SUPPLEMENTARY INFORMATION

Petrology of iron and copper slags from historical smelting activity in southern Tuscany

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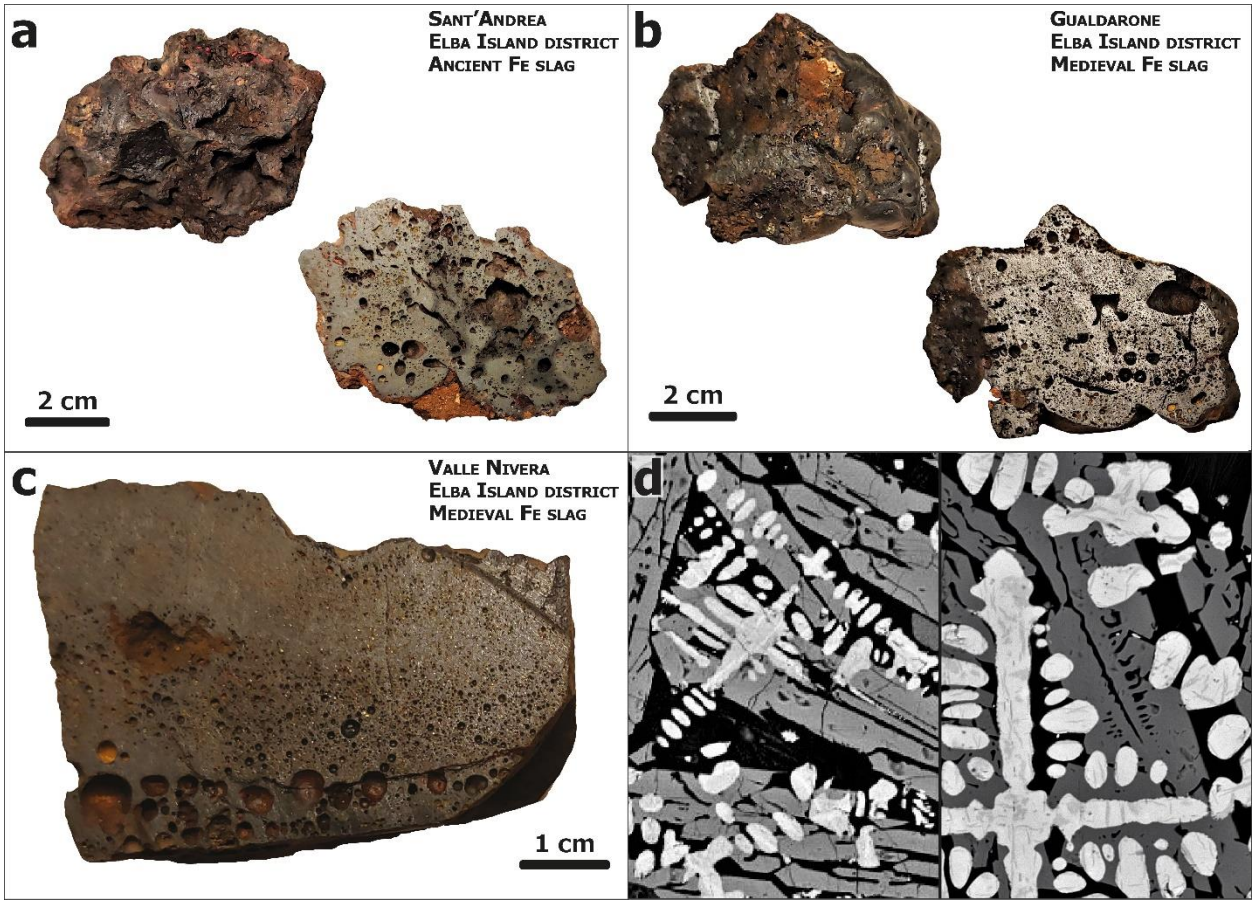

Fig. S1 – Macroscopic images of: (a) an ancient Fe slag from Sant'Andrea site showing a vesiculated texture; (b) a medieval Fe slag from Gualdarone site; (c) the spongy texture in a medieval Fe slag from Valle della Nivera site. (d) Backscattered electron images of Fe-oxides crystals in the Fe slags, composed of two different phases: ancient Fe slag from San Giovanni site (left), medieval Fe slag from Valle della Nivera site (right).

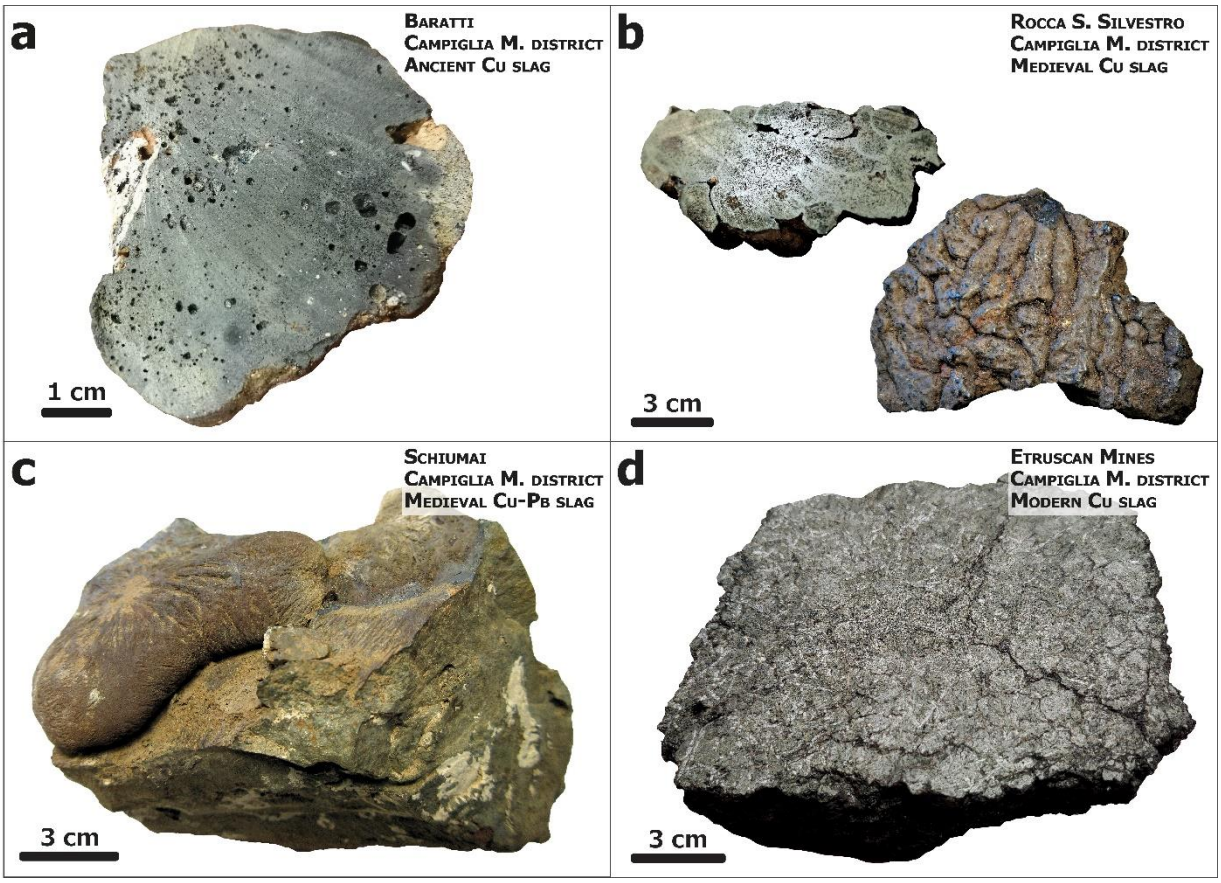

Fig. S2 – Macroscopic images of: (a) a Cu slag from Baratti site showing many vesicles and inclusions; (b) a medieval Cu slag from Rocca San Silvestro mining village showing flow textures both on the surface and on the cut portion of the sample; (c) medieval Cu slag from Schiumai site showing a flow of molten slag that rapidly cooled on an already solidified one; (d) a modern Cu slag from Etruscan Copper Mines site, showing large crystals of olivine and clinopyroxene.

