

Platinum group and related minerals from the Ivrea-Verbano sulfide deposits

GIORGIO GARUTI, ROMANO RINALDI *

Istituto di Mineralogia e Petrologia dell'Università, Via S. Eufemia 19, 41100 Modena

ABSTRACT. — A systematic electron microprobe and reflected light microscopy investigation was carried out on a considerable number of Pd-, Pt-, Ni-, Ag-, Pb-, and Bi-telluride grains and associated Co-, Ni-, Fe-, and Ir-sulfarsenides from the Ivrea-Verbano sulfide deposits. The analytical data confirm the existence of solid solution among the melonite-group tellurides melonite, merenskyite, and moncheite although with the possibility of a miscibility gap corresponding to the Pd-poorer compositions. Although experimental confirmation is needed, restricted phase relations seem to exist in the Pd-Pt-Ni-Te quaternary system, when considering coexisting composition. Different paragenetic associations of the tellurides are found in the sulfide deposits possibly related to the different geological settings and different textures of the sulfide, sometimes indicating late to post magmatic mobilization.

Key words: platinum group minerals, tellurides, electron probe microanalysis, Ivrea-Verbano.

RIASSUNTO. — Uno studio sistematico in luce riflessa e in microsonda elettronica ha consentito l'individuazione e caratterizzazione chimica di un gran numero di tellururi di Pd, Pt, Ni, Ag, Pb, Bi, e di solfarseniuri di Co, Ni, Fe e Ir ad essi associati nei depositi a solfuri dell'Ivrea-Verbano. I dati analitici confermano l'esistenza di una soluzione solida tra i tellururi melonite, merenskyite e moncheite, anche se è probabile la presenza di una lacuna di miscibilità tra le composizioni più povere in Pd. Inoltre se si prendono in considerazione le composizioni di grani coesistenti alla scala del campione, sembrano emergere relazioni di fase più restrittive all'interno del sistema quaternario Pd-Pt-Ni-Te, anche se queste necessitano di conferma sperimentale. I depositi a solfuri presentano differenti associazioni paragenetiche dei tellururi correlabili al diverso assetto geologico ed al diverso

tipo tessiturale della mineralizzazione che indica talora una mobilizzazione da tardo a post magmatica del solfuro.

Parole chiave: minerali del gruppo del platino, tellururi, microanalisi elettronica, Ivrea-Verbano.

Introduction

The Fe-Ni-Cu sulfide mineralizations of the Sudbury type, occurring within the Ivrea-Verbano layered intrusion, contain trace amounts of Pd and Pt (FERRARIO et al., 1982) which were recently substantiated by the finding of specific platinum group minerals (PGM) (GARUTI and RINALDI, 1985) along with other precious and heavy metal minerals. The aim of the present work is the identification and complete chemical characterization of a considerable number of grains of such minerals, although their dimensions, mostly in the range of a few micrometers, posed a serious challenge to the technique especially as regards the quantitative analysis. The Pd- and Pt-bearing minerals pertain to the melonite-merenskyite-moncheite solid solution of tellurides, which is part of the melonite group of minerals (FLEISCHER, 1983) with the general formula $(\text{Ni}, \text{Pd}, \text{Pt})(\text{Te}, \text{Bi})_2$ and whose stoichiometries and fields of existence are better defined by the present data. The complete paragenesis includes hessite (Ag_2Te), altaite (PbTe), wehrlite (BiTe), and irarsite (IrAsS) as well as Au-Ag alloys (electrum) and (Co,Ni)-sulfarsenides. The platinum group minerals described represent the first documented occurrence in Italy.

* Now at: Dipartimento di Scienze della Terra, Università di Cagliari, Via Trentino 51, I-09100 Cagliari.

Experimental

The grains of precious minerals were investigated in situ by both reflected light microscopy and systematic SEM scanning of 4 cm diameter polished sections; the total area explored varied from 20 to about 70 cm² for each sample yielding an average of 1 grain per 2-3 cm². The grains were generally very small, ranging from 40 to 5 µm and less in size, thus observation of the optical properties and quantitative microprobe analyses were normally limited to the larger grains (≥ 10 µm). The grains smaller than 10 µm across were at least qualitatively confirmed by electron microprobe. Due to their minuteness and the lack of a specialized technique for their recovery from the sulfide ore, no grain could be extracted for X-ray diffraction, thus attribution to the mineral species was solely based on chemical composition and optical properties. The latter were generally consistent with those listed by CABRI (1981) and RAMDHOR (1980), although slight variations of the anisotropy colours, including a peculiar faint bluish tint were observed in Bi-bearing melonites and merenskyite.

Electron probe microanalysis was carried out in the wavelength dispersive mode with a fully automated ARL-SEM-Q instrument operated at various settings of accelerating voltage and probe current, experimentally established for each mineral species, in order to minimize analytical artifacts mostly due to fluorescence uncertainty and atom migration. On-line data reduction was performed by the use of a modified version of the MAGIC IV program (COLBY, 1968). Analyzing crystals, X-ray lines, and (synthetic standards) were as follows: ADP: TeL α (PdTe₂); PET: PdL α (PdTe₂), PtM α (PtTe), BiM α (Bi and Bi₂Te₃), AgL α (Ag₂S and Ag₂Te), PbM α (PbS and PbTe), AuM α and AgL α (Au Ag); LIF: NiK α (NiCr) and NiAs). Synthetic (Pd,Ni)Te₂ was repeatedly analyzed as reference material for the telluride analyses.

The presence of varying amounts of Fe and S in the microprobe analyses of small telluride grains included in a sulfide matrix has often been considered to represent a true composition (WATKINSON et al., 1978), although these authors did not exclude the possibility of fluorescence from the host base

metal sulfides. During our investigation the presence of induced characteristic fluorescence (fluorescence uncertainty; REED, 1975) was monitored by varying the excitation potential and the distance of the analysis point from the grain boundary on a selection of grains of medium size (5-10 µm across). A marked decrease was obtained in the S and Fe spurious counts by utilizing accelerating voltages in the range between 14 and 15 kV, thereby reducing the interaction volume but still maintaining an effective electron beam in terms of ionization potential (RINALDI, 1985). Confirmation of the quantitative results was obtained by comparison with appropriate sulfide standards. Furthermore, the best analytical results on the telluride grains were obtained by utilizing modest values of the probe current (10-15 nA on brass) to avoid fluctuations of the apparent compositions such as those observed for the silver-gold telluride petzite (RUCKLIDGE and STUMPFL, 1968). These effects, although not fully understood, can be ascribed to migration and/or diffusion phenomena taking place within the electron beam-solid interaction volume in response to local electric field and temperature gradients generated in semiconductor materials.

Paragenetical associations and occurrences

Information on the localities, host sulfide mineralogy and paragenesis of the mineralized samples are listed in table 1. The various sulfide occurrences are grouped according to their different geological settings, following the distinction proposed by BIGIOGGERO et al. (1979): 1) Fe-Ni-(Cu) mineralization in ultramafic fractionation layers in the lower part of the intrusion (cyclic units); 2) Fe-Cu-Ni mineralization in ultramafic fractionation layers of the main gabbro (middle and upper part of the intrusion); 3) Fe-Ni-Cu mineralization in discordant to subconcordant ultramafic bodies (pipes) crosscutting the upper part of the main gabbro or injected into the country roof rocks as offsets (Fei di Doccio).

