GEOCHEMICAL CONSTRAINTS ON THE CONCENTRATIONS OF PLATINUM GROUP ELEMENTS IN URAL-ALASKAN TYPE COMPLEXES

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Porphyry Cu-Mo-Au deposits

Continental volcanic arc



Traditionally not regarded as target locations for magmatic sulfide mineralizations of Cu, Ni and PGE

Ural-Alaskan type complexes

- Ultramafic in composition
- Concentric lithological zoning:

Dunite at the center followed in sequence by peridotite, olivine clinopyroxenite and hornblende clinopyroxenite.

- Absence of orthopyroxene and plagioclase in the ultramafic rocks (with very rare exceptions)
- Small in size, have funnel shaped cross-sections and occur as linear belts in subduction zone settings

Ural-Alaskan type complexes

- Relatively higher abundance of magnetite in pyroxenites
- Occurrence of chromite only in the dunites as stratiform segregations and irregular veins
- Association with economic PGE-rich placer deposits
- Occasional presence of sulfide minerals

Modes of PGE Mineralization in Ural-Alaskan type Complexes:

Associated with chromitites of dunite cores: Nizhni Tagil (Russia); Union Bay, Goodnews Bay (Alaska); Fifield (Australia)

Pt-Fe alloys: Konder (Russia); Alto Condo (Columbia)

Magnetite rich clinopyroxenites around dunite core: Owendale (Australia)

Sulfide horizons in clinopyroxeneites: Salt Chuck (Alaska); Duke Island (Alaska)



Southeastern Alaska



Southeastern Alaska

Modified from Werdon, Szumigala and Davidson, 2000; Himmelberg and Loney, 2005

Duke Island (Irvine, 1974; Saleeby et al., 1991; Butler et al., 2001)



Union Bay (Van Treeck, 2009)



Salt Chuck (Loney and Himmelberg, 1992)











Percentage abundance of sulfur in four drill cores

Sulfide-rich intervals are present in the Duke Island Complex, but in detail the distribution of sulfide minerals in the ultramafic rocks shows a high degree of spatial variability.





Massive

t cm

Network textured



Disseminated









Origin of magmatic sulfide ore deposits

If the Ural-Alaskan type complexes represent feeder channels to extensive arc-type andesitic volcanism (e.g. the Gravina arc volcanic sequence) it seems probable that the intrusions were parts of conduit systems through which large volumes of magma may have passed.

Thus, the sulfide liquid generated in the magmas may have interacted with sufficient quantities of metal-bearing magmas to produce economic Cu-Ni-PGE-rich intersects in the sulfide zones of the complexes.





Controlling factors for concentrations of PGE in magmatic rocks

- 1. PGE content of the source magma
- 2. Relative mass of silicate liquid to immiscible sulfide liquid (R-factor; Campbell and Naldrett, 1979) and the extent of interaction between them
- 3. Fractional crystallization of non-sulfide minerals in which some PGE may be compatible, such as olivine and chromite
- 4. Fractional crystallization of mono-sulfide solid solution from immiscible sulfide liquid
- 5. Post-magmatic redistribution of PGE caused by the interaction of sulfide assemblages with hydrothermal fluids

Modeling magmatic crystallization and formation of PGE-rich sulfides

Sulfide saturation, and accompanying reduction in the Ni content of olivine was achieved near the point when clinopyroxene was a liquidus phase, at ~10% fractional crystallization of an ankaramitic parental magma.

Sulfide saturation at this point was related to the introduction of external sulfur; the attainment of sulfide saturation via fractional crystallization alone would not have occurred until ~30% crystallization.

Figure 20. Variation of sulfur content at sulfide saturation (SCSS) and S content of an ankaramitic magma with fractional crystallization at QFM+2 and QFM. Crustal contamination caused reduction of the magma from QFM+2 (green) to QFM (yellow). Assimilation of crustal S (path AB) caused sulfide saturation of the magma at about 10% crystallization, much earlier than otherwise would have resulted simply via fractional crystallization.

