

## CHROMIUM-PLATINUM GROUP ELEMENTS (PGE) MINERALIZATION AS PETROGENETIC INDICATORS: AN EXAMPLE FROM THE METASOMATIC SUB-CONTINENTAL MANTLE OF FINERO (WESTERN ALPS, ITALY)

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Small-size podiform chromitites associated with the metasomatized sub-continental mantle of the Finero complex (Ivrea Zone, Western Alps, Italy), have been investigated for the chromian spinel composition and for their platinum-group elements (PGE) geochemistry and mineralogy. Our data indicate that the chromite-PGE mineralization in the Finero massif significantly differs from other podiform chromitites, being they hosted in the oceanic mantle of supra-subduction zone ophiolites, or in the lithospheric mantle (i.e. Serrania de Ronda massif), suggesting a different genesis. In particular the Finero chromitites are characterized by high  $\text{TiO}_2$ , the presence of abundant “exotic” minerals, such as zirconolite, baddeleyite, thorianite, uraninite, thorite or huttonite and zircon, and a quite constant Rh positive anomaly, expressed by the presence of abundant Rh minerals. Among these Rh minerals, those corresponding to the formula  $(\text{Rh}_{0.42}\text{Ru}_{0.3}\text{Ir}_{0.19})_{1.01}(\text{S}_{1.36}\text{Sb}_{0.6})_{1.99}$ , probably represents a new mineral specie. The residual mantle of Finero reacted with an alkaline-carbonatite metasomatizing and not with a basaltic melt, as proposed for the ophiolites. This metasomatic fluid generated in the mantle itself and its interaction between restitic peridotite caused the instability of Cr-diopside and the crystallization of abundant chromian spinel in the Finero complex. The presence of alkaline-carbonatite metasomatizing fluid would appear distinctive of a mantle plume setting. These observation suggest that the formation of the Finero chromitites in a compressive regime as typical of the subduction zone is very unlike, supporting the concept of metasomatism of the Finero mantle as a result of mantle diapirism at the base of the continental crust, induced by extensional tectonics in pre-Hercynian times.

**Key words:** *chromium-platinum mineralization, chromitites, massif Finero, metasomatism, sub-continental mantle, Rh minerals.*

### INTRODUCTION

Spinel has been used as useful “petrogenetic indicator” since this term was first applied to them [20, 21]. Although this role of the spinels has been recently questioned [35], theoretical considerations, experimental results and the study of a great number of natural occurrences confirm, since many years, that the formation of chromitites and the composition of the chromian spinel are mainly controlled by the geological environment in which they formed [2, 6, 37, 39]. In the last decades, due to developments in analytical techniques and increasing available data, the potential of platinum-group elements (PGE), as petrogenetic indicators of evolution of mafic-ultramafic rocks has been also recognized, although they occur, generally, as ultra-trace elements in their host rocks. The chromitites are important hosts for platinum group elements (PGE), being strongly enriched in these noble metals compared to their country rocks. The PGE are carried in specific phases, the platinum group minerals (PGM), and they did not occur in solid solution in the spinel lattice. The majority of PGM occur as nano-minerals (generally

less than 10 microns in size) included in the crystals of chromian spinel and more rarely, in the silicate matrix, mainly composed of olivine and pyroxene and their alteration products such as chlorite and serpentine. Small-size podiform chromitites have been described in the metasomatized sub-continental mantle of the Finero complex (Ivrea Zone, Western Alps, Italy). These chromitites have been investigated for PGM [9, 12] but data on PGE are fragmentary, due to high values of the detection limits of the used analytical method [17]. Therefore the trends of chondritic-normalized PGE patterns obtained so far, remind undefined. In this paper we present a comprehensive investigation of PGE geochemistry and mineralogy as well as the composition of chromian spinels obtained in selected samples of the Finero chromitites. Our data confirm the importance of chromitites as petrogenetic indicators and collector for these noble metals. In particular, they show that the mineralization in the Finero complex are very peculiar being very different when compared with other podiform chromitites. This feature can be considered distinctive of the Cr-PGE forming system in a mantle-plume regime under the strong influence of metasomatizing fluids.

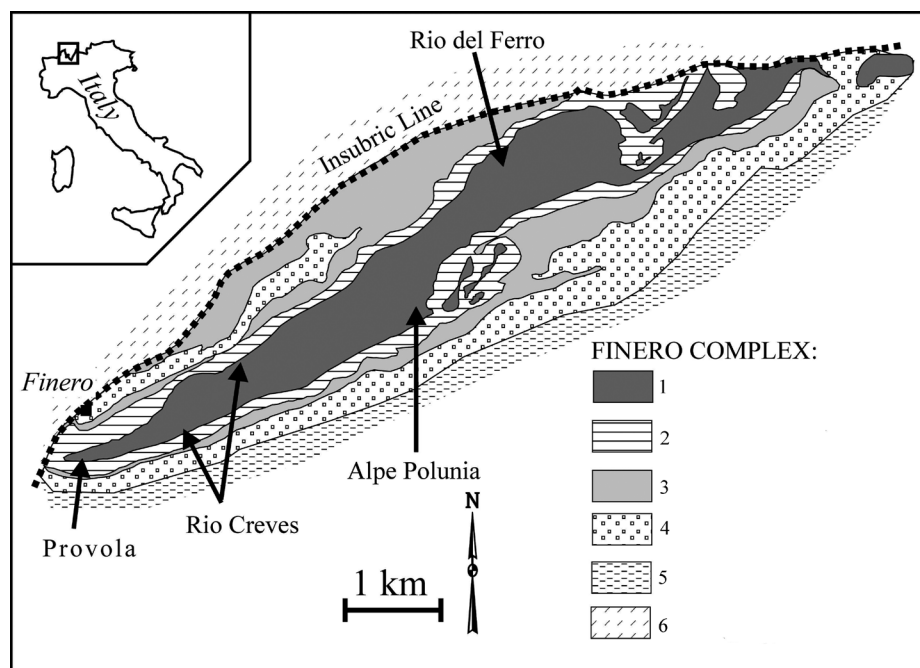
# GEOLOGICAL BACKGROUND AND DESCRIPTION OF THE FINERO CHROMITITES