The sulfides generally occur as interstitial disseminations that are believed to be of magmatic origin although in places they

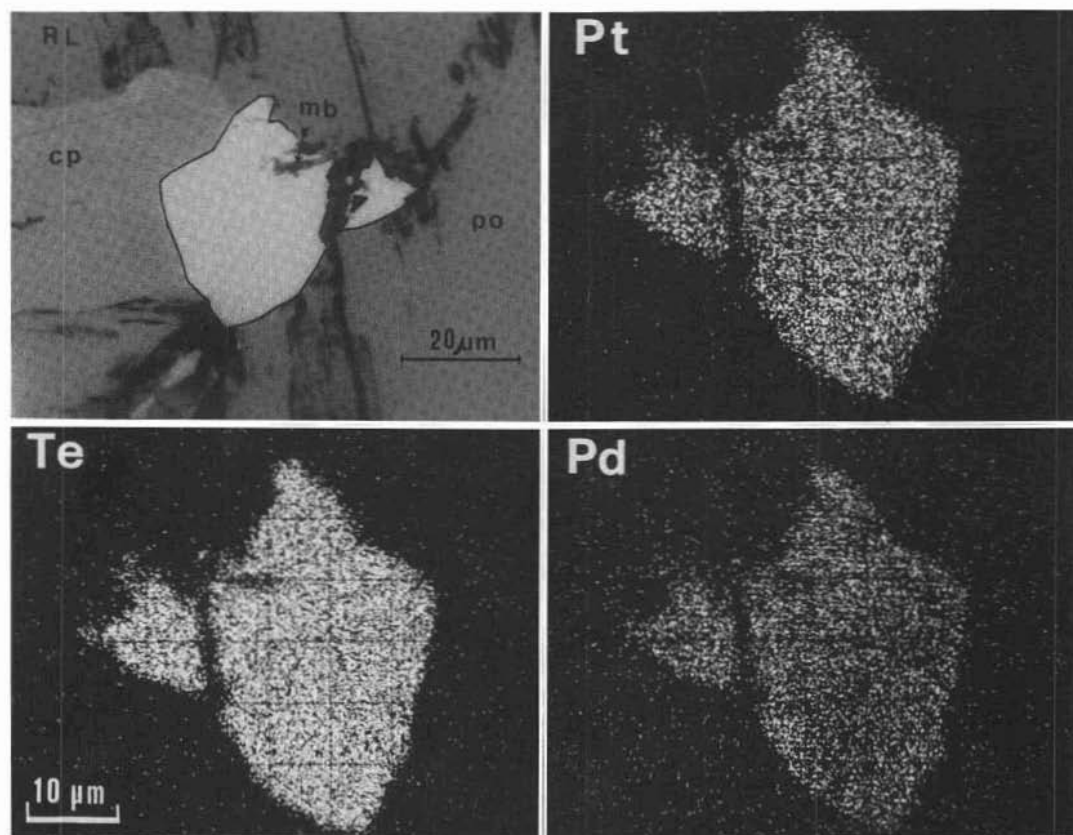


Fig. 1. — Moncheite associated with chalcopryrite (*cp*) and molybdenite (*mb*) in pyrrhotite (*po*); grain SB2PX (analysis 3, table 3). RL = reflected light. (X-ray lines and instrumental parameters as reported in the text apply to all figures).

show to have undergone mobilization and redeposition during late to post magmatic deformation events generating high-grade to massive ore bodies (GARUTI et al., 1986). In the three groups of sulfide occurrence the precious metal minerals are found included in, or in contact with the base metal sulfides pyrrhotite, pentlandite and chalcopryrite without any obvious preference, indicating their origin to be related with the deposition of these phases. Systematic SEM scanning of polished sections did not reveal any of these minerals as free grains within the silicate gangue, although in some cases they were found at the sulfide-silicate contact. Unusual intergrowths of the tellurides are seen at Gula (cyclic units) with molybdenite and cobaltite and at Stella Bassa (main gabbro) with pyrite and molybdenite (see for example fig. 1).

Usually, the melonite group tellurides as well as hessite, altaite and wehrilite occur as blebs, beans, or rods, and other irregular shapes. Idiomorphic growth of crystals is rare, it was observed only for some melonites. Electrum and irarsite are idiomorphic as well as the Ni-Co sulfarsenides that sometimes display a typical skeletal morphology. The three groups of sulfide mineralizations and textural associations show the following different telluride parageneses as reported in table 1.

In the cyclic units, the tellurides are melonite and merenskyite found exclusively in the mobilized sulfide with the typical « breccia cementing texture » (samples BT8, AL7273, IS7276, GU6334 and GU4RM).

This is also the case for most of the samples from the main gabbro (SB1, SB2PX, SB3RM) where moncheite may be present

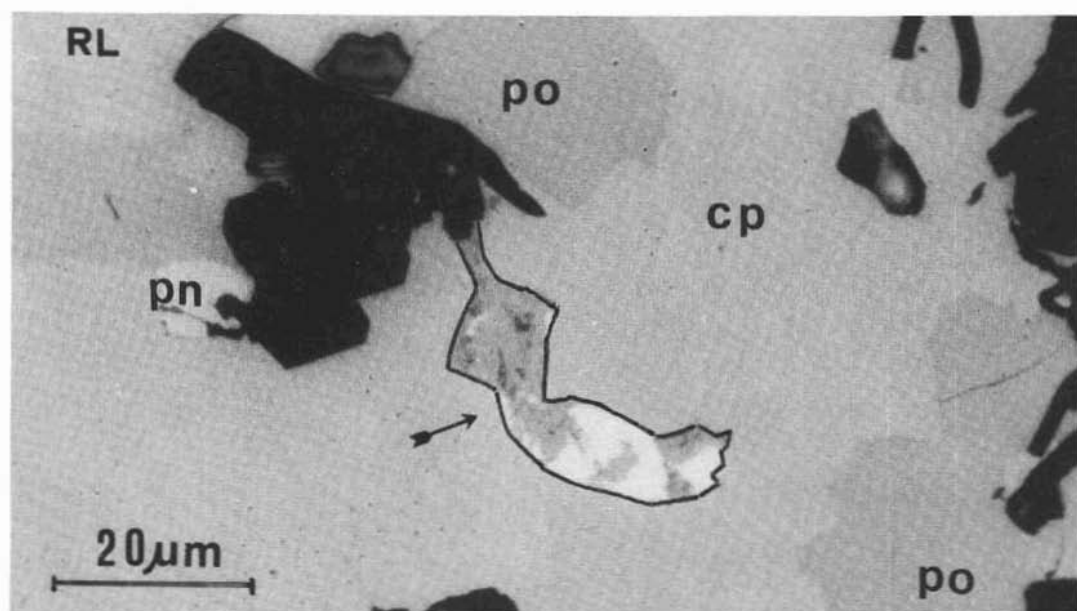
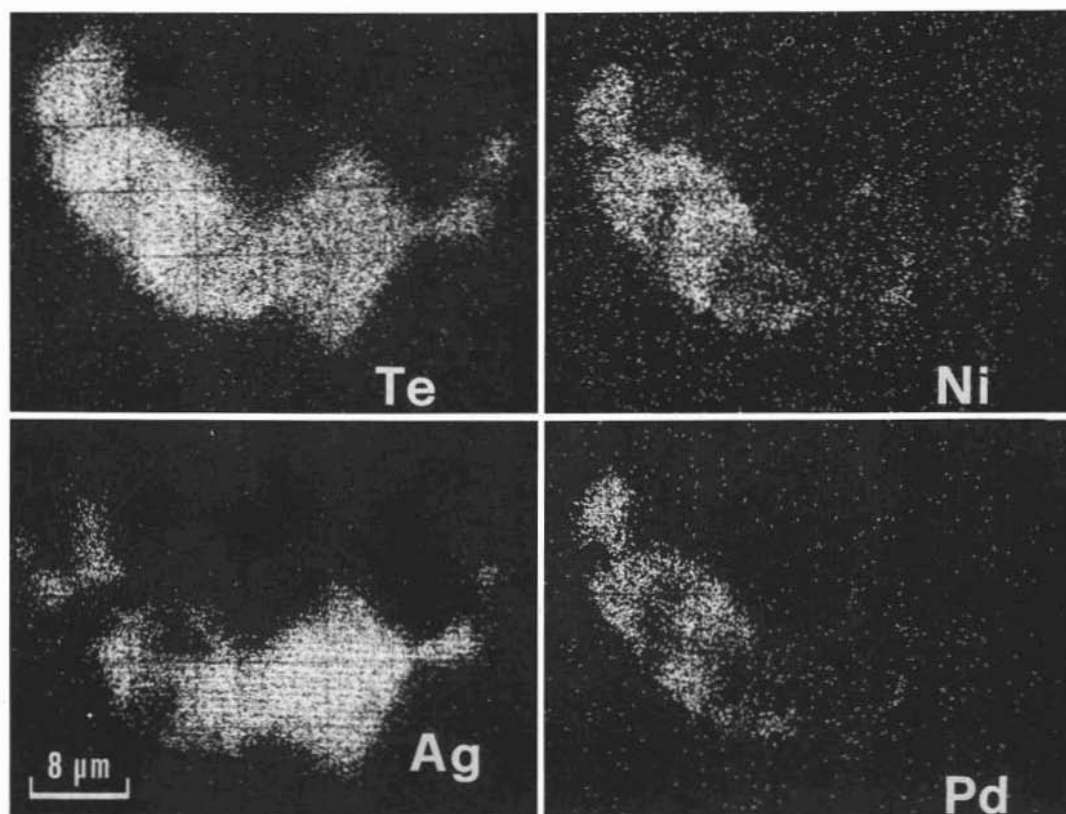


Fig. 2. — Melonite + hessite intergrowth in chalcopyrite, grain VM12E1 1A (analysis 26, table 4).

