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Petrological and metallogenic outlines of the Valmaggia ultramafic pipe (Ivrea zone), NW Alps, Italy

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ABSTRACT. — The Valmaggia pipe intrudes the uppermost part of the Main gabbro (Basic Complex, Ivrea-Verbano Zone, Italy). The ore body associated with the pipe consists of a stockwork and disseminated Fe-Ni-Cu sulphide mineralisation, with accessory Platinum Group Elements (PGE). The pipe consists of a roughly ellipsoidal main body. shortened along a WNW-ESE axis and elongated along a NNE-SSW axis, dipping steeply (70°-90°) towards WNW. Fe-Ni-Cu sulphide mineralisation is hosted in the internal margins of the pipe, from the contact with the host gabbro to a distance of 4-5 metres inside the pipe. The ore mineral paragenesis comprises sulfides (pyrrhotite, pentlandite, chalcopyrite, cubanite), tellurides (altaite, wehrlite, hessite) and PGM (merenskyte).

Cross-sections of the pipe mapped from the drives, together with petrographic and metallogenic observations, show that the pipe is concentrically zoned, with a homogeneous core and a heterogeneous rim.

On the basis of textural evidences and mineral chemistry we suggest that the pipe is primarily composed of a crystal mush comprising relatively low Fo olivine including buck-shot textured Fe-Ni sulphides and hercynite, which is cemented by products of the residual liquid. Crystallisation proceeded from the rim to the core, where residual melt was no more in equilibrium with cumulus phases, that were replaced extensively by late hydrous phases. PGE-sulphide mineralisation formed in the early stages of crystallisation and is limited to the rim portions of the pipe. It is possible, mainly on the basis of age relationships, to envisage a correlation between the restitisation process that occured in Finero ultramafic body and production of melt that formed Valmaggia and other pipes of Ivrea Verbano Zone. PGE chondritic profiles of sulphidepoor and sulphide-rich portions are generally similar and reflect the primary PGE content of the magma.

RIASSUNTO. — Il pipe di Valmaggia si intrude nella porzione più elevata del Main gabbro (Complesso Basico di Ivrea, Zona Ivrea-Verbano, Italia). Il corpo minerario associato al pipe consiste di una mineralizzazione, da stockwork a disseminata di solfuri di Fe, Ni e Cu, con accessori elementi del gruppo del platino (PGE).

Il pipe è costituito da un corpo principale approssimativamente ellissoidico, con un asse di massimo allungamento in direzione NNE-SSO, con un'inclinazione elevata (tra i 70° e i 90°) verso ONO. La mineralizzazione a solfuri di Fe, Ni e Cu è presente unicamente al margine del pipe, dal contatto con il gabbro incassante verso l'interno per una distanza fino a 4-5 m. La paragenesi della mineralizzazione comprende solfuri (pirrotina, pentlandite, calcopirite, cubanite), tellururi (altaite, wehrlite, hessite) e PGM (merenskyte).

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Sezioni del pipe tracciate in galleria, insieme alle osservazioni petrografiche e metallogeniche, evidenziano la natura concentrica del pipe, con un nucleo omogeneo ed un bordo disomogeneo.

Sulla base di evidenze tessiturali e della mineral chemistry si suggerisce che il pipe si sia formato a partire da un crystal mush comprendente olivina relativamente bassa in Fo, solfuri di Fe e Ni con tessitura a buck shot ed ercinite, il quale è stato successivamente cementato dal liquido residuale. La cristallizzazione è proceduta dal bordo verso il nucleo, dove il fuso residuale non era più in equilibrio con le fasi di cumulus, le quali sono state quindi sostituite da fasi idrate tardive. La mineralizzazione a PGE e solfuri si è formata negli stadi iniziali della cristallizzazione ed è limitata unicamente alle parti marginali del pipe.

È possibile, principalmente sulla base delle relazioni temporali, ipotizzare una correlazione tra il processo di restitizzazione riscontrato nel corpo ultrafemico di Finero e la produzione di fusi che ha portato alla formazione del pipe di Valmaggia e degli altri pipe della Zona Ivrea Verbano.

I profili condritici dei PGE, sia delle porzioni povere che di quelle ricche in solfuri, sono simili e riflettono il contenuto primario di PGE del magma.

KEY WORDS: Nickel, ore deposit, peridotite, Ivrea, PGE

INTRODUCTION

The studied ultramafic pipe is located on the left side of the lower part of Sesia Valley, not far away from the small village of Valmaggia (fig. 1).

The pipe intrudes the uppermost part of the Main gabbro (Basic Complex, Ivrea-Verbano Zone). The morphology of the ultramafic body was drawn after a detailed mapping of the accessible portions of the abandoned mine (fig. 2).

The pipe hosts a sulphide ore body, comprised within a 2 to 5 m-wide band at the contact with the enclosing gabbro. The ore assemblage is pyrrhotite-pentlanditechalcopyrite, with minor mineral phases including mackinawite, Platinum Group Minerals (PGM), Pb-tellurides; graphite and dolomite are common and ubiquitous accessory interstitial minerals. The ore was mined at various stages between 1865 and 1943. Other pipe-like ultramafic bodies are located at the Main Gabbro-Diorites transition (Sella Bassa, Castello di Gavala, Piancone), or injected as offset bodies into the metasediments and metavolcanics of the Kinzigite Formation (Fej di Doccio) (Ferrario *et al.*, 1982; Garuti *et al.*, 1990; Garuti *et al.*, 2001).

