

## HIGH-MG FAIENCES FROM GRANGES-LE-BOURG (HAUTE SAÔNE, FRANCE)

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**Abstract:** 40 faiences from the manufacture of Granges-le-Bourg and 7 local clays were studied by X-ray fluorescence and X-ray diffraction. The faience is rich in MgO (5-10 wt. %) and can be distinguished from known French reference groups. Local Triassic marls contain high concentrations of dolomite and are chemically similar to the High-Mg faience. As shown by vertical profiles of two raw material outcrops, there is a decarbonatisation towards the surface. Firing temperatures lie < 950°C for the biscuits and between 950-1050°C for the enamelled pieces, indicating a two chambered kiln.

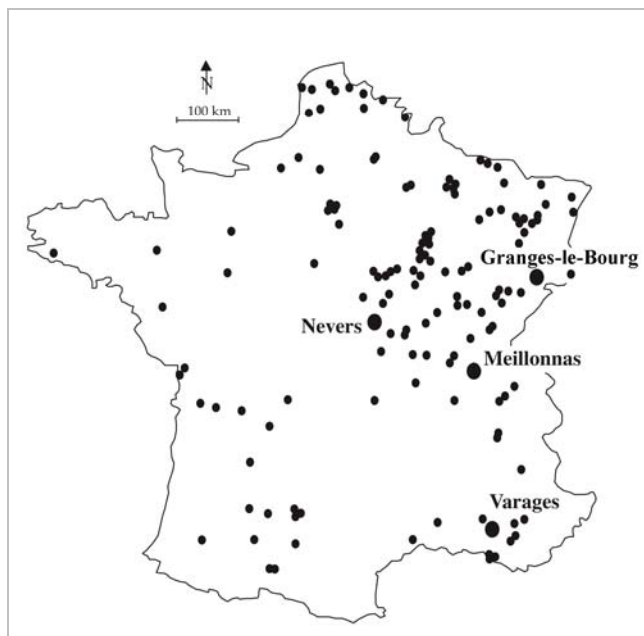
**Keywords:** Faience, Granges-le-Bourg, Chemistry, Mineralogy, Dolomite.

### INTRODUCTION

From 2003 until 2006, excavations were carried out at the site of the former brickyard of Granges-le Bourg (**Fig. 1**). Three kilns and a variety of brick and tile waste were discovered (*Morin & Morin-Hamon 2004*). The production can be dated back to the end of 18<sup>th</sup> / beginning of 19<sup>th</sup> century. However, according to archive entries, manufacture was already taking place during the 16<sup>th</sup> century (Archives Départementales de Haute-Saône, ref. ADHS E-180). As shown by a number of biscuits with a reddish paste discovered on the site, a kiln was used before the 19<sup>th</sup> century to produce faience. Unglazed biscuits accounted for most of the fine ceramic found. The material available for analysis consists of plates/dishes and jars/pots of different forms. In addition, several fragments of painted faience and of technical ceramics (saggars, firing plates, spacers, props) were available. In this workshop, architectural ceramics and crockery were produced simultaneously, which is a rare case. Until now, this crockery had been completely unknown and unmentioned in the archives.

Therefore, the following questions needed to be addressed: (1) to characterize the pottery chemically (are biscuits and faiences identical?); (2) to form a “reference group” for the faience production at this site (is this reference group different from other known reference groups?); (3) to identify the raw materials exploited and their treatment (where is the source within the local area? Was there any mixing of clays?) and (4) to infer the ancient firing temperature by mineralogical analyses (what kind of kiln did the potters use ?).

A total of 46 samples, consisting of 33 unglazed biscuits (GLB 18, 25-29, 31, 35-36, 39-50, 57-68), 6 glazed faiences (GLB 72-77) and 7 clays (GLB 1+ GLB2: at the site, just below the surface, GPS 318 150/5270 800/GLB 52: 0.5m below the surface, foundations of a new house,



**Fig. 1** Map of France showing location of places mentioned in the text as well as the faience workshops (dots) active in the 18<sup>th</sup> century (from Rosen 2001)

100 m NNW of the site, GPS 318 060/5270 800/GLB 53: Brownish clay, on top of GLB 52, 0.3m below the surface, foundations of a new house, 100 m NNW of the site, GPS 318 060/5270 800/GLB 54: Greyish clay, on top of GLB 53, 0.2m below the surface, foundations of a new house, 100 m NNW of the site, GPS 318 060/5270 800/GLB 55: Yellow-greyish clay, 1.5m below the surface, foundations of a new house in Granges-le-Bourg, GPS 318 140/5270 900/GLB 56: Brown clay, on top of GLB 55, 0.4m below the surface, foundations of a new house in Granges-le-Bourg, GPS 318 140/5270 900) were examined (**Table 1**). The analysis was focused on the unglazed biscuits, because their raw material was most likely to be of local origin.