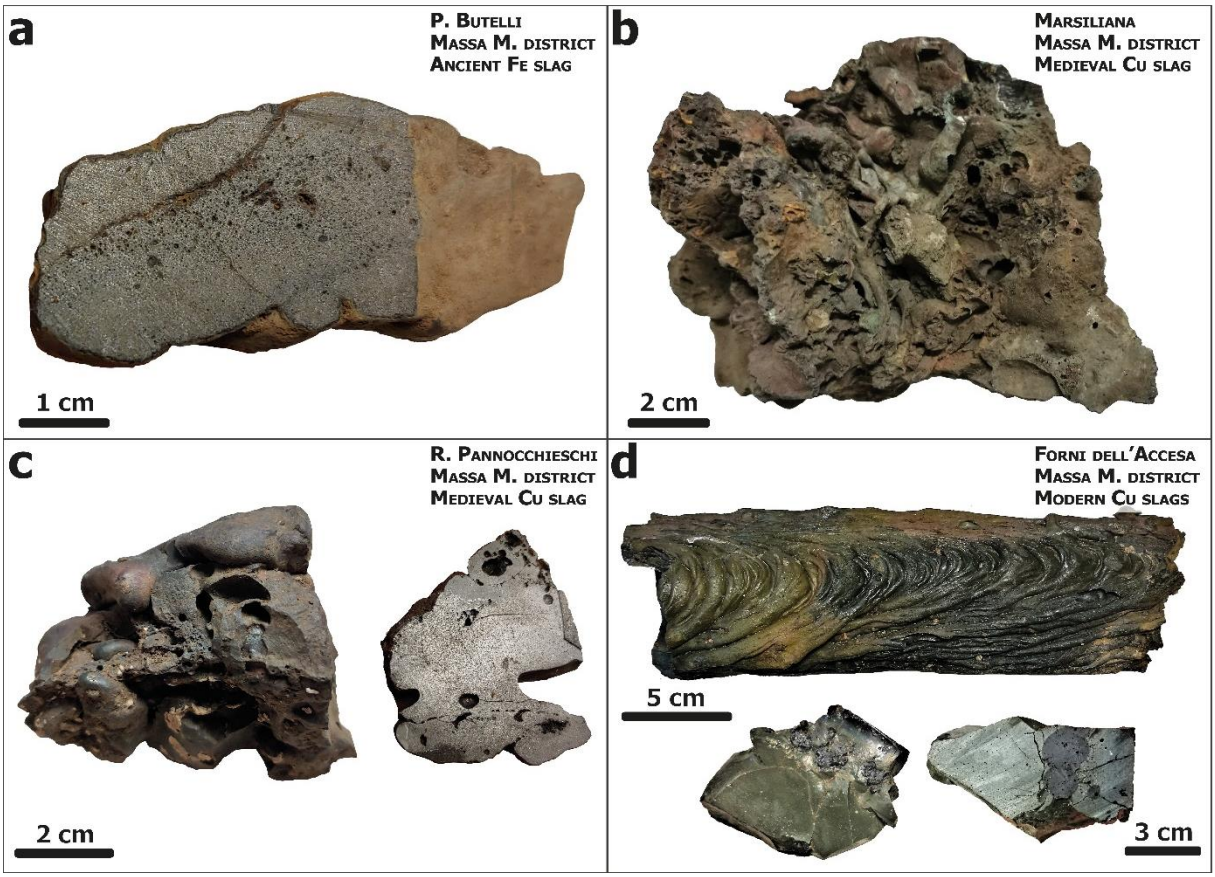

Fig. S3 – Macroscopic images of: (a) an ancient Fe slag from Poggetti Butelli site, owning a vesiculated texture and a weathered outer layer; (b) a medieval Cu slag from Marsiliana site showing an uneven and partially shattered surface; (c) a medieval Cu slag from Rocchette Pannnocchieschi site; (d) two examples of modern Cu slags from Forni dell'Accesa site, a large crystalline sample showing well defined flow textures and a smaller glassy sample strongly resembling a natural obsidian except for the greenish colour.

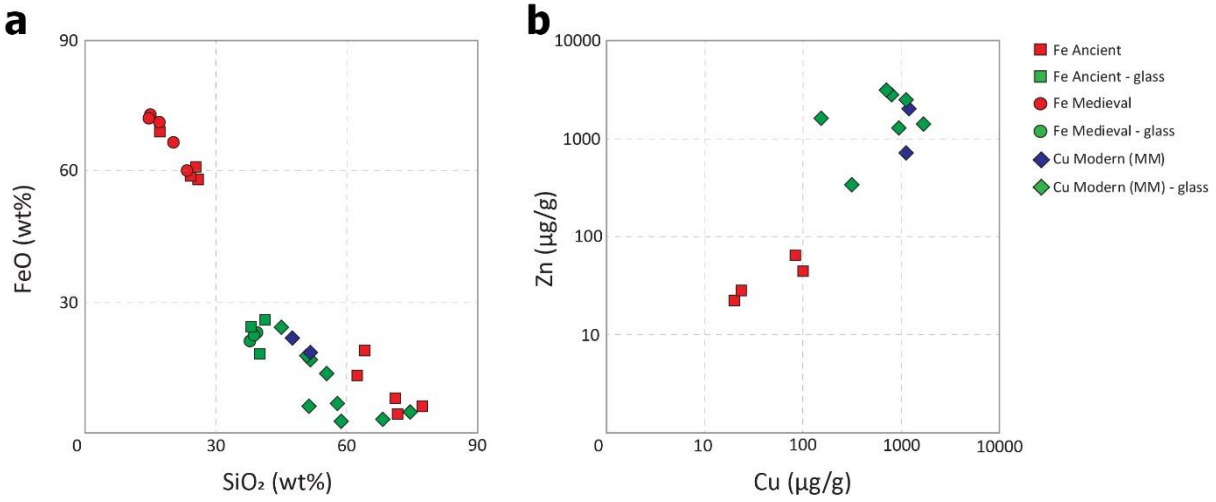

Fig. S4 –Electron microprobe analyses of elements concentration in glass compared to bulk chemistry composition of slag samples. Samples from Massa Marittima district are reported as "(MM)".

