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Platinum-group mineral formation: Evidence of an interchange process from the entropy of activation values

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Abstract

Small grains of Ru–Os–Ir sulfides or alloys that formed in the early stages of the crystallization of basaltic magmas occur as inclusions in chromitites from many ophiolite complexes, Ural/Alaskan-type and layered intrusions. The nature of platinum-group elements is debated, i.e., whether they originally occurred in a metallic state or bonded with sulfur or other ligands. The application of kinetics and suggestions regarding the mechanisms of PGE formation may contribute to a better understanding of the genetic processes for platinum-group mineral (PGM) formation. The aim of the present study is to investigate the type of mechanism (associative, dissociative or interchange) and the possibility of direct formation of PGM from the reaction of free metals with sulfur, defining also the structure of possible intermediate species.

The literature on the grain sizes (r) of platinum-group minerals (PGM) and their formation temperatures (range between 700 and 1100 °C) reveals an Arrhenius temperature dependence. The activation energy was estimated to be 450 ± 45 kJ mol^{-1}. Applying the Eyring equation to the same data, a linear relationship between $2.5\ln(r) + \ln(T)$ versus $1/T$ was obtained, leading to an estimation of the free energy of activation, $\Delta G^{\neq} = 440 \pm 43$ kJ mol^{-1}. The thermodynamic relation $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$, used together with the relation $\Delta \mathrm{H}^{\neq} = E_{\mathrm{act}} - RT$ leads to the calculation of $\Delta S^{\neq}$ at various temperatures. The estimated entropy of activation at various temperatures being almost zero, we suggest an interchange mechanism for PGM formation.

The possibility of PGM formation from the direct reaction of free metals with sulfur would be inconsistent with the estimated entropy of activation values ($\Delta S^{\neq} \sim 0$) at various temperatures. In the cases of PGMs of known r, the formation temperatures can be estimated, and then the free energy of activation obtained, applying $2.5\ln(r) + \ln(T)$ versus $1/T$ (straight line). From that value, the entropy of activation can be calculated [$\Delta S^{\neq} = -R + (E_{\mathrm{act}} - \Delta G^{\neq})/T$], and an interchange mechanism is proposed. Furthermore, applying the relation of $2.5\ln(r) + \ln(T)$ versus $1/T$ on PGM grains of known r and T, an interchange mechanism for their formation can be suggested if they fit the above line.

1. INTRODUCTION

The petrogenetic processes controlling the deposition of platinum-group elements (PGE) and the formation of platinum-group minerals (PGM), either directly precipitated from silicate melts or formed from immiscible sulfide liquids, are subjects of great interest to many investigators (Hiemstra, 1979; Keays, 1982, 1995; Stockman and Hlava, 1984; Tredoux et al., 1995; Naldrett et al., 1996, 1999; Melcher et al., 1997; Ohnenstetter et al., 1999; Bowles et al., 2000; Johan et al., 2000; Cabri, 2002; Augé et al., 2005; Mungall, 2005; Ballhaus et al., 2006 and references cited therein). An adequate thermodynamic description of micro-nuggets or clusters, as they can be called if they are of colloidal size (Tredoux et al., 1995), has not yet been presented, and their relevance to natural systems remains an open question. Field and experimental evidence

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demonstrate that under appropriate conditions of T, P, fO_2 and fS_2, it is possible for laurite (RuS_2) and (Ir-group) IPGE alloys to precipitate directly from basaltic liquids/silicate magmas (Borisov and Palme, 1997, 2000; Brenan and Andrews, 2001; Bockrath et al., 2004). The platinum-group elements (PGE) tend to exist in the metallic state or bonded with sulfur, oxygen or other ligands (Amosse et al., 1990, 2000; Wood, 2002; Hanley, 2005; Mungall, 2005; Brenan, 2008; Finnigan et al., 2008), but the mechanism of their formation remains unclear.

Examples of mineral formation from nature and experimental data have been explained by kinetic factors, proposing as a mechanism solid-state diffusion (Lennie and Vaughan, 1992; Lennie et al., 1995; Rosso and Vaughan, 2006; Hunger and Benning, 2007). However, a mechanism for PGM formation has not yet been suggested.

The application of kinetics and the suggestion of mechanisms during PGE deposition may contribute to a better understanding of the molecular-scale chemistry of the genetic processes for platinum-group mineral (PGM) formation. More specifically, the correlation of data in the literature concerning the grain sizes (r) of platinum-group minerals (PGM) and their formation temperatures (range between 700 and 1100 °C) revealed an Arrhenius temperature dependence, and the activation energy for the formation of IPGM (Ir–platinum-group minerals) was thus calculated. The activation energy, that is, the minimum energy required for reactants to give products, was estimated to be $450 \pm 45\ \text{kJ mol}^{-1}$ (Petrou and Economou-Eliopoulos, 2009).

2. PGE-MINERALS AND THEIR OCCURRENCE

Small inclusions of Ru–Os–Ir sulfides or alloys that formed in the early stages of the crystallization of basaltic magmas have been described as inclusions in chromitites or along grain boundaries from many ophiolite complexes, Ural/Alaskan-type and layered intrusions (Augé, 1985; Prichard and Tarkian, 1988; Garuti and Zaccarini, 1997; Cabri, 2002; Tsoupas and Economou-Eliopoulos, 2008). There is acceptance of both a primary magmatic nature of the IPGE-minerals hosted in chromitites as well as remobilization of PGEs at relatively low temperatures during post-magmatic stages (Melcher et al., 1997; Garuti and Zaccarini, 1997). Available geological, mineralogical and geochemical data indicate a multistage evolution of PGE mineralization in ophiolite complexes. The presence of extremely abundant solitary platinum-group element minerals (PGM) within massive chromite samples located along a shear zone in the Veria area of Greece has been attributed to post-magmatic processes (Tsoupas and Economou-Eliopoulos, 2008). In general, the presence of Os-, Ir-, Ru- and Rh-bearing PGMs within PGE-enriched altered chromitites from some ophiolite complexes may indicate both *in situ* alteration or/and remobilization and redeposition of PGEs.

