na}_2\text{O-K}_2\text{O}$  system (Partyka *et al.* 2015). These factors forced northern  
488 potters to seek other siliceous raw materials for their glaze recipe, and not just to rely on such  
489 body materials. From our chemical and Sr isotopic results of Xing glazes, we can see this quite  
490 clearly.

491 The results of Sr isotope and chemical analysis of our early porcelain samples from Xing kilns  
492 show that body material was not the sole siliceous material in the glaze formula. Although green  
493 stoneware glaze from Xing kilns is not studied in this work, from its chemical composition  
494 reported in Huang *et al.* (2020), we can see that it has a very similar chemical composition to Xing  
495 early porcelain, and there is also a  $\text{Na}_2\text{O}$  content discrepancy between Xing green stoneware  
496 body and glaze which suggests that another raw material, apart from body material and wood  
497 ash, was included in the glaze recipe.

498 When white slip porcelain came along, Xing potters not only used a new calcareous flux in its  
499 recipe, they also gave up using body material in the glaze completely. Five Dynasty Ding potter  
500 also inherited this approach. It was first noticed by Wood (1999) that the  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  contents  
501 of Xing white slip porcelain glaze are too low for the body material to be the main siliceous  
502 material in the recipe and our Sr isotopic results also suggest the same.

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

512

### 513 **6.3 The porcelain glaze recipes of the Ding kilns**

514 Previous studies of Ding kilns porcelain glazes have reached quite different conclusions about the  
515 raw materials used in Ding glazes, especially for the flux. According to the high MgO contents in  
516 Ding glazes and the rich dolomite resources in the vicinities of the Ding kiln complex, Li and Guo  
517 (1983) suggested that the flux for Ding glazes was either dolomite or dolomitized limestone.  
518 According to the low  $\text{CaO/P}_2\text{O}_5$  ratio of Ding glaze, Kerr and Wood (2004) suggested wood ash  
519 could still be the flux in the Ding glaze recipe. Based on the negative correlation of MgO and CaO  
520 and the relatively high  $\text{P}_2\text{O}_5$  content, Cui and *et al.* (2012) suggested that two raw materials were  
521 involved: one was wood ash but the other was unknown. By analysing some possible glaze raw  
522 materials unearthed by excavation, Kang and *et al.* (2014) suggested a limestone based powder,  
523 which is made by firing limestone using wood as fuel, was the flux for Ding glazes.

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

527 Our Sr isotopic results suggest that the three glazes studied in this work, which were made in

528 different parts of Ding kilns complex during different historical periods, were made by three  
529 different recipes. Is this the reason why we get contradictory interpretations from the previous  
530 studies? These studies were trying to simplify a singular approach for the entire duration of Ding  
531 glaze production. But the real situation for glaze making at the Ding kilns may have kept changing  
532 throughout its production and perhaps even between different workshops at the same time.

533 Our Sr isotopic compositions of Ding Five dynasties white slip glaze produced at Beizhen village  
534 do suggest dolomitized limestone was used as the flux for this glaze, and we have explained why  
535 it has comparatively high  $P_2O_5$  content

536 The possible glaze making raw materials analysed by Kang *et al.* (2014) were unearthed from a  
537 Northern Song dynasty workshop located at Jianci village and the analytical results suggest that a  
538 fairly pure (not highly dolomitized) limestone was the flux used at the site. This limestone powder  
539 was pulverized by burning cypress wood because cypress ash has been identified in the powder.  
540 This suggestion is also consistent with our Sr isotopic results for Ding Northern Song fine  
541 porcelain glaze produced at Jianci village<sup>5</sup>.