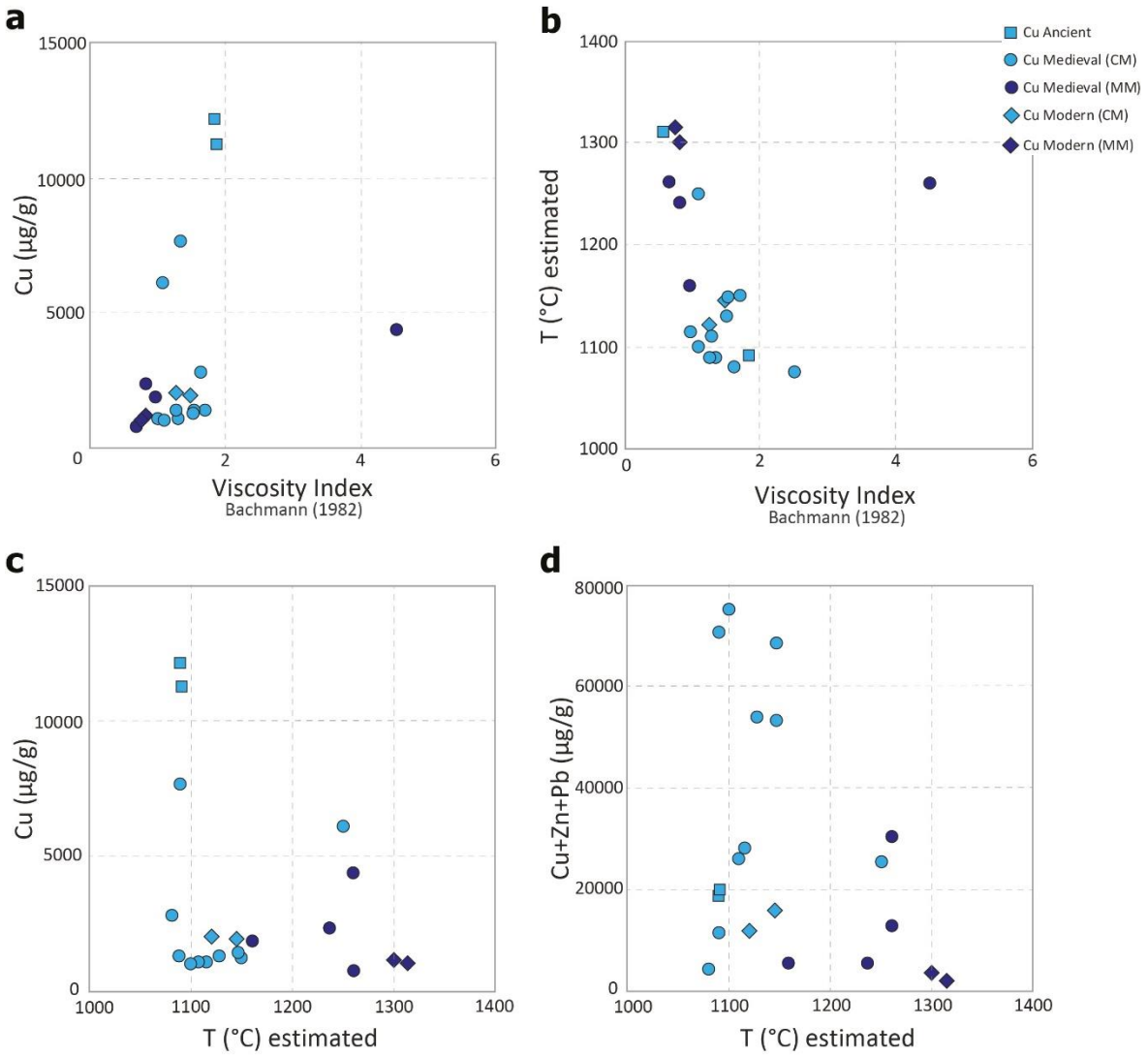

Fig. S5 – Viscosity index after Bachmann (1982) plotted versus copper concentration in the copper slag samples (a), and viscosity after Giordano et al. (2008) (b) calculated for temperature = 1100 °C. Estimated temperatures after Bachmann (1980) and Allibert et al. (1995) plotted versus copper concentration (c), and Cu+Zn+Pb concentration (d), in the copper slag samples. Legend: CM: Campiglia Marittima; MM: Massa Marittima.

Table S1 – Electron microprobe analyses of glasses from two modern copper slags from Forni dell'Accesa site (Massa Marittima), one ancient iron slag sample from San Giovani site (Elba Island) and one medieval iron slag sample from Valle della Nivera site (Elba Island).

	Copper slags												Iron slags					
	Massa Marittima												Elba Island					
site	Forni dell'Accesa				Forni dell'Accesa								San Giovanni			Valle della Nivera		
wt%	RA_02				RA_03								TS_SG1			M1B		
SiO_2	51.5	51.1	51.7	51.0	51.4	45.4	55.5	74.5	59.0	58.1	51.3	68.3	38.1	41.2	40.4	39.0	37.9	38.4
TiO_2	0.17	0.15	0.18	0.19	0.09	0.14	0.14	0.16	0.35	0.45	0.02	0.16	0.30	0.11	0.15	0.15	0.18	0.17
Al_2O_3	4.86	4.74	4.68	4.80	24.3	5.46	5.62	7.11	9.99	11.8	0.00	9.54	19.9	18.6	24.1	20.8	21.1	20.4
FeO	17.6	17.6	16.7	18.0	6.12	24.1	13.8	4.67	3.05	7.13	0.21	3.21	24.5	25.9	18.1	23.5	21.7	22.9
MnO	0.13	0.21	0.22	0.22	0.04	0.19	0.27	0.01	0.12	0.33	<dl	0.10	0.02	0.06	0.04	0.04	0.03	0.03
MgO	0.71	0.74	0.83	0.71	0.08	0.68	0.89	0.58	0.85	2.77	0.01	0.72	0.02	0.03	0.02	0.05	0.04	0.05
CaO	22.7	22.9	23.7	22.5	11.1	18.1	20.5	5.81	19.6	13.4	47.9	11.0	8.68	5.53	6.49	6.64	8.06	6.05
Na_2O	0.11	0.09	0.11	0.12	0.41	0.10	0.14	0.14	0.17	0.19	<dl	0.17	0.75	1.81	6.76	1.66	1.54	2.14
K_2O	1.20	1.15	1.18	1.26	5.48	2.70	2.99	4.70	5.88	4.82	0.08	6.94	4.50	8.06	3.59	7.68	7.55	7.78
P_2O_5	0.20	0.28	0.27	0.27	0.18	1.39	0.16	0.31	0.14	0.22	0.23	0.09	0.51	0.42	0.43	0.86	0.81	0.68
total	*99.1*	*99.0*	*99.6*	*99.1*	*99.2*	*98.2*	*100.0*	*97.9*	*99.1*	*99.3*	*99.8*	*100.3*	*97.3*	*101.8*	*100.0*	*100.4*	*99.0*	*98.7*
µg/g																		
S	2044	2374	2119	2627	164	3563	1395	970	1034	734	<dl	493	2544	2221	2268	2972	3491	3557
Cu	133	276	450	664	<dl	738	939	757	1153	1638	319	151	<dl	<dl	<dl	<dl	573	<dl
Zn	1228	2110	1915	962	1677	3111	1276	2877	2487	1436	345	1688	<dl	<dl	<dl	<dl	<dl	<dl
Sr	1498	1268	<dl	808	964	118	<dl	112	568	1629	109	<dl	<dl	489	<dl	244	<dl	<dl
Ag	<dl	13.0	65.2	<dl	150	<dl	789	<dl	<dl	273	<dl	<dl	93.1	159	590	173	<dl	<dl
Sn	<dl	47.3	<dl	<dl	<dl	<dl	<dl	195	<dl	<dl	<dl	<dl	<dl	138	28	382	<dl	516
Sb	<dl	51.2	<dl	294	1125	309	1767	473	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl
Ba	779	432	<dl	382	1693	<dl	662	179	173	<dl	61.8	<dl	737	669	116	398	1269	119
W	1294	<dl	<dl	970	1253	<dl	<dl	2005	<dl	<dl	95.2	<dl	3544	4086	3307	4697	6256	8980
Pb	386	162	<dl	448	<dl	200	<dl	<dl	<dl	<dl	615	<dl	<dl	161	87	<dl	<dl	<dl

Table S2 – Electron microprobe analyses of silicate phases (olivine and clinopyroxene). Results are reported in wt% and in a.p.f.u. calculated on the basis of 4 oxygens for the olivine and 6 oxygens for the pyroxene.

