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Fe in P-doped basaltic melts: a Mössbauer spectroscopy study

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Abstract

The addition of P to a basalt causes a change in the environment of Fe. At low P contents iron is located in the glass structure and the Fe^{3+}/Fe^{2+} ratio is about 80/20. Further addition of P causes a collapse of the glass structure related to a phase separation that triggers the crystallization of a more reduced iron-containing phosphate phase with a crystalline structure similar to that of stanfieldite, and Mössbauer parameters similar to those of the alluaudite group, together with the formation of a Fe^{3+}-Fe^{2+} disordered phase. Their presence increases the viscosity of the melt.

Keywords: Fe environment; redox state; basaltic glass; structure; stanfieldite

1. Introduction

Sewage sludge (SS) is a high volume, potentially toxic waste. The European Union proposes its use in agriculture in substitution of fertilizers due to its high concentrations of phosphorus and nitrogen when sludge complies with regulations on heavy metal contents[1]. The two main alternatives are incineration and landfilling, which generate waste by-products, and space availability and cost issues respectively. Sewage sludge may be mixed with other toxic wastes such as waste mold sands to increase its silica contents and obtain a basalt-like composition to make a valorized product with potential applications in construction[2]. Like basalt, SS-like melts vitrify easily due to their low viscosity above the liquidus and bind the toxic metals[3,4]. Moreover, basic melts may host phosphorus up to the wt% range. However, high concentrations of phosphorus have strong effects on glass structure (polymerization, immiscibility, redox ratio, and macroscopic properties[5–7]).

P_2O_5 may alter the ratio of ferric to ferrous iron[8] Phosphorus has the highest reducing power of all major cations in a ferrobasalt bearing up to 9.45 wt% P_2O_5[6]. Variations in the ferric-ferrous ratio significantly change both density and viscosity of iron-bearing silicate melts. Iron is generally assumed to have a dual role in glasses according to its oxidation state. In silicate glasses, Fe^{3+} is in tetrahedral coordination, acting as a network former, whereas Fe^{2+} is generally in octahedral coordination and plays the role of a network modifier[5]. In phosphate glasses, it is commonly found in distorted octahedral sites regardless of the oxidation state[9].

The objective of this paper is to determine the effect of increasing phosphorus concentrations on the Fe environment and redox state of a series of P-doped basaltic glasses simulating environmentally-friendly glasses for the inertization of sewage sludge.

2. Materials and methods

The P-doped basaltic glasses have been prepared from 100 g mixtures of basalt from Sant Joan les Fonts (Catalonia) and up to 32% of reagent grade $NH_4H_2PO_4$ (ADHP, Reag-Ph.Eur, PA-ACS 131126.1211). The samples are named BXP, where X stands for P_2O_5 concentration in wt%. Each sample has been heated at 200 ºC during 2 h to decompose ADHP and then at 1450 ºC for 4h in SuperKanthal® furnaces, using Pt-Rh crucibles, and under air atmosphere. All the melts have been cast in a Cu plate except B32P, which has been quenched by immersing the bottom of the crucible in water due to its inability to flow.

The chemical composition of the basalt has been analyzed by X-Ray Fluorescence as lithium tetraborate pearls, using a sequential X-ray spectrophotometer Phillips PW2400. Powder X-Ray diffraction (XRD) patterns have been acquired in a Bragg-Brentano PANAnalytical X'Pert Diffractometer.

Room temperature Mössbauer spectra have been collected in transmission geometry over the velocity range ±4 mm/s using a constant acceleration spectrometer, with a 25 mCi source of ^{57}Co(Rh). Several sets of paramagnetic doublets have been fitted to the spectra, using a Voigt curve profile with a natural width (half with at half maximum of 0.24 mm/s) (NORMOS programs R.A. Brand, Laboratorium fur Angewandte Physik, Univ. Duisburg) to take into account the Gaussian distribution

of hyperfine parameters associated to the variability of sites due to cation substitution in crystalline

structures and in disordered and glass structures. The hyperfine parameters fitted for each doublet are

the isomer shift (IS), relative to α-Fe, the quadrupole splitting (QS) and the full width at half

maximum of the absorption lines (Γ). The Fe^{2+} and Fe^{3+} ratios with respect to total Fe, are based on

fitted peak areas.