One common feature of many mafic layered intrusions is the occurrence of platinum-group minerals with either oxide (mostly chromite) or silicate minerals, whereas base-metal sulfides are scarce or completely absent. Important examples of sulfide-poor mineralization are found in Bushveld, South Africa, and Stillwater, Montana (Merkle, 1992; Mathez, 1999; Maier and Barnes, 1999; Barnes and Maier, 2002; Cawthorn et al., 2002; Zientek et al., 2002). These authors discussed potential geochemical models regarding the formation of PGE reefs and explained the association of PGEs with chromitites, emphasizing the importance of redox conditions.

The most common PGMs in silicate matrices include a variety of Pt–Fe alloys, Pd–Pt tellurides, arsenides and antimonides. Helmy et al. (2007) argued that many natural tellurides coexisting with sulfides may be metastable, i.e. modified by exsolution of a Ni–Te component from the coexisting high-temperature sulfides. Li et al. (2008) provided mineralogical and textural evidence that indicates alteration of base-metal sulfides and mobilization of metals and S during hydrothermal alteration in the main sulfide zone of the Great Dyke, Zimbabwe and the precious metals zone of the Sonju Lake Intrusion, Minnesota, USA, both mineralized intrusions. On the basis of stable isotopic data, they suggested that the fluids involved in the alteration were of magmatic origin in the Great Dyke but that a meteoric water component was involved in the alteration of the Sonju Lake Intrusion. They concluded that Pt and Pd tellurides, antimonides, and arsenides may form during both magmatic crystallization and subsolidus hydrothermal alteration.

3. SOLUBILITY AND MAJOR LIGANDS FOR PGES AT HIGH TEMPERATURES

Magmatic platinum-group element (PGE) deposits can be classified into several types based on a variety of criteria, including classification into sulfide-poor and sulfide-rich. The platinum-group elements (Os, Ir, Ru, Rh, Pt and Pd) are known to have high metal silicate partition coefficients and are termed highly siderophile elements (HSE). Experimental studies on the solubility of HSEs contribute to a better understanding of the behaviors of these elements during the formation of partial melts from the upper mantle and during the separation of sulfides from these melts, as exemplified by the HSE solubility data. It has been shown that these elements are dissolved as oxide components in silicate melts, implying a dependence of the metal/silicate and metal/sulfide partition coefficients on the oxygen fugacity (Borisov and Palme, 1997, 2000; Cottrell and Walker, 2006; Finnigan et al., 2008). Platinum-phases commonly crystallize directly from the sulfide liquid at an early stage, e.g. prior to monosulfide solid solution (MSS) crystallization, to give a PtFe alloy in Fe-rich systems or PtS in Ni–Cu-rich systems (Fleet et al., 1993; Li et al., 1996). Experimental data have also shown that there is a strong correlation between the distribution of Pt and As in quenched sulfide liquids, suggesting that in As-rich systems, sperrylite may preferentially crystallize directly from the sulfide liquid (Fleet et al., 1993). Brenan et al. (2005) provided an upper bound on Os solubility in a silicate melt of 10 ppb, and concluded that the solubilities of Os, Ru and Ir in silicate melt are comparable to the concentrations of these elements in primitive, sulfur-poor magmas, suggesting that they could be metal-saturated. Finnigan et al.

(2008) concluded based on experimental data that PGM formation is redox-controlled and that PGE sulfides can crystallize at the chromite–melt interface as a result of decreased fO_2. They also concluded that chromite crystallization or re-equilibration with a melt could explain the chromite–PGM association in natural magmatic systems, as a consequence of the selective uptake of trivalent Cr and Fe from the melt by spinel relative to the divalent species.

Models concerning a high-temperature hydrothermal origin for the PGE concentrations in layered intrusions have been described by Boudreau and Meurer (1999) and Willimore et al. (2000). They suggested that the stratigraphic distribution of S, Cu and the PGE in layered intrusions cannot be explained solely by the precipitation of sulfide as a cotectic phase. According to Boudreau and Meurer (1999), a Cl-rich volatile phase interstitial to crystals dissolves PGE, S, and base metals from sulfide minerals precipitated during an earlier stage. The metal and S-bearing fluid rises upward, dissolving into a fluid-undersaturated magma, and the PGE, base metals, and S precipitates out of solution as PGM and base-metal sulfides.

Wood (2002) provided a thorough review of the current state of knowledge about the solubility and speciation of PGEs and concluded that the timing of the involvement of a volatile phase is not clear. A volatile phase may be present early in the evolution of the layered intrusions, at a temperature of around 1200 °C. Also, at very high temperatures the roles of the pH and $f(O_2)$ are not critical for PGE transport by chloride and Cl-rich magmatic volatiles (either aqueous or H_2O-free), and may be responsible for the primary concentration and redistribution of the PGE. In the absence of H_2O, the vapor transport of the PGE is only significant above 1000 °C and is enhanced by the presence of both Cl and S in the vapor phase (but not S alone). Brenan (2008) suggested that platinum-group elements (PGEs) tend to exist in the metallic state or bonded with sulfur or other Group Va and VIa ligands, occurring as trace accessory minerals in rocks.