	Copper/lead slags																				Iron slags			
	Campiglia Marittima																Massa Marittima				Elba Island			
site	Baratti					Schiumai					Rocca San Silvestro				Etruscan Mines				Rocchette Pannocchieschi		Forni dell'Accesa		San Giovanni		Valle della Nivera	
	BB_03					RS_05					A2000				MR_234_03_B1				RPS		RA_03		TS_SG1		M1B	
	Kirschst.	Fayalite		Hedenbergite		Kirschsteinite	Fayalite		Hedenbergite		Fayalite		Hedenbergite		Fayalite		Hedenbergite		Kirschsteinite		Hedenbergite		Fayalite		Fayalite	
	$CaFeSiO_4$	Fe_2SiO_4		$CaFeSi_2O_6$		$CaFeSiO_4$	Fe_2SiO_4		$CaFeSi_2O_6$		Fe_2SiO_4		$CaFeSi_2O_6$		Fe_2SiO_4		$CaFeSi_2O_6$		$CaFeSiO_4$		$CaFeSi_2O_6$		Fe_2SiO_4		Fe_2SiO_4	
		(n=7)		(n=5)			(n=8)		(n=5)		(n=4)		(n=4)		(n=8)		(n=10)		(n= 7)		(n=10)		(n=7)		(n=4)	
wt%		average	st. dev.	average	st. dev.			average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.
SiO_2	32.1	30.7	0.23	45.1	0.26	34.3	31.4	31.0	0.38	41.3	*0.83*	28.0	6.18	48.6	0.51	30.7	0.28	46.2	2.07	32.2	2.08	47.9	1.05	30.8	0.71	30.3	0.22
TiO_2	0.02	0.02	0.01	0.08	0.04	0.05	0.08	0.05	0.03	0.28	*0.11*	0.02	0.03	0.02	0.02	0.03	0.02	0.07	0.03	0.11	0.11	0.15	0.10	0.06	0.02	0.04	0.03
Al_2O_3	0.01	0.02	0.01	3.04	0.19	1.75	0.11	0.37	0.61	10.0	*3.14*	0.22	0.34	0.52	0.69	0.10	0.26	3.10	2.20	3.73	3.93	4.58	4.75	0.28	0.10	0.37	0.07
FeO	43.6	60.0	2.34	29.0	0.44	38.1	40.9	53.6	8.01	22.5	*5.09*	63.3	2.30	29.0	1.40	59.4	3.24	26.5	1.77	33.9	5.84	22.3	3.20	66.3	2.61	67.2	0.43
MnO	1.92	3.29	0.34	0.97	0.11	0.77	0.80	1.21	0.31	0.30	*0.10*	1.81	0.91	1.47	0.37	3.57	0.64	1.24	0.22	0.29	0.12	0.26	0.11	0.20	0.03	0.12	0.02
MgO	0.07	1.14	0.73	0.19	0.05	0.11	0.26	0.88	1.00	0.12	*0.10*	0.58	0.44	0.30	0.25	0.33	0.31	1.18	1.44	1.35	0.52	0.98	0.52	1.87	0.53	2.34	0.42
CaO	20.98	4.69	2.22	21.2	0.08	21.2	23.0	8.89	7.40	19.1	*3.23*	2.41	0.84	20.0	2.07	5.37	2.20	21.3	0.35	24.4	2.71	20.7	5.62	0.62	0.21	0.63	0.05
Na_2O	0.21	0.11	0.05	0.16	0.04	0.53	0.23	0.30	0.12	0.61	*0.57*	0.06	0.03	0.03	0.06	0.13	0.05	0.13	0.10	0.30	0.19	0.07	0.07	0.02	0.02	0.03	0.03
K_2O	0.09	0.01	0.01	0.01	0.01	1.13	0.07	0.18	0.36	1.25	*1.65*	0.01	0.01	0.07	0.15	0.01	0.03	0.10	0.28	1.67	2.02	1.18	2.13	0.01	0.01	0.04	0.01
ZnO	2.60	1.69	0.58	1.17	0.34	0	3.84	2.83	2.55	1.78	*2.66*	0.28	0.11	0.11	0.06	1.79	0.43	0.68	0.26	0.13	0.14	0.28	0.11	0.02	0.03	0.01	0.02
total	*101.6*	*101.7*		*101.0*		*97.9*	*100.8*	*99.4*		*97.2*		*96.6*		*100.0*		*101.4*		*100.4*		*98.1*		*98.3*		*100.2*		*101.1*	
a.p.f.u.		average	st. dev.	average	st. dev.			average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.
Si	1.01	1.00	0.00	1.87	0.01	1.07	1.00	1.02	0.02	1.73	0.02	0.97	0.10	2.00	0.01	1.01	0.00	1.89	0.06	0.99	0.03	1.95	0.06	1.02	0.03	0.99	0.00
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	0.00	0.00	0.00	0.15	0.01	0.06	0.00	0.01	0.02	0.50	0.16	0.01	0.02	0.03	0.03	0.00	0.01	0.15	0.11	0.13	0.14	0.22	0.22	0.01	0.00	0.01	0.00
Fe^{2+}	1.15	1.64	0.06	1.00	0.02	0.99	1.08	1.47	0.24	0.79	0.17	1.87	0.22	1.00	0.05	1.63	0.10	0.91	0.07	0.88	0.17	0.76	0.11	1.83	0.06	1.85	0.02
Mn	0.05	0.09	0.01	0.03	0.00	0.02	0.02	0.03	0.01	0.01	0.00	0.05	0.02	0.05	0.01	0.10	0.02	0.04	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00
Mg	0.00	0.06	0.04	0.01	0.00	0.00	0.01	0.04	0.05	0.01	0.01	0.03	0.02	0.02	0.02	0.02	0.01	0.07	0.09	0.06	0.02	0.06	0.03	0.09	0.03	0.11	0.02
Ca	0.71	0.16	0.08	0.94	0.00	0.71	0.78	0.31	0.25	0.86	0.14	0.09	0.02	0.88	0.08	0.19	0.08	0.94	0.02	0.81	0.10	0.90	0.25	0.02	0.01	0.02	0.00
Na	0.01	0.01	0.00	0.01	0.00	0.03	0.01	0.02	0.01	0.05	0.05	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.01	0.01	0.07	0.09	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.06	0.08	0.06	0.11	0.00	0.00	0.00	0.00
Zn	0.06	0.04	0.01	0.04	0.01	0.00	0.09	0.07	0.06	0.05	0.08	0.01	0.00	0.00	0.00	0.04	0.01	0.02	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
total	*3.00*	*3.00*		*4.06*		*2.94*	*3.01*	*2.98*		*4.07*		*3.03*		*3.99*		*3.00*		*4.04*		*2.98*		*3.97*		*2.98*		*3.00*	

Table S3 – Electron microprobe analyses of sulfides. Only results for copper/lead slags are presented as no sulfides have been detected in the iron slags. Results are reported in wt% and in atomic percentages.