GEOLOGY OF THE IVREA BASIC COMPLEX

The Ivrea-Verbano Zone is made up of two main units: the Basic Complex and the Kinzigite Formation (Garuti et al., 1980; Pin and Sills, 1986; Sinigoi et al., 1994) (fig. 1). On the basis of structural data many authors (e.g. Rivalenti et al., 1984; Quick et al., 1994) demonstrated that the contact between these units is magmatic. The deepest units of the Basic Complex outcrop at its western edge along the Insubric Lineament, and are made up of a series of peridotitic bodies (i.e. Balmuccia, Finero and Baldissero): these are thought to be subcontinental mantle slices and are mainly constituted of lherzolite, with minor harzburgite and dunite. The fabric is compared to a mantle tectonite (Garuti, 1977) with foliated, protogranular and porphyroclastic textures.

In its central portion, the Basic Complex is then composed of cyclic units, consisting of a sequence of layers including peridotites, pyroxenites, gabbro-norites and anorthosites, with intercalated metasediments. The cyclic sequence envelopes and rests on top of the peridotitic bodies. Septa and layers of metasedimentary rocks of the crustal sequence (Kinzigite Formation), with thickness up to ten metres, alternate with the layers of the cyclic units (Ferrario *et al.*, 1982).

One of the largest metasedimentary intercalations, which extends for about 5 km in strike and can reach up to 100 m in thickness, marks the boundary on the east between the cyclic units and a huge body of almost homogeneous amphibole gabbro (Main Gabbro). This gap in the magmatic sequence



Fig. 1 - Geological sketch of the Ivrea Verbano Zone. The location of the ultramafic pipes of Valmaggia, Bec d'Ovaga, Castello di Gavala, Fej di Doccio, Sella Bassa and Piancone is shown.

suggests that the two formations represent separate intrusive events (Ferrario *et al.*, 1982; Garuti *et al.*, 2001), and Pin and Sills (1986) show geochemical and isotopic data in agreement with a different origin for Cyclic Units and Main Gabbro parental magmas. On the other hand different sets of petrographic, geochemical and isotopic data suggest a cogenetic origin of all units of the Basic Complex (Rivalenti *et al.*, 1975; Voshage *et al.*, 1990; Sinigoi *et al.*, 1994). The gabbro grades upwards into diorites, and constitutes the uppermost portion of the whole Basic Complex.

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The Kinzigite Formation is structurally located above the Basic Complex: it consists of a prograde metamorphic sequence (from middle amphibolite up to granulite facies) of metapelites, paragneisses, amphibolites, marbles, quartzites and meta-basic igneous rocks (Ferrario *et al.*, 1982, 1983; Garuti *et al.*, 2001). Locally, these rocks underwent intense partial melting and melt segregation (Schnetger, 1994; Bea and Montero, 1999).



Fig 2. - Main Ni-Cu sulfides concentrations in the Valmaggia ore deposit. Significative vertical sections with the massive and stockwork mineralized bodies.

GEOLOGY OF THE VALMAGGIA PIPE

The geology of the area is poorly exposed, due to dense vegetation and extensive debris deposits: there is only one small outcrop of the pipe (fig. 2). On the basis of underground mapping it was possible to outline the morphology of the pipe and the contact with the host gabbro that is sharp when not dislocated by faults (fig. 3A).

The pipe consists of a roughly ellipsoidal main body, smoothened along WNW-ESE and lengthened along NNE-SSW, dipping steeply (70°-90°) towards WNW. Ore mineralisation is hosted in the internal margins of the pipe, from the contact with the host gabbro up to a distance of 4-5 metres inside the pipe.

Portions of the pipe which have been displaced by faults show tectonic contacts with the host gabbro: along these faults, sulphide mineralisation is rare or absent.

The size of the pipe cannot be defined precisely as investigations inside the mine are limited to a restricted area, mainly because some levels of the abandoned mine are collapsed and others are flooded. Crosssections of the pipe along transversal galleries showed that it is concentrically zoned with a homogeneous core and a heterogeneous rim.

ANALYTICAL METHODS

Petrographic and microtextural characters were analysed in thin and polished section. Electron microprobe (EMP) analyses for major and minor elements in silicates, oxides, sulphides and tellurides were performed using an ARL-SEMQ microprobe at the University of Milan, Department of Earth Sciences and National Research Council. The analytical conditions were as follows: cup current of 300 nA, 20 kV and 20s peak counting time for sulphides and tellurides analyses, and 300 nA, 15 kV and 10-80s peak counting time for the analyses of silicates and oxides. Platinum Group Element (PGE) whole rock contents were analyzed with ICP-MS at ACTLABS in Ancaster (Ontario, Canada): detection limits were: Os 2ppb, Ir 0.1 ppb, Ru 5 ppb, Rh 0.2 ppb, Pt 5 ppb. Data were then normalised to chondritic values from C1 chondrites (Naldrett and Duke, 1980).

PETROGRAPHIC FEATURES OF THE PIPE

Rim portions

The rim portions of the pipe mainly consist of a hydrated peridotite, whose texture is commonly equigranular with olivine crystals between 3 and 7mm in size. Texture locally becomes cumulitic, and the mineral grain size of the rock does not exceed 3 mm (fig. 3B). Textural and petrographic characters are overall rather dishomogeneous: changes in grain size and texture are visible at the metrescale, and can be observed along various pipegabbro contacts.

