A PRELIMINARY PETROGRAPHIC AND LA-ICP-MS TRACE ELEMENTS STUDY OF THE IRON SULFIDE-RICH DEPOSITS OF LOMBARD SOUTHERN ALPS: EVIDENCES OF A HYDROTHERMAL ORIGIN?

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ESM 1 - A SHORT HISTORY OF LIMONITE IRON MINING IN THE LOMBARD ALPS

The iron sulphide-rich ore bodies were exploited in the past for limonite, in fact these deposits are characterized by the presence of extensive gossans. In general, the Lombard southern Alps are rich in iron ore deposits exploited since antiquity, mainly siderite-hematite hydrothermal veins/stratabound bodies. According to the archaeological evidence it seems that at first the early iron metallurgists were attracted more by the limonite ores of the presently studied deposits (linked to sulfide weathering) than by the far richer hematite and siderite veins. While the former ores are in soft calcareous rocks and the nature itself of the ore makes its digging easier, the latter are often hosted by hard rocks with barite and massive quartz veins.

The earliest limonite iron mining area in Lombardy so far discovered is in the outskirts of the main Lombard Iron Basin: the site of Piani d'Erna near Lecco a complex of mining and smelting activities was archaeologically investigated (Tizzoni et al., 2006). Similar yet undated and unpublished groups of mines were recently discovered in the Mt. Bronzone area near Iseo Lake and at Sasso Rancio on the shore of Como Lake (Gaeta mine). These soft limonite deposits were dug with simple picks and the miners followed the ore vein avoiding digging the sterile rock. Because of this the mine's shape mirrors the ore deposit. Moreover, some of these limonite deposits are in far more reachable places and closer to the sites in the plain where iron was forged and traded. According to 19th century metallurgists this limonitic ore was reduced with far greater ease than the manganiferous siderite/hematite ores (Curioni, 1877).

At Piani d'Erna (Lecco) the metallurgical activities had begun in the 2nd century B. C. during the La Téne period and lasted for about three centuries (Tizzoni et al., 2006). We do not know if the people here were Celts, or local Celticized groups as suggested by the burials found in nearby Valsassina.

The earliest iron reduction technology used at this site points to a Celtic tradition, but it was soon abandoned in favour of a more proficient smelting technique of Roman tradition by the end of the 1st century B. C., possibly when this site was taken over by a Latin or by a Romanized Celtic entrepreneur (Tizzoni et al., 2006). The iron made from this ore was an excellent ferrite with very little amounts of sulfides (Fluzin, 2006) thanks to its roasting and, as we know from historical documents, to its "seasoning" (after roasting the ore was left in the open for a long time in order to be "purified" by rain and snow).

Successively these limonite deposits were exploited probably during the Middle Ages and some mines that were even opened in more recent times. The Gaeta deposit, the largest limonite-rich ore body of the Lombard Alps, was extensively exploited for iron production until the end of 19th century and again for pyrite and galena (Pb and Ag) mining in the early 20th century.

ESM 2 - FIELD OBSERVATIONS

A detailed description of the various studied ore bodies is reported.

Como Lake - Valsassina area, Gaeta mine

Gaeta mine exploited the largest limonite-rich deposit of Lombardy. This mine is formed by over 2 km of galleries on six levels with stopes up to 80x30x25 m (the so called Pini room). Its ore forms mainly stockwork veinlets in the heavy fractured host rock, where pyrite is common. It may form also lenticular bodies and fault-hosted vertical veins. In the mine's upper part there are sulfide-rich bodies, with pyrite and Pb-Zn sulfides, along the contact within Esino and Bellano Fms. There are sulfides sporadic disseminations also in an arenaceous matrix of Bellano Fm. Galena being the main ore in these mineralized bodies. Pb-Zn non-sulfides (characterized by EDS analyses) as cerussite, anglesite, wulfenite, hemimorphite and smithsonite are common in the weathered areas. Sulfates casts are common in this mine, suggesting the presence of weathering pyrite within the limonite-rich masses and sulfur-rich waters percolating.

Como Lake-Valsassina area, Valsassina mines

Pasturo mine exploited various limonite-pyrite fault-hosted vertical veins; stockwork pyrite-quartz veinlets are also present. Sulfate casts are common as pyrite weathered relicts within the limonite too. In the deeper zone of the ore bodies there are massive fine-grained marcasite and pyrite masses over 1 m thick, with sporadic Pb-Zn sulfides. Disseminations of small (0.5-1 mm) pyrite cubic crystals can be found within the dolomitized host rocks. In the Balisio area weathered pyrite stockwork veinlets are hosted by a fault zone with iron sulfides as cement of a fault breccia. In the Barzio area similar deposits characterize high Val Ferrera, Campo del Ferro and Prato dell'Orso mines. In Val Ferrera the pyrite-limonite deposits are very similar to those of the Balisio area, moreover on Mount Ferrera various massive barite veins with coarse-grained galena and pyrite can be found. At Campo del Ferro and Prato dell'Orso there are various vertical fault-hosted limonite veins. They are characterized by hemimorphite, smithsonite and minor cerussite. At the Piani d'Erna mines, exploited for limonite mainly in antiquity and for barite in recent times, the iron gossan forms irregular masses and veinlets. Often pyrite relicts and coarse-grained lamellar barite are common. To the North of the main mining area of this site the mineralized body becomes progressively pyrite-poor. Massive white barite and sporadic coarse-grained galena with minor pyrite and sphalerite are its main ores.

Val Seriana-West Iseo Lake area, Büs del Fer mine

Büs del Fer (Albino) deposit is hosted by the Albenza Fm. Various limonite lenses and veinlets both concordant and discordant form its ore body. Sulfides or other minerals are not visible within the ore deposit or in the host rocks. Limonite forms compact masses and stockwork veinlets set along limestone fractures and banded concordant tabular bodies. Various vertical karst cavities crosscut the mining works.

