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## To be purple or not to be purple? How different production parameters influence colour and redox in manganese containing glass



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## ABSTRACT

The purpose of this paper is to understand why manganese containing Roman glass could be purple or colourless in spite of having very similar chemical compositions. The strategy followed to tackle this question consists in the production of glass with the same chemical composition as Roman glass whereby various production parameters were controlled and systematically analysed. It is shown that redox and colour of glass is more likely to have been managed through internal control through the choice of raw materials and the addition of organic matter. The main difference between ancient and modern glass production relies on the lower melting temperature of Roman furnaces, so that sulphate would have played a less important role in the redox determination.

### 1. Introduction

Glass is a commonly used material produced industrially at a large scale: > 370 float furnaces produce over 1,000,000 tons of glass each week (Nascimento, 2014). However, glass was already produced in the 16th century B.C. in Mesopotamia and Syria (Moretti and Hreglich, 2013; Pfaender, 1996; Rehren, 2014). During Roman times, glass production reached a large scale for a pre-industrial society. The centralised model for glass production is nowadays commonly accepted and proposes that raw materials were melted in large primary factories on the southeastern coast of the Mediterranean Sea and then sent throughout the Roman Empire to secondary workshops where raw glass was re-melted and formed into objects (Freestone et al., 2002; Nenna et al., 2000; Whitehouse, 2003). At primary workshops, slabs of glass weighing a few tons of glass could be produced as is attested by the 9-ton glass slab found at Bet She'arim (Freestone et al., 2000; Gorin-Rosen, 2000).

Furthermore, apart from producing delicate vessels, Roman glassmakers were also able to control the production parameters to achieve certain colours. Iron, being a sand impurity, is always present in Roman

glass in a rather reduced form, thus causing the glass to have a bluish colour with an absorption peak at 1100 nm (Ceglia et al., 2014). Through the addition of antimony or manganese oxides, iron in glass was oxidised to its yellowish form (main absorption peaks at 380, 420 and 435 nm) thus giving the impression of a colourless glass (Foster and Jackson, 2010; Jackson, 2005). However, the case of manganese is rather complex. Indeed, manganese in glass can either act as a purple colourant (if manganese is present as  $Mn^{3+}$  thus leading to an absorption peak at 490 nm) or as a decolourant, in which case it has been referred to as 'glassmaker's soap' (Bamford, 1977; Möncke et al., 2014). There are two ways in which manganese can affect the colour of a glass containing iron. First, it can oxidise the bluish reduced iron (ferrous) to its yellowish oxidised form (ferric) or it can be present in its oxidised form giving the characteristic purple colour to the glass. The reaction that would occur between iron and manganese is given by Eq. (1).



Secondly, a colour compensation occurs between the blue reduced iron and the purple oxidised manganese. This causes a general 'greying' of the glass where no wavelength is absorbed more than others, but the

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absorption background increases thus giving thicker samples a greyish appearance (Möncke et al., 2014).

Chemical analyses of Roman glasses have shown that purple and manganese-decoloured glasses have very similar chemical compositions, respectively 67.2 wt% of SiO<sub>2</sub>, 16.13 wt% of Na<sub>2</sub>O and 8.00 wt% of CaO for purple glass and 68.7 wt% of SiO<sub>2</sub>, 16.70 wt% of Na<sub>2</sub>O and 7.53 wt% of CaO for manganese-decoloured glass. For example, Gliozzo (2017) recently drew an inventory of a large quantity of Roman decoloured glasses and calculated based on 104 samples that manganese-decoloured glass contains on average  $1.10 \pm 0.63$  wt% of MnO with a maximum of 2.43 wt%. While the 57 purple Roman glass fragments found in the literature contain on average  $2.1 \pm 0.9$  wt% of MnO, the manganese oxide concentration interval goes from 0.95 to 3.82 wt% (Arletti et al., 2013, 2010; Bonnerot et al., 2016; Boschetti et al., 2017; Cagno et al., 2014; Cosyns et al., 2014; Freestone and Stapleton, 2015; Gallo et al., 2013; Ganio et al., 2012; Mirti et al., 2008; Möncke et al., 2014; Rehren et al., 2015; Rosenow and Rehren, 2014; Schibille et al., 2016; Silvestri et al., 2014; Van Der Linden et al., 2009). There are thus many glasses with virtually the same concentrations in iron and manganese oxides which have totally different colours.

To understand how glass with similar compositions could have been purple or colourless, it is not possible to count on ancient written evidence. There is a lack of clear and precise ancient recipes. Indeed, interpretations of ancient texts are not straightforward and it is difficult to relate the recommendation of Pliny, in Roman times, or Theophilus, in medieval times, to a glass production recipe. For example, hypotheses have been made about Pliny's mention to *magnes lapis* and it is likely that it could have been magnetite (Freestone, 2008). However, this does not explain whether and how manganese could have been used in the production of purple or decoloured glass. In spite of all the chemical composition analyses carried out on ancient glass, how purple and colourless glass could be obtained remains so far unclear. Yet, it has important implications on our understanding of Roman glass production. This archaeometric interrogation raises further glass science questions related to reduction-oxidation (redox) reactions for which more literature is available in the modern glass production. Therefore, we can draw a comparison between ancient and modern glass production centred around the redox control issue. Despite some important differences between ancient and modern glass making such as melting temperatures, our modern understanding of glass redox control could be used as an insight into Roman coloured glass production. Therefore, a brief theoretical background is given in the Appendix B to set up the general context. This allows for the outline of the strategy followed in this study where the influence of different parameters on glass colour and iron redox is analysed systematically.

## 2. Objectives and experimental strategy

The question that sparked this study is to understand how Roman glassmakers obtained different colours from glasses having similar chemical composition. Chemical analyses of ancient glass cannot answer this question directly so that other methods have to be envisaged. This initial interrogation can be decomposed into a wide-range of sub-questions. In this paper, the aim is to address some of them by specifically looking at six central glass production parameters which can affect glass colour and redox.

1. Theoretically, raw materials and carbon should have an influence on iron redox ratios (Simpson and Myers, 1978), but the extent of their influence has not been probed yet in Roman production. We are thus left without a practical understanding of their impact on ancient glass compositions. This raises the need to analyse quantitatively the effect of **different iron and manganese raw materials**.
2. It has been noted in Roman glass that the decolouring effect of manganese is related to its relative concentration compared to iron (Silvestri et al., 2005). What the importance of the **ratio of iron**

**towards manganese** on the colour and redox ratio of the glass is, remains yet unknown from an experimental perspective.

3. **Sulphates** are important additives to the glass batch. They are currently systematically added in modern glass production and chemical composition analyses also show that some sulphates are retained in ancient glass. Indeed, chemical composition analyses of ancient glass measured that there is on average 0.15 wt% SO<sub>3</sub> retained, with a range between 0.05 and 0.50 wt% (Ceglia et al., 2015a). This raises the question of the extent to which sulphates can have an impact on redox in glass in ancient and modern glass production.
4. Very often in archaeological science, **organic matter** is mentioned as an efficient reducing agent. However, carbon is burnt so that none will be retained in glass. As such, it is difficult to assess how much and what the effect of carbon was in ancient glass recipes. This remains nevertheless an important question and needs to be verified.
5. Redox reactions are governed by diffusion processes. As such, they evolve with the square root of time. As a consequence, the melting time and the geometry of the melt container can play a role. How this **melting time** is interrelated with other parameters needs to be considered.
6. Industrial glass melting temperatures are in theory above the onset temperature of sulphate decomposition (1450–1500 °C), while Roman furnaces would not have reached > 1200 °C (Bingham and Jackson, 2008; Freestone, 2006). The influence of this difference in **melting temperature** remains under-studied in the ancient glass analyses.

To answer such questions, the strategy developed in this study consists in the production of experimental glasses where these different production parameters are well-controlled and systematically examined. First, the glass chemical composition is chosen so as to imitate major oxides concentrations in Roman glasses (Gliozzo, 2017; Silvestri, 2008; Silvestri et al., 2008). The basic chemical composition of the glasses studied here is given in Table 1. The iron content is given as Fe<sub>2</sub>O<sub>3</sub>, it represents 0.26 wt% of Fe. It should also be taken into account that the average redox ratio, defined as the ratio of ferrous iron (Fe<sup>2+</sup>) to the total amount of iron, in Roman glass containing neither colouring nor decolouring agents (i.e. only iron is present) is  $0.60 \pm 0.15$ , which is much more reduced than glass produced in a float furnace (Ceglia et al., 2016).