Since the question of the original existence of bonds between metallic PGEs and sulfur or other ligands is still under debate, we applied molecular-scale chemistry to the PGE mineralization processes in order to investigate the mechanisms of reactions controlling the initiation of PGE formation. Literature data on the grain sizes (r) of platinum-group minerals (PGMs) and their formation temperatures revealed an Arrhenius temperature dependence (Petrou and Economou-Eliopoulos, 2009). Three sets of data were used: one of small IPGM grains from IPGE-rich chromite ores hosted mostly in the mantle sequences of ophiolite complexes (temperatures between 1030 and 1100 °C), a second one of large IPGMs associated with Pt-Pd, formed at lower temperatures (between 700 and 850 °C), related mainly to Ural/Alaskan-type intrusions and ophiolite complexes, and a third one based on the experimental data that defined the stability limit of RuS_2 at a temperature of 1275 °C. A straight line was obtained, the slope of which was used to estimate the activation energy (Petrou and Economou-Eliopoulos, 2009).

4. MECHANISMS OF SUBSTITUTION REACTIONS

Substitution reactions can in general be presented as follows: $LM + L' \rightarrow L'M + L$.

The above formula actually means that L' is transferred from the bulk of the environment to M and L is released from M to the environment. Substitution reactions can be classified according to the mechanism by which they proceed.

4.1. Associative (*A*) mechanism

The first reaction of the mechanism is an addition reaction (addition of L'), followed by the removal of L:

$$\begin{array}{ll} LM + L' \rightarrow LML' & k \text{ (first stage, slow)} \\ LML' \rightarrow ML' + L & \text{(second stage, fast)} \\ \hline LM + L' \rightarrow ML' + L & \text{(overall reaction)} \end{array}$$

The first stage (slow) is the rate-determining step; $R = k[LM][L']$.

The above elementary reactions reflect the molecular processes. For simplicity, we use ML, i.e. one ligand L around the metal M.

For an A (associative) mechanism, the randomness of the transition state $[LML']^{\neq}$ is smaller than that of the initial state $[LM + L']$, and $\Delta S^{\neq} < 0$. (Katakis and Gordon, 1987) (see Fig. 1).

4.2. Dissociative (*D*) mechanism

The first reaction of this mechanism is a decomposition, but M in the presence of the ligand L' is not stable, and it reacts with it:

$$\begin{array}{ll} LM \rightarrow L + M & k \text{ (first stage, slow)} \\ M + L' \rightarrow ML' & \text{(second stage, fast)} \\ \hline LM + L' \rightarrow L + ML' & \text{(overall reaction)} \end{array}$$

The first stage (slow) is the rate-determining step, and $R = k[LM]$.

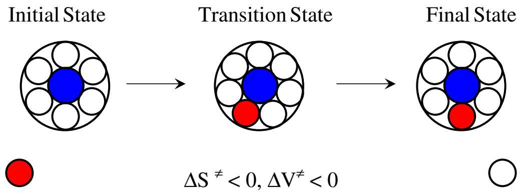

Fig. 1. Schematic representation of ligand exchange reactions proceeding by Associative mechanism. The blue circle in the middle of the idealized ‘flat’ complex represents the central atom. The small open circles represent the bound ligands. The red circle represents the incoming ligand. The large circles enclosing the small ones represent the boundaries of the first coordination sphere. For an A mechanism the entropy and volume of activation are negative. (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

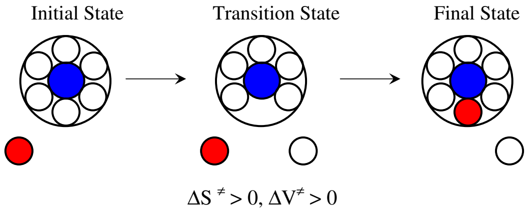

Fig. 2. Schematic representation of ligand exchange reactions proceeding by Dissociative mechanism. The blue circle in the middle of the idealized 'flat' complex represents the central atom. The small open circles represent the bound ligands. The red circle represents the incoming ligand. The large circles enclosing the small ones represent the boundaries of the first coordination sphere. For a *D* mechanism, the entropy and volume of activation are positive. (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

The above elementary reactions reflect the molecular processes.

For a *D* (dissociative) mechanism, in going from the initial state $[L' + LM]$ to the transition state $[M, L, L']^{\neq}$, there is an increase in disorder, that is, the entropy has increased, so $\Delta S^{\neq} > 0$. (Katakis and Gordon, 1987) (see Fig. 2).

4.3. Interchange (*I*) mechanism

For an interchange mechanism, an outer-sphere complex is first formed (an outer-sphere complex is a structure where the coordination spheres of the involved molecules are retained) and then the group that is leaving moves from the inner to the outer coordination sphere, while the entering group simultaneously moves from the outer to the inner coordination sphere:

$L'M' + LM = L'M'LM$ K_1 (fast, diffusion-controlled equilibrium)
$L'M'LM = L'LM + M'$ K_2 (fast, diffusion-controlled equilibrium)
$L'LM \rightarrow L'M + L$ k

$L'M' + LM = L'M + L + M'$ (overall reaction)

For an *I* (Interchange) mechanism, intermediate values of the entropy of activation are expected. For an ideal interchange mechanism, $\Delta S^{\neq} = 0$, while for an I_a $\Delta S^{\neq} \leqslant 0$, and for an I_d $\Delta S^{\neq} \geqslant 0$, but generally for an *I* mechanism, $\Delta S^{\neq} \approx 0$ (Katakis and Gordon, 1987) (see Fig. 3).

The present study is an attempt to gain insight into "what happens at the molecular level during the critical elementary step that governs the rate of the reaction and thus the mechanism." Negative entropies of activation are in general indicative of an associative mechanism (*A*), and positive entropies of activation of a dissociative mechanism (*D*). The volume of activation $\Delta V^{\neq}$ that can be determined by high-pressure experiments, on going from the reactants to the transition state, changes if a mechanism is associative (negative $\Delta V^{\neq}$) or dissociative (positive $\Delta V^{\neq}$). For interchange mechanisms, intermediate values are expected.

