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The activation energy values estimated by the Arrhenius equation as a controlling factor of platinum-group mineral formation

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Abstract

In ophiolite complexes and Ural/Alaskan-type intrusions the platinum-group element minerals (PGM) occur as laurite (RuS_2), erlichmanite (OsS_2), irarsite (IrAsS) and alloys (Os–Ir–Ru and Pt–Fe). They are commonly found as small inclusions (normally less than 10 μm, occasionally up to 100 μm) in chromite. The origin of coarse-grained PGM, in the form of 0.5–10 mm nuggets, in placer deposits related with mafic/ultramafic complexes remains still unclear. Literature data on grain size (r) of platinum-group minerals (PGM) and their formation temperature (range of temperatures between 700 and 1100 °C), revealed an Arrhenius temperature dependence. Correlation of the rate of crystal formation that depends on temperature (T) with the size (r) of the grain results in a linear relationship between $\ln(r)$ and 1/T. From the slope of the line $n \times \ln(r) = -\text{const.} + E_{act}/RT$ the activation energy for the formation of IPGM (Ir–platinum-group minerals) was estimated, for the first time in the present study, to be approximately 450 ± 45 kJ mol^{-1}. Applying the Arrhenius equation, the corresponding formation temperature for extremely large IPGM grains (up to 1.3 mm) in chromite ores related to ophiolites was found to be approximately 740 °C. It seems to be consistent with a lower formation temperature than with the typical formation temperature of small PGM grains associated with ophiolitic chromitites. This suggests that coarse-grained PGM in mafic/ultramafic complexes, along the permeable shear zones, may have been re-crystallized during plastic deformation at relatively lower temperatures (700–800 °C), under appropriate pressure, temperature, redox conditions and an increased H_2O content. Thus, applying the plot of $\ln(r)$ versus 1/T on large Os–Ir–Ru-minerals (sulfides or alloys), characterized by an r value falling into the linear part of the graph and having evidence supporting their formation at relatively high temperatures, then the corresponding formation temperature of those IPGM can be found.

1. INTRODUCTION

The platinum-group elements (Ru, Rh, Pd, Os, Ir, and Pt), which are the most valuable elements, are of strategic importance due to their growing use in advanced technologies. They have been described in a wide range of geotectonic settings but the conditions under which platinum-group elements (PGE) are concentrated remains still unclear. More specifically, the origin of coarse-grained platinum-group minerals (PGM) located in many placers associated with ultramafic–mafic complexes, such as Ural/Alaskan- and ophiolitic-type and in laterites related with the Freetown layered gabbro, Sierra Leone and many other deposits worldwide, have been a subject of debate for several years, due to the paucity of coarse-grained PGM in parental rocks. Some authors have suggested that coarse-grained PGM have formed at low-temperature, during the weathering of mafic rocks and sedimentation in placers (Augustithis, 1965; Ottemann and Augustithis, 1967;

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Cousins and Kinloch, 1976; Bowles, 1986; Barker and Lamal, 1989; Bowles et al., 2000) whilst others suggested that such coarse-grained PGM have crystallized at relatively high temperature, in a magmatic environment (Cabri and Harris, 1975; Hattori and Hart, 1991; Johan et al., 1991; Slansky et al., 1991; Cabri et al., 1996; Johan et al., 2000; Malitch and Thalhammer, 2002; Hattori et al., 2004; Tolstykh et al., 2005).

Thermodynamically favorable processes have occurred in nature both in biological and geological systems. Thermodynamics being concerned with original and final states is independent on (chemical) reaction mechanism, it foresees whether a reaction will take place and say nothing about the rate by which the reaction will take place, whilst kinetics involves the rate of the reaction. The Arrhenius equation is a simple but remarkably accurate formula for the temperature dependence of the rate constant, and therefore the rate of a chemical reaction. It is seen as an empirical relationship and can be used to model the temperature-variance of diffusion coefficients, population of crystal vacancies, creep rate, and many other thermally-induced processes (Kenneth, 1990; Laidler, 1997). Based on mineralogical, phase mineral chemistry and formation temperature data for platinum-group minerals (PGM) associated with Ural/Alaskan-type and ophiolite complexes we suggest the application of the Arrhenius equation incorporating the grain-size of PGM and the temperature of their formation for the estimation of the activation energy for Ru, Os, Ir-sulfides and alloys (only minerals of the Ir-group minerals). The activation energy value estimated and presented here, for the first time, may contribute to the better understanding of the PGE mineralization, in particular of the coarse-grained IPGM (Ir–platinum-group minerals) related to mafic/ultramafic complexes.

2. CHARACTERISTIC FEATURES OF PLATINUM-GROUP MINERALS

The occurrence, crystallographic, physical properties of platinum-group minerals, their chemical composition, textural relationships to other species have been studied extensively and reviewed by several authors (Cabri, 2002; Oberthür et al., 2004). Sulfides of the iridium group PGE (IPGE) such as laurite (RuS_2), erlichmanite (OsS_2) and irarsite (IrAsS) have been identified as small inclusions (normally less than 10 μm, occasionally up to 100 μm) within chromite grains in many mafic–ultramafic complexes, including ophiolite, and Ural/Alaskan-type complexes (Talkington et al., 1984; Augé, 1985; Prichard and Tarkian, 1988; Garuti and Zaccarini, 1997; Melcher et al., 1997; Garuti et al., 1999a,b; Tarkian et al., 1992; Hattori and Hart, 1991; Hattori et al., 2004; Augé and Maurizot, 1995; Cabri et al., 1996).