To this basic chemical composition, sulphates, carbon and/or manganese were added in order to tackle each of the six aspects previously described in a systematic way. As there can be different ways of expressing the concentration in iron and manganese depending on the oxide chosen, we chose to give the weight percent of elemental iron and manganese. The glass production strategy is shown in Fig. 1.

The six experimental choices and angles outlined here are aimed to answer directly the six research questions developed previously.

1. To understand the effect of different ratios of iron to manganese, glasses are produced containing iron only (0.26 wt%), stoichiometric proportions of iron and manganese (0.26 wt% of iron and manganese), typical amounts of iron and manganese found in glass that could be either purple or decoloured (0.26 wt% Fe and 1 wt% Mn) and a large excess of manganese towards iron (0.26 wt% Fe and 2 wt% Mn).
2. Two raw materials for iron (FeO and Fe<sub>2</sub>O<sub>3</sub>) and three for

**Table 1**  
Basic chemical composition of the glasses studied (wt%).

SiO <sub>2</sub>	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	Fe <sub>2</sub> O <sub>3</sub>
70.7	17.0	8.42	2.28	0.63	0.63	0.37

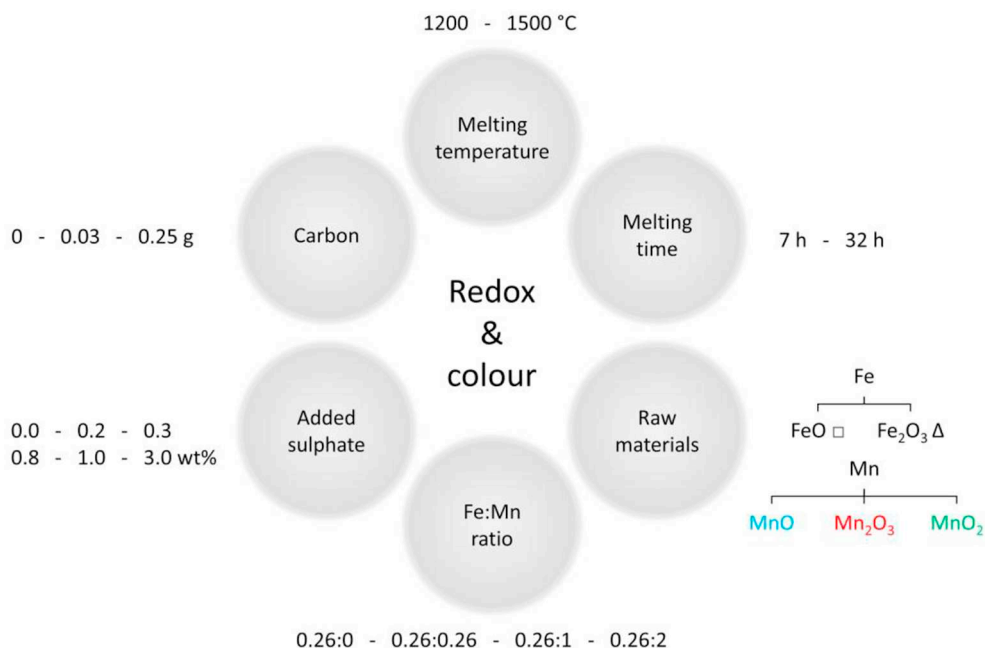


Fig. 1. Schematic overview of the different production parameters studied and the glass production strategy.

manganese (MnO, Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>) are used. Fe and Mn have an initial oxidation state of: 2 for FeO and MnO, 3 Fe<sub>2</sub>O<sub>3</sub> and Mn<sub>2</sub>O<sub>3</sub>. MnO<sub>2</sub> would theoretically correspond to Mn<sup>4+</sup> but only divalent and trivalent manganese can be present in glass (Bamford, 1977). MnO<sub>2</sub> corresponds to the commonly encountered pyrolusite, a manganese ore often considered to have been used as a manganese source by Roman glassmakers (Gliozzo, 2017).

- The amount of sulphate added and sulphate retained is not the same. Six concentrations of sulphates added were considered: 0, 0.2, 0.3, 0.8, 1.0 and 3.0 wt%.
- In some glasses, carbon was added, either 0.03 or 0.3 g were added to a batch of around 100 g of glass.
- Glasses were melted either for 7 h or 32 h.
- Two melting temperatures are considered: 1200 °C as it is a likely temperature for Roman glass furnaces (Bingham and Jackson, 2008) and 1500 °C, a temperature that can be attained in modern glass production.

The legends used in all the figures of this paper correspond to the code given in Table 2. The same legends are used whether the glass is melted at 1200 °C or 1500 °C and for the different initial concentrations of sulphate added. When these parameters vary, it will be carefully detailed.

### 3. Experimental methods

#### 3.1. Glass synthesis

Each batch contained around 100 g of raw materials, these are: SiO<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, K<sub>2</sub>CO<sub>3</sub>. Raw materials were weighed so as to have the concentrations given in Table 1. Depending on the batch, carbon (activated charcoal containing maximum 0.01 wt % SO<sub>3</sub>) and Na<sub>2</sub>SO<sub>4</sub> were also added. To evaluate quantitatively the influence of different raw materials, glasses are produced using iron as FeO or Fe<sub>2</sub>O<sub>3</sub> with or without MnO, Mn<sub>2</sub>O<sub>3</sub> or MnO<sub>2</sub> in different proportions. In the case where FeO was used, it was weighed in a glove box with a controlled argon atmosphere. MnCO<sub>3</sub> is used as a source of MnO thanks to its decarbonation.

All elements are added as chemicals with a minimum purity of minimum 99.1%. These raw materials are then melted during 7 or 32 h at 1200 °C or 1500 °C in a cylindrical Pt-Rh crucible of 6 cm diameter and 8 cm height in an electrical furnace providing approximately 140 cm<sup>3</sup>. Each glass was cast, crushed and re-melted three times in order to ensure homogeneity. The optical basicity  $\Lambda$  of all the glasses is around 0.57 calculated using tabulated values (Dimitrov and Komatsu, 2010; Moretti, 2005). If the formula proposed by Duffy (1993) is used, which linearly related  $\log \frac{[Fe^{2+}]}{[Fe^{3+}]}$  to the optical basicity  $\Lambda$ , the redox

Table 2  
Legend used throughout this study.

		/	0.26 wt% Mn			1 wt% Mn			2 wt% Mn
			MnO	Mn <sub>2</sub> O <sub>3</sub>	MnO <sub>2</sub>	MnO	Mn <sub>2</sub> O <sub>3</sub>	MnO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>
0.26 wt% Fe	FeO	■	■	■	■	■	■	■	
	FeO + carbon	●	●	●	●	●	●	●	●
	Fe <sub>2</sub> O <sub>3</sub>	▲	▲	▲	▲	▲	▲	▲	

ratio would be around 0.25 for all glasses.

For each glass, the chemical composition was verified using Wavelength Dispersive X-ray fluorescence (WDS-XRF, Siemens Bruker S4 PIONEER, Cu K $\alpha$  radiation) on polished samples. The determination of the sulphate concentration was quantitative and based on a calibration using 5 standards.

The glasses are described based on the raw materials which are present, their chemical composition is given as the weight percent of elemental iron and manganese so as to avoid any confusion with the raw materials. Stoichiometric proportions refer to molar concentrations but in the case of iron and manganese can be simplified by using weight percent. The sulphates concentrations given refer to the amount of sulphates added based on the theoretical decomposition of Na<sub>2</sub>SO<sub>4</sub>.

### 3.2. Optical spectroscopy

Ultraviolet-visible-Near Infrared spectroscopy was carried out on polished samples and flat samples. Samples were illuminated using two lamps as light source, a 30 W deuterium lamp for the UV spectral region and 20 W halogen lamp emitting in the visible and infrared regions. Optical fibres guide the light from the light sources to a plano-convex lens, which focused the light to the samples to a spot size of around 3 mm of diameter. The light was collected using an integration sphere with an aperture of 6 mm, which was connected via optical fibres to two spectrometers: the AvaSpec-3648 and the AvaSpec-256-NIR1.7 from Avantes (Ceglia et al., 2016; Meulebroeck et al., 2010). Spectra were thus recorded between 200 and 1650 nm with a spectral resolution of 1.4 nm.

Once the spectra were collected, they were normalised to a sample of 1 mm thickness thanks to an accurate and precise measurement of the sample thickness with a resolution of 0.001 mm beforehand. Secondly, Fresnel reflection losses at the surface were taken into account considering that the incident angle did not exceed 20° and that glass refractive index is 1.5 so that the reflectance was 4% for each surface (Bamford, 1977; Ceglia et al., 2015b).