TABLE 1
Sample locality, sulfide mineralogy, and paragenesis of PGM and related minerals

Setting, Locality	Sample	Sulfide		PGM and
		Type ⁽¹⁾	Assemblage ⁽²⁾	related minerals ⁽³⁾
Cyclic Units				
Bottrorno	BT8	CB	hpo-pn-cp-sph-mb	mr-ml
Alpe Lavaggio	AL7273	CB	hpo-pn-cp-sph	mr-ml
Isola di Vocca	IS7276	CB	hpo-pn-cp-mck	mr-ml
Gula	GU6334	MS	hpo-pn-cp-mck-mb	ml-cb
	GU4RM	CB	hpo-pn-cp-mb	mr
Main Gabbro				
Piancone	PC1220A	ND	mpo-pn-cp-py	ml
Sella Bassa	SBDS	ND	hpo-pn-cp-mb	ml
	SB1	MS	mpo-pn-cp-py	mr-mn-ml
	SB2PX	CB	mpo-pn-cp-py-mb	mr-mn
	SB3RM	MS	mpo-pn-cp-py	mr-ml
Pipes				
Valmaggia	VM1	ND	tr-pn-cp-mck-cbn	ml
	VM3RM	MB	mpo-pn-cp-py	ml
	VM9	MB	mpo-pn-cp-py	ml
	VM12E	ND	hpo-tr-pn-cp-mck	ml-hs-al
Bec d'Ovaga	BO4	ND	hpo-pn-cp-mck	mr-ml
Castello di Gavala	GV1233	ND	hpo-pn-cp	el
Fei di Doccio	FD1	ND	hpo-tr-pn-cp-mb	hs-al-wr-el-cb-gd-ir
	FD3	MB	mpo-pn-cp-py	hs-cb
	FD4	ND	hpo-tr-pn-cp	al-gd
	FD6519	ND	hpo-tr-pn-cp	ml-cb
	FD6531	ND	hpo-pn-cp	hs-cb

(1) CB = cementing breccia, MS = massive, MB = mobilized, ND = nodular.

(2) po = pyrrhotite, hpo = hexagonal po, mpo = monoclinic po, tr = troilite, pn = pentlandite, cp = chalcopyrite, py = pyrite, mb = molybdenite, mck = mackinawite, cbn = cubanite, sph = sphalerite.

(3) mr = merenskyite, ml = melonite, mn = moncheite, hs = hessite, al = altaite, wr = wehrlite, el = electrum, ir = irarsite, cb = cobaltite, gd = gersdorffite.

along with melonite (in one case forming a composite grain, SB1 C 1) and merenskyite. However, a few grains of melonite also occur related with interstitially disseminated sulfide of primary magmatic origin in samples SBDS and PC1220A.

In the pipes, melonite is by far the most important carrier of Pd and Pt. In the primary sulfide mineralization with a nodular texture, it is part of a complex assemblage consisting of hessite, altaite, wehrlite, irarsite, electrum, and sulfarsenides of the cobaltite-gersdorffite series (samples VM1, VM12E, FD1, FD4, FD6519, and GV1233). The following associations were observed as composite grains: melonite + hessite ± altaite (fig. 2); hessite + altaite ±

wehrlite (fig. 3 and 4); cobaltite + hessite; gersdorffite + irarsite. In the mobilized portions of the sulfide mineralization, melonite (and merenskyite in one case) appears as the dominant telluride (samples BO4, VM3RM, and VM9).

Results of the microprobe analysis

Electron microprobe analyses of the tellurides and the associated Ni-Co sulfarsenides are listed in tables 2 to 6, together with the indication of the minerals in contact with the analyzed grain. The symbols reported after the numerals for each analysis consist of the sample name, as reported in

TABLE 2
Electron microprobe analyses of Merenskyite

No	Sample	Assoc. ⁽²⁾	El. wt% ⁽¹⁾						Atomic %				
			Ni	Pd	Pt	Bi	Te	Tot.	Ni	Pd	Pt	Bi	Te
1	BT8 AQ 2	po	3.6	24.8	0.28	0.19	71.1	99.97	7.18	27.29	0.17	0.11	65.25
2	BT8 AQ 3	pn	9.7	18.6	0.10	-	71.7	100.10	18.31	19.37	0.06	-	62.26
3	BT8 Q 1	po	4.0	22.2	0.13	0.26	71.1	97.69	8.15	24.96	0.08	0.15	66.66
4	BT8 CS 1	cp	3.9	23.1	0.24	1.0	71.7	99.94	7.80	25.50	0.14	0.56	66.00
5	BT8 CS 2	cp	7.8	16.3	0.56	2.1	71.8	98.56	15.42	17.78	0.33	1.17	65.30
6	AL7273 2	po	8.1	15.4	1.5	-	75.2	100.20	15.68	16.45	0.87	-	66.99
7	AL7273 3	po	5.1	19.1	1.6	-	73.1	98.90	10.25	21.18	0.97	-	67.60
8	IS7276 1	po	3.2	23.4	0.9	0.47	71.6	99.57	6.47	26.11	0.55	0.27	66.60
9	IS7276 2	po	2.8	23.3	1.3	0.52	71.5	99.42	5.70	26.19	0.80	0.30	67.01
10	SB1 C 2	cp px	3.0	23.4	0.29	2.7	71.3	100.69	6.05	26.05	0.18	1.53	66.19
11	SB3RM 3	po px	1.1	27.5	0.33	-	71.1	100.03	2.24	30.91	0.20	-	66.65
12	BO4 2	cp	6.2	15.7	5.0	4.0	68.0	98.90	12.71	17.76	3.08	2.30	64.15

(1) Sb and Se were tested but not detected; the detected amounts of Fe and S were attributed to fluorescence uncertainty (see text).

(2) Minerals in contact with merenskyite; px = pyroxenes; other abbreviations as in Table 1.

TABLE 3
Electron microprobe analyses of Moncheite

No.	Sample	Assoc. ⁽²⁾	El. wt% ⁽¹⁾						Atomic %				
			Ni	Pd	Pt	Bi	Te	Tot.	Ni	Pd	Pt	Bi	Te
1	SB1 A 2	py po	2.2	6.9	28.3	0.51	62.2	100.11	5.08	8.80	19.68	0.33	66.11
2	SB1 C 1 ⁽³⁾	ml pn	6.9	7.1	18.8	0.66	66.1	99.56	14.66	8.32	12.02	0.39	64.61
3	SB2PX	cp mb	0.55	3.3	37.1	0.18	58.9	100.03	1.35	4.48	27.44	0.12	66.61

(1) Analytical notes as in Table 2.

(2) Minerals in contact with moncheite; abbreviations as in Table 1.

(3) Some Ni could derive from induced fluorescence from the matrix.

table 1, followed by the name of the section and the grain number. The reported compositions were obtained by averaging at least two point analyses with differences within the experimental error. With the exception of one melonite grain (analyses 28 and 29, table 4; see X-ray map in fig. 4), all the minerals appear chemically unzoned.

The melonite group tellurides were classified by plotting their compositions in the

PdTe₂-PtTe₂-NiTe₂ ternary diagram (fig. 5) where analyses from the literature (CABRI and LAFLAMME, 1976; CABRI, 1981; HUDSON and DONALDSON, 1984) are also reported for comparison.