Val Seriana-West Iseo Lake area, Mt.Bronzone mines

Mt. Bronzone mines exploited various limonite ore bodies hosted by the Albenza Fm. and Sedrina Limestone Fm. As reported for Büs del Fer deposit sulfides and other minerals are not observable within the deposits. Pyrite is present sporadically as weathered relicts only at Ducone mine. There are calcite veinlets, massive lenses and geodes within the limonite masses. Weathered siderite is visible locally. Limonite forms compact stockwork veinlets along limestone fractures and banded concordant tabular bodies, in the latter iron-bearing calcite is common. Pyrite weathered crystals, from 1 to 15 mm are common within the limonite. In some areas limonite pseudomorph after pyrite can be so common, widespread and concentrated to suggest an origin of the limonitic masses from massive pyrite weathering. Discordant stockwork veinlets of weathered pyrite crystals substituted by iron hydroxides are hosted within fractures of the host rocks.

ESM 3 - FURTHER CONSIDERATIONS ABOUT THE GOSSAN ORES

In the Valseriana-Mt. Bronzone area karst cavities are common in the mining areas, crosscutting the limonite-rich beds. Moreover, in the karst areas there are conglomerate bodies from lenticular to irregular in shape. These rocks include angular to rounded host rock, speleothems calcite/aragonite and limonite clasts within a micritic carbonate matrix. These conglomerates derive probably from the lithification of material sedimented within the karst cavities. Moreover, there can be limonite as a filler of pre-existing karst cavities, usually it is earthy and has banded textures.

As previously reported, two different limonite types were selected for LA-ICP-MS analyses from Mt. Bronzone mines: black limonite pseudomorph on pyrite coarse-grained crystals and ochraceous laminated limonite. The two different Mt. Bronzone limonitic ores (massive and banded) have slightly different REE enrichment patterns. Mt. Bronzone limonite has a LREE fraction ($(La/Sm)_N = 3.25$) for limonite after pyrite, $(La/Sm)_N = 2.09$ for earthy laminated limonite and total REE fraction ($(La/Yb)_N = 10.50$) for limonite after pyrite and ($(La/Yb)_N = 3.26$ for earthy laminated limonite) higher than HREE fraction ($(Gd/Yb)_N = 2.78$ and $(Gd/Yb)_N = 1.65$ for limonite after pyrite and for earthy laminated limonite). Mt. Bronzone limonite has negative Eu and Ce anomalies for both the limonite-type, with a very enhanced Ce negative anomaly ($\log (Ce/Ce^*) = -6.88$) for earthy banded limonite. In general, they have a Ce and Eu negative and a Y positive anomaly, with REE patterns typical of marine oxidizing waters and river-phreatic waters in carbonate basins (Möller et al., 2021). Mt. Bronzone limonite-rich ore from the paleo-karstic cavities (ochraceous laminated limonite) has a stronger Ce negative anomaly if compared to that of pseudomorphs on pyrite coarse-grained crystals. Moreover, it is generally more REE enriched (24-150 ppm against 10-36 ppm ∑REE). The formation of both ores is probably linked to the interaction of the original pyrite with strongly oxidizing waters. The ore-filled paleo-karstic cavities within Albenza and Sedrina Fm. are not related to a subaerial exposure event linked to a sea level fall. Because of this, the paleo-karstic cavities hosting limonite bodies (ochraceous laminated limonite) may be related to a supergene iron-oxides reprecipitation from underground waters.

In the deposits of the Como Lake-Valsassina area, there are indeterminate manganese oxides/hydroxides as micro-aggregates of lamellar and acicular crystals inside the iron rich ore. The presence of these manganese minerals may not be linked directly to the secondary assemblage of this deposit, but to subsequent water percolation. Dendrites of Mn are quite common in the host rock, even in areas far from the mineralized bodies.