The optical spectra were used to determine the colour coordinates and the iron redox ratio. The CIE Lab 1976 colour system was used here because it has the advantage of quantifying colour in a linear Cartesian system which can be compared to other analyses of glass colour (Alberghina et al., 2014; Ceglia et al., 2016; Silvestri et al., 2011). L\* varies from 0 to 100 and represents the lightness factor (L\* = 0: black; L\* = 100: white) while a\* and b\* are the chromaticity coordinates: for a\*, negative values represent green and positive values red, while for b\*, negative values represent blue and positive values yellow. The ferrous amount was determined using Beer-Lambert law knowing that Fe<sup>2+</sup> absorbs at 1100 nm in soda-lime silicates (Bamford, 1977; Ceglia et al., 2015b; Möncke et al., 2014; Weyl, 1951). Fig. S2 in the Supplementary materials shows the importance of the absorption peak of Fe<sup>2+</sup> on the optical spectra of three glasses having a wide-range of redox ratios. The calibration curve established by Ceglia et al. (2015a, 2015b) was used to determine the ferrous concentration. The redox ratios presented are the ratios of the amount of ferrous iron to the total amount of iron measured by WDS-XRF. The error on the redox ratios given combines the error on ferrous iron (based on the error of the determination of the linear absorption coefficient as proposed by Ceglia et al. (2015a, 2015b)) and the error on the total amount of iron (maximum of 0.03 wt% Fe). It can also be noticed that Fe<sup>3+</sup> absorbs at

380, 420 and 435 nm and Mn<sup>3+</sup> at 490 nm. Nevertheless, it is not possible to determine the manganese redox ratio because no unique extinction coefficient was found in the literature (Bamford, 1977; Möncke et al., 2014).

## 4. Results and discussion

The complete set of data is given in the Appendix A with the measured chemical compositions, redox ratio and colour coordinates determined using optical spectroscopy. In the text, figures and tables, the glass samples are designated by the raw materials and concentration of iron and manganese. Each glass can thus be found in the Appendix A based on these characteristics (raw material and iron-manganese concentration) in the Appendix A using the first columns. In section 4.1 and 4.2, all the glasses are melted for 32 h.

### 4.1. Iron and manganese proportions and raw materials

In this first part, the proportions of iron to manganese as well as the raw materials are discussed. All glasses here are produced at 1200 °C with 0.15 to 0.2 wt% of SO<sub>3</sub> added which corresponds to Roman conditions.

Fig. 2 gives optical spectra obtained with iron added as Fe<sub>2</sub>O<sub>3</sub> for glasses containing iron only, iron and manganese in stoichiometric proportions (Fig. 2a) and an excess of manganese compared to iron (Fig. 2b).

In Fig. 2a, where iron and manganese are in stoichiometric proportions, it can be observed that there is no significant absorption of Mn<sup>3+</sup> when MnO or MnO<sub>2</sub> are used, but that a little absorption peak occurs in presence of Mn<sub>2</sub>O<sub>3</sub>. There are some slight differences in the absorption of Fe<sup>2+</sup>, the glass containing MnO showing the strongest absorption of Fe<sup>2+</sup> while the glass containing Mn<sub>2</sub>O<sub>3</sub> has the weakest Fe<sup>2+</sup> absorption. The case of an excess of manganese compared to iron (respectively 1 wt% and 0.26 wt%), shown in Fig. 2b, is useful because it represents a typical chemical composition of Roman purple or de-coloured glass. In that case, the Mn<sup>3+</sup> absorption peaks are very strong only for the glass containing Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> as raw materials for manganese which makes them appear purple. Based on such optical spectra, the amount of Fe<sup>2+</sup> and the colour coordinates can be quantified. The optical spectra of all the other glasses in the production strategy were also recorded but have not all been shown for a better readability.

Table 3 gives the redox ratios of these glasses produced at 1200 °C from different raw materials with sulphates added to the batch between 0.15 and 0.20 wt SO<sub>3</sub>. In case where carbon was added, it was always 0.03 wt% from the initial raw materials. The colours of the columns are given as an indication of oxidation (yellow) and reduction (blue) of iron.

Whether manganese is present or not, the iron is more reduced if FeO was used initially (0.34 ± 0.03 without manganese) and most oxidised if it is produced from Fe<sub>2</sub>O<sub>3</sub> (0.12 ± 0.01 without manganese). If carbon was added to the initial batch, iron was even more reduced (0.65 ± 0.07 without manganese). This value is the closest to Roman glass that contains only iron (Ceglia et al., 2016), thus suggesting that the presence of an organic additive in ancient glass-forming melts is quite likely. It can also be noted that the glass produced from Fe<sub>2</sub>O<sub>3</sub> is not entirely oxidised while the glass produced from FeO is not

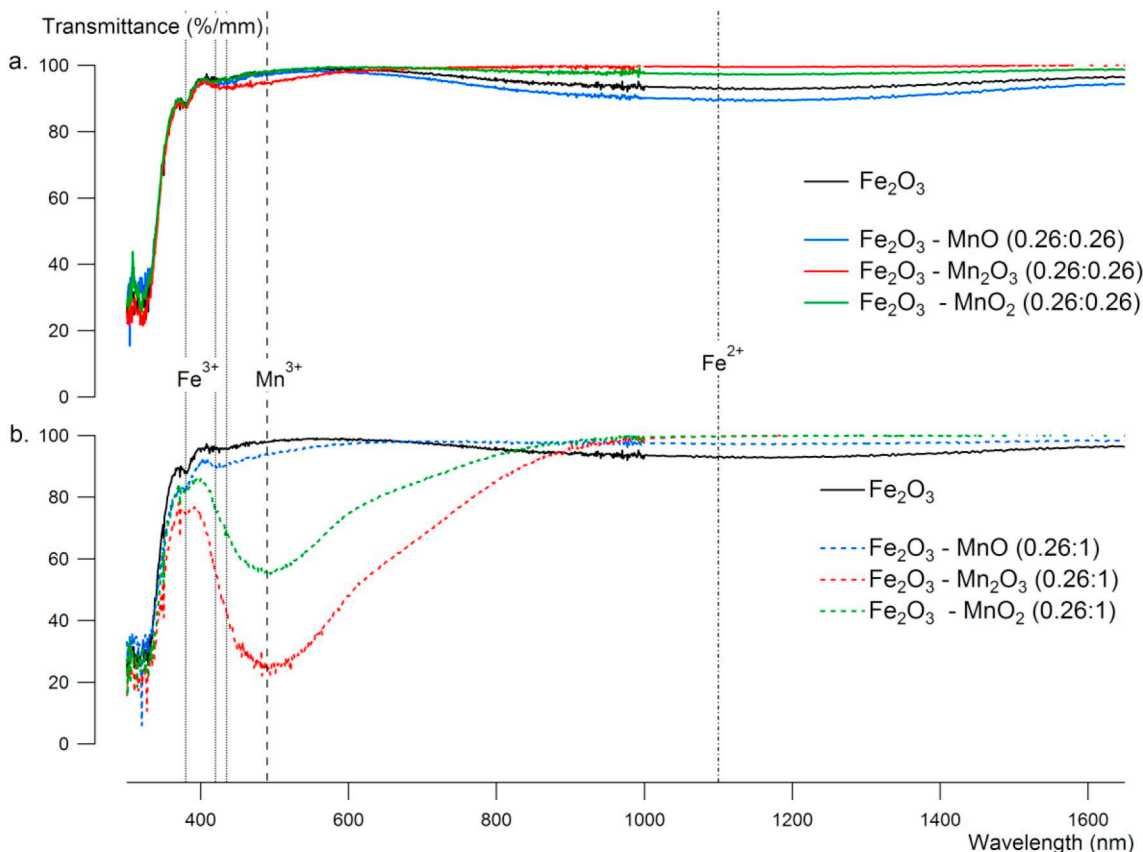


Fig. 2. Optical spectra with the wavelengths characteristic of the absorption of Fe<sup>3+</sup>, Fe<sup>2+</sup> and Mn<sup>3+</sup>, a. Iron alone and iron-manganese in stoichiometric proportions, b. iron alone and manganese in excess of iron.

