METAMORPHISM OF CHROMITITES IN THE TAPO ULTRAMAFIC MASSIF, EASTERN CORDILLERA, PERU

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Abstract. Metamorphosed chromite crystals in massive chromitite ore-bodies from the Tapo ultramafic massif (Peru) show distinct petrographic features and chemical patterns of zoning different from those exhibited by disseminated chromites. The observed differences can be explained in terms of prograde metamorphism up to the lower-amphibolite facies, under the control of the chromite/silicate ratio, chromite grain size and degree of fracturing.

Keywords. Ophiolite, Chromite, Metamorphism, Tapo Ultramafic Massif.

1 Introduction

Metamorphism can deeply modify the chemical composition of chromite affecting its commercial grade. However, the degree of alteration suffered by chromite crystals in chromitites does not only depend on the metamorphic grade, since it is relatively frequent to observe chromitites in high-grade metamorphic terranes, with very variable, but scarce alteration. Correlation between chromitite alteration and metamorphic grade of the host is not always evident. To investigate what other factors may control the extent of the alteration of chromitites we have selected a set of small chromitite deposits located in the Tapo ultramafic massif in the Eastern Cordillera of Central Perú. Four samples of massive chromitites selected for analysis by EMPA were collected from the San Felipe (samples 33 and 6A), Tomasa (sample 30) and Cerro Chacciapata (sample 21) bodies. Four additional, selected samples with disseminated texture come from the Rumicruz-Tomasa-Felipito area (samples 16, 19, 61 and 61X).

2 Geological setting

The Tapo ultramafic massif is a NW-SE elongated body,

located 3km west of the Tapo village in the Eastern Cordillera (Fig. 1). It is ~5km long and 1-2km wide, and



Figure 1. Simplified geological map of the Tapo Ultramafic Massif, showing the location of the different chromite mines and showings.

occurs tectonically emplaced upon Lower Carboniferous sedimentary rocks (Ambo Group, Mégard et al, 1996). The latter consist of conglomerates, sandstones and pelites interbedded with volcanic tuffs. The overall structure of the massif corresponds to a NW-SE trending, thrust bounded synform. (Further information in Castroviejo et al., 2009).

The Tapo massif consists of highly serpentinized peridotites which locally preserve evidences of their harzburgitic and, to a lesser extent, dunitic protoliths. Serpentinites contain 1-2 km long, but thin (< 100 m thick) bands of amphibolites and metagabbros along their SW contact. They also contain several small (few tens of metres long) bodies of chromitites which were worked in the past in the San Felipe Manto, Rumicruz, Tomasa and Felipito mines. San Felipe and Manto mines occur near the NE contact of the massif whereas Rumicruz, Tomasa and Felipito mines, as well as the Cerro Chacciapata chromite showing are aligned parallel to the SW contact, close to the amphibolite/metagabbro bands (Fig. 1). These chromitites display massive (>85% chromite), semi-massive (60-85% chromite) and/or disseminated (<60% chromite) textures.

3 Petrography and texture of chromite

Massive and semi-massive chromitites consist of coarsegrained aggregates of rounded and sub-rounded chromite crystals. The latter are highly fractured and exhibit irregular zoning caused by alteration. Most frequent zoning consists of two or three distinct optical zones, which are not equally developed in all samples. Zoning is usually concentric, advancing from rims and, at lesser extent, fractures inwards, although irregular and patchy patterns of zoning are also present (Fig. 2). Alteration zones contain variable amounts of hydrous silicate inclusions, mainly chlorite and serpentine. Nearly homogeneous, slightly altered grains are preserved only in very coarse-grained, non-fractured portions of massive chromitites.



Figure 2. Back-scattered electron photomicrographs illustrating typical patters of zoning of chromite: (A) massive chromitite and (B) disseminated chromite.

Disseminated chromite occurs as variably fractured, irregular grains, showing four distinct optical zones arranged concentrically from grain boundaries inward. The contacts between the different optical zones are sharp. Like in massive-textured chromites, the outermost alteration zone contains abundant inclusions of chromite and minor serpentine. These zoned grains are usually coated by a layer of minute, subhedral crystals of magnetite. These zoned, disseminated chromite crystals are equivalent to "type 2 spinels" defined by Barnes (2000).

4 Chromite composition

Most unaltered cores of chromite crystals from massive chromitites show a restricted composition, having Cr# [Cr/(Cr+Al)]=0.40-0.57, Mg# [Mg/(Mg+Fe)]=0.70-0.80 and Fe³⁺# [Fe³⁺/(Fe³⁺+Cr+Al)]<0.16 (Fig. 3). However some optically homogeneous cores exhibit a modified composition characterized by significant increase in Cr_2O_3 (with loss of Al₂O₃, resulting in Cr# up to 0.74) and Fe^{2+} (Mg# decreases down to 0.51) without any increase in Fe₂O₃ content. In the first alteration zone, depletion of Al₂O₃ continues, compensated by slight residual enrichment in Cr₂O₃ and the incorporation of significant amounts of Fe₂O₃ (up to 16 wt.%). This zone also contains increasing amounts of FeO (Mg# decreases down to 0.2), as well as high MnO (up to 6.4wt.%) and, locally, ZnO (up to 5wt.%); its NiO content is very low (<0.45wt.%). The outermost zone can be considered an intermediate phase between chromite and magnetite; it is called ferritchromite. Its composition is characterized by very small amounts of Al₂O₃ and similar Cr₂O₃ (from 34 to 38wt.%) and Fe₂O₃ contents (20 to 36wt.%; Fig. 3).