There are no strict limits on $\Delta S^{\neq}$ for the various mechanisms. Values of $\Delta S^{\neq}$ can be used to suggest (define) a mechanism, provided that the reaction is simple, and $\Delta S^{\neq}$ is not a composite of some equilibrium and kinetic parameters. Anything within ±10 J mol^{-1} K^{-1} is a good candidate for an interchange mechanism. Obviously, other considerations apply, and these vary and depend on the particular reaction, solvent, charges, etc. Still, $\Delta S^{\neq}$ typically does not exceed about ±100 J mol^{-1} K^{-1} (dissociative/associative), and even that is relatively high (although there are exceptions and even larger numbers have been reported in the literature).

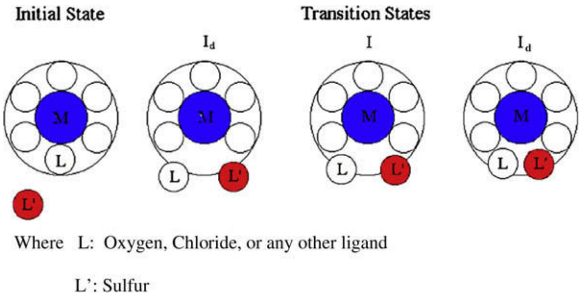

Fig. 3. Schematic representation of an exchange reaction proceeding by the Interchange (*I*) mechanisms. The blue circle in the middle of the idealized "flat" octahedral complex represents the metal ion (in our case Os, Ru, Ir). The small circles represent the bound ligands. The red circle represents the incoming ligand. In an Interchange mechanism an outer-sphere complex is formed first, and then the leaving group (*L*, in our case Oxygen, Halogen, etc.) moves from the inner to the outer coordination sphere and simultaneously the entering group (*L*′, in our case Sulfur) moves from the outer to the inner coordination sphere. During the critical concerted Interchange step, in a dissociative-like (I_d) mechanism there is only weak bonding to the entering and leaving groups, whereas in an associative-like (I_a) mechanism the bonding is stronger. In this figure bonding is symbolized by placing the leaving and incoming groups at different distances from the central metal ion (after Petrou, 2002). (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

The above brief analysis gives the salient features of the expected trends, but it is certainly idealized. It does not include the reorganization of the solvent outside the first coordination sphere. Thus, although the general trend is indeed observed, $\Delta S^{\neq}$ is not always a reliable criterion, even when its value is known fairly accurately.

The empirical criteria for deciding the mechanism of substitution are: (a) the observed rate law, (b) the dependence on the nature of the entering ligand, (c) detection of intermediates, (d) the entropy of activation, (e) the volume of activation, and (f) the effect of the non-leaving ligands.

The mechanism of a given substitution sometimes changes. Examples are available in which two mechanisms operate simultaneously, while other cases show a change in the environment causing a change in the mechanism (Katakis and Gordon, 1987). The aim of the present study is to investigate the type of mechanism (associative, dissociative or interchange) and the possibility of a direct formation of PGMs from the reaction of free metals with sulfur, defining also the structure of possible intermediate species.

4.4. Uncertainties concerning the suggestion of a mechanism

In suggesting a possible mechanism for a process, one must remain aware that there are many experimental difficulties and uncertainties in identifying species. For example, one general conclusion is that the observed rate law by itself without other criteria cannot give conclusive evidence in support of one mechanism or another since the rate law is ambiguous regarding the concentration of the solvent or a reagent in excess. A mechanism that is labeled dissociative $[R=k'(ML)]$ may in fact be associative with the participation of a solvent molecule or a reactant in excess $[R=k(ML)(L')=k'(ML)$ since $(L')=$ (solvent, or reagent in excess) $=$ constant].

5. MECHANISMS OF ADDITION REACTIONS

5.1. Entropy of activation for a mechanism involving a direct reaction between free metals and sulfur

An addition reaction between free metals (Ru, Os, Ir) and sulfur is:

$$(Ru\text{–}Os\text{–}Ir)+\frac{2}{n}S_n \rightarrow (Ru\text{–}Os\text{–}Ir)S_2 \quad \text{or} \quad M_{\text{metal}}+x/_4S_2=MS_{x/2,\text{melt}}$$

where x is the valence state of the metal species, which is considered to be unknown.

The transition state for the slow step of the above reaction would involve the existence of attractive forces between the reactants (metals and sulfur). The distances between the reactants would continuously decrease, together with the degrees of freedom, and finally the products would form. Such a scheme would lead to negative entropies of activation, since the transition state is more organized than the reactants. More organization leads to less freedom, hence less randomness, and thus a negative $\Delta S^{\neq}$ ($S_{\text{transition state}}-S_{\text{reactants}}$). Since the estimated entropy of activation for PGE formation (Section 7) is ~zero, this means that the above reaction and consequently the above mechanism is not taking place; it is thus discarded. In other words, an addition reaction is not taking place.

6. THE EYRING OR ACTIVATED COMPLEX THEORY RELATION

The Eyring equation relates the reaction rate constant (k) to the temperature (T). It follows from the transition state or activated complex theory and is based on statistical thermodynamics. The general form of the Eyring equation resembles the Arrhenius equation:

$$k=\kappa\frac{RT}{Nh}e^{-\frac{\Delta G^{\neq}}{RT}} \tag{1}$$

The Eyring or activated complex theory relation uses $\Delta H^{\neq}$ (the activation enthalpy) and $\Delta S^{\neq}$ (the activation entropy) by applying the thermodynamic relation

$$\Delta G^{\neq}=\Delta H^{\neq}-T\Delta S^{\neq} \tag{2}$$

$$k=\kappa\frac{RT}{Nh}e^{\frac{\Delta S^{\neq}}{R}}e^{-\frac{\Delta H^{\neq}}{RT}} \tag{3}$$

