

UDC 547.489+549.212

Towards to Extraction of Nanodispersed Noble Metals From Natural Black Graphite Shales

¹ Victor G. Zavodinsky² Alexander I. Khanchuk³ Elena A. Mikhailenko

¹ Institute for Material Science of the Khabarovsk Science Center, the Far Eastern Branch of the Russian Academy of Sciences, Russia

680042, Khabarovsk, Tikhookeanskaya str., 153

Dr. (Physics), Director of Institute

E-mail: vzavod@mail.ru

² Far Eastern Geological Institute, the Far Eastern Branch of the Russian Academy of Sciences, Russia

690022, Vladivostok, 100-letiya Vladivostoka av., 159.

Dr. (Geology), academician of RAS, Director of Institute

E-mail: khanchuk@fegi.ru

³ Institute for Material Science of the Khabarovsk Science Center, the Far Eastern Branch of the Russian Academy of Sciences, Russia

680042, Khabarovsk, Tikhookeanskaya str., 153

Dr. (Physics), research scientist

E-mail: mea80@list.ru

Abstract. A theoretical approach based on the density functional theory and the pseudopotential method was applied to consider diffusion and accumulation of Au, Pt, and Pd in graphite. It is shown that Pt atoms migrate easily inside graphite. They can stop at structure defects and accumulate there, attracting each other and forming plate clusters. Atoms of gold do not penetrate into graphite but link with edge atoms of broken graphite crystallites, forming three-dimensional metallic particles. Palladium behavior is intermediate between platinum and gold. Addition of silicon into graphite can promote the extraction of noble metals because Si atoms force out Pt, Pd, and Au atoms from their bonded states. Last effect can be used as a mechanism of striking off metals from graphite and their extraction from shales.

Keywords: noble metals; graphite shales; accumulation; ab initio simulation.

1. Introduction. Accumulations of gold and platinum group elements in black graphite shales have recently been discovered in south regions of the Russian Far [1-4] Khanchuk et al. 2004; 2007; 2010]. It has been concluded that gold forms visible grains in graphite shales but platinum is present there by dispersive way mainly [5]. Concentrations of noble metals in local areas can reach several tens of grammas in ton. However, the level of their scrutiny is fragmentary due to difficult detecting of noble metals in carbon minerals and their high dispersion (single atoms or nanoparticles). Nowadays there is no clear understanding in what form these metals are included in shales, in what way they penetrate there, and how they accumulate inside [6-10]. The decision of this problem can be significantly advanced with use of methods of quantum-mechanical simulation. The problem of the noble metals behavior within graphite was considered recently [11] in the quantum-chemical approach. However, the authors could not obtain any reliable data on the energetics of the noble metals interaction with graphite.

The goal of this study is to investigate behavior of typical noble metals (Au, Pt, and Pd) in graphite taken as the simplest model of black shales. Graphite crystals are the arrangement of

graphite sheets, e.g., AA, AB, or ABC sequence, along the Z-axis. In general, natural graphite adopts an AB-stacking sequence [12] therefore we studied here Pt, Pd, and Au behaviors in the AB stacked (two-layers) type of graphite.

2. Methods and approaches. All calculations were performed within the framework of the density functional theory [13, 14] using the plane wave basis set, the generalized gradient approximation [15], and the pseudopotential method [16], as implemented in the FHI96md package [17]. For an Au case we used a spin-polarized version of the FHI96md package because atomic gold demonstrate a non-zero magnetic moment in contact with carbon [18].

The pseudopotential for carbon was the same as utilized by Zavodinsky and Mikhailenko [19] and Zavodinsky [20, 21] where carbon contained systems were considered. Pseudopotentials for gold, platinum, palladium and silicon have been constructed in the scheme of Troullier-Martins [22]; they were checked for the absence of 'ghost' states and tested for determining the equilibrium lattice parameters a_0 and the bulk elastic modules B . The values of a_0 and B were found using the Murnaghan equation of state [23].