	Campiglia Marittima																Massa Marittima											
site	Baratti			Schiumai				Rocca San Silvestro			Etruscan Mines						Rocchette Pannocchieschi		Forni dell'Accesa						Forni dell'Accesa			
	BB_03			RS_05				A2000			MR_234_03_B1						RPS		RA_02						RA_03			
	Covellite		Chalcoc.	Galena		Pyrrhotite		Wurtzite	Covellite	Chalcop.	Bornite	Pyrrhotite		Bornite		Wurtzite	Pyrrhotite		Bornite		Chalcopyrite		Pyrrhotite		Bornite		Pyrrhotite	
	CuS		Cu_2S	PbS		$Fe_{1-x}S$		(Zn,Fe)S	CuS	$CuFeS_2$	Cu_5FeS_4	$Fe_{1-x}S$		Cu_5FeS_4		(Zn,Fe)S	$Fe_{1-x}S$		Cu_5FeS_4		$CuFeS_2$		$Fe_{1-x}S$		Cu_5FeS_4		$Fe_{1-x}S$	
				(n=5)								(n=6)		(n=3)			(n=4)		(n=4)				(n=3)		(n=3)		(n=3)	
wt%				average	st. dev.							average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.			average	st. dev.	average	st. dev.	average	st. dev.
S	29.1	28.3	21.1	13.2	1.42	34.7	34.5	32.2	25.9	29.5	28.9	34.4	0.26	25.0	0.56	32.4	0.10	32.8	2.96	24.8	1.23	32.7	27.9	34.1	0.40	24.0	0.82	34.4	0.24
Fe	1.07	0.35	0.40	4.96	4.99	62.0	63.3	30.6	4.73	21.4	14.4	64.1	0.33	12.5	2.19	38.3	0.76	64.7	0.76	15.4	2.21	42.6	21.0	63.9	0.44	15.1	2.83	63.9	0.86
Cu	68.0	69.7	78.7	0.38	0.25	2.06	0.73	0.001	68.0	48.1	55.2	0.61	0.29	62.0	3.60	0.80	0.43	0.65	0.21	59.3	3.64	23.8	51.5	1.14	0.76	58.2	3.66	0.66	0.26
Zn	0.04	0.13	0.11	0.34	0.47	<dl	<dl	36.2	<dl	0.01	0.07	0.11	0.18	0.05	0.09	28.3	0.54	<dl	<dl	0.07	0.07	0.23	0.14	0.03	0.04	0.04	0.06	<dl	<dl
Ag	0.10	0.05	0.03	<dl	<dl	<dl	<dl	<dl	0.14	0.07	0.16	0.01	0.01	0.08	0.06	0.01	0.02	0.02	0.02	0.05	0.04	0.06	0.03	0.02	0.02	0.05	0.07	0.01	0.01
Sn	<dl	0.01	0.03	0.06	0.04	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl	0.02	0.03	<dl	<dl	<dl	<dl	0.005	0.01	<dl	<dl	<dl	<dl	0.01	0.01	<dl	<dl
Ba	0.16	0.13	0.24	0.03	0.05	0.01	0.04	0.02	0.14	0.05	0.14	0.01	0.01	0.14	0.04	<dl	<dl	0.00	0.00	0.13	0.07	0.10	0.17	0.03	0.02	0.11	0.07	0.03	0.06
W	<dl	<dl	<dl	0.19	0.20	<dl	<dl	0.11	0.14	0.04	<dl	0.06	0.09	0.05	0.07	<dl	<dl	<dl	<dl	0.05	0.11	0.00	0.10	0.07	0.03	0.02	0.03	0.03	0.05
Pb	<dl	<dl	<dl	80.5	7.86	<dl	<dl	0.11	0.02	<dl	<dl	<dl	<dl	<dl	<dl	0.01	0.02	0.01	0.01	0.04	0.05	0.00	0.16	<dl	<dl	0.01	0.02	<dl	<dl
total	*98.5*		*100.6*	*99.6*		*98.8*	*98.6*	*99.3*	*99.1*	*99.2*	*98.9*	*99.3*		*99.9*		*99.8*		*98.1*		*99.8*		*99.5*	101.0	*99.3*		*97.5*		*99.0*	
atomic %				average	st. dev.							average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.			average	st. dev.	average	st. dev.	average	st. dev.
S	45.4	44.3	34.5	45.7	5.18	48.6	48.5	47.7	41.1	44.6	44.4	48.0	0.22	39.3	0.87	47.2	0.20	46.6	2.56	38.9	1.57	47.2	42.20	47.8	0.17	38.6	0.62	48.1	0.42
Fe	0.96	0.32	0.38	9.78	9.78	49.9	51.0	26.0	4.31	18.6	12.7	51.43	0.21	11.30	1.98	32.0	0.61	52.9	2.70	13.9	1.85	35.3	18.23	51.4	0.38	14.0	2.84	51.4	0.60
Cu	53.6	55.2	64.9	0.66	0.44	1.46	0.52	0.00	54.4	36.7	42.8	0.43	0.20	49.2	2.85	0.59	0.32	0.46	0.14	47.0	3.34	17.3	39.34	0.81	0.53	47.3	2.33	0.47	0.19
Zn	0.03	0.10	0.09	0.59	0.80			26.3		0.005	0.05	0.08	0.13	0.04	0.07	20.2	0.42			0.05	0.05	0.16	0.10	0.02	0.02	0.03	0.04		
Ag	0.05	0.02	0.01						0.07	0.03	0.07	0.01	0.01	0.04	0.03	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.03	0.03	0.00	0.00
Sn		0.00	0.01	0.06	0.04									0.01	0.01					0.002	0.004					0.003	0.003		
Ba	0.06	0.05	0.09	0.03	0.04	0.00	0.01	0.01	0.05	0.02	0.05	0.00	0.00	0.05	0.01			0.00	0.00	0.05	0.02	0.03	0.06	0.01	0.01	0.04	0.03	0.01	0.02
W				0.11	0.12			0.03	0.04	0.01		0.01	0.02	0.01	0.02					0.01	0.03	0.00	0.03	0.02	0.01	0.01	0.01	0.01	0.01
Pb				43.1	4.48			0.03	0.01							0.003	0.01	0.001	0.002	0.01	0.01	0.00	0.04			0.003	0.004		

Table S4 – Electron microprobe analyses of iron oxides. Magnetite and wüstite in the iron slags were finely intertwined, at a scale finer than the size of the analytical spot, with dominant magnetite composition in sample TS_SG1, while the opposite holds for sample M1B. Results are reported in wt% and in a.p.f.u. calculated on the basis of 4 oxygens for magnetite and 1 oxygen for wüstite. For magnetite, the FeO/Fe2O3 ratio was calculated following Droop (1987).