Well-developed crystals of platinum-group minerals (PGM) and nuggets, ranging in size from <1 mm to some mm in placers deposits (Cabri, 2002; Weiser, 2002; Melcher et al., 2005). Alluvial PGM from the Freetown intrusion, Sierra Leone have been described by Bowles (1986) and Bowles et al. (2000). Platinum–iron alloy, (Pt_3Fe) is the principal component and forms large (0.5–7 mm) irregular grains. Laurite–erlichmanite and osmium–iridium alloy occur both as separate grains and are associated with Pt–Fe alloys. The laurite–erlichmanite forms pyritohedral crystals of 0.5–2 mm. Ru–Ir–Os and Pt–Fe alloys with grain size up to >1 mm have been found in the alluvial placer deposits of the Meratus–Bobaris area, southern Kalimantan, Indonesia (Burgath, 1988). Although monophase grains of Pt–Fe alloy are the most common platinum-group minerals (PGM) recovered from alluvial sediments by panning on the farm Maandagshoek, easterm Bushveld, Ru–Os–Ir–Pt alloy and laurite are also present. All authors who have studied platinum–PGM from the Bushveld complex agree that the grain sizes of the PGM are much larger in the Merensky Reef (~10–200 μm, even up to 1 mm) compared to those of the UG-2 (<10–30 μm), and both are smaller compared to the dominant grain size of detrital PGM (more than 6000 grains). The latter are all >40 μm, commonly their size is in the range of 100–200 μm, and up to 1.6 μm is the size of the Pt–Fe alloy grains (Oberthür et al., 2004; Oberthür and Melcher, 2005). Multi-component (Os–Ir–Ru–Rh–Pt) detrital grains have been described in the Somabula gravels of the Great Dyke in Zimbabwe, and detrital grains of Pt–Fe alloy are ubiquitous in the alluvial sediments along the Makwiro river (Oberthür et al.,1998; Oberthür, 2002; Oberthür et al., 2003; Melcher et al., 2005; Oberthür and Melcher, 2005). Geological and geographical constraints indicate that the possible sources of those PGM grains are the Merensky Reef, the UG-2 or other PGM-bearing seams (Tarkian and Stumpfl, 1975; Cawthorn, 2001; Oberthür et al., 2004 and references cited therein). Tarkian and Stumpfl (1975) reported that grain sizes of Pt–Fe alloy grains reach up to 1 mm, and Wagner and Mellor (1925) have described Pt–Fe nuggets in the form of cubic crystals and irregular particles up to 5 mm in size from the eluvial gravels surrounding the Mooihoek and Onverwacht pipes.

Also, an isoferroplatinun–iridium paragenesis has been established in the Fifield placer of Australia. The reported grain size ranges from 80 to 1600 μm (Slansky et al., 1991; Weiser, 2002; Tolstykh et al., 2005). Hexagonal, coarse-grained Os–Ir–Ru alloys, ranging from 100 μm to 2 mm have been located in the Papua New Guinea placers derived from ophiolites. They are often characterized by an unusually high Pt content, an association with Pt–Fe alloys and have been probably derived from ophiolites of the Papuan Ultramafic Belt (Johan et al., 2000; Malitch and Thalhammer, 2002). Euhedral macrocrystals of Pt–Fe alloy from the Kondyor PGE placer, Khabarovskiy Kray, eastern Siberia, Russia, exhibit inclusions suggesting a petrogenetic association with the late apatite—magnetite—phlogopite clinopyroxenite bodies rather than the dunite-dominant main intrusion (Malitch and Thalhammer, 2002; Shcekas et al., 2004).

It has been suggested that well-developed crystals (up to 10 mm) of laurite, erlichmanite and irarsite PGM in placer deposits are detrital grains, derived from PGM-bearing rocks in the source area by weathering and erosion. However, there is a debate as to whether all PGM grains in placer deposits represent transported minerals or they have formed either in the weathered rock or in placers, due mostly to the paucity of large PGM in the parent rocks and differences in the chemical composition of PGM (Ottemann and Augustithis, 1967; Cabri and Harris 1975; Cousins and Kinloch 1976; Bowles, 1981, 1986, 1988; Burgath, 1988; Cabri et al., 1996; Bowles et al., 2000; Johan et al., 2000; Tsintsov, 2001; Weiser, 2002; Hattori et al., 2004; Oberthür et al., 2004; Oberthür and Melcher, 2005; Tolstykh et al., 2005). Laurite (RuS_2), with a size ranging from 700 to 1100 μm (average 900 μm), from the sediments in the main channel of the river Pontyn River and Tambanio River, Borneo, exhibit inclusions, such as Ca–Al amphibole, chalcopyrite, bornite, pentlandite, heazlewoodite. On the basis of the type and composition of the inclusions it has been suggested that these PGM may have been derived from ophiolites (Cousins and Kinloch, 1976; Barker and Lamal, 1989). The stability fields and paragenetic relationships of isoferroplatinum, Os–Ir–Ru alloys, laurite, and sperrylite occurring in placer deposits as well as in related zoned Alaskan/Ural-type and ophiolite complexes can provide the valuable evidence that distinguishes the parent rocks (Tolstykh et al., 2005).

According to Bavkov et al. (2005) Ir-dominant Ir–Os–(Ru–Pt) alloys, subordinate Os-dominant alloys, and minor Ru-rich alloys and rutheniridosmine, are less common in British Columbia placer deposit, and they are commonly slow intergrowths with large Pt–Fe–(Cu) alloy grains. The zoned Pt–Fe–Cu alloys were interpreted as having formed by fractional crystallization under closed-system conditions. The compositions of inclusions and exsolution lamellae of Os- and Ir-dominant alloys in Pt–Fe alloys imply uniform temperatures of equilibration within the range 750–800 °C. Furthermore, the above authors based on the terrane affinities, compositions and associations of those placer PGM suggested that they are derived from two types of potential source-rocks, being Alaskan-type intrusions and the Atlin ophiolite complex, and that the preservation of faceted morphologies on many PGM grains from that area implies a relatively short distance of transport from their source.