Olivine is a primary and abundant phase occurring as equigranular subcentimetric rounded crystals; it contains drop-like inclusions of hercynite. Orthopyroxene and green amphibole are more abundant in the rim than in the core of the pipe, and show heteraccumulus texture, where inclusions are rounded olivine crystals; mirmekytic-like inclusions of hercynite are also included within these phases.

Brown amphibole and phlogopite are less abundant than in the core of the pipe. While amphibole is still the most abundant hydrated phase and occurres as idiomorphic centimetric crystals engulfing and replacing clinopyroxene, green amphibole, orthopyroxene and olivine, phlogopite is present in much lower amounts, and occurs as idiomorphic lamellae, commonly associated to brown amphibole, and which show evidence of intracrystalline deformation (kink banding). Phlogopite replaces brown amphibole in some areas. The replacement of clinopyroxene, green amphibole, orthopyroxene and olivine by brown amphibole and phlogopite is much less marked than in the core of the pipe.

Significant accessory phases such as



Fig. 3 - Schematic section of the ultramafic pipe and the host amphibole gabbro (not to scale). A: Underground view of the contact between the ultramafic pipe and the host gabbro. B: Relationships between silicates (olivine, orthorhombic pyroxene, phlogopite) and interstitial sulfides. This is the rim portion of the pipe where the ore is contained. C: The central part of the pipe is characterized by very little sulfide mineralization. Poikilitic texture of Ti-rich amphiboles and phlogopites around olivine. Opaques are magnetite, ilmenite, Ti-magnetite and very little pyrhotite. (Ol) Olivine, (Phl) Phlogopite, (Amph) Amphibole.

magnetite and ilmenite are located within olivine and in association with drop-like inclusions of hercynite. Apatite and dolomite are rare but ubiquitous.

Sulphides are very abundant, grading into the ore body, and occur as a dissemination of droplets and nodular patches interstitial to silicates. The typical sulphide assemblage is composed of pyrrhotite, pentlandite, chalcopyrite, with minor cubanite, mackinawite and pyrite. The sulphide assemblage as well as its abundance can vary greatly in different rim portions.

Core portion

The core portion of the pipe shows homogenous textural and petrographic characters, unlike the rim of the pipe. Lithologically it consists of a hydrated peridotite: the texture of the rock is poikilitic, with the presence of centimetric (>3cm) idiomorphic crystals of orthopyroxene, brown amphibole, and phlogopite, containing submillimetric rounded crystals of olivine (fig. 3C). Drop-like inclusions of hercynite are present within orthopyroxene and, in minor amounts, olivine. Clinopyroxene and green amphibole are relics as they are nearly completely replaced by phlogopite and brown amphibole.

Brown amphibole and phlogopite are the most abundant phases in the core portion of the pipe: they are commonly associated to form plagues which replace almost completely clinopyroxene and green amphibole and, in minor amount, orthopyroxene and olivine. Phlogopite replaces brown amphibole in some areas.

Significant accessory phases such as magnetite and ilmenite are located at the contacts between olivine and other phases. Apatite and dolomite are rare but ubiquitous. Sulphide phases are extremely rare: only submillimetric blebs of pyrrhotite \pm pentlandite are present within olivine or at the contacts between olivine and other phases.

MINERAL CHEMISTRY OF SILICATES IN THE PIPE

The composition of olivine is nearly constant in the various portions of the pipe (tab. 1-2; fig. 4): the MgO content ranges between 39.44 and 40.12 wt%, corresponding to Fo₇₅₋₇₇. NiO content ranges between 0.02 and 0.18 wt%, but does not show any correlation with Fo# or silicate-sulphide assemblage, and MnO content plots in a narrow range around 0.30 wt%.

Orthopyroxene (tab. 1-2) has MgO contents ranging between 26.60 and 29.50 wt% (En₆₄₋₇₆), MnO between 0.26 and 0.41 wt%, CaO between 0.10 and 0.50 wt%, while NiO never reaches 0.07 wt%. TiO₂ and Cr₂O₃ contents both range between 0.05 and 0.15 wt%. A significant difference in the Cr content is noticed between those crystals which are almost completely replaced by Cr-rich brown amphibole and those which are still relatively well preserved, the former being the most depleted in this element.

Clinopyroxene (tab. 1-2) was found almost exclusively in the rim portions of the pipe: its composition is diopsidic, with Cr_2O_3 contents ranging between 0.26 and 0.37 wt%. Na₂O and TiO₂ contents ranging between 0.74 and 1.12 and between 0.26 and 0.80 wt% respectively. The X_{Mg} of clinopyroxene is, on average, higher than that of olivine and orthopyroxene.

Two types of amphiboles were found, a green and a brown one. The former belongs to the primary paragenesis, while the latter crystallised later and replaced orthopyroxene, clinopyroxene and green amphibole. Both green and brown amphiboles are Mghastingsites (tab. 1-2): the brown one contains on average around 15 wt% MgO, while the green contains on average around 16 wt% MgO. Brown amphibole has significant TiO₂ and Cr₂O₃ contents, respectively higher than 2.00 and higher than 0.39 wt% and up to 3.35 and 0.73 wt%; alkalis also are relatively high, Na_2O and K_2O being respectively higher than 3.28 and 0.44 wt%, and up to 3.58 and 0.84 wt%. Green amphibole has very little TiO₂ and Cr_2O_3 , the former being lower than 0.25 wt% and the latter being lower than 0.13 wt%. Na₂O