**Table 1** Description of the samples

| Analysis No. | Description  | Inv. No.   | Analysis No. | Description  | Inv. No.          |
|--------------|--|------------|--------------|--|-------------------|
| GLB 1        | Clay. At the site, just below the surface. GPS 318 150/5270 800  |            | GLB 55       | Yellow-greyish clay, 1.5m below the surface, foundations of a new house in Granges-le-Bourg, GPS 318 140/5270 900          |                   |
| GLB 2        | Clay. At the site, just below the surface. GPS 318 150/5270 800  |            | GLB 56       | Brown clay, on top of GLB 55, 0.4m below the surface, foundations of a new house in Granges-le-Bourg, GPS 318 140/5270 900 |                   |
| GLB 18       | Biscuit  | 03-CD12-03 | GLB 57       | Biscuit  | G11, 05/G11/81    |
| GLB 25       | Biscuit  | 04-E11-13  | GLB 58       | Biscuit  | G11, 05           |
| GLB 26       | Biscuit  | 04-E11-14  | GLB 59       | Biscuit  | G11, 05           |
| GLB 27       | Biscuit  | 04-E11-15  | GLB 60       | Biscuit  | G11, 06           |
| GLB 28       | Biscuit  | 04-E11-17  | GLB 61       | Biscuit  | G11, 05/G11/84    |
| GLB 29       | Biscuit  | 04-E11-24  | GLB 62       | Biscuit  | U.S.02,05/G 12/61 |
| GLB 31       | Biscuit  | 04-E11-26  | GLB 63       | Biscuit  | F11, 05/F11/75    |
| GLB 35       | Biscuit  | 04-E11-30  | GLB 64       | Biscuit  | F11, 05/F11/54    |
| GLB 36       | Biscuit  | 04-E11-31  | GLB 65       | Biscuit  | F11, 05/F11/48    |
| GLB 39       | Biscuit  | 04-G10-08  | GLB 66       | Biscuit  | F11, 05/Fosse     |
| GLB 40       | Biscuit  | 04-G10-09  | GLB 67       | Biscuit  | F11, 05/Fosse     |
| GLB 41       | Biscuit  | 04-G10-10  | GLB 68       | Biscuit  | E12,05/E12/57     |
| GLB 42       | Biscuit  | 04-G10-18  | GLB 72       | Faience  | 05/F12/18         |
| GLB 43       | Biscuit  | 04-G10-19  | GLB 73       | Faience  | 05/F12/11         |
| GLB 44       | Biscuit  | 04-G10-20  | GLB 74       | Faience, overfired   | 05/F11, fosse     |
| GLB 45       | Biscuit  | 03-I11-02  | GLB 75       | Faience  | 05/F12/68         |
| GLB 46       | Biscuit  | 04-I11-05  | GLB 76       | Faience  | 05/F12/68         |
| GLB 47       | Biscuit  | 04-I11-06  | GLB 77       | Faience  | 05/F12/68         |
| GLB 48       | Biscuit  | 04-I11-07  |              |  |                   |
| GLB 49       | Biscuit  | 04-JK11-21 |              |  |                   |
| GLB 50       | Biscuit  | 04-JK11-22 |              |  |                   |
| GLB 52       | Clay, 0.5m below the surface, foundations of a new house, 100 m NNW of the site. GPS 318 060/5270 800                            |            |              |  |                   |
| GLB 53       | Brownish clay, on top of GLB 52, 0.3m below the surface, foundations of a new house, 100 m NNW of the site. GPS 318 060/5270 800 |            |              |  |                   |
| GLB 54       | Greyish clay, on top of GLB 53, 0.2m below the surface, foundations of a new house, 100 m NNW of the site. GPS 318 060/5270 800  |            |              |  |                   |

Only few samples were taken from the faiences, because some of them could also have been imported, with exception for the kiln waster GLB 74.

## EXPERIMENTAL

### *Powder preparation*

From the ceramic objects, a small sample was obtained by cutting with a saw. This sample (6.5 – 28 g) was ground in a tungsten carbide mill after removal of the possibly contaminated surface and the enamel or the glaze, if present. The clays were dried and 10 g of each clay milled in a tungsten carbide mill. The briquettes of the firing experiments were divided with the diamond

saw in external (3 mm of the rim) and internal sub-samples and ground in the tungsten carbide mill.

### *Chemical analyses by X-ray fluorescence (XRF)*

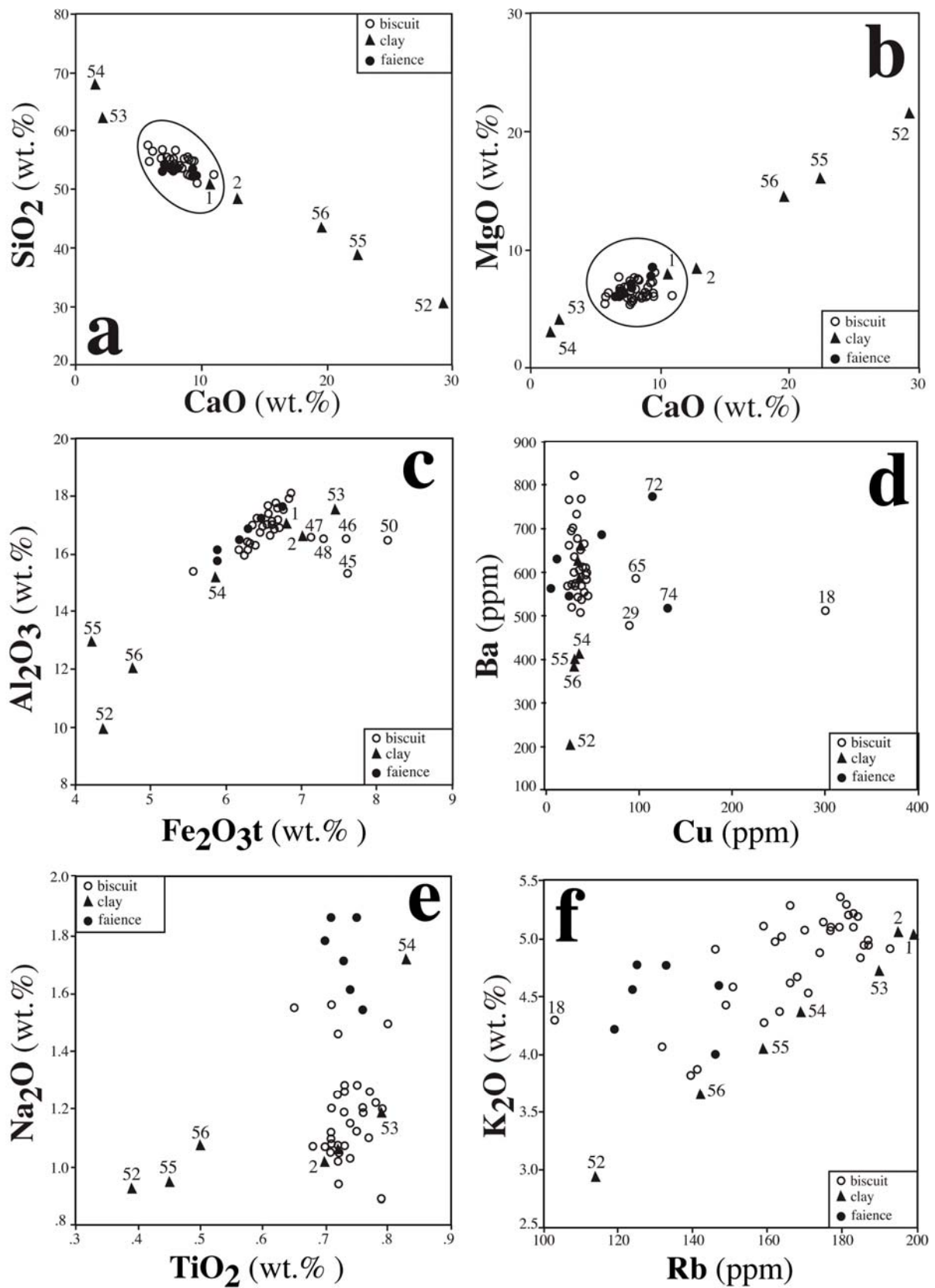
2 g of powdered sample were calcined at 1000°C for 1 hour to obtain the loss on ignition (LOI). 0.700 g of calcined powder was carefully mixed with 6.650 g of MERCK spectromelt A10 (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) and 0.350 g of MERCK lithium fluoride (LiF). This mixture was put into a platinum crucible and melted at 1150° C for 10 minutes (PHILIPS PERL X-2) in order to obtain a glassy tablet. These tablets were analysed for major, minor and trace elements using a PHILIPS PW 2400 wavelength-dispersive spectrometer (Rhodium tube, 60 kV et 30 mA) (**Table 2**).

