

CHROMITE–PLATINUM-GROUP ELEMENT MAGMATIC DEPOSITS

Giorgio Garuti

University of Modena and Reggio Emilia, Italy

Keywords: chromite, platinum-group elements, magmatic ore deposits, geotectonic setting

Contents

1. Introduction
 - 1.1. Chromium
 - 1.2. Platinum-Group Elements (PGE)
 2. Chromium and PGE Geochemistry in Magmatic Systems
 3. Types and Geotectonic Setting of Chromite–PGE Magmatic Deposits
 4. Mineral Residence of PGE in Chromitites
 - 4.1. Mineralogy
 - 4.2. Primary and Secondary Platinum-Group Minerals (PGM)
 - 4.3. Origin of Primary PGM Inclusions in Chromite: the “Metallic Cluster” Model
 5. PGE Abundance in Chromitites
 - 5.1. Stratiform Chromitites in Continental Layered Intrusions
 - 5.2. Podiform and Layered Chromitites in Ophiolite Complexes
 - 5.3. Podiform Chromitites in Orogenic Lherzolites
 - 5.4. Segregation Chromitites in Zoned Ultramafic Complexes
 6. Conclusions
- Acknowledgments
Glossary
Bibliography
Biographical Sketch

Summary

Magmatic chromite deposits (chromitites) are the only source of chromium for industrial use, and in some case they may carry subeconomic to economic amounts of platinum-group elements (PGE). The chromitites are classified into two descriptive types: a) the stratiform chromitites, mainly associated with layered igneous intrusions; and b) the podiform chromitites associated with ophiolite complexes, orogenic lherzolites, and zoned mafic–ultramafic complexes. Although large chromite deposits occur preferentially in layered intrusions and ophiolite complexes, PGE are, at present, only economically recovered from the UG2 chromitite layer of the Bushveld complex in South Africa. Extensive exploration has shown that the chromitites vary from PGE-mineralized—generally enriched in the valuable metals Pt, Pd, and Rh—to almost PGE-barren—with prevalence of the low-priced Os, Ir, and Ru. Among various factors, achievement of sulfur saturation in the chromite-forming system is interpreted as a necessary condition for precipitation of Pt, Pd, and Rh to occur. Platinum mineralization in chromitites from zoned mafic–ultramafic complexes would appear to be the only relevant exception to this rule.

The great bulk of PGE associated with chromitites are carried in specific platinum-group minerals (PGM) consisting of alloys, sulfides, sulfarsenides, arsenides, and various compounds with Te, Sb, Bi, and rare oxides. PGM mainly occur as microscopic inclusions—up to some 10 microns—in chromite or associated with interstitial Fe–Ni–Cu sulfides. The solution of problems related to the separation of these ultrafine particles from the chromite ores will probably make a good number of chromitites a potential source for PGE recovery, especially in view of the expansion of the future demand for these metals on the international market.

1. Introduction

Chromium (Cr) and the platinum-group elements (PGE = Pt, Os, Ir, Ru, Rh, and Pd) have become essential commodities to human life because of their use in the manufacture of a number of consumer products and the important role they play in several industrial processes and modern engineering technologies. In nature, chromium and PGE can be economically recovered from orthomagmatic chromite deposits (chromitites) occurring associated with large bodies of mafic–ultramafic plutonic rocks. This article provides an overview of the geology, petrography, and mineralogy of economic and subeconomic chromitites in the world, with particular reference to their PGE potential.

1.1. Chromium

Chromium as a new element was first isolated from crocoite (PbCrO_4) in 1797 by Louis Nicolas Vauquelin, professor at the School of Mines in Paris. Soon after, chromium was identified as the major constituent of a new mineral of the spinel group now known in mineralogy as “chromite” ($\text{Fe}^{2+}\text{Cr}_2\text{O}_4$). In the mining industry, the term “chromite” has been extended to all members of the chromian-spinel solid solution whose composition is described by the general formula $(\text{Mg,Fe}^{2+})(\text{Cr,Al,Fe}^{3+})_2\text{O}_4$, in which Cr and total Fe can vary from 16–65 wt% Cr_2O_3 and 9–40 wt% FeO respectively. Chromite is the essential mineral component of chromitites and represents the only mineral source of chromium for industrial use. Presently, it is marketed in the international trade as “chromite ore” under three major ore grades, namely:

- “metallurgical ore” ($\text{Cr}_2\text{O}_3 > 48\%$ and $\text{Cr/Fe} > 2$);
- “chemical ore” ($\text{Cr}_2\text{O}_3 > 45\%$); and
- “refractory ore” ($\text{Cr}_2\text{O}_3 > 30\%$, high Al_2O_3 , and $\text{SiO}_2 < 2.5\%$).

