Earth-Science Reviews 131 (2014) 1–21

Contents lists available at ScienceDirect

Earth-Science Reviews

journal homepage: www.elsevier.com/locate/earscirev

Platinum in Earth surface environments

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ARTICLE INFO

Article history:
Received 22 September 2012
Accepted 18 January 2014
Available online 24 January 2014

Keywords:
Platinum
Cycling
Geochemistry
Mobility
Geobiology
Anthropogenic

ABSTRACT

Platinum (Pt) is a rare precious metal that is a strategic commodity for industries in many countries. The demand for Pt has more than doubled in the last 30 years due to its role in the catalytic conversion of CO, hydrocarbons and NO_x in modern automobiles. To explore for new Pt deposits, process ores and deal with ecotoxicological effects of Pt mining and usage, the fundamental processes and pathways of Pt dispersion and re-concentration in surface environments need to be understood. Hence, the aim of this review is to develop a synergistic model for the cycling of Pt in Earth surface environments. This is achieved by integrating the geological/(biogeo)chemical literature, which focuses on naturally occurring Pt mobility around ore deposits, with the environmental/ecotoxicological literature dealing with anthropogenic Pt dispersion. In Pt deposits, Pt occurs as sulfide-, telluride- and arsenide, native metal and alloyed to other PGEs and iron (Fe). Increased mining and utilization of Pt combined with the burning of fossil fuels have led to the dispersion of Pt-containing nano- and microparticles. Hence, soils and sediments in industrialized areas, urban environments and along major roads are now commonly Pt enriched. Platinum minerals, nuggets and anthropogenic particles are transformed by physical and (bio)geochemical processes. Complexation of Pt ions with chloride, thiosulfate, ammonium, cyanide, low- and high molecular weight organic acids (LMWOAs and HMWOAs) and siderophores can facilitate Pt mobilization. Iron-oxides, clays, organic matter and (micro)biota are known to sequester Pt-complexes and -particles. Microbes and plants are capable of bioaccumulating and reductively precipitating mobile Pt complexes. Bioaccumulation can lead to toxic effects on plants and animals, including humans. (Bio)mineralization in organic matter-rich sediments can lead to the formation of secondary Pt particles and -grains. Ultimately, Pt is enriched in oceanic sediments, where Pt is commonly concentrated in manganese (Mn) oxides. When these sediments are subducted, Pt re-enters the magmatic cycle. In conclusion, this review demonstrates that geological, geochemical as well as biological and most recently anthropological processes are strongly interlinked in driving the cycling of Pt in surface environments.

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0012-8252/$ – see front matter © 2014 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.earscirev.2014.01.003

1. Introduction

Platinum is one of the rarest elements in the Earth's crust (Fig. 1; Wedepohl, 1995). It is one of six platinum group elements (PGEs), which also include osmium (Os), iridium (Ir), palladium (Pd), ruthenium (Ru), and rhodium (Rh). PGEs are highly sought after because of their unique physical and chemical properties (Macdonald, 1987). Platinum is a non-reactive refractory metal with high boiling- and melting-points, which makes it resistant to oxidation and corrosion (Bond, 1991). Hence, Pt compounds are commonly used as catalysts in (de)hydrogenation-, dehalogenation-, isomerisation- and oxidation reactions (Bond, 1991). Currently, the most important use of Pt is in automobile catalytic converter units (Fig. 2). But Pt is also required as catalyst in fuel cells, the production of petroleum and other petrochemicals from crude oil, and the oxidation of ammonia (Fig. 2C). In addition, Pt is used in resistance thermometers and thermocouples, glassmaking, jewelry, dentistry, prosthetics and anticancer drugs (Brenan, 2008). Because of these widespread industrial uses and its rarity, Pt has become a strategic commodity for many countries, e.g., the USA, China and the Euro-zone countries (Fig. 2; Koek et al., 2010; Mudd, 2012).