Recently, Cabral et al. (2006) presented the first evidence of a natural Hg-bearing Pt–Pd alloy, with an empirical composition close to $(Pt,Hg)_2Pd$, as well as evidence for Pd–Pt crystals from Córrego Bom Sucesso, Serro, Minas Gerais, Brazil. They exhibit arborescent, botryoidal form, reaching a maximum length of 2.5 mm and a compositional zoning in platinum, palladium and mercury contents, from core outward. Also, they are characterized by the lack of base metals and mineral inclusions other than gold, open spaces between arborescent grains and a seleniferous signature, such as all Pd–Pt-bearing deposits of economic importance in Brazil within metasedimentary rocks. Those peculiar nuggets of platinum and palladium from Córrego Bom Sucesso have been considered to have formed under oxidizing conditions and subjected to weathering (i.e., residual primary grains), whilst the origin of the alluvial Pt–Pd nuggets from Sucesso, Serro, Minas Gerais, Brazil remains still unclear (Cabral et al., 2006 and references herein).

3. PETROGENETIC PROCESSES CONTROLLING GRAIN SIZE OF PGM

Platinum-group element mineralization is still a subject of debate. The petrogenetic processes controlling the deposition of the PGE, and the formation of platinum group minerals (PGM), such as the directly precipitated from silicate melt, the immiscible sulfide liquids, and the magmatic volatile phases are subjects of great interest for many investigators. Experiments at 1250 and 1200 °C on synthetic laurite and Ru–Os–Ir alloy (Andrews and Brenan, 2002), indicated that grains of Ru–Os alloy are relatively small (<10 μm) whilst those of Ir-bearing alloy tend to be larger (20–30 μm). Also, innovative experiments at temperatures from 1150 to 1200 °C and pressures from 10^5–4×10^8 Pa, showed mixing or immiscibility between basalts of different composition, and between hydrous fluids and chromite (Matveev and Ballhaus, 2002). A salient feature was the strong immiscibility between an olivine chromite melt and a hydrous fluid. Upon olivine and chromite precipitation, chromite would collect in the hydrous liquid droplets, accompanied by PGE-rich metallic alloys, whilst olivine would be collected in the basaltic melt. Although the high solubilities of the PGE in basaltic magma would preclude direct nucleation and crystallization of PGM from silicate melt, laurite (RuS_2) and alloys occurring as inclusions within natural chromite crystals may have formed by direct crystallization from a silicate magma under appropriate conditions of T, P, f_{O2} and f_{S2}. Thus, sulfides of the laurite–erlichmanite solid solution series are the most common monophase inclusions in chromite. These minerals are often associated with enstatite–pargasite and clinopyroxenite–phlogopite aggregates, suggesting a hydrous magmatic origin. It has been suggested that Ir–platinum-group phases (Ir, Os, Ru; the IPGE) associated with chromite have formed at very early stage, and are trapped in chromites (Stockman and Hlava, 1984; Melcher et al., 1997; Ohnenstetter et al., 1999; Johan et al., 2000; Augé et al., 2005 and references cited therein).

The most common phase that is implicated in the generation of PGE deposits is sulfide liquid, which forms immiscible droplets dispersed within the silicate melt. All of the chalcophile elements Cu, Ni, Co, Au, and the PGE, are extremely compatible with sulfide liquid relative to silicate melt. The separation of sulfide liquid from basaltic magma will collect all of the chalcophile elements present unless the modal proportion of sulfide is very small (Mungall, 2005). In a multidisciplinary study by Ohnenstetter et al. (1999) it has been emphasized that (a) within all platinum-group deposits locally high sulfur fugacity conditions may be developed even in low-sulfur assemblages during the final stages of the PGE deposition, (b) fluid-driven multistage platinum-mineralization could be widespread and (c) subsolidus reactions may be occurred progressively during cooling of the formed PGE-mineralization. Thus, some remobilisation and recrystallization of PGE-deposits may have taken place during regional metamorphism, but the system is considered to be a closed system with respect to PGE.

Although most Alaskan-type complexes contain primary PGE mineralization, they are much better known as the source of economic PGE placer concentrations (Johan et al., 2000; Weiser, 2002). A characteristic feature of the Alaskan/Ural-type complexes is the dominance of Pt–Fe alloys, in particular compared to the ophiolite complexes dominated by Os–Ir–Ru sulfides and alloys. According to experimental data and natural occurrences Pt–Fe, Os–Ir–Ru alloys and traces of laurite have probably formed at a very early stage of magmatic differentiation under low fugacity of sulfur, high-temperature conditions and the presence of a fluid phase (Johan et al., 1989). In Ural/Alaskan-type complexes and the related economically important placer deposits, the occurrence of oriented lamellae of Os–Ir phases in Pt–Fe alloys is common, and this has been interpreted in light of the miscibility-gaps in the binary systems Os–Ir, Ir–Pt and Os–Pt. Estimated equilibrium temperatures for the Pt–Fe, Os–Ir and Ir–Os alloys from Pt–Fe nuggets of economically important placer deposits closely linked to clinopyroxenite–dunite massifs of the Siberian Platform (Kondyor, Inagli, Guli) and the Middle Urals (Nizhny Tagil), Russia, range from 850 to 800 °C (Malitch and Thalhammer, 2002). Such a temperature estimated range is in a good agreement with studies of PGM associations from Fifield (NSW, Australia; Slansky et al., 1991), Inagli massif (Tolstykh et al., 2005), and from the Kompiam area, Papua New Guinea (Johan et al., 2000). Euhedral macrocrystals of Pt–Fe alloy from the Kondyor PGE placer, Khabarovskiy Kray, eastern Siberia, Russia, exhibit inclusions suggesting a petrogenetic association with the late apatite—magnetite—phlogopite clinopyroxenite bodies rather than the dunite-dominant main intrusion. The large size of the crystals has been attributed to crystal growth in a pegmatitic environment, i.e., from residual liquids that eventually reached fluid saturation (Johan et al., 2000; Malitch and Thalhammer, 2002; Shcekas et al., 2004; Cabral et al., 2006).

