A Model for Co-Precipitation of Platinum-Group Minerals with Chromite from Silicate Melts

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Introduction

The Platinum-Group Elements (PGE) show enigmatic behaviour during crystallization of chromite in mafic silicate magmas. Whereas Rh, Pt and Pd (PPGE) are incompatible with crystallizing chromite, the Ir-group (Ir, Os, Ru; the IPGE) tend to be included in chromite crystals, leading to their depletion in the residual melt. Here I show that the association of IPGE with natural and experimentally grown chromite can be understood as a result of local perturbation of the redox state of silicate melt surrounding growing chromite crystals.

Background

The reason for the inclusion of IPGE in chromite and other magmatic spinels has been contentious. Experimental and field studies employing indirect or bulk analytical techniques to characterize the composition of magmatic chromites have shown large apparent Nernst partitioning coefficients $D_{IPGE}^{Ch/melt}$ (e.g., Brugmann et al., 1987; Capobianco and Drake, 1990; Capobianco et al., 1994; Puchtel and Humayun, 2001). Microtextures, thermodynamic constraints, and the results of microanalytical studies confirm that the IPGE are not actually incorporated in the crystal structure of chromite but occur as discrete inclusions of Platinum-Group Minerals (PGM) (e.g., Sattari et al., 1999). The inclusions range in size from nanometer-scale (and hence invisible during optical examination) to sub-millimeter-scale, and include laurite ($(Ru,Os,Ir)S_2$ alloy), Os-Ir alloy, and a host of subsidiary alloy and sulfide phases of the other PGE (Merkle, 1992; Ballhaus and Sylvester, 2000). The amount of IPGE present within magmatic chromite grains generally exceeds the amount represented by what is observable by conventional optical and Scanning Electron Microscope (SEM). Based on the results of time-resolved Laser-Ablation Inductively Coupled Mass Spectrometry (LA-ICPMS), the greater part of the PGM present within chromite crystals appear to be contained in submicroscopic grains of PGE and base metal alloys despite the predominance of the sulfide phase laurite at the scale observable at the microscopic scale (e.g., Sattari et al., 1999; Ballhaus and Sylvester, 2000).

Field observations (Peck et al., 1992) and experimental studies show that Ru-Os-Ir alloys can precipitate directly from silicate melts. Laurite is the most common magmatic IPGE sulfide, and also can be grown experimentally under conditions representative of natural mafic magmas (Brenan and Andrews, 2001). The solubility of IPGE alloys are known to be strong functions of fO_2. Through comparison of possible dissolution reactions such as

$$Ru_{alloy} + n/4\ O_2 = RuO_{n/2(melt)} \qquad K \quad (1)$$

with observed dependences of IPGE metal solubility on fO_2 it has been possible to infer that Ru and Os dissolve in magmas at commonly observed fO_2 in the trivalent state (e.g., Borisov and Nachtweyh, 1998; Borisov and Walker, 2000), whereas Pt, Ir and Rh are thought to dissolve predominantly in the divalent state, and Pd in the monovalent state (Borisov and Palme, 1994, 1995; Borisov et al., 1997; Ertel et al., 1999). Comparison of observed IPGE concentrations in mafic silicate magmas with their measured solubilities suggests that many natural magmas exist in states near to IPGE alloy saturation and could be perturbed into precipitating the alloys by small reductions in their intrinsic oxidation state. Indeed, a major obstacle to the accurate measurement of PGE solubility in silicate melts has been the ease with which submicroscopic "micronuggets" of alloy form upon reduction in alloy solubility due to changes in melt redox state (Ertel et al., 1999).

It follows from equation 1 that the solubility of a PGE will depend on fO_2 as follows

$$\log X_{Ru^{+n}} = -\log \gamma_{Ru^{+n}} - \log K - n/4 \log fO_2 \qquad (2)$$

with the result that the solubilities of the trivalent PGE will show markedly stronger dependences on fO_2 than those of the divalent ones. Reductions in oxygen fugacity will therefore promote precipitation of all of the PGE, but more extensive

precipitation of the more highly oxidized species is expected.

Model

The association of IPGE alloys and laurite with magmatic chromite and spinel may be understood by consideration of what happens as the crystal grows from the silicate melt. A crystal grows in response to some change in the intensive parameters of its local thermodynamic system. For example, a melt may be perturbed into a state of chromite supersaturation by a change in temperature or by mixing with another magma along the chromite-olivine cotectic (Irvine, 1977). A chromite grain might nucleate and begin to grow or a pre-existing grain formerly at equilibrium with its host melt may begin to grow anew. Initially, although the system as a whole will not have reached equilibrium, local reversibility may be assumed, and the crystal-melt partitioning will still obey equilibrium thermodynamic constraints at the interface (e.g., Liang, 1999). Growth of the chromite grain will be accomplished by diffusive transfer of chromite components from a steadily increasing volume of silicate melt, for as long as the melt between widely separated chromite grains remains supersaturated with chromite.