3. Results and Discussion

The fitted Mössbauer spectra of the glasses are shown in Figure 1. The wide bands are

consistent with the amorphous nature of the samples. The estimated Mössbauer parameters IS, QS and

Γ are summarized in Table 1. The spectra corresponding to glasses B0-B4P show the overlapping of

two doublets corresponding to Fe^{3+} and Fe^{2+} in the glass structure. The doublet with IS values

between 1.04-1.05 mm/s and QS between 1.91-1.94 mm/s is assigned to Fe^{2+} in octahedral

coordination. Besides, the doublet with IS of 0.19 mm/s and QS between 1.25-1.27 mm/s is assigned

to Fe^{3+} in tetrahedral coordination. Iron is mainly present as Fe^{3+} and the total $Fe^{3+}/\Sigma Fe$ slightly

increases (from 74 to 80 %) with the addition of P. The hyperfine parameters correspond well to Fe in

a basaltic glass structure. Fe^{2+} in octahedral coordination is consistent with a network-modifying role.

Fe^{3+} in a tetrahedral environment may be replacing Si^{4+} as a network modifier.

Increasing the P content up to 8% (B8P), two broad doublets can be observed. The first, with

an IS of 0.40 mm/s and a QS of 0.72 mm/s is assigned to Fe^{3+} in octahedral coordination. The second,

with an IS of 0.85 mm/s and a QS of 2.0 mm/s corresponds to a site where both Fe^{3+} and Fe^{2+} are

present and consequently the hyperfine parameters show intermediate values corresponding to the

phenomenon known as valence exchange. Similar parameters are often seen in oxide disordered and

nano-sized structures. In the spectra corresponding to samples B16P and B32P, three doublets can be

clearly identified (Figure 1). The first has an IS of 0.7 mm/s and a QS of 1.2-1.3; the second has an IS

of 0.36-0-38 mm/s and a QS of 0.66-0-69 mm/s and the third has an IS of 1.08-1.12 mm/s and a QS of

2.40-2.48 mm/s. The last two correspond to Fe^{3+} and Fe^{2+} in octahedral coordination consistent with a

crystalline phosphate with Mössbauer parameters similar to those of the alluaudite group -

$NaCaFe^{2+}(Mn,Fe^{2+},Fe^{3+},Mg)_2(PO_4)_3$ [10]. In this case, the broadness of the peaks is due to Fe sharing its position with the other cations in the alluaudite structure. The first doublet showing intermediate $Fe^{3+}Fe^{2+}$ values correspond most probably to a disordered or nano-size oxide. The presence of a phase of this nature has been suggested in vitrified SS ash[4].

The formation of crystalline Ca-Mg-Fe anhydrous phosphates in B16P and B32P is consistent with the XRD spectra of the as-quenched glasses (Figure 2). Stanfieldite, $Ca_4(Mg,Fe,Mn)_5(PO_4)_6$ and Powder Diffraction File (PDF) 73-1182, is a phosphate found in stony-iron meteorites; unfortunately, there is no Mössbauer spectroscopy data in the literature. The composition of stanfieldite matches very well our basalts (~10% MgO, ~10% CaO and ~10% FeO). In addition, the broad reflection at 2Theta = 35.522° - the position of the 100% intensity peak of magnetite - consistent with a low crystallinity or nano-size phase.