4. MECHANISMS OF CRYSTAL GROWTH—FACTORS CONTROLLING THE GRAIN-SIZE OF PGM

Extensive studies have been carried out on magmas at thermodynamic equilibrium (although there is geochemical evidence of disequilibrium) on the dependency of the effective distribution coefficient upon growth rates, on the roughness of interfaces and on the crystallographic orientations. Most of the experimental work on crystal growth has been done using model systems or natural crystals in synthetic melts (Kirkpatrick et al., 1979; Lofgren, 1980; Kirkpatrick, 1981; Muncill and Lasaga, 1987). In general, rates of crystal growth from a melt are mainly controlled by any of three principal processes: (l) interfacial kinetics or the rate of attachment at the crystal face, (2) transport of material by diffusion or a combination of diffusion and advection through the melt phase, and (3) transport of latent heat of crystallization away from the crystal face. Although considerable research has focused on studying the crystal growth and resultant crystal size distributions (CSDs) there is a controversy with respect to the interpretation of crystal growth, size-independent (constant) vs. size-dependent (proportionate) growth (Eberl et al., 2002). According to experimental evidence by Kile and Eberl (2003) crystal growth mechanisms are governed by the nature of the transport of reactants to the crystal surface. Constant, size-independent growth results when reactant supply to crystal surfaces is diffusion-limited, whereas proportionate, size-dependent growth results when reactants are supplied by advection. Thus, proportionate growth is expected whenever the rate of reactant supply by advection exceeds that by diffusion. An understanding of kinetic-related features in igneous rocks requires detailed models of reactions in igneous systems. The importance of the dynamic crystallization and kinetics, has been emphasized by Lofgren (1980) and Kirkpatrick (1981).

The rate (u) of crystal growth is (by definition) measured by the growth of one linear size of the primary crystals with respect to time. The rate is governed by the rate of diffusion between the reacting species (Belcher and Gordon, 1987). Chemical diffusivities are widely reported to obey an exponential dependence on reciprocal temperature over considerable ranges in temperature, a type of relation referred to as Arrhenian.

$$D = D_0 e^{-\frac{E_{\mathrm{act}}}{RT}} \qquad (1)$$

The Arrhenian relation can be derived from absolute rate theory since species (ions) move from one location in the magma to another in discrete diffusive jumps. Each jump requires a species (an ion) vibrating within a stable potential energy in the melt to acquire sufficient kinetic energy to rise over a potential energy barrier, to move to an adjacent stable site in the structure. The pre-exponential factor D_0 can be related to the frequency of the vibration, which allows diffusive steps to occur. It has been called the frequency factor and is for most purposes a constant.

5. ARRHENIUS ACTIVATION ENERGY AND MINIMUM ENERGY PATHWAYS

The energy required to bring reactants to a condition necessary to form products is called the activation energy (E_{act}), whilst a proper orientation (relative position) of reactants is also necessary to result in product formation. The activation energy is independent of reactant concentration and is expressed in kJ per mol. However, the role of concentration in the development of Eq. (11) and the final graph from which calculation of the activation energy is obtained, is in detail discussed below. The activation energy is also independent on temperature; at higher temperature a larger portion of reactant molecules will have the required E_{act} to react. Thus, rates of reaction depend on activation energy, reactant orientations (relative positions) during collisions and temperature,

$$k_{\mathrm{obs}} = A e^{-\frac{E_{\mathrm{act}}}{RT}} \qquad (2)$$

where k_{obs} is the rate constant at the (absolute) temperature T, the constant A is called a frequency factor and contains information about molecule collision frequency and the