The three telluride minerals melonite, merenskyite and moncheite have trigonal symmetry (P3m1) probably with a niccolite-type structure, in which many of the metal sites may be left vacant either randomly or

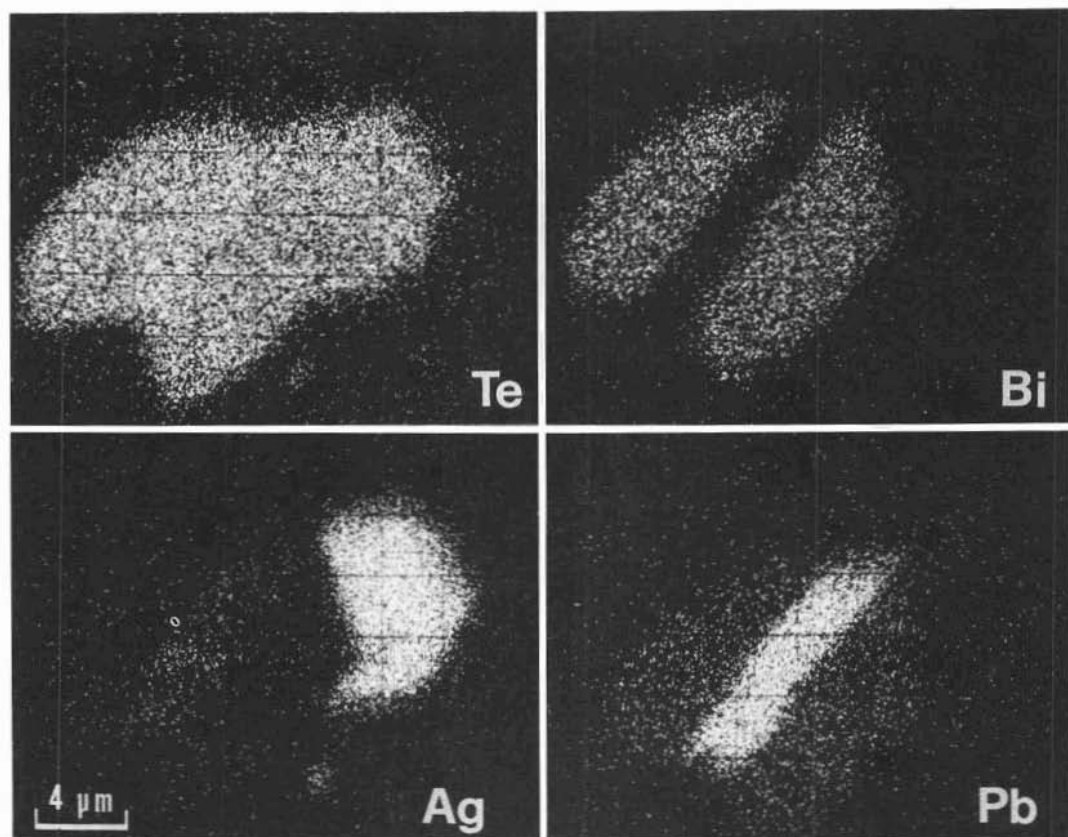


Fig. 3. — Composite grain (FD1 7B) displaying the association of hessite (Ag), altaite (Pb), and wehrilite (Bi). Partial substitutions of Ag and Pb are evident in altaite and wehrilite respectively. The corresponding analyses are reported in table 5 (analyses 9, 10, and 11).

along planes normal to the c axis (VAUGHAN and CRAIG, 1978). This must be frequent for the phase melonite where the existence of a solid solution between NiTe_2 and NiTe has been postulated (RAMDOHR, 1980). As a matter of fact, the anions to cations average ratio of the Ivrea-Verbano melonite is 1.85, thus remarkably lower than those of moncheite and merenskyite, 1.95 and 1.97 respectively. Furthermore, as shown in fig. 6, the $(\text{Te} + \text{Bi})/\text{metal}$ ratio tends to decrease with increasing Ni content therefore giving further support to the existence of a solid solution between melonite and the term NiTe .

Substitution of Bi for Te is frequent, being more pronounced in Pd- and Pt-poor melonites where it reaches a maximum value of 4.36 atomic percent. Therefore these minerals can be classified as bismuthian melonites

(PIISPANEN and TARKIAN, 1984). Figure 7 shows one example corresponding to analysis 16, table 4. Sb was tested but not detected.

Melonite and merenskyite usually contain less than 1 atomic percent Pt and show an almost continuous variation of the Pd/Ni ratio, therefore including mineral phases that, according to the IMA rules for the nomenclature of minerals (HEY and GOTTARDI, 1980), can be referred to as melonite, palladian melonite, Pd-rich melonite, Ni-rich merenskyite and nickelian merenskyite (fig. 8 and 9). End-member merenskyite compositions were not found in the Ivrea-Verbano samples where considerable Ni always substitutes for Pd.

The present data provide further evidence for the postulated existence of a complete solid solution along the $\text{PdTe}_2\text{-NiTe}_2$ join (RUCKLIDGE, 1969; CABRI, 1981). Solid so-

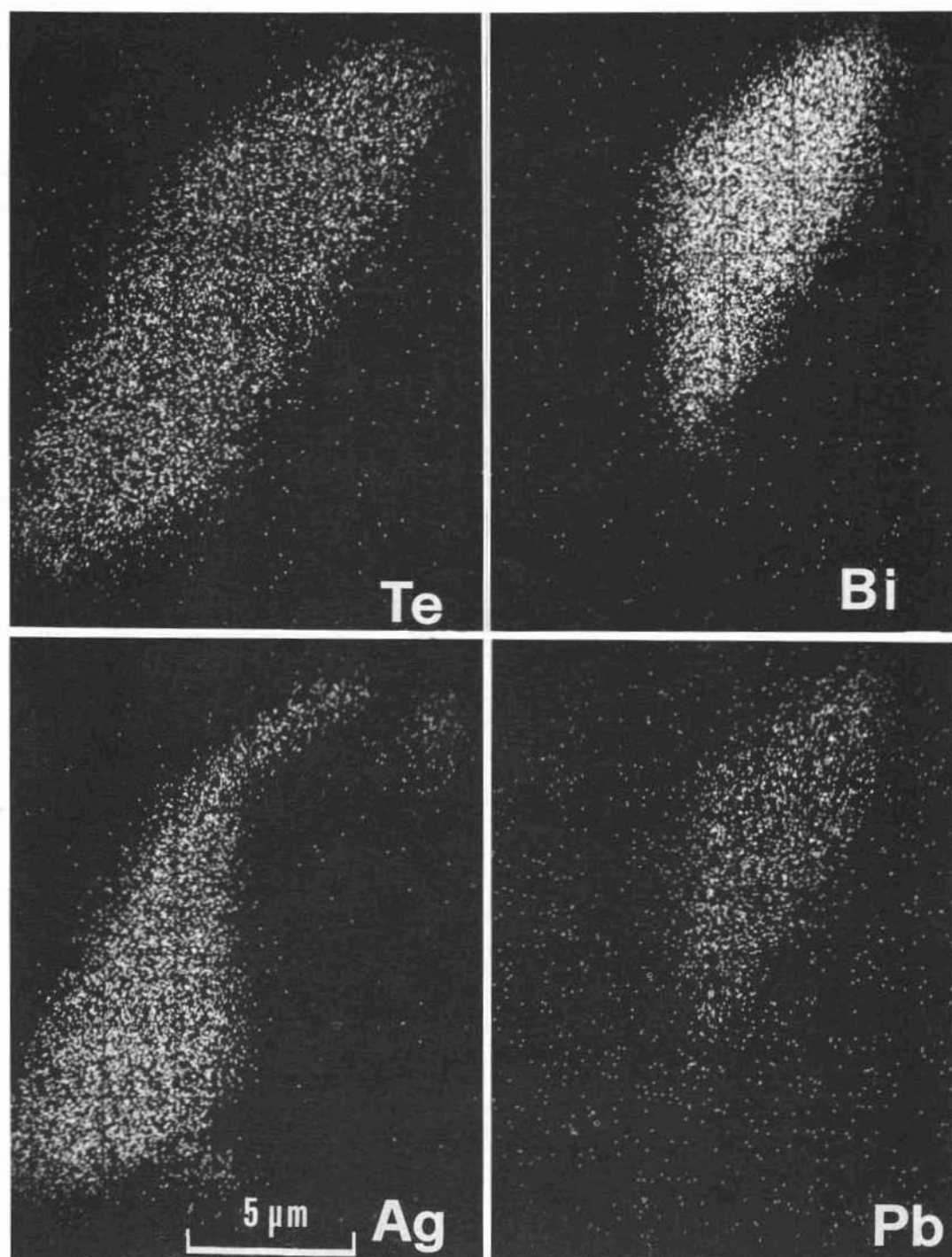


Fig. 4. — Composite grain (FD1 B 1) of hessite (Ag) and wehrlite (Bi) displaying partial substitution of Pb for Bi (analyses 12 and 13, table 5).

lution probably exists also between Ni-poor merenskyite and moncheite (CABRI and LAFLAMME, 1981) and between palladian melonite and palladian moncheite (HUDSON, communication at the 4th International Platinum Symposium, Toronto, 1985). A marked solubility gap seems to exist along the melonite-moncheite join, suggesting the need for considerable Pd substitution to promote solid solution between these two phases. Furthermore, when considering the compositions encountered in the Ivrea-Verbano samples, either within the same hand specimen or even within the same ore locality, the phase relations pertaining to the Ni-Pd-Pt-Te quaternary system seem to undergo a considerably more restrictive rule. In fact no melonite containing less than about 8 atomic percent Pd was found coexisting with merenskyite, nor with members of the palladian moncheite to palladian melonite series.