Electron microprobe representative analyses of minerals from the core portions of Valmaggia ultramafic pipe (wt%). Samples housed in the Geology Department, University of Milano, Italy 1. Sample I 2, Level 691m, Valmaggia; 2. SampleM 7, Level 648m, Valmaggia

	Olivine				Pyroxen	9		Amp	hibole		Phlogopite	
samples	<u> </u>	Ι	1		1	1	2	2	<u>1</u>	Г	T	
SiO ₂	39.20	39.27	38.78	52.12	52.11	50.99	41.86	41.41	41.60	41.56	37.30	
TiO_2	0.02	0.00	0.00	0.07	0.15	0.35	0.32	1.28	2.73	3.35	4.52	
$Al_2 \tilde{O}_3$	0.00	0.00	0.00	2.66	5.72	1.20	15.75	15.28	14.59	14.23	17.19	
Cr_2O_3	0.03	0.01	0.02	0.07	0.06	0.06	0.06	0.13	0.47	0.42	0.42	
Fe ₂ O ₃	0.00	0.00	0.00	5.43	1.24	6.23	5.65	4.09	6.45	5.41	0.00	
FeO	21.01	20.92	20.48	10.62	13.96	0.00	1.67	3.64	2.40	3.57	6.97	
MnO	0.29	0.33	0.31	0.31	0.36	0.15	0.10	0.06	0.15	0.15	0.00	
NiO	0.10	0.09	0.11	0.07	0.08	0.07	0.08	0.02	0.00	0.00	0.09	
MgO	39.89	39.16	40.14	28.75	26.76	17.95	16.15	15.76	15.09	14.86	20.36	
CaO	0.00	0.02	0.02	0.11	0.27	23.61	11.93	11.97	10.45	10.61	0.00	
Na ₂ O	-	-	-	0.00	0.00	0.26	3.17	3.40	3.54	3.38	1.54	
$K_2 \tilde{O}$	-	-	-	0.00	0.00	0.00	0.46	0.42	0.44	0.49	8.00	
$\tilde{H_2O}$	-	-	-	-	-	-	2.09	2.08	2.09	2.09	4.18	
Total	100.55	99.80	99.86	100.21	100.71	100.87	99.30	99.54	100.01	100.11	100.57	

Electron microprobe representative analyses of minerals from the rim portions of Valmaggia ultramafic pipe (wt%). Samples housed in the Geology Department, University of Milano, Italy 1. Sample I 3, Level 691m, Valmaggia; 2. Sample I 7, Level 691m, Valmaggia

3. Sample 110, Level 691m, Valmaggia

samples	Olivine			Pyroxen	e			Phlogopite			
	1	2	1	2	1	3	1	1	1	1	1
SiO2	38.87	39.07	54.29	53.41	52.41	41.89	41.22	41.06	41.50	41.23	36.76
TiO2	0.00	0.00	0.08	0.07	0.08	2.53	2.46	2.94	0.20	0.17	4.34
Al2O3	0.00	0.00	1.63	2.59	4.17	13.90	14.45	13.91	15.67	15.52	16.69
Cr2O3	0.08	0.00	0.16	0.18	0.37	0.61	0.59	0.80	0.04	0.06	0.42
Fe2O3	0.00	0.00	2.26	2.71	2.57	4.16	4.77	3.35	9.22	8.75	0.00
FeO	21.95	21.73	12.67	11.62	2.66	4.92	4.51	5.14	0.00	0.35	8.29
MnO	0.25	0.28	0.39	0.28	0.10	0.08	0.14	0.08	0.12	0.06	0.03
NiO	0.02	0.06	0.02	0.02	0.08	0.02	0.03	0.02	0.00	0.07	0.00
MgO	39.44	39.65	28.93	28.85	15.71	15.06	14.86	15.14	16.34	15.81	19.21
CaO	0.01	0.04	0.23	0.43	21.14	11.46	11.41	11.83	11.83	11.59	0.00
Na2O	-	_	0.00	0.00	1.12	3.13	3.12	2.90	3.02	3.11	0.42
K2O	-	-	0.00	0.00	0.09	0.72	0.84	0.82	0.23	0.26	9.57
H2O	-	-	-	-	-	2.09	2.08	2.07	2.11	2.08	4.10
Total	100.62	100.83	100.68	100.17	101.22	100.56	100.48	100.07	100.29	99.06	99.83



Fig. 4 - Microprobe analyses of olivine crystals in various textural settings of the ultramafic pipe do not show any significative difference in composition. Note that the Ni content of olivine is unrelated to the magnesium content.



Fig.5 - Microprobe analyses of primary (green) and secondary (brown) amphibole crystals. The primary green amphibole (Ti-poor) has lower average K content.

content is very similar to that of brown amphibole, while K_2O is lower, ranging between 0.23 and 0.32 wt% (fig. 5).

Mica composition is essentially a titanian annite-phlogopite solid solution (tab. 1-2), shifted towards the phlogopite end-member (fig. 6). MgO content ranges between 19.21 and 21.14 wt%, K_2O between 6.96 and 9.96 wt%, Na_2O is higher than 0.42 wt%, Cr_2O_3 ranges between 0.28 and 0.47 wt% and TiO₂ is in all cases higher than 3.14 wt%. The Na/K ratio of mica is higher in the core portion of the pipe with respect to the rim portion.

METALLOGENIC FEATURES OF THE PIPE AND OF THE HOST GABBRO

A schematic overview of the various mineralised zones of the pipe and the host gabbro is shown in fig. 3, and selected sulphide analyses are in tab. 3.

