ORIGIN OF SLAG FROM EARLY MEDIEVAL AGE FURNACES IN NITRA

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Summary Two types of archaeological artefacts from remains of Early Medieval Age furnaces excavated in Nitra are analysed. They are supposed to originate from slag of glass and iron production. Employing Mössbauer spectrometry, iron crystallographic sites are identified and compared. In all samples, Fe^{2+} and Fe^{3+} structural positions were revealed. Some of the archaeological artefacts including those that were supposed to originate from glass production show a presence of metallic iron and/or magnetic oxides. Based on the results of Mössbauer effect measurements performed at room temperature as well as 77 K (liquid nitrogen temperature) analytical evidence is provided that the iron sites identified are not as those usually encountered in glasses. Consequently, a conclusion is proposed that neither of the investigated furnaces was used for glass production.

1. INTRODUCTION

In 1960, remains of four furnaces from Early Medieval Age were excavated in Nitra [1] (Fig. 1). Because a lot of glass–like findings were found on this site the function of furnaces was considered as being used for production of glass even though no analytical tests were performed. These dig-outs were divided into two groups: The first group contains dark glass–like archaeological fragments which were interpreted as a waste (slag) of a glass production. The second group consists of archaeological artefacts which were thought to be a slag from iron production.

Fig. 1. Schematic reconstruction of an Early Medieval Age furnace from Nitra (after [1]).

D. Staššíková–Štukovská discusses in works [2, 3] the interpretation of four furnaces and from the results of her research it follows that the first group of archaeological artefacts are in fact slag formers which were used for iron production. It is considered that the furnaces were not used for glass production but more probably for iron production.

This work aims in verifying the above mentioned assumptions using Mössbauer effect experiments. [57]Fe Mössbauer spectrometry is an analytical tool which uniquely identifies structural positions of iron atoms contained in the investigated material. Due to this feature Mössbauer spectrometry finds broad

applications in archaeological research [4]. It is widely used for the analysis of corrosion products [5] or clays and pottery [6]. By the help of Mössbauer spectrometry, firing conditions comprising the type of atmosphere and consequent formation of different colours were examined in fragments of archaeological pottery [7].

2. EXPERIMENTAL DETAILS

Samples for Mössbauer effect experiments were prepared by crushing to powder pieces from two groups of species: (i) glass-like material (denoted as G), and (ii) slag-like leftovers (S) collected from furnaces which were supposed to be used for glass- and iron-production, respectively. Three types of samples were prepared from each group of archaeological artefacts. Each sample was measured at room (RT) and liquid nitrogen (LNT) temperature in transmission geometry using a [57]Co(Rh) source. Calibration was performed with α-Fe. Hyperfine parameters of the spectra were refined using the CONFIT fitting software [8]. We have applied a model which consisted of up to four doublets for paramagnetic components and one or two sextets for magnetically split components if any.

3. RESULTS AND DISCUSSION

Room temperature [57]Fe Mössbauer spectra of all samples are shown in Fig. 2. They exhibit well developed doublet-like features which consist of four doublets with different isomer shift (*IS*) and quadrupole splitting (*QS*). According to these spectral parameters, the identification of particular iron positions is possible and even the coordination number can be estimated.

Apart from dominating quadrupole doublets, small contributions of magnetically split lines are revealed in G1, G2, and in S1. The sextets were identified by the help of their hyperfine magnetic fields *B* to belong to α-Fe and α-Fe_2O_3 (hematite).