About 85% of the world production of chromite ore (~12 million tonnes (Mt)) is consumed by the metallurgical industry. For metallurgical purposes, the chromite ore is blended with fluxes and smelted to form ferrochrome, ferro-silicochrome, and nonferrous-chrome alloys, which are mainly used as sources of chromium by the steel industry. The use of chromite by the chemical industry is substantially smaller than that of the metallurgical industry, running around 8% of the world production. The chemical ore represents the feed material for the preparation of sodium chromate, from which many other chromium chemicals (i.e., sodium and potassium dichromates, chromic acid, and chromic oxide) are produced. The end uses of chromium chemicals are quite diverse and include metal finishing, leather tanning, pigments, wood preservation,

electroplanting, and pharmaceuticals. About 7% of chromite ore production goes to the refractory industry. Refractory chromites are generally used in the natural state; after crushing and grinding they are blended with magnesia to make shaped and unshaped refractory products (i.e., furnace-lining briquettes and foundry molding sands). The Republic of South Africa (RSA) is the major producer of chromite ore, with about 4.5 Mt in the year 2000; followed by Kazakhstan (~2 Mt), Turkey (1.4 Mt), India (1.2 Mt), Finland (0.5 Mt), Zimbabwe (0.5 Mt), and Brazil (0.2 Mt).

1.2. Platinum-Group Elements (PGE)

Platinum was discovered by Julius Scaliger in 1735. Palladium, rhodium, osmium, and iridium were officially described between 1803 and 1804 by W. Wollstone and S. Tenant, whereas ruthenium was identified only in 1844 by K. Klaus. From the second half of the twentieth century onwards, PGE have become essential to modern industry, assuming such a relevant role in a number of advanced technologies that they have gained the reputation of “miracle metals.” Their innumerable applications are based on physical properties such as electrical conductivity and high resistance to heat, oxidation, and chemical corrosion, though what makes some of the PGE even more extraordinary is their rather unique ability to act as extremely efficient catalysts in several chemical reactions. Worldwide demand for PGE by application in 2000 is shown in Table 1. A remarkable increase was recorded in the 1990s, mainly because of the adoption of restrictive laws for the emission of poisonous exhaust gases from internal combustion engines (autocatalysts) in most industrialized countries. Further expansion of demand is expected as a result of the development of fuel-cell technology, which will certainly play a prominent role in the production of clean energy and the construction of electrical vehicles in the not too distant future, when consumption will have critically dwindled our reserves of natural combustibles (oil, coal, fissionable elements). In that moment, our energy supply will not be able to do without the platinum metals, which will become a strategic commodity for human life.

Year 2000	Pt (545)	Pd (682)	Rh (1998)	Ru (130)	Ir (415)
Autocatalyst *	1370	5420	715		14
Chemical	270	260	35	79	
Electrical	455		6	97	19
Glass	255		42		
Dental		820			
Electronics		2140		235	59
Petroleum	105				
Jewelry	2840	200			
Investment	140				
Other **	365	60	9	28	35
Total	5800	8900	807	439	127

Notes:

* = Recovery excluded.

** = Mainly crucibles for Ir.

Numbers in brackets: prices in US\$ per oz.

Table 1. Worldwide demand for PGE by application in units of 1000 oz

For a long while—straddling the nineteenth and twentieth centuries—platinum was only won from nuggets in placer deposits, mainly located downstream of mafic–ultramafic magmatic complexes in Colombia, Canada, and Russia. Lode deposits were not mined until the early 1920s, at first in Canada and subsequently in Transvaal (RSA), where PGE occur associated with magmatic sulfides and are gained as either coproducts or byproducts of Ni and Cu mining. The only chromitite-hosted PGE deposit worked to day is the UG2 chromitite layer of the Bushveld complex (RSA), carrying estimated resources amounting to more than 13×10^6 kg Pt, with an average recovery grade of about 2.5 g t^{-1} , and even more economically attractive than its companion PGE–sulfide reefs. Although UG2 still remains a unique, remarkable exception, literature data show that PGE mineralization is associated with a number of chromite deposits in the world.

