

Au-Ag-Te-Se deposits

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The formation of Pt, Pd and Ni tellurides during cooling of Fe-Ni-Cu sulfide: Results of experiments and implications for natural systems

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Abstract. In this study we evaluate the role of temperature and Te concentration in the crystallization of Pt, Pd and Ni tellurides (melonite-group minerals). We add Pd, Pt and Te at two Pt+Pd/Te ratios of 0.50 'mixture A' and 0.65 'mixture B' to the (Fe,Cu,Ni)_{1-x}S melt at various temperatures from 1015 to 370 °C. Significant differences in the phase chemistry and the tellurides assemblage are observed in the two experimental sets. 1) The solubility of Pt and Pd in the monosulfide solid solution (Mss) decreases with the increase of Te concentration in the starting material. 2) The solubility of Te in Mss decreases from 0.3 wt.% (mixture A) to 0.2 wt.% (mixture B). 3) The Pt and Pd telluride assemblage is moncheite-merenskyite-melonite solid solution (mixture A) and moncheite-kotulskite-unnamed Pd₃Te₂ phase (mixture B). The relatively high solubility of Te in the mss at a wide-range of temperatures makes it is likely that no PGE tellurides form before the decomposition of the mss to pentlandite and pyrrhotite (below 250°C). The melonite-group mineralogy and chemistry is mainly controlled by the Te concentration in the ore fluids.

Key words: Melonite group, platinum, palladium, nickel, tellurides, synthetic experiment

Introduction

Pd, Pt and Ni-tellurides have been described from magmatic, hydrothermal and metamorphosed Cu-Ni-PGE deposits. Among Pt and Pd tellurides, moncheite and merenskyite (minerals of the melonite group) are the most abundant. In Cu-Ni-PGE deposits, which preserve magmatic textures, moncheite and merenskyite are commonly hosted in pyrrhotite and pentlandite. In hydrothermal and metamorphosed deposits, these minerals are commonly hosted in mobilized chalcopyrite, violarite and secondary silicates.

A wide-range of temperatures (>600 to 300°C) was suggested for crystallization of the

melonite-group members based on ore texture and associated silicate assemblage.

In the present study, we evaluate the role of temperature and Te concentration in the crystallization of Pt, Pd and Ni tellurides (the melonite-group minerals; MGM). Because of the common association of MGM with base-metal sulfides, it is reasonable to consider the problems of MGM formation in close connection with the processes of crystallization in the Fe-Ni-Cu sulfide systems. We add Pd, Pt and Te at two Pt+Pd/Te ratios: 0.50 ('mixture A') and 0.65 ('mixture B') to the sulfide melt at various temperatures; 1000, 900, 700; 600, 500 and 400°C (for mixture A) and 1015, 920, 825, 725, 625, 500 and 370°C (for mixture B).

Experiments with the Te-rich mixture (Mixture A):

Sulfide

The monosulfide solid solution (mss): mss was encountered only at 900°C, it was not found at 1000°C, where the mixture is superliquidus. The mss persisted to 400°C where it existed with iss, moncheite and merenskyite-melonite solid solution. Significant amounts of Te are detected in mss (0.29-0.31 wt.%) in all runs. No Pt or Pd is detected in mss at any of the temperatures.

Intermediate solid solution (iss): iss appeared in the 700°C experiment and existed down to 400°C. All telluride melt grains at 900°C and lower temperatures are concentrated in the iss. The iss contains higher amounts of Te (0.23-0.44 wt.%) relative to the mss. Both Pt and Pd contents in iss are close to, or below the microprobe detection limit (0.05%).

Tellurides

Moncheite: Pd-Ni-rich moncheite began to crystallize at 900°C and coexisted with a merenskyite-melonite solid solution at 500 and 400°C. The Pd and Ni contents in moncheite varied between 2.3-1.9 wt.% and 1.85-1.2 wt.%, respectively.

Merenskyite-melonite solid solution: Moncheite is commonly surrounded by a merenskyite-melonite solid solution. The Pt content of the merenskyite-melonite solid solution decreases from 3.5 wt.% (at 500°C) to 0.6 wt.% (at 400°C).