Table 3

Iron redox ratio (Fe<sup>2+</sup>/Fe<sub>tot</sub>) for glasses melted at 1200 °C produced from different Fe and Mn raw materials with SO<sub>3</sub> added between 0.15 and 0.20 wt%. Different Mn/Fe (wt% of elemental manganese and iron) ratios are studied: 0.26:0 (Fe alone), 0.26:0.26 (Fe and Mn in stoichiometric proportions, both being at 0.26 wt%), 0.26:1 (Fe = 0.26 wt% and Mn = 1 wt%) and one glass with 0.26:2. Where the text is purple and bold indicates which glasses appear purple, the colours of the glasses can be observed in Fig. 3.

	Alone	Stoichiometric (0.26:0.26)			(0.26:1)			(0.26:2)
		MnO	Mn <sub>2</sub> O <sub>3</sub>	MnO <sub>2</sub>	MnO	Mn <sub>2</sub> O <sub>3</sub>	MnO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>
FeO	0.34 ± 0.03	0.38 ± 0.04	0.19 ± 0.02	0.26 ± 0.03	0.21 ± 0.02	<b>0.05 ± 0.01</b>	<b>0.17 ± 0.01</b>	
FeO + carbon	0.65 ± 0.07	0.78 ± 0.08	0.40 ± 0.04	0.64 ± 0.07	0.37 ± 0.04	<b>0.36 ± 0.04</b>	<b>0.32 ± 0.04</b>	<b>0.04 ± 0.01</b>
Fe <sub>2</sub> O <sub>3</sub>	0.12 ± 0.01	0.15 ± 0.01	0.04 ± 0.01	0.07 ± 0.01	0.07 ± 0.01	<b>0.04 ± 0.01</b>	<b>0.04 ± 0.01</b>	

entirely reduced. This can be due to the decomposition of the carbonates during the glass melt, which can cause some variations of the partial pressure of oxygen in the melt. This observation is quite important for glass production, where equilibrium with the atmosphere is usually not attained (Bingham and Jackson, 2008). Thus, as explained previously, the system would be closed and internal control of the redox would prevail.

It is useful to understand how iron and manganese interact in stoichiometric proportions before looking at other proportions of iron and manganese. In stoichiometric proportions (second section in the columns of Table 3), iron tends to get slightly reduced if MnO is added compared to a glass with iron only. In that case, the reaction shown in Eq. (1) is slightly shifted to the left, i.e. the Mn<sup>2+</sup> initially present reacts with Fe<sup>3+</sup> to form more reduced Fe<sup>2+</sup>. The most efficient oxidation of

iron occurs when manganese is present as Mn<sub>2</sub>O<sub>3</sub>, whereas if MnO<sub>2</sub> was added initially, the iron gets only slightly oxidised. It could be considered that Mn<sup>4+</sup> oxidises iron in a similar way as Mn<sup>3+</sup> as shown in Eq. (1) but Mn<sup>4+</sup> is not stable in glass (Möncke et al., 2014). However, it appears that Mn<sub>2</sub>O<sub>3</sub> is a more efficient oxidising agent: not only does iron get more oxidised in presence of Mn<sub>2</sub>O<sub>3</sub> than MnO<sub>2</sub> but the Mn<sup>3+</sup> absorption peak is much stronger in the presence of Mn<sub>2</sub>O<sub>3</sub> (Fig. 2). The hypothesis can thus be made that MnO<sub>2</sub> in glass has an intermediate role between MnO and Mn<sub>2</sub>O<sub>3</sub>.

In Roman decoloured and purple glass, the proportions of iron and manganese are not stoichiometric and manganese is in excess; this is the reason why glass with 0.26 wt% Fe along with 1 wt% Mn are studied. In this case, manganese always plays the role of an oxidising agent even if MnO is added initially. Yet, Mn<sub>2</sub>O<sub>3</sub> is still the most efficient oxidising



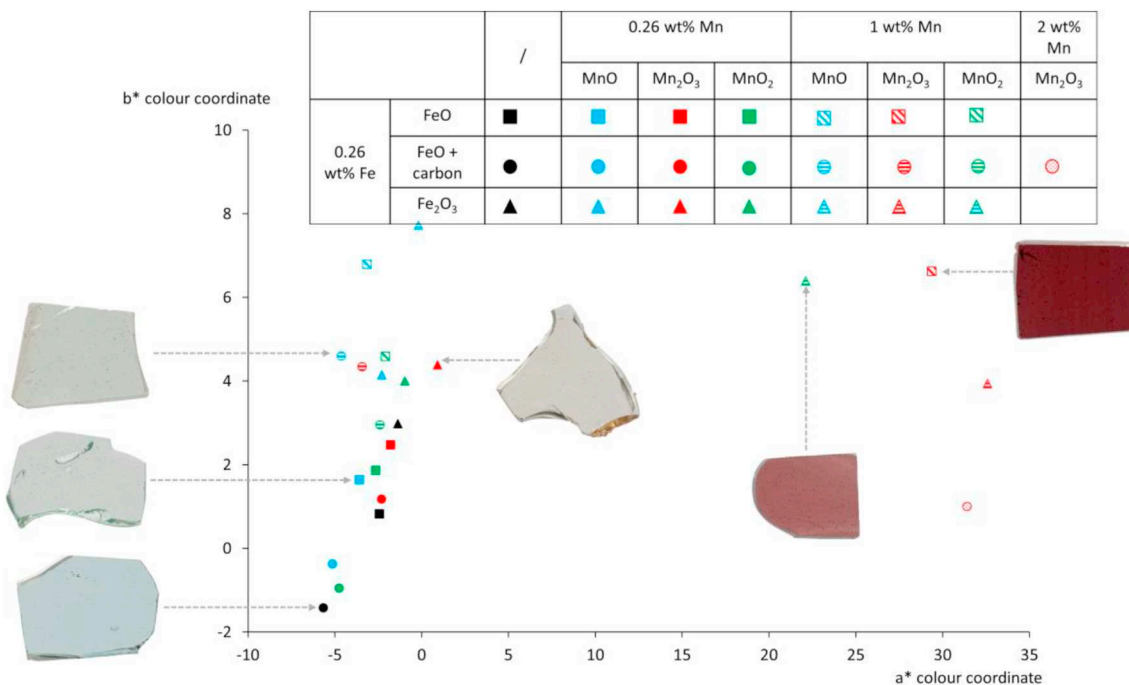


Fig. 3. Colour coordinates a\* and b\* of the different glasses studied. In black: iron only, in blue: iron with MnO, in red: iron with Mn<sub>2</sub>O<sub>3</sub>, in green: iron with MnO<sub>2</sub>; square: FeO, circle: FeO and carbon, triangle: Fe<sub>2</sub>O<sub>3</sub>. The proportion of iron and manganese are determined based on the full and striped symbols. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

agent, whereas MnO only slightly oxidises iron and MnO<sub>2</sub> has an intermediate role.

The choice of raw materials has a crucial influence to determine whether the glass is purple. This colour is generated by the presence of Mn<sup>3+</sup> causing an absorption at 490 nm as can be seen in Fig. 2. CIELab colour coordinates from the different glass envisaged here are represented in Fig. 3 along with pictures of some glass fragments, giving a better overview of the colour of the samples. The colour coordinate b\*, which quantifies how blue/yellow a glass is, is represented as a function of a\* characterising how green/red a sample is. To understand how colours in glass are generated by multivalent elements, it is important to keep in mind that there are two aspects. On the one hand, there can be colour variations associated to redox changes of the multivalent element. Indeed, Fe<sup>2+</sup> is well known for causing a blue colour and Mn<sup>3+</sup> a purple one (Bamford, 1977). On the other, colours can compensate each other so that the overall colour perceived from a glass is a combination of the different colours that would have been generated by the different multivalent elements (Möncke et al., 2014).

From Fig. 3, four glasses can be considered purple:

- Fe<sub>2</sub>O<sub>3</sub>:MnO<sub>2</sub> (0.26:1),
- FeO:Mn<sub>2</sub>O<sub>3</sub> (0.26:2) with carbon,
- FeO:Mn<sub>2</sub>O<sub>3</sub> (0.26:1),
- Fe<sub>2</sub>O<sub>3</sub>:Mn<sub>2</sub>O<sub>3</sub> (0.26:1).

The inherent cause to obtaining purple glass is the presence of

Mn<sup>3+</sup>. For this oxidation state of manganese to be present in sufficient concentration to colour the glass purple, raw materials of iron and manganese, as well as their proportions, play a key role. The following observations can be made.