Ore hosted in the rim portions of the pipe

The rim portions of the pipe host the mined ore body, which is distributed along a 2-4 mwide band at the contact with the host gabbro. The sulphides are, in order of decreasing abundance: pyrrhotite, pentlandite. chalcopyrite, cubanite, isocubanite, mackinawite, sphalerite, Pd-Pt melonite. Violarite and minor valleriite are common secondary minerals. Associated to the Base Metal Sulphides (BMS) are: ilmenite, magnetite, Ti-magnetite, graphite and Ag-Pb-Bi tellurides.

Sulphides occur both as a dissemination of droplets and as nodular patches filling spaces between silicates: the size of these patches ranges between 1mm and 1-2 cm, with some tennis ball-like sulphide aggregates exceeding 5 cm in diameter. Sulphide patches may penetrate along amphibole crystallographic planes; sulphides also form millimetric blebs



Fig. 6 - The last growing silicate is phlogopite that locally replaces the amphiboles. The phlogopite plots in a restricted compositional field sharply separated from that of the brown micas of the host gabbro.

Electron microprobe representative analyses of Fe-Ni-Cu sulfides from Valmaggia ultramafic pipe (wt%). Specifc description of each type of sulfide in the text: (a) monocline pyrrhotite, (b) pyrrhotite in aggregates, (c) buck shot texture, (d) flame-like exsolutions, (e) veins, (f) associated to drop-like

		Pyrrhotite												
Туре	a	a	a	b	b	b	с	с	c	•				
Sample	1	1	1	2	2	2	3	2	2					
Co	0.11	0.10	0.11	0.07	0.11	0.11	0.10	0.11	0.06					
Pt	0.07	0.13	0.12	-	-	-	-	-	-					
Ni	0.55	0.64	0.48	0.03	0.05	0.12	0.00	0.03	0.00					
S	38.42	38.63	39.10	36.32	36.11	36.23	36.39	36.39	36.21					
As	0.21	0.20	0.18	-	-	-	-	-	-					
Fe	59.21	58.99	58.75	63.35	63.08	63.20	62.93	63.31	63.26					
Те	0.02	0.00	0.00	-	-	-	-	-	-					
Pd	0.00	0.00	0.02	-	-	. –	-	-	-					
Pb	0.79	0.83	0.90	-	-	-	-	-	-					
Bi	0.16	0.26	0.07	-	-	-	-	-	-					
Cu	-	-	-	0.00	0.00	0.00	0.00	0.03	0.08					
Total	99.54	99.78	99.73	99.77	99.35	99.66	99.42	99.87	99.61					

which are included in olivine and orthopyroxene.

Pyrrhotite is the most abundant sulphide mineral. When in blebs pyrrhotite is usually the only sulphide, it is extremely rich in Fe and has a hexagonal structure. Rarely it can be associated to lamellar pentlandite. When in nodular patches pyrrhotite is usually monoclinic and is associated to other sulphides, among which the most abundant and common ones are pentlandite and chalcopyrite.

Pentlandite forms irregularly shaped patches in association with pyrrhotite and other sulphides. Pentlandite crystals are euhedral and contain dendritic and lamellar exsolutions of isocubanite and mackinawite. Pentlandite, occurring as an unmixing flame-shaped phase, is located along the lamellar planes of pyrrhotite or in cross-cutting veins. Finally, pentlandite can rarely be associated to droplike pyrrhotite. Compositional differences among various pentlandite crystals in different textural settings are outlined in fig. 7. Pentlandite is commonly extensively substituted by violarite, which grows preferentially along fractures and often completely replaces pentlandite.

All other BMS are much less abundant than pyrrhotite and pentlandite. Chalcopyrite is never associated to blebs of pyrrhotite, but it forms patches of various size together with other sulphides. It shows unmixing lamellar structures of cubanite. Chalcopyrite can also form drop-like inclusions inside patches of pyrrhotite, (g) euhedral crystals, (h) euhedral crystals containing merenskyte type tellurides. Samples housed in the Geology Department, University of Milano, Italy 1= Sample I 8, Level 691m, Valmaggia; 2= Sample I 1, Level 691m, Valmaggia; 3= Sample I 3, Level 691m, Valmaggia; 4= Sample M 9, Level 648m, Valmaggia; 5= Sample M 12, Level 648m, Valmaggia; 6= Sample I 7, Level 691m, Valmaggia

Chal	lcopyrite		Pentlandite									
	_	d	d	e	f	g	h	g				
6	6	3	3	3	5	3	5	3	2	4		
0.06	0.09	1.38	1.62	2.56	2.07	2.80	2.42	2.97	0.05	0.05		
-	-	-	-	-	-	-	-	-	-	-		
0.07	0.05	25.26	26.94	25.69	28.27	27.91	30.65	28.43	0.01	0.04		
35.10	35.11	33.76	33.23	33.38	33.36	32.98	33.12	33.21	35.16	34.95		
-	-	0.12	0.10	0.06	-	0.09	-	0.09	-	-		
30.38	30.32	39.76	38.04	37.87	36.74	35.70	31.29	35.37	41.05	40.12		
-		-	-	-	-	-	0.45	-	-	· _		
-		-	-	-	-	-	0.15	-	-	-		
-		-	-	-	-	-	-	-	-	-		
-		-	-	-	-	-	-	-	-	-		
33.31	33.10	-	-	-	0.00	-	0.00	-	22.23	23.86		
98.92	98.67	100.28	99.93	99.56	100.44	99.48	98.08	100.07	98.50	99.02		

pyrrhotite, or intergranular films which crosscut already formed silicates. Cubanite forms lamellar millimetric inclusions within chalcopyrite, or more rarely, allotriomorphic patches within pentlandite. Isocubanite is usually associated to mackinawite and as a dendritic unmixing phase within pentlandite.