Observed olivine compositions compared with theoretical olivine compositional trends for the magma. The initial picritic magma was in equilibrium with olivine in the compositional domain of X. One chamber underwent reduction with early separation of sulfide liquid and crystallized dunite-B (path XB), while another chamber still in the initial oxidation state of QFM+2 underwent fractional crystallization along the path XA to form dunite-A. Further crystallization and reduction of the magma to the oxidation state of QFM at point C caused the magma to follow the path CDE. The separation of the sulfide liquid at D resulted in a drop in the Ni content of the silicate magma (e.g. D to F and D to H) and continued crystallization of olivine with depleted Ni concentrations (paths DFG and DHI).

Modeling the concentration of PGE in sulfide minerals

With variable degrees of crustal sulfide addition, R-factors may have varied over a wide range. We used the R-factor of Campbell and Naldrett (1979):

 $Y_i = [X_{i(o)} \cdot D^s_i \cdot (R + 1)]/(R + D^s_i)$

where $X_{i(o)}$ = initial concentration of metal i in the silicate liquid; Y_i = concentration of i in the sulfide liquid and D_i^s = distribution coefficient for partitioning of i between silicate and sulfide liquids.

We used D-values of 10⁴ for all the PGEs (Peach et al., 1994; Fleet et al., 1999).

Most Pt , Pd and Os concentrations in the sulfides at Duke Island could have been produced from an initial liquid with Os: 0.04ppb Pt: 1.08 ppb Pd: 2.17 ppb at R-factors between 100 and 500.

Fractionation of Os relative to Pt and Pd: importance of R-factors

The strong fractionation of Pt and Pd relative to Os, Ru, and Ir in the sulfide mineralization of the Duke Island Complex may be related to fractional crystallization, attainment of sulfide saturation and variable R-factors.

We calculated the changes in the concentrations of Os, Pt and Pd in a magma caused solely by early fractional crystallizations of olivine and chromite using D (olivine –magma) values for Os, Pt and Pd of 2, 0.01 and 0.01 respectively (Brenan et al., 2003) and D (chromite – magma) values for Os, Pt and Pd of 20, 0.2 and 0.02 respectively (Brenan et al., 2012).

We utilized initial Os (0.05 ppb), Pt (1ppb), and Pd (2 ppb) values of an arc picrite from Woodland et al. (2002).

After 8% crystallization (shortly before sulfide saturation) the concentrations of Os, Pt and Pd are 0.04, 1.08 and 2.17 ppb, respectively. The depletion in Os and enrichment in Pt and Pd in the residual liquid are sufficient to produce the strong fractionation

Fractionation of sulfide liquid

We utilized the Rayleigh expression to compute the concentration in the residual sulfide liquid:

 $C_f = C_i \cdot F^{(D-1)}$, where

 C_i = concentration of the element in the initial liquid;

 C_{f} = concentration of the element in the fractionated liquid;

F = weight fraction of the remaining liquid and

D = partition coefficient of the element between the fractionated solid and the residual liquid.

D values between mono-sulfide solid solution and sulfide liquid were 5.0 for Os and 0.1 for each of Pt and Pd (Fleet and Stone, 1991; Fleet et al., 1993; Li et al., 1996; Barnes et al., 1997).

Pt (ppb)

Hydrothermal alteration and potential PGE re-distribution

Some of the variability shown in the PGE contents of sulfidebearing samples from Duke Island may also be a result of hydrothermal processes.

The serpentinization of dunites has involved up to three stages of meteoric water introduction

Several researchers (e.g. Gammons et al., 1992; Gammons and Bloom, 1993; Wood, 2002) have shown that Pt and Pd, in particular, are mobile in various types of fluids. Both Pt and Pd can be transported as bisulfide complexes, and in sulfide-rich environments Pd is more soluble in a fluid than Pt.

Primitive mantle normalized plots of PGE in the sulfide samples of Duke Island Complex in the three textural types: massive, net-textured and disseminated. The PGE data was recalculated to 100% sulfide before mantle normalization. The red lines indicate samples with anomalously low Pt contents that are indicative of possible hydrothermal origin.