The composition of hessite is very close to the theoretical stoichiometry Ag_2Te , although minor amounts of Pb and/or Bi may be present especially when hessite is intergrown with altaite and/or wehrilite (see analyses 9 to 15, tab. 5). Altaite shows a slight metal enrichment with respect to Te, which is consistent with compositions reported from Sudbury (CABRI and LAFLAMME, 1976), and always contains substantial amounts of Ag. Only two reliable analyses could be obtained for wehrilite (analyses 11 and 13, tab. 5) because of the small size of the grains and the close association with hessite and/or altaite (see for example fig. 3 and 4) causing induced fluorescence effects. The two analyses show (Bi, Pb, Ag): Te ratios of 1.58 and 1.25 respectively, both within the range between 1.10 and 1.78 observed at Sudbury.

Most of the Ni-Co sulfarsenides were found in samples from the pipes at Fei di Doccio (FD1, FD3, FD6531), only two grains occurred in one sample from the cyclic units at Gula (GU6334) although with distinctive compositions. The sulfarsenides from Fei di Doccio vary from Co-rich gersdorffite to Ni-rich cobaltite and contain substantial amounts of Fe (up to 7.4 wt%). The two grains from Gula proved to be Ni-poor cobaltite with low Fe contents. KLEMM (1965) has shown that, at tempe-

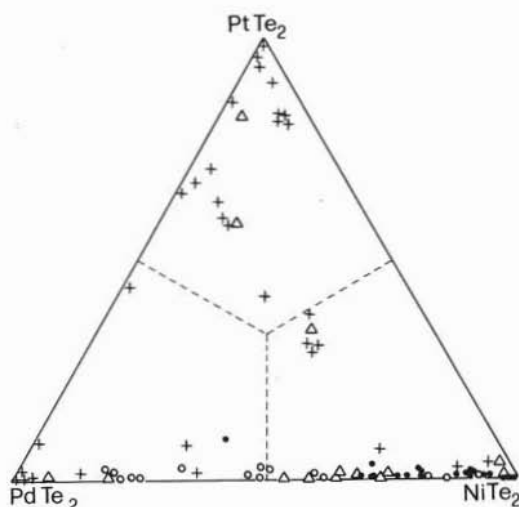


Fig. 5. — PdTe_2 - PtTe_2 - NiTe_2 ternary diagram and corresponding solid solution fields of merenskyite, moncheite, and melonite. Open circles = cyclic units; triangles = main gabbro; dots = pipes; crosses = data from the literature.

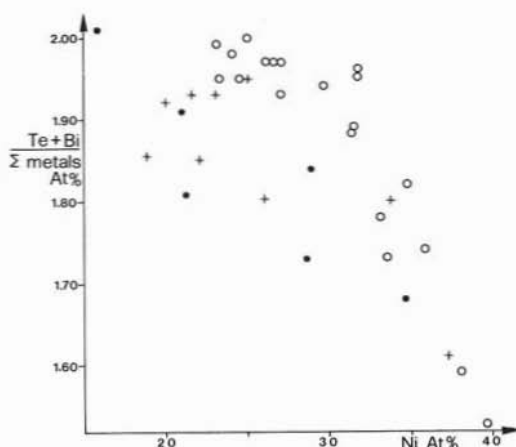


Fig. 6. — Plot of melonite stoichiometries versus Ni contents displaying a negative correlation. Dots = cyclic units; crosses = main gabbro; open circles = pipes.

ratures near 650°C , a wide solid solution field extends from the cobaltite-gersdorffite join towards arsenopyrite compositions in the CoAsS - NiAsS - FeAsS ternary diagram (fig. 10). A miscibility gap appears upon cooling below about 550°C where the stability fields shrink, with decreasing temperatures, towards the pure CoAsS and NiAsS end members. According to these experi-

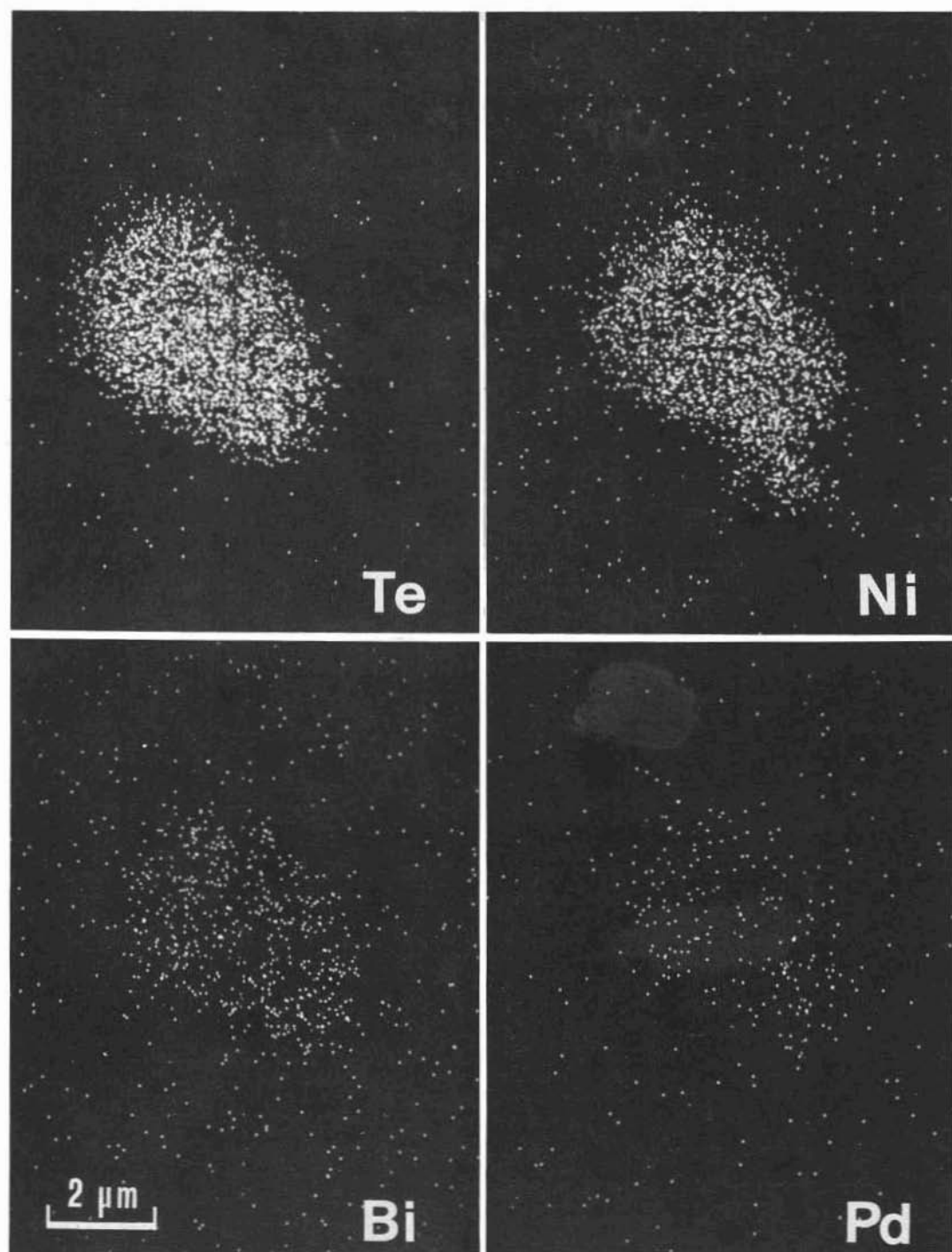


Fig. 7. — X-ray maps of bismuthian melonite grain VM1 1 corresponding to analysis 16 of table 4.