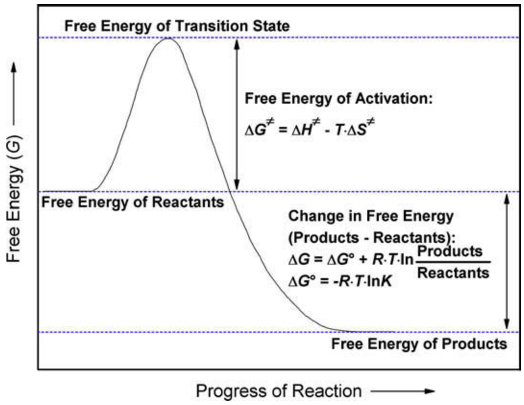

Fig. 4. Transition state or activated complex theory postulates that the reaction proceeds through formation of an activated complex that is in equilibrium with the reactants.

The pre-exponential shows a first-power temperature dependence. The transmission coefficient κ is usually taken as unity (Espenson, 1981).

$\Delta G^{\neq}$ is the Gibbs Free Energy of activation, h is Planck's constant, R is the universal gas constant and N is Avogadro's number (see Fig. 4).

$$\Delta G^{\neq}=G_{(\text{transition state})}-G_{(\text{reactants})},$$
$$\Delta H^{\neq}=H_{(\text{transition state})}-H_{(\text{reactants})},$$
$$\Delta S^{\neq}=S_{(\text{transition state})}-S_{(\text{reactants})},$$
$$\Delta G=G_{(\text{products})}-G_{(\text{reactants})},$$
$$\Delta H=H_{(\text{products})}-H_{(\text{reactants})},$$
$$\Delta S=S_{(\text{products})}-S_{(\text{reactants})}$$

The linear form of the Eyring equation is:

$$\ln(k/T)=(-\Delta H^{\neq}/R)(1/T)+\ln(\kappa R/Nh)+\Delta S^{\neq}/R \tag{4}$$

This relation is used to suggest a mechanism for a certain reaction in the following way: the reaction is performed at various temperatures in which the reaction rate constant is determined. The plot of $\ln(k/T)$ versus $1/T$ gives a straight line with the slope $-\Delta H^{\neq}/R$, from which the enthalpy of activation can be derived, and with intercept $\ln(\kappa R/Nh)+\Delta S^{\neq}/R$, from which the entropy of activation is calculated. The term $\ln(\kappa R/Nh)$ has a known constant value. The calculated value of the entropy of activation is used to suggest a mechanism (associative, dissociative or interchange; see below).

6.1. Relation between E_{act} and $\Delta H^{\neq}$

The relation between E_{act} of the Arrhenius equation

$$k=Ae^{-\frac{E_{\text{act}}}{RT}} \tag{5}$$

and $\Delta H^{\neq}$ of the Eyring equation (activated complex theory) is (Espenson, 1981):

$$\Delta H^{\neq}=E_{\text{act}}-RT \tag{6}$$

By differentiating $\ln(k)$ with respect to T [$\ln(k)=\ln A-E_{act}/RT$], Eq. (7) is obtained.Thus,

$$\mathrm{d}\ln(k)/\mathrm{d}T=-E_{act}/R\ (-1\times T^{-2})=E_{act}/RT^{2}$$

$$\text{or}\quad E_{act}=RT^{2}\ \mathrm{d}\ln(k)/\mathrm{d}T \tag{7}$$

From Eq. (3) we get,

$$\ln(k) = \ln C + \ln(T) + \Delta S^{\neq}/R - \Delta H^{\neq}/RT \tag{8}$$

Hence,

$$\mathrm{d}\ln(k)/\mathrm{d}T = \mathrm{d}\ln(T)/\mathrm{d}T - \Delta H^{\neq}/R\mathrm{d}(1/T)/\mathrm{d}T \quad \text{and} \tag{9}$$

$$\mathrm{d}\ln(k)/\mathrm{d}T = 1/T - \Delta H^{\neq}/R(-1)(T^{-2}) = 1/T + \Delta H^{\neq}/RT^2. \tag{10}$$

By substituting $\mathrm{d}\ln(k)/\mathrm{d}T$ into Eq. (7), the empirical definition of activation energy, we get $E_{act} = RT^2\mathrm{d}\ln(k)/\mathrm{d}T = RT^2\ (1/T + \Delta H^{\neq}/RT^2) = RT^2\ (T + \Delta H^{\neq})/RT^2 = RT + \Delta H^{\neq}$ or

$$\Delta H^{\neq} = E_{act} - RT \tag{11}$$

Thus, near room temperature (the thermodynamic temperature, 25 °C), E_{act} is roughly 2.5 kJ mol^{-1} larger than $\Delta \mathrm{H}^{\neq}$. At the level of the temperatures that are used in this work (for example 1000 °C), E_{act} is approximately 10.6 kJ mol^{-1} larger than $\Delta \mathrm{H}^{\neq}$.

7. SUGGESTION OF AN INTERCHANGE MECHANISM FOR PGM FORMATION

Estimation of the free energy of activation $\Delta G^{\neq}$ and the entropy of activation $\Delta S^{\neq}$:

The rate (u) of a process is proportional to the concentration of the various reactants (C^a).

$$u = \frac{\partial c}{\partial t}, \tag{12}$$

$$u = k_{\mathrm{obs}} \times C^a \tag{13}$$

$C^a_{\mathrm{reactants}} = C_1^k C_2^l C_3^m \cdots\cdots$ where $C_1, C_2, C_3 \ldots$ are the concentrations of the various reactants and $k, l, m, \ldots$ are the orders of the reaction with respect to the certain reactants.