The abrupt change on Fe environment – including the formation of the $Fe^{3+}Fe^{2+}$ nano-size oxide phase (Figure 3) – and the structural collapse at 8 wt% P_2O_5 (Figure 1) are correlated with the nucleation of a spinel-like oxide structure and the onset of a phase separation process in P-doped ferrosilicate systems[6,7]. Although this phase cannot be precisely identified by Mössbauer spectroscopy, it is consistent with the presence of a spinel-like oxide with mixed Fe^{2+}-Fe^{3+} sites – $(X,Fe^{2+})(Y,Fe^{3+})_2O_4$ with X=Mg,Mn and Y=Al⁻, such as magnetite-hercynite – $Fe^{2+}(Al,Fe^{3+})_2O_4$ – nanolites observed in iron aluminosilicate melts by Transmission Electron Microscopy[11]. Moreover, the addition of phosphorus to ferrobasalt is known to cause the formation of stable Fe^{3+}-PO_4^{3-} complexes in the melt that inhibit the crystallization of magnetite, probably by reducing the activity coefficient of Fe^{3+}[12]. Fe^{3+}-PO_4^{3-} complexing enhances the formation of the disordered spinel-like oxide and triggers the crystallization of the phosphate phase. If these complexes exist in the liquidus region, they may explain the increase of viscosity that prevented the casting of sample B32P, in good agreement with research on calcium aluminosilicate melts[8]. At low P contents, Fe^{3+}/Fe^{2+} increases due to phosphate complexing as the balance of network formers to network modifiers varies only slightly. At high P contents this balance is much in favor of the network formers, enhancing crystallization. The formation of crystalline phosphates also accounts for the increase of Fe^{2+}.

4. Conclusions

The addition of phosphorus to a basaltic melt causes the oxidation of the resulting glass as long as there is no significant increase of the concentration of network-forming cations ($Si^{4+}+Al^{3+}+P^{5+}$). Fe is located in the glass structure. Further addition of P triggers a structural collapse related to the unmixing of the melt into a silicate and a phosphate phases together with the formation of a $Fe^{3+}Fe^{2+}$-containing disordered/nano-sized oxide phase. An anhydrous phosphate mineral then crystallizes with a structure similar to that of stanfieldite and Mössbauer parameters similar to the alluaudite group, increasing the viscosity of the melt and preventing its casting. The Fe^{3+}/Fe_T ratio decreases due to Fe being mostly in the reduced form in minerals.

References

[1]   European Council, Directive 86/278/EEC of the European Council on the protection of the environment, and in particular of soil, when sewage sludge is used in agriculture, Off. J. Eur. Communities. L Ser. L 269 (1986) 1–13. doi:2004R0726 - v.7 of 05.06.2013.

[2]   M. Tarragó, H. Esteves, M. Garcia-Valles, S. Martínez, D.R. Neuville, Effect of Ca in P-doped basaltic glass-ceramics: Application to waste inertization, Mater. Lett. 220 (2018) 266–268. doi:10.1016/j.matlet.2018.03.020.

[3]   O.M. Hannant, S.D. Forder, P.A. Bingham, R.J. Hand, Structural studies of iron in vitrified toxic wastes, Hyperfine Interact. 192 (2009) 37–42. doi:10.1007/s10751-009-9944-5.

[4]   O.M. Hannant, P. a. Bingham, R.J. Hand, S. Forder, The structural properties of iron in vitrified toxic waste ashes, Glas. Technol. J. Glas. Sci. Technol. Part a. 49 (2008) 27–32. http://shura.shu.ac.uk/4976/.

[5]   B.O. Mysen, P. Richet, Silicate Melts: Properties and Structure, 1st ed., Elsevier B.V, 2005.

[6]   M.J. Toplis, D.B. Dingwell, G. Libourel, The effect of phosphorus on the iron redox ratio, viscosity, and density of an evolved ferro-basalt, Contrib. to Mineral. Petrol. 117 (1994) 293–304. doi:10.1007/BF00310870.

[7]   F.J. Ryerson, P.C. Hess, The role of P_2O_5 in silicate melts, Geochim. Cosmochim. Acta. 44 (1980) 611–624. doi:10.1016/0016-7037(80)90253-7.

[8]   B.O. Mysen, Iron and phosphorus in calcium silicate quenched melts, Chem. Geol. 98 (1992) 175–202. doi:10.1016/0009-2541(92)90184-7.