TABLE 4
Electron microprobe analyses of Melonite

No.	Sample	Assoc. ⁽¹⁾	El. wt%						Atomic %					
			Ni	Pd	Pt	Bi	Te	Tot.	Ni	Pd	Pt	Bi	Te	
1	BT8 AQ 1	po	11.1	12.9	0.10	0.17	75.6	99.87	20.91	13.41	0.06	0.09	65.53	
2	BT8 AQ 4	pn	11.3	13.8	0.11	-	74.6	99.81	21.21	14.29	0.06	-	64.43	
3	AL7273 1	po	8.1	14.5	1.4	-	75.5	99.5	15.80	15.61	0.82	-	67.77	
4	GU6334 1	pn mb	15.7	6.2	0.17	0.1	76.6	98.77	28.84	6.28	0.09	0.05	64.73	
5	GU6334 2	pn cb	15.6	4.6	-	0.11	79.0	99.31	28.61	4.66	-	0.06	66.67	
6	GU4RM 1	pn	19.6	2.7	-	0.04	77.2	99.54	34.62	2.63	-	0.02	62.73	
7	PC1220A 1	cp	18.6	0.67	2.4	0.24	76.9	98.81	33.73	0.67	1.31	0.12	64.17	
8	PC1220A 2	cp	21.2	0.91	0.64	0.14	76.3	99.19	37.17	0.88	0.34	0.07	61.55	
9	SBDS 1	po sl	12.2	10.3	0.09	0.30	75.0	97.89	23.24	10.82	0.05	0.16	65.73	
10	SBDS 2	po pn	13.5	8.3	0.75	0.18	77.6	100.33	24.97	8.5	0.42	0.09	66.05	
11	SBDS 3	pn cp	12.1	12.4	0.10	0.11	76.3	101.01	22.36	12.64	0.06	0.06	64.88	
12	SB1 C 1	pn	11.4	11.2	1.1	3.6	73.1	100.4	21.69	11.76	0.63	1.92	64.00	
13	SB3RM 2	pn	9.8	15.3	0.21	-	73.5	98.81	18.80	16.20	0.12	-	64.88	
14	SB3RM 5	pn	10.5	13.5	0.08	-	75.0	99.08	20.01	14.19	0.05	-	65.75	
15	SB3RM 6	pn	14.2	9.5	0.05	-	76.0	99.75	26.09	9.63	0.03	-	64.25	
16	VM1 1	cp	21.5	0.54	0.05	7.1	71.0	100.19	38.07	0.53	0.03	3.53	57.84	
17	VM1 3	cp	19.1	0.72	-	6.9	73.0	99.72	34.71	0.72	-	3.52	61.04	
18	VM1 5A	po	19.8	0.71	0.16	8.6	71.1	100.37	35.76	0.71	0.09	4.36	59.08	
19	VM3RM 1	po chl	14.7	6.0	0.95	-	78.5	100.15	27.01	6.08	0.53	-	66.38	
20	VM3RM 2	po chl	14.4	5.9	1.2	-	77.2	98.70	26.90	6.08	0.67	-	66.35	
21	VM9 3	cp	16.4	4.0	0.43	0.28	78.8	99.91	29.78	4.01	0.23	0.14	65.84	
22	VM9 5	pn	17.3	3.3	0.51	0.41	78.5	100.02	31.17	3.28	0.28	0.21	65.07	
23	VM9 6	po	17.7	3.1	0.17	0.19	79.8	100.96	31.48	3.04	0.09	0.09	65.30	
24	VM9 7	po	18.6	3.0	0.26	-	76.5	98.36	33.49	2.98	0.14	-	63.38	
25	VM12E 1	po	18.7	2.8	-	0.91	77.5	99.91	33.30	2.75	-	0.46	63.50	
26	VM12E1 1A	po hs	14.0	7.2	-	-	77.0	98.2	26.22	7.44	-	-	66.34	
27	VM12E1 1B	pn	13.6	7.8	-	-	77.8	99.2	25.33	8.01	-	-	66.66	
28	VM12E1 5	po pn sl	13.1	9.1	-	-	76.8	99.0	24.51	9.39	-	-	66.10	
29	VM12E1 5	po pn sl	17.7	2.1	-	-	79.9	99.7	31.82	2.08	-	-	66.09	
30	VM12E1 6	cp	12.3	10.2	0.15	-	76.2	98.85	23.19	10.61	0.09	-	66.11	
31	VM12E1 7A	po	14.7	6.5	0.17	-	76.8	98.17	27.39	6.68	0.10	-	65.84	
32	VM12E1 8	po	17.5	2.0	-	-	79.2	98.7	31.79	2.01	-	-	66.20	
33	VM12E1 9	cp	12.8	9.3	0.10	-	77.1	99.30	23.95	9.60	0.06	-	66.39	
34	B04 1	cp	12.2	8.6	1.8	6.7	71.7	101.00	23.3	9.06	1.03	3.59	63.02	
35	FD6519 21	pn	22.4	0.07	0.31	5.9	71.2	99.88	39.33	0.07	0.16	2.91	57.53	

(1) Minerals in contact with melonite; sl = silicate; chl = chlorite; other abbreviations as in Tables 1 - 3.

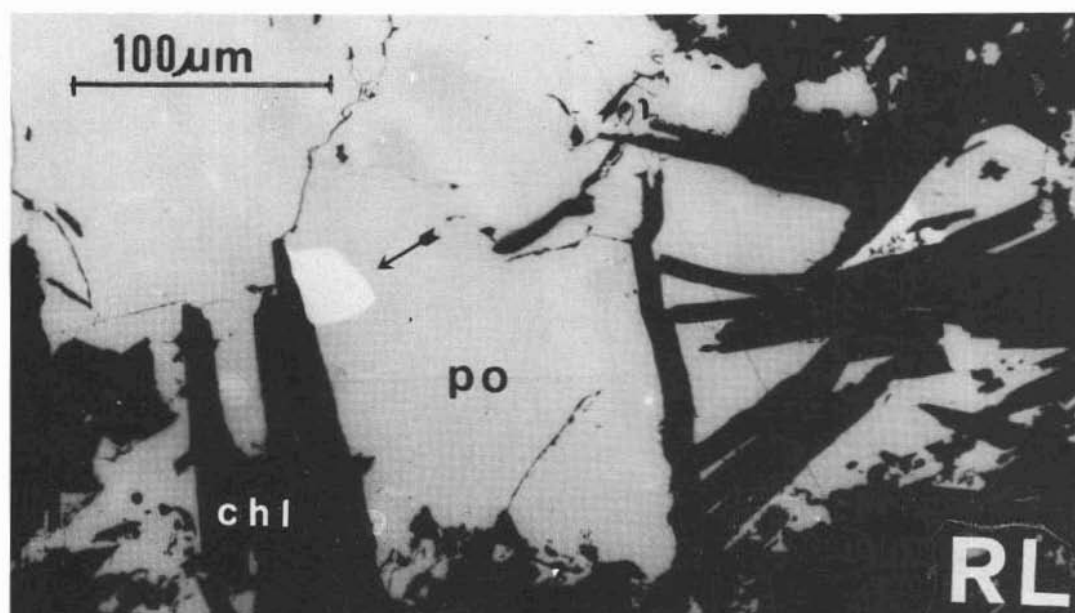
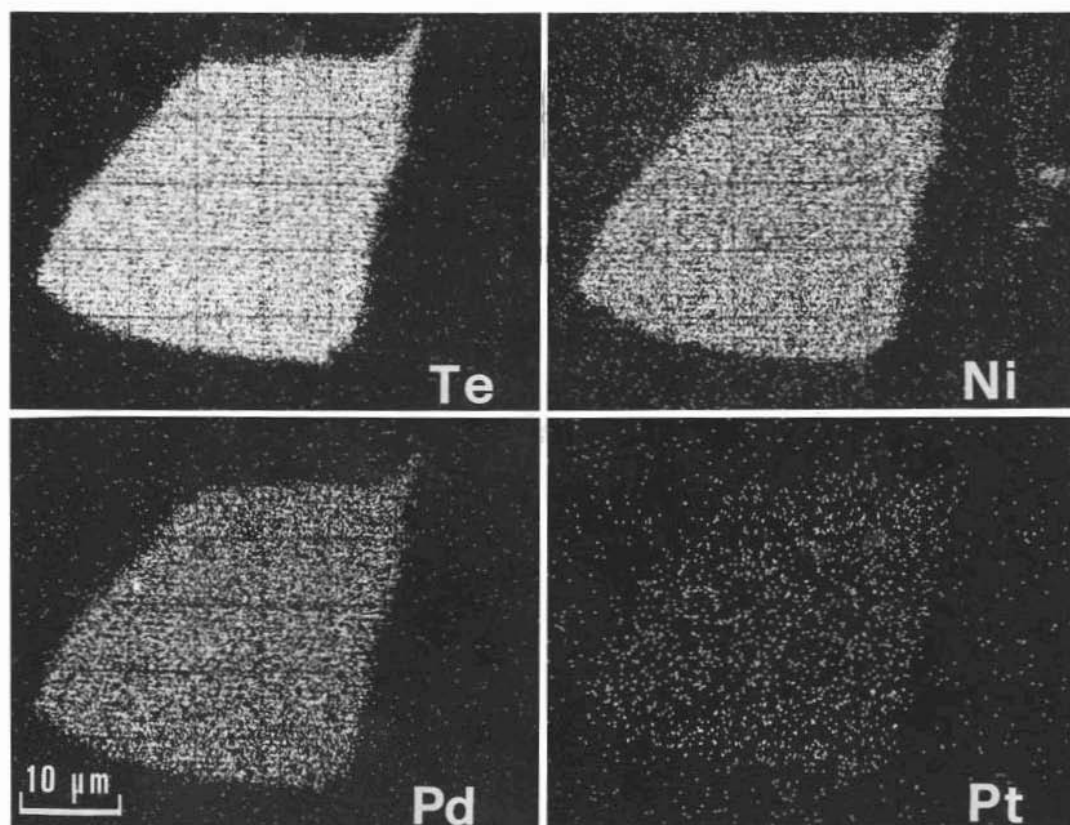


Fig. 8. — Melonite in monoclinic pyrrhotite (*po*) intergrown with chlorite (*chl*), grain VM3RM 1 (analysis 19, table 4).