First, the proportion of manganese towards iron is determining: none of the glasses with stoichiometric proportions of iron and manganese turned purple. An excess of manganese is thus necessary to colour the glass purple. However, the opposite is not true: it is not because there is an excess of manganese that the glass will be purple. Comparing the colour to the iron redox ratio, it appears that the purple glasses are also those that were most oxidised (iron redox ratio < 0.05). Based on Eq. (1), it could be suggested that all the Mn<sup>3+</sup> initially present will oxidise the iron, i.e. with the reaction shifted to the right. Once there is no more Fe<sup>2+</sup> to be oxidised, Mn<sup>3+</sup> remains and colours the glass purple.

Secondly, a crucial role is played by the raw materials, i.e. the initial oxidation state of the element. For the purple colour to occur, Mn<sup>3+</sup> needs to be present in the glass. This can happen either if Mn<sub>2</sub>O<sub>3</sub> or MnO<sub>2</sub> are used but not in presence of MnO. The source of iron needs to be considered in parallel. Indeed, if iron is already quite oxidised in the raw material, more Mn<sup>3+</sup> will be present thus allowing for the purple colour. This explains why the glass produced using Fe<sub>2</sub>O<sub>3</sub> in presence of MnO<sub>2</sub> is purple even though MnO<sub>2</sub> does not contribute to this colour in any other glass. If carbon is present, the glass does not get purple. This could be due to a reduction by carbon of both iron and manganese. Here again, the proportion of manganese to iron can alleviate the effect

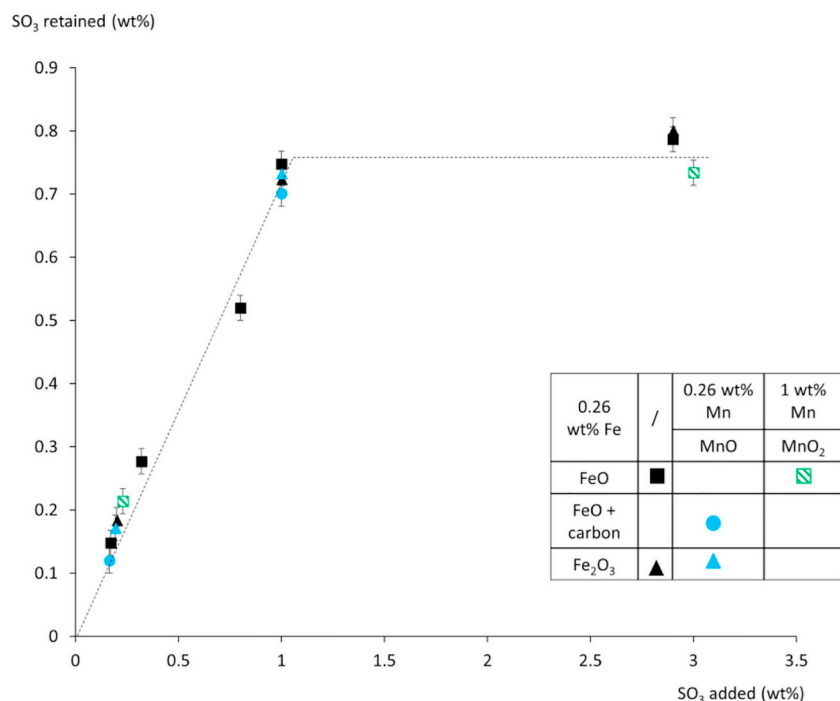


Fig. 4. Sulphate retained as a function of sulphate added in glass melted for 32 h at 1200 °C, the maximum solubility is just below 0.8 wt%.

of carbon, as a very large excess of manganese (FeO:Mn<sub>2</sub>O<sub>3</sub> (0.26:2) with carbon) still allowed for the appearance of purple.

As a conclusion, an excess of manganese is necessary for the purple colour to appear. This explains why Roman glasses with the highest concentrations of manganese are not colourless or greenish. However, in the intermediate range of concentrations, the raw materials are crucial: sources of manganese and/or iron which are already oxidised initially favour purple in the glass.

#### 4.2. The particular case of sulphates and carbon

After having discussed the importance of raw materials and proportions of iron to manganese, it is necessary to address the issue of other additives. Sulphates and carbon are additives which have been considered to have an important role in adjusting the redox ratio (Simpson and Myers, 1978) and thus on the glass colour. How this relates to ancient glass is tackled in this second part, where the effect of sulphate is first studied and then followed by the analysis of carbon.

How sulphate is retained in glass melted at 1200 °C for 32 h is presented in Fig. 4. Fig. 4 gives the concentration of sulphate retained (as measured quantitatively on WDS-XRF on the final glass samples) as a function of sulphate added originally in the batch (based on the amount of Na<sub>2</sub>SO<sub>4</sub>). The error corresponds to the error of weighed Na<sub>2</sub>SO<sub>4</sub> for the SO<sub>3</sub> added and to repetitive WDS-XRF measurements for

the SO<sub>3</sub> retained. It can be observed that there is a linear correlation between the amount of sulphate added and retained until a plateau is reached which corresponds to the maximum solubility of sulphates in a melt at 1200 °C around 0.8 wt% of SO<sub>3</sub>. It is also interesting to note that, whatever the raw materials and iron/manganese proportions used, the trend in sulphate retained is the same for all the glasses. This indicates that sulphate behaves independently from the action of manganese. For glasses melted with 3.0 wt% of sulphate added, it was observed that the remaining sulphur separates from the melt as an immiscible gall which has been considered to be almost pure sodium sulphate (Beerkens, 2003). The presence of this gall in ancient glass production is quite likely depending on the glass composition and it has been proposed that this gall was removed from the glass surface once the glass had cooled down (Freestone, 2006).

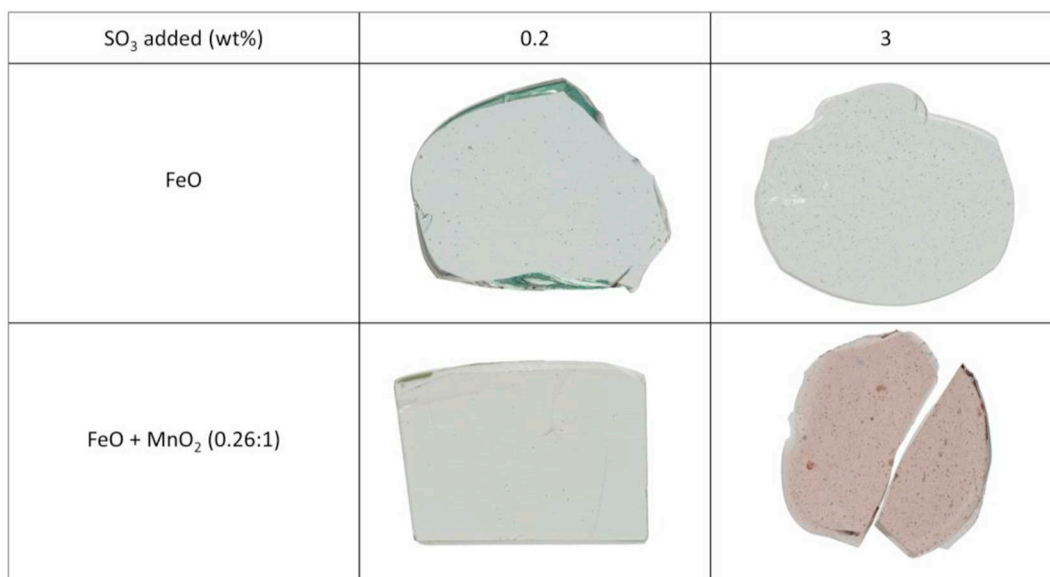
Another interesting conclusion that can be drawn from Fig. 4 is the initial sulphate concentration that must have been added in Roman glass. Indeed, as mentioned previously, there is on average 0.15 wt% of residual SO<sub>3</sub> in Roman glass. Given the hypothesis that Roman furnaces would not have reached higher temperatures than 1200 °C, it can be considered that < 0.20 wt% of sulphate would have entered the batch on average.

Furthermore, sulphate has an influence on the iron redox ratio. This can be observed in Table 4 which gives sulphate added in the glass and its redox ratio for different chemical compositions melted at 1200 °C for

Table 4

Redox ratio of the glasses melted at 1200 °C for different composition and different amounts of sulphates added initially.