2. Chromium and PGE Geochemistry in Magmatic Systems

Chromium is a transition metal belonging to group VIa of the periodic table of elements characterized by lithophile geochemical behavior: it tends to partition into oxide minerals and silicates rather than metals or sulfides during crystallization of natural magmas. Chromium is a minor elements in igneous rocks. Its concentration in the earth's mantle has been estimated to vary between 0.3 wt% and 0.7 wt% Cr_2O_3 —depending on the authors and methods of calculation—and decreases to figures of 0.01–0.05 wt% Cr_2O_3 in basaltic magmas derived from mantle partial melting. The Cr^{3+} ion is the most common form of chromium within basaltic magmas. The Cr^{3+} ion has very low solubility in silicate melts and therefore tends to precipitate as highly refractory oxides (chromite and chromian spinels) in the early stages of magmatic crystallization. Owing to the low Cr content of the parent magmas the total amount of crystallizing chromite is usually low ($< 2.0 \text{ vol}\%$), forming low-grade disseminations in ultramafic rocks, mainly consisting of olivine and pyroxenes. The origin of almost all monomineralic accumulations of chromite (chromitites) associated with mafic–ultramafic plutonic complexes requires that chromite is the sole crystallizing phase during long periods of the fractional crystallization of the parent melt. Experimental models indicate that different factors (i.e., variations in oxygen fugacity, total pressure, and silica activity, promoted by mixing of different magmas or reaction of a mafic magma with solid ultramafic rocks) may contribute to expand the stability field of chromite in magmatic systems, leading to the formation of essentially silicate-free, massive chromite deposits representing important mineral resources.

PGE (Ru, Rh, Pd, Os, Ir, Pt) pertain to Group 8 of the transition metals. Because of their siderophile nature, PGE have extremely high metal/silicate partition coefficients of the order of 10^6 , therefore they were forced to collect into the earth's core during the early differentiation of the planet—probably at trace concentrations of 0.000003–0.000008%—as deduced from the study of iron meteorites. The PGE content of the earth's mantle is estimated from the analysis of alpine-type peridotites and mantle xenoliths, and reflects the composition of the carbonaceous chondrites (CC1) by a factor of 0.00815 (Os = 4.2×10^{-9} , Ir = 4.4×10^{-9} , Ru = 5.6×10^{-9} , Rh = 1.6×10^{-9} , Pt = 8.3×10^{-9} , and Pd = 4.4×10^{-9}). Surprisingly, these concentrations are at least one order of magnitude higher than would be expected if metal/silicate equilibrium had been achieved between the (Fe–Ni) core and (Fe–Mg–Si) mantle during the earth's differentiation. The reason for this anomaly has long been debated and not completely

understood; however, there is now general agreement that it might have resulted from the addition of chondritic material to the primitive mantle by meteoritic bombardment (the Late Veneer model) in the early history of the earth. The average concentration of PGE in the earth's crust is in the order of a few mg t^{-1} , too low to allow an economic recovery of these metals. However, substantial amounts of PGE were extracted from the earth's mantle by partial melting and transferred into the crust by upwards injection of the produced mafic silicate melts, several times during the history of the earth. These melts generally had basaltic composition, and although not particularly concentrated in PGE, they represented the natural precursors to the formation of economic PGE deposits at crustal levels. Although PGE represent a coherent group of highly refractory and siderophile metals, they exhibit slightly different geochemical behaviors during formation and evolution of terrestrial basalts. On this basis they have been divided into two subgroups: the high-melting IPGE, including Ir, Os, and Ru, characterized by a relatively low solubility in silicate melts; and the low-melting PPGE (Pd, Pt, and Rh), characterized by a relatively more soluble character. In silicate magmas PGE are chalcophile, having a strong affinity for the magmatic sulfide phase, so that if sulfur saturation is achieved, they will partition strongly into the resulting Fe–Ni–Cu sulfide liquid with sulfide/silicate partition coefficients of the order of 10^3 – 10^6 . In sulfur-poor systems, the magma may become saturated with refractory PGE minerals, which are collected together with the early-crystallizing refractory silicates and oxides. The geological classification of magmatic PGE deposits apparently reflects a geochemical behavior of PGE mainly based on their chalcophile and siderophile properties, showing that PGE concentrations occur mainly when associated with the accumulation of Fe–Ni–Cu magmatic sulfides (the sulfide association) or in close relation with fractional crystallization of chromite and olivine (the oxide/silicate association).

-
-
-

TO ACCESS ALL THE 21 PAGES OF THIS CHAPTER,
Visit: <http://www.eolss.net/Eolss-sampleAllChapter.aspx>

Bibliography

Cabri L.J. (ed.) (1981). *Platinum-Group Elements: Mineralogy, Geology, Recovery*, special Vol. 23, 267 pp. Ottawa, Canada: Canadian Institute of Mining and Metallurgy. [This book represents the first comprehensive treatise addressing the origin of PGE deposits, based on modern geological and mineralogical concepts.]