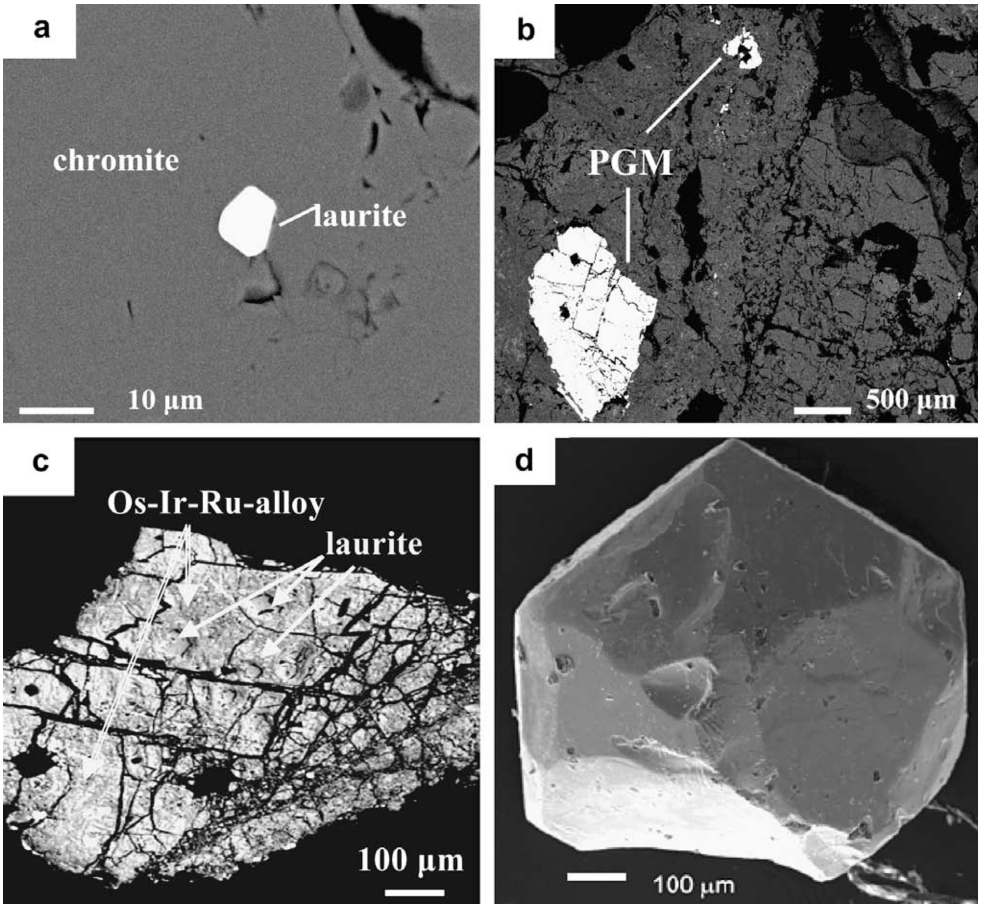

Fig. 1. Back-scattered electron images of typical small laurite within unaltered chromite (a), coarse-grained IPGM within strongly fragmented chromite along a shear zone (b), detail of coarse-grained IPGM (b) consisting of remnants of laurite and Os–Ir–Ru alloy (c) and IPGM from a placer deposit (d), after Tsoupas and Economou-Eliopoulos (2008) and Hattori et al. (2004).

probability that the collisions are favorably oriented for reaction to occur.

Under the special conditions at which chemical processes usually proceed, there is a statistical distribution in the relative orientations (positions, pathways) of the (usually nonspherical) reacting molecules as they move and approach each other. The energy required to bring reactants to a condition necessary to form products is called the activation energy and the more favorable energetically orientations (positions, pathways) are called the minimum energy pathways (Espenson, 1981; Katakis and Gordon, 1987). Hence, we applied the Arrhenius equation to various data obtained from the literature in order to estimate the minimum energy (E_{act}) that is needed for the process of various IPGM formation.

6. ESTIMATION OF ACTIVATION ENERGY FROM THE LITERATURE DATA

The rate (u) of a reaction/process is proportional to the concentration of the reactants (C^{a}).

$$u = \frac{\partial c}{\partial t} \tag{3}$$

$$u = k_{\mathrm{obs}} \times C^{a} \tag{4}$$

It is also well-known that high temperatures of reacting media result in high rates of crystal formation and lead to small crystal sizes, whilst low temperatures lead to small 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, then $u \propto \frac{1}{r^n}$, where r is a dimension of the crystal. In the case where $n = 3$ we refer to the volume of the crystal, and $n = 2$ to the surface area.

The rate is governed by the rate of diffusion (Belcher and Gordon, 1987). Attempts to model crystal growth mathematically often fail to predict either the commonly observed lognormal size distribution or the associated crystal size variance (Eberl et al., 2002). Eqs. (2) and (4) give:

$$u = Ae^{-\frac{E_{\mathrm{act}}}{RT}}C^{a} \tag{5}$$

$$\Rightarrow \frac{1}{r^n} = A'C^{a}e^{-\frac{E_{act}}{RT}} \tag{6}$$

Hence, combining constants, A' and C^{a} we obtain:

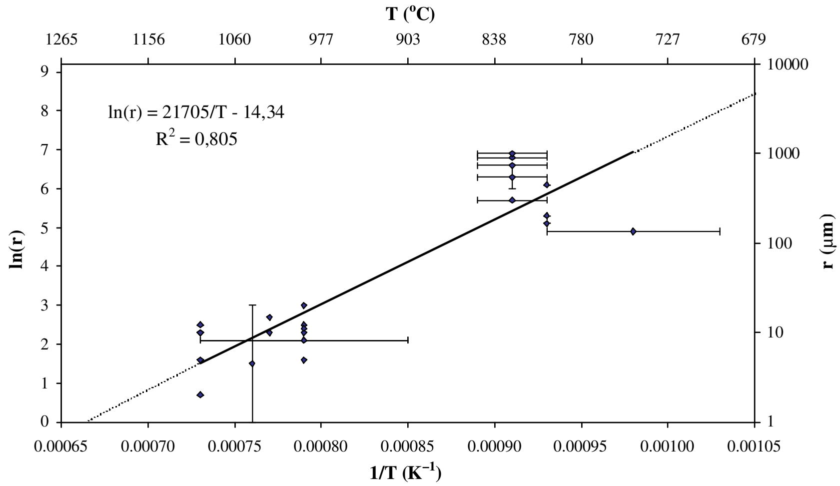

Fig. 2. Plot of ln(r) versus $1/T$ for the estimation of the required (minimum) activation energy of the Ru, Os, Ir-sulfide and alloy formation. Data from Table 1. [ln(r) = 21705/T − 14.34].

$$\frac{1}{r^n} = A'' e^{-\frac{E_{\mathrm{act}}}{RT}} \tag{7}$$

$$\ln\left(\frac{1}{r^n}\right) = \ln(A'') - \frac{E_{\mathrm{act}}}{RT} \tag{8}$$

$$\Rightarrow -\ln(r^n) = \text{const.} - \frac{E_{\mathrm{act}}}{RT} \tag{9}$$

$$\Rightarrow -n \times \ln(r) = \text{const.} - \frac{E_{\mathrm{act}}}{RT} \tag{10}$$

$$n \times \ln(r) = -\text{const.} + \frac{E_{\mathrm{act}}}{RT} \tag{11}$$

An assumption is made here concerning the concentration: the concentration of the reactants (C^a) is assumed to be constant, and this is true in the case of mineral formation from a large body of magma, though 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.