**Table 2** XRF analyses of the ceramics and clays from Granges-le-Bourg. Oxides and LOI in wt. %, elements in ppm. Fe<sub>2</sub>O<sub>3t</sub> = total Fe as Fe<sub>2</sub>O<sub>3</sub>.

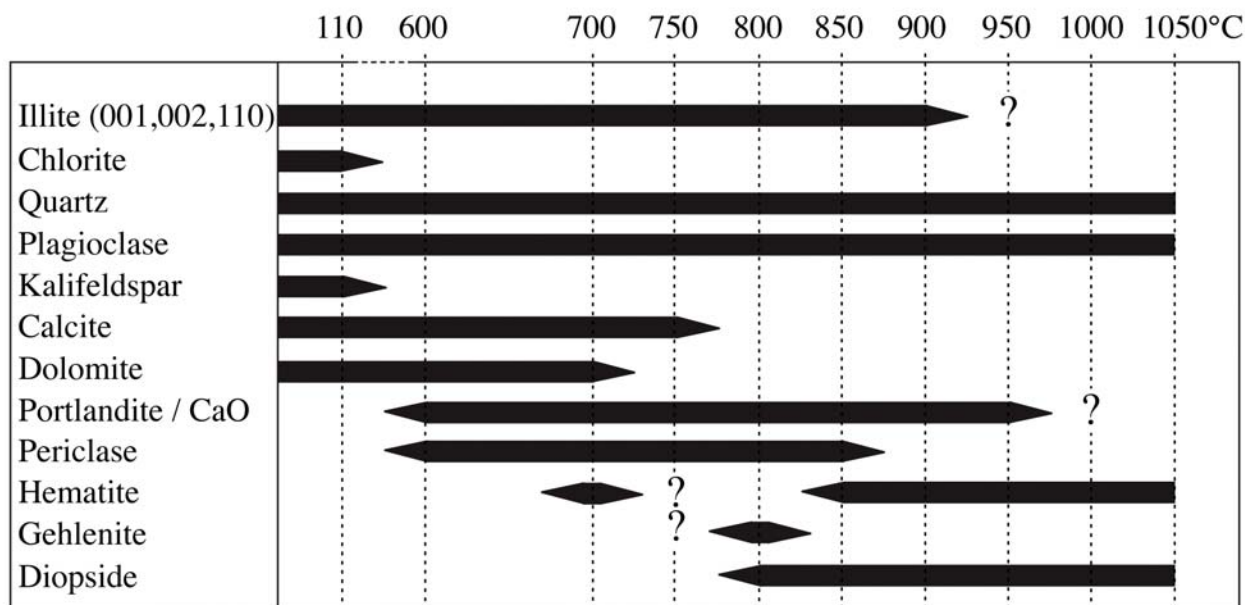
| Sample | SiO <sub>2</sub> | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3t</sub> | MnO  | MgO   | CaO   | Na <sub>2</sub> O | K <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> | Sum    |
|--------|------------------|------------------|--------------------------------|---------------------------------|------|-------|-------|-------------------|------------------|-------------------------------|--------|
| GLB1   | 50,61            | 0,72             | 16,97                          | 6,79                            | 0,12 | 7,70  | 10,62 | 1,05              | 5,02             | 0,18                          | 99,91  |
| GLB2   | 48,19            | 0,70             | 16,53                          | 7,00                            | 0,13 | 8,25  | 12,89 | 1,01              | 5,05             | 0,15                          | 100,06 |
| GLB18  | 51,06            | 0,65             | 15,41                          | 5,56                            | 0,09 | 8,00  | 9,67  | 1,55              | 4,30             | 0,20                          | 99,31  |
| GLB25  | 67,09            | 0,83             | 16,59                          | 5,42                            | 0,11 | 2,17  | 1,14  | 1,12              | 4,62             | 0,16                          | 99,83  |
| GLB26  | 67,12            | 0,83             | 16,48                          | 5,47                            | 0,13 | 2,16  | 1,04  | 1,15              | 4,56             | 0,15                          | 99,71  |
| GLB27  | 64,44            | 0,90             | 18,99                          | 6,40                            | 0,16 | 2,21  | 0,55  | 1,11              | 5,17             | 0,14                          | 100,25 |
| GLB28  | 54,77            | 0,71             | 16,12                          | 6,28                            | 0,10 | 7,27  | 9,33  | 1,05              | 4,27             | 0,20                          | 100,27 |
| GLB29  | 55,40            | 0,71             | 16,34                          | 6,32                            | 0,10 | 6,03  | 8,94  | 1,12              | 4,37             | 0,16                          | 99,68  |
| GLB31  | 52,44            | 0,71             | 16,72                          | 6,44                            | 0,09 | 6,10  | 10,96 | 1,20              | 4,53             | 0,18                          | 99,55  |
| GLB35  | 57,56            | 0,77             | 16,99                          | 6,35                            | 0,10 | 5,42  | 5,75  | 1,10              | 4,91             | 0,18                          | 99,35  |
| GLB36  | 55,02            | 0,73             | 16,71                          | 6,44                            | 0,10 | 6,41  | 7,70  | 1,26              | 4,84             | 0,20                          | 99,69  |
| GLB39  | 55,45            | 0,76             | 16,99                          | 6,54                            | 0,10 | 6,03  | 6,80  | 1,19              | 4,99             | 0,23                          | 99,32  |
| GLB40  | 53,94            | 0,73             | 16,79                          | 6,62                            | 0,10 | 6,81  | 8,04  | 1,28              | 5,09             | 0,22                          | 99,78  |
| GLB41  | 53,95            | 0,72             | 16,68                          | 6,58                            | 0,09 | 7,51  | 8,07  | 1,46              | 4,58             | 0,22                          | 99,99  |
| GLB42  | 56,69            | 0,71             | 15,97                          | 6,24                            | 0,10 | 7,10  | 7,91  | 1,10              | 3,87             | 0,18                          | 100,05 |
| GLB43  | 53,88            | 0,72             | 16,82                          | 6,64                            | 0,09 | 7,26  | 8,02  | 0,94              | 4,88             | 0,22                          | 99,66  |
| GLB44  | 53,85            | 0,73             | 16,91                          | 6,69                            | 0,10 | 6,73  | 8,05  | 1,19              | 5,10             | 0,21                          | 99,74  |
| GLB45  | 55,39            | 0,68             | 15,30                          | 7,61                            | 0,24 | 6,02  | 8,69  | 1,07              | 3,82             | 0,20                          | 99,18  |
| GLB46  | 52,53            | 0,72             | 16,52                          | 7,59                            | 0,16 | 5,98  | 9,03  | 1,06              | 5,19             | 0,25                          | 99,19  |
| GLB47  | 52,36            | 0,72             | 16,60                          | 7,12                            | 0,20 | 6,03  | 9,53  | 1,02              | 5,29             | 0,28                          | 99,34  |
| GLB48  | 52,22            | 0,71             | 16,52                          | 7,28                            | 0,21 | 6,14  | 9,48  | 1,56              | 5,35             | 0,27                          | 99,92  |
| GLB49  | 55,24            | 0,74             | 17,08                          | 6,59                            | 0,09 | 6,71  | 7,30  | 1,03              | 4,67             | 0,15                          | 99,77  |