Experiments with the Te-poor mixture (Mixture B)

Sulfides

The mss was encountered in all runs from 1015 to 370°C. It occurs as variable size masses - smaller in the run at 1015°C, and larger in the 370°C experiment. In the 825°C experiment, fine lamellae of Cu-rich iss are commonly encountered. The Te content of the mss stays constant around 0.2 wt.% in all runs. The Pd

content increases from 0.19 wt.% in the 1015°C run to 0.43 wt.% in the 625°C run. In the 500°C run, the Pd content decreases again to 0.21 wt.% before it goes below the electron microprobe detection limit (0.05 wt.%) in the 370°C run. Detectable Pt contents were found in the 1015 and 920°C runs (0.29 and 0.22 wt.%, respectively), but went below the detection limit in other runs.

Intermediate solid solution (iss): the iss appeared in the 920°C run and lasted down to 370°C temperature, where it exists with mss, moncheite, Cu-rich melt, kotulskite and a Pd_3Te_2 phase. Contents of both Pt and Pd are below the EMP detection limit. Detectable Te contents (0.17 wt.%) were found in the iss at 825°C, but close to the detection limit at lower temperatures.

Tellurides

Moncheite, the first PGE telluride to form, appeared at 920°C and existed down to 370°C. It coexists with a $\text{Pd}_{0.43}\text{Te}_{0.53}\text{Pt}_{0.01}\text{Ni}_{0.3}$ melt at 920°C, with a $\text{Pd}_{0.5}\text{Te}_{0.5}$ melt at 825°C, and kotulskite and $\text{Pd}_{0.59}\text{Te}_{0.37}\text{Pt}_{0.01}$ melt at 725°C. At 500°C, moncheite always contains small exsolutions of PdTe phase commonly oriented in the direction of elongation of the crystals.

Kotulskite: (PdTe) appeared at 725°C where it existed with moncheite and a $\text{Pd}_{0.59}\text{Pt}_{0.01}\text{Cu}_{0.01}\text{Te}_{0.37}$ melt. This phase was also encountered in the 625, 500 and 370°C runs.

Pd-Te melt: This melt form a minor phase with a composition $\text{Pd}_{0.59}\text{Pt}_{0.01}\text{Cu}_{0.01}\text{Te}_{0.37}$ existed at 725°C. This melt disappeared in the 625°C run.

Pd_3Te_2 Unnamed phase: This phase occurs as small (30 μm) brownish yellow euhedral grains in iss. It has not been observed in mss. This phase is considered the last telluride phase to form in our experiments.

Discussion

Experimental data

According to previous studies (Makovicky et al., 1990; Ballhaus and Ulmer, 1995; Li et al.,

1996), it was expected that the Mss in our experiments will host high contents of Pt and Pd. However, this is not the case and only traces of Pt (0.29 and 0.22 wt% at 1015 and 920°C, respectively) and Pd (0.19 and 0.29 wt% at 1015 and 920°C, respectively) were detected in Mss of the Te-poor runs. These values are very low relative to pure sulfide

systems at the same temperature (maximum solubility of Pt and Pd in Fe_{1-x}S at 810°C are about 1.1 and 6.5 wt.%, respectively; Ballhaus and Ulmer, 1995). No Pt was detected in the Mss at temperatures lower than 920°C (Fig. 1). It is suggested that the individual Pt and Pd crystallizing phases affect the solubility of Pt and Pd in the Mss.