In order to investigate diffusion and clusterization of metal atoms we used a periodic graphite supercell consisting of two graphene layers with twelve hexagon rings in each layer and with the 0.335 nm distance between layers. A fragment of this supercell is shown in Fig. 1. (The third layer is shown for clearness.) Interlayers in which metal atoms are placed are separated each from other by empty interlayers. For all calculations the 8 k -points of the Brillouin zone (Γ -point (0,0,0) with a $2 \times 2 \times 2$ grid as proposed by the Monkhorst-Pack scheme [24]) were used with the kinetic energy cutoff of 680 eV.

The energy of binding of a metal atom with graphite, E_{bind} , was calculated as follows:

$$E_{\text{bind}} = E_{\text{tot}} - E_{\text{graphite}} - E_{\text{atom}} ,$$

where E_{tot} , E_{graphite} , and E_{atom} are, respectively, energies of the metal-graphite system, the graphite cell, and a free metal atom. To determine the diffusion barrier inside graphite layers, values of E_{bind} were calculated along the line connecting the T (top), H (hollow), T^{H} (top-hollow), and T (top) points as marked in Fig. 1. It must be noted that T and T^{H} points are not equivalent, namely: the T-atom is situated under another T-atom, while the T^{H} -atom is located under a hollow center.

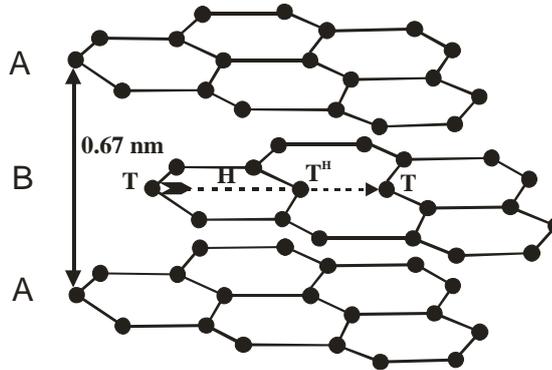


Fig. 1. Atomic scheme of graphite. The dotted line represents a diffusion path for a metal atom, moving from one equivalent position to another (T-H- T^{H} -T)

3. Results and discussion. Calculations have shown that the binding energy for single Pt, Pd, and Au atoms is minimal when metal atoms are placed just above carbon atoms of a graphite layer (Fig. 2). The binding energies are listed in Table 1, and the energy schemes of energy migration calculated for Pt and Pd atoms are shown in Fig. 3. The Au migration within an interlayer was not considered because gold penetration into the interlayer space is very difficult.

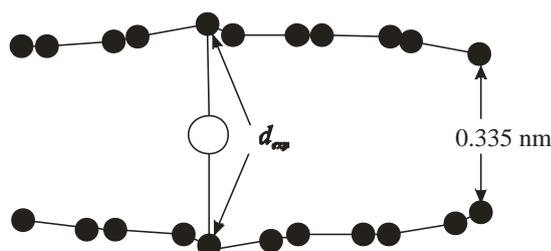


Fig. 2. An atomic scheme of interaction of a single metal atom with graphite layers

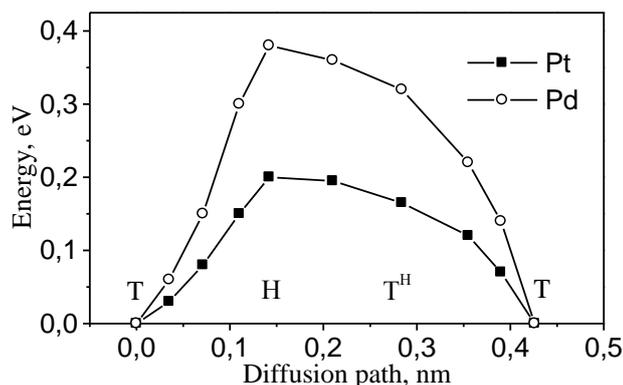


Fig. 3. Energy barriers for Pt and Pd atomic migration along graphite layers

Table 1.