| GLB50  | 52,37            | 0,71             | 16,49                          | 8,14                            | 0,20 | 5,96  | 9,15  | 1,08              | 5,21             | 0,32                          | 99,78  |
| GLB52  | 29,97            | 0,39             | 9,93                           | 4,36                            | 0,23 | 21,31 | 29,38 | 0,92              | 2,94             | 0,12                          | 99,71  |
| GLB53  | 61,99            | 0,79             | 17,50                          | 7,44                            | 0,27 | 3,89  | 2,21  | 1,18              | 4,72             | 0,16                          | 100,40 |
| GLB54  | 67,84            | 0,83             | 15,08                          | 5,85                            | 0,22 | 2,72  | 1,53  | 1,71              | 4,37             | 0,18                          | 100,49 |
| GLB55  | 38,30            | 0,45             | 13,03                          | 4,20                            | 0,13 | 15,80 | 22,47 | 0,94              | 4,05             | 0,08                          | 99,60  |
| GLB56  | 43,34            | 0,50             | 12,06                          | 4,75                            | 0,19 | 14,31 | 19,63 | 1,07              | 3,65             | 0,14                          | 99,82  |
| GLB57  | 56,75            | 0,72             | 16,39                          | 6,26                            | 0,09 | 7,75  | 6,92  | 1,05              | 4,07             | 0,16                          | 100,31 |
| GLB58  | 54,98            | 0,72             | 16,12                          | 6,17                            | 0,10 | 6,98  | 9,13  | 1,25              | 4,43             | 0,24                          | 100,30 |
| GLB59  | 54,12            | 0,76             | 17,52                          | 6,75                            | 0,11 | 6,60  | 7,05  | 1,20              | 5,14             | 0,22                          | 99,66  |
| GLB60  | 56,45            | 0,78             | 17,24                          | 6,41                            | 0,10 | 6,41  | 6,07  | 1,22              | 5,07             | 0,18                          | 100,17 |
| GLB61  | 54,92            | 0,77             | 17,57                          | 6,68                            | 0,10 | 5,88  | 7,59  | 1,26              | 4,97             | 0,27                          | 100,14 |
| GLB62  | 55,19            | 0,79             | 17,72                          | 6,64                            | 0,10 | 5,43  | 7,71  | 1,20              | 5,28             | 0,24                          | 100,45 |
| GLB63  | 53,58            | 0,74             | 17,14                          | 6,68                            | 0,09 | 7,31  | 8,31  | 1,15              | 5,11             | 0,18                          | 100,43 |
| GLB64  | 54,89            | 0,80             | 17,92                          | 6,83                            | 0,10 | 5,96  | 5,81  | 1,49              | 5,10             | 0,21                          | 99,42  |
| GLB65  | 54,14            | 0,79             | 17,62                          | 6,55                            | 0,09 | 5,66  | 7,89  | 0,89              | 5,07             | 0,26                          | 99,13  |
| GLB66  | 53,70            | 0,78             | 18,04                          | 6,85                            | 0,10 | 6,63  | 7,59  | 1,22              | 5,20             | 0,21                          | 100,47 |
| GLB67  | 53,72            | 0,73             | 16,99                          | 6,62                            | 0,09 | 7,43  | 8,27  | 1,07              | 4,91             | 0,20                          | 100,18 |
| GLB68  | 54,82            | 0,76             | 17,39                          | 6,56                            | 0,10 | 6,37  | 7,60  | 1,20              | 5,01             | 0,25                          | 100,19 |
| GLB72  | 53,94            | 0,73             | 16,46                          | 6,19                            | 0,10 | 6,30  | 7,09  | 1,71              | 4,56             | 0,33                          | 99,27  |
| GLB73  | 53,24            | 0,76             | 17,57                          | 6,73                            | 0,10 | 6,90  | 7,90  | 1,54              | 4,59             | 0,19                          | 100,02 |
| GLB74  | 54,14            | 0,74             | 16,89                          | 6,30                            | 0,09 | 6,26  | 7,11  | 1,61              | 4,77             | 0,17                          | 99,71  |
| GLB75  | 53,07            | 0,75             | 17,24                          | 6,45                            | 0,09 | 5,98  | 6,89  | 1,86              | 4,77             | 0,15                          | 99,20  |
| GLB76  | 52,57            | 0,71             | 16,10                          | 5,88                            | 0,08 | 8,52  | 9,47  | 1,86              | 4,00             | 0,17                          | 100,03 |
| GLB77  | 53,20            | 0,70             | 15,71                          | 5,88                            | 0,09 | 7,74  | 9,35  | 1,78              | 4,22             | 0,19                          | 99,81  |