The Finero complex forms an elliptical body about 12 km long and 3 km wide. It occurs in the Western Alps of Italy and crops out at the base of the lower continental crust that is composed of high-grade metasediments (kinzigite, stromalite) (fig. 1). To north-west the Finero complex is cut by the Insubric line and it is in tectonic contact with rocks of the Austroalpine domain. The Finero complex can be divided, from core to rim, in four main units: (1) the mantle rock consists of a phlogopite-bearing harzburgite containing small pods of chromitites, with minor clinopyroxenite dikes and dunite, (2) the layered internal zone with amphibole and garnet gabbros, amphibole websterite, amphibole peridotite, with rare layers of anorthosite, (3) the amphibole peridotite made up of layered cumulate of amphibole lherzolite with subordinate dunite and wehrlite, (4) the external gabbro composed of massive amphibole and garnet gabbros, with rare pyroxenitic and anorthositic layers.

The phlogopite-bearing harzburgite has been interpreted to represent a slice of mantle that was metasomatically enriched in incompatible elements and tectonically emplaced into the deep crust. Metasomatism caused the extensive crystallization of phlogopite, amphibole, apatite, carbonates, and the abnormal re-enrichment in Rb, Ba, K, Pb, Sr, LREE, Na and Au [8, 10, 18, 31, 41]. The metasomatic process was initiated  $293 \pm 13$  Ma ago [5, 50] by reaction of the depleted protolith

with an alkaline, volatile-rich fluid phase that, according with some authors, may have derived from a crustal slab in a subduction setting [18, 31, 53]. An alternative interpretation is that the Finero phlogopite peridotite may represent depleted and re-enriched parts of a mantle plume emplaced at the base of the sub-continental crust by extension and thinning of the lithosphere, in pre-Hercynian times [8, 10, 19, 40, 41, 52].

The presence of small bodies of chromitite in the Finero complex was described more than 60 years ago, in the 1948 [38]. A more recent investigation on these chromitites was carried out by Ferrario and Garuti [9]. These authors recognized that all the chromitites occurred in the marginal zone of the mantle phlogopite peridotite. The chromitite forms distinct layers, elongated lenses and schlieren, inside coarse grained harzburgite and dunite. The morphological characters are similar to podiform chromitites from the mantle tectonite of ophiolites, although the ore bodies are distinctly smaller, and the effects of low  $P$ - $T$  oceanic metamorphism are lacking. Some authors [9] suggested that the chromitites formed concomitantly with the episode of alkaline metasomatism. Recently, using the composition of "exotic" minerals, such as zirconolite, baddeleyite, thorite, uraninite, thorite or huttonite and zircon found in the Finero chromitites, it has been proposed a carbonatitic-alkaline character of metasomatism at Finero [52]. The chromitite samples, object of the present investigations, were collected in the following localities: Alpe Polunia, Rio Creves, Rio del Ferro, and Provola (Fig.1).



**Fig. 1.** Geological sketch map of the Finero complex, showing the location of the investigated chromitites.

1–4 – Finero complex: 1 – mantle phlogopite harzburgite, 2 – layered gabbros, pyroxenite and peridotite, 3 – amphibole peridotite, 4 – external gabbros; 5, 6 – country rocks: 5 – kinzigite-stromalite, 6 – Austroalpine domain.

## ANALYTICAL METHODS

All the six PGE were analyzed by a simple and very effective procedure. The samples were previously crushed in an agata mill. Subsequently they were spiked with enriched isotopes and digested in a HNO<sub>3</sub>/HCl (5 + 2) acid mixture at 300°C and 125 bar pressure in a high pressure asher (HPA-S, Anton Paar) for 4 to 12 hours. The PGE were then measured in an ICP-MS after a simple on-line matrix removal determined with an ICP-MS system [27, 28]. The concentrations are determined via the isotope ratio through isotope dilution and external calibration (Rh). Through the on-line separation, the isobaric and molecular interferences were controlled over which results in highly reproducibly data.

The PGM grains were previously located by scanning the polished sections with the reflected light microscope at a magnification of 250–800. Their electronic images were obtained with a Philips 40 scanning electron microscope using 20 kV accelerating voltage and 10 nA beam current. Electron microprobe quantitative analyses of PGM and chromium spinel were performed in WDS mode using a Superprobe Jeol JXA 8200 (Laboratory Eugen F. Stumpfl, University of Leoben, Austria, and an ARL-SEMQ (Department of Earth Sciences, University of Modena and Reggio Emilia, Italy), operating with an accelerating voltage of 20–15 kV, a beam current of 10 nA and a beam diameter of 1 µm. The proportion of trivalent iron in chromian spinel was calculated assuming the ideal stoichiometry.

## RESULTS

**Chromitite texture and chromian spinel composition**

The investigated chromitites of Finero display a peculiar texture not comparable to either the podiform chromitites hosted in the mantle sequence of ophiolites or to stratiform chromitites of layered intrusions. Massive chromitite at Finero consists of coarse grained (up to 2–3 mm) chromian spinel, characterized by rounded and lobate boundaries with the silicates, with frequent amoeboid intergrowths and reciprocal inclusions. This texture suggests the concomitant crystallization of oxides and silicates. The chromian spinel-silicate assemblages are characterized by the presence of symplectitic intergrowths of chromite and olivine, and orthopyroxene rims between chromian spinel and olivine, indicating a reaction among these minerals.

