

# Platinum-Group Element Geochemistry in Chromitite and Related Rocks of the Bracco Gabbro Complex (Ligurian Ophiolites, Italy)

Roberto Cabella<sup>1</sup>, Giorgio Garuti<sup>2</sup>, Massimo Oddone<sup>3</sup> and Federica Zaccarini<sup>2</sup>

<sup>1</sup>Department for the study of the Territory and its Resources, University of Genoa, Italy

<sup>2</sup>Department of Earth Sciences, University of Modena, Italy,

<sup>3</sup>Department of General Chemistry, University of Pavia, Italy

e-mail: cabella@dipteris.unige.it

## Introduction

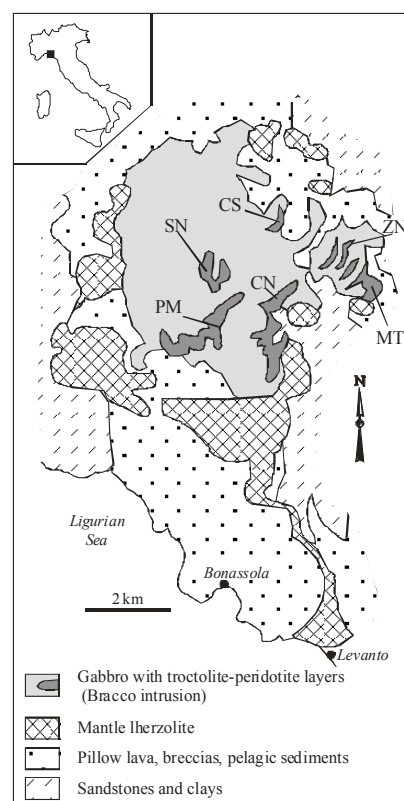
The ophiolites in the Northern Apennines of Italy are believed to represent fragments of the Mesozoic Tethys oceanic crust, exhumed during the Alpine-age orogeny. The Bracco gabbro complex belongs to the so-called Internal Ligurides that, in a commonly accepted structural model, consist of a crystalline basement made up of mantle tectonite intruded by gabbroic bodies (the Bracco gabbro complex), overlain by MORB-like basalts, ophiolitic breccias and pelagic sediments (Cortesogno et al. 1987). Trace element and isotope geochemistry indicate that volcanics, intrusive gabbros, and mantle tectonite are not linked by melt-residue relationships, the residual mantle being even interpreted as a relic of an old subcontinental lithosphere involved in the Jurassic extension (Rampone et al., 1996).

This paper reports on the composition of chromian spinel and geochemistry of the Platinum-group element (PGE) in chromitites and related mafic-ultramafic rocks of the Bracco gabbro complex.

## Geological setting and petrography of the chromitites

The Bracco gabbro complex (Fig. 1) covers an area of about 12 km<sup>2</sup> with an estimated thickness of 500 meters, and consists of layered gabbro with minor layering of peridotite, troctolite and anorthosite. The ultramafics are largely serpentinized while gabbroic rocks generally display evidences of polyphase ocean-floor metamorphic evolution grading from high-T to low-T hydrothermal conditions (Cortesogno and Lucchetti 1984). The whole ophiolitic sequence has been affected by a tectono-metamorphic overprint under prehnite-pumpellyite facies conditions (Cortesogno et al. 1987). Although the primary mineralogy is largely modified by metamorphism, the original cumulus textures are well preserved throughout the complex. Chromian spinel is a common accessory phase in peridotite and troctolite generally occurring as euhedral to subhedral grains (0.1-3 mm) interstitial to cumulus olivine, or inside

the intercumulus plagioclase. Monomineralic pods, veins, ribbon-like bodies and regular layers of Cr-spinel ranging in thickness from 0.1 to 10 cm occur associated with troctolite and peridotite at the transition zones with predominant gabbro cumulates (Fig.1). Bezzi and Piccardo (1970) for the first time recognized the cumulate texture of the chromite mineralization, and emphasized the strong similarity of the rhythmic chromitite layering inside peridotite-troctolite-anorthosite cyclic units at M. San Nicolao (SN) with the chromitite-anorthosite layering observed in other layered intrusions of the world (i.e.: Bushveld, Rhum, Skaergaard).



