Antimicrobial Fe2O3-CuO-P2O5 glasses

MITCHELL, Alexandra L., LEE, Sung Hoon, MCENROE, David J., NULL, Eric L., STERNQUIST, Daniel A., HUFZIGER, Kathryn A., RICE, Brian J., SCRIMSHIRE, Alex, BINGHAM, Paul <http://orcid.org/0000-0001-6017-0798> and GROSS, Timothy M.

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Supplementary Information

Title: **Antimicrobial Fe_2O_3-CuO-P_2O_5 glasses**

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Supplementary Table 1. FeCuP glass compositions used for the AIMD simulations, taking oxidation state into account. The Fe content for glass #6 was lowered and P content raised compared to experimental values so that the composition could be distinguished from glass #5.

	1	2	3	4	4	5	6
# Atoms	**Not Simplified (No Fe)**	**Simplified (All Fe as FeO)**			**Not Simplified (FeO & Fe_2O_3)**	**Simplified (All Fe as FeO)**	
P	44	44	44	44	55	44	48
Fe	0	2	4	6	9	4	2
Cu	24	20	22	20	25	20	20
O	128	128	128	128	163	128	136
Sum	196	194	198	198	252	196	206
O/P Ratio	*2.91*	*2.91*	*2.91*	*2.91*	*2.96*	*2.91*	*2.83*

Supplementary Table 2. FeCuP glass compositions (Series A = Glasses #1-#4 and Series B = Glasses #4-#6)

Analyzed composition (mol%)	1	2	3	4	5	6
P_2O_5	46.4	46.1	45.3	44.7	47.5	49.4
Fe_2O_3	0.0	4.3	8.7	13.1	9.1	8.8
CuO	53.2	49.4	45.3	41.2	42.2	40.5
SiO_2	0.5	0.3	0.7	1.0	1.2	1.3

Supplementary Table 3. Analyzed atom ratios in bulk glasses and in the Day 5 solution showing that about half the expected P was released during leaching. Data in 3a is normalized to Cu (as the largest component of the leachate) and in 3b is normalized to P (as the glass former).

Table 3a

	Initial		*Day 5 Solution*	
Glass #	**Fe/Cu**	**P/Cu**	**Fe/Cu**	**P/Cu**
1	0.00	1.74	0.00	0.76
2	0.17	1.86	0.15	0.89
3	0.38	2.00	0.30	0.87
4	0.64	2.17	0.51	1.00
5	0.43	2.25	0.41	1.05
6	0.44	2.44	0.37	1.16

Table 3b

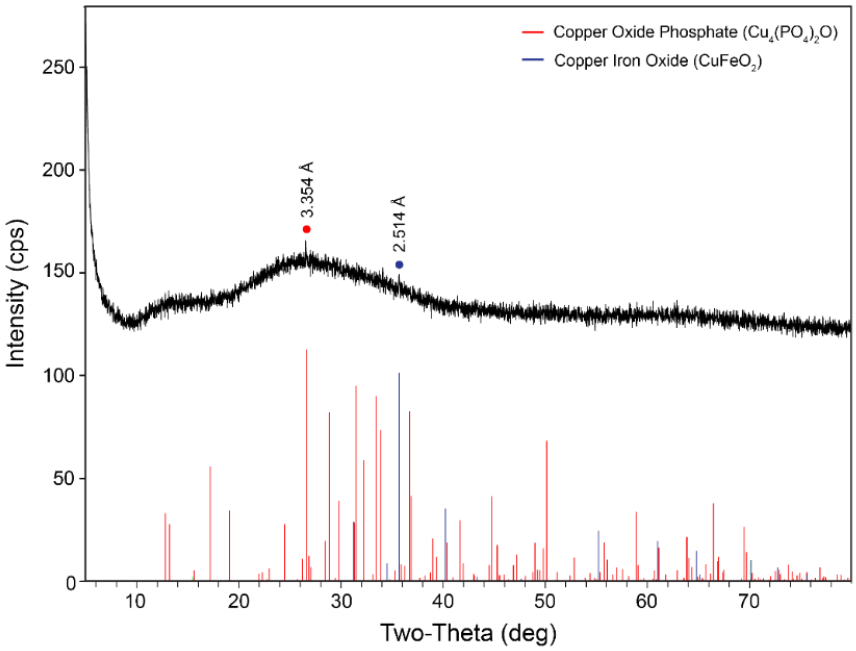
	Initial		*Day 5 Solution*	
Glass #	**Fe/P**	**Cu/P**	**Fe/P**	**Cu/P**
1	0.00	0.57	0.00	1.32
2	0.09	0.54	0.17	1.13
3	0.19	0.50	0.35	1.15
4	0.29	0.46	0.51	1.00
5	0.19	0.44	0.39	0.96
6	0.18	0.41	0.32	0.87