Chromite incorporates Fe^{+3} and Fe^{+2} with a Fe^{+3}/Fe^{+2} ratio always exceeding that of the melt, and furthermore incorporates Cr^{+3} to the complete exclusion of Cr^{+2} despite the presence of Cr in both valencies in the silicate melt (Roeder and Reynolds, 1991). A compositional boundary layer may be defined as the region between the melt-crystal interface and the outermost extent of the region in which diffusion occurs due to chromite growth. This boundary layer will be depleted in both Cr^{+3} and Fe^{+3}. The homogeneous reaction

$$Fe^{+3} + Cr^{+2} = Fe^{+2} + Cr^{+3} \qquad (3)$$
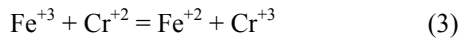
may be assumed to take place instantaneously, so that the fO_2 defined by each of the chromic/chromous and ferric/ferrous ratios will be identical. Due to the net loss of the oxidized species Fe^{+3} and Cr^{+3}, the melt as a whole will be somewhat reduced throughout the compositional boundary layer, increasingly so toward the melt-crystal interface.

I have employed simple empirical relations published by Roeder and Reynolds (1991) for chromic/chromous and ferric/ferrous ratios as functions of fO_2, combined with a least-squares fit to their data for chromite solubility in diabase melt 401 as a function of fO_2 to estimate the composition of the melt in the interface surrounding a chromite crystal growing from a melt initially containing 4,000 ppm Cr_2O_3* at 1300 °C with an ambient intrinsic fO_2 of 10^{-7} (~ FMQ). The melt in the boundary layer is significantly depleted in Fe+3 and Cr+3, with an equilibrium Cr_2O_3* content of 1230 ppm and an intrinsic fO_2 of $10^{-7.14}$.

As discussed above, many magmas from which chromite precipitates are probably near to alloy saturation so that even small changes in redox state can cause micronuggets of alloy to form throughout the compositional boundary layer. In the example above the reduction of fO_2 by 0.14 log units will diminish Os and Ru solubility each by $100-10^{(0.14 \times 0.75)} = 22\%$. Solubilities of the divalent PGE will be reduced by about 15%. The formation of micronuggets would be promoted most strongly in the immediate interfacial region because this is where the fO_2 is reduced the most. Micronuggets with sizes in the nanometer to micrometer range will have negligible Stoke's flow velocities, with the result that they will not be advected away from the growing crystal face by their own negative buoyancy. Whereas melt components rejected by the growing crystal (including PGE not present in micronuggets) can diffuse away from the interfacial region with diffusivities in mafic liquids on the order of 10^{-6} cm^2s^{-1} (e.g., Mungall, 2002a), the removal of nm-scale micronuggets from the interfacial region by Brownian motion will be impeded by their relatively large size. The Stokes-Einstein relation predicts a diffusivity for micronuggets on the order of 2 orders of magnitude less than the network-former diffusivity in a given melt if the particles in question are about 2 orders of magnitude larger than the network-forming tetrahedra. Larger particles will be even more sluggish, with the result that alloy micronuggets, once formed, will tend to be overgrown by the advancing crystal-melt interface, thus becoming inclusions in the growing chromite crystal.

The effects of chemical diffusion in the compositional boundary layer do not stop at the imposition of a locally disturbed intrinsic fO_2. Two other factors related directly to diffusion of the PGE themselves will contribute to the effect. First, the diffusivities of the trivalent PGE are expected to be substantially smaller than those of the divalent and monovalent PGE (Mungall, 2002b), so that these relatively slowly-moving species will tend to become concentrated by diffusive "pileup" in the interfacial region before a rapidly growing crystal (e.g., Smith et al., 1955). If the melt in the interfacial region is already saturated with PGE alloys, the result will be inefficient diffusive removal of the rejected IPGE and additional growth of alloy micronuggets.

The combined results of the micronugget formation and diffusive pileup around the growing crystal will cause $D_{IPGE}^{Ch/melt}$ to tend toward 1 even if the true equilibrium value of $D_{IPGE}^{Ch/melt}$ is much less than 1. However these effects cannot bring $D_{IPGE}^{Ch/melt}$ to values > 1.