0.26 wt% Fe	SO <sub>3</sub> added (wt%)					
	0	0.2	0.3	0.8	1.0	3.0
FeO	0.48 ± 0.05	0.34 ± 0.03	0.34 ± 0.04	0.30 ± 0.03	0.32 ± 0.04	0.20 ± 0.02
Fe <sub>2</sub> O <sub>3</sub>		0.12 ± 0.01			0.10 ± 0.01	0.09 ± 0.01
Fe <sub>2</sub> O <sub>3</sub> – MnO (0.26 wt% Mn)		0.15 ± 0.01			0.17 ± 0.01	0.09 ± 0.01
FeO + carbon – MnO (0.26 wt% Mn)		0.78 ± 0.08			0.24 ± 0.03	
FeO – MnO <sub>2</sub> (1 wt% Mn)		0.17 ± 0.01				0.07 ± 0.01



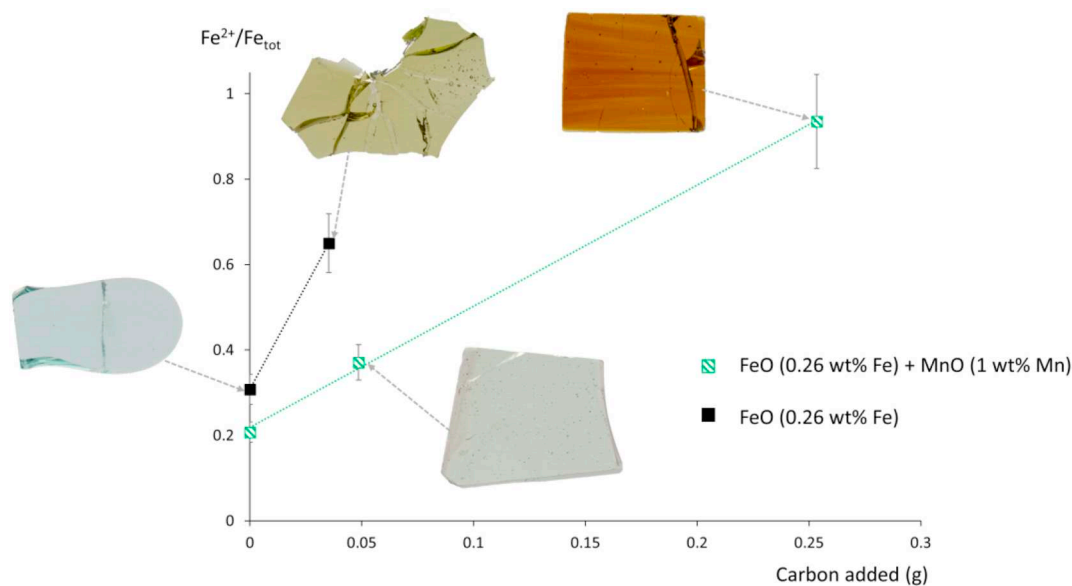
**Fig. 5.** Pictures of glasses with different amounts of sulphate added (0.2 and 3 wt%) for different chemical compositions. A very high addition of sulphate leads to the presence of many small bubbles and can cause colour differences.

32 h. These are the same samples as those presented in Fig. 4.

As expected, for one given chemical composition, the more sulphate is added to the batch, the more oxidised the glass is. For example, for a glass produced with FeO, the redox ratio decreases from  $0.48 \pm 0.05$ , for a glass without sulphate, to  $0.20 \pm 0.02$ , if 3.0 wt% of sulphate is added. As a comparison, a glass with Fe<sub>2</sub>O<sub>3</sub> to which 3 wt% of SO<sub>3</sub> was added has a redox ratio of  $0.09 \pm 0.01$ , whereas the ratio is  $0.12 \pm 0.01$  with 0.2 wt% of added sulphate. Consequently, the amount of sulphates in glass made with Fe<sub>2</sub>O<sub>3</sub> has less impact on the redox ratio than in presence of FeO. For the most reduced glass, i.e. the glass with carbon and stoichiometric amounts of iron and manganese added as FeO and MnO, the redox ratio is  $0.78 \pm 0.08$  when only 0.2 wt% of sulphate is added, but it decreases to  $0.24 \pm 0.03$  for 1.0 wt % of sulphate. This means that sulphate does not play an important role for already quite oxidised glasses, whether through the use of Fe<sub>2</sub>O<sub>3</sub> as a raw material or the presence of manganese as an oxidising agent

(MnO<sub>2</sub>). On the other hand, when the glass is much more reduced, sulphates allow for an oxidation of the iron. Furthermore, the spread in redox ratios for glasses where only 0.2 wt% of sulphate is added is much larger (from 0.78 to 0.12) than the range of redox ratios for 3 wt% of sulphate initially added (0.07 to 0.20). However, it should be kept in mind that the concentration of sulphate retained in archaeological usually does not exceed 0.50 wt%. The implications of this will be discussed later, once the effects of all parameters have been assessed.

Fig. 5 gives pictures of the glass produced with either 0.2 wt% or 3 wt% SO<sub>3</sub> added. Two main observations can be made. First, it can be noted that the addition of high amounts of sulphate causes the presence of either many trapped bubbles or recrystallised Na<sub>2</sub>SO<sub>4</sub>. It is not possible to distinguish these due to their very small size. These could be bubbles because sulphate is a well-known fining agent, meaning that its decomposition creates many bubbles. These absorb those already present in the melt and rise by buoyancy, thus getting rid other trapped



**Fig. 6.** Redox ratio as a function of carbon added for glasses melted at 1200 °C with around 0.15 wt% SO<sub>3</sub>. Three glasses contain both iron and manganese (respectively 0.26 wt% Fe and 1 wt% Mn), the other two containing only iron as FeO (0.26 wt% Fe). The more carbon is added, the more reduced the glass is and the darker it becomes.



gasses in the melt (Beerkens, 2009a; Wondergem-de Best, 1994).

Secondly, as can be observed in Fig. 5, the glass remains bluish despite the presence of an excess of manganese if only 0.2 wt% of  $\text{SO}_3$  was added. However, in the case where 3 wt% of  $\text{SO}_3$  added, a purplish tinge occurs. This means that sulphate can contribute to colour modifications through the oxidation of the multivalent elements present. However, for this to occur, very high initial concentrations of sulphate is necessary.

It should be kept in mind that sulphate acts upon the redox of glass through two mechanisms. On the one hand, sulphate has a positive contribution to the redox number (Simpson and Myers, 1978). On the other, their thermal decomposition releases oxygen which oxidises iron. This latter decomposition occurs above  $T_{\text{onset}}$  as explained previously. In this case, the glasses are melted at  $1200^\circ\text{C}$ , a temperature below  $T_{\text{onset}}$ . Therefore, all the observations made in this part are due to the action of sulphate as a direct oxidising agent. How sulphate acts at higher temperatures will be the subject of the next part of the discussion.

Carbon is another component that can be used to adjust the redox ratio and influence the colour without changing the chemical composition. Its addition in the form of charcoal is likely in ancient glass production (Jackson et al., 2009; Paynter and Jackson, 2017). Furthermore, in the 19th century, Bontemps (1868) explains how to decolour or colour glass using manganese. He describes that if there is too much manganese the glass can become purple and that this effect can be overcome through the mixing of the glass-forming melt with a wooden stick, which is instantly burnt. Basically, this process consists in the addition of a source of carbon to the batch, which will reduce the glass and correct the batch redox number to achieve the desired colour.

Fig. 6 presents the iron redox ratio as a function of carbon added for one glass containing only iron as FeO (0.26 wt% Fe) and another with both iron and manganese (added as FeO and MnO with 0.26 wt% Fe and 1 wt% Mn). Around 0.2 wt%  $\text{SO}_3$  was added to both sets of samples which were melted at  $1200^\circ\text{C}$  for 32 h. Clearly, the more carbon is added to the glass, the more reduced the iron is and the darker the glass appears, this results in the typical amber colour (Paynter and Jackson, 2017). As discussed based on Table 3, the presence of carbon is correlated with iron being in its most reduced form in all the different cases. This goes well with the early production of Roman black glass,

where it is not the amount of iron but rather the addition of carbon which would have been responsible for the dark colour (Ceglia et al., 2014). Unless a large excess of  $\text{Mn}_2\text{O}_3$  was added to the batch (2 wt% Mn), none of the glasses with carbon became purple (Fig. 3). Manganese can thus also be affected by the presence of carbon. If there is a large amount of carbon added in the batch (0.25 g of carbon), the glass becomes very reduced and brown, even though manganese is present in excess. In that case, we propose that the ferri-sulphide complex is formed, causing its characteristic amber colour (Chopin et al., 2002; Paynter and Jackson, 2017).

Carbon is thus a very efficient reducing agent in glass, whereas sulphate can oxidise the glass but, in the concentration detected in Roman glass, i.e. on average 0.15 wt% of residual sulphate (Ceglia et al., 2015a; Freestone, 2006), it could not have played a decisive role in defining the redox ratio at  $1200^\circ\text{C}$ .