The Republic of South Africa and the Russian Federation control more than 95.9% of the 80,000 t known PGE reserves (Fig. 2B; Koek et al., 2010). With their large deposits in the Bushveld Complex and Norilsk they also account for more than 90% of the annual global production (Mudd, 2012). Production in other countries is limited to the mining of smaller deposits including placers, refining of Pt from Ni-rich secondary lateritic deposits and recycling of Pt from industrial wastes (Mungall and Naldrett, 2008; Mudd, 2010). To break the South

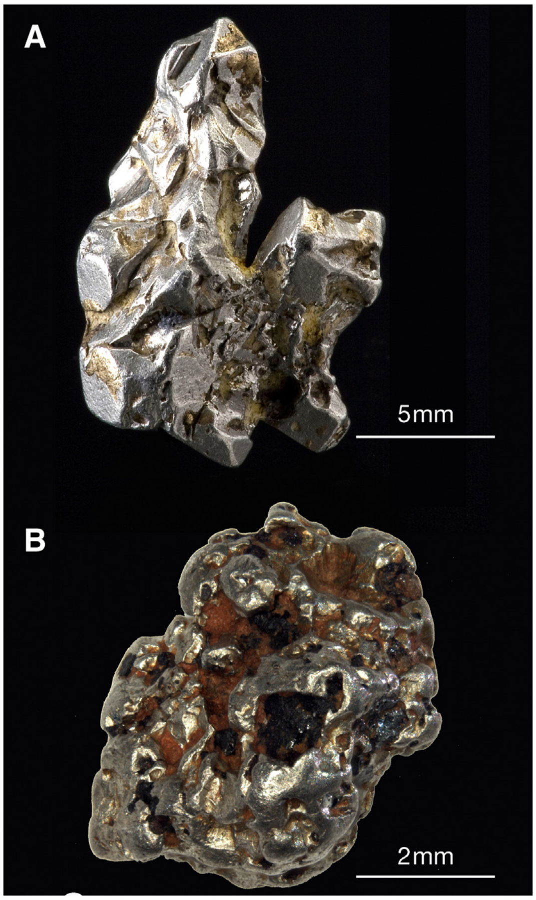

Fig. 1. Optical micrographs of Pt nuggets. (A) Cubic primary nugget from the Kondyer Massif, Siberia, Russia; (B) subhedral surface transformed placer nugget from Platina Deep Lead, Fifield, New South Wales, Australia.
Panel A is after Cook (2011); image J. Budd.