	Copper/lead slags													Iron slags			
	Campiglia Marittima									Massa Marittima				Elba Island			
site	Baratti		Schiumai		Rocca San Silvestro		Etruscan Mines			Rocchette Pannocchieschi				San Giovanni		Valle della Nivera	
	BB_03		RS_05		A2000		MR_234_03_B1			RPS				TS_SG1		M1B	
	Magnetite		Magnetite		Magnetite		Magnetite		Wüstite	Magnetite		Wüstite		Magnetite		Wüstite	
	$Fe^{2+}Fe^{3+}{}_2O_4$		$Fe^{2+}Fe^{3+}{}_2O_4$		$Fe^{2+}Fe^{3+}{}_2O_4$		$Fe^{2+}Fe^{3+}{}_2O_4$		FeO	$Fe^{2+}Fe^{3+}{}_2O_4$		FeO		$Fe^{2+}Fe^{3+}{}_2O_4$		FeO	
	(n=6)		(n=6)		(n=4)		(n=6)		(n=1)	(n= 5)		(n=6)		(n=6)		(n=6)	
wt%	average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.		average	st. dev.	average	st. dev.	average	st. dev.	average	st. dev.
SiO_2	0.69	0.09	1.44	0.64	1.26	0.66	0.69	0.53	0.21	0.44	0.34	0.18	0.01	0.79	0.57	0.22	0.04
TiO_2	0.34	0.04	1.47	0.79	0.09	0.09	0.50	0.51	0.03	0.51	0.22	0.17	0.07	0.36	0.07	0.25	0.04
Al_2O_3	1.58	0.14	5.63	2.25	0.43	0.25	1.52	1.31	<dl	4.39	3.10	0.52	0.18	0.52	0.18	0.58	0.08
Fe_2O_3	65.6	0.36	53.5	3.14	65.96	1.88	64.7	3.04		61.7	3.70			65.1	2.46		
FeO	31.0	0.59	31.7	2.06	32.08	0.61	31.1	0.86	97.3	31.8	0.82	96.2	0.49	31.9	0.38	98.2	2.10
MnO	0.56	0.10	0.25	0.10	0.31	0.07	0.50	0.17	2.30	0.15	0.04	0.16	0.04	0.05	0.05	0.05	0.05
MgO	0.12	0.08	0.18	0.15	0.09	0.05	0.03	0.03	0.05	0.26	0.20	0.60	0.26	0.05	0.03	0.21	0.05
CaO	0.05	0.04	0.18	0.14	0.34	0.23	0.12	0.13	0.01	0.35	0.38	0.15	0.10	0.06	0.02	0.02	0.02
ZnO	1.16	0.61	1.79	1.97	0.18	0.13	0.99	0.80	0.33	0.02	0.04	<dl	<dl	0.04	0.07	<dl	<dl
total	*101.0*		*96.1*		*100.7*		*100.1*		*100.3*	*99.6*		*98.0*		*98.9*		*99.5*	
a.p.f.u.																	
Si	0.03	0.00	0.06	0.02	0.05	0.02	0.03	0.02	0.00	0.02	0.01	0.00	0.00	0.03	0.02	0.00	0.00
Ti	0.01	0.00	0.04	0.02	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00
Al	0.07	0.01	0.25	0.10	0.02	0.01	0.07	0.06		0.19	0.14	0.01	0.00	0.02	0.01	0.01	0.00
Fe^{3+}	1.86	0.01	1.55	0.11	1.88	0.06	1.85	0.11		1.75	0.13			1.89	0.05		
Fe^{2+}	0.98	0.01	1.02	0.05	1.02	0.02	0.99	0.02	0.96	1.00	0.02	0.97	0.01	1.03	0.02	0.97	0.00
Mn	0.02	0.00	0.01	0.00	0.01	0.00	0.02	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00
Ca	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.03	0.02	0.05	0.05	0.00	0.00	0.03	0.02	0.00	0.00	0.00			0.00	0.00		
total	*3.0*		*3.0*		*3.0*		*3.0*		*1.0*	*3.0*		*1.0*		*3.0*		*1.0*	

Table S5 – Chemical analyses of iron slags. Major elements analyses by ICP-OES, trace elements by ICP-MS. LOI has been corrected inferring the total iron content as Fe2+.

iron slags														
	Ancient									**Medieval**				
site	**Baratti**	**Poggetti Butelli**			**San Giovanni**			**Sant'Andrea**	**Polverata**	**Valle della Nivera**	**Valle Literno (P)**	**Marmi**	**Valle Literno (M)**	**Gualdarone**
Sample	B1	TS_PB2	TS_PB3	TS_PB4	SG1	SG2	TS_SG1	R1B	R3E	M1B	M2B	M3E	M4C	M5A
major elements (wt%)														
SiO_2	70.9	77.1	25.3	64.3	71.6	62.3	24.3	17.2	26.1	16.7	20.3	15.3	23.5	15.3
TiO_2	0.46	0.43	0.22	0.46	0.32	0.49	0.18	0.13	0.24	0.18	0.13	0.15	0.18	0.16
Al_2O_3	11.4	9.39	5.36	9.40	13.5	14.8	5.11	4.41	6.83	4.36	4.10	3.36	4.54	4.44
$FeO_{(t)}$	8.04	6.27	61.0	19.2	4.38	13.5	59.4	69.1	58.1	71.3	66.7	72.5	60.3	73.0
MnO	0.13	0.08	0.12	0.14	0.03	0.10	0.13	0.07	0.08	0.08	0.13	0.07	0.38	0.16
MgO	1.52	0.72	0.68	0.84	0.65	0.83	0.85	0.50	0.66	0.82	0.77	0.59	0.75	0.68
CaO	1.54	0.52	2.68	1.46	0.74	0.84	2.36	1.45	1.61	1.21	1.32	0.92	1.16	1.95
Na_2O	1.94	1.44	0.45	1.16	1.45	0.67	0.49	0.29	0.50	0.32	0.30	0.29	0.24	0.42
K_2O	2.47	2.68	1.44	1.99	3.99	4.58	1.08	1.10	1.38	1.18	1.34	0.93	1.30	1.49
P_2O_5	0.12	0.06	0.13	0.11	0.05	0.16	0.13	0.14	0.15	0.20	0.24	0.18	0.24	0.23
LOI	1.26	1.00	0.67	1.05	1.40	1.65	0.64	0.58	0.83	0.64	0.65	0.52	0.69	0.67
Tot	*99.8*	*99.7*	*98.0*	*100.1*	*98.1*	*100.0*	*94.7*	*95.1*	*96.5*	*97.0*	*96.0*	*94.8*	*93.4*	*98.6*
trace elements (µg/g)														
V			42.0			53.0	35.0	21.0	35.0	38.0	27.0	33.0	29.0	
Cr			59.0			49.0	45.0	11.0	29.0	26.0	21.0	27.0	22.0	
Co			1.11			3.44	1.44	2.89	0.75	0.85	1.06	1.86	1.96	
Ni			1.78			13.10	2.30	2.50	2.00	0.87	1.14	1.81	2.36	
Cu			24.0			84.0	12.0	100.0	20.0	22.0	14.0	17.0	<8	
Zn			28.0			65.0	<18	45.0	22.0	<18	<18	<18	<18	
Rb			35.0			237	53.0	61.0	80.0	48.0	56.0	33.0	50.0	
Sr			77.0			76.0	94.0	78.0	88.0	53.0	66.0	44.0	77.0	
Zr			56.0			117	43.0	35.0	63.0	39.0	34.0	38.0	49.0	
Sn			120			30.0	48.0	41.0	87.0	88.0	57.0	95.0	42.0	
Sb			16.7			63.0	<1.5	2.60	2.64	<1.5	<1.5	1.95	<1.5	
Ba			120			423	100	89.0	147	81.0	108	81.0	145	
W			1030			628	1463	628	1426	1171	814	657	598	
Pb			78.0			282	14.0	11.0	19.0	6.00	5.00	10.0	5.00	
Bi			0.08			0.63	0.10	0.11	<0.03	0.13	0.08	0.08	0.28	