Calculated binding energies (E_{bind}), and the expansion distances (d_{exp}) for single metal atoms within a graphite interlayer (T-position). Literature data [Ishii et al. 2009] are shown in parentless

	Pt	Pd	Au
E_{bind} , eV	-1.82	-0.40	+1.62
d_{exp} , nm	0.408	0.410	0.414
E_{bar} , eV	0.20 (0.18)	0.38 (0.20)	1.62

One can see that in the Pt case, the graphite layers are very slightly deformed, the metal-carbon distance is the same as on graphene, therefore E_{bind} and E_{bar} very slightly differ from the Pt-graphene case. In the Pd case, graphite is strained much more, a metal atom is pressed strongly, which results in significant decreasing of the binding energy and in increasing of the migration barrier. The Au atom is pressed very strongly: $d_{\text{exp}}/2 = 0.207$ nm instead of $d_{\text{M-C}} = 0.240$ nm on graphene. It leads to a great energy loss and to impossibility for gold to penetrate into the interlayer space. Thus, single Pt and Pd atoms can easily migrate along interlayers of perfect graphite even at room temperatures and can be found in any site of it, but gold cannot.

However, in natural graphite minerals there are a lot of defects which can play a role of traps. The simplest and the most widespread of them is a carbon vacancy. Our calculations show that a carbon vacancy indeed catches single noble atoms (all binding energies are negative; their absolute values are listed in Table 2).

Table 2.

Absolute values of calculated binding energies (E_{bind}) for metal atoms trapped by a carbon vacancy

n	Pt _n			Pd _n			Au _n		
	1	2	3	1	2	3	1	2	3
E_{bind} , eV	7.95	5.12	4.02	5.41	3.08	2.33	2.91	0.62	0.0

The binding energy for Pt₁ (7.95 eV) is very large and exceeds the cohesive energy of metallic platinum for which our calculation provides 6.16 eV, and a published experimental value is equal to 5.84 eV [25]. This binding energy is even comparable with the graphite cohesive energy, the calculated value of which has been reported of 8.74 eV [20], and experimental value is equal to 7.37 eV [26]. The platinum atom which has got to such trap cannot migrate even at the raised temperatures: at least while graphite still remains stable. Palladium and gold single atoms demonstrate weaker bonding with a point graphite defect than platinum atom. Calculations show that decreasing of the single-atom binding energies in the Pt-Pd-Au row (7.95-5.41-2.91 eV) correlates with increasing of the metal-carbon distances (0.177-0.198-0.211 nm).

Differences of metal-graphite interactions for Pt, Pd, and Au became clearer if we consider the accumulation process for metal atoms near a carbon vacancy. A scheme of the first stage of such accumulation is shown in Fig. 4; metal-carbon ($d_{\text{M-C}}$) and metal-metal distances (d_{1-2} , d_{1-3} , d_{2-3}) for 3-atoms clusters localized near a carbon vacancy are listed in Table 3; the binding energies for two-atoms and three-atoms clusters are presented in Table 2.

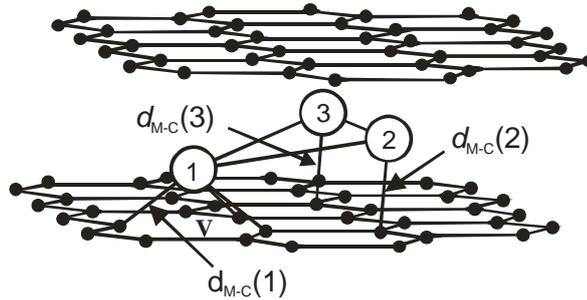


Fig. 4. Atomic scheme of a three atomic metallic cluster near a carbon vacancy: 1) the first atom trapped by a carbon vacancy; 2) and 3) the second and third atoms linked with the first atom. The vacancy position is marked as V

Table 3.

Metal-carbon ($d_{\text{M-C}}$) and metal-metal distances (d_{1-2} , d_{1-3} , d_{2-3}) for 3-atoms clusters localized near a carbon vacancy

	Pt ₃	Pd ₃	Au ₃
$d_{\text{M-C}}(1)$, nm	0.177	0.198	0.211
$d_{\text{M-C}}(2)$, nm	0.208	0.210	0.210
$d_{\text{M-C}}(3)$, nm	0.208	0.210	0.215
d_{1-2} , nm	0.278	0.278	0.388
d_{1-3} , nm	0.278	0.278	0.326
d_{2-3} , nm	0.300	0.302	0.440

As it follows from Table 3, in the three-atoms cases the metal-carbon distances ($d_{\text{M-C}}(1)$) for atoms trapped directly by a carbon vacancy are the same as in the single-atom cases. The second interesting fact is very large distances between gold atoms (up to

0.44 nm). This result correlates with abrupt reduction of the binding energy: 2.91 eV for Au₁, 0.62 eV for Au₂, and 0.0 eV for Au₃. In other words, calculations demonstrate their pushing away instead of accumulation.