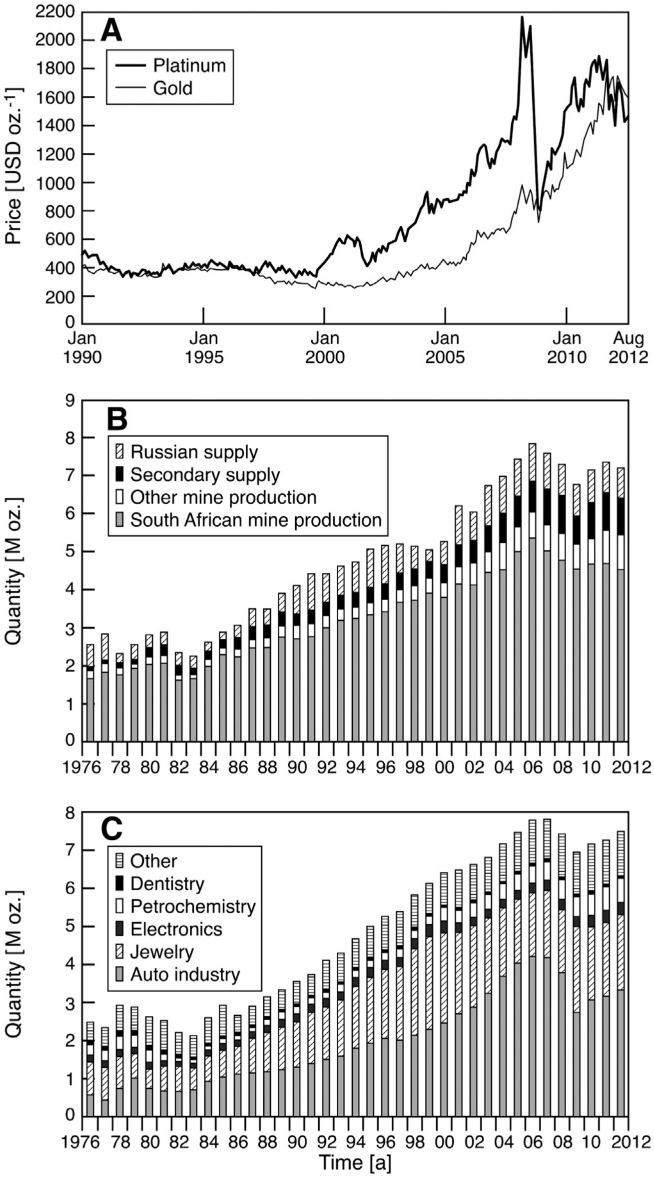

Fig. 2. Economics of Pt. (A) Comparison of Pt and Au prices from 1990 to August 2012; world production (B) and demand of Pt by industry (C) since 1976.
After Butler (2012) and CPM-Group (2012).

Fig. 3. World map showing the location of the largest primary Pt deposits, placer and other secondary Pt deposits described in the text, and also shows the countries with at least two known localities of Pt minerals.
After Weiser (2002) and Mindat (2012).

African and Russian strangle hold on Pt supplies, exploration for Pt deposits and research into their genesis has increased sharply in the last 20 years (Maier, 2005). Potentially prospective areas in the USA, Canada, Finland, Australia and parts of Africa have been the focus of large geophysical and geochemical exploration campaigns (Fig. 3; e.g., Hoatson, 1998; Fiorentini et al., 2010; Lapworth et al., 2012). However, because many Pt deposits are small, pinpointing them is extremely difficult, especially in areas where extensive weathering has led to the formation of hundreds of meters of in situ or transported weathered materials (Hoatson, 1998). Weathered materials may overlie primary Pt mineralization or in themselves contain economic quantities of Pt resulting from surface enrichment processes (Hoatson, 1998; Mungall and Naldrett, 2008). Consequently, to successfully explore for Pt environmental dispersion- and concentration mechanisms need to be understood. In this context, it is very important to be able to differentiate Pt contamination derived from anthropogenic sources from geochemical signals from underlying mineralization.

The use of Pt in catalytic converters, which contain between 1 and 3 g of Pt, and the burning of fossil fuels release large quantities of Pt into the environment; Pt mining and other industrial uses add to this anthropogenic dispersion. This release has given rise to highly elevated concentrations of Pt in soils and sediments in many industrialized areas. This may affect resident microbial communities and lead to Pt enrichment in plants and animals (e.g., Ek et al., 2004; Kalbitz et al., 2008). Laboratory experiments have shown that Pt complexes, such as *cis*-diaminedichloroplatinum(II), commonly known as cisplatin, strongly inhibit binary fission in the bacterium *Escherichia coli* by cross linking DNA (Rosenberg et al., 1965). Naturally occurring Pt-complexes, e.g., Pt-thiosulfate and -chloride, complexes with LMWOAs and Pt nano-particles, may also adversely affect biota. In turn, (micro)biota may affect the dispersion and re-concentration of Pt in surface environments by facilitating its solubilization, transport and precipitation.

We now recognize that metal cycles in Earth surface environments are strongly influenced by biological processes. Metal cycling is driven largely by microbiota due to their high metabolic rates, their ability to obtain metabolic energy from metal respiration and their extensive metal detoxification capabilities (Ehrlich and Newman, 2009). Microbes also control redox- and pH conditions and the formation and secretion

Table 1
Principal Pt minerals found in the supergene zone.