Mantle normalized PGE distribution in dunite (A) and pyroxenite (B) reported from Utkus, Tagil and Kachkanar Ural-Alaskan intrusions by Garuti et al. (1997)

Mantle-normalized plots of average PGE contents in the three textural types: massive, net-textured and disseminated, from Duke Island Complex compared with massive and disseminated ore samples in the Eastern Deeps deposit of the Voisey's Bay Complex (Naldrett et al., 2000) and the Partridge River intrusion of the Duluth Complex (Hauck et al., 1997)

The Dynamic Model

The origin of the ultramafic magmatic complex can be modeled by multiple stages of emplacement of cumulate crystal mushes in a dynamic conduit system, fed by a staging magma chamber at depth

This model explains the observed geochemistry of Cu, Ni and PGE in the sulfide zones

This model is consistent with the origin of Ural-Alaskan type complexes as feeder reservoirs of subduction zone volcanoes.

The magma evolves progressively by fractional crystallization and attains sulfide saturation upon interaction with the surrounding sulfide-rich rocks.

Immiscible sulfide droplets start to form which concentrate Cu-Ni-PGE and sink to the floor by gravity

With continued addition of sulfur into the system and progressive fractional crystallization cumulate crystal mushes concentrate on the floor along with the heavy immiscible sulfide liquid in the interstices. A Cu-Ni-PGE depleted but sulfidesaturated magma rests on the upper part of the magma chamber.

Renewed influx of fresh magma into the chamber pushes the old, evolved magma upwards and entrains a part of the cumulate crystals into a flowing channel along an upper conduit.

The entrained cumulate crystals are deposited in an intermediate magma chamber (which forms the Duke Island Complex) while the residual magma is released to feed the surface volcanoes.

On the way along the conduit the sulfide-saturated magma incorporates additional sulfur from the surrounding rocks to result in renewed production of sulfide liquid. This liquid forms the sulfide zones in the Duke Island Complex.

The Cu-Ni-PGE enriched sulfide liquid formed in the first stage, remains trapped along the conduit system

Conclusions

1. Although most Ural-Alaskan type complexes are sulfide-deficient, the Duke Island Complex in southeastern Alaska is a rare example of a Ural-Alaskan type complex where significant zones of sulfide mineralization have been found.

2. Sulfide assemblages consist of pyrrhotite, chalcopyrite, cubanite and pentlandite, and are found primarily in the olivine clinopyroxenite unit of the complex. Intervals of disseminated, net-textured and massive sulfides occur irregularly in the unit, indicating that multiple pulses of sulfide-rich magmas contributed to the mineralized zones.

3. PGE concentrations in the sulfide mineralization are low relative to those of most sulfide-rich magmatic ore deposits. Mantle-normalized metal trends are characterized by relative depletion in Ni, Os, Ir, and Ru, and enrichment in Pt, Pd and Cu. The trends are similar to those observed in several S-poor intrusions from the Ural Pt-Belt (Garuti et al., 1997).

Conclusions

4. The general PGE depletion and strong relative enrichment in Pt and Pd appear to be general features of Ural-Alaskan intrusions and are related to processes that affected parent melts at source and possibly by early crystallization history.

5. In the case of the Duke Island Complex mantle-normalized Ni-Cu-PGE trends were modified by fractional crystallization of olivine and chromite (concentrating Ni, Ir, Ru and to a lesser extent Os and Rh), followed by the introduction of S from crustal rocks when clinopyroxene was appearing as a liquidus mineral. The sulfide liquids that formed were characterized by relative depletion in Ni and the IPGE, and strong enrichment in Pt, Pd and Cu.

6. Most of the inter-element variations observed in the sulfide horizons can be related to variations in R-factors, with minor contributions resulting from mixing of cumulus mono-sulfide solid solution and fractionated liquid, and redistributions from low-T interaction with hydrothermal fluids.

Conclusions

7. Although processes that occur in the mantle source region appear to control the starting PGE content, sulfide segregation events in staging magma chambers could be responsible for PGE depletions in the observed sulfide assemblages.

8. The sulfide liquid segregated from the magma at the early stage of crystallization must have been extremely enriched in PGE, and if discovered, will be regarded to be a very rich ore of PGE.

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