An assumption is made here concerning the concentration: the concentrations of the reactants (C^a) are assumed to be constant; this is true in the case of mineral formation from a large body of magma, although recent studies include the effect of mineral formation on the magma composition. At lower temperatures, when diffusive effects become more important, the concentration may vary (Petrou and Economou-Eliopoulos, 2009).

It is also well-known that high temperatures of reacting media result in high rates of crystal formation and lead to small crystal sizes, while low temperatures lead to low rates of crystal formation and large crystal sizes (Belcher and Gordon, 1987). In addition, the rate of cooling allows the development of coarse-grained rocks. Thus, assuming that the three dimensions of the crystals are similar, $u \propto \frac{1}{r^n}$, where r is a dimension of the crystal. In the case where $n = 3$, we refer to the volume of the crystal, and $n = 2$ refers to the surface area (Petrou and Economou-Eliopoulos, 2009).

Eqs. (1) and (13) give:

$$u = kC^a = C^a \frac{\kappa RT}{Nh} e^{-\frac{\Delta G^{\neq}}{RT}} \quad \text{and} \tag{14}$$

$$\frac{1}{r^n} = (\text{const.})\ (T) e^{-\frac{\Delta G^{\neq}}{RT}} \tag{15}$$

$$\frac{1}{r^n T} = \text{const.}\ e^{-\frac{\Delta G^{\neq}}{RT}} \tag{16}$$

$$\ln\left(\frac{1}{r^n}\frac{1}{T}\right) = \text{const}'. - \frac{\Delta G^{\neq}}{R}\left(\frac{1}{T}\right) \tag{17}$$

$$\ln\left(\frac{1}{r^n}\right) + \ln\left(\frac{1}{T}\right) = \text{const}'. - \frac{\Delta G^{\neq}}{R}\left(\frac{1}{T}\right) \tag{18}$$

$$-n\ln(r) - \ln(T) = \text{const}'. - \frac{\Delta G^{\neq}}{R}\left(\frac{1}{T}\right) \tag{19}$$

$$n\ln(r) + \ln(T) = (-\text{const}'.) + \frac{\Delta G^{\neq}}{R}\left(\frac{1}{T}\right) \tag{20}$$

By plotting $n\ln(r) + \ln(T)$ versus $\left(\frac{1}{T}\right)$, we get a straight line with a slope $= \frac{\Delta G^{\neq}}{R}$ and intercept $= -\text{const}'$.

Assuming that $n = 3$, we have the volume of a grain and we get a value for $\Delta G^{\neq}$. If $n = 2$, we refer to the surface area of the grains and we get another value for $\Delta G^{\neq}$. Assuming that the grains of platinum-group minerals described in various geotectonic environments (Table 1) can be roughly described by $n = 2.5$, an estimated value of $\Delta G^{\neq}$ can be found from Eq. (21)

$$2.5\ln(r) + \ln(T) = (-\text{const}'.) + \frac{\Delta G^{\neq}}{R}\left(\frac{1}{T}\right) \tag{21}$$

From the slope of the obtained line (Fig. 5), we calculate $\Delta G^{\neq} = 440 \pm 43$ kJ mol^{-1}. Applying the thermodynamic relation (2), we get

$$\Delta G^{\neq} = E_{\mathrm{act}} - RT - T\Delta S^{\neq} \tag{22}$$

$$\Delta S^{\neq} = -R + \left(E_{\mathrm{act}} - \Delta G^{\neq}\right)/T \tag{23}$$

By substituting the known value of E_{act}, we can calculate $\Delta S^{\neq}$ at various temperatures, i.e., 1250 °C, 1000 °C and 700 °C, to examine whether the same mechanism applies at the various temperatures, since a mechanism of a reaction may change if conditions, i.e. temperature, change.

(a) T=1523 K (1250 °C)

440 kJ mol^{-1} = 450 kJ mol^{-1} − 8.31 J mol^{-1} K^{-1} (1523 K) − (1523 K) $\Delta S^{\neq}$

$\Delta S^{\neq} = -1.8$ J mol^{-1} K^{-1}. This $\Delta S^{\neq}$ value implies an *interchange mechanism.*

(b) T = 1273 K (1000 °C)

440 kJ mol^{-1} = 450 kJ mol^{-1} − 8.31 J mol^{-1} K^{-1} (1273 K) − (1273 K) $\Delta S^{\neq}$

$\Delta S^{\neq} = -0.5$ J mol^{-1} K^{-1}

Again, the $\Delta S^{\neq}$ value suggests an *interchange mechanism.*

(c) T=973 K (700 °C)

440 kJ mol^{-1} = 450 kJ mol^{-1} − 8.31 J mol^{-1} K^{-1} (973 K) − (973 K) $\Delta S^{\neq}$

$\Delta S^{\neq} = +2$ J mol^{-1} K^{-1}.

This $\Delta S^{\neq}$ value is indicative of an *interchange mechanism.*

We also plot $\Delta S^{\neq}$ against $1/T$ (Eq. (23), Fig. 6); the various regions of the $\Delta S^{\neq}$ values (positive and negative) can easily be seen. The levels of $\Delta S^{\neq}$ considered to indicate

Table 1
Characteristic features of refractory platinum-group minerals.