Name	Formula	Crystal symmetry[a]	Unit cell
Bowieite	$(Rh,Ir,Pt)_2S_3$	O *Pnca*	a = 8.454, b = 5.995, c = 6.143
Braggite	$(Pt,Pd)S$	Tet $P4_2/m$	a = 6.367, c = 6.561
Cooperite	PtS	Tet $P4_2/mmc$	a = 3.470, c = 6.1096
Genkinite	$(Pt,Pd)_4Sb_3$	Tet n.d.	a = 7.736, c = 24.161
Hongshiite	$PtCu$	H $R32$, $R3m$, $R-\quad 3m$	a = 10.713, c = 13.192
Irarsite	$(Ir,Ru,Rh,Pt)AsS$	C $Pa3$	a = 5.777
Isoferroplatinum	Pt_3Fe	C n.d.	a = 3.866
Malanite	$CuPt_2S_4$	C	a = 9.910
Niggliite	$PtSn$	H $P6_3/mmc$	a = 4.100, c = 5.432
Platarsite	$(Pt,Rh,Ru)AsS$	C $Pa3$	a = 5.790
Platinum	Pt	C $Fm3m$	a = 3.9231
Rustenburgite	$(Pt,Pd)_3Sn$	C $Fm3m$	a = 3.991
Sperryite	$PtAs_2$	C $Pa3$	a = 5.967
Sudovikovite	$PtSe_2$	Trig n.d.	
Tetraferroplatinum	$PtFe$	Tet n.d.	a = 3.850, c = 3.693
Tulameenite	$PtFe_{0.5}Cu_{0.5}$	Tet n.d.	a = 3.891, c = 3.557

[a] Crystal symmentry: Orthorhombic, O; Trigonal, Trig; Hexagonal, H; tetragonal, Tet; cubic C.

Table 2
Examples of Pt concentrations in environmental samples.

Environmental compartment	Material	Locality	Source	Concentration average, *Min–Max*, N[a]	Unit	Reference
Earth crust	Crustal rocks	Global overall	G[b]	0.4	µg kg^{-1}	Wedepohl (1995)
Unweathered rocks	Mafic rocks					
	Lherzolites	Spain, Morocco, Italy, France, Japan, Egypt	G	10, >*1.–18*, 110		Crocket (2002)
	Harzburgites	Spain, Morocco, Japan, Egypt,	G	5.1, >*1.–7.8*, 29		
	Dyke rocks	Spain, Italy, Morocco	G	*11.0–15.0*, 28		
	Abyssal peridotites (oceanic)	Mid Atlantic Ridge, East Pacific Rise	G	>*1.–7.8*, 12		
	Abyssal peridotites (continental)	Tanzania, Sth. Africa, Australia	G	5.6, >*1–6.5*, 21		
	Komatiites	Sth, Africa, Australia, Columbia Russia, Norway, Columbia	G	10.5, >*1*–15, 61		
	Mafics assoc. with Kommatiites (komatiitic basalt, tholeiite, dolerite, norite)	Sth, Africa, Australia, Columbia Russia, Norway, Antarctica, Canada, Columbia	G	>*1*–25.0, 53		
	Kimberlites	Sth. Africa, Brazil	G	4.4–13.5, 31		
	Lamprophyres	Canada	G	1.7–3.2, 37		
	Ophiolites	Cyprus, Canada, Mexico, Australia, Philippines, Oman, Finland, Italy	G	*3.6–135.0*, 314		
	Ocean island basalt	Hawaiian Island, Indian Ocean, Nth./Sth. Atlantic, Sth. Pacific	G.	4.3, >*1–9.7*, ≥117		
	Continental flood basalts and assoc. mafic dykes and Sheets	Russia, Brazil, Greenland, Australia, USA, Canada	G	6.2, >*1–10.7*, 257		
	Currently economic deposits—sulfide-poor mineralized rock	UG2, Sth. Africa	G	1850		Cameron and Hattori (2005)
		Merensky, Sth. Africa	G	1530		
		Great Dyke, Zimbabwe	G	1560		
		Stillwater, USA	G	890		
		Lac des Iles, Canada	G	4740		
	Currently economic deposits—sulfide-rich mineralized rock	Sudbury, Canada	G	511		
		Talnakh, Russia	G	9980		
		Lennon Shoot	G	1899		
		Suhanko, Finland	G	11,030		
		Pechenga, Russia	G	386		
Weathered rock and soil	Saprolitic materials					
		Saprolite, Mt. Carnage, Yilgarn. Australia[c]	G	138, *94–175*		Butt et al. (2001)
		Serpentine, Lomie, Cameroon	G	*19.2–63.8*		Ndjigui and Bilong (2010)
		Black shale, Clay City, USA[a]	G	*1.3–2.2*		Jaffe et al. (2002)
	Gossans and duricrusts					
		Ferruginous and manganiferous zone, Mt Carnage[c]	G	723, *66–1300*		Butt et al. (2001)
		Ferruginous and manganiferous zone, Mt. Keith, Australia[c]	G	*70–125*		
		Aguablanca Gossan, Spain[c]	G	*44–1763*, 14		Suárez et al. (2008)
	Soils (unpolluted)					
		Lateritic, Australia[a,c]	G	<*5–70*		Reimann and Caritat (1998)
		Southern British Columbia, Canada[c]	G	*2–155*		Fletcher (1988)
		Background, Germany[a]	G	*0.4–0.8*		Schaefer and Puchelt (1998)
	Soils (polluted, roadside)					
		Perth, Australia	A[d]	*31.0–152.2*		Whiteley and Murray (2003)
		Germany	A	*50.4–261*		Wichmann et al. (2007)
		Seoul, Korea	A	*3.8–444.0*		Lee et al. (2012)
Sediments	River					
		Moelndal, Sweden (1999)	A/G	53.9		Rauch et al. (2000)
		Stour, UK	A/G	*0.3–4.2*		De Vos et al. (2002)
		Rhine, Germany	A	*73–31,220*		WHO (2000)
	Lake and harbor					
		Boston Harbor (1987, 1993, 1996)	A	*3.8–4.6*		Tuit et al. (2000)
		Lac Sheen	G	>*0.3–122.0*		Wood and Vlassopoulos (1990); Cook et al. (1992)
		Lake Nipigon, Canada	G	<0.3–6.6		Hattori and Cameron (2004)