The second diffusive effect on effective PGE partitioning results from the fact that supersaturation of Ru and Os will not have resulted from a change in their chemical activities, but through a change in the oxygen fugacity. Crystallization of nuggets of alloy in the compositional boundary layer will consequently reduce their activities, imposing an activity gradient on the affected PGE between the more distant melt and the boundary layer. In response to the development of this activity gradient, Ru and Os will diffuse inward from the far-field toward the growing crystal, being continuously consumed by the formation of more alloy. This process of inward IPGE diffusion will continue for as long as the chromite crystal growth continues to impose a reduced fO_2 in its compositional boundary layer. As a result of this net inward flux of PGE toward the zone of alloy saturation, the effective $D_{IPGE}^{Ch/melt}$ can be raised to values significantly greater than 1, as is observed in nature and experiment.

Formation of laurite

The reaction to form laurite from a melt containing S^{-2} and Ru^{+3} ions requires a net addition of oxygen, as shown below

$$4FeS_{(melt)} + 2Ru^{+}{}_{3(melt)} + 1/2O_2 =$$
$$RuS_{2(laurite)} + FeO_{(melt)} + 3Fe^{+2}{}_{(melt)} \quad (4)$$
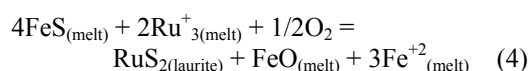
so that laurite solubility should show a weak negative dependence on oxygen fugacity. If reaction 4 is correct, then it should be impossible for laurite to form in the reduced compositional boundary layer around a growing chromite crystal even if the silicate melt was initially saturated with laurite. The common observation within chromite of laurite grains that are volumetrically minor but nonetheless large compared to the more abundant alloy micronuggets demands an explanation.

A simple explanation that is consistent with the data and the model presented above would be that the growth of chromite grains in response to magma mixing will not proceed by a simple, one-stage event as described above, but will rather involve a complex history in which the degree of supersaturation of Cr fluctuates wildly as the chromite crystal is advected through a turbulent and incompletely mixed magma. During periods when the crystal is surrounded by melt supersaturated

with chromite it will grow, and the effects described above will operate. When the crystal is immersed in melt that is not chromite-saturated (i.e., the Cr concentration in the far-field is less than in the boundary layer) the crystal will either remain unchanged or may even be temporarily redissolved. At any time when the far-field Cr concentration is too low to feed further chromite growth, the compositional boundary layer will quickly be erased by diffusion, and the local depression of fO_2 surrounding the chromite grain will be relieved. At this time the PGE alloy grains that have been collecting Os and Ru from the surrounding alloy-undersaturated melt will themselves enter a metastable state of undersaturation, and will begin to redissolve.

Since the boundary layer will have collected excess IPGE from the surrounding melt, redissolution of the alloys will cause it to contain higher IPGE concentrations than the melt farther away from the crystal. Diffusion of the IPGE will then tend to occur in a sense opposite to that which fed the growth of alloy micronuggets during chromite growth. At fS_2 slightly below that required for sulfide melt liquation and at typical mafic magmatic temperatures, IPGE alloy can coexist with laurite (Brenan and Andrews, 2001). If the equilibrium solubility of laurite falls at a value in between the (higher) solubility of alloy in the now-oxidized boundary layer and the original (lower) concentration of Ru and Os that obtained before chromite growth began, then the imposition of the alloy saturation during diffusive re-equilibration of the boundary layer will now have placed the boundary layer temporarily within the field of laurite stability. Laurite will therefore precipitate in the region containing dissolving alloy micronuggets, and as long as some alloy remains to be dissolved the laurite will consume all of the IPGE being released by alloy dissolution, not permitting it to diffuse away. A few large grains of laurite can be generated in this way, spatially associated with the margins of chromite grains which contain invisible micronuggets. Resumption of chromite growth can then lead to incorporation of a few relatively large laurite grains into the newly added chromite.

Conclusion

The growth of chromite crystals from mafic magmas slightly undersaturated with IPGE alloys should lead to the coprecipitation of abundant micronuggets of IPGE alloy. Micronuggets dominated by Os and Ru but including all the PGE will be incorporated in the growing chromite crystals because they cannot

move out of the way. Inward diffusion of the components feeding the growing alloy micronuggets will cause enrichment of Os and Ru far in excess of the amount that could be caused by simple diffusive pileup of rejected components. During hiatuses in chromite growth the alloys in the compositional boundary layer will react with the melt to form small numbers of relatively large grains of laurite, which will tend to be incorporated into the chromite grains if these begin to grow again in response to random fluctuations in intensive parameters during turbulent magma mixing.

The model presented here accounts for paradoxical observations of PGE alloy and laurite growth associated exclusively with chromite in magmas that show no other signs of havingn been saturated with PGMs, and permits reconciliation of observations of both bulk $D_{IPGE}^{Ch/melt} > 1$ and true thermodynamic $D_{IPGE}^{Ch/melt} \ll 1$.

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