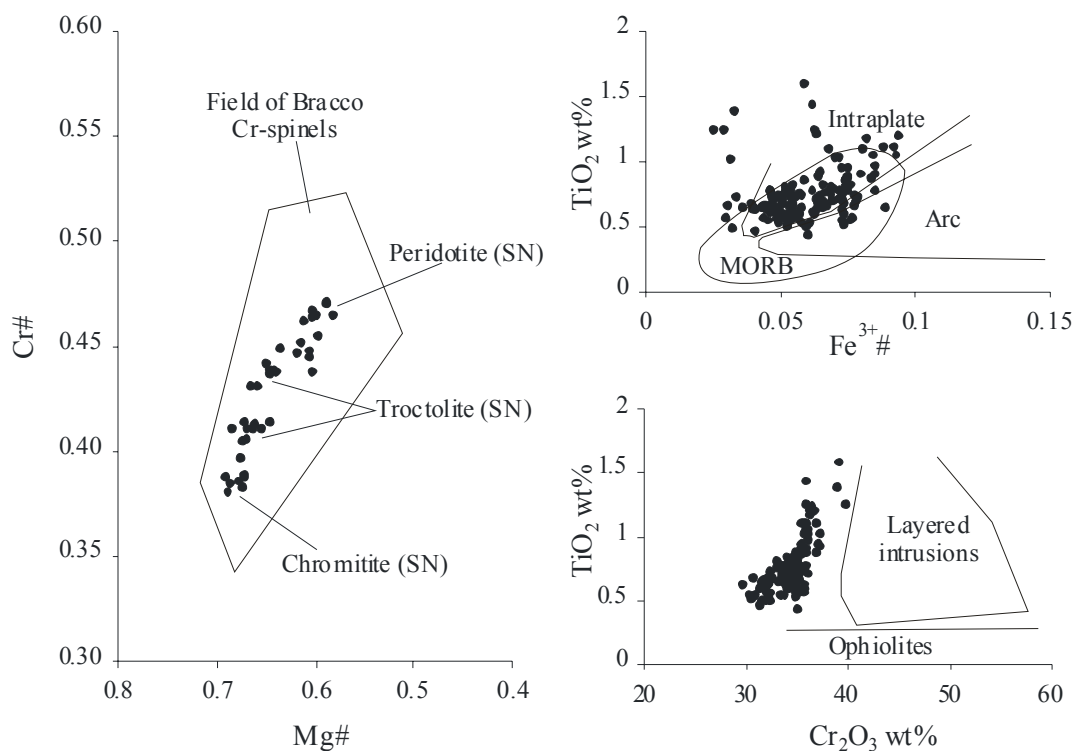
**Figure 1.** Geological sketch map of the Bracco complex. Chromite localities: SN = M. San Nicolao, PM = Pian della Madonna, CS = Case Pian Romè, CN = Canegreca, MT = Mattarana, ZN = Zona.

The cumulus texture of chromitites is locally masked by adcumulus overgrowth, sintering, or late alteration. Ferrian-chromite rims are common, however, the primary chromite is usually encountered at the cores of partially altered grains. The chromite usually contains inclusions of silicates (clinopyroxene, orthopyroxene, Na-rich phlogopite and Ti-rich pargasite), sulfides (chalcopyrite – pentlandite – pyrrhothite  $\pm$  bornite  $\pm$  pyrite), and oxydes (rutile, Mn- or Mg-rich ilmenite and Fe-rich pyrophanite). Other relevant accessory minerals are loweringite, baddeleyite, and titanite, mainly occurring associated with primary silicates and oxydes (Cabella et al., 1997). Pyrite, sphalerite and other sulfides of predominant secondary origin (heazlewoodite, millerite, violarite and mackinawite) occur disseminated in peridotite, troctolite and chromitite, and account for bulk-rock sulfur contents of up to 0.27, 0.84, and 0.44 wt% S, supporting that sulfur saturation was attained during fractionation of the Bracco intrusion.

#### Chromian spinel mineral chemistry

The mineral chemistry of spinels from the Bracco chromitites is presented in Figure 2. The compositions plot in the field of Cr-spinels close to

the limit of Al-chromite. Their low Cr# (0.37-0.51) and narrow range of Mg# (0.73-0.58) would be apparently consistent with MORB spinels (Roeder 1994), or with Al-rich chromites from ophiolitic supra-Moho cumulates (Stowe 1994). However the Bracco spinels distinguish for  $\text{TiO}_2$  contents from 0.43 up to 1.6 wt%, that are higher than those expected for ophiolitic chromitites, and in diagrams involving  $\text{TiO}_2$ - $\text{Fe}^{3+}$  relationships, most compositions straddle the fields of MORB and intraplate basalts (Arai 1992). Compositional variations through the chromitite layering in the locality of M. San Nicolao (SN) show a decrease in Cr#,  $\text{Fe}^{3+}$ , and Ti, with increasing Mg#, from the spinels disseminated in peridotite, to spinels in troctolite and in massive seams interlayered with melatroctolite and anorthosite. This trend is not consistent with that expected from common magmatic differentiation. It was described previously in chrome-spinels from the layered intrusion of Rhum (Henderson 1975), and can be interpreted as a result of the periodic mixing of incoming primitive magma, with a more differentiated liquid resident in the magma chamber (Dunham and Wadsworth 1978).