TABLE 5
Electron microprobe analyses of Hessite, Altaite, and Wehrlite

No. Sample	Assoc. ⁽¹⁾	El. wt%					Atomic %				
		Ag	Pb	Bi	Te	Tot.	Ag	Pb	Bi	Te	
1 VM12E1 1A	po ml	62.2	—	—	37.1	99.3	66.48	—	—	33.52	
2 VM12E1 11	cp	60.5	—	—	39.1	99.6	64.67	—	—	35.33	
3 VM12E1 12	po	62.8	0.03	0.35	36.9	100.08	66.68	0.02	0.19	33.11	
4 FD1 B 2	po	62.1	—	0.47	37.2	99.77	66.21	—	0.26	33.53	
5 FD1 1	po	0.32	62.3	—	37.3	99.92	0.50	50.45	—	49.05	
6 FD1 2B	po	5.9	61.1	—	33.0	100.00	8.99	48.49	—	42.52	
7 FD1 5	po	0.36	62.4	—	37.1	99.86	0.56	50.59	—	48.85	
8 FD4 1	po	0.34	62.9	—	36.7	99.94	0.53	51.08	—	48.39	
9 FD1 7B	po	63.3	0.14	0.43	35.8	99.67	64.44	0.08	0.24	32.24	
10 FD1 7B	po	3.3	59.9	—	36.9	100.1	5.02	47.48	—	47.50	
11 FD1 7B	po	0.2	4.3	67.8	28.0	100.3	0.33	3.66	57.27	38.74	
12 FD1 B 1	po	62.6	0.08	0.02	36.9	99.6	66.71	0.05	0.01	33.23	
13 FD1 B 1	po	0.19	5.3	61.0	32.7	99.19	0.31	4.44	50.72	44.53	
14 FD1 B 6	cp	62.9	0.18	—	36.8	99.88	66.84	0.10	—	33.06	
15 FD1 B 6	cp	0.32	61.1	—	36.9	98.82	0.51	50.23	—	49.26	

(1) Minerals in contact with tellurides; abbreviations as in Table 1.

mental data, the compositions of the sulfarsenides from Fei di Doccio would reflect a temperature of crystallization close to 600°C and certainly above 500°C. The

Ivrea-Verbano sulfarsenides are slightly metal rich which is consistent with the Sudbury occurrence (CABRI and LAFLAMME, 1976), although cobaltites have $As \leq S$ and the slight arsenic excess, found only in gersdorffite, never results in an As/S ratio above 1.04 as compared with that of 1.2 observed at Sudbury.

The sulfarsenides at Fei di Doccio may be in contact with hessite and irarsite (see analyses 3, 6, 9, 12, and 13 of table 6). Hessite usually occurs as tiny chips attached to the grain border, whereas irarsite is typically included at the core of the sulfarsenides as small, idiomorphic crystals. Due to the extremely small size of irarsite crystals, no reliable analyses could be obtained.

Two grains of electrum were analyzed, one included in chalcopyrite (Sample GV 1233) the other included in pentlandite (Sample FD1). They both proved to be pure Au-Ag alloys, but the grain included in chalcopyrite had a remarkably higher gold content (83.2 wt%) with respect to that included in pentlandite (70.5 wt%).

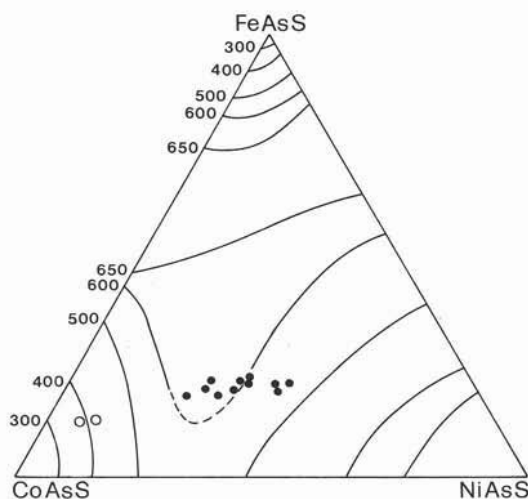


Fig. 10. — CoAsS-NiAsS-FeAsS ternary diagram displaying the relative temperatures of stability according to KLEMM (1965). Symbols as in fig. 5.

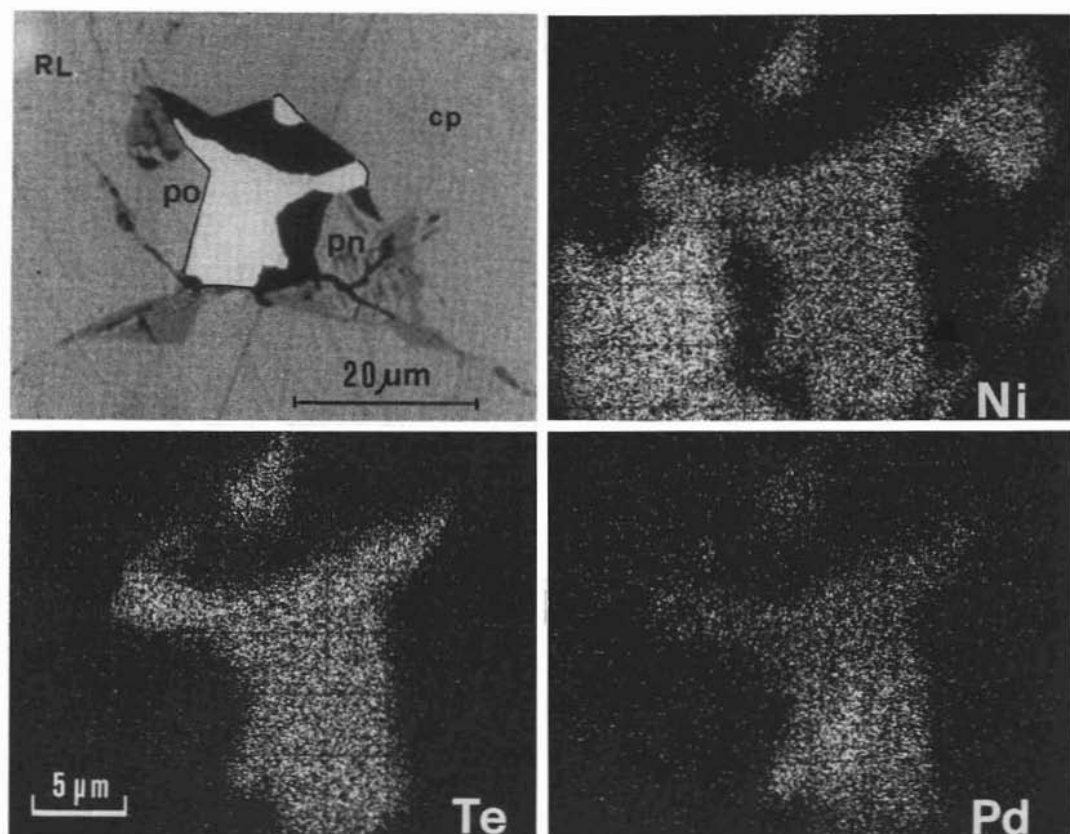


Fig. 9. — Compositional zoning in melonite grain VM12E 5 (analyses 28 and 29, table 4) associated with chalcopyrite (*cp*), pyrrhotite (*po*), and pentlandite (*pn*).