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	Zn	Fe	S	Mn	Co	Ni	Cu	Ga	Ge	As	Mo	Cd	In	Sn	Sb	Bi
GAE - ls - 1	60,86	1,23	32,76	1,179	3,632	0,108	93,831	346,474	2,718	0,811	0,018	35185,291	0,981	3,238	0,917	0,004
GAE - ls - 2	61,67	1,26	32,73	4,512	2,503	0,085	266,459	353,558	12,196	2,623	0,030	26763,640	0,196	3,449	26,759	0,005
GAE - ls - 3	62,87	1,22	32,77	0,988	3,595	0,044	1797,797	1926,177	435,456	51,769	0,099	13177,892	0,322	5,465	87,010	0,031
GAE - ls - 4	61,09	1,24	33,24	1,509	3,249	0,055	292,819	560,912	7,182	2,026	0,151	32459,711	3,792	9,102	8,287	0,004
GAE - ls - 5	61,44	1,22	32,77	0,642	3,876	0,082	1118,738	753,685	259,287	34,899	0,137	28749,715	3,052	13,314	64,856	0,021
GAE - ls - 6	60,54	1,24	32,75	1,094	3,340	0,085	99,655	595,800	3,800	0,647	0,011	37956,431	1,635	7,072	1,873	0,005
GAE - ls - 7	61,10	1,26	32,73	2,587	2,136	0,078	259,445	742,416	2,575	0,762	0,021	32003,062	1,751	4,693	16,477	0,006
GAE - ls - 8	61,46	2,56	31,43	1,491	6,493	0,186	2624,319	4124,918	631,923	141,590	2,140	11351,428	< d.l.	31,223	200,252	0,112
GAE - ls - 9	62,76	1,31	32,68	0,563	2,918	0,026	1010,228	217,148	229,587	27,018	0,191	15239,826	0,442	4,216	74,075	0,026
GAE - ls - 10	63,42	1,40	32,59	1,735	3,202	0,080	582,745	1319,500	84,189	30,458	0,099	6722,691	0,080	1,123	149,315	0,012
GAE - ls - 11	62,72	1,32	32,67	0,606	2,796	< d.l.	1139,415	360,434	233,508	22,256	0,320	15446,746	0,986	8,859	53,290	0,030
GAE - es - 1	64,03	1,39	32,6	3,663	0,670	0,427	476,840	549,909	66,175	13,714	< d.l.	1664,581	0,003	0,414	263,101	0,004
GAE - es - 2	64,02	1,37	32,62	0,702	0,490	< d.l.	230,133	399,230	17,075	7,515	< d.l.	2123,064	< d.l.	0,211	134,447	< d.l.
GAE - es - 3	62,92	1,71	32,28	1,359	< d.l.	< d.l.	269,358	< d.l.	< d.l.	< d.l.	< d.l.	10166,373	< d.l.	80,347	< d.l.	< d.l.
GAE - es - 4	63,99	1,23	33,23	0,745	0,444	0,049	7,648	0,180	< d.l.	0,220	< d.l.	4280,998	< d.l.	0,201	0,190	< d.l.
GAE - es - 5	64,10	1,17	33,17	1,315	0,619	0,149	394,149	186,854	3,007	10,574	0,018	3510,367	0,008	1,010	152,189	0,009
GAE - es - 6	63,96	1,24	33,24	1,151	1,141	0,077	996,739	115,631	0,935	36,815	< d.l.	4210,466	0,018	0,846	998,465	0,003
GAE - es - 7	64,08	1,27	32,72	0,919	0,529	0,101	250,763	345,922	16,933	6,968	< d.l.	2478,408	0,002	0,164	163,279	0,001
GAE - es - 8	64,00	1,32	32,67	1,061	0,601	< d.l.	50,097	64,075	4,078	1,458	< d.l.	3148,776	< d.l.	0,190	24,314	0,003
GAE - es - 9	64,11	1,27	32,72	1,085	0,428	0,020	37,067	18,792	2,712	0,563	< d.l.	2549,402	0,002	0,202	23,080	0,003
GAE - es - 10	64,14	1,28	32,71	2,039	0,527	0,522	368,058	492,554	35,311	8,170	< d.l.	1604,320	< d.l.	0,238	169,698	0,006
GAE - es - 11	63,92	1,38	32,61	12,720	0,867	0,152	377,525	207,366	18,910	12,850	< d.l.	3175,477	< d.l.	0,154	332,244	0,004
GAE - es - 12	64,14	1,29	33,29	0,502	0,407	< d.l.	29,070	39,573	2,285	2,180	< d.l.	2059,084	< d.l.	0,609	1,603	< d.l.
GAE - es - 13	60,24	1,25	33,25	1,167	0,395	0,412	269,388	398,351	20,622	5,124	0,008	1078,652	0,015	0,344	68,101	< d.l.
GAE - es - 14	64,04	1,41	32,58	16,598	1,104	0,157	21,458	23,050	1,896	0,027	< d.l.	1915,121	0,001	0,195	2,073	0,003
GAE - es - 15	64,01	1,44	32,55	2,696	0,732	0,198	566,880	348,437	64,354	14,534	< d.l.	1520,228	< d.l.	0,206	280,316	< d.l.
GAE - es - 16	63,89	1,57	32,42	0,950	0,652	0,023	87,327	97,793	44,370	3,218	< d.l.	1625,293	0,005	0,927	76,072	0,001
GAE - es - 17	63,04	1,51	32,48	1,450	1,997	0,055	465,593	184,188	9,263	28,204	< d.l.	10737,932	0,016	0,481	344,388	0,031
GAE - es - 18	63,68	1,74	32,25	6,747	4,954	0,267	387,162	367,447	18,591	3,516	0,114	1795,596	0,003	0,429	35,568	0,002
GAE - es - 19	61,72	1,79	32,2	6,598	2,665	0,259	219,097	39,287	20,606	5,935	< d.l.	1244,695	0,001	0,147	143,635	0,003
GAE - es - 20	63,92	1,51	33,51	1,376	1,009	0,078	201,679	127,118	8,967	3,545	< d.l.	1946,616	0,013	1,697	81,240	0,007
GAE - es - 21	63,92	1,53	32,46	0,722	0,456	0,013	22,207	9,400	23,997	0,755	< d.l.	1924,573	0,005	1,902	12,739	0,003
GAE - es - 22	63,91	1,54	32,45	3,635	0,995	0,109	84,436	12,303	5,026	2,174	< d.l.	1901,630	0,005	1,194	47,910	0,002

Table ESM 1: Major EDS (Zn, Fe, S - Wt%), minor and trace elements LA-ICP-MS (concentrations in ppm) analyses of two sphalerite generations from Gaeta mine. EDS major elements analyses have been carried out using sphalerite as external standard. GAE: Gaeta mine, es: early stage sphalerite, ls: late stage sphalerite