**Figure 2.** Composition of chromian spinels from the Bracco Complex.  $\text{Cr\#} = \text{Cr}/(\text{Cr} + \text{Al})$ ,  $\text{Mg\#} = \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ,  $\text{Fe}^{3+\#} = (\text{Fe}^{3+} + \text{Cr} + \text{Al})$ . Fields for MORB, Arc- and Intraplate-basalts redrawn after Arai (1992).

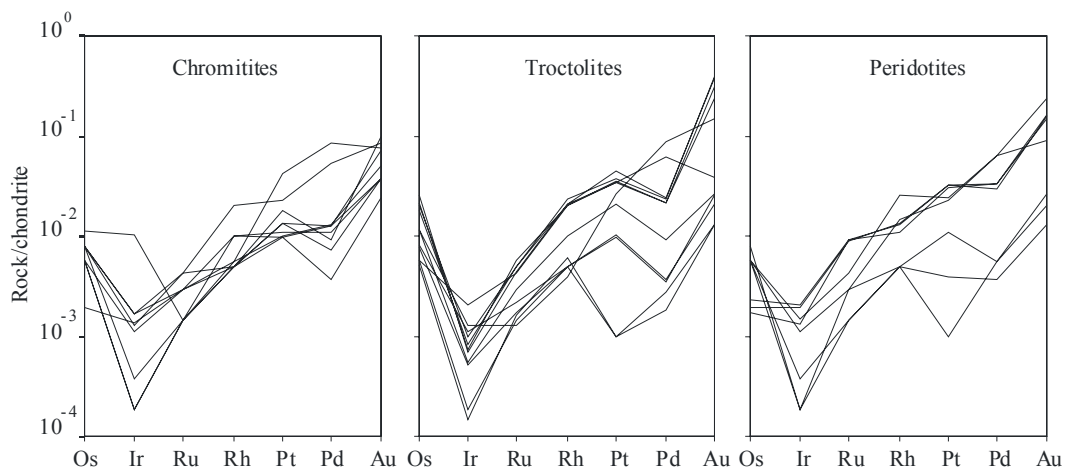
### Platinum-group element geochemistry

A total of 30 samples, 10 chromitites, 12 troctolites, and 8 peridotites were analyzed for PGE and Au by INAA at the University of Pavia. Overall PGE contents do not vary substantially with rock type, ranging 17-100 ppb, 7-78 ppb and 9-72 ppb in chromitites, troctolites and peridotites respectively. The Au concentrations are very low in chromitites (< 7 ppb) but reach up to 25 ppb and 60 ppb in peridotites and troctolites. All rocks have positive PGE patterns (Fig. 3) with Pd, Pt, and Rh abundances in the range of 0.05 to 0.1 times chondritic abundance, while the Os, Ir and Ru abundances are generally below 0.01 times chondritic, and Ir displays a marked negative anomaly. The positive correlation of the  $(\text{Pd}+\text{Pt}+\text{Rh})/(\text{Os}+\text{Ir}+\text{Ru})$  ratio with the S content (Fig. 4) supports the contention that the PGE distribution in the Bracco samples is a function of the original sulfide content (Naldrett and Von Gruenewaldt, 1989), and therefore we assume that it was the segregation of sulfide the mechanism responsible for the precipitation of the PPGE (Pd,Pt,Rh), and generation of the positive PGE profiles. The fact that at a given sulfide content, the  $(\text{Pd}+\text{Pt}+\text{Rh})/(\text{Os}+\text{Ir}+\text{Ru})$  ratio decreases sensibly from peridotites to chromitites and troctolites suggests that the "R" factor (silicate/sulfide mass ratio) was probably increasing in the early stages of fractionation, to drop down during crystallization of the main gabbroic mass, in which interstitial sulfides are very rare or absent.