542 The low  $CaO/P_2O_5$  in Ding glaze was noted by Kerr and Wood (2004) and by Cui *et al.* (2012). They  
543 suggested that wood ash was the flux used: we have observed this but only in Jin dynasty fine  
544 porcelain glaze from Jianxi village. The  $CaO/P_2O_5$  of this glaze is actually the lowest value among  
545 all the glazes studied in this work. It is even lower than the confirmed wood ash green stoneware  
546 glaze from Gongyi kilns. Our results agree with those published by Cui *et al.* (2012) who found  
547 that the lowest  $CaO/P_2O_5$  was in samples made at Jin dynasty Jianxi village<sup>6</sup>. This low  $CaO/P_2O_5$   
548 also coincides with our Sr isotopic results for the glaze which suggest that the flux used may have  
549 switched back to wood ash.

550 Technologically reverting back from a limestone based glaze to wood ash based one is  
551 retrogressive. Limestone is a far superior calcareous raw material than wood ash: pulverized  
552 limestone is much easier to produce in large quantities than wood ash given the abundance of  
553 limestone in the area, and pulverized limestone is much purer with lower levels of e.g.  $P_2O_5$  and  
554  $MnO$  for making colourless porcelain glaze than wood ash. When pottery production progresses  
555 and develops in a normal way, this technological retrogression should not have happened.  
556 However, the Ding kilns did get devastated at the end of the northern Song dynasty when Jurchen  
557 invaded and took Heibei province where the Ding kilns were located. According to historical  
558 records and archaeological excavations, after the devastation the production of Ding kilns did not  
559 recover for another 30 years when the Jurchen Jin had stabilized the governance in the area (Li  
560 and Bi 1987). Many skilled Ding potters fled from Quyang during the turmoil, and some of them  
561 went to Jingdezhen, which is southern Song territory, to carry on their practice. The Ding type  
562 wares made at Jingdezhen during this period were called southern Ding wares (Liu 1974). At the  
563 end of 30 years of this disruption when Ding kilns resumed their production, it seems that the  
564 technology used (in the Jin dynasty), at least for production in Jianxi village, was not the same as  
565 northern Song Ding technology. A comparatively less developed technology was used instead.  
566 Ding kilns did recover to mass production during the Jin dynasty, but to what extent the old

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<sup>5</sup> Our Northern Song dynast fine porcelain samples and the samples studied in Kang *et al.* (2014) were from the same excavation

<sup>6</sup> Our Ding kiln samples and samples studied in Cui *et al.* (2012) are also from the same excavations.

567 fashioned glaze recipe replaced the northern Song Ding glaze recipe should be addressed by  
568 further studies.

569 Different authors agree on the use of siliceous raw materials to make Ding glazes: a body material  
570 may have been used in the formula but it was not the main siliceous material used because the  
571  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  contents of the glazes are too low for the body material to be the main  
572 siliceous raw material used in the formula (Wood 1999, Cui *et al.* 2012, Kang *et al.* 2014). The Sr  
573 isotopic composition is not a very suitable index to suggest what specific siliceous raw materials  
574 were used in glaze formulae, but we can still see from the mixing lines of the three Ding glazes  
575 studied here that their siliceous raw materials were all different: a material with high Sr  
576 concentration (c. 400 ppm) and high  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $\geq 0.72$ ) was used as the main siliceous material for  
577 Five Dynasties white slip glaze; a material with a low Sr concentration ( $\leq 100$  ppm) and high  
578  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $\geq 0.72$ ) was used in the formula of Northern Song dynasty fine glaze; and body material  
579 was used in Jin fine porcelain glaze. Although it is not very sound to infer the nature of the  
580 siliceous raw material used in a glaze formula by the Sr isotopic composition suggested by mixing  
581 lines, the high  $^{87}\text{Sr}/^{86}\text{Sr}$  signature and chemical composition of the siliceous materials used in  
582 Ding Five Dynasties white slip glaze, Ding northern Song dynasty fine glaze and Xing white slip  
583 porcelain glaze do suggest they could have derived from (possibly weathered products of) felsic  
584 rocks with very old ages<sup>7</sup>. The Precambrian gneissose granitic complex is the main felsic outcrop  
585 on the eastern slope of the Taihang Mountain (Figure 1), and one K-feldspar sample collected  
586 from this outcrop near Ding kilns has very high  $^{87}\text{Sr}/^{86}\text{Sr}$  at 0.762020. Therefore some weathered  
587 felsic rocks from the eastern slope of Taihang Mountain, especially the light colour sort with low  
588  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  contents (Ren *et al.* 2009), which has the same chemical composition as the rocky  
589 materials unearthed in the excavation of Ding kilns in 2009 (Wood 2013), could have been the  
590 siliceous material used for relevant Xing and Ding glazes.