	Fe	S	Co	Ni	Cu	Zn	As	Mo	Sb	Te	Bi	Ti	V	Ag	Au	Tl	Pb	Co/Ni
GAE-Py-1	45,61	52,63	0,427	21,326	15,545	1883,212	765,633	190,130	32,418	< dl	< dl	3,227	2,466	206,279	0,002	184,328	2143,868	0,020
GAE-Py-2	45,52	52,64	2,166	25,961	19,878	2571,791	820,434	185,618	31,148	7,758	< dl	1,873	2,224	236,912	< dl	269,211	2149,133	0,083
GAE-Py-3	45,47	53,25	10,043	58,904	21,286	1729,914	855,041	254,146	37,766	< dl	0,007	109,903	4,531	215,097	< dl	137,164	3577,123	0,170
GAE-Py-4	45,45	52,65	9,952	75,247	15,472	3049,743	390,786	141,587	16,065	4,505	< dl	0,278	< dl	171,248	< dl	253,706	2921,371	0,132
GAE-Py-5	45,79	52,92	1,049	11,636	14,968	554,867	425,527	114,573	16,345	< dl	< dl	21,674	4,189	172,498	< dl	248,541	1996,437	0,090
GAE-Py-6	45,74	52,62	0,139	3,906	31,054	634,343	702,970	156,668	26,535	< dl	0,001	40,582	2,813	292,782	< dl	336,723	1912,359	0,036
GAE-Py-7	45,78	52,68	0,265	5,613	14,972	782,873	377,457	93,947	14,371	4,295	< dl	12,846	2,948	165,550	0,003	125,317	2095,529	0,047
GAE-Py-8	45,76	52,55	0,964	15,220	32,171	662,023	605,587	198,014	24,532	2,428	0,001	39,190	2,925	137,523	< dl	138,070	2080,979	0,063
GAE-Py-9	45,66	52,63	0,153	2,533	17,902	1301,284	579,847	158,414	15,904	< dl	< dl	5,129	2,718	210,674	0,003	121,169	2481,155	0,060
GAE-Py-10	45,62	53,13	1,476	29,043	62,326	1605,868	609,446	149,877	44,191	5,627	0,008	20,984	3,963	480,811	< dl	181,793	2240,745	0,051
GAE-Py-11	45,75	52,62	11,696	2,087	15,492	1287,132	738,294	243,981	18,247	0,730	0,011	0,288	0,014	0,519	< dl	42,668	1667,733	5,604
GAE-Mar-1	45,50	52,64	0,021	2,773	18,648	1979,567	508,653	131,337	15,739	< dl	0,006	0,975	2,136	210,486	0,004	159,516	3468,880	0,008
GAE-Mar-2	44,98	52,70	0,187	9,582	24,534	8016,351	868,766	206,315	30,613	0,090	0,001	10,132	3,259	321,765	< dl	358,847	1862,111	0,019
GAE-Mar-3	44,61	53,33	0,283	8,277	30,155	11701,892	469,610	150,969	29,868	< dl	< dl	11,209	2,865	389,888	0,002	555,030	2075,438	0,034
GAE-Mar-4	45,73	52,62	0,336	10,426	20,857	502,179	735,318	223,500	30,657	0,113	0,010	7,206	3,466	204,623	0,019	264,209	2266,097	0,032
GAE-Mar-5	45,72	52,99	0,034	3,385	27,431	576,236	751,318	210,156	32,222	< dl	< dl	3,040	2,872	253,142	< dl	249,627	2248,408	0,010
GAE-Mar-6	45,72	52,82	0,784	11,181	26,139	521,695	637,862	204,031	29,504	0,185	0,002	3,269	2,646	256,430	< dl	391,344	2270,017	0,070
GAE-Mar-7	45,16	52,68	0,113	7,703	16,895	4934,189	499,673	168,935	14,495	< dl	0,004	0,507	2,931	185,418	0,005	153,189	3921,412	0,015
GAE-Mar-8	44,98	52,70	0,021	5,518	14,640	6467,362	488,191	137,385	13,328	< dl	0,003	0,356	2,538	182,136	0,006	169,241	4253,779	0,004
GAE-Mar-9	45,65	55,36	0,131	5,602	12,639	1067,716	352,412	99,957	11,924	< dl	0,003	0,202	1,285	152,411	0,005	283,941	3042,391	0,023
GAE-Mar-10	45,66	52,63	1,209	16,517	20,575	2038,908	490,304	177,734	20,562	0,020	< dl	4,103	2,159	191,619	0,011	288,275	1667,782	0,073
BRZ-Py-1	46,07	52,79	1,210	0,924	6,973	23,612	510,139	193,286	6,536	3,827	0,008	0,142	0,019	0,222	< dl	28,101	26,390	1,309
BRZ-Py-2	45,95	53,00	0,514	0,268	0,821	1,492	841,877	1064,831	1,496	3,499	< dl	0,321	0,008	0,032	< dl	13,985	1,977	1,915
BRZ-Py-3	46,00	52,99	0,089	0,034	0,514	1,278	893,999	501,540	0,422	2,867	0,001	0,229	0,007	0,016	< dl	14,164	1,574	2,583
BRZ-Py-4	46,03	52,81	3,737	1,135	12,285	8,691	875,261	224,735	5,063	3,567	0,010	0,597	0,023	0,175	< dl	26,158	19,782	3,293
BRZ-Py-5	45,79	53,02	1,596	1,203	27,307	4,239	3056,699	346,853	24,524	3,233	0,005	0,380	0,021	0,818	0,005	109,431	60,968	1,327
BRZ-Py-6	45,80	53,19	4,420	2,423	84,802	13,584	2786,841	311,976	77,249	4,437	0,039	1,905	0,125	1,821	0,022	75,602	217,197	1,824
BRZ-Py-7	45,97	53,25	0,169	0,711	3,400	2,550	947,037	788,190	0,901	3,387	< dl	0,348	0,016	0,067	< dl	12,342	3,262	0,237
BRZ-Py-8	46,04	52,95	10,669	1,589	16,255	2,493	728,094	219,811	12,756	3,719	0,015	0,367	0,011	0,447	< dl	34,500	24,781	6,713
BRZ-Py-9	45,96	53,30	0,127	0,317	2,527	1,699	772,500	1078,442	0,509	4,363	< dl	0,478	0,008	0,020	< dl	13,271	3,862	0,403