The refined spectral parameters of individual components including isomer shift (*IS*), quadrupole splitting (*QS*), as well as spectral area A_{rel} are listed
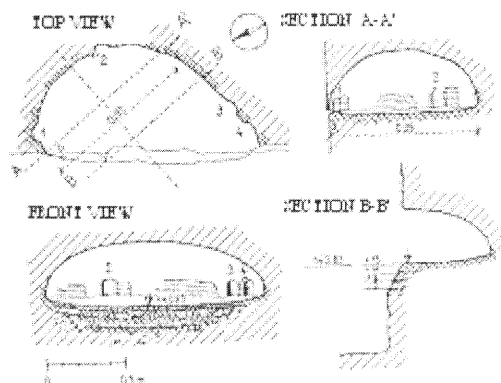
in Table 1 for room (300 K) temperature Mössbauer effect experiments. Errors in their determination are of ±0.02 mm/s, ±0.02 mm/s, and ±0.5 %, correspondingly.
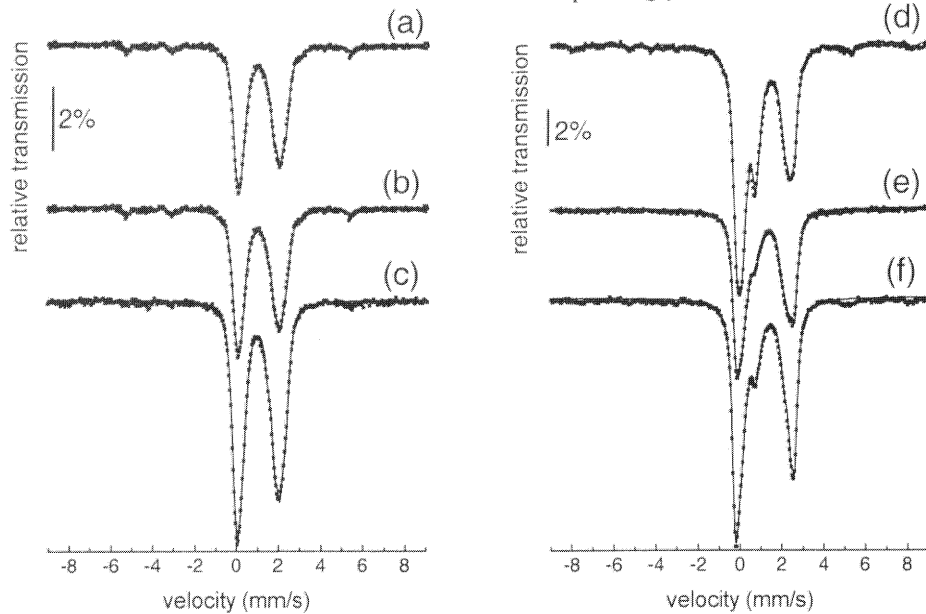

Fig. 2. ^{57}Fe Mössbauer spectra of G1 (a), G2 (b), G3 (c), S1 (d), S2 (e), and S3 (f) recorded at room (300 K) temperature.

Tab. 1. Parameters of Mössbauer spectra recorded at room temperature for G1-G3 and S1-S3 samples: IS – isomer shift, QS – quadrupole splitting, A_{rel} – relative area, and B – hyperfine field (for sextets only). Identification of spectral components is provided under "note" together with the corresponding coordination number.

sample's number	sample G				sample S			
	IS (mm/s)	QS (mm/s)	A_{rel} (%)	note	IS (mm/s)	QS (mm/s)	A_{rel} (%)	note
1	0.01	0.00	5	α-Fe (B = 33.08 T)	0.00	0.00	2	α-F (B = 32.90 T)
	-	-	-	-	0.26	-0.28	4	Fe_2O_3 (B = 50.23 T)
	1.19	2.23	12	Fe^{2+}, 6	1.16	2.82	12	Fe^{2+}, 4
	1.14	1.84	53	Fe^{2+}, 4	1.11	2.51	12	Fe^{2+}, 4
	0.82	1.92	21	Fe^{2+}, 4	1.11	2.02	35	Fe^{2+}, 4
	0.75	1.46	9	Fe^{3+}, 6	0.38	0.70	35	Fe^{3+}, 4
2	0.01	0.00	4	α-Fe (B = 33.08 T)	-	-	-	-
	1.19	2.24	19	Fe^{2+}, 6	1.17	2.86	24	Fe^{2+}, 4
	1.19	1.80	31	Fe^{2+}, 4	1.14	2.56	22	Fe^{2+}, 4
	0.89	1.96	29	Fe^{2+}, 4	1.13	2.02	31	Fe^{2+}, 4
	0.82	1.52	17	Fe^{3+}, 6	0.38	0.75	23	Fe^{3+}, 4
3	1.08	2.46	21	Fe^{2+}, 4	1.18	2.80	25	Fe^{2+}, 4
	1.05	2.04	32	Fe^{2+}, 4	1.17	2.26	35	Fe^{2+}, 4
	1.02	1.62	33	Fe^{3+}, 6	0.92	2.12	20	Fe^{2+}, 4
	0.94	1.12	14	Fe^{3+}, 6	0.48	0.48	20	Fe^{3+}, 4