Mackinawite is included within pentlandite either as dendritic or as unmixing lamellae. Timagnetite can be associated to pyrrhotite and/or pentlandite as allotriomorphic submillimetric crystals. It can also occur as isolated, idiomorphic crystals in intergranular position. Ilmenite either forms lamellae included within Ti-magnetite, or it occurs as single crystals in contact with hercynite. Sphalerite is rare and is found only as allotriomorphic submillimetric inclusions within patches of pyrrhotite and pentlandite. Primary magnetite is associated to hercynite. It occurs as rounded crystals and as exsolutions within orthopyroxene and amphibole. Secondary magnetite is abundant within serpentine veins and commonly shows a dendritic shape. Molybdenite and graphite are accessory phases, while Ag-Pb-Bi tellurides and Pd-Pt melonite seem to be peculiar of this deposit and occur as a fine dissemination within monoclinic pyrrhotite crystals forming nodular patches.

Ore hosted in the core portion of the pipe

In the core portion the Fe-Ni sulphide and Fe-Ti oxide mineralisation are quantitatively



Fig. 7 - The different types of pentlandite are defined according to their textural position: in flame-like exsolutions (full squares), in filling veins (open squares), in euhedral crystals (open diamonds), and associated to drop-like pyrrhotite (full diamonds).

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poor: the mineral assemblage is made up of pyrrhotite, pentlandite, ilmenite, magnetite and Ti-magnetite. Pyrrhotite is hexagonal and is the most abundant sulphide: it forms buck-shot textures or droplets occurring mainly within olivine crystals, but also along the intergranular boundaries of silicates. In the former case pyrrhotite is usually associated to ilmenite and hercynite, in the latter mostly to magnetite.

Pentlandite is extremely rare, and no Cubearing phase has been detected.

Ore hosted in gabbro

Minor stockwork ore is hosted in the enclosing gabbro. When present, sulphide mineralisation is restricted along the sharp contacts with the pipe and can reach up to 1-2 metres in thickness. In the gabbro the sulphides occur as irregularly shaped patches never exceeding 3-4 mm in size along intergranular boundaries of silicate minerals.

The ore assemblage comprises pyrrhotite, pentlandite and chalcopyrite, with violarite and goethite as accessory phases. Pyrrhotite is the most abundant sulphide and occurs either as idiomorphic crystals or as inter- and intragranular films: the former show the typical hexagonal to monoclinic pyrrhotite breakdown texture, the latter are embedded along brown amphibole crystallographic planes. Pyrrhotite is partially replaced by chalcopyrite. Pentlandite forms subidiomorphic crystals along pyrrhotite grain boundaries, and it shows flame-shaped exsolutions orthogonal to grain boundary. Pentlandite is commonly partially substituted by violarite.

Chalcopyrite is rare but more abundant here than within the pipe: it forms either millimetric blebs included in pyrrhotite or, more often, intergranular films in the silicatic matrix.

PGE, PGM and Ag-Bi-Pb tellurides

Ferrario *et al.* (1982) first pointed out the existence of subeconomic concentrations of Pd and Pt in the Ivrea-Verbano Zone: PGEs were described to form discrete phases, mainly tellurides, associated with massive and

disseminated sulphide concentrations. In the present study, 6 samples from the Valmaggia pipe were analysed for PGEs. PGE whole-rock content is low, ranging from 3.2 to 41 ppb (tab. 4), and enriched in Pt and Pd (fig. 8), thus confirming the Pt and Pd enriched patterns of Garuti et al. (1990; 2001). These patterns are similar to those of other pipes in the area (i.e. Castello di Gavala, Bec d'Ovaga and Fej di Doccio), and are the most primitive of the Ivrea-Verbano Zone (Garuti et al., 1990). The PGE chondritic profiles of sulphide-poor and sulphide-rich portions are broadly similar and seem to reflect the primary PGE content of the magma. Nonetheless, lower values were found in the core of the pipe and higher values in its sulphide-rich rim portions.

Garuti *et al.* (1986b) described in detail the mineralogy of the PGM, which mainly include melonite-group tellurides (such as merenskyite and moncheite), Ir sulfarsenides (irarsite), Ag-Bi-Pb tellurides (such as hessite, altaite and fine mixtures of hessite and pilsenite), and Au-Ag alloys (electrum) occurring at different localities in the Basic Complex. In the present study PGM were observed within pentlandite grains, occurring in nodular patches, in the form of small (less than 10 microns) euhedral grains of the melonite-merenskyte group (Ni, Pd)Te₂, with up to 15 wt% Pd (Fiorentini, 1999; Ferrario *et al.*, 2000). PGM-bearing pentlandite can contain up to 0.15 wt% Pd.

Small euhedral grains (less than 10 microns) of Ag, Bi and Pb tellurides are common and usually included within monoclinic pyrrhotite. The tellurides comprise altaite (PbTe), the most abundant species with minor Fe and highly variable Bi, Bi-telluride with minor Fe and Ag, and hessite (Ag₂Te), with minor Fe (tab. 5).