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu	Y	Y/Ho	La/Sm	Gd/Yb	La/Yb	Eu/Eu*
GAE-Py-1	0,150	0,074	0,005	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	0,006	-	-	-	-	-
GAE-Py-2	0,007	0,009	0,002	< dl	0,013	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	0,011	-	0,345	-	-	-
GAE-Py-3	0,058	0,082	0,012	0,013	0,028	0,017	< dl	0,002	< dl	< dl	< dl	< dl	< dl	0,081	-	-	-	-	-
GAE-Py-4	< dl	0,002	< dl	< dl	< dl	< dl	0,017	< dl	< dl	< dl	< dl	< dl	< dl	< dl	-	-	-	-	-
GAE-Py-5	0,020	0,042	0,003	0,012	0,012	< dl	0,017	< dl	0,009	< dl	< dl	< dl	< dl	0,042	-	1,041	-	-	-
GAE-Py-6	0,031	0,051	0,009	0,048	0,016	0,005	0,017	0,001	< dl	0,002	< dl	< dl	< dl	0,055	28,660	1,255	-	-	1,375
GAE-Py-7	0,035	0,100	0,011	0,023	0,017	0,006	0,013	0,002	< dl	< dl	0,006	< dl	< dl	0,034	-	-	-	-	1,566
GAE-Py-8	0,040	0,052	0,009	0,043	0,002	< dl	0,016	< dl	0,015	0,001	0,013	< dl	< dl	0,004	2,808	11,529	-	-	-
GAE-Py-9	0,002	0,008	< dl	0,003	0,012	0,002	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	-	-	-	-	-
GAE-Py-10	0,190	0,271	0,026	0,069	0,029	0,004	0,008	< dl	< dl	< dl	< dl	< dl	< dl	0,044	-	4,133	-	-	1,501
GAE-Py-11	0,168	0,467	0,073	0,535	0,155	0,039	0,224	0,027	0,164	0,026	0,048	0,035	0,001	0,853	32,324	0,689	8,095	5,235	0,651
GAE-Mar-1	0,002	0,003	< dl	0,004	0,016	0,001	< dl	0,002	<0.001	0,001	< dl	0,001	0,001	0,006	4,330	1,091	-	-	-
GAE-Mar-2	0,014	0,026	0,003	0,010	0,019	< dl	0,002	< dl	< dl	0,001	0,004	< dl	0,002	0,021	27,876	-	-	-	-
GAE-Mar-3	0,100	0,125	0,011	0,039	0,017	< dl	< dl	<0.001	0,001	0,002	0,001	0,005	0,001	0,023	12,527	-	-	-	-
GAE-Mar-4	0,020	0,032	0,006	0,012	0,009	0,003	< dl	0,002	0,007	0,001	0,003	0,004	< dl	0,014	20,471	0,965	-	-	-
GAE-Mar-5	0,006	0,012	0,002	0,008	0,013	0,001	0,002	<0.001	0,008	< dl	0,002	0,005	< dl	0,018	-	13,924	-	-	1,482
GAE-Mar-6	0,030	0,054	0,005	0,027	0,016	0,001	< dl	< dl	< dl	0,001	0,006	< dl	<0.001	0,008	7,496	2,328	-	-	-
GAE-Mar-7	0,001	0,002	<0.001	< dl	0,013	0,002	< dl	< dl	< dl	< dl	0,002	< dl	<0.001	0,001	-	-	-	-	-
GAE-Mar-8	0,001	0,001	0,001	0,005	0,004	< dl	< dl	<0.001	0,003	< dl	< dl	0,007	<0.001	0,001	-	-	-	-	-
GAE-Mar-9	< dl	0,001	< dl	< dl	0,005	< dl	0,001	0,001	0,001	< dl	0,002	< dl	0,001	< dl	-	-	-	-	-
GAE-Mar-10	0,024	0,026	0,001	0,018	0,004	< dl	< dl	0,001	0,007	0,001	0,003	0,006	0,001	0,023	17,560	-	-	-	-
BRZ-Py-1	0,023	0,071	0,013	0,073	0,013	0,007	0,024	0,004	0,016	0,002	< dl	< dl	< dl	0,089	38,824	-	-	-	-
BRZ-Py-2	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	-	0,080	-	-	-
BRZ-Py-3	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	-	0,445	2,220	12,808	-
BRZ-Py-4	0,009	0,022	0,003	< dl	0,006	0,002	< dl	0,001	< dl	< dl	< dl	< dl	< dl	0,036	-	3,711	-	-	-
BRZ-Py-5	0,002	0,014	0,002	< dl	<0.001	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	0,022	-	-	-	-	-
BRZ-Py-6	0,013	0,051	0,007	0,021	0,003	< dl	0,019	0,002	0,017	< dl	< dl	< dl	< dl	0,069	-	0,296	-	-	-
BRZ-Py-7	< dl	0,003	< dl	< dl	< dl	< dl	0,004	< dl	< dl	< dl	< dl	< dl	0,001	< dl	-	-	-	-	-
BRZ-Py-8	0,001	0,009	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	0,014	-	-	-	-	-
BRZ-Py-9	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	-	-	-	-	-

	Y/Ho	La/Sm	Gd/Yb	La/Yb	Eu/Eu*
GAE-Py III	21,264	3,165	8,095	5,235	1,273
GAE-Mar	15,043	4,577	-	-	1,482
BRZ-Py	38,824	1,133	2,220	12,808	-

Table ESM 2: Major EDS (Fe, S - Wt%), minor and trace elements LA-ICP-MS (concentrations in ppm) analyses of iron sulfides from Gaeta and Mt. Bronzone mines
EDS major elements analyses have been carried out using pyrite as external standard. GAE: Gaeta mine, BRZ: Mt. Bronzone mines, py: pyrite, mar: marcasite