Thus, trapping of platinum and palladium atoms at a vacancy defect of graphite gives a start for formation of their clusters (nanoparticles). However, the binding energies per atom decrease when particles increase; therefore the bonding of single Pt and Pd atoms with graphite defects is more preferable. Anyway, the particles growth is limited by the interlayer space of graphite, and formation of three-dimensional Pt and Pd particles is difficult.

Natural graphite has a lot of defects much more complicated than single carbon vacancies. A typical complicated defect is a break of one or several graphene sheets where metal atoms can interact with several carbon atoms having unsaturated covalent bonds. Such graphene breaks can border with internal empty spaces (cavities) and serve as places of possible formation of metallic particles. Graphene sheets may be broken by different ways. We have studied here two main of them, namely: zigzag and armchair edges. Schemes of these metal-graphite systems are shown in Fig. 5, calculated binding energies are listed in Table 4.

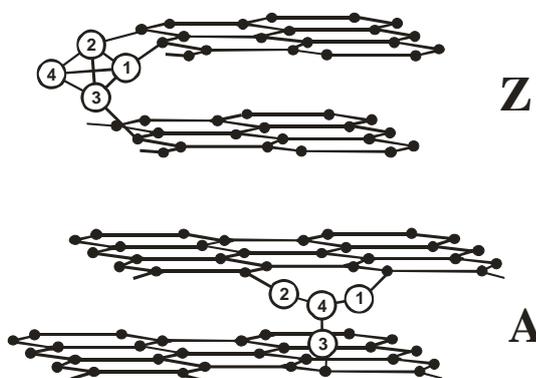


Fig. 5. Schemes of formation for metallic particles at edges of broken graphite sheets: A) armchair case; Z) zigzag case

Table 4.

Absolute values of the binding energy for Pt_n, Pd_n, and Au_n clusters (n=1-4) formed at graphite zigzag (Z) and armchair (A) edges

n		Pt _n				Pd _n				Au _n			
		1	2	3	4	1	2	3	4	1	2	3	4
E _{bind} , eV per atom	Z	5.10	5.61	5.50	5.30	4.40	3.95	3.50	3.10	3.06	3.65	3.62	3.54
	A	4.37	5.20	4.90	4.72	4.37	4.10	3.44	3.02	3.11	3.56	3.67	3.72

In all cases the binding energies for single Pt and Pd atoms are less than in the case of trapping of these single atoms by a carbon vacancy (Table 3). However, the next Pt and Pd atoms are linked stronger with graphite edges than with an internal carbon vacancy saturated by the first atoms. Thus, platinum and palladium atoms prefer to migrate along graphite interlayers and to saturate all internal defects, before these atoms start to accumulate at broken edges.

The gold binding energy per atom is larger than the binding energy for a single gold atom trapped by a vacancy point defect (2.91 eV). Besides, as mentioned above, Au atoms

need to overcome the barrier of 1.62 eV to penetrate into a graphite interlayer and to find a vacancy defect. Thus, gold prefers to accumulate at graphite edges than within interlayers.

As a rule, graphite of natural shales contains some mineral pollutions. Silicon is the main one of them. Silicon can be included there in different ways, for instance as a substitutable dopant. Our calculations show that a single Si atom links with a carbon vacancy with the binding energy of 8.7 eV, that is practically the same as the binding energy of a C atom and is larger than the binding energy of Pt in graphite. Thus, silicon can passivate vacancy defects in graphite, interfering with atoms of noble metals to collect on them. On another hand, Si atoms being placed at vacancy sites can attract noble metals. Namely, a Si atom attracts Pt and Pd atoms with the binding energy of -2.15 and -0.58 eV, respectively, while gold atoms run away off the trapped silicon.