	Marine					
		Carbonaceous and siliceous sediments, Eastern Pacific	G	*1.1–3.0*		Hodge et al. (1985)
		Terrigenous sediments (Japan)	A/G	3.1, *2.7–3.7*, 108		Terashima et al. (2002)
		Plelagic sediments (Japan)	A/G	9.5, *5.8–22.8*, 153		
	Marine manganese-nodules					
		Northwest Pacific nodule belt (1120–3780 m)	G	<*5–145*		Agiorgitis and Gundlach (1978)
		Pacific (1700–4200 m)	G	*138–940*		Hodge et al. (1985)
		Sth Tasmania, Dampier Ridge, Midpac 2b, Java Trench	G	*83.6–328*		Cabral et al. (2009b)
	Coal					
		North Carolina, Indiana, North Dakota, Illinois, West Virginia, Pennsylvania	G	<*2–6*	ng kg^{-1}	Finkelman and Aruscavage (1981)
		Ash from German coal	G	< *1000*		Goldschmidt and Peter (1933)
		Tulameen, Canada	G	*n.d.–170*, 53		Van der Flier-Keller (1991)
Water	Groundwater					
		Germany	G/A	*3–38*		Ravindra et al. (2004)
		Yilgarn Australia	G	>*1–91*		Noble et al. (2011)
	River and lake					
		Salween, Mekong, Chiang Jian, Hong, Huang He, Duman, Mt. Baekdu, Amur, Lena, Yana, Indgirka, Kolyma	G	0.07, >*0.02–1.1*, 200		Soyol-Erdene and Huh (2012)
		Ferguesson Lake, Canada	G	*0.2–2.8*		Coker et al. (1991)
		Lac Sheen and Lac Long, Canada	G	*0.16–0.26*		Wood and Vlassopoulos (1990); Cook et al. (1992)
	Ocean					
		Worldwide range	G	*0.026–0.332*		Soyol-Erdene and Huh (2012); Ravindra et al. (2004)
		Indian Ocean (below 500 m)		*0.055–0.074*		
		Baltic Sea		2.2		
	Rain and drinking					
	Rain	Germany, UK	G/A	*1.4–74*		Laschka and Nachtwey (1993)
	Rain	Sweden (1999)	G/A	22		Eriksson (2001)
	Tap	Liverpool, UK	G/A	60		WHO (2000)
	Ice and snow					
		Greenland, the Alps	G/A	*0.0008–2.7*		Barbante et al. (1999, 2001)
		Mont Blanc	G/A	*0.08–0.62*		Van de Velde et al., 2000
		Antarctica	G/A	*0.0047–0.076*		Soyol-Erdene et al. (2011)
Air	Cities					
		Rome, Italy	A	*2.8–60.1*	pg m^{3}	Bocca et al. (2003)
		Copenhagen (1995–97)	A	*250–2740*		Probst et al. (2001)
		Frankfurt, Germany (2001/2002)	A	*8.7–29.3*		Zereini et al. (2004)
	Rural regions					
		Italy	A	< 0.5		Bocca et al. (2003)
		California	A	< 0.05		Ravindra et al. (2004)
		near Frankfurt, Germany (2001/2002)	A	5.2, *3.0–7.9*		Zereini et al. (2004)
Biota	Plants in unpolluted environments					
	Pinus sylvestris wood ash	Siberia, Russia[a,c]	G	>1–< 5000, ≥25,000	μg kg^{-1}	Kovalevsky (2001)
	Pinus flexilis/Pseudotsuga menziesii twig ash	Stillwater, USA[c]	G	*12.–3000.0*, >60		Fuchs and Rose (1974) Riese and Arp (1986)
	Grass	remote area[a]	G	*0.2–0.5*		Hoppstock and Sures (2004)
	Plants in polluted environments					
	Roadside grass	Germany	A	*0.1–4.6*		Ravindra et al. (2004)
	Pine needles	Palermo, Italy and surrounds	A	*1.0–102.0*		Dongarra et al. (2003)
	Beans	Dortmund, Germany	A	*130–642*		Ravindra et al. (2004)
	Animals					
	Asellus aquaticus	Urban	A	> 38		Moldovan et al. (2001)
	Falcon peregrines (feathers, blood, eggs, feces, liver and kidney)	Sweden	G/A	0.1–3.4		Ek et al. (2004)
	Humans		A			
	Uptake	Australia, UK	G/A	1–1.44	μg d^{-1} person^{-1}	WHO (1991) Vaughan and Florence (1992)