Decomposition of a typical Mössbauer spectrum into its components is shown as an example in Fig. 3. Though minute in relative amount, the involvement of magnetically split spectral components (sextets) is unambiguously recognized.

In G samples of glass-like group (i), we have found two types of divalent Fe atoms with coordination numbers 4 and 6, and trivalent Fe^{3+} in coordination 6. On the other hand, S samples of slag from iron production (group (ii)) exhibit a presence of Fe^{2+} with coordination number 4 and Fe^{3+} also in tetrahedral coordination. It is noteworthy that

divalent Fe atoms with coordination number 4, which are identified in samples of both groups (i) and (ii), have diverse values of isomer shift IS and quadrupole splitting QS. These differences in spectral parameters imply distinctions in particular structural positions of the resonant atoms even though they depict the same valence and coordination.

Mössbauer spectra of the samples measured at liquid nitrogen (77 K) temperature which are shown in Fig. 4 show no changes in the number of components. In addition, none of paramagnetic
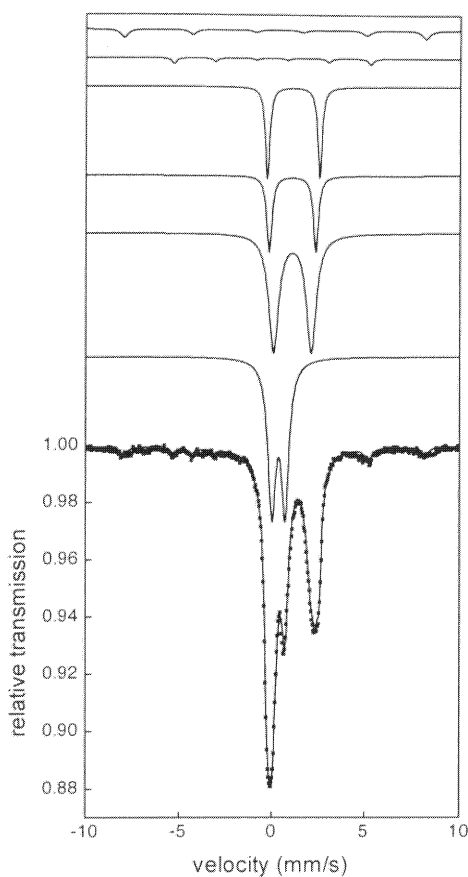
Fig. 3. Room temperature Mössbauer spectrum of S1 decomposed into its components.

positions. The spectral parameters derived are listed in Table 2.

Presence of metallic iron in structural positions of glasses is very improbable. Iron in glass is usually in the form of Fe_2O_3 located either in structural Fe^{3+} tetrahedral positions which are characterised by quadrupole doublets or as octahedral Fe^{3+} typical for extra frame positions [9]. The latter are demonstrated as magnetically split sextets. From this point of view, presence of Fe^{3+} with tetrahedral coordination in all samples from group (ii) as well as traces of α-Fe_2O_3 in S1 may suggest that these archaeological artefacts originate from glass production furnaces. However, presence of α-Fe rules this conclusion out. Most probably the hematite which was revealed in S1 is a corrosion product of extra frame metallic iron which was also found in this sample.