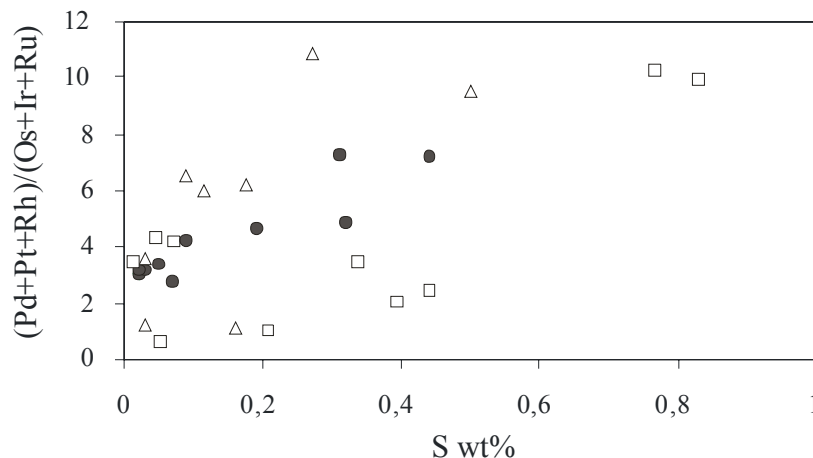
### Conclusions

Stratigraphic position of chromitites in the

Bracco gabbroic complex and the compositional variations of chromian spinel support the view that the chromitites formed as a result of the mixing of a primitive magma with a more differentiated melt that was laying over the ultramafic cumulates and had plagioclase on the liquidus. Petrographic evidence indicates that the mixed melt attained sulfur saturation at the time of chromite precipitation, and maintained such a condition during fractionation of melatroctolite and troctolite interlayered with the chromitites. The resulting sulfide liquid acted as a collector for the PPGE (mainly Pt and Pd) originating positive PGE patterns in chromitites, peridotites and troctolites. Several characters of the chromite-PGE mineralization of the Bracco gabbroic complex (i.e. chromite-anorthosite association, chromian spinel composition, PGE patterns) are not strictly consistent with the chromite-PGE mineralizations commonly observed in supra-MOHO ultramafic cumulates of ophiolite complexes, but have some similarity with those associated with Tertiary layered intrusions of the Scottish Hebrides (Henderson 1975, Bell and Claydon 1992) derived from mantle plume activity at the opening of the north Atlantic Ocean. The implication is that gabbros intruding the mantle basement of the Ligurian ophiolites may not represent typical MORB magmatism from an evolved mid-ocean spreading center, but possibly reflect the initial magmatic activity at the beginning of the Tethyan rifting, in Middle Jurassic times (Lemoine et al. 1987).



**Figure 3.** Chondrite-normalized PGE patterns for the Bracco Complex. See references in Naldrett and Von Gruenewaldt (1989) for chondrite normalization values.



**Figure 4.** Correlation between the sulfur content (S wt %) and the (Pt+Pd)/(Os+Ir+Ru) ratio in the Bracco samples. Dot = chromitite, Triangle = troctolite, Squares = peridotite.

## References

- Arai, S. 1992, Chemistry of chromian spinel in volcanic rocks as a potential guide to magma chemistry. *Min. Mag.*, 56, 173-184.
- Bell, B.R. and Claydon, R.V. 1992, The cumulus and post-cumulus evolution of chrome-spinels in ultrabasic layered intrusions: evidence from the Cuillin Igneous Complex, Isle of Skye, Scotland. *Contrib. Mineral. Petrol.*, 112, 242-253.
- Bezzi, A. and Piccardo, G.B. 1970, Studi petrografici sulle formazioni ofiolitiche della Liguria. Riflessioni sulla genesi dei complessi ofiolitici in ambiente appenninico e alpino. *Rendiconti della Soc. It. Mineral. Petrol.*, 26, 1-42.
- Cabella, R., Gazzotti, M. and Lucchetti, G. 1997, Loverigite and baddeleyite in layers of chromian spinel from the Bracco ophiolitic unit, Northern Apennines, Italy. *Canad. Mineral.*, 35, 899-908.
- Cortesogno, L. & Lucchetti, G., 1984, Ocean floor metamorphism of the volcanic and sedimentary sequences in the Northern Apennine ophiolites: mineralogical and paragenetic features. *Ofoliti* 9, 363-400.
- Cortesogno, L., Galbiati, B. and Principi, G. 1987, Note alla "Carta geologica delle ofioliti del Bracco" e ricostruzione della paleogeografia Giurassico-Cretacea. *Ofoliti*, 12, 261-342.
- Dunham, A.C. and Wadsworth, W.J. 1978, Cryptic variation in the Rhum layered intrusion. *Min. Mag.*, 42, 347-356.
- Lemoine, M., Tricart, P. and Boillot, G. 1987, Ultramafic and gabbroic ocean floor of the Ligurian Tethys (Alps, Corsica, Apennines): In search of a genetic model. *Geology*, 15, 622-625.
- Naldrett, A.J. and Von Gruenewaldt G. 1989, Association of Platinum-group elements with chromitites in layered intrusions and ophiolite complexes. *Economic Geology*, 84, 180-187.
- Rampone, E., Hofmann, A.W., Piccardo, G.B., Vannucci, R., Bottazzi, P. and Ottolini, L. 1996, Trace element and isotope geochemistry of depleted peridotites from an N-MORB type ophiolite (Internal Liguride, N. Italy). *Contrib. Mineral. Petrol.*, 123, 61-76.
- Roeder, P.L. 1994, Chromite: from the fiery rain of chondrules to the Kilauea Iki lava lake. *Canad. Mineral.*, 32, 729-746.
- Stowe, C.W. 1994, Compositions and tectonic settings of chromite deposits through time. *Econ. Geol.*, 89, 528-546.