**Table 2 continued** XRF analyses of the ceramics and clays from Granges-le-Bourg. Oxides and LOI in wt. %, elements in ppm. Fe<sub>2</sub>O<sub>3t</sub> = total Fe as Fe<sub>2</sub>O<sub>3</sub>.

| Sample | Ba  | Cr  | Cu  | Nb | Ni | Pb    | Rb  | Sr  | Y  | Zn  | Zr  | LOI   |
|--------|-----|-----|-----|----|----|-------|-----|-----|----|-----|-----|-------|
| GLB1   | 619 | 95  | 34  | 15 | 48 | 22    | 199 | 176 | 19 | 85  | 136 | 14,20 |
| GLB2   | 656 | 104 | 37  | 14 | 45 | 17    | 195 | 177 | 17 | 77  | 117 | 15,77 |
| GLB18  | 512 | 69  | 300 | 16 | 45 | 26411 | 103 | 138 | 46 | 97  | 191 | 6,22  |
| GLB25  | 571 | 78  | 48  | 17 | 39 | 4223  | 211 | 162 | 30 | 158 | 241 | 0,63  |
| GLB26  | 502 | 81  | 52  | 18 | 41 | 4599  | 208 | 155 | 32 | 165 | 241 | 0,56  |
| GLB27  | 522 | 96  | 47  | 18 | 49 | 61    | 236 | 155 | 31 | 120 | 253 | 0,48  |
| GLB28  | 591 | 68  | 43  | 15 | 47 | 128   | 159 | 164 | 19 | 98  | 151 | 5,35  |
| GLB29  | 479 | 74  | 90  | 15 | 48 | 377   | 163 | 108 | 18 | 104 | 156 | 8,57  |
| GLB31  | 603 | 63  | 35  | 15 | 46 | 256   | 171 | 157 | 19 | 89  | 146 | 9,95  |
| GLB35  | 768 | 79  | 37  | 16 | 45 | 365   | 193 | 155 | 23 | 106 | 173 | 2,99  |
| GLB36  | 730 | 74  | 33  | 16 | 44 | 938   | 185 | 188 | 20 | 94  | 168 | 3,64  |
| GLB39  | 821 | 97  | 30  | 17 | 46 | 469   | 187 | 173 | 20 | 86  | 177 | 3,35  |
| GLB40  | 600 | 81  | 42  | 16 | 48 | 103   | 177 | 146 | 20 | 97  | 149 | 5,10  |
| GLB41  | 546 | 93  | 45  | 14 | 47 | 76    | 151 | 153 | 20 | 91  | 147 | 6,42  |
| GLB42  | 675 | 85  | 33  | 14 | 48 | 216   | 141 | 133 | 22 | 94  | 168 | 5,96  |
| GLB43  | 610 | 85  | 42  | 15 | 48 | 109   | 174 | 143 | 20 | 88  | 147 | 5,54  |
| GLB44  | 596 | 84  | 31  | 15 | 47 | 68    | 179 | 131 | 22 | 89  | 146 | 5,98  |
| GLB45  | 611 | 76  | 40  | 15 | 47 | 80    | 140 | 118 | 20 | 98  | 165 | 4,10  |
| GLB46  | 539 | 82  | 37  | 16 | 46 | 91    | 184 | 182 | 19 | 84  | 153 | 8,55  |
| GLB47  | 584 | 82  | 43  | 15 | 46 | 413   | 181 | 164 | 19 | 86  | 149 | 7,44  |
| GLB48  | 664 | 59  | 40  | 17 | 46 | 178   | 180 | 170 | 19 | 86  | 148 | 7,56  |
| GLB49  | 552 | 69  | 41  | 16 | 49 | 208   | 168 | 110 | 22 | 98  | 155 | 7,60  |
| GLB50  | 506 | 76  | 37  | 16 | 45 | 97    | 183 | 183 | 18 | 84  | 149 | 8,31  |
| GLB52  | 199 | 44  | 26  | 9  | 22 | 448   | 114 | 90  | 16 | 583 | 91  | 32,50 |
| GLB53  | 580 | 105 | 35  | 17 | 52 | 416   | 190 | 103 | 30 | 545 | 207 | 8,48  |
| GLB54  | 397 | 112 | 31  | 17 | 39 | 242   | 169 | 111 | 30 | 275 | 270 | 6,97  |
| GLB55  | 407 | 80  | 35  | 11 | 31 | 92    | 159 | 103 | 16 | 536 | 104 | 26,85 |
| GLB56  | 379 | 79  | 30  | 12 | 28 | 456   | 142 | 102 | 19 | 401 | 153 | 25,09 |
| GLB57  | 701 | 97  | 28  | 16 | 45 | 110   | 132 | 134 | 25 | 93  | 157 | 7,49  |
| GLB58  | 570 | 69  | 28  | 14 | 42 | 148   | 149 | 147 | 24 | 103 | 160 | 4,61  |
| GLB59  | 766 | 83  | 25  | 14 | 45 | 216   | 175 | 199 | 25 | 93  | 153 | 4,27  |
| GLB60  | 572 | 91  | 28  | 17 | 43 | 970   | 177 | 157 | 26 | 105 | 171 | 0,83  |
| GLB61  | 696 | 105 | 27  | 15 | 43 | 80    | 162 | 154 | 27 | 94  | 163 | 7,12  |
| GLB62  | 576 | 97  | 32  | 15 | 42 | 196   | 166 | 176 | 26 | 90  | 164 | 5,33  |
| GLB63  | 660 | 97  | 24  | 15 | 43 | 51    | 159 | 127 | 24 | 91  | 144 | 5,48  |
| GLB64  | 635 | 78  | 29  | 17 | 48 | 1339  | 183 | 186 | 28 | 94  | 182 | 1,52  |
| GLB65  | 585 | 123 | 96  | 17 | 44 | 81    | 170 | 176 | 26 | 88  | 172 | 5,33  |
| GLB66  | 567 | 122 | 31  | 16 | 47 | 125   | 182 | 185 | 26 | 90  | 154 | 2,52  |
| GLB67  | 567 | 82  | 24  | 16 | 47 | 39    | 146 | 145 | 25 | 89  | 144 | 6,13  |
| GLB68  | 520 | 107 | 27  | 16 | 46 | 59    | 164 | 172 | 27 | 98  | 161 | 4,95  |
| GLB72  | 772 | 103 | 115 | 15 | 40 | 17083 | 124 | 146 | 43 | 93  | 188 | 1,43  |
| GLB73  | 682 | 118 | 59  | 15 | 44 | 3720  | 147 | 162 | 29 | 95  | 153 | 0,55  |
| GLB74  | 518 | 82  | 131 | 16 | 43 | 14757 | 133 | 149 | 41 | 86  | 192 | 0,67  |
| GLB75  | 626 | 96  | 13  | 16 | 42 | 17943 | 125 | 157 | 46 | 89  | 197 | 0,34  |
| GLB76  | 562 | 74  | 6   | 15 | 43 | 5075  | 146 | 124 | 29 | 77  | 154 | 0,50  |
| GLB77  | 547 | 82  | 25  | 14 | 43 | 8116  | 119 | 126 | 34 | 90  | 170 | 1,27  |