	Na	P	K	V	Cu	Sr	Ag	Sb	Au	Tl	Bi	Ti	Mn	Co	Ni	Zn	As	Mo	Pb	Th	U
GAE-lm-1	78,294	113,639	85,112	6,760	123,534	1,824	518,442	61,657	0,228	5,624	0,009	13,683	40,872	0,121	0,334	807,407	2204,457	210,145	17,598	0,011	0,113
GAE-lm-2	48,278	108,189	153,018	5,005	141,435	2,132	27,268	105,188	0,563	2,812	0,015	21,110	19,148	0,043	0,344	674,809	1868,396	229,514	13,286	0,029	0,425
GAE-lm-3	72,281	114,160	488,861	6,823	141,095	2,073	163,247	63,026	0,186	7,861	0,008	65,196	17,410	0,053	0,350	735,767	1680,890	208,298	49,220	0,074	0,652
GAE-lm-4	63,884	119,620	411,691	4,929	144,226	1,808	210,227	122,741	0,099	6,187	0,009	19,913	20,403	0,031	0,166	7,577	1733,019	349,884	28,399	0,031	0,329
GAE-lm-5	204,256	116,985	413,356	7,212	132,271	3,376	537,402	126,158	0,122	179,108	0,003	26,833	16,044	0,035	0,143	794,037	2026,624	408,304	2190,296	0,040	0,411
GAE-lm-6	196,514	237,742	726,121	14,066	138,353	2,410	17,386	1394,486	0,016	6,466	0,079	20,318	23,422	0,119	2,358	2475,546	2783,295	2098,188	148,753	0,042	1,842
GAE-lm-7	81,258	266,859	1392,260	27,144	122,097	2,390	11,055	1089,667	0,032	5,240	0,075	58,374	17,343	0,053	0,977	1004,384	2496,476	1666,718	49,231	0,032	1,341
GAE-lm-8	222,742	200,292	1889,185	19,250	141,635	4,058	459,955	1475,878	0,033	269,301	0,082	70,213	19,131	0,086	1,690	1446,159	2503,743	2058,929	3112,578	0,099	1,492
GAE-lm-9	143,248	142,852	3059,306	8,002	132,430	3,393	2832,670	14,637	0,162	15,236	0,009	159,487	26,990	0,057	0,320	1200,507	1116,385	52,630	45,417	0,217	1,476
GAE-lm-10	48,537	108,981	1165,501	4,234	120,794	1,395	18,232	66,991	0,066	3,645	0,011	30,823	32,652	0,028	0,355	2022,060	913,121	306,705	83,753	0,162	1,274
GAE-lm-11	51,687	124,300	4712,782	8,638	128,975	2,028	65,810	16,682	0,052	23,129	0,000	224,824	26,864	0,054	0,212	1007,035	536,798	88,456	23,272	0,128	0,409
BRZ-blm-1	26,678	691,096	17,916	49,816	4,956	7,463	< dl	3,174	< dl	1,624	0,019	6,805	518,350	1,910	11,359	121,922	77,066	1827,920	4,454	0,476	0,346
BRZ-blm-2	20,481	467,738	2,733	8,050	6,036	6,085	< dl	1,247	< dl	0,186	0,012	0,726	241,182	0,459	3,584	140,789	10,068	351,533	2,443	0,166	0,716
BRZ-blm-3	37,803	475,664	14,286	14,624	5,565	5,872	< dl	1,060	< dl	1,009	0,015	0,781	346,045	2,682	6,313	122,628	17,328	585,379	3,548	0,301	1,658
BRZ-blm-4	26,595	471,495	6,802	15,123	5,648	5,700	< dl	1,072	< dl	0,636	0,016	1,234	348,903	2,294	6,685	121,931	17,276	569,272	3,125	0,270	2,437
BRZ-blm-5	36,407	374,449	27,816	6,122	6,699	6,502	< dl	1,782	< dl	0,278	0,027	14,644	332,371	0,580	2,571	77,668	16,463	953,518	3,479	0,190	1,323
BRZ-elm-1	19,228	1023,844	9,636	83,846	1,749	12,338	0,000	0,986	< dl	0,092	< dl	0,057	6,517	0,017	1,679	14,773	48,180	30,829	0,155	< dl	0,568
BRZ-elm-2	9,717	616,491	3,248	42,769	0,279	7,713	0,013	1,317	< dl	0,063	< dl	0,076	22,829	0,030	1,069	3,141	45,739	9,149	2,610	< dl	0,401
BRZ-elm-3	14,954	1108,387	8,461	103,281	0,495	14,984	0,012	1,229	< dl	0,020	< dl	0,020	8,185	0,008	2,166	14,295	65,095	85,259	0,322	0,006	0,806
BRZ-elm-4	9,137	832,481	6,122	75,585	0,514	12,638	< dl	0,958	< dl	0,021	< dl	0,033	6,957	0,001	1,453	10,556	63,346	73,457	< dl	< dl	0,498
BRZ-elm-5	35,626	1160,967	53,413	142,019	113,349	17,635	0,114	6,669	0,151	0,066	0,102	12,770	19,302	0,162	5,171	156,070	68,180	87,864	12,196	0,503	1,509
BRZ-elm-6	14,962	919,156	12,420	74,160	9,721	11,217	0,020	0,981	< dl	0,073	0,007	0,510	6,833	0,021	1,321	33,497	40,369	86,326	0,397	0,057	0,618