[9]   P.A. Bingham, R.J. Hand, O.M. Hannant, S.D. Forder, S.H. Kilcoyne, Effects of modifier additions on the thermal properties, chemical durability, oxidation state and structure of iron phosphate glasses, J. Non. Cryst. Solids. 355 (2009) 1526–1538. doi:10.1016/j.jnoncrysol.2009.03.008.

[10]   M.D. Dyar, E.R. Jawin, E. Breves, G. Marchand, M. Nelms, M.D. Lane, S.A. Mertzman, D.L. Bish, J.L. Bishop, Mössbauer parameters of iron in Phosphate minerals: Implications for interpretation of martian data, Am. Mineral. 99 (2014) 914–942. doi:10.2138/am.2014.4701.

[11]   D.R. Neuville, Y. Linard, P. Richet, Rheology of iron aluminosilicate melts, Eos (Washington. DC). 77 (1996) F798.

[12]   M.J. Toplis, G. Libourel, M.R. Carroll, The role of phosphorus in crystallisation processes of basalt: An experimental study, Geochim. Cosmochim. Acta. 58 (1994) 797–810. doi:10.1016/0016-7037(94)90506-1.

Figure and table captions

Figure 1. [57]Fe Mössbauer spectra of the glasses.

Figure 2. XRD spectra of the as-quenched glasses.

Figure 3. Isomer shift, quadrupole splitting and concentration of Fe species.

Table 1. a) Chemical composition of the basalt. b) Hyperfine parameters of the fitted spectra. The statistical error is given as the standard deviation in brackets.