**Fig. 2** Correlation diagrams of selected oxide and element pairs for biscuits (n = 33), faïences (n = 6) and clays (n = 7)



**Fig. 3** Stability of minerals in the dolomitic marl GLB 1 during controlled firing (rim subsamples)

Calibration was made on 40 international standards. Accuracy and precision were checked using laboratory reference samples. Error has been evaluated to be less than 5% for all elements analysed.

#### Statistics

The statistical treatment of the chemical analyses was obtained with the program SPSS 11. For the principal component analysis (PCA), logarithmically transformed data of 16 variables were used: SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, Ba, Cr, Ni, Rb, Sr, Zn, Zr. Cluster analysis was performed with non transformed data of the same variables (Ward method, squared eucl. distances).

#### Experimental firing

Small briquettes (8.1 x 4.1 x 1.2 cm) of clay GLB 1 were dried (110°C, 12 h), then fired in an electric kiln under an oxydising atmosphere at steps of 50°C between 600 and 1050°C. The temperature elevation was of 100°C/hour. The holding time at peak temperature was one hour. The kiln was cooled without temperature control.

#### Mineralogical analyses by X-ray diffractometry (XRD)

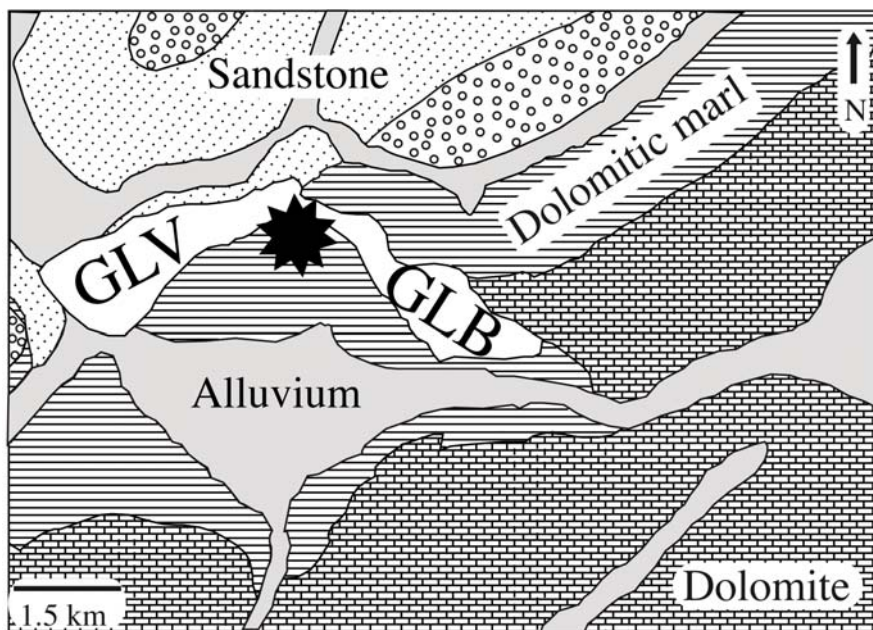
The mineralogical composition was determined through powder X-ray diffraction (PHILIPS PW 1800 diffractometer, CuK $\alpha$ , 40 kV, 40 mA, 2 $\theta$  2-65°, measuring time 1 sec./step).

## RESULTS

#### Chemical composition

The correlation diagram CaO-SiO<sub>2</sub> indicates well the homogeneity of the crockery, (i.e. the biscuits and the faiences) for these two oxides (**Fig. 2a**). This diagram shows clearly the similarities among the compositions of the clays GLB 1 and 2 collected at the site of the faience works, and the biscuits and faiences.

However, clays from the base of two houses located 100m to the north-west (GLB 52, 53, 54) and 80m to the north of the excavation site (GLB 55, 56), show a higher CaO content with increasing depth. The CaO-MgO diagram indicates a positive correlation between CaO and MgO, as well as a magnesian nature of the crockery's and the 'deep' clays (**Fig. 2b**). This correlation points to the presence of dolomite CaMg(CO<sub>3</sub>)<sub>2</sub> in the raw material, a mineral that was detected by X-ray diffraction, in the studied clays (see below). **Fig. 2c** reveals a sound correlation between aluminium and iron, except for biscuits GLB 45-48 and GL 50, which show an increased iron content. GLB 18 has considerable copper (**Fig. 2d**). The lead content of the local clays and most biscuits, remains below 500 ppm, except for biscuits GLB 18 (2.6 wt.%!), 25, 26, 60 and 64. In the faiences, Pb concentrations of 0.4 and 1.8 wt% were observed, which is significantly higher than in the clays. The analyses show that biscuits and faiences are chemically similar. However, faience pieces have higher Na<sub>2</sub>O contents and tend to be lower in K<sub>2</sub>O and Rb.