The chromian spinels and the silicate matrix are completely fresh in most cases. The composition of chromian spinel from the Finero chromitites is compared with the compositional fields of chromitites from different geological settings in fig. 2.

The fields portrayed refer to massive chromite ores and do not include compositions of accessory spinel from mafic and ultramafic rocks. The Finero chromitites have compositions similar to ophiolitic podiform chromitites, when relations among major oxides are considered, although the Finero samples display a slight Fe enrichment. The TiO<sub>2</sub> content, however, can be much higher than normal for ophiolitic chromitites (<0.25 wt %), varying in the range 0.15–0.95 wt %, similarly to the stratiform chromitites or, in same case, with the chromitite hosted in the sub-continental lithospheric mantle of Serrania de Ronda (Spain) (Fig. 2b).

**PGE geochemistry**

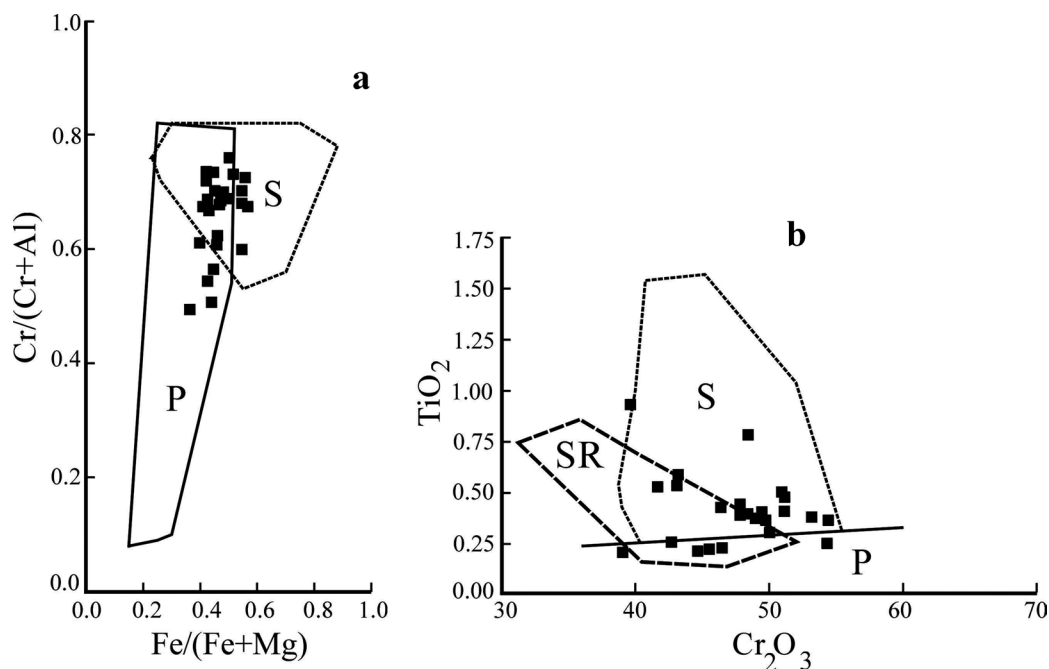
The total PGE amount of the Finero chromitites are very low (45 ppb, average on 10 samples) and only in one chromitite sample the total PGE contents is 292 ppb (table 1). Our results, normalized to the C1 chondrite [32] show a peculiar shape, very different when compared with the PGE pattern of the chromitites hosted in the mantle sequence of the ophiolites (fig. 3a) as well as with those of the sub-continental mantle of Serrania de Ronda (Fig. 3b). In the Finero chromitites Os, Ir, Ru are unfractionated (5–8 times the mantle concentration), forming flat patterns. Their content of Rh is quite high (about 10 times the mantle concentration) giving a positive anomaly in all the analyzed chromitites, except for the richest sample (Fig. 3a). Low contents of Pt > Pd (less than the mantle concentration) are reflected in a strong negative slope (Fig. 3a).

**PGE mineralogy**

Despite of the low PGE contents, more than 50 (PGM) have been identified in a total of about 60 polished sections. According to [9, 12] the most common PGM

**Table 1.** PGE analyses of the Finero chromitites (ppb)

Sample	Os	Ir	Ru	Rh	Pt	Pd	Sum PGE
Alpe Polunia							
FN1	9	10	19	7	4	1	50
FN2	15	12	28	7	4	1	67
FN3	19	16	32	10	5	0	82
FN4	19	20	36	13	6	1	95
FN5	21	11	21	10	3	1	67
Rio del Ferro							
FN11	59	78	115	23	16	1	292
RF1393	13	10	24	5	3	1	56
RF1398	4	4	7	4	1	1	21
Rio Creves							
CR1339	14	9	24	6	3	1	57
CR1367	12	12	25	9	2	0	60
Provola							
PR1372	4	6	8	10	4	1	33



**Fig. 2.** Composition of chromite from chromitites from the Finero complex.

a – relationships between  $\text{Cr}/(\text{Cr} + \text{Al})$  and  $\text{Fe}/(\text{Fe} + \text{Mg})$ ; b – Weight %  $\text{TiO}_2$  versus weight %  $\text{Cr}_2\text{O}_3$ . Compositional fields of stratiform (S), podiform (P) and Serranía de Ronda (SR) chromitites are reported for comparison. The Serranía de Ronda field is based on unpublished microprobe data available to the authors.

is laurite, accompanied by abundant cuprorhodsite-cuproiridsite grains with rare other PGM (Pt-Cu, Ir-Rh alloys, Rh sulfide, Ru-pentlandite and unidentified Rh-Sb-S mineral). The PGM forms both single phase and composite grains, with a size generally less than 10 microns. Most of them occur enclosed in the chromian spinel. Occasionally the PGM have been found in the contact chromian spinel-silicate matrix, and only one laurite has been found enclosed in olivine. The majority of the PGM are considered to have formed during the precipitation of chromite. Only few grains were altered after their formation. Examples of the PGM morphology and textural relations are illustrated in fig. 4 and selected analyses of PGM from Finero are given in table 2.