Cabri L.J. and Naldrett A.J. (1984). The nature of the distribution and concentration of platinum-group elements in various geological environments. *27th International Geological Congress* (Proceedings of the 27th International Geological Congress, Moscow, USSR, 1984), Vol. 10, *Mineralogy* (ed. VNU Science Press), pp. 17–46. [This article presents the first coherent classification of PGE deposits in different geological settings.]

Cawthorn R.G. (1999). The platinum and palladium resources of the Bushveld complex. *South African Journal of Sciences* **95**: 481–489. [Based on a wide literature, the article gives a reliable figure of the platinum and palladium resources enclosed in the Bushveld complex.]

Daltry V.D.C. and Wilson A.H. (1997). Review of platinum-group mineralogy, compositions and elemental associations of the PG-minerals and unidentified PGE-phases. *Mineralogy and Petrology* **60**: 185–229. [This article presents the most recent comprehensive updating of the PGM mineralogy, including a list of minerals still on record.]

Leblanc M. and Nicolas A. (1992). Ophiolitic chromitites. *International Geology Review* **34**(7): 653–686. [This article provides a modern revision of the geology and petrology of chromite ore deposits related with ophiolite complexes.]

Malitch K.N. (1998). Peculiarities of platinum-group elements distribution in ultramafites of clinopyroxenite-dunite massives as an indicator of their origin. *International Platinum* (ed. N.P. Laverov and V.V. Distler), pp. 129–140. St Petersburg and Athens: Theophrastus Publications. [This paper represents a review of PGE distribution in Inagli-type zoned complexes of Russia, including recent data on related chromite–PGE mineralization.]

Martin R.F. (ed.) (1990). Advances in the study of platinum-group elements. *The Canadian Mineralogist, Journal of the Mineralogical Association of Canada* **28**(3): 1–690. [This is a wide compilation of scientific articles providing a complete picture of the state of the art at the beginning of the 1990s.]

Naldrett A.J. and Von Gruenewaldt G. (1989). Association of platinum-group elements with chromitite in layered intrusions and ophiolite complexes. *Economic Geology* **84**: 180–187. [This article discusses the role of sulfur saturation in determining PGE distribution in precipitating chromitites, based on a revision of a large number of PGE analyses. It has been used as data source in drawing diagrams in Figure 4.]

Prichard H.M., Potts P.J., Bowles J.F.W., and Cribb S.J. (ed.) (1987). *Geoplatinum* 87, 422 pp. London and New York: Elsevier Applied Science. [This book is a wide compilation of scientific articles describing different aspects of the mineralogy, geochemistry, and geology of PGE.]

Tredoux M., Lindsay N.M., Davies G., and McDonald I. (1995). The fractionation of platinum-group elements in magmatic systems, with the suggestion of a novel causal mechanism. *South African Journal of Geology* **98**: 157–167. [This article provides a re-interpretation of the geochemical and crystallochemical behavior of PGE, based on the metallic cluster model for transition elements.]

Biographical Sketch

Giorgio Garuti received his title of Doctor in Geological Sciences from the University of Modena, Italy, in 1969. After military service, he spent three years as a postdoctoral fellow at the same institution. Since 1975 he has held research and teaching positions at the Department of Mineralogy and Petrology of the University of Modena, where he is currently Professor of Ore Deposits. He has extensive expertise in the fields of structural petrography, petrology, mineralogy, and metallogeny of mafic–ultramafic rocks in the following areas: Ivrea-Verbano Zone (western Alps) and Betico-Rifean Cordillera (southern Spain and northern Morocco); Mesozoic ophiolites of Liguria (Italy), Greece, Albania, and Cyprus; Paleozoic ophiolites of the Urals and Precambrian ophiolites of the eastern desert of Egypt; layered intrusion in the cratons of South America (Goias and Bahia State) and South Africa (Bushveld); and concentrically zoned mafic–ultramafic complexes of the Urals and mafic–ultramafic rocks of Argentina. Much of his research has focused on the geochemistry, mineralogy, and economic geology of platinum group elements (PGE), Fe–Ni–Cu sulfides, and chromite. Professor Garuti was associate editor of *The Canadian Mineralogist*, 1997–9, and is the Italian representative of the International Association on the Genesis of Ore Deposits (IAGOD). More information is available on the web page <www.terra.it/georisorse/index.htm>.