4. Conclusion

Ab initio calculations show that platinum and palladium atoms can migrate through graphite even at room temperatures. They can link with structure defects of graphite layers, attract each other and accumulate, forming plate clusters. It seems that these clusters can grow up, till their increasing is not stopped by strengths in deformed graphite. Atoms of gold do not penetrate into graphite layers but concentrate at graphite breaks, forming three-dimensional particles, which sizes are mainly limited by sizes of adjacent cavities. Palladium also can form three-dimensional clusters at graphite breaks as well as accumulate near carbon vacancies. Silicon can passivate vacancy defects in graphite, interfering with atoms of noble metals to collect on them. Last effect can be used as a mechanism of striking off metals from graphite and their extraction from shales.

References:

1. Plyusnina L.P., Khanchuk A.I., Goncharov V.I., Sidorov V.A., Goryachev N.V., Kuzmina T.V., Likhoydov G.G. Gold, platinum and palladium in ores of the Natalka deposit (the High-Kolyma region). // *Doklady RAN (in Russian)* 2003. V. 391(3). P. 383-387.
2. Khanchuk A.I., Plyusnina L.P., Molchanov V.P. The first information on gold-platinum ores within carbonic minerals of the Khanka massive and prediction of a large deposit of noble metals in Primorsky region. // *Doklady RAN (in Russian)*. 2004. V. 397(4). P. 524-529.
3. Khanchuk A.I., Plyusnina L.P., Molchanov V.P., Medvedev E.I. Noble metals in rich-carbonic metamorphic minerals of the Khanka massive, Primorie. // *Tikhookeanskaya Geologiya*. 2007. V. 26(1). P. 70-80.
4. Khanchuk A.I., Plyusnina L.P., Molchanov V.P., Medvedev E.I. Carbonization and geochemical specification of graphite-contained minerals of the North region of the Khanka massive, Primorie. // *Geokhimiya*. 2010. V. 2. P. 115-125.
5. Khanchuk A.I., Didenko A.N., Rasskazov I.Yu., Berdnikov N.V., Alexandrova T.N. Graphite shales as a perspective source of noble metals at the Far East of Russia. // *Vestnik DVO RAN (in Russian)*. 2010. V. 151(3). P. 3-12.
6. Coveney R.M. Jr., Murowchick J.B., Grauch R.I., Chen N., Glascock M.D. Gold and platinum in shales with evidence against extraterrestrial sources of metals. // *Chem. Geol.* 1992. V. 99. P. 101-114.
7. Juvonen R., Lakomaa T., Soikkeli L. Determination of gold and the platinum group elements in geological samples by ICP-MS after nickel sulphide fire assay: difficulties encountered with different types of geological samples. // *Talanta*. 2002. V. 58. P. 595-603.
8. Mossman D.J. The formation of graphitizing carbons from the liquid phase. // *J. Geochem. Explor.* 1999. V. 66. P. 241-247.
9. Orberger B., Pasava J., Gallien J.P., Daudin L., Trocellier P. Se, As, Mo, Ag, Cd, In, Sb, Pt, Au, Tl, Re traces in biogenic and abiogenic sulfides from Black Shales (Selwyn

Basin, Yukon territories, Canada): A nuclear microprobe study. // Nucl. Instr. and Meth. in Phys. Res. 2003. V. 210. P. 441-448.

10. Pasava J. Anoxic sediments — an important environment for PGE: An overview. // Ore Geol. Rev. 1993. V. 8. P. 425-445.

11. Medkov M.A., Khanchuk A.I., Voyt A.V., Plyusnina L.P., Molchanov V.P., Medvedev E.I. Quantum-chemical study of interactions of Au(O), Pt(O), and Ag(O) clusters with graphene fragments, taken as models of graphite structure. // Doklady RAN (in Russian). 2010. V. 434(4). P. 518-521.