Most of the laurite are characterized by a perfect euhedral shape and they occur enclosed in the chromian spinel (Fig. 4a, b). A few grains of laurite have been found in contact with spinel symplectite in olivine (Fig. 4c), enclosed in olivine (Fig. 4d) and at the contact spinel-silicate (Fig. 4e). Laurite at Finero may occur as solitary inclusion (Fig. 4a, d) or associated with Base Metal sulfide (Fig. 4b) and other PGM (Fig. 4e, g). One xenomorphic crystal of laurite accompanied by Ru-pentlandite and an unknown Rh-Sb-S has been found in contact with spinel and partially serpentinized olivine (Fig. 4g). The shape of this grain as well as its textural position suggests that it formed during some alteration processes. The composition of laurite-erlichmanite has been plotted, as atomic proportion in fig. 5. Laurite at Finero displays remarkable

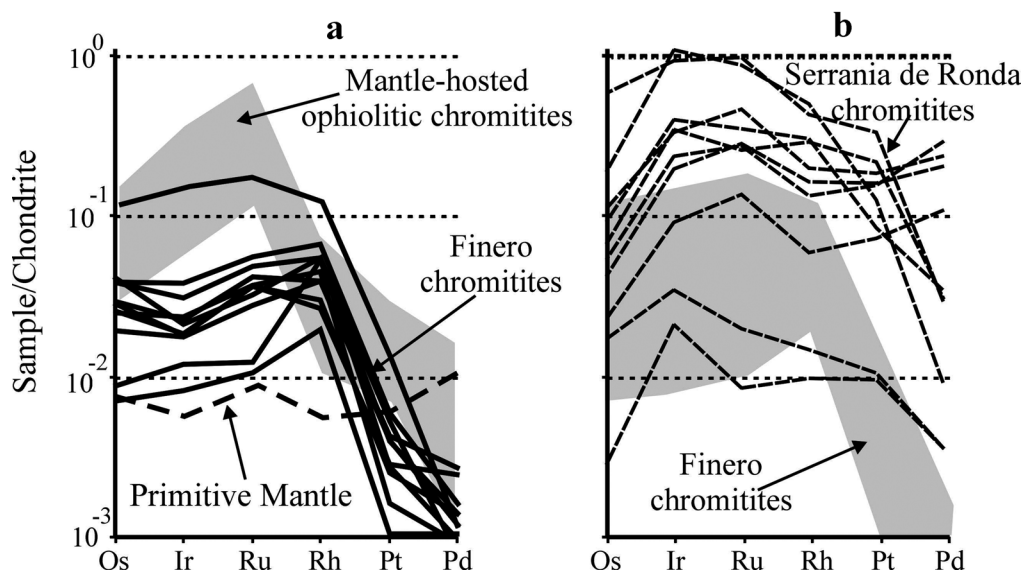
substitution of Rh (up to 6.88 wt %), Ir (up to 8.89 wt %) and As (up to 2.40 wt %). Also the Os content is quite high (up to 28.3 wt %), although only one composition falls in the erlichmanite field (Fig. 5). Base metals, Pt and Pd may be present as minor constituent. The laurite found in contact with altered silicate is Os and Ir-free, corresponding to the Ru end member of the laurite-erlichmanite series (Fig. 5).

The cuprorhodsite-cuproiridsite minerals form polygonal grains often in association with laurite and Cu sulfides (Fig. 4e, f). They occur almost exclusively in the chromian spinels. Only one grain of cuprorhodsite associated with laurite has been found at the contact between chromian spinel and olivine (Fig. 4e). Five grains of cuprorhodsite and one of cuproiridsite were analyzed. The Pt content, in most of the analyzed grains, varies from 0 up to 5.17 wt %. Only one grain of cuprorhodsite associated with laurite contains up to 25.38 wt % of Pt. The composition (at %) of cuprorhodsite and cuproiridsite from Finero chromitites have been plotted in the ternary diagram of figure 5.

One polypahsic grain found at the contact between chromian spinel and serpentinized olivine is composed of Rh sulfide, Pt-Cu and Ir-Rh alloys (Fig. 4H). Due to the small size of the crystals, they have been only qualitatively checked.

Rh-Sb-S mineral corresponding to the formula  $(\text{Rh}_{0.42}\text{Ru}_{0.3}\text{Ir}_{0.19})_{1.01}(\text{S}_{1.36}\text{Sb}_{0.6})_{1.99}$  (calculated on three atoms per formula unit, average on the three analyses reported in table 2) was identified as part of a composite grains





**Fig. 3.** Comparison of PGE chondrite-normalized patterns from the Finero chromitites.

a – with chromitites hosted in the mantle sequence of different ophiolites (see the text for bibliography). Primitive mantle values from C1 Chondrite  $\times 0.00815$ .

b – with “Cr-ores” and “Cr-Ni-ores” from the Betic Cordillera ([16, 46] and unpublished data available to the authors). Chondrite-normalization values from [32].

(Fig. 4G) with laurite and Ru-pentlandite containing up to 11.36 wt % of Ru (table 2). Compared to laurite, the unknown mineral appears yellowish and, although only qualitatively estimated, with a reflectance slightly higher. It seems to be isotropic. The polyphasic grain is associated with chromian spinel and partially serpentinized olivine.