Location	Rock-type	Mineral	Description	Grain size (mm)	Temperature (°C)	Ref.
Othrys, Greece	Ophiolites	Laurite	Inclusion in chromite	10	1030	Garuti et al. (1999a,b)
Vourinos, Greece	Ophiolites	Ru-rich laurite	Inclusion in chromite	10	1100	Garuti and Zaccarini (1997)
Skyros, Greece	Ophiolites	Laurite	Inclusion in chromite	12	1100	Tarkian et al. (1992)
Ray-Iz, Polar Urals, Russia	Ophiolites	Laurite	Inclusion in chromite	10	1000	Garuti et al (1999b)
Tropoja, Albania	Ophiolites	Laurite	Inclusion in chromite	8	900–1100	Ohnenstetter et al. (1999)
Kempirsai, Urals, Russia	Ophiolites	Laurite	Inclusion in chromite	1–20	1050	Melcher et al. (1997)
CED, Egypt	Ophiolites	Os-rich laurite	Inclusion in chromite	12	1000	Ahmed (2007)
Borneo	Ophiolites	Laurite	Placer	900 ($n = 13$)	800–850	Hattori et al. (2004)
Russia	Alaskan-type	Ru-rich laurite	Inclusion in isoferroplatinum	300	800–850	Tolstykh et al. (2005)
Nevado, Colombia	Alaskan-type	Laurite	Inclusion in Pt–Fe	170	800	Weiser (2002)
Othrys, Greece	Ophiolites	Erlichmanite	Inclusion in chromite	15	1030	Garuti et al. (1999a,b)
Ray-Iz, Polar Urals, Russia	Ophiolites	Erlichmanite	Inclusion in chromite	11	1000	Garuti et al (1999b)
Freetown, Sierra Leone	Layered intrusion	Erlichmanite	Placer	400–700	800–850	Hattori and Hart (1991)
Russia	Alaskan-type	Erlichmanite	Placer	200	800	Malitch and Thalhammer (2002)
Vourinos, Greece	Ophiolites	Irarsite	Inclusion in chromite	2	1100	Garuti and Zaccarini (1997)
Ethiopia	Ophiolites	Irarsite	Placer	1000	800–850	Johan et al. (2000)
Vourinos, Greece	Ophiolites	Os–Ir alloy	Inclusion in chromite	10	1100	Garuti and Zaccarini (1997)
Tropoja, Albania	Ophiolites	Os-rich alloys	Inclusion in chromite	20	1000	Ohnenstetter et al. (1999)
Ray-Iz, Polar Urals, Russia	Ophiolites	Os–Ir–Ru alloy	Inclusion in chromite	5	1000	Garuti et al (1999b)
SED, Egypt	Ophiolites	Os–Ir–Ru alloy	Inclusion in chromite	5	1100	Garuti et al (1999b), Ahmed (2007)
Bulqiza, Albania	Ophiolites	Isoferroplatinum	Inclusion in chromite	8	900–1100	Ohnenstetter et al. (1999)
Durance river, France	Alaskan-type	Isoferroplatinum	Placer	130	700–800	Garuti et al. (1999b)
Fifield, Australia		Isoferroplatinum	Placer	ca. 450	800	Johan et al. (1991), Slansky et al. (1991)
Russia	Alaskan-type	Isoferroplatinum	Placer	700	800–850	Johan et al. (2000)

associative, dissociative and interchange mechanisms are shown. We can see that $\Delta S^{\neq}$ ($440\ \mathrm{kJ\ mol^{-1}} - 450\ \mathrm{kJ\ mol^{-1}} + 8.31\ \mathrm{J\ mol^{-1}\ K^{-1}} (T\ \mathrm{K}) + (T\ \mathrm{K})\ \Delta S^{\neq} = 0$) becomes zero ($\Delta S^{\neq} = 0$) when $T = 1203$ K (930 °C), and $\Delta S^{\neq}$ is positive at $T < 1203$ K, whereas it becomes negative at $T > 1203$ K. The range of temperatures used in Table 1 is 700–1100 °C, that is, 973–1373 K, (i.e., $1/T = 0.00103$–0.00073) and the value of $\Delta S^{\neq}$ varies between $-2 < \Delta S^{\neq} < +2$. The mechanism would become dissociative, $\Delta S^{\neq} > 10\ \mathrm{J\ K^{-1}\ mol^{-1}}$, at $T < 546$ K (<273 °C, $1/T > 0.0018$), and would become associative, $\Delta S^{\neq} < -10\ \mathrm{J\ K^{-1}\ mol^{-1}}$, at the impossible temperatures $T > -5917$ K.

It is obvious (Fig. 6) that the only mechanism that can apply in our case is interchange.

As we have seen (Section 4.3) in the interchange mechanism, an outer-sphere "complex" is initially formed. Then, the leaving group (in our case oxygen or chloride or any other ligand, assuming that these compounds containing oxygen, chloride or other ligands formed during an earlier stage) move from the inner to the outer coordination sphere, while simultaneously the entering group (in our case sulfur) moves from the outer to the inner coordination sphere.

Since the valence of the PGE is still a subject of debate, the general equation is used:

$$ML_{x/2(\mathrm{melt})} + x/_4L'_2 \rightleftarrows ML'_{\mathrm{x/2(sulfide)}} + x/_4L_2$$

where $L = O$, $\mathrm{Cl_2}$, or any other ligand, and $L' = S$.

For an interchange process, we focus on the dynamic changes occurring during the critical concerted interchange step. This step can be associative-like interchange (I_a), where the incoming group helps the leaving group depart, or dissociative-like (I_d), where the determining factor is the release of the leaving group while the group that will eventually enter "waits just outside" and moves in to fill the "void" (Katakis and Gordon, 1987). In the I_d mechanism, there is only weak bonding to the entering and leaving groups, while in I_a the bonding is stronger but not quite as strong as for the associative mechanism (Fig. 3).

