

THE ALKALI-METAL RATIO IN ROMANO-BRITISH BLOOMERY SLAGS, SEVERN ESTUARY LEVELS, SOUTHWEST BRITAIN: VALUES AND IMPLICATIONS

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A further assessment of geochemical data previously reported on the composition of Romano-British bloomery slags from the Severn Estuary Levels (16 sites, 113 analyses) reveals that the $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio for furnace bottoms from non-tappable bowl furnaces in general is significantly higher than for the tap-slags from tappable devices. As sodium is the more volatile of the two metals, the difference in the ratio could indicate that the smelting process in the tappable furnace, most likely to have been of the shaft variety, was generally of a longer duration and/or at a higher temperature than in the simple bowl furnaces.

INTRODUCTION

Iron has been smelted since the Iron Age in the Forest of Dean and surrounding area, part of the Bristol Channel Orefield (Young and Thomas 1998), first by the bloomery batch process and then, from the sixteenth century onward, by the continuous blast-furnace method (Hart 1971; Meredith 2006). The important Roman industry is fairly well known in terms of smelting sites, ores and residues, but not with regard to the location of mines from which the rich ores of the Forest – chiefly goethite but some haematite (Sibly and Lloyd 1927; Young and Thomas 1998) – were extracted for use (Walters 1992; Allen 2009). It would appear, however, that most smelting was done away from the mines (Fulford and Allen 1992), and that ores were exported eastward by land and water to many sites up and down the Severn Estuary Levels, especially in the later Roman period (Allen 2009). Both tappable and simple bowl furnaces (Tylecote 1986) were in use at this time on the Levels, at many sites apparently together, yielding smelting slags of very different

character. From the tappable furnaces came tap-slags with lava-like flow markings on their upper surfaces. The bowl furnaces afforded basin-shaped furnace bottoms weighing up to a few kilograms that typically preserved on the undersides the moulds of the marks of the tools used to dig the hollows in which smelting took place.

An intensive geochemical study (16 sites, 113 samples) using x-ray fluorescence analysis showed these residues compositionally to be fayalite-wüstite slags (Allen 2009), the silicate component deriving from either the lining of the furnaces or dried/burnt clay deliberately included as a reactant in the charges of ore and charcoal fuel, and to some extent from the fuel itself (Fulford and Allen 1992; Thomas and Young 1999). Although the furnace bottoms and tap-slags clearly belonged to the same chemical family in terms of the major and minor elements present, small but significant differences between the two types of residue were found in the case of certain element-ratios, suggesting that the procedures/processes involved in the use of non-tappable and tappable furnaces were not exactly the same. What the differences were remain unclear, but the extension of the analysis to the alkali-metal ratio ($\text{Na}_2\text{O}/\text{K}_2\text{O}$), reported in this note, seems to begin to narrow the field. The use of ratios in geochemical analysis is in general to be preferred over reference to raw proportions, as it circumvents the problems of assessing numerical data available only in closed-number systems (Buccianti *et al* 2006).

GEOCHEMICAL SUMMARY

Previous work showed that the tap-slags and

Table 1. Summary of alkali ratios ($\text{Na}_2\text{O}/\text{K}_2\text{O}$) (data of Allen, 2009, Appendix A). Footnotes: 1 = average (standard deviation); 2 = single analysis; 3 = furnace bottom/tap-slag.