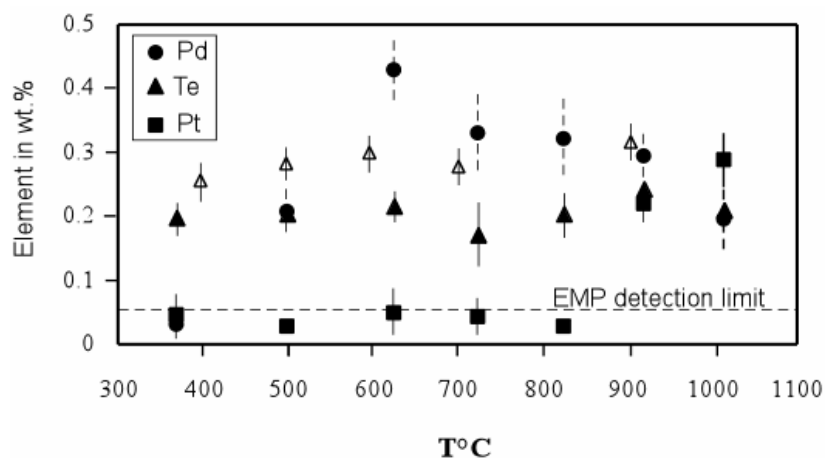


Fig. 1. The effect of Te concentration and temperature on the solubility of Pt, Pd and Te in monosulfide solid solution. Open marks for mixture A and closed marks for mixture B

At higher bulk Te in the system, the solubility of Pt and Pd in mss sharply decreases; neither Pt nor Pd was detected in the Mss of all of the Te-rich runs. It is clear that Te concentration increases the incompatibility of Pd and Pt towards the mss. Tellurium is complexing Pd and Pt so strongly that these metals no longer fit in the mss lattice and are instead retained in the melt. It is likely that very small concentrations of Te (and possibly Bi and Sb) can stabilize PGE in solution in silicate melt as well. The solubility of Te in the mss increases with the bulk content of Te in the system. It is likely that Te replaces for S in the Mss.

Natural occurrences of the melonite group minerals

According to the results of our experiments, the three end members of the MGM will never

form unless the Te concentration exceeded the concentration of Pd and Pt (at least $\text{Te}/\text{Pd}+\text{Pt} \geq 2$). The $\text{Te}/\text{Pd}+\text{Pt}$ ratio in primitive mantle is slightly more than 1 (1.1; McDonough and Sun, 1995). Te, Pt and Pd are closely related to sulfides during the generation of basaltic magmas and display similar partition coefficients between sulfide and basalt melts.

Pd, Pt and Ni-tellurides have been described from magmatic (Garuti and Rinaldi, 1986), hydrothermal (Barkov et al., 1999) and metamorphosed (Helmy et al., 1995) Cu-Ni-PGE deposits. Among Pt and Pd tellurides, moncheite and merenskyite (minerals of the melonite group) are the most abundant. In Cu-Ni-PGE deposits which preserve magmatic textures, moncheite and merenskyite are commonly hosted in pyrrhotite and pentlandite. In hydrothermal and metamorphosed deposits,

these minerals are commonly hosted in mobilized chalcopyrite, violarite and secondary silicates.

All three end members of the melonite group have been described from Wellgreen and Kambalda (Barkov et al., 2002; Hudson, 1986). It is hard to explain the PGE telluride mineralogy at Wellgreen and Kambalda deposits according to the orthomagmatic concept alone. This assemblage cannot be formed without involvement of Te from an external source (latter in the mineralization history). A complete solid solution between melonite and merenskyite (Rucklidge, 1969), Ni-poor merenskyite and moncheite (Cabri and Laflamme, 1976), and melonite and moncheite (Hudson, 1986) has been suggested. Figure 2 illustrates the compositional variations among the melonite group minerals both in experiments (2A) and in specimens from Wellgreen and Kambalda (Barkov et al., 2002; Hudson, 1986). Compared to our experimental results, the Pt-Pd-Ni substitutions in natural occurrences are substantially different. The scatter shown in Fig. 2B reflects sub-solidus re-equilibration and substitutions rather than primary crystallization from ore fluids. The

linear relationship between Pt and Pd+Ni in both natural and experimental MGM (Fig. 3) suggests that the crystal structure is the controlling factor in elemental substitutions.