Plotting ln(r) versus $1/T$ we obtain a straight line, with Slope = $E_{\mathrm{act}}/R \times n$ and intercept = −const/n.

The relationship between ln(r) and $1/T$ will not be a straight line if the concentration is not constant since the "−const." term contains C^a. Since C^a decreases with increasing $1/T$, that is at lower temperatures, the term $A' \times C^a = A''$ also decreases, and thus $\ln(A'')$ = const. is reduced. The "const." being reduced, "−const." increases and so the intercept (−const/n) also increases. Thus, the E_{act} value resulting from Eq. (11) will be smaller. The straight line equation (graph 1, Fig. 2), is valid at high temperatures whilst at low temperatures the line curves (see below graph 2, Fig. 3). Finally r tends to become independent of temperature as is implied by the relation $u \propto \frac{1}{r^n}$, since the product $u \times r^n$ cannot exceed a certain value. When u is high, at high temperature, r is small, when u is low at lower temperature, r is large. At very high temperature and thus high u, r approaches a very small value (invisible 1 μm, the lower limit), close to the stability limit of laurite (Brenan and Andrews, 2001). At very low temperatures u becomes very small and r very large, but certainly having an upper limit. Various data of grain size and the corresponding temperatures ($T = T$(°C) + 273 K) are presented in Table 1.

Plotting ln(r) versus $1/T$ (Fig. 2; data from Table 1, in a range of temperature between 700 and 1100 °C), where r is the grain size of platinum-group minerals (PGM), an Arrhenius temperature dependence is obtained. From the slope of the straight line the activation energy was estimated: −const/n = −14.34 and $E_{\mathrm{act}}/n \times R$ = slope = 21705 K, hence $E_{\mathrm{act}} = 21705 \times n \times 8.31 = 180368.6 \times n$ J mol^{-1} = $n \times 180.4$ kJ mol^{-1}. Assuming that $n = 3$ (volume of a grain), then $E_{\mathrm{act}} = 541.2$ kJ mol^{-1}. If $n = 2$ (surface of the grain) then $E_{\mathrm{act}} = 360.8$ kJ mol^{-1}. Therefore, assuming that grains of platinum-group minerals described in various geotectonic environments (Table 1) can be roughly described by $n = 2.5$, the estimated average value is approximately 450 ± 45 kJ mol^{-1}. As far as we are aware, the value of the activation energy for the platinum-group minerals of the Ir–platinum group (IPGE) is still missing from the literature. In the present study the estimated value of the activation energy from the slope of the plot of ln(r) versus $1/T$ (Fig. 2) of approximately 450 ± 45 kJ mol^{-1} seems to be comparable to the activation energy (387 kJ mol^{-1}) given in previous studies for spinel growth over the same temperature range at or near atmospheric pressure (Watson and Price, 2001).

Furthermore, we applied the plot of ln(r) versus $1/T$ on PGE data on extremely large PGM grains, ranging from 0.5 to 8 mm in Ethiopia, 0.5–10 mm in Freetown, Borneo, 1–3 mm in Colombia, 5 mm in Fifield and 1.6 mm Bushveld (Wagner and Mellor, 1925; Bowles, 1981, 1986, 1988; Burgath, 1988; Bowles et al., 2000; Tsintsov, 2001; Malitch and Thalhammer, 2002; Malitch et al., 2002; Oberthür et al., 2004; Bavkov et al., 2005), assuming that these grains are Ru, Os, Ir-sulfides and alloys. The application is conducted considering two cases: (a) if the PGM grains have formed at relatively low temperatures, ranging from 30 to 100 °C, during the weathering of parent rocks and sedimentation-diagenesis, then there is an upper limit since the product $u \times r^n$ cannot exceed a certain value (the curve becomes