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu	La/Sm	Gd/Yb	La/Yb	Eu/Eu*	Ce/Ce*
GAE-lm-1	0,041	0,036	0,003	0,023	0,028	0,001	< dl	< dl	< dl	0,001	0,011	< dl	0,001	0,925	-	-	-	0,872
GAE-lm-2	0,024	0,044	0,006	0,011	< dl	< dl	0,006	< dl	0,013	0,006	0,019	0,004	< dl	-	1,333	4,738	-	1,087
GAE-lm-3	0,107	0,117	0,016	0,045	< dl	< dl	0,038	< dl	0,023	0,006	0,029	0,016	0,005	-	1,98	4,739	-	1,033
GAE-lm-4	0,073	0,109	0,013	0,03	0,022	< dl	< dl	0,002	< dl	0,004	0,013	1,537	< dl	2,13	-	0,033	-	1,047
GAE-lm-5	0,1	0,125	0,013	0,061	0,016	< dl	0,014	0,001	0,024	0,004	0,021	0,019	< dl	4,08	0,575	3,608	-	0,925
GAE-lm-6	0,108	0,191	0,034	0,248	0,04	0,011	0,061	0,007	0,053	0,011	0,027	0,011	0,003	1,694	4,559	6,841	1,848	0,933
GAE-lm-7	0,07	0,098	0,014	0,044	< dl	< dl	0,032	0,004	0,04	0,006	0,012	0,031	< dl	-	0,841	1,602	-	1,026
GAE-lm-8	0,233	0,231	0,032	0,153	0,061	0,01	0,042	0,008	0,03	0,01	0,055	0,029	0,011	2,413	1,177	5,579	-	0,961
GAE-lm-9	0,234	0,274	0,025	0,081	0,13	0	0,045	0,008	0,052	0,013	0,07	0,083	0,019	1,149	0,448	1,979	-	0,955
GAE-lm-10	1,291	1,847	0,329	1,622	0,394	0,068	0,593	0,063	0,485	0,098	0,296	0,157	0,033	2,084	3,072	5,734	1,167	0,988
GAE-lm-11	0,465	0,67	0,091	0,453	0,08	0,014	0,128	0,013	0,127	0,031	0,092	0,055	0,012	3,693	1,916	5,961	1,499	0,937
BRZ-blm-1	6,747	4,553	1,553	7,438	1,464	0,279	1,692	0,177	1,147	0,224	0,649	0,437	0,071	2,932	3,158	10,794	1,041	-1,291
BRZ-blm-2	4,931	5,243	1,074	4,822	0,787	0,16	1,01	0,105	0,702	0,137	0,465	0,284	0,056	3,987	2,904	12,145	1,158	-1,077
BRZ-blm-3	2,719	2,392	0,66	3,284	0,581	0,133	0,707	0,078	0,487	0,107	0,284	0,223	0,035	2,978	2,585	8,521	1,300	-1,125
BRZ-blm-4	3,209	3,399	0,796	3,723	0,723	0,159	0,781	0,085	0,578	0,103	0,306	0,253	0,043	2,825	2,52	8,878	1,286	-1,100
BRZ-blm-5	1,995	1,921	0,426	1,831	0,355	0,079	0,385	0,042	0,281	0,062	0,164	0,115	0,018	3,573	2,74	12,168	1,442	-1,093
BRZ-elm-1	21,492	0,121	5,745	28,647	6,526	1,501	8,582	1,037	7,741	1,623	5,299	4,423	0,804	2,096	1,582	3,396	0,742	-7,061
BRZ-elm-2	4,563	0,136	1,337	7,127	1,661	0,389	2,497	0,289	2,01	0,466	1,375	1,018	0,202	1,748	2	3,132	0,990	-2,597
BRZ-elm-3	27,75	0,12	7,764	38,032	8,636	2,027	11,665	1,39	10,385	2,158	6,981	6,184	1,166	2,044	1,538	3,136	0,679	-10,885
BRZ-elm-4	20,655	0,043	5,417	26,698	6,045	1,481	9,173	1,065	7,554	1,607	5,343	3,998	0,774	2,174	1,871	3,61	0,724	-7,803
BRZ-elm-5	34,289	0,618	9,713	43,397	9,736	2,417	13,52	1,92	12,878	2,561	8,416	7,601	1,453	2,241	1,45	3,152	0,665	-7,386
BRZ-elm-6	14,96	0,175	4,276	19,14	4,201	1,038	5,895	0,754	5,394	1,13	3,696	3,335	0,623	2,266	1,441	3,135	0,841	-5,526

	Eu/Eu*	Ce/Ce*	La/Sm	Gd/Yb	La/Yb
GAE-lm-1	1,505	0,979	2,271	1,767	4,081
BRZ-blm-1	1,245	-1,137	3,259	2,781	10,501
BRZ-elm-1	0,773	-6,876	2,095	1,647	3,26

Table ESM 3: LA-ICP-MS trace elements analyses (concentrations in ppm) of iron hydroxides from Gaeta and Bronzone mines
GAE: Gaeta mine, BRZ: Mt. Bronzone mines, lm: limonite, blm: black limonite, elm: earthy limonite