FeO content of ferritchromite in massive chromitites does not change with respect to that of chromite from the first alteration zone (Figure 3). In contrast, it contains lower MnO (<2wt.%) and ZnO (<0.65wt.%), but higher NiO (up to 1.3wt.\%).



Figure 3. Chemical composition of massive and disseminated chromite in terms of their Mg# and Cr_2O_3 , Al_2O_3 and Fe_2O_3 contents.

Unaltered nuclei of disseminated chromites have a composition very close to those from massive chromitites (Cr#=0.52-0.54, Mg#=0.63-0.67 and Fe³⁺#=0.04-0.05). Similarly to the latter, there are some optically homogeneous nuclei having slightly lower Cr#

(0.50-0.52) and higher Fe³⁺# (up to 0.09), together with significant enrichment in FeO (Mg# decreases down to 0.43) and ZnO (varies from <0.1 to 0.6wt.%). In contrast, the subsequent alteration zones in disseminated chromites show a continuous trend of Fe₂O₃ enrichment, Cr₂O₃ depletion and strong loss of Al₂O₃ contents (Fig. 3), reaching the proportions of these oxides in magnetite. These chemical changes among the trivalent cations are accompanied by continuous increase of FeO substituting for MgO (Fig. 3). The latter is leached out from chromite and concentrated in the hydrous phyllosilicates (chlorite and serpentine) of the host silicate matrix. Minor oxides show variable trends: MnO first increases from 1.4 to 3.7wt.% and then decreases down to 0.0wt.%; NiO increases from 0.15 to 0.7wt.%; ZnO decreases from the first alteration band to the contact with magnetite (from 1.0 to <0.1wt.%); TiO₂ remains constant (<0.45wt.%) except in one sample where it correlates possitively with FeO and Fe₂O₃, reaching 1.83wt.% The outermost rim of magnetite contains small amounts of Cr₂O₃ (up to 8wt.%) and traces of NiO (<0.68wt.%), TiO2 (<0.65wt.%), MnO (<0.4wt.%) and ZnO (<0.2wt.%).

5 Discussion

Petrographical and chemical data evidence that the extent of the alteration of chromite in the Tapo Ultramafic Massif mainly depend on the chromite/silicate ratio and, at lesser extent, on chromite grain size and degree of fracturing. Thus, the less altered crystals are those occurring in coarse-grained, slightly fractured, massive chromitites whereas highly altered chromite tends to be small in size (<1mm across) and/or strongly fractured, and occurs disseminated in the serpentinites.

Chromite alteration is always characterized by continuous depletion in Al2O3 and MgO, coeval with enrichment in FeO. Cr₂O₃ slightly increases in massive chromites but decreases in the disseminated ones. In contrast, Fe₂O₃ shows smooth increase in massive chromites (it tends to be opposite to the trend shown by Cr_2O_3) and strong enrichment in disseminated chromites with the progress of alteration. These alteration trends can be better explained referring them to the metamorphic facies of Cr-spinels defined by Purvies et al. (1972), Evans and Frost (1975), and Suita and Streider (1996) (Fig. 4). According to this figure, the trend defined by the studied disseminated chromites clearly follows that expected in chromites metamorphosed under low-temperature amphibolite facies. However, most of the occurrences in massive chromitites preserve inner alteration bands which show chemical trends generated during previous metamorphic events under greenschist facies. The absence of equilibrium of the outermost alteration bands in chromite from massive chromitites, under lower amphibolite facies metamorphism, is caused by the slow diffusion of trivalent cations in the spinel structure as well as the low permeability of these rocks for the intergranular flow of metamorphic fluids. The latter are essential for the necessary supply of iron (both Fe^{2+} and Fe^{3+}) to form ferritchromite. Furthermore, the small amount of serpentine matrix around massive chromite limit the

extent of the extraction of Al_2O_3 from chromite as show the reaction proposed by Mellini et al. 2005:

 $\begin{array}{ll} MgAl_2O_4 + 1.5Mg_3Si_2O_5(OH)_4 + H_2O + 0.083O_2 \rightarrow \\ Al-Spinel & serpentine \end{array}$

 $\rightarrow Mg_5AlSi_3O_{10}(OH)_8 + 0.167(M)_3O_4$ chlorite Cr-magnetite

This reaction shows that the Al-rich component of

chromite reacts with serpentine to form chlorite and either a residual Cr-rich chromite or ferritchromite, depending on Fe^{3+} availability.



Figure 4. Chromite composition of the Tapo ultramafic massif plotted on a Cr-Fe³⁺-Al triangular diagram.

6 Conclusions

The alteration trends observed in the chromites of Tapo reflect the effect of metamorphic reactions. The intensity of these reactions depends on the chromite/silicate ratio and the fracturing grade.

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