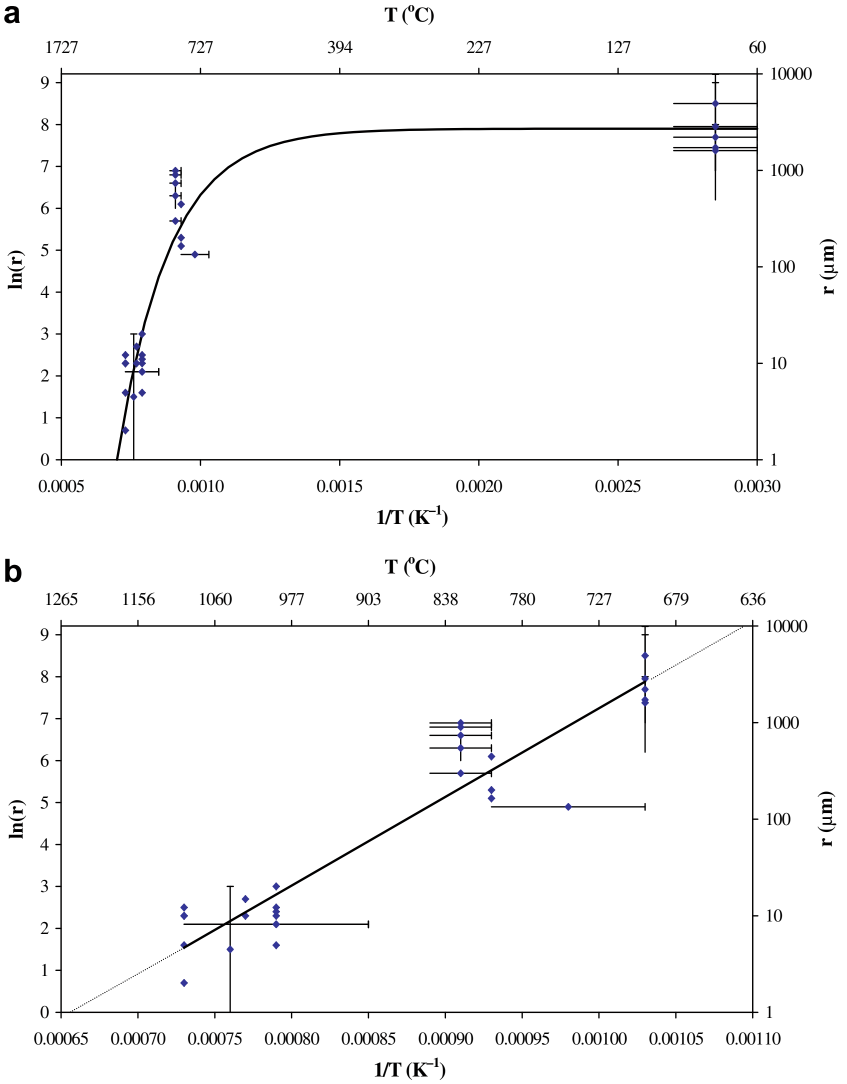

Fig. 3. Plot of ln(r) versus $1/T$ of the Ru, Os, Ir-sulfides and alloys formation data (Table 1; Fig. 2) extrapolated to literature data of large detrital PGM (Table 1). (a) Assuming that these large PGM grains coming from placer deposits are IPGM (Ru, Os, Ir-sulfides and alloys) and correspond to a formation temperature between 30 and 100 °C, during the weathering of parent rocks and sedimentation, then the curve becomes asymptotic and gives an upper limit. The $\ln(r) = 0$, $r = 1$ μm, when $1/T = 0.0007$, $T = 1429$ K, $T = 1160$ °C. (b) If these large IPGM grains have formed at a temperature of approximately 700 °C, then b is obtained [$\ln(r) = 21141/T - 13.893$, and the $\ln(r) = 0$, $r = 1$ μm, when $T = 1522$ K, $T = 1250$ °C].

asymptotic, Fig. 3a), (b) if the PGM grains have formed at temperature approximately 700 °C, in the associated mafic–ultramafic rocks, then the plot remains linear (Fig. 3b, $\ln(r) = 21141/T - 13.893$).

7. ESTIMATION OF THE ACTIVATION ENERGY OF THE *IN SITU* DESULFURISATION OF PGM SULFIDES

Based on scanning electron microscopy (SEM) and the electron microprobe analysis literature data on the relationship between PGM-sulfides and associated alloys, it is realized that the sulfur content decreases gradually outwards the periphery or cracks of relatively small (a few tens of microns) laurite grains in chromite ores hosted in serpentinized peridotites. The replacement of laurite by Os–Ir–Ru alloys, enriched in Ir, Pt, Pd, Fe, Ni, Co and Mn, and/or metallic phases, such as metallic Ru has been interpreted as a replacement association, characterized by *in situ* desulfurisation products of the PGM sulfides, at relatively low (350–500 °C) temperature (Stockman and Hlava, 1984; Tarkian and Prichard, 1987; McElduff and Stumpfl, 1990; Garuti and Zaccarini, 1997; Melcher et al., 1997; Tsoupas and Economou-Eliopoulos, 2008).

The association of primary with secondary PGM reflects a difference in the stability field, e.g., differences in the element diffusion rates. Diffusing atoms movement requires activation energy. The application of Arrhenius equation allowed us to estimate the sulfur mobility. Assuming that the diffusion of sulfur starts from the cen-

Table 1
Characteristic features of refractory platinum-group minerals.

Location	Rock-type	Mineral	Description	Grain size (μm)	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	Garuti et al. (1999b); 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 et al. (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. (1991)
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	c.a. 450	800	Johan et al. (1991); Slansky et al. (1991)
Russia	Alaskan-type	Isoferroplatinum	Placer	700	800–850	Johan et al. (2000)
Meratus-Bobaris, Kalimantan, Indonesia	Ophiolites	Laurite-erlichmanite	Placer	2000	[*]	Burgath (1988)
Hokkaido, Japan	Ophiolites	Os–Ir–Ru alloy	Placer	1300	[*]	Nakagawa and Franco (1997)
Samar, Philippines	Ophiolites	Os–Ir–Ru alloy	Placer	1000	[*]	Nakagawa and Franco (1997)
Freetown, Sierra Leone	Layered intrusion	Laurite-erlichmanite	Placer	5000	[*]	Bowles (1981, 1986)

[*] Two cases have been examined corresponding to formation temperature of these PGM grains: (a) at 30–100 °C and (b) at about 700 °C (Fig. 3).

ter of the grain, then the distance Δx that it has traveled in laurite grains (up to the edge of the grains), with average size 20 μm, can be taken as 10 μm, at approximately 425 °C (average between the range 350–500 °C, (McElduff and Stumpfl, 1990). With respect to the large grain (1300 μm) of Os–Ir–Ru-alloy with small remnants of laurite from the Veria area (Fig. 1b,c) then Δx is 650 μm at about 700 °C, assuming that desulfurisation has taken place before brittle deformation resulted in fragmentation of the crystal (Fig. 1c).