The discussion at this point was mainly focused on the chemical composition of the batch which basically relates to a redox number as proposed by Simpson and Myers (1978). However, melting time and temperature are also important parameters that need to be taken into consideration.

#### 4.3. The effect of melting time and temperature on redox and colour

At this point, all the results presented were for glasses melted for 32 h at  $1200^\circ\text{C}$ . Here melts of 7 h and 32 h are compared as well as  $1200^\circ\text{C}$  and  $1500^\circ\text{C}$ . For more clarity, the lines of the appendix give the elemental weight percent of iron and manganese, as well as the melting temperature and time and the amounts of sulphate added and retained.

As can be observed in Appendix A, it was verified that there is no significant difference in the redox ratios for melting times of 7 h and 32 h for all the glasses except for one composition melted at  $1500^\circ\text{C}$ . The glass with FeO (0.26 wt% Fe) melted at  $1500^\circ\text{C}$  containing neither manganese nor sulphate is significantly more oxidised after 32 h of melt ( $\text{Fe}^{2+}/\text{Fe}_{\text{tot}} = 0.30 \pm 0.03$ ) than after 7 h of melt ( $\text{Fe}^{2+}/\text{Fe}_{\text{tot}} = 0.53 \pm 0.06$ ). As a comparison for glasses melted at  $1200^\circ\text{C}$  with neither manganese nor sulphate, the redox ratios are not significantly different (respectively  $0.53 \pm 0.07$  and  $0.48 \pm 0.05$  for 7 h and 32 h of melting). This difference in redox ratio due to melting time occurs only at the higher temperature because redox in glass is due to

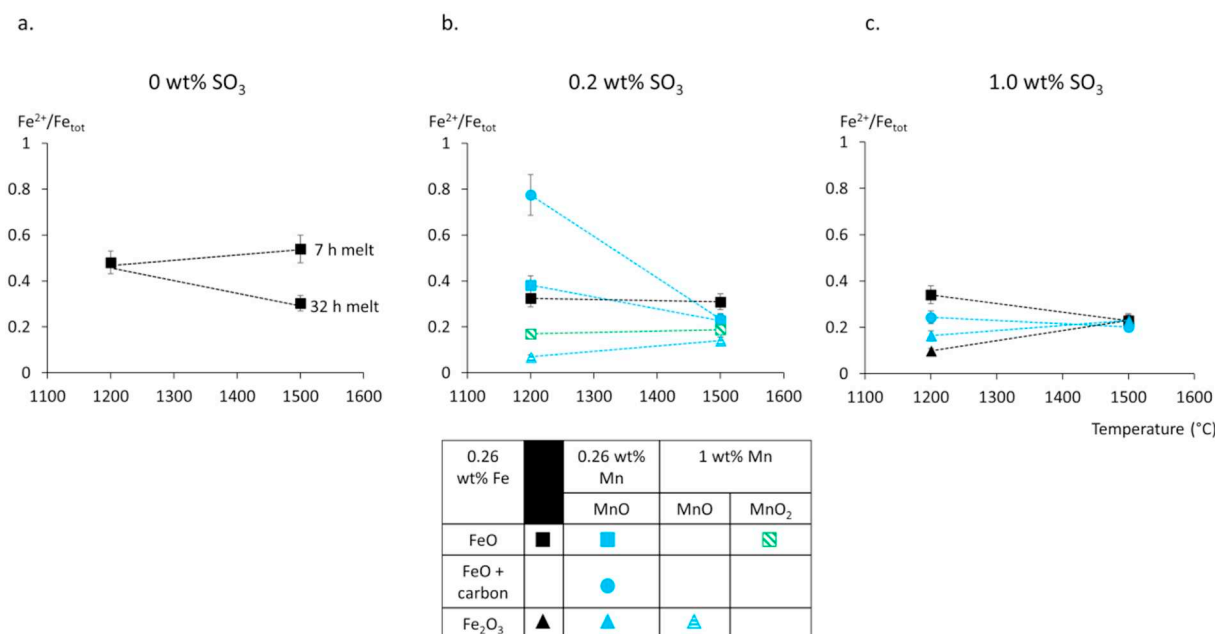


Fig. 7. Redox ratio as a function of melting temperature: the higher the temperature, the more the redox ratios tend to converge for glasses with different chemical compositions. a. no  $\text{SO}_3$  added initially, b. 0.2 wt%  $\text{SO}_3$  added initially, c. 1.0 wt%  $\text{SO}_3$  added initially.

diffusion processes and are therefore exponentially related to the melting temperature following the Arrhenius equation (Schreiber, 1986). As a result, the higher the melting temperature is, the higher the oxygen diffusion coefficients are and thus the more oxidised the glass will be. In the same way as when iron is alone in the melt, no significant redox ratio difference is noted in glasses melting for 7 h or 32 h if either manganese and/or sulphate are present. For the rest of this discussion, glasses melted for 32 h will be considered because glass melted for only 7 h at 1200 °C can still contain some unmelted parts. The only exception would be for the glass melted at 1500 °C without sulphate (only FeO). In that case, we propose that the data of the glass melted for 7 h rather than 32 h is more relevant. Indeed, the glass is more oxidised after 32 h of melt because of the diffusion of oxygen from the atmosphere and this is not due to any other internal effect. As it is the only glass where this was observed and given the fact that such an oxidation does not occur at 1200 °C, it is reasonable to consider that this effect is exceptional in the glass production strategy developed here.

The melting temperature has an important influence on the iron redox ratio. The precise onset temperature, i.e. the temperature at which sulphate thermally decomposes and determine the redox ratio of the glass, varies depending on the chemical composition of the glass and particularly the quantity of SO<sub>3</sub> dissolved in the glass. As a result, the glass will be oxidised due to the decomposition of sulphate instead of being reduced by higher temperatures. Yet, it should be between 1400 °C and 1500 °C for soda-lime silicates (Beerkens, 1999).

How different melting temperatures affect the redox ratio of various glasses is shown in Fig. 7, which gives the redox ratio of the glass as a function of melting temperature in three different cases: a. when no sulphate is added, b. when 0.2 wt% of sulphate is added (i.e. corresponding to archaeological glass), c. when 1.0 wt% of sulphate is added. Different chemical compositions are envisaged: glasses contain either only iron or both iron and manganese and some initially melted with carbon. The first observation is that as temperature increases, redox ratios tend to converge.

Concerning the glasses that contain only iron as FeO (black full squares), in the absence of sulphate (Fig. 7a), the glass melted for 7 h at 1500 °C is slightly more reduced than if it was melted at 1200 °C. This can be explained by the fact that reductions are endothermic and that in a closed system the higher the temperature is, the more reduced the glass becomes (Schreiber, 1986). The oxidising effect of sulphate is enhanced at higher temperature. When 1 wt% of sulphate is added initially in a glass that contains no manganese, the redox ratio goes from  $0.34 \pm 0.04$  at 1200 °C to  $0.24 \pm 0.02$  after a melt at 1500 °C.

For glasses where both manganese, sulphates and sometimes even carbon are present, the redox ratios are spread at 1200 °C and converge at 1500 °C. At 1500 °C, a common melting temperature of modern glass, the redox ratio of all the chemical compositions are between  $0.15 \pm 0.02$  and  $0.30 \pm 0.03$ . Comparatively, at 1200 °C, a commonly accepted melting temperature for Roman furnaces, redox ratios range from  $0.07 \pm 0.01$  to  $0.78 \pm 0.09$ . This effect is enhanced for glasses where 1 wt% of sulphate is added: at 1200 °C redox ratios range from  $0.34 \pm 0.04$  to  $0.09 \pm 0.01$  whereas the range is  $0.20 \pm 0.02$  to  $0.22 \pm 0.02$  at 1500 °C. This allows us to draw an important conclusion. Sulphates have a much more important impact on redox at higher temperature than at archaeological furnace temperatures. This is due to

the fact that 1200 °C is below  $T_{\text{onset}}$  whereas 1500 °C should be above. As such, in the latter case, the effect of sulphate is not only limited to its contribution to the redox number of the batch (Simpson and Myers, 1978) but also due to the thermal decomposition of sulphates. While the amount of sulphate initially added can also have an impact on the redox ratio at 1200 °C (Table 4), it has a much more pronounced effect at 1500 °C. There is thus clearly a difference between glasses produced nowadays and in Roman times. At modern melting temperatures, sulphate has a strong impact on the redox ratio, while the chemical composition and batch redox has a major influence at lower temperatures.