Table S6 – Chemical analyses of copper/lead slags. Major elements analyses by ICP-OES, trace elements by ICP-MS. (*) Data after Muti (2012), (**) analyses of samples of inferred charge used for the copper smelting furnaces. LOI has been corrected inferring the total iron content as Fe2+.
The low total for sample US2255 is plausibly related to the high amount of metals (not analysed by ICP-OES) in this type of material.

copper slags																												
	Ancient (Baratti)		**Medieval (Campiglia Marittima)**										**Medieval (Massa Marittima)**						**Modern (Campiglia Marittima)**									**Modern (Massa Marittima)**		
site	Baratti		Valle di Capattoli			Monte Coronato			Rocca San Silvestro				Marsiliana			Rocchette Pannocchieschi			Etruscan Mines									Forni dell'Accesa		
Sample	BB_01	BB_03	BVC_02	RVC_01	RVC_04	TS_MC3	RS_03	RS_05	US 2289	US 2291	US 2465	A 2000	US2255 (**)	FO	FO3	FOA-B	RPS	TS_RP2	TS_RP5	MR.234.03.A2 (*)	MR.234.03.B1	MR.235.03 (*)	MR.235.01 (*)	MR.235.02 (*)	MR.234.01	MR.234.02 (*)	MR.235.NE.02 (**)	MR.235.NE.03 (**)	RA_02	RA_03	RA_06
major elements (wt%)																														
SiO_2	31.2	31.7	42.6	35.7	36.6	31.1	27.6	30.9	37.7	44.9	38.6	35.2	15.2	45.4	46.4	45.9	13.1	18.7	14.1		43.8				36.8		17.17	17.59	51.5	47.4	75.9
TiO_2	0.05	0.05	0.04	0.17	0.22	0.20	0.19	0.17	0.06	0.08	0.06	0.03	0.00	0.16	0.39	0.16	0.26	0.30	0.25		0.04				0.03		0.03	0.02	0.17	0.21	0.50
Al_2O_3	1.43	1.37	1.62	4.10	5.16	4.25	4.20	3.75	1.63	2.24	1.62	0.96	0.19	4.51	10.6	4.61	3.70	5.45	4.01		1.74				1.30		0.43	0.42	4.83	6.42	14.5
$FeO_{(t)}$	50.0	49.4	39.0	42.0	42.1	41.2	43.8	42.4	38.8	28.6	30.0	47.6	7.69	32.3	20.5	31.0	65.0	54.3	64.0		39.4				38.4		45.3	39.0	18.4	22.3	3.85
MnO	1.75	2.00	2.10	1.09	0.85	0.88	0.70	0.87	1.97	4.08	2.95	1.47	1.35	0.37	1.00	0.28	0.17	0.23	0.14		2.17				2.31		0.21	0.16	0.21	0.27	0.03
MgO	0.64	0.63	0.42	0.71	0.81	0.88	0.90	0.78	0.57	0.98	0.62	0.39	0.06	1.08	3.02	0.87	0.71	1.09	0.85		0.95				0.77		0.12	0.15	0.72	0.78	0.41
CaO	8.77	8.88	5.88	5.74	9.12	10.3	7.68	8.30	11.0	12.5	10.6	9.52	0.24	12.3	12.4	7.76	9.05	12.1	10.9		14.8				15.2		6.23	9.08	22.7	20.0	1.24
Na_2O	0.12	0.14	0.07	0.25	0.39	0.19	0.24	0.20	0.08	0.16	0.09	0.03	0.01	0.31	0.25	0.23	0.16	0.27	0.19		0.14				0.08		0.05	0.08	0.12	0.11	0.18
K_2O	0.21	0.28	0.49	1.12	1.53	0.91	0.95	0.85	0.29	0.83	0.43	0.04	< 0.01	2.28	2.38	2.00	0.91	1.58	1.16		0.27				0.10		0.15	0.11	1.25	1.58	3.42
P_2O_5	0.09	0.11	0.09	0.32	0.33	0.31	0.27	0.28	0.17	0.22	0.18	0.06	0.09	0.29	0.24	0.21	0.22	0.26	0.28		0.06				0.03		0.03	0.03	0.13	0.16	0.06
S													13.6														8.29	7.57			
LOI	1.43	1.29	2.14	0.32	-1.47	0.96	-0.48	0.64	4.59	-0.45	0.25	4.12	11.4	0.00	-0.08	6.87	0.80	1.33	-0.60	0.00	0.45	0.00	0.00	0.00	0.71	0.00	25.14	23.74	-0.28	0.19	0.43
Tot	*95.6*	*95.8*	*94.4*	*91.4*	*95.6*	*91.1*	*86.1*	*89.1*	*96.9*	*94.2*	*85.4*	*99.4*	*49.8*	*99.1*	*97.1*	*99.8*	*94.0*	*95.7*	*95.4*		*103.8*				*95.7*		*103.2*	*98.0*	*99.7*	*99.4*	*101*
trace elements (µg/g)																														
V	10.6	8.53	7.92	39.8	43.0	38.5	30.0	29.1	10.8	12.9	8.32	5.08		23.7	74.1	26.1	48.0			26.0	13.0	16.0	10.0	12.0	9.00	9.00	5.00	9.00	37.1	43.2	34.7
Cr	38.3	25.5	25.8	65.2	80.6	56.2	46.3	45.6	34.3	47.9	<30	17.3		31.7	50.7	26.8	<40			40.0	19.0	20.0	12.0	12.0	15.0	18.0	8.00	31.0	30.5	41.1	24.2
Co	431	363	30.4	17.4	11.6	15.6	12.5	18.1	128.2	28.5	54.3	74.6		15.9	9.45	14.3	7.01			33.0	81.5	94.3	117	86.1	80.0	90.8	39.4	46.6	11.2	17.3	3.88
Ni	14.13	11.93	6.25	10.83	11.23	12.04	7.42	14.21	12.54	6.29	8.19	4.98		9.43	7.32	9.31	28.6			4.00	4.00	4.00	5.00	5.00	4.00	6.00	5.00	7.00	8.55	14.4	19.3
Cu	11288	12191	6132	1371	1105	1314	1390	1351	7678	1108	1034	2817		1879	796	2383	4381			1890	2030	3300	2460	2560	1960	2060	5340	5220	1085	1175	153
Zn	7011	7598	16998	18004	12501	31293	42483	24016	3215	22553	47322	1345		2769	9493	2341	7638			14003	9751	6300	9590	7523	13945	6860	1300	1380	698	2113	110
Rb	5.53	7.97	9.42	30.2	39.5	37.8	30.9	21.6	9.36	29.3	13.9	1.35		66.1	95.4	59.4	38.0			9.60	10.5	8.50	5.70	3.80	4.10	6.30	4.90	6.10	44.3	59.1	155
Sr	54.04	47.09	29.8	123	142	171	146	146	35.1	72.3	62.1	21.4		218	264	166	152			101	99.8	80.5	89.7	88.5	68.1	79.9	17.8	46.5	702	617	123
Zr	16.6	15.6	9.91	29.5	47.1	42.3	42.3	32.5	15.4	22.5	13.8	10.3		32.7	62.7	28.4	43.0			19.0	11.0	14.0	9.00	7.00	7.00	8.00	6.60	9.40	38.0	44.2	90.2
Sn	9.32	8.29	53.8	142	90.0	112	144	118	27.3	7.09	7.41	13.5		<1	1.00	<1	2.00			28.0	25.0	16.0	29.0	42.0	19.0	35.0	35.0	78.0	0.53	1.86	2.67
Sb	<8	<8	<8	15.7	36.1	206	515	59.3	<8	<8	161	<4		13.6	216	33.9	3835			3.20	6.60	4.50	6.10	6.10	6.60	8.00	6.70	12.6	5.15	13.9	30.5
Ba	<180	<180	<180	<900	199	187	<450	574	<180	<180	<450	<90		363	3519	333	4892			270	130	113	56.0	54.0	151	133	25.0	52.0	239	354	832
W	4.94	4.35	3.44	15.0	9.6	20.9	13.0	18.7	1.86	4.24	<4	1.76		30.6	46.8	28.4	<200			2.80	3.00	3.70	2.50	1.50	2.40	3.70	4.90	1.60	28.2	29.3	3.35
Pb	961	323	2289	51284	12583	20430	24562	28505	460	4566	26986	200		395	2714	478	18457			62.0	147	127	160	210	141	226	1710	1200	42.1	135	128
Bi	57.5	48.3	5.06	12.5	0.79	2.07	1.42	4.72	150	4.83	4.41	40.7		3.83	1.44	14.4	<0.2			8.80	21.8	20.2	41.6	44.2	21.0	54.0	1280	1560	3.75	9.86	0.88