Conclusions

- 1) The Pt and Pd telluride assemblage in sulfide and the solubility of Pd, Pt and Te in monosulfide solid solution is dependent on the bulk Te content of the sulfide melt.
- 2) No Pt, Pd or Ni tellurides will form in natural sulfide ores at temperatures above 250°C due to the normally low concentration of these elements in the original melt and their high solubility in the mss.
- 3) The assemblages moncheite-merenskyite-Pd-rich melonite and moncheite-kotulskite-Pd₃Te₂ (unknown phase) will form at Te/Pd+Pt ratios >2 and <2, respectively. The occurrence of merenskyite and kotulskite in the same deposit implies that the Te concentration varied during the evolution of the mineralization.

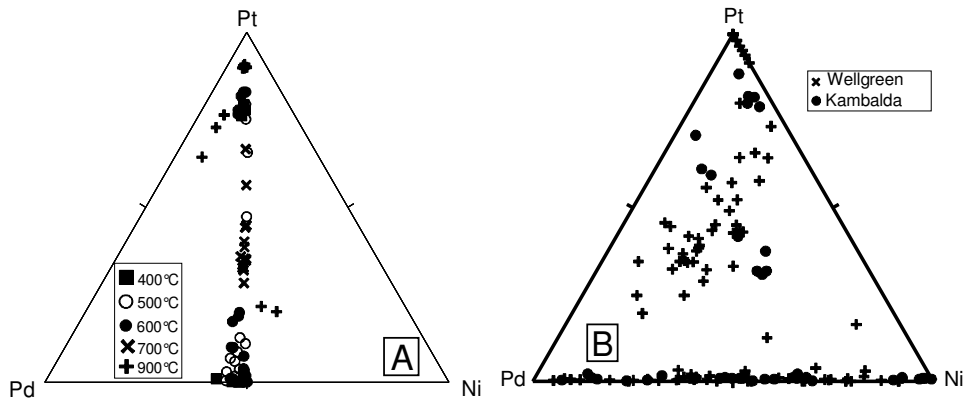


Fig. 2. The PdTe₂-PtTe₂-NiTe₂ system in experimental run products and natural sulfide-PGE ores

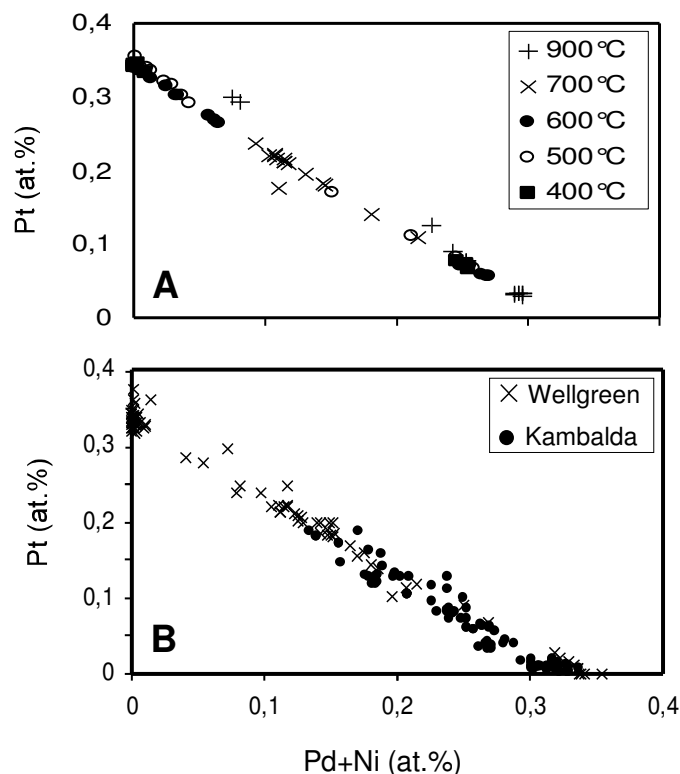


Fig. 3. The variation of Pt versus Pd+Ni in Pd and Pt tellurides from experimental runs (A) and natural sulfide-PGE ores (B)

- 4) It is suggested that textures among melonite-group minerals and their compositions, as observed in nature, are a consequence of very low-temperature (<100°C) equilibration of assemblages over geological time scales.

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