Site	Tap-slag ¹	Furnace bottom ¹	Ratio ³
<i>West bank</i>			
Awre	0.34 (0.11)	0.48 (0.48)	1.41
Lydney Park Farm	0.21 (0.12)	1.25 ²	-
Ley Pill	0.12 (0.058)	0.57 (0.41)	4.75
Horse Pill	0.60 (0.69)	0.77 (0.92)	1.28
Pill House	0.22 (0.096)	0.41 ²	-
Rumney Great Wharf	-	0.76 (0.22)	-
<i>East bank</i>			
Elmore	0.25 (0.086)	0.48 (0.66)	1.92
Longney C	0.24 (0.17)	2.08 ²	-
Longney A	0.30 (0.082)	0.40 (0.24)	1.33
Longney B	0.20 (0.083)	-	-
Arlingham	0.31 (0.12)	-	-
Whitminster	0.19 (0.10)	-	-
Hills Flats	0.32 (0.15)	0.65 (0.44)	2.03
Oldbury (Home Farm)	0.20 (0.10)	0.61 (0.45)	2.25
Oldbury Flats	0.37 (0.21)	0.62 (0.25)	1.68
Chesters villa	0.17 (0.096)	-	-

furnace bottoms were similar in the proportions of SiO_2 and Fe_2O_3 , the two major components, the former being slightly the more siliceous for a given amount of iron (Allen 2009, fig 8). The iron oxide content for both types of residue varied from *c* 50-60 wt % to *c* 95 % and the proportion of silica from *c* 10% to *c* 35%. The alkali metals among the minor elements are represented in the analyses as Na_2O and K_2O . Their combined total relative to alumina, $(\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{Al}_2\text{O}_3$, ranged from *c* 0.05 to *c* 0.8 and, although there was overlap, proved to be significantly lower for furnace bottoms (Allen 2009, fig 9). The alkaline earths were analysed as MgO and CaO . Their sum relative to alumina, $(\text{MgO}+\text{CaO})/\text{Al}_2\text{O}_3$, varied even more, from *c* 0.1 to in excess of 2, with an average of 0.84 for tap-slugs and 0.41 for furnace bottoms, as compared to a value of 0.36 for ‘average’ shale. The high values for the tap-slugs suggested that carbonate-bearing rocks could have been used as a fluxing agent. At some sites the alkali-alumina and alkaline earth-alumina ratios for the furnace bottoms appeared to show a systematic variation with the weight of the residue, although the pattern was not consistent in form (Allen 2009, figs 11-12). On the face of it,

the $\text{Fe}_2\text{O}_3/\text{SiO}_2$ ratio for furnace bottoms declined with weight but, when the three heaviest of the analysed residues are treated as outliers and consequently excluded, appeared to increase slightly for the majority, weighing less than *c* 1 kg (Allen 2009, fig 13).

THE $\text{Na}_2\text{O}/\text{K}_2\text{O}$ RATIO

Sodium and potassium expressed as their oxides are present in the slags to no more than a few per cent by weight in total (Allen 2009, Appendix A). At one of the 16 sites (Rumney Great Wharf) no tap-slugs are known, and at four (Longney B, Arlingham, Whitminster, Chesters villa) there are no furnace bottoms. The ratios can therefore be compared at only half the sites.

Table 1 lists the alkali ratio, $\text{Na}_2\text{O}/\text{K}_2\text{O}$, for the furnace bottoms and tap-slugs recovered from the 16 sites, in terms of the average and standard deviation. The site average for tap-slugs has a five-fold range between 0.12 and 0.60, clustering around 0.2-0.3. For the furnace bottoms, ignoring single analyses, the range is from 0.40 to 0.77, that is, up to almost five times as much.