## DISCUSSION

### Comparison with the podiform chromitites in the ophiolites and in the Serrania de Ronda massif

The podiform chromitites typically occur as irregular chromite-rich bodies in the following two alpine-type complexes: 1) ophiolites and 2) mantle diapirs. Most of the huge deposits of podiform chromitites are hosted in the mantle sequence of the ophiolites, that formed originally in the oceanic setting. Distinct model have been proposed for the genesis of these podiform deposits. [4] considered the mantle chromitites as a residue of partial melting of the mantle harzburgite. However this model do not explain the cumulate texture sometimes presents in the podiform chromitites and the variation of Cr/Fe ratio in chromite with depth observed in many ophiolites [3]. The formation of podiform chromitites in the mantle where they crystallized at different times and at different places by crystallization of basaltic melt, is widely accepted. Recently it has been proposed that the podiform chromitites formed by reaction between rising basaltic melts and the host peridotites. This reaction causes the incongruent dissolution of pyroxenes in the host peridotite, producing a melt

enriched in  $\text{SiO}_2$  [24]. The formation of this melt drives the system into the stability field of chromite. This model explains also the presence of depleted dunite envelope that often can be found around the podiform chromitite bodies.

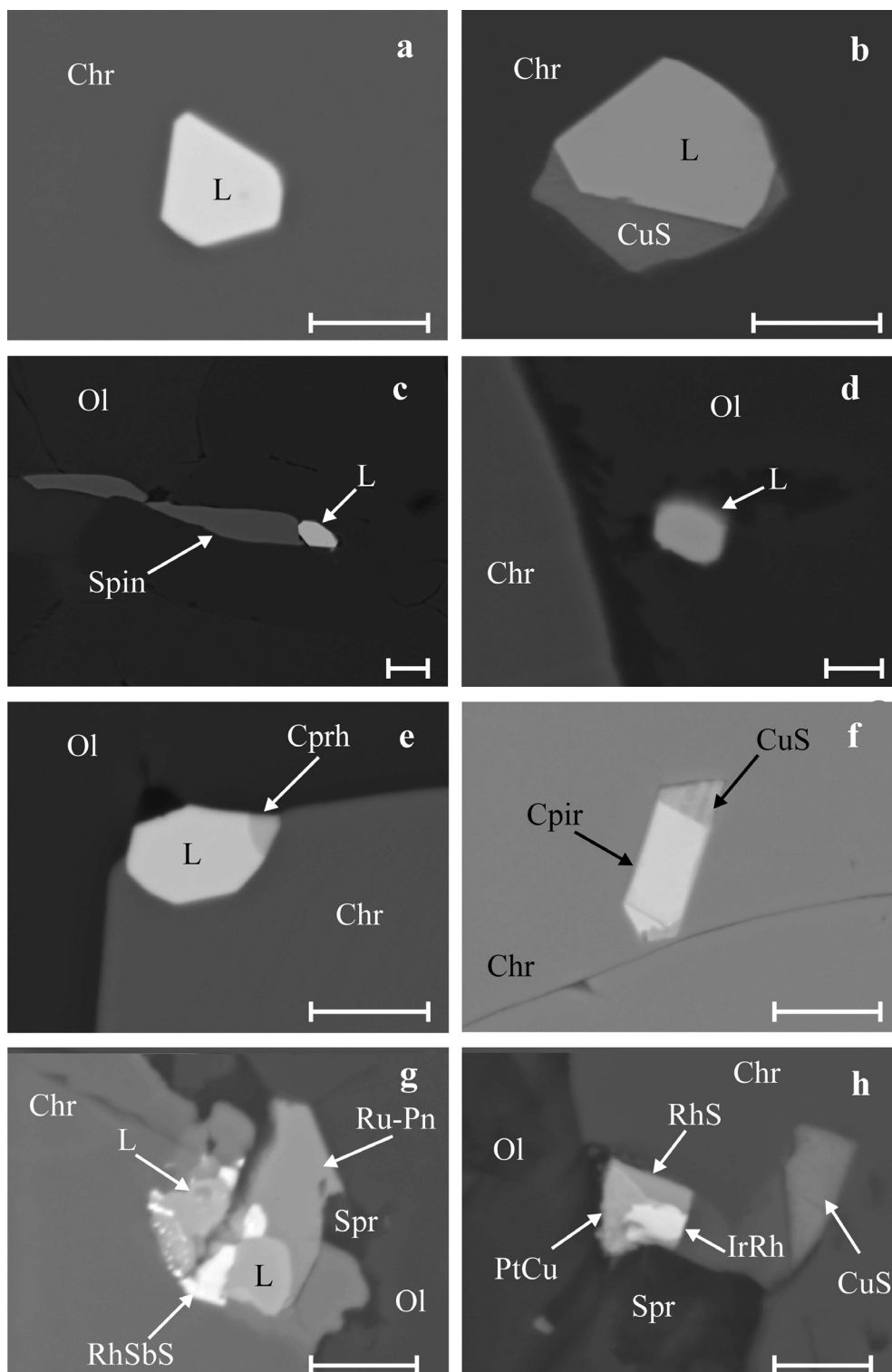
Mantle diapirs are believed to represent diapiric emplacement in the deep continental crust of mantle material in a solid state, under variable  $P$ - $T$  conditions. Chromite concentrations in these bodies are limited to a few small pods of little economic importance. The complexes of Finero and Serrania de Ronda (Spain) probably provide the only two examples of mantle diapirs with the occurrence of chromitites.

### Finero versus supra-subduction ophiolites

We have compared the ophiolitic chromitites, for which all the six PGE have been analyzed and PGM data are available, with those of the Finero complex. The selected ophiolitic complexes are the following: Kraubath, Hochgrössen (Austria) [44, 45]. Vourinos, Otrhys, Pindos (Greece) [1, 7, 13, 14, 22, 23], Bulqiza (Albania) [7, 34], Rhodope (Bulgaria) [7, 42], Troodos (Cyprus) [26], Ray-Iz, Kempirsai, Kluchevskoy (Urals, Russia) [15, 25, 29, 30, 51], Muğla, Eskişehir, Kahramanmaraş (Turkey) [42, 47–49] and Mayarí-Baracoa (Cuba) [36]. Most of these ophiolites contain huge chromite deposits and they generated in a supra-subduction zone.