**Fig. 4** Schematic geological map of the surroundings of Granges-le-Bourg (GLB), Granges-la-Ville (GLV) and the manufacture (black star). Dots and circles = Triassic sandstones (from Contini et al. 2000).

#### Mineralogical composition

The clays GLB 1 and GLB 2 consist of quartz, plagioclase, potassium feldspar, illite, chlorite, dolomite and calcite. The raw materials GLB 52-56 are lacking chlorite and calcite. The fine ceramics can be assigned to four different mineral-associations:

- a) Quartz + plagioclase + dolomite + illite (002, 110) + hematite, +/- portlandite, calcite, diopside (?): GLB 18, 27, 29, 35, 36, 41, 43-50, 57, 59, 61-65, 67, 68.
- b) Quartz + plagioclase + illite (110) + hematite + diopside + gehlenite + calcite +/- dolomite: GLB 28, 31, 39, 40, 42, 58, 66.
- c) Quartz + plagioclase + hematite + diopside +/- calcite: GLB 25, 72-77.
- d) Quartz + plagioclase + hematite + diopside + gehlenite: GLB 26, 60.

#### Firing experiments

**Fig. 3** illustrates the mineralogical evolution for marl GLB 1 from the unfired (110°C) to the fired rim subsamples (600-1050°C). The first change in the mineralogical composition is the breakdown of chlorite and kalifeldspar, which occurs at temperatures < 600°C. Dolomite disappears between 700 and 750°C and calcite between 750 and 800°C. Hematite crystallizes between 600 and 700°C, is absent between 750 and 850 and present above 850°C. Newly formed phases are lime (CaO) between 600 and 1000°C, which reacts after firing to portlandite, periclase (MgO) between 600 and 900°C, gehlenite between 750 and 850°C and pyroxene

(diopside) > 750°C. The height of the plagioclase peak increases markedly above 800°C. These results are compatible with former studies of the thermal behaviour of dolomite-bearing to dolomitic raw materials (*Peters & Jenni 1973, Maggetti 1979, Jornet 1982, Béarat 1992, Benghezal 1989, 1994*). Astonishingly, there are no differences between the rim and core subsamples. Macroscopically, the matrix of phase association d is sprinkled with little typical yellow dots, giving a spotted appearance.

#### DISCUSSION

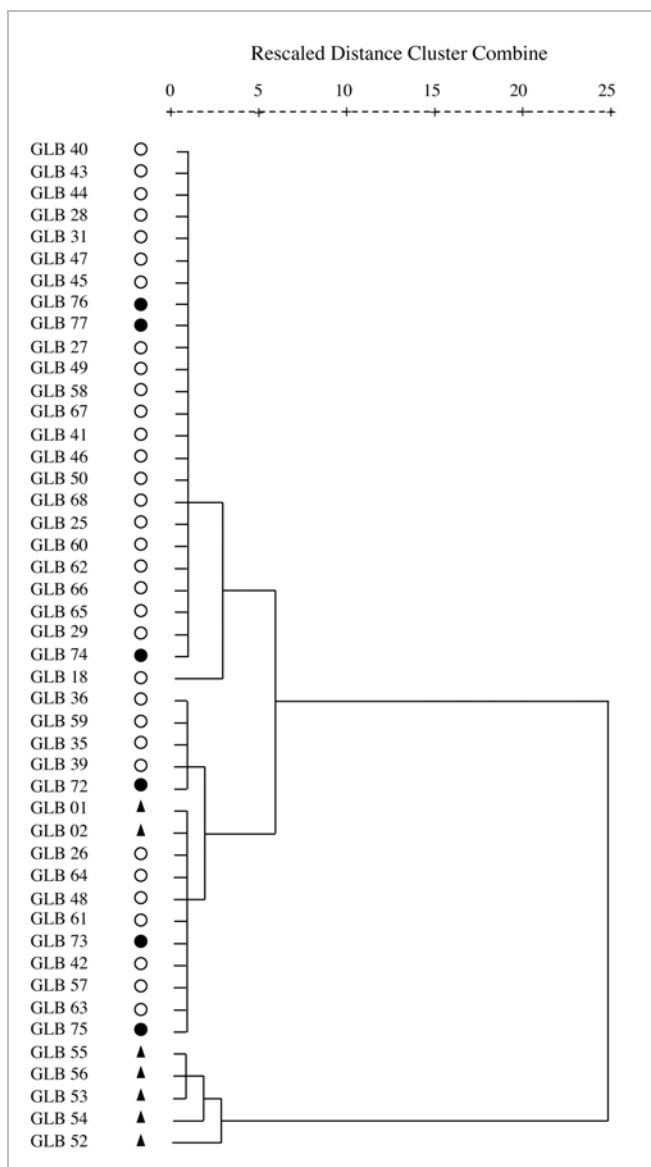
##### Lead-contamination

Local marls contain less than 500 ppm of Pb. Each of the examined faiences shows a significantly higher concentration, which indicates contamination. This can be due to: (1) an insufficient removal of the lead glaze/enamel; (2) the porous biscuit was infiltrated by the water glaze suspension during glazing; (3) the porous ceramic shard was infiltrated with fused glaze during firing and/or (4) infiltration through Pb-vapour during firing.

Biscuits can be contaminated during firing by penetrating Pb-vapour only, provided no lead-bearing substance was added to the clay before firing, as can be deduced from low Pb-contents found in most biscuits.

##### Raw materials

According to the geological map 1: 50'000 sheet LURE (**Fig. 4**), the brick & tile and faience works of Granges-le-Bourg are located on the dolomitic, gypsiferous marls of the Middle Muschelkalk (Middle Anisian), not far from



**Fig. 5** Dendrogram based on cluster analysis of 33 biscuits (circles), 7 clays (triangles) and 6 faiences (dots)

the alluvial resp. colluvial terrains further south (Contini 2000, Contini et al. 2000). Looked at from the bottom upwards, these Triassic marls consist of red, grey and white layers, which can be as thick as 70 m. Five clays from the site were examined in two profiles. There are differences as far as the contents of CaO and MgO are concerned (from deeper layers upwards). In the layers close to the surface, concentrations of these two oxides are low. These layers may therefore belong to leached Triassic marls, while the lower CaO- and MgO-rich layers are truly Triassic marls. However, their yellowish colour is not at all compatible with the red, grey or white colour expected of such marls according to the literature. So, it is possible that they are unleached alluvial or colluvial sediments. The high MgO content is due to a high concentration of dolomite detected by XRD.