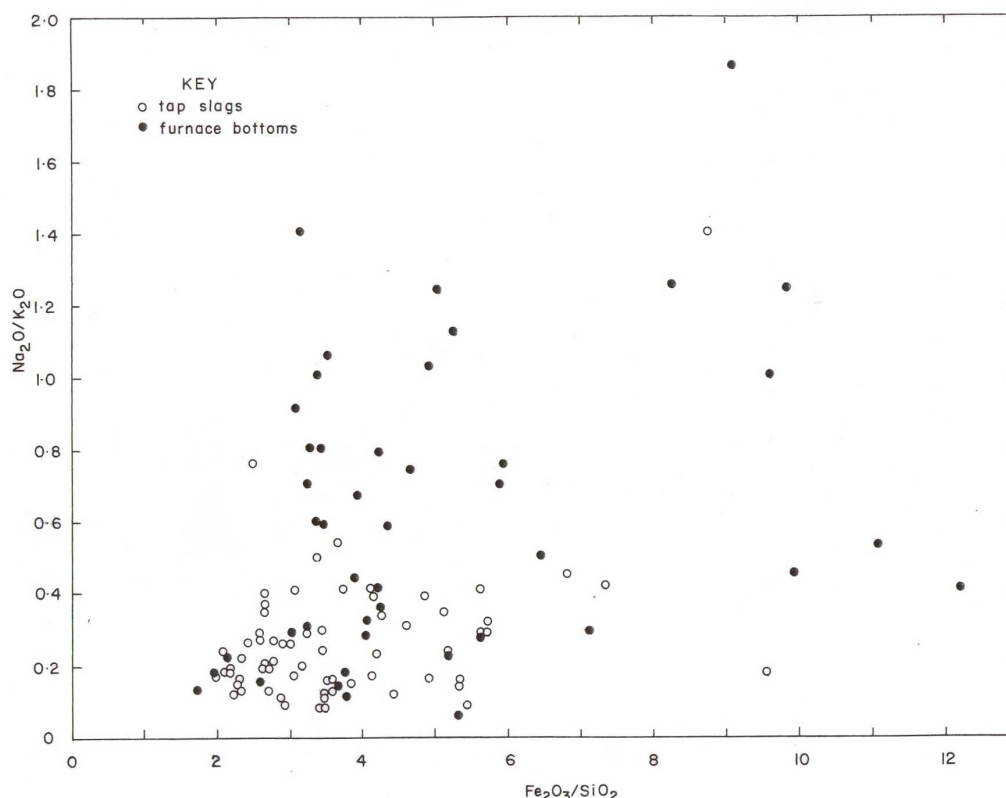


Figure 1. The alkali ratio, $\text{Na}_2\text{O}/\text{K}_2\text{O}$, as a function of the iron oxide/silica ratio, all sites and slags.

Where multiple analyses are available, the site ratio is invariably in favour of furnace bottoms. It is worth noting that it is also in their favour where only a single bottom could be analysed. Relative to 'average' shale, for which a ratio of 0.401 is quoted by Klein and Hurlbut (1999), tap-slags appear to be depleted in sodium relative to potassium.

The individual data appear in Figure 1 as a plot of $\text{Na}_2\text{O}/\text{K}_2\text{O}$ against the major-element ratio $\text{Fe}_2\text{O}_3/\text{SiO}_2$. The data for the two kinds of residue overlap, but furnace bottoms stray toward much higher values of the alkali ratio than is generally true of the tap-slags. There is no trend with the major oxide ratio.

As with the alkali/alumina and alkaline earth/alumina ratios discussed above, there are indications that the alkali ratio may also vary with the weight of furnace bottoms. The scatters for bottoms from Ley Pill, Rumney Great Wharf, Elmore, Longney A and Oldbury (Home Farm) hint at a possible inverse relationship (Figure 2). On the contrary, possible direct relationships

seems to be indicated by the plots for bottoms from a second, smaller group of sites: Horse Pill, Hills Flats and Oldbury Flats (Figure 3).

DISCUSSION

Like the alkali/alumina and alkaline earth/alumina ratios, the alkali ratio for the slags suggests that on the Severn Estuary Levels during the Roman period there were significant differences between the bloomery process as practiced in non-tappable bowl furnaces and tappable devices, the latter most likely to have been of the shaft type, going by the evidence from the Forest of Dean (Walters 1992) and Chesters villa (Fulford and Allen 1992). The differences may originate in some combination of a number of factors: (1) the choice of clay for fluxing agent and/or furnace lining, (2) the plant-sources of the carbon fuel, (3) the fuel-ore ratio, (4) the size of the charge, (5) the general temperature reached during the smelt, and (6) the duration of the smelt. The first two are site-specific, but the others relate to the components and management of the smelting process itself.