Table S8 – Initial composition in oxides for the easyMelts software, calculated liquidus temperature and selected oxygen fugacity.

	Ancient (Baratti)		**Medieval (Campiglia Marittima)**						**Medieval (Massa Marittima)**		**Modern (Campiglia Marittima)**		**Modern (Massa Marittima)**	
			Valle di Capattoli		Schiumai		Rocca S. Silvestro		Marsiliana		Etruscan Copper Mines		Forni dell'Accesa	
Initial melt composition (wt%)	BB_01	BB_03	RVC_01	RVC_04	TS_MC3	RS_05	US 2289	A 2000	FO3	FOA-B	MR.234.03.B1	MR.234.01	RA_02	RA_03
SiO_2	33.4	33.5	39.1	37.6	34.4	34.9	40.8	36.8	47.6	49.2	42.3	38.6	51.5	47.6
TiO_2	0.05	0.05	0.19	0.23	0.22	0.19	0.07	0.03	0.40	0.17	0.04	0.03	0.18	0.22
Al_2O_3	1.49	1.45	4.49	5.31	4.70	4.23	1.77	1.01	11.05	4.95	1.68	1.37	4.95	6.58
Fe_2O_3	1.58	1.64	1.59	1.60	1.99	1.71	2.13	2.09	1.41	1.73	2.18	2.37	1.82	1.94
FeO	51.1	50.7	44.5	41.8	43.8	46.3	40.0	48.0	19.9	31.7	36.1	38.2	16.6	20.7
MnO	1.86	2.12	1.19	0.87	0.97	0.98	2.13	1.55	1.04	0.30	2.10	2.42	0.22	0.29
MgO	0.68	0.67	0.78	0.83	0.97	0.88	0.62	0.41	2.98	0.94	0.92	0.81	0.51	0.63
CaO	9.38	9.38	6.28	9.38	11.4	9.36	11.9	9.97	12.5	8.3	14.3	16.0	22.6	20.1
Na_2O	0.13	0.15	0.27	0.40	0.21	0.23	0.09	0.03	0.26	0.25	0.14	0.08	0.12	0.11
K_2O	0.22	0.30	1.23	1.57	1.01	0.96	0.31	0.04	2.48	2.15	0.26	0.11	1.30	1.64
P_2O_5	0.10	0.12	0.35	0.34	0.34	0.32	0.18	0.06	0.25	0.23	0.06	0.03	0.14	0.17
T (°C)	1397	1339	1198	1328	1146	1245	1092	1083	1133	1113	1114	1106	1128	1123
fO_2 buffer	COH	COH	COH	COH	COH	COH	COH	COH	COH	COH	COH	COH	COH	COH

Table S7 – Comparison between the temperatures (in °C) estimated from phase ternary diagrams An-SiO_2-FeO (Fig. 5a) and SiO_2-CaO-FeO (Fig. 5c), and the temperatures (in °C) obtained from the modelling using easyMelts software.

	Estimated temperatures		Modelled temperatures
	An-SiO_2-FeO	**SiO_2-CaO-FeO**	**easyMelts**
Baratti (BB_01)	1090	1145	1397
Baratti (BB_03)	1090	1145	1339
Capattoli Valley (RVC_01)	1090	1200	1198
Capattoli Valley (RVC_04)	1110	1150	1328
Schiumai (TS_MC3)	1150	1120	1146
Schiumai (RS_05)	1130	1130	1245
Rocca San Silvestro (US 2289)	1090	1145	1092
Rocca San Silvestro (A 2000)	1080	1125	1083
Etruscan Mines (MR.234.03.B1)	1120	1140	1114
Etruscan Mines (MR.234.01)	1145	1130	1106
Marsiliana (FO3)	1260	1400	1133
Marsiliana (FOA-B)	1240	1450	1113
Forni dell'Accesa (RA_02)	1315	1350	1128
Forni dell'Accesa (RA_03)	1300	1280	1123

References

Allibert, M., Gaye, H., Geiseler, J., Janke, D., Keene, B. J., Kirner, D., Kowalski, M., Lehmann, J., Mills, K. C., & Neuschütz, D., 1995. Slag Atlas 2nd edition. Verlag Stahleisen GmbH, Düsseldorf.

Bachmann, H. G., 1980. Early copper smelting techniques in Sinai and in the Negev as deduced from slag investigations. In P. T. Craddock (Ed.), Scientific studies in early mining and extractive metallurgy, vol. 20, 103–134. British Museum.

Bachmann, H. G., 1982. The identification of slags from archaeological sites. Occasional Publication (University of London, Institute of Archaeology), 6, 1–37.

Droop, G. T. R., 1987. A general equation for estimating Fe^{3+} concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria. Mineralogical Magazine, 51(361), pp. 431–435. https://10.1180/minmag.1987.051.361.10

Giordano, D., Russell, J. K., and Dingwell, D. B., 2008. Viscosity of magmatic liquids: A model. Earth and Planetary Science Letters, 271(1–4), pp. 123–134. https://doi.org/10.1016/j.epsl.2008.03.038

Muti, G., 2012. Studio geochimico di suoli, sedimenti e scorie metallurgiche nell'area della ex discarica Ginepraie, San Vincenzo, Livorno. Master's thesis, University of Pisa.