Figure 1

Figure 2

Stf: stanfieldite

NOx: nano-oxide

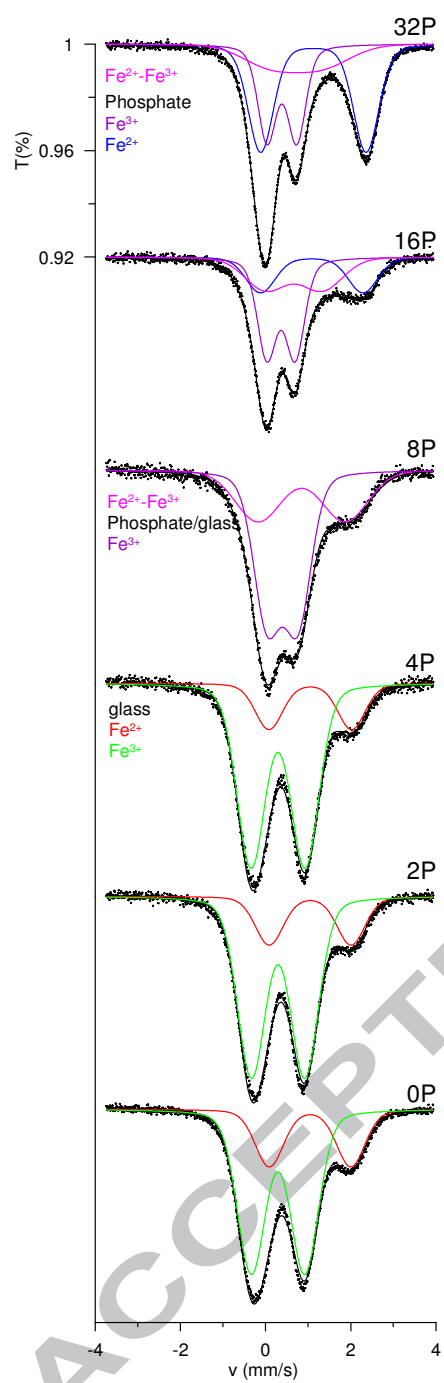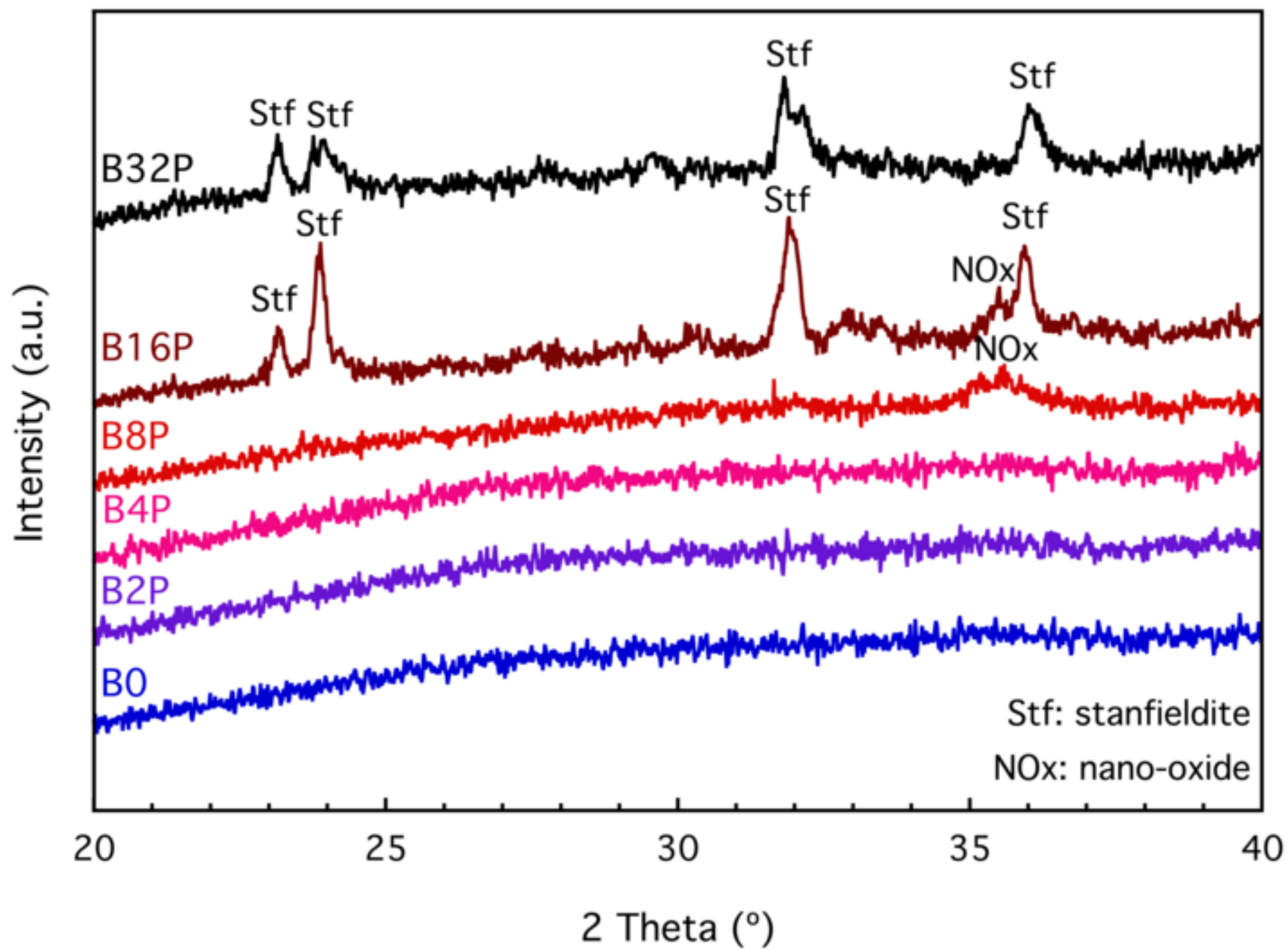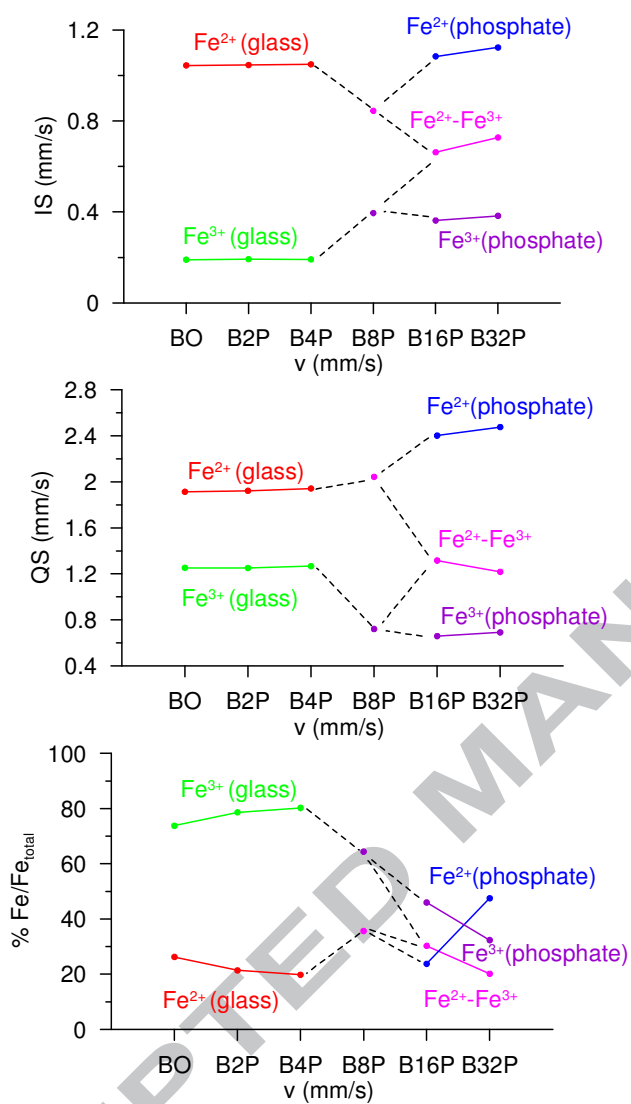**Figure 3**