Supplementary Table 4. The center shifts (CS) and quadrupole splitting (QS) obtained from room temperature Mössbauer spectra for Fe^{2+} and Fe^{3+} ions. Redox ratios were calculated assuming the room temperature recoil-free fraction ratio $f(Fe^{3+}) / f(Fe^{2+}) = 1.3$.

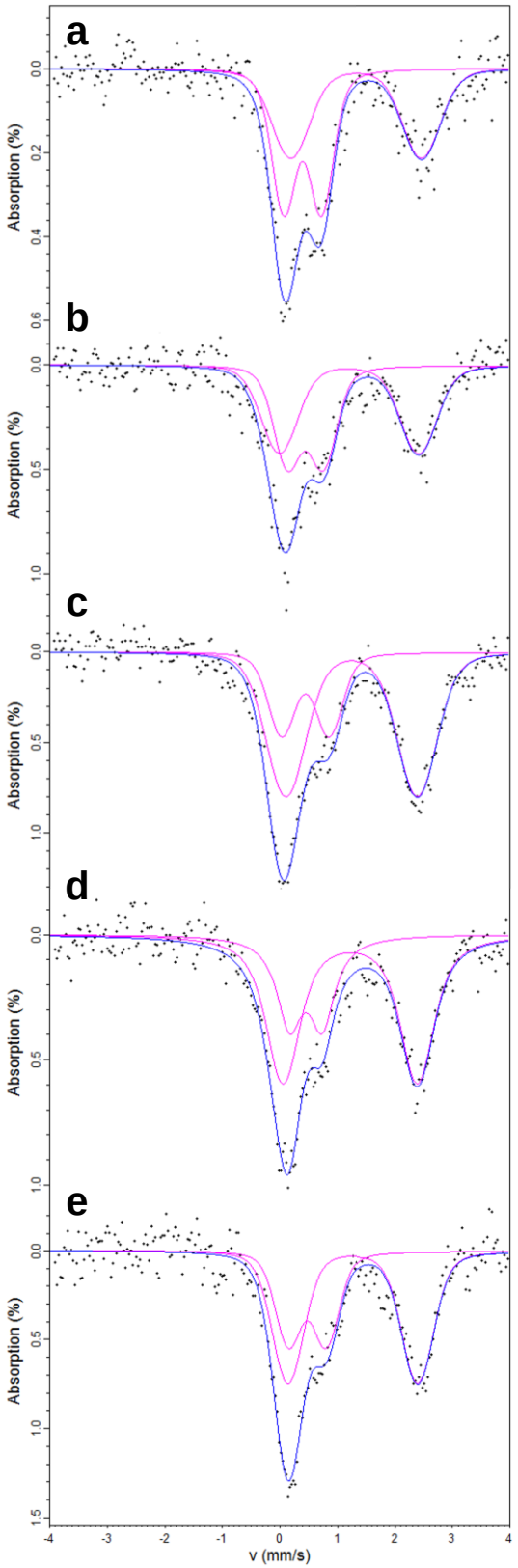
	Glass #2		Glass #3		Glass #4		Glass #5		Glass #6	
Center Shift (mm s^{-1})	0.40	1.33	0.44	1.20	0.44	1.25	0.45	1.22	0.48	1.27
Quadropole Splitting (mm s^{-1})	0.65	2.27	0.62	2.52	0.82	2.28	0.57	2.33	0.65	2.25
$Fe^{2+}/\Sigma Fe$ (%)	58	42	53	47	35	65	40	60	45	55
Assignment	(III)	(II)	(III)	(II)	(III)	(II)	(III)	(II)	(III)	(II)
Reduced X^2	0.621		0.698		0.783		0.595		0.594	

Supplementary Table 5. AIMD results corresponding to data shown in Figure 5.