It is possible to determine theoretically the maximum content of dolomite present in the magnesiferous marls, by considering the MgO and CaO concentrations and neglecting the fact that magnesium could be bound in other mineral, such as chlorite: GLB 1 = 18.3 / GLB 2 = 19.8 / GLB 52 = 50.7 / GLB 53 = 3.8 / GLB 54 = 2.6 / GLB 55 = 37.8 / GLB 56 = 33.7 wt.%.

#### *Paste recipe*

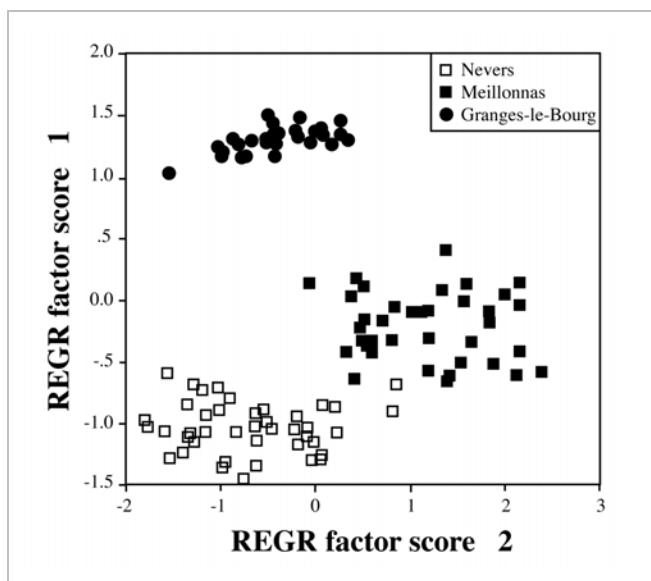
Chemical analyses have shown that there is no significant chemical difference between the biscuits and the faiences. The six faiences were therefore produced at the workshop of Granges-le-Bourg. The tendency for lower K<sub>2</sub>O and Rb contents in the faiences as compared to the biscuits was also found in the faience manufacture of Fribourg/Switzerland (Blanc 2007). It is possible that diffusion processes between the ceramic body and the glaze may have been involved (Blanc 2008), however, more faiences would need to be examined in order to obtain a clearer picture. This also applies to the interpretation of the Cu- and Na<sub>2</sub>O values. Using a carbonate-rich mixture to make faiences corresponds to the common production 'norms' for this type of ceramic (Caiger-Smith 1973). Were two clays, a carbonated and a non-carbonated one, mixed, as was often the case in the production of faiences? **Fig. 2** could substantiate such a procedure, because the crockery is located on the correlation line between the dolomitic marls and the non-dolomitic clays. However, it may also be assumed that on site, potters found dolomitic marl with an 'ideal' chemical composition close to the surface (GLB 1 and GLB 2). These correspond well to the fine ceramic (**Fig. 5**).

#### *A new reference group*

The 33 biscuits and 6 faiences examined in this study, form a new reference group, which differs significantly from the French reference groups published to date, i.e. Meillonas (Rosen 2000) und Nevers (Rosen et al. 2007) (**Fig. 6**). Five faiences from Varages (South of France) are set apart clearly (not shown in **Fig. 6**) from the Granges-le-Bourg production, due to their minimal MgO value of 11 wt.% (Schmitt 1990).

#### *Firing temperatures and kiln typology*

By comparing the results obtained by firing experiments to the identified phases, the following firing temperatures can be postulated: for phase association a (all biscuits) < 750-800°C, for b (all biscuits) 800-950°C and for c+d (3 biscuits, 6 faiences) 950-1050°C. Calcite is a secondary crystal in phase associations b and c. Most of the 33 biscuits were therefore fired at low temperatures, i.e. below 950°C. However, the final product, the enamelled faience, was subjected to significantly higher firing temperatures (950 to 1050°C).



**Fig. 6** PCA plot of the faience reference groups of Granges-le-Bourg ( $n = 39$ , this work), Meillonas ( $n = 39$ , Rosen 2000) and Nevers ( $n = 44$ , Rosen et al. 2007)

This seems to indicate that the faience works in Granges-le-Bourg did not use a single chamber kiln, but a two level faience kiln, as was common practice in French faience production by the end 18<sup>th</sup> / beginning 19<sup>th</sup> century (Rosen 1995). In a single chamber kiln, the dried, unfired objects and the enamelled biscuits are fired together in the same firing chamber and consequently at the same temperature (Maggetti 2007). In a two chambered kiln, however, the dried objects are fired in the upper chamber with lower temperatures than in the level below, where the enamelled biscuits are fired. The variation in temperature observed in the biscuits, shows that temperature was not distributed evenly in the upper chamber. This is not surprising, because temperatures in a kiln's firing chamber may vary, at different places, as much as 550°C, from lowest temperatures of 500°C to highest of 1050°C (Wolf, 2002).

## CONCLUSIONS

The questions raised above may be answered as follows: (1) chemically, biscuits and faiences are very similar and they are characterised by a high MgO-content. The faience examined in this study was therefore produced locally; (2) the fine ceramic analysed in this study forms a homogeneous group in terms of their chemical composition. This allows for the definition of a new reference group, rich in MgO, which differs significantly from the French reference groups published so far (Meillonas and Nevers); (3) local dolomitic Triassic marls of the Anisian and the fine ceramic correspond chemically. It remains unclear, however, if the potters used to mix higher (decarbonated) and deeper layers (rich in carbonate) or if they purposely chose middle layers

with a suitable composition; (4) due to the considerable differences in the inferred firing temperatures of biscuits (< 950°C) and faiences (950 -1050°C), a two chambered kiln was most likely used at the manufacture of Granges-le-Bourg.

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