591

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

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

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## 605 7. Conclusions

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<sup>7</sup> The estimation is based on the growth of radiogenic  $^{87}\text{Sr}$  equation:  $\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \frac{^{87}\text{Sr}}{^{86}\text{Sr}_0} + \frac{^{87}\text{Rb}}{^{86}\text{Sr}}(e^{\lambda t} - 1)$ ,  $\lambda$   
 $= 1.42 \times 10^{-11} \text{ yr}^{-1}$  ( $^{87}\text{Rb}$  decay constant),  $\frac{^{87}\text{Sr}}{^{86}\text{Sr}_0} = 0.699$  (primordial meteorite value),  $\frac{^{87}\text{Rb}}{^{86}\text{Sr}} = 0.53$  (average  
concentrations of rubidium in terrestrial rocks) (Faure and Powell 1972).

606 The profound differences in the raw materials used for northern and southern ceramic glaze  
607 production made it very difficult for northern potters to retain the glaze making principles which  
608 initially derived from the south, namely the use of body material plus calcareous flux. This is very  
609 clear to see in the practice followed by the Xing kilns. Though Xing potters kept the wood ash flux  
610 during the early years, they added another material to their glaze formula with high Na<sub>2</sub>O in the  
611 earliest phase of their production. Soon Xing potters came up with a completely new approach to  
612 manufacturing porcelain by using white slip to improve the whiteness of the wares and limestone  
613 as a glaze flux. At this point during the Sui to mid-Tang dynasty (late 6<sup>th</sup>-early 9<sup>th</sup> Century)  
614 limestone was, for the first time, used as a glaze flux in Chinese high-fired ceramic making, and it  
615 was probably used in a mixture along with wood ash. This approach completely freed porcelain  
616 production at the Xing kilns from the limitation imposed by sourcing scarce resources, namely  
617 white-firing clay and wood ash. Xing potters also gave up using body material as the main  
618 siliceous raw material in the glaze, possibly because they did not want the grey-firing body  
619 material to compromise the whiteness of the ware. The white slip was very easy to copy,  
620 although the new limestone-based glaze formula may have been kept secret until the Xing  
621 technology relocated to Quyang to found the Ding kilns. The new fine porcelain and the new  
622 glaze formula associated with the fine porcelain saw the quality peak of Ding kilns during the  
623 Northern Song dynasty and before the Jurchen invasion devastated this production site. When  
624 production of Ding kilns recovered again some 30 years later, at least at some workshops, an old  
625 fashioned glaze recipe based on wood ash and body material was picked up again.

626

## 627 **Acknowledgement**

628 This work was supported by the National Natural Science Foundation of China (Grant No.  
629 51802017) and British Geological Survey (Grant No. IP-1810-0618). The authors are indebted to  
630 Professor Sun Xinmin from Henan provincial institute of Cultural Heritage and Archaeology for  
631 providing Gongyi kilns samples. Special gratitude is paid to Professor Nigel Wood for the advices  
632 on certain issues addressed in this paper.

633

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735 *Figure 1 the simplified location maps and surrounding geologies of Gongyi kilns, Xing kilns and Ding*  
736 *kilns*

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738 *Figure 2A (left) and 2B (right) Sr isotopic composition of Gongyi green stoneware glaze (GY-GS), Gongyi*  
739 *Tang white slip porcelain glaze (GY-TP) and some relevant raw materials*

740

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

743

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

751

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

755