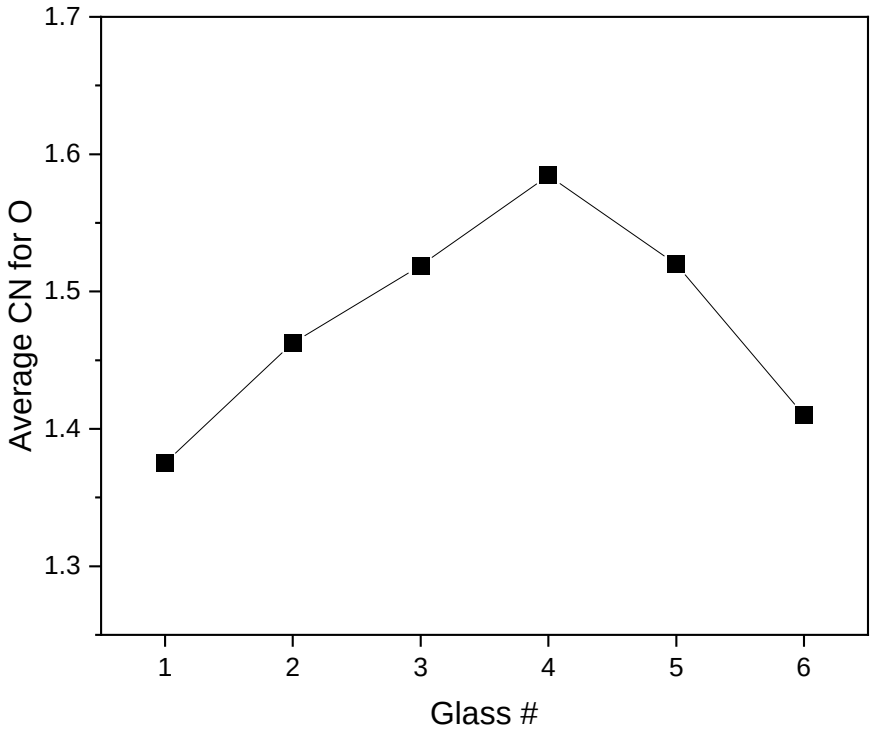
% Bond Type	1	2	3	4	4	5	6
	Not Simplified (No Fe)	Simplified (All Fe as FeO)			Not Simplified (FeO & Fe_2O_3)	Simplified (All Fe as FeO)	
P–O–P	37.5 ± 0.0	38.6 ± 1.2	36.9 ± 0.7	36.1 ± 0.7	35.4 ± 1.6	37.5 ± 0.8	37.2 ± 0.7
P–O–Fe, Fe		0.2 ± 0.3	0.2 ± 0.3	1.3 ± 0.8	1.6 ± 0.5	0.5 ± 0.4	0.2 ± 0.4
P–O–Fe		6.9 ± 2.8	13.6 ± 1.9	18.6 ± 1.9	18.8 ± 2.7	13.1 ± 2.5	6. 5± 1.4
Fe–O–Fe		0.5 ± 0.7	1.1 ± 0.4	1.3 ± 0.9	2.5 ± 0.0	0.6 ± 0.9	0.2 ± 0.4
Fe–O–x		0.8 ± 0.6	0.2 ± 0.3	0.2 ± 0.3	0.4 ± 0.5	0.9 ± 0.4	2.5 ± 0.4
P–O–x	62.5 ± 0.0	53.1 ± 0.6	48.1 ± 1.4	42.7 ± 0.9	41.3 ± 0.9	47.3 ± 1.4	53.5 ± 0.7
Sum	100	100	100	100	100	100	100