The main differences of the Cr-PGE mineralization at Finero and in the ophiolitic mantle are summarized in the following:

(1) A distinctive character of the ophiolitic mantle is the occurrence of economically important chromite



**Fig. 4.** BSE images of PGM associated with chromitite of Finero.

a – primary single phase laurite in chromite; b – primary laurite associated with Cu sulfide in chromite; c – laurite in contact with spinel symplectite, enclosed in olivine; d – primary single phase laurite in olivine; e – magmatic grain of laurite and cuprorhodsite at the contact chromite-olivine; f – primary cuproiridsite associated with Cu sulfide, in chromite; g – secondary PGM in contact with chromite, serpentine and olivine, composed of laurite, Ru-rich pentlandite and unknown  $(\text{Rh}, \text{Ir}, \text{Ru})(\text{Sb}, \text{S})_2$ ; h – secondary PGM in contact with chromite, serpentine and olivine, composed of Pt-Cu and Ir-Rh alloys and Rh sulfides (only qualitatively analyzed).

Abbreviations: L – laurite, Cprh – cuprorhodsite, Cpir – cuproiridsite, Ru-Pn – Ru-rich pentlandite, RhSbS –  $(\text{Rh}, \text{Ir}, \text{Ru})(\text{Sb}, \text{S})_2$ , PtCu-RhS-IrRh – unidentified PGM, Chr – chromite, Spin – spinel symplectite, Ol – olivine, Spr – serpentine, CuS – Cu-sulfide. Scale bar – 10 microns.

**Table 2.** Selected microprobe composition of PGM from the Finero chromitites

	Os	Ir	Ru	Rh	Pt	Pd	Fe	Cu	Ni	S	As	Sb	Tot
Cuprorhodsite (wt %)													
1	0.04	7.54	0.00	44.80	0.35	0.00	4.50	10.97	1.35	31.32	0.00	n.a	100.87
2	0.00	7.81	0.00	43.95	0.28	0.00	4.51	11.36	1.34	31.75	0.00	n.a	101.00
3	0.04	7.02	0.00	43.96	0.70	0.00	4.62	10.84	1.30	31.48	0.00	n.a	99.96
4	0.00	15.92	0.00	17.63	25.38	0.00	1.85	11.28	0.10	26.61	0.00	n.a	98.77
5	0.00	16.06	0.00	18.13	23.81	0.00	1.99	11.69	0.09	26.58	0.00	n.a	98.35
6	0.00	15.95	0.00	17.79	24.20	0.00	1.88	11.40	0.02	26.63	0.00	n.a	97.87
Cuprorhodsite (at %)													
1	0.01	2.26	0.00	25.32	0.10	0.00	4.65	9.96	1.33	56.36	0.00	n.a	
2	0.00	2.33	0.00	24.67	0.08	0.00	4.63	10.24	1.31	56.74	0.00	n.a	
3	0.01	2.11	0.00	24.92	0.21	0.00	4.79	9.87	1.28	56.81	0.00	n.a	
4	0.00	5.80	0.00	12.09	9.11	0.00	2.32	12.43	0.12	58.12	0.00	n.a	
5	0.00	5.83	0.00	12.39	8.52	0.00	2.49	12.84	0.11	57.84	0.00	n.a	
6	0.00	5.82	0.00	12.23	8.70	0.00	2.36	12.59	0.02	58.27	0.00	n.a	
Laurite (wt %)													
1	17.58	3.90	36.72	4.52	0.07	0.55	1.04	0.00	0.07	33.80	1.30	n.a	99.55
2	1.00	1.32	46.25	5.76	0.07	0.43	3.69	0.12	1.38	37.21	2.45	n.a	99.68
3	15.31	7.54	34.10	5.07	0.00	0.36	1.20	0.52	0.28	34.18	1.00	n.a	99.56
4	29.01	8.01	26.13	3.62	0.00	0.50	1.16	0.23	0.00	30.82	1.05	n.a	100.54
5	14.29	5.10	38.31	5.51	0.00	0.70	1.48	0.11	0.11	33.59	1.09	n.a	100.30
6	16.45	5.37	35.24	5.54	0.00	0.56	1.15	0.08	0.21	34.12	2.00	n.a	100.72
Laurite (at %)													
1	5.72	1.25	22.47	2.71	0.02	0.32	1.15	0.00	0.07	65.20	1.07	n.a	
2	0.29	0.38	25.22	3.09	0.02	0.22	3.64	0.10	1.30	63.95	1.80	n.a	
3	4.96	2.42	20.78	3.04	0.00	0.21	1.32	0.50	0.29	65.66	0.82	n.a	
4	10.22	2.79	17.32	2.36	0.00	0.31	1.39	0.24	0.00	64.41	0.94	n.a	
5	4.60	1.62	23.21	3.28	0.00	0.40	1.62	0.11	0.11	64.15	0.89	n.a	
6	5.28	1.71	21.28	3.28	0.00	0.32	1.26	0.08	0.22	64.95	1.63	n.a	
Ru-pentlandite (wt %)													
1	0.00	0.00	11.36	1.67	0.07	0.07	16.89	0.00	36.09	30.02	0.92	n.a	97.09
2	0.00	0.00	11.12	1.41	0.08	0.00	16.93	0.00	36.65	29.98	0.92	n.a	97.09
Ru-pentlandite (at %)													
1	0.00	0.00	5.55	0.80	0.02	0.03	14.93	0.00	30.35	47.71	0.61	n.a	
2	0.00	0.00	5.42	0.68	0.02	0.00	14.94	0.00	30.77	47.57	0.61	n.a	
Unidentified Rh-Sb-S (wt %)													
1	6.67	16.03	10.93	17.99	n.a.	n.a.	n.a.	n.a.	n.a.	16.80	0.88	29.71	99.01
2	6.69	14.92	11.60	17.53	n.a.	n.a.	n.a.	n.a.	n.a.	17.06	0.93	30.38	99.10
3	7.24	13.74	14.73	17.06	n.a.	n.a.	n.a.	n.a.	n.a.	18.77	0.99	28.00	100.53
Unidentified Rh-Sb-S (at %)													
1	0.20	0.48	0.33	0.54	n.a.	n.a.	n.a.	n.a.	n.a.	0.50	0.03	0.89	
2	0.20	0.45	0.35	0.53	n.a.	n.a.	n.a.	n.a.	n.a.	0.51	0.03	0.91	
3	0.22	0.41	0.44	0.51	n.a.	n.a.	n.a.	n.a.	n.a.	0.56	0.03	0.84	