TABLE 6
Electron microprobe analyses of Cobaltite and Gersdorffite

No Sample	Assoc. ⁽¹⁾	El. wt%						Atomic %					
		Co	Ni	Fe	S	As	Tot.	Co	Ni	Fe	S	As	
1 GU6334 1	pn mb ml	26.9	3.3	4.3	19.6	44.4	100.5	26.83	3.08	4.21	33.45	32.43	
2 GU6334 2	pn ml	29.9	2.3	4.4	19.5	44.0	100.1	27.87	2.15	4.33	33.40	32.25	
3 FD6519 181	pn hs	14.4	15.1	6.6	18.5	45.0	99.6	13.59	14.31	6.58	32.10	33.42	
4 FD6519 182	pn	18.7	11.1	6.3	19.5	43.0	98.6	17.62	10.50	6.26	33.76	31.86	
5 FD1 3	pn cp cx	14.0	14.5	7.0	18.5	43.9	97.9	13.40	13.93	7.07	32.55	33.05	
6 FD1 7A 1	po hs	21.1	8.8	6.3	19.3	44.2	99.7	19.75	8.27	6.22	33.21	32.55	
7 FD1 7A 2	po	17.7	12.2	6.7	18.7	43.3	98.6	16.79	11.61	6.70	32.60	32.30	
8 FD1 7E	po cp	16.3	13.1	7.0	19.1	45.1	100.8	15.17	12.24	6.88	32.68	33.03	
9 FD1 8	po ox ir	13.1	15.6	7.2	18.8	44.8	99.5	12.34	14.75	7.16	32.55	33.20	
10 FD1 8A	po	16.4	12.2	7.4	19.2	44.9	100.1	15.32	11.44	7.29	32.96	32.99	
11 FD3 2B	sl	19.8	10.2	7.1	19.2	44.7	101.0	18.34	9.48	6.94	32.68	32.56	
12 FD3 3	po pn hs	18.7	10.0	7.0	19.5	44.9	100.1	17.43	9.36	6.88	33.41	32.92	
13 FD6531	po pn hs	16.3	13.2	7.2	19.1	44.7	100.5	15.17	12.34	7.07	32.69	32.73	

(1) Minerals in contact with Ni-Co sulfarsenides; ox = oxide;
other abbreviations as in Tables 1 - 5.

Concluding remarks

The analysis of a large number of grains pertaining to the melonite, merenskyite, and moncheite species, confirms the existence of solid solution among the $\text{PdTe}_2\text{-NiTe}_2$, $(\text{Pt,Pd})\text{Te}_2\text{-(Ni,Pd)Te}_2$, and $\text{NiTe}_2\text{-NiTe}$ series in the Pd-Pt-Ni-Te quaternary system. The observed paragenetical associations suggest the existence of phase relations between relatively narrow compositional fields corresponding to the coexistence of Ni-merenskyite, Pd-moncheite, and Pd-melonite which, on the other hand, are never found associated with members of the $\text{NiTe}_2\text{-NiTe}$ series characterized by very low to absent Pd. Experimental data are needed to confirm this observation.

Although a more extensive investigation is still in progress, the present data provide a better definition of the Ivrea-Verbano occurrence of PGM and related minerals. Differences in the assemblages and compositions of the investigated minerals are evident between the deposits of the cyclic units and the main gabbro on one hand and those of the pipes on the other.

The first group is characterized by a relatively Pd- and Pt-rich telluride assemblage consisting of melonite, merenskyite and moncheite mainly associated with the mobilized portions of the sulfide mineralization. The sporadic association with pyrite,

molybdenite, and cobaltite of these minerals may be of some significance.

The second group displays more complex assemblages associated with sulfide mineralizations having different textures and settings. The presence of melonite dominates the primary nodular sulfide along with hessite, altaite, wehrilite and minor electrum. Abundant Ni-Co sulfarsenides and minor irarsite occur typically associated with this assemblage in the offset deposits (Fei di Doccio), in analogy with the Sudbury occurrence. Melonite and rare merenskyite predominate in sulfide affected by postmagmatic mobilization.

These different assemblages are likely to be related to a higher $(\text{Ag} + \text{Au} + \text{Pb} + \text{Bi})/(\text{Pd} + \text{Pt})$ ratio in the original sulfide melt of the pipes with respect to the cyclic units and the main gabbro. Furthermore, some of the investigated occurrences seem to indicate the relevance of a mobilization process of the host sulfides to the deposition of Pd + Pt tellurides.

Acknowledgements. — The authors thank the Italian Ministry of Public Education (MPI) for financial support, and the Italian National Research Council (CNR) for financing the electron microprobe Laboratory at Modena University. Thanks are also due to RIMIN S.p.A. and Prof. A. FERRARIO (Milano University) for providing some of samples used in the present investigation.

REFERENCES

- BIGIOGGERO B., BRIGO L., FERRARIO A., GREGNANIN A., MONTRASIO A., ZUFFARDI P. (1979) - *Strona Valley (Fe-Ni-Cu) and (Fe-Ba) ore deposits: Excursion book*. Mem. Ist. Geol. Min. Univ. Padova, 33, 33-39.
- CABRI L.J. (1981) - *The platinum-group minerals*. In: *Platinum-Group Elements: Mineralogy, Geology, Recovery*. Cabri L.J. Ed., Can. Inst. Mining Metall. Spec. Vol. 23, 83-150.
- CABRI L.J., LAFLAMME J.H.G. (1976) - *The mineralogy of the platinum-group elements from some copper-nickel deposits of the Sudbury area, Ontario*. Econ. Geol., 71, 1159-1195.
- CABRI L.J., LAFLAMME J.H.G. (1981) - *Analyses of minerals containing platinum-group elements*. In: *Platinum-Group Elements: Mineralogy, Geology, Recovery*. Cabri L.J. Ed., Can. Inst. Mining Metall. Spec. Vol. 23, 151-173.
- COLBY J.W. (1968) - *Magic IV. A computer program for quantitative electron microprobe analysis*. Bell Telephone Labs., Allentown, Pennsylvania, U.S.A.
- FERRARIO A., GARUTI G., SIGHINOLFI G.P. (1982) - *Platinum and palladium in the Ivrea-Verbano basic complex, western Alps, Italy*. Econ. Geol., 77, 1548-1555.
- FLEISCHER M. (1983) - *Glossary of mineral species*. Mineralogical Record, Tucson, AZ, U.S.A., 186.
- GARUTI G., RINALDI R. (1985) - *Mineralogy of melonite-group PGM and other tellurides from the Ivrea-Verbano basic complex, Western Italian Alps*. Fourth Intern. Platinum Symposium, Abstract, Can. Mineralog., 23, 303.
- GARUTI G., FIANDRI P., ROSSI A. (1986) - *Sulfide composition and phase relations in the Fe-Ni-Cu ore deposits of the Ivrea-Verbano basic complex (western Alps, Italy)*. Mineral. Deposita, 21, 22-34.

- HEY M.H., GOTTARDI G. (1980) - *On the use of names, prefixes and suffixes, and adjectival modifiers in the mineralogical nomenclature*. Can. Mineralog., 18, 261-262.
- HUDSON D.R., DONALDSON M.J. (1984) - *Mineralogy of platinum group elements in the Kambalda nickel deposits, Western Australia*. In: Sulphide deposits in mafic and ultramafic rocks. Buchanan D.L. and Jones M.J. Eds. The Institute of Mining and Metallurgy, London, U.K., 55-61.
- KLEMM D.D. (1965) - *Synthesen und analysen in den dreiecksdiagrammen $FeAsS-CoAsS-NiAsS$ und $FeS-FeS_2-NiS_2$* . N. Jb. Miner. Abh., 103, 3, 205-255.
- PIISPANEN R., TARKIAN M. (1984) - *Cu-Ni-PGE mineralization at Rometolvas, Koillismaa layered igneous complex, Finland*. Mineral. Deposita, 19, 105-111.
- RAMDOHR P. (1980) - *The ore minerals and their intergrowths*. Pergamon Press, Frankfurt, F.R.G.
- REED S.J.B. (1975) - *Electron microprobe analysis*. Cambridge Univ. Press, Cambridge, U.K.
- RINALDI R. (1985) - *Microanalisi-X: recenti sviluppi e aspetti pratici*. Rend. Soc. It. Mineral. Petrol., 40, 2, 241-254.
- RUCKLIDGE J. (1969) - *Electron microprobe investigation of platinum metal minerals from Ontario*. Can. Mineralog., 9, 617-628.
- RUCKLIDGE J., STUMPFL E.F. (1968) - *Changes in the composition of petzite (Ag_3AuTe_2) during analysis by electron probe*. N. Jb. Mineral. Mh., 61-68.
- VAUGHAN D.J., CRAIG J.R. (1978) - *Mineral chemistry of metal sulfides*. Cambridge Univ. Press, Cambridge, U.K.
- WATKINSON D.H., HAK J., MORTON P., JOHAN Z. (1978) - *Merenskyite from the Shebandowan Nickel-Copper mine, Northwestern Ontario*. Can. Mineralog., 16, 659-663.