The fact that we have found α-Fe in some of group (i) samples suggests that this glass-like material is not a slag from glass production either. Moreover, Fe^{3+} iron sites identified in the G1 – G3 samples do not represent tetrahedral coordination. We can speculate that in spite of their "glassy" look, group (i) samples do not originate from glass production and that they were used as additives for iron production.

4. CONCLUSIONS

^{57}Fe Mössbauer effect measurements performed upon two groups of archaeological artefacts provided information about the composition of these materials. Presence of metallic iron in two samples originally assumed to be of glass production waste means that this specification is most probably

doublets observed at room temperature has split into sextet at low temperature which might indicate that some of the doubles would represent small magnetically active particles in extra frame
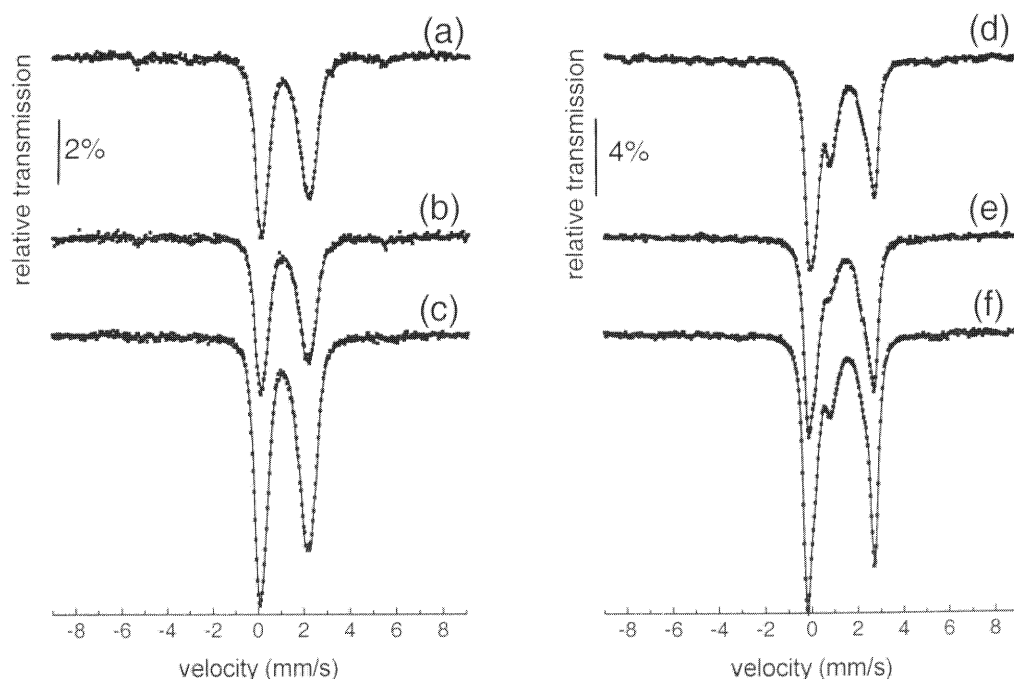

Fig. 4. ^{57}Fe Mössbauer spectra of G1 (a), G2 (b), G3 (c), S1 (d), S2 (e), and S3 (f) recorded at 77 K.

incorrect. It seems that the origin of these samples (group (i)) is the same as that of the group (ii). All

samples are probably iron slag or slag formers which were used for iron production.