n.a. = not analyzed

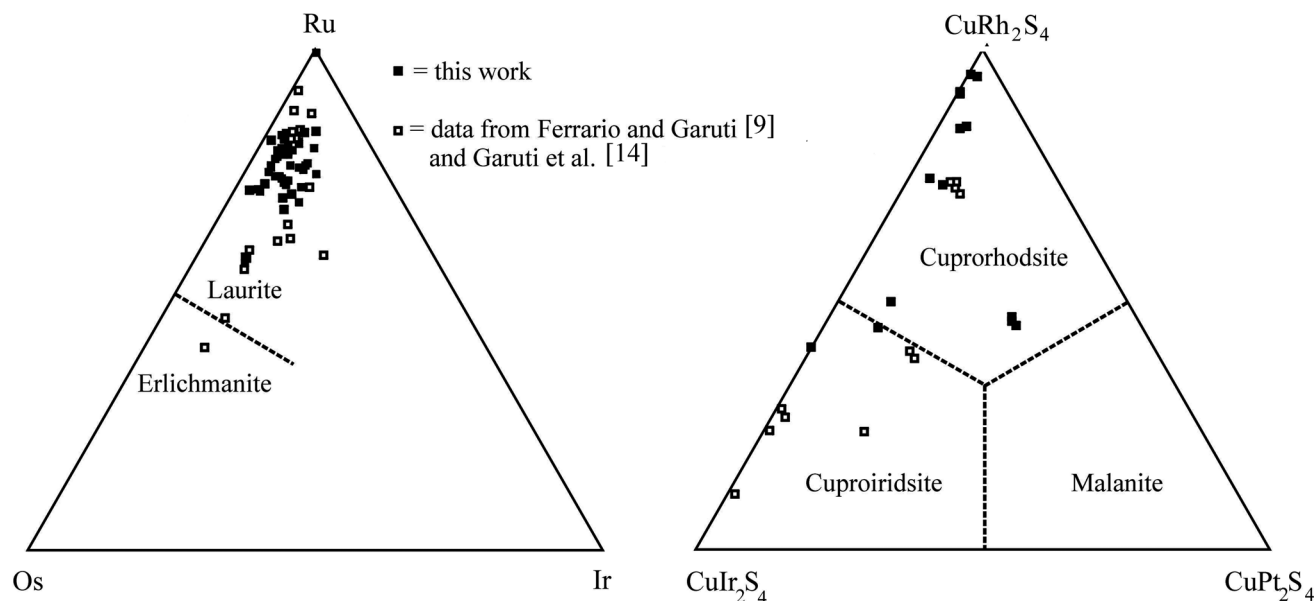


Fig. 5. Compositions of PGM (atomic %) from the Finero chromitites.

deposits, whilst at Finero the chromitites form very small bodies.

(2) The chromitites from Finero and the associated silicates are completely fresh and they show a peculiar texture characterized by rounded and lobate boundaries with the silicates. On the contrary most of the chromian spinels of the ophiolitic chromitites are deformed and brecciated, often altered in ferrian-chromite with the matrix that is mainly composed of serpentine. The Finero chromitites definitely differ from high-Cr, low-Ti podiform chromitites hosted in the mantle section of ophiolites, in which the composition of the spinel matches that crystallized from boninitic basalts in suprasubduction zones.

(3) The total amounts of PGE in the Finero chromitites are lower when compared with those reported from the ophiolitic chromitites, especially as it regards the Os-Ir-Ru contents. The PGE patterns of the Finero chromitites are characterized by a constant Rh positive anomaly, whilst the ophiolitic chromitites display a pronounced Ru positive anomaly. We have calculated the anomalies of Rh and Ru in 140 published analyses of PGE of mantle hosted ophiolitic chromitites (see the bibliography previously listed) and in 11 Finero samples. We used the formula given by [11] using the C1 chondrite values instead of the primitive mantle: Rh anomaly =  $(\text{Rh}/200)/\sqrt{(\text{Ru}/690 \times \text{Pt}/1020)}$ , Ru anomaly =  $(\text{Ru}/690)/\sqrt{(\text{Ir}/540 \times \text{Rh}/200)}$ . The two type of chromites are characterized by very different Ru and Rh anomalies: Ru = 1.1 at Finero and 2.8 in the ophiolitic chromitites, Rh = 4.2 at Finero and 1.5 in the ophiolitic chromitites.

(4) The PGM assemblage found in the Finero chromitites is consistent with the high Rh positive anomaly. Laurite, the most abundant PGM, is

accompanied by a number of cuprorhodsite, Rh-rich cuproiridsite and other Rh-bearing minerals. The Os-Ru-Ir alloys, that are very common in the ophiolitic chromitites, are absent at Finero.