MINING SITE	DEPOSIT TYPE	FeO	ZnO	PbO_2	SO_3	MgO	SiO_2	Al_2O_3	CaO	K_2O	MnO	AgO	P_2O_5
Gaeta mine	Como Lake-Valsassina	68,41	4,95	10,98	2,30	0,88	2,18	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
Gaeta mine	Como Lake-Valsassina	46,52	5,69	1,08	0,99	5,04	12,78	8,64	7,55	2,69	< d.l.	< d.l.	< d.l.
Gaeta mine	Como Lake-Valsassina	64,88	7,10	0,33	0,58	3,47	6,45	3,67	3,33	1,59	< d.l.	< d.l.	< d.l.
Gaeta mine	Como Lake-Valsassina	50,12	6,47	0,68	0,75	5,41	10,49	5,58	7,96	2,52	< d.l.	< d.l.	< d.l.
Gaeta mine	Como Lake-Valsassina	36,11	18,53	< d.l.	9,47	13,80	0,88	<d l	11,17	< d.l.	< d.l.	< d.l.	< d.l.
Gaeta mine	Como Lake-Valsassina	46,30	17,27	0,67	4,67	4,25	1,14	<d l	14,63	< d.l.	< d.l.	< d.l.	< d.l.
Gaeta mine	Como Lake-Valsassina	71,64	5,19	< d.l.	2,85	< d.l.	2,29	<d l	1,67	< d.l.	< d.l.	0,75	< d.l.
Gaeta mine	Como Lake-Valsassina	77,60	4,45	1,65	1,17	1,04	3,83	0,99	0,93	< d.l.	< d.l.	< d.l.	< d.l.
Gaeta mine	Como Lake-Valsassina	74,71	4,21	1,78	1,56	0,66	4,15	1,53	1,08	< d.l.	0,27	< d.l.	< d.l.
Gaeta mine	Como Lake-Valsassina	40,59	1,98	0,66	0,69	16,04	3,88	0,58	24,07	0,47	0,99	< d.l.	< d.l.
Gaeta mine	Como Lake-Valsassina	75,86	3,35	4,77	1,11	< d.l.	3,15	1,11	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
Pasturo mine	Como Lake-Valsassina	81,27	< d.l.	< d.l.	6,87	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
Pasturo mine	Como Lake-Valsassina	75,09	0,75	3,16	11,52	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	1,11	< d.l.
Pasturo mine	Como Lake-Valsassina	75,66	< d.l.	2,80	10,71	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	1,08	< d.l.
Pasturo mine	Como Lake-Valsassina	53,98	1,13	9,91	21,87	< d.l.	< d.l.	< d.l.	< d.l.	1,88	< d.l.	1,05	< d.l.
Pasturo mine	Como Lake-Valsassina	49,91	3,25	10,45	26,15	< d.l.	< d.l.	< d.l.	< d.l.	1,92	< d.l.	< d.l.	< d.l.
Campo del Ferro mine	Como Lake-Valsassina	52,19	10,23	3,89	0,70	< d.l.	10,61	4,35	7,64	1,06	< d.l.	< d.l.	< d.l.
Campo del Ferro mine	Como Lake-Valsassina	64,92	11,91	3,24	1,78	< d.l.	5,37	1,28	1,11	0,72	< d.l.	< d.l.	< d.l.
Campo del Ferro mine	Como Lake-Valsassina	52,34	24,51	3,58	1,95	< d.l.	4,61	1,69	1,24	0,63	< d.l.	< d.l.	< d.l.
Piani d'Erna mines	Como Lake-Valsassina	59,57	4,37	4,50	3,24	< d.l.	3,46	1,21	< d.l.	0,75	< d.l.	< d.l.	< d.l.
Piani d'Erna mines	Como Lake-Valsassina	55,97	6,15	3,98	4,61	< d.l.	3,37	< d.l.	< d.l.	0,81	< d.l.	< d.l.	< d.l.
Piani d'Erna mines	Como Lake-Valsassina	40,96	24,47	7,34	6,26	< d.l.	< d.l.	< d.l.	< d.l.	1,95	< d.l.	< d.l.	< d.l.
Bronzone mines	Val Seriana-West Iseo Lake	72,33	< d.l.	< d.l.	< d.l.	0,86	9,39	6,07	0,63	0,70	< d.l.	< d.l.	0,59
Bronzone mines	Val Seriana-West Iseo Lake	80,44	< d.l.	< d.l.	< d.l.	< d.l.	4,60	3,79	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
Bronzone mines	Val Seriana-West Iseo Lake	83,55	< d.l.	< d.l.	< d.l.	< d.l.	3,35	3,08	< d.l.	< d.l.	< d.l.	< d.l.	0,65
Bronzone mines	Val Seriana-West Iseo Lake	82,66	< d.l.	< d.l.	< d.l.	0,66	4,11	1,82	0,51	< d.l.	< d.l.	< d.l.	0,37
Bronzone mines	Val Seriana-West Iseo Lake	84,23	< d.l.	< d.l.	< d.l.	< d.l.	1,17	1,17	< d.l.	< d.l.	< d.l.	< d.l.	1,41
Bronzone mines	Val Seriana-West Iseo Lake	88,31	< d.l.	< d.l.	< d.l.	< d.l.	0,73	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	0,81
Bronzone mines	Val Seriana-West Iseo Lake	88,83	< d.l.	< d.l.	< d.l.	< d.l.	2,45	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
Bronzone mines	Val Seriana-West Iseo Lake	78,82	< d.l.	< d.l.	< d.l.	1,77	5,40	3,38	0,60	< d.l.	< d.l.	< d.l.	0,40
Bronzone mines	Val Seriana-West Iseo Lake	79,05	< d.l.	< d.l.	< d.l.	1,29	5,07	4,14	0,42	< d.l.	< d.l.	< d.l.	0,27
Bronzone mines	Val Seriana-West Iseo Lake	75,18	< d.l.	< d.l.	< d.l.	1,37	6,05	2,48	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
Büs del Fer mine	Val Seriana-West Iseo Lake	83,22	< d.l.	< d.l.	< d.l.	< d.l.	2,45	0,96	< d.l.	< d.l.	< d.l.	< d.l.	0,55
Büs del Fer mine	Val Seriana-West Iseo Lake	85,12	< d.l.	< d.l.	< d.l.	< d.l.	3,44	1,11	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
Büs del Fer mine	Val Seriana-West Iseo Lake	81,76	< d.l.	< d.l.	< d.l.	1,87	4,50	2,08	< d.l.	< d.l.	< d.l.	< d.l.	0,73

Table ESM 4: EDS major element analyses on mixed limonite-rich ores from various deposits. The EDS analyses have been carried out on polished gossan samples. The analyses have been carried out on selected areas of around 1 mm^2*, using the following standards: Fe on hematite, Zn on sphalerite, Pb on galena, S on pyrite, Mg on chlorite, Al, Si and K on biotite, Mn on rhodonite and, finally, Ca and P on apatite (Ag standardless).*