Tab. 2. Parameters of Mössbauer spectra recorded at liquid nitrogen (77 K) temperature for G1-G3 and S1-S3 samples: IS – isomer shift, QS – quadrupole splitting, A_{rel} – relative area, and B – hyperfine field (for sextets only). Identification of spectral components is provided under "note" together with the corresponding coordination number.

sample's number	sample G				sample S			
	IS (mm/s)	*QS* (mm/s)	A_{rel} (%)	note	*IS* (mm/s)	*QS* (mm/s)	A_{rel} (%)	note
1	0.03	0.00	4	α-Fe ($B = 33.61$ T)	0.02	0.00	2	α-F ($B = 33.50$ T)
	-	-	-	-	0.28	-0.10	3	Fe_2O_3 ($B = 51.14$ T)
	1.04	1.88	24	Fe^{2+}, 6	1.23	2.92	23	Fe^{2+}, 4
	1.35	2.25	22	Fe^{2+}, 4	1.20	2.56	18	Fe^{2+}, 4
	1.06	2.32	30	Fe^{2+}, 4	1.12	2.04	19	Fe^{2+}, 4
	1.02	1.32	20	Fe^{3+}, 6	0.45	0.72	35	Fe^{3+}, 4
2	0.00	0.00	3	α-Fe ($B = 33.61$ T)	-	-	-	-
	1.03	1.92	26	Fe^{2+}, 6	1.28	2.92	37	Fe^{2+}, 4
	1.34	2.24	26	Fe^{2+}, 4	1.13	2.88	16	Fe^{2+}, 4
	1.05	2.36	23	Fe^{2+}, 4	1.18	2.16	24	Fe^{2+}, 4
	1.03	1.34	22	Fe^{3+}, 6	0.45	0.74	23	Fe^{3+}, 4
3	1.18	2.67	17	Fe^{2+}, 4	1.23	2.92	34	Fe^{2+}, 4
	1.14	2.25	26	Fe^{2+}, 4	1.24	2.38	28	Fe^{2+}, 4
	1.10	1.82	37	Fe^{3+}, 6	0.99	2.18	18	Fe^{2+}, 4
	1.03	1.32	20	Fe^{3+}, 6	0.51	0.56	20	Fe^{3+}, 4

REFERENCES

[1] Chropovský, B. 1974: Das frühmitelalterliche Nitrava. In: Vor- und Frühformen der europäischen Stadt im Mittelalter, vol. 2, Göttingen, 159-175.

[2] Staššíková-Štukovská D., Plško A.: K otázke interpretácie sklovitej hmoty z tzv. sklárskych pecí v Nitre, Archeologia technica 14 (2003) 27 - 34.

[3] Pribulová, A., Mihok, Ľ., Staššíková-Štukovská, D.: Železiarske trosky z nálezov pozostatkov pecí v Nitre na Leningradskej ulici, Archeologia technica 13 (2002) 18 - 22.

[4] Wagner F. E., Kyek A.: Mössbauer spectroscopy in archaeology, Hyperfine Interactions 154 (2004) 3 - 33.

[5] Balasubramaniama R., Ramesh Kumar A.V.: Characterization of Delhi iron pillar rust by X-ray difraction, Fourier transform infrared spectroscopy and Mössbauer spectroscopy, Corrosion Science 42 (2000) 2085-2101.

[6] Wagner F. E., Wagner U.: Mössbauer spectra of clays and ceramics, Hyperfine Interactions 154 (2004) 35 - 82.

[7] Lipka J., Rausz J., Gajdošová M., Fusek G., Sitek J., Hucl M.: Study of ancient pottery from Slovakia, Hyperfine Interactions 57 (1990) 2257-2260.

[8] Kučera J., Veselý V., Žák T.: Mössbauer Spectra Convolution Fit for Windows 98/2K, 1986-2004, ver. 4.161.

[9] Kukkadapu R.K., Hong Li, Smith G. L., Crum J. D., Keoung J. S. Poisl W. H., Weinberg M. C.: Mössbauer and optical spectroscopic study of temperature and redox effects on iron local environments in Fe-doped (0.5 mol% Fe_2O_3) $18Na_2O$-$72SiO_2$ glass, *J. Non-Cryst. Solids* **317** (2003) 301-318.