#### Finero versus Serrania de Ronda massif

The Serrania de Ronda lherzolite massif (Betic Cordillera, Southern Spain) is thought to be a fragment of sub-continental mantle uplifted to crustal levels, during alpine age orogeny [33]. The massif contains two types of Cr-PGE mineralization: chromite (Cr ores) and chromite-Ni arsenides (Cr-Ni ores). They are considered to be genetically-related having segregated by differentiation of magmas that migrated from the core to the border of the mantle under decreasing  $P$ - $T$  conditions [16]. Similar to Finero, the Cr ores of Serrania de Ronda are very small in size, generally extending over less than a few square meters, but they are randomly distributed in the plagioclase lherzolite zone of the ultramafic massif whilst, at Finero, the chromitites occur in the phlogopite-bearing harzburgite. The chromite composition in both the chromitites, Finero and Serrania de Ronda, is characterized by a  $\text{TiO}_2$  content quite high. However, the Serrania de Ronda chromitites display a negative correlation between  $\text{TiO}_2$  and  $\text{Cr}_2\text{O}_3$ , not present in the Finero chromitites (Fig. 2b). The PGE chondrite normalized patterns are completely different in the two chromitites. At Finero the PGE distribution is very similar in all the chromite bodies, showing a constant Rh positive anomaly. On the contrary, the chromitites of Serrania de Ronda are characterized by extremely variable PGE abundance (Fig. 3b). The contents of Pt and Pd, in the Serrania de Ronda chromitites are higher than those found in



the Finero chromitites. Furthermore, the Serrania de Ronda chromitites are distinguished by the presence of specific PGM containing all the six PGE, by the abundance of sulfarsenides and arsenides and by the frequency of Pt and Pd bearing PGM [46]. On the contrary, in the Finero chromitites, PGE sulfarsenide-arsenides and Pd minerals are absent, whilst Pt specific minerals are extremely rare.

### CONCLUSIONS

The data presented in this paper confirm the importance of chromitites as petrogenetic indicators and collector for PGE. They show that the chromite-PGE mineralization in the Finero massif significantly differs from other podiform chromitites, being they hosted in the oceanic mantle (ophiolites) or in the lithospheric mantle (i.e. Serrania de Ronda massif), suggesting a different genesis. In particular the Finero chromitites are characterized by a quite constant Rh positive anomaly, expressed by the presence of abundant Rh minerals, high  $\text{TiO}_2$  content in the chromite and the presence of abundant "exotic" minerals, such as zirconolite, baddeleyite, thorianite, uraninite, thorite or huttonite and zircon. We believed that residual mantle of Finero reacted with an alkaline-carbonatite metasomatizing and not with a basaltic melt, as proposed for the ophiolites. This metasomatic fluid generated in the mantle itself and its interaction between restitic peridotite caused the instability of Cr-diopside and the crystallization of abundant chromian spinel in the Finero complex. The presence of alkaline-carbonatite metasomatizing fluid would appear distinctive of a mantle plume setting. This provides a further evidence that the formation of the Finero chromitites in a compressive regime as typical of the subduction zone [18, 31, 53] is very unlikely, supporting the concept of metasomatism of the Finero mantle as a result of mantle diapirism at the base of the continental crust, induced by extensional tectonics in pre-Hercynian times, as proposed by several authors [8, 10, 19, 40, 41, 52].

Among the Rh minerals found in the Finero chromitites, those corresponding to the formula  $(\text{Rh}_{0.42}\text{Ru}_{0.3}\text{Ir}_{0.19})_{1.01}(\text{S}_{1.36}\text{Sb}_{0.6})_{1.99}$ , probably represents a new mineral specie. However, due to its small size (about 5 microns) it was impossible to give a crystallographic characterization to the degree required for acceptance as new mineral species.

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## Cr-платиноидная минерализация как петрогенетический индикатор на примере метасоматизированной подконтинентальной мантии комплекса Финеро (Западные Альпы, Италия)

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Исследованы составы хромистой шпинели а также геохимия и минералогия элементов платиновой группы (МПГ) в небольших подиформных телах хромититов, связанных с метасоматизированной подконтинентальной мантией комплекса Финеро (Зона Ивреа, Западные Альпы, Италия). Наши данные указывают на то, что хромит-платиновая минерализация в массиве Финеро значительно отличается от других подиформных хромититов, расположенных в надсубдукционных зонах офиолитов океанической или литосферной мантии (например, в массиве Серрания де Ронда), что предполагает их разное происхождение. В частности, хромититы Финеро характеризуются высоким содержанием  $\text{TiO}_2$ , присутствием обильных “экзотических” минералов типа цирконолита, бадделеита, торинита, уранинита, торита или хаттонита и циркона, а также весьма постоянной Rh положительной аномалией, выраженной в присутствии обильных минералов родия. Среди этих родиевых минералов, соответствующих формуле  $(\text{Rh}_{0.42}\text{Ru}_{0.3}\text{Ir}_{0.19})_{1.01}(\text{S}_{1.36}\text{Sb}_{0.6})_{1.99}$ , вероятно присутствует новый минеральный вид. Остаточная мантия Финеро подвергалась воздействию щелочно-карбонатитового метасоматоза, а не базальтового расплава, как полагают для офиолитов. Взаимодействие метасоматического флюида, образованного непосредственно в мантии, с реститовым перидотитом привело в комплексе Финеро к неустойчивости Сг-диопсида и кристаллизации обильной хромистой шпинели. Присутствие щелочно-карбонатитового метасоматирующего флюида – отличительная особенность обстановки мантийного плюма. Это наблюдение предполагает, что формирование хромититов Финеро в типичном для зоны субдукции режиме сжатия неправдоподобно и поддерживает концепцию метасоматоза мантии Финеро в результате диапиризма мантии в основание континентальной коры, вызванного интенсивным тектогенезом в догерцинское время.

Ключевые слова: хром-платиноидная минерализация, хромититы, метасоматоз, массив Финеро, субконтинентальная мантия, родиевые минералы.