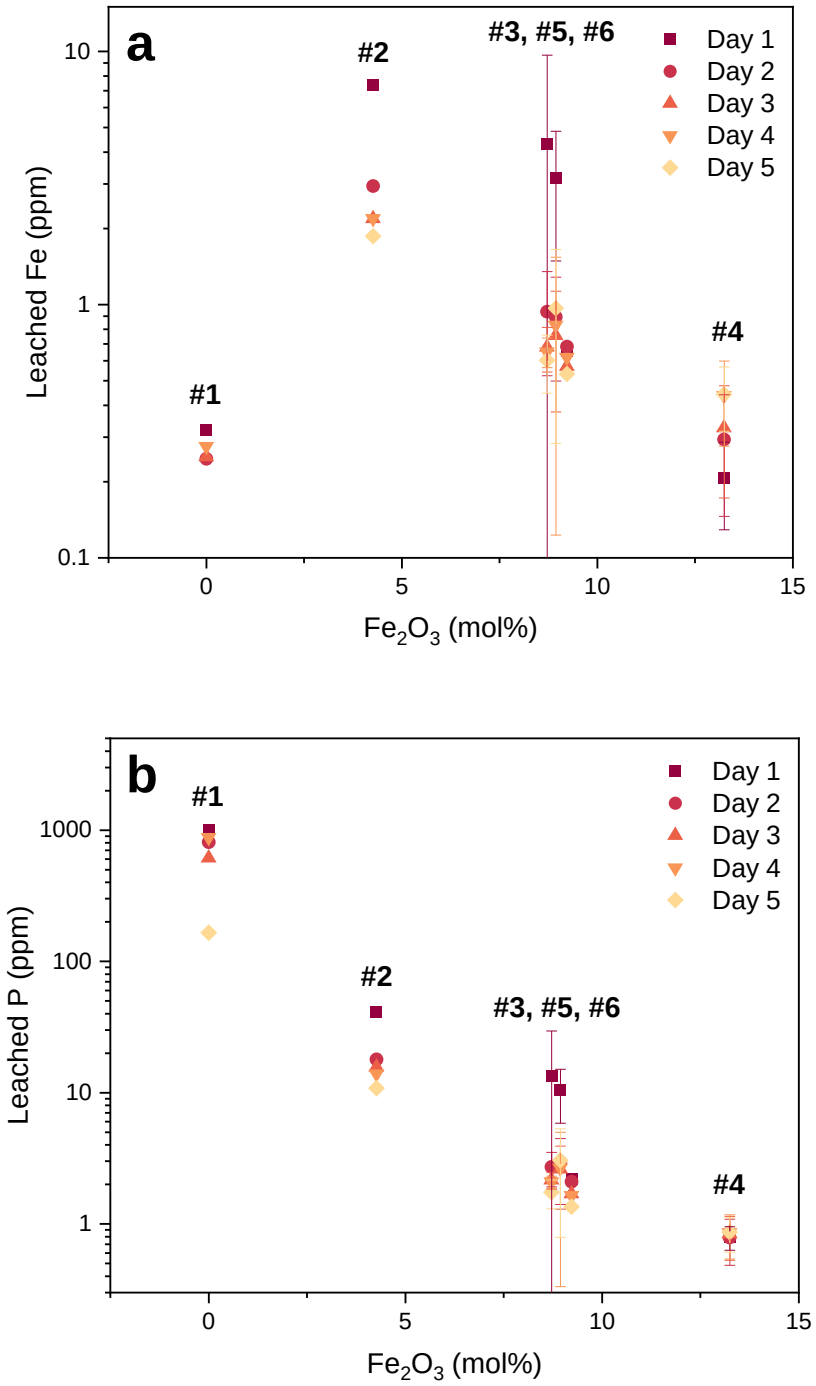
Supplementary Figure 1. XRD data for glass #4 showed low levels of crystallinity.



Supplementary Figure 2. Room temperature ^{57}Fe Mössbauer spectra and fits for glasses **a)** #2, **b)** #3, and **c)** #4 (top to bottom), with CS relative to α-Fe.



Supplementary Figure 3. Average coordination number for oxygen, which links neighboring P- and Fe-polyhedra as a function of glass #. Values were determined by *ab-initio* molecular dynamics simulations for the analyzed compositions.



Supplementary Figure 4. The amount of leached a) Fe and b) P as a function of Fe_2O_3 content (mol%).