Table 1. a) Chemical composition of the basalt. b) Hyperfine parameters of the fitted spectra. The statistical error is given as the standard deviation in brackets.

a) wt%	Al_2O_3	SiO_2	CaO	TiO_2	Na_2O	MgO	MnO	FeO	K_2O	P_2O_5
Basalt	14.37	44.63	10.26	2.55	3.36	10.20	0.17	11.88	2.01	0.56

b)			B0	B2P	B4P	B8P	B16P	B32P
glass	Fe^{2+}	Γ	0.68(0.04)	0.67(0.03)	0.65(0.07)			
		IS	1.01(0.02)	1.05(0.02)	1.05(0.03)			
	(o)	QS	1.91(0.03)	1.92(0.04)	1.94(0.05)			
		%	26(1)	21(1)	20(1)			
	Fe^{3+}	Γ	0.67(0.01)	0.67(0.02)	0.68(0.02)			
		IS	0.19(0.01)	0.19(0.01)	0.19(0.01)			
	(t)	QS	1.25(0.01)	1.25(0.01)	1.27(0.02)			
		%	74(1)	79(1)	80(1)			
	$Fe^{2+}Fe^{3+}$	Γ				1.2(0.2)	1.1(0.2)	1.5(0.2)
		IS				0.85(0.05)	0.7(0.1)	0.7(0.2)
		QS				2.0(0.2)	1.3(0.3)	1.2(0.6)
		%				36(5)	30(8)	20(5)
Phosphate	Fe^{3+}	Γ				0.64(0.04)	0.43(0.05)	0.40(0.04)
		IS				0.40(0.03)	0.36(0.04)	0.38(0.01)
	(o)	QS				0.72(0.03)	0.66(0.09)	0.69(0.03)
		%				64(4)	46(6)	32(4)
	Fe^{2+}	Γ					0.71(0.05)	0.60(0.04)
		IS					1.08(0.04)	1.12(0.01)
	(o)	QS					2.40(0.09)	2.48(0.03)
		%					24(6)	48(3)

Highlights

- The addition of P to a ferrobasalt causes a structural collapse.

- At low contents, P enters the glass structure as a network former.

- At high contents, P causes a structural collapse linked to a phase separation.

- A disordered nano-oxide and stanfieldite increase melt's viscosity.

- The Mössbauer parameters of stanfieldite are similar to those of the alluaudite group.