(continued on next page)

Table 2 (*continued*)

Environmental compartment	Material	Locality	Source	Concentration average, *Min–Max*, N[a]	Unit	Reference
	Urine	Australia, Belgium, Germany, Sweden, USA	A	*0.001–1180*	μg kg^{-1}	Ravindra et al. (2004)
	Blood	Australia, Sweden, Germany, UK	A	*0.1–3.8*		
Anthropogenic materials	Car exhaust fumes					
	Three-way petrol (new)	n.a.[e]	A	*27–313*	ng km^{-1}	Moldovan et al. (2002)
	Three-way petrol (aged)	n.a.	A	*6–8*		Palacios et al. (2000)
	Diesel	n.a.	A	*47–170*		Moldovan et al. (2002)
	Sewage sludge					
		Sheffield, Birmingham, Widnes, London, Reading, UK	A	*26–192*	μg kg^{-1}	Jackson et al. (2010)
		Southern Australia (urban, industrialized)	A	<*0.5–157.0*		Kabata-Pendias and Mukherjee(2007)
		Southern Australia (rural)	A	<*0.5–6.5*		
	Road dust					
		Perth, Australia	A	*53.8–419.2*		Whiteley and Murray (2003)
		M25 motorway, London, UK	A	*101.6–764.2*		Kan and Tanner (2005)
		San Diego, USA	A	*100–680*		Hodge and Stallard (1986)
	Incinerator ash (from sewage)					
		Stuttgart Germany (1972 and 1994)	A	<100, >300		Helmers and Kuemmerer (1999)
		Sheffield, Birmingham, Widnes, London, Reading, Leeds, UK (2007)	A	*33–602*		Jackson et al. (2010)
		Sheffield, Birmingham, UK (1998–2003)	A	*9–463*		

[a] Material overlying a mineralized zone (background).

[b] G, geogenic source.

[c] Material overlying a mineralized zone.

[d] A, anthropogenic source.

[e] n.a., not applicable.