12. Bernal J.D. The Structure of Graphite. // Proc. Roy. Soc. London A. 1924. V. 106. P. 749-773.

13. Hohenberg H., Kohn W. Inhomogeneous Electron Gas. // Phys. Rev. 1964. V. 136. P. B864-B871.

14. Kohn W., Sham J.L. Self-Consistent Equations Including Exchange and Correlation Effects. // Phys. Rev. 1965. V. 140. P. A1133-A1138.

15. Perdew J.P., Wang Y. Accurate and simple density functional for the electronic exchange energy. // Phys. Rev. B. 1986. V. 33. P. 8800-8802.

16. Cohen M.L., Heine V. Pseudopotential theory of cohesion and structure. // In: Ehrenreich H, Seitz F, Turnbull D (editors) Solid State Physics., Academic Press, New York, 1970. V. 24. P. 38-249.

17. Beckstedte M., Kley A., Neugebauer J., Scheffler M. Density functional theory calculations for poly-atomic systems: electronic structure, static and elastic properties and ab initio molecular dynamics. // Comp. Phys. Commun. 1997. V. 107. P. 187-205.

18. Durgun E., Dag S., Bagci V.M.K., Gülseren O., Yildirim T., Ciraci S. Systematic study of adsorption of single atoms on a carbon nanotube. // Phys Rev B. 2003. V. 67. P. 201401-201405.

19. Zavodinsky V.G., Mikhailenko E.A. Quantum-mechanics simulation of carbon nanoclusters and their activities in reactions with molecular oxygen. // Comp. Mater. Sci. 2006. V. 36. P. 159-165.

20. Zavodinsky V.G. Ab initio simulation of diamond epitaxial growth on copper. // Comp. Mater. Sci. 2006. V. 36. P. 139-142.

21. Zavodinsky V.G. Small tungsten carbide nanoparticles: Simulation of structure, energetics, and tensile strength // Int J Refract Metals & Hard Materials. 2010. V. 28. P. 446-450.

22. Troullier N., Martins J.L. Efficient pseudopotentials for plane-wave calculations. // Phys Rev B. 1991. V. 43. P. 1993-2006.

23. Murnaghan F.D. The compressibility of media under extreme pressures. // Proc. Natl. Acad. Sci. USA. 1944. V. 30. P. 244-247.

24. Monkhorst H.J., Pack J.D. 1976. Special points for Brillouin-zone integrations. Phys. Rev. B. 1976. V. 13. P. 5188-5192.

25. Kittel C. Introduction to Solid State Physics, 6th ed. // Wiley, New York, 1986.

26. CRC Handbook of Chemistry and Physics, 65 ed. CRC Press Inc, Boca Raton, 1984-1985.

УДК 547.489+549.212

**К извлечению нанодисперсных благородных металлов
из черных графитовых сланцев**

¹ Виктор Григорьевич Заводинский

² Александр Иванович Ханчук

³ Елена Альбертовна Михайленко

¹ Институт материаловедения ХНЦ ДВО РАН, Хабаровск, Россия
680042, г. Хабаровск, ул. Тихоокеанская, 153.

Доктор физико-математических наук, директор.

E-mail: vzavod@mail.ru

² Дальневосточный геологический институт ДВО РАН, Владивосток, Россия
690022, г. Владивосток, просп. 100-летия Владивостока, 159.

Доктор геологических наук, директор.

E-mail: khanchuk@fegi.ru

³ Институт материаловедения ХНЦ ДВО РАН, Хабаровск, Россия
680042, г. Хабаровск, ул. Тихоокеанская, 153.

Кандидат физико-математических наук, научный сотрудник.

E-mail: mea80@list.ru

Аннотация. Теоретический подход, основанный на квантовой механике, применен к рассмотрению процессов диффузии атомов благородных металлов (платины, палладия и золота) и их накопления в графите. Показано, что атомы платины и палладия могут легко мигрировать по графиту. Они могут закрепляться на структурных дефектах и накапливаться, притягиваясь друг к другу, формируя плоские кластеры. Атомы золота не проникают внутрь слоев графита, а связываются на краях разломов графита, формируя трехмерные частицы. Примеси кремния могут способствовать извлечению благородных металлов из графитовых минералов.

Ключевые слова: благородные металлы; графитовые сланцы; накопление; моделирование из первых принципов.