More or less bonding is symbolized in Fig. 3 by placing the leaving and incoming groups at different distances from the central atom. In an ideal interchange mechanism, $\Delta S^{\neq} = 0$ and $\Delta V^{\neq} = 0$. In an I_a mechanism, $\Delta S^{\neq}$ and $\Delta V^{\neq}$ are close to zero but slightly negative, and in an I_d mechanism $\Delta S^{\neq}$ and $\Delta V^{\neq}$ are close to zero but slightly

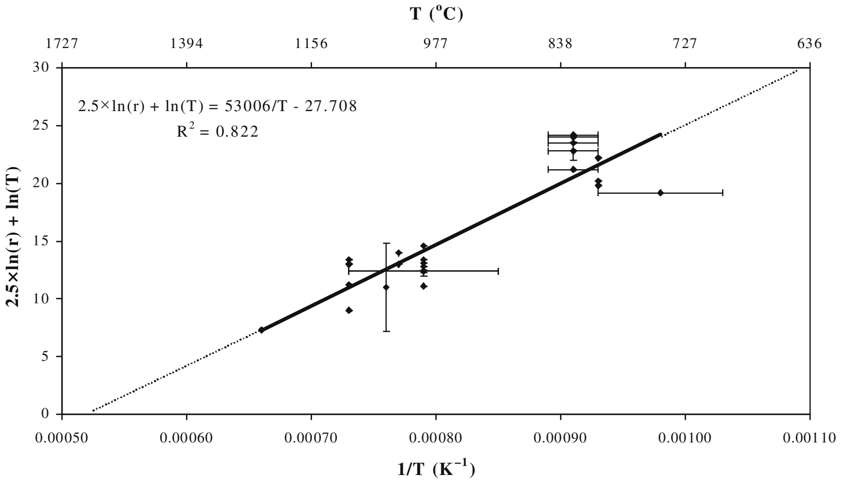

Fig. 5. All data (r, T) were taken from literature (Table 1). The point with coordinates $y = 2.5\ln(1) + \ln(1523) = 7.33$ and $x = 1/1523 = 0.00066$, that is, the point $r = 1$ and $T = 1250$ °C or 1523 K is also included in the graph (last lower point of the solid line).

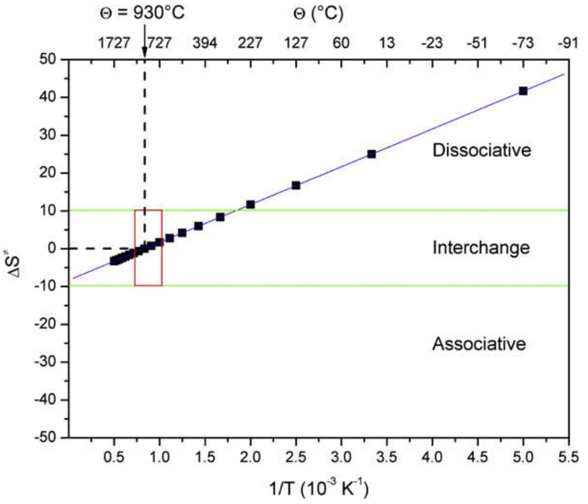

Fig. 6. Plot of $\Delta S^{\neq}$ versus $1/T$ [equation $\Delta S^{\neq} = -R + (E_{\text{act}} - \Delta G^{\neq})/T$] for the determination of the limits of $\Delta S^{\neq}$ and T that are considered to indicate associative, dissociative and interchange mechanisms. The area that is included in the red parallelogram corresponds to the values of T, $700 < T < 1100$ °C and of $\Delta S^{\neq}$, $-10 < \Delta S^{\neq} < +10$ J K^{-1} mol^{-1}. The squares that appear in the graph correspond to the values of T, $200 < T < 2000$ K and to the resulting values of $\Delta S^{\neq}$ (application of the above equation for 100 K intervals). (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

positive. The $\Delta S^{\neq}$ value is the entropy change between the transition state and the reactants, and $\Delta V^{\neq}$ the corresponding change in volume. The transition state is the state that the reactants reach upon receiving the activation energy that is required for the reaction to take place. Positive $\Delta S^{\neq}$ and $\Delta V^{\neq}$ values mean a less well-organized transition state compared to the reactants (dissociative mechanism). A negative $\Delta S^{\neq}$ value means a more structured, more organized transition state than the reactants (associative mechanism). In an ideal interchange mechanism, there is no difference in the entropy, that is, in the organization and degree of freedom, between the reactants and the transition state (Katakis and Gordon, 1987; Petrou, 2002).

The possible errors involved in the calculation are large and are derived from the errors in the activation energy and the free energy of activation. Further work to improve these data is necessary.

8. CONCLUSIONS

The application of molecular-scale chemistry to the genetic processes for platinum-group mineral (PGM) formation, i.e., the suggestion of possible mechanisms taking place during PGE formation, may contribute to a better understanding of the above processes. We draw the following conclusions from our study:

1. Applying the Eyring equation to literature data for the platinum-group element minerals (PGM), we obtained a linear relationship between $2.5\ln(r) + \ln(T)$ and $1/T$, leading to an estimation of the free energy of activation, $\Delta G^{\neq} = 440 \pm 43$ kJ mol^{-1}.
2. The estimated entropy of activation values at various temperatures being approximately zero suggests a possible interchange mechanism rather than an associative or dissociative mechanism for PGM formation.
3. The possibility of formation of PGM from the direct reaction of free metals with sulfur is inconsistent with the estimated entropy of activation values ($\Delta S^{\neq} \sim 0$) at various temperatures.
4. By applying the plot of $\ln(r)$ versus $1/T$ (straight line) to PGM grains of known r, we can estimate the formation temperatures, and then by applying the relation of $2.5\ln(r) + \ln(T)$ versus $1/T$ (straight line, Fig. 5), the free energy of activation can be obtained. From that value, the entropy of activation can be calculated using the relation $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} = E_{\text{act}} - RT - T\Delta S^{\neq}$, and an interchange mechanism is proposed, consistent with the data/results.

5. Applying the relation $2.5\ln(r) + \ln(T)$ versus $1/T$ on PGM grains of known r and T, we can suggest an interchange mechanism for their formation if they fit the above (Fig. 5) straight line.

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