#### 4.4. Archaeological implications of the glass production strategy and hypotheses

Everything considered, it appears that the most important factor to determine if a glass becomes purple is the amount of manganese added in Roman furnace conditions (i.e. melt at 1200 °C for 0.2 wt% SO<sub>3</sub> added). Indeed, in stoichiometric proportions, no glass was purple, whereas in glasses with high manganese concentrations, the glass became purple. It thus appears that an excess of manganese is necessary for glass to become purple. This answers the first question of this paper as the ratio manganese to iron is crucial in determining the glass redox ratio and colour. At this stage, it is also necessary to keep in mind that, while manganese would have been a deliberate addition to the batch, the iron was present as an impurity of the sand.

Nevertheless, there are many cases in which there is no large excess of manganese, but Roman glass is still purple (Arletti et al., 2013; Boschetti et al., 2017; Möncke et al., 2014). The second factor is thus the choice of raw materials. It has been hypothesized that Roman glassmakers were using pyrolusite (MnO<sub>2</sub>) as a manganese ore (Gliozzo, 2017). As has been shown, MnO<sub>2</sub> has an intermediate behaviour between MnO and Mn<sub>2</sub>O<sub>3</sub> containing raw materials and did cause a purple colour in the glass made with FeO. In the case where it is not the amount of manganese that determines the colour, we propose three hypotheses to explain how manganese was either colouring or decolouring a glass.

First, it is possible that glass makers used different manganese ores or that different parts within one ore were kept for the production of different glasses. This remains a hypothesis but appears quite likely. Indeed, Huisman et al. (2017) proposed that manganese ores used for Iron Age coloured glass beads had one single provenance but that there was a very high variability within the deposits used. It is also suggested that the same ores would have been used in the Iron Age as in Roman times. Therefore, we hypothesize that some parts of the ore (more oxidised) would have been kept for the production of purple glass based on the empirical know-how of glassmakers.

Secondly, in the case of antimony opacified glass, Lahlil et al. (2010) proposed that stibnite must be roasted prior to being added to the glass batch. In a similar way, one could assume a processing of the manganese ore in a first step in order to obtain a more oxidised manganese source, which could then be used as a colouring agent. It would be interesting to carry out roasting experiments of pyrolusite prior to the addition of the manganese in the glass batch. Huisman et al. (2017) propose that manganese ores would have occurred as by-products of

metals extraction in ancient times. In that case, it is likely that the manganese further used as a (de)colouring agent would have undergone various heat treatments which could have influenced the oxidation state of the manganese.

The third hypothesis concerns the additives and processing of the glass itself (carbon and sulphates). As has been described carbon is a very powerful reducing agent and its presence impedes the purple colour of glass. The addition of organic matter, whether intentional or unintentional, is very likely in ancient glass production, for example in the form of charcoal (Jackson et al., 2009; Paynter and Jackson, 2017). For the production of purple glass, it could thus be considered that particular care was taken to avoid or at least limit the incorporation of charcoal or any other organic matter in the batch. A source of manganese would gradually have been added and the colour tested until the desired hue was reached.

Beyond its role of fining agent, high amounts of sulphates can also favour the appearance of a purple colour (Fig. 5). Yet, in ancient glass we hypothesize that the concentration of sulphate added is not a determining parameter for two main reasons. Glasses containing manganese (HIMT, manganese decoloured and purple glass) tend to have higher concentrations of residual sulphate, up to 0.5 wt% (Ceglia et al., 2015b; Cholakova et al., 2016; Gallo et al., 2013; Maltoni and Silvestri, 2016; Rosenow and Rehren, 2014; Schibille et al., 2017; Silvestri et al., 2011, 2005; Zoleo et al., 2015). However, based on Fig. 4, for a maximum of 0.5 wt% SO<sub>3</sub> to be retained in a glass melted at 1200 °C, it is unlikely that > 1 wt% of SO<sub>3</sub> would have entered the batch initially. This amount of sulphate would not have been sufficient to play an important role in the colouring of the glass. Furthermore, sulphate content is not a parameter that ancient glassworkers could have controlled easily as it came as an impurity from the natron which brought the sodium carbonates. Schreurs and Brill (1984) consider it unlikely for sulphur to have been added intentionally to the glass, rather it would have been present as a contaminant whose content could have been quite variable depending not only on the exact location of the natron but also on the season (Shortland et al., 2006). Actually, analyses of ancient glass have revealed that glass contained a large range of residual SO<sub>3</sub>: between 0.05 and 0.5 wt% (Freestone, 2006).

Glasses produced nowadays and in Roman times are quite similar, not only in their properties but also in their chemical composition. However, the major difference in redox control is related to the melting temperature. The temperatures reached in modern glass furnaces are close to the thermal decomposition of sulphate, strongly influencing the final glass redox. It should however be noted that the maximum temperature is not reached throughout the full glass melt in modern furnaces (Beerkens, 2009b). Therefore, in certain parts of the glass-forming melt in modern furnaces, it could be considered that T<sub>onset</sub> is not necessarily reached. In these lower temperature zones, raw materials would prevail in the determination of the redox ratio. Yet, in Roman glass furnaces, such high temperatures could not be reached anywhere in the furnace so that sulphate had less influence and the impact of raw materials was crucial.

Like in modern glass production, it seems relatively unlikely that furnace atmosphere would have been the principal factor to determine the redox and colour. Indeed, the atmosphere only influences the redox of the upper part of the batch due to diffusion of oxygen from air. Actually, a discussion about furnace atmosphere should carefully examine the melt geometry and melting times. In the case where the glass-forming melt has large dimension, such as would have been the case for primary workshops, it is quite unlikely that furnace atmosphere would have modified the glass redox throughout the melt thickness. However,

## Appendix A

in pot furnaces, which would have been used in secondary workshops, the glass is melted in smaller-sized crucibles. Paul (1990) determined that for 10 g of glass melted at 1400 °C in a crucible of 3 cm diameter, it takes > 30 h to reach equilibrium with the atmosphere (at a redox ratio of 0.15). So, for very long melting times, some interaction with the furnace atmosphere could be envisaged.

## 5. Conclusions

To understand why manganese containing glass can be either purple or decoloured, the strategy followed in this study relied on the production of glass with similar compositions as ancient glass. Different production parameters are systematically analysed to evaluate their influence on glass redox and colour. In total, only 5 glasses can be considered purple or having a purplish tinge (a\* > 7 and b\* > 3):

- FeO:MnO<sub>2</sub> (0.26:1) with higher amounts of sulphates (3 wt% of SO<sub>3</sub> added),
- Fe<sub>2</sub>O<sub>3</sub>:MnO<sub>2</sub> (0.26:1),
- FeO:Mn<sub>2</sub>O<sub>3</sub> (0.26:2) with carbon,
- FeO:Mn<sub>2</sub>O<sub>3</sub> (0.26:1),
- Fe<sub>2</sub>O<sub>3</sub>:Mn<sub>2</sub>O<sub>3</sub> (0.26:1).

The most important parameter is the amount of manganese: an excess of manganese relative to iron is necessary for the glass to become purple. For lower concentrations of manganese, the glass is more likely to appear only weakly coloured. Secondly, raw materials play an essential role. While, manganese added as MnO can even reduce slightly the iron, thus causing the glass to be bluish, the addition of manganese in the form of Mn<sub>2</sub>O<sub>3</sub> oxidises the iron. As a result, without an excess of manganese, the glass would be colourless whereas an excess of Mn<sub>2</sub>O<sub>3</sub> leads to the production of purple glass. MnO<sub>2</sub> which is the most likely source of manganese in ancient times has an intermediate impact on glass. Finally, carbon is a very powerful reducing agent whereas sulphates would have played a relatively minor role even at the maximum melting temperature possible in ancient furnaces. This is the most important difference between ancient and modern glass production. In modern furnaces, temperatures close to the onset temperature are reached so that the influence of sulphates is determining in the glass colour and redox ratio. This would not have been the case in Roman glass.

The empirical colour control of ancient glassmakers is impressive and it is not possible to give a univocal recipe for the production of purple and decoloured manganese containing glass. Rather, different hypotheses are suggested involving either thermal treatments of raw materials prior to their incorporation in the batch, or an informed choice of raw materials. That furnace atmosphere would have played a role in the redox control is a hypothesis often upheld in archaeological science, but which we do not support for primary production. Instead, many other factors come into play and would have participated more efficiently to colour and redox control.

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## Appendix B. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jasrep.2019.101975>.

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