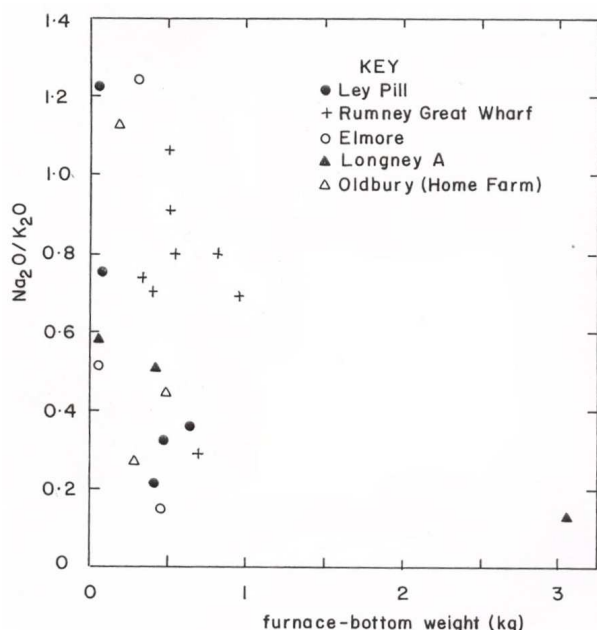


Figure 2. The alkali ratio, $\text{Na}_2\text{O}/\text{K}_2\text{O}$, as a function of weight for furnace bottoms from the smelting sites at Ley Pill, Rumney Great Wharf, Elmore, Longney A and Oldbury (Home Farm).

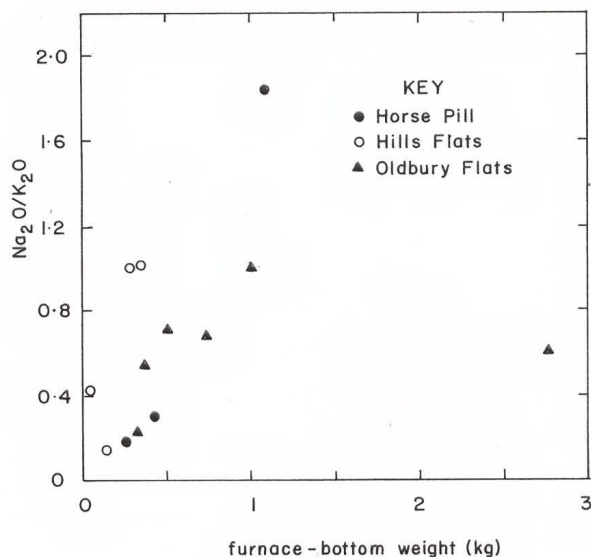


Figure 3. The alkali ratio, $\text{Na}_2\text{O}/\text{K}_2\text{O}$, as a function of weight for furnace bottoms from Horse Pill, Hills Flats and Oldbury Flats.

The possible significance of the alkali ratio is that it compares the abundance of two elements of which sodium is the more volatile and potassium the more stable. The finding that furnace bottoms in general yield higher values of the ratio than tap-slugs may suggest that the

bloomery process in bowl furnaces afforded less opportunity than in shaft furnaces for the more volatile sodium to be lost from among the reactants. It is conceivable that this arose from a typically shorter duration and/or lower temperature of smelting in simple bowl as compared to shaft furnaces. It is also worth noting that to achieve a higher temperature, a higher rate of fuel consumption would have been required; this could have contributed to a lowering of the $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio in the case of residues from shaft furnaces through an enhanced contribution of potassium from the fuel ash. Some support for this suggestion comes from the relatively high values of $\text{Na}_2\text{O}+\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio typically yielded by the tap-slugs (Allen 2009, fig 9).

The correct explanation lies in the future and will only be obtained by systematic smelting experiments, in which careful attention is given not just to the question of mass-balance but also to the detailed physics and chemistry of the process.

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