Applying the Arrhenius equation on the rate by which sulfur has been transferred outside the above grains and using additional literature data (Garuti and Zaccarini, 1997) we have:

$$u = \frac{\Delta x}{\Delta t} = Ae^{-\frac{E_{\mathrm{act}}}{RT}}C^{a} \tag{12}$$

hence

$$\Delta x = C' e^{-\frac{E_{\mathrm{act}}}{RT}} \tag{13}$$

and

$$\ln(\Delta x) = C'' - \frac{E_{\mathrm{act}}}{RT} \tag{14}$$

thus $\ln(\Delta x) = f(\frac{1}{T})$ should give a straight line with slope $= -\mathrm{E}_{\mathrm{act}}/R$ and intercept $= C''$.

Actually plotting $\ln(\Delta x)$ versus $1/T$ we obtained a straight line, and from its slope we estimated the approximate activation energy value for diffusion of sulfur to be 60 kJ mol^{-1}. However, this estimation is only a rough approach since more data are required (this work is still in progress). Nevertheless, the low value of the sulfur diffusion activation energy, 60 kJ mol^{-1}, compared to the activation energy for the formation of platinum-group minerals of the Ir–platinum-group (IPGE), 450 kJ mol^{-1}, seems to be consistent with the sulfur incompatible behavior, and the expected higher activation energy for the formation than the diffusion of the elements.

8. APPLICATION OF THE ESTIMATED ACTIVATION ENERGY

8.1. Paucity of PGM in extruded komatiites

By extrapolating the obtained line (Fig. 2) to the point where it meets the horizontal axes (1/*T*), a value of $1/T = 0.00066\ \mathrm{K}^{-1}$ is found, which gives $T = 1513.6$ K (1240 °C), corresponding to $\ln(r) = 0$, and hence $r = 1$ μm. Mathematical solution of the equation of the straight line: $y = 21705x - 14.34$ gives the same results. The obtained values $r_{\max} = 1$ μm and $T = 1240$ °C are in very good agreement with the very small (∼1 μm) grain size of the IPGM-phases ("*invisible PGM*") at the experimental temperature of 1275 °C (Brenan and Andrews, 2001). In addition, they are consistent with the paucity of PGM in extruded komatiites, where the high temperature exceeds the maximum thermal stability of the PGM in mafic magmas. Such an agreement between values of temperature and grain size from experimental work and those obtained by application of the proposed plot (Fig. 2) provides a strong support to the reliability of the slope of the straight line and hence the estimated activation energy value.

8.2. Origin of coarse-grained PGM *in situ*

Given that Os–Ir–Ru-minerals (sulfides or alloys) are mostly found as inclusions in chromite related to mafic/ultramafic complexes, using the plot of ln(*r*) versus 1/*T* (Fig. 2), a brief estimation of the formation temperature is possible if only the grain size of PGM is available. Two large, up to 1300 μm laurite grains from the Veria (Greece) ophiolites, are located exclusively along shear zones, cementing strongly fractured (brittle-deformed) chromite (Tsoupas and Economou-Eliopoulos, 2008). The corresponding temperature of the extremely large PGM grain (Fig. 1b) was found from the plot of Fig. 2, to be approximately 740 °C. It seems to be consistent with a lower formation temperature than with the typical formation temperature of small PGM grains associated with ophiolitic chromitites (Tsoupas and Economou-Eliopoulos, 2008) and confirms the possibility of remobilisation and recrystallization during metamorphism in a closed system for PGE (Ohnenstetter et al., 1999).

Furthermore, the Arrhenius equation could be applied to relatively large size IPGM crystals described to mafic–ultramafic complexes (Johan et al., 2000; Malitch and Thalhammer, 2002; Shcekas et al., 2004; Tolstykh et al., 2005; Cabral et al., 2006). Applying the plot of ln(*r*) versus 1/*T* (Fig. 2) when the grain-size (*r*) of IPGM is known, then the corresponding formation temperature can be found.

8.3. Origin of coarse-grained detrital PGM

In the present study we applied the Arrhenius equation incorporating the grain-size of IPGM and the formation temperature for Ru, Os, Ir-sulfides and alloys (only minerals of the Ir–platinum group minerals). Applying the plot of Fig. 2 in large IPGM from placer deposits of Papua, New Guinea and Bulgaria (Tsintsov, 2001; Malitch and Thalhammer, 2002), which contain inclusions of Pt–Fe alloys, with grain size 300, 500, 800 and 2000 μm, the corresponding temperatures were found to be 800, 780, 760 and 720 °C, respectively. The activation energy that is obtained from the slope of the plot of Fig. 2, is valid only for minerals having similar composition, that is, having the same A (pre-exponential or frequency factor) in the Arrhenius equation. For this reason, it was not applied to find the corresponding temperature for numerous of detrital large (in the order of mm) PGM grains, such as those related with the Great Dyke, Zimbabwe, which are mostly Pt–Fe (Oberthür et al., 1998; Oberthür, 2002; Oberthür et al., 2003), Bushveld complex (Wagner and Mellor, 1925; Oberthür et al., 2004), and elsewhere since those are Pt–Fe alloys.

9. CONCLUSIONS

The agreement between values of temperature and grain size from experimental data and those resulted by application of the Arrhenius equation (Fig. 2) provides a strong support to the reliability of the slope of the straight line and hence the estimated, in the present study, activation energy value (approximately 450 ± 45 kJ mol^{-1}).

The straight line equation (graph 1, Fig. 2) can be applied at high temperatures (closed system, approximately constant concentration), whilst at lower temperatures (open system, varying concentration), the line should be curving and any application of the above equation should take this into account.

Applying the plot of $\ln(r)$ versus $1/T$ (straight line) on large grain-size (of known r) IPGE-minerals, characterized by Pt–Pd and Pt–Fe alloys, sulfides and/or other inclusions (formation at relatively high temperatures), the corresponding formation temperature can be found.

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