DISCUSSION AND CONCLUSIVE REMARKS

In spite of non conclusive isotopic and age data, that show extensive overlap between pipes and Basic Complex, field, textural and petrographic data support an intrusive origin of the pipe, as suggested also by Garuti *et al.*,

Pipe Name	Sample	Os	Ir	Ru	Rh	Pt	Pd
Valmaggia	I 1	<2	0.3	<5	0.7	20	20
	I 2	<2	< 0.1	<5	0.2	<5	3
	I 3	<2	< 0.1	<5	< 0.2	18	3
	I 4	na	na	na	na	7.4	6
	I 6	na	na	na	na	<5	6
	I 7	na	na	na	na	<5	8
	M 12	<2	< 0.1	<5	0.8	18	18
	VM 123*	nd	0.7	nd	1.1	nd	nd
	VM 1304*	8	9.4	nd	3.7	33.5	75.7
	VM 1316*	nd	1.9	nd	2.3	58.7	36.9
Castello di Gavala	GV 1232*	33.3	23.7	25.2	19.5	114.6	76.5
	GV 1262*	nd	0.4	6.5	nd	107.7	39.6
	GV 1265*	19.6	15.3	16.5	7.1	97.4	66.1
	GV 1279*	nd	nd	nd	nd	nd	81.6
	GV 1280*	28.7	22.6	28.7	18.5	162	89.4
Bec d'Ovaga	BO 04*	13.1	10.8	14.3	10.9	85.5	143.7
U	BO 1270*	4.3	4.3	6.2	4.9	37.5	130.4
Fej di Doccio	FD 1*	nd	0.4	nd	nd	nd	nd
U	FD 3*	15.5	11.5	8.9	4.4	48.5	84.4
	FD 6*	nd	0.5	nd	nd	nd	nd

 TABLE 4

 PGE whole rock contents analyzed with ICP-MS (ppb)

(*) data from Garuti et al.. 1990.

(2001). Pipes inside the Basic Complex and within other host rocks show similar features, the contacts, well and extensively exposed inside the mine, is sharp and sometimes mineralization intrudes the gabbro, finally even if many ages overlap Biino and Meisel (1996) found a Re-Os age of Valmaggia pipe of 217 ± 6 Ma, much younger than the age of host gabbro.

On the basis of a broad but partially contrasting set of data, Garuti *et al.* (2001) concluded that the whole set of geochemical features that characterises the ultramafic pipes fits a model in which high-Mg hydrous magmas, enriched in volatiles and incompatible elements with an alkaline signature, were produced by metasomatism of a depleted mantle source and then intruded into the deep crust of the Ivrea-Verbano Zone during the late Carboniferous. They also concluded that the melt, according to their S, Nd and Sr data, did not undergo any significant crustal contamination during its ascent.

Field observations and textural and petrographic analyses carried out in the present study at the pipe-gabbro sharp contact do not show any significant interaction between the intruding ultramafic melt and the host rock, thus confirming the already assessed lack of contamination after emplacement within the mafic unit. The distribution of mineral phases, their composition and their textures also show that the pipe emplacement occurred within a relatively cold gabbro. The significant difference in temperature between the pipe and the host rock can explain the absence of



Fig. 8 – Chondrite-normalised patterns of Platinum Group Elements and gold. Data for Castello di Gavala, Bec d'Ovaga and Fej di Doccio are from Garuti *et al.*, (1990).

assimilation processes: the very small mass of melt intruding the gabbro could not provide enough heat to cause partial melting of any mineral phase within the host rock.

The core-rim distribution of the silicatic phases within the pipe shows that crystal fractionation occurred along a rim-to-core vector, and that cooling was not driven by gravity, with the late stage phases, such as brown amphibole and phlogopite, being concentrated in the core of the pipe. The rimto-core zoning observed in the silicatic paragenesis is not associated with a similar zoning in their mineral chemistry: on average, the composition of silicates does not change significantly from rim to core. The only silicatic phase that significantly changes its composition is amphibole, with Ti-rich brown amphibole extensively replacing the Ti-poor green one in the core of the pipe. We suggest that the change in amphibole composition was related to the capability to accept Ti and Cr, elements that could not form oxydes (i.e. rutile and ilmenite and chromite) due to the very low oxygen fugacity of the melt (Garuti *et al.*, 1986a) and were therefore strongly concentrated in the residual melt. Substitution of green amphibole by brown amphibole

Electron microprobe representative analyses of tellurides from the rim portions of Valmaggia ultramafic pipe (wt%) Samples housed in the Geology Department, University of Milano, Italy

1. Sample I 8, Level 691m, Valmaggia; 2. Sample I 1, Level 691m, Valmaggia; 3. Sample M12, Level 648m, Valmaggia

		Altaite				Wehrlite			h tellurid	es	Hessi	Hessite Merens	
Samples	1	1	1	2	1	2	1	1	2	2	1	2	3
Co	0.02	0.02	0.09	0.02	0.02	0.03	0.07	0.06	0.06	0.03	0.00	0.04	0.32
Pt	0.00	0.00	0.00	0.00	1.30	1.08	0.00	0.00	0.00	0.00	0.15	0.17	0.98
Ni	0.05	0.00	0.47	0.04	0.02	0.06	0.08	0.08	0.18	0.06	0.00	0.01	7.13
S	0.23	0.21	0.16	0.22	0.20	0.20	0.35	3.59	9.04	1.38	0.24	0.30	3.84
As	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
Fe	2.35	2.36	2.18	2.33	2.36	2.41	3.91	4.57	15.48	5.15	1.68	1.15	2.50
Te	38.28	37.33	33.40	37.82	29.45	29.00	35.71	33.66	22.80	34.96	32.61	33.09	48.90
Pd	0.03	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	15.27
Pb	59.09	58.24	53.45	57.44	6.05	7.22	55.37	50.30	33.45	56.82	5.77	6.19	0.43
Bi	0.75	0.87	6.11	2.67	52.56	51.70	3.96	2.36	0.50	0.98	0.37	0.06	20.33
Ag	0.01	0.01	3.85	0.02	7.50	7.50	0.00	4.55	17.55	0.00	56.85	57.03	0.00
Total	100.81	99.04	99.72	100.56	99.46	99.20	99.46	99.17	99.06	99.38	97.67	98.04	99.70

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reflects disequilibrium of earlier green amphibole with a highly residual Cr and Tienriched melt.

Petrography, texture and mineral chemistry of silicates thus suggest that crystallisation occurred at low oxygen fugacity condition and started with olivine, whose high Fe content is related to the reduced conditions of Fe in the melt (Garuti *et al.*, 1986a). Crystal fractionation was driven by temperature gradient, and crystallisation proceeded with formation of orthopyroxene and clinopyroxene. Late crystallising phases are brown amphibole and phlogopite: they are abundant and strongly enriched in alkalis, thus confirming the hydrated and metasomatised nature of the melt source.

Early crystallisation of the sulphide melt was dominated by a homogeneous Fe-(Ni)-(Cu)-S phase comparable with a monosulphide solid solution (Mss) (Garuti et al., 1986a). The core of the pipe hosts only very small droplets of sulphides included in olivine (buck-shot textured near-troilite pyrrhotite ± Fe-rich lamellar pentlandite), droplets that are found as inclusions in olivine also in the rim portions of the pipe. Unmixing of a sulphide melt must have occurred quite soon, prior or contemporaneously to olivine crystallisation, probably during ascent of the melt. It is likely that sulphide droplets were entrapped within olivine at high temperature; their composition, similar to the Mss and very different from that of ore sulphides, confirms this hypothesis.

The Mss crystallised during the first stages of cooling in a very restricted temperature range, and concentrated within the rim portions of the pipe. The present sulphide assemblages were formed entirely by subsolidus exsolution from the Mss upon cooling (Garuti *et al.*, 1986a). Silicate minerals crystallised over a much wider temperature range, due to the high water and alkalis content of the melt. On the basis of textural evidences and mineral compositions we suggest that the pipe is mainly composed of a crystal mush made up of relatively low Fo olivine including buck-shot textured Fe-Ni sulphides (near-troilite pyrrhotite \pm Fe-rich lamellar pentlandite) and hercynite, which is cemented by products of the residual liquid. Accumulation of the crystal mush occurred first near the rim of the pipe; the residual melt, containing crystals of the same nature, concentrated in the core of the pipe and being no more in equilibrium with cumulitic phases caused extensive substitution of them by late brown amphibole and phlogopite.

PGE chondritic profiles of sulphide-poor and sulphide-rich portions are overall similar and reflect the primary PGE content of the magma. Enrichment in Pt and Pd compared with both chondrite (Naldrett and Duke, 1980) and primitive mantle (Barnes et al., 1988) is probably due to a process that occurred in the mantle before the ascent of melt into the crust. In particular, lower PGE values were found in the core of the pipe and higher values were found in its sulphide-rich rim portions, consistent with the incompatible and chalcophile behaviour of PGEs in a sulphursaturated system (Amossé et al., 1987; Naldrett, 1989; Fleet et al., 1993; Peck and Keays, 1990; Keays, 1995;).

Garuti *et al.* (2001) showed similarities of mineral assemblages in the Ivrea pipes with those of metasomatised mantle xenoliths (Haggerty, 1995; Ionov, 1998); however this conclusion is at odds with the observed Pt and Pd-enriched pattern which characterises the pipes, since mantle xenoliths show an opposite trend (Lorand and Alard, 2001).

Garuti *et al.* (2001) suggested a common origin for the agents that caused the metasomatic events in the source of the melts that produced the ultramafic pipes and in the Finero peridotite. Yet parallelism of all PGE patterns at Valmaggia and other pipes argues for absence of metasomatic processes; unlike Finero, the pipes do not show any PGE fractionation (Garuti *et al.*, 1990). In Finero metasomatic processes strongly affected PGE distributions and resulted in a variety of different PGE patterns depending on grade and modality of metasomatic processes(Grieco *et al.*, 2001).

The age determinations are again not

conclusive, anyway for the pipes age was estimated at 292 to 288 Ma (Garuti *et al.*, 2001), similar to the 285 Ma age of the diorites of the mafic unit (Pin, 1986) and much older than the 207.9 Ma of the metasomatic process in Finero (Grieco *et al.*, 2001), or to 217 \pm 6 Ma, that, even if much closer, is anyway older than the age of metasomatism in Finero.

A process for melt origin alternative to the refertilisation of a depleted mantle (Garuti et al., 2001) and that, in our opinion, can better explain the whole set of data and the age relationships, is a low degree of partial melting of a fertile mantle, that can similarly produce melts enriched in incompatible elements, alkalis and water (Menzies, 1990). A melting event is recorded in the Ivrea Verbano Zone by the strongly restitic peridotite at Finero. This event, older than 207 Ma, could be related to the production of parental melts of the pipes Metasomatism at Finero occurred later and refertilised the restitic peridotite, but was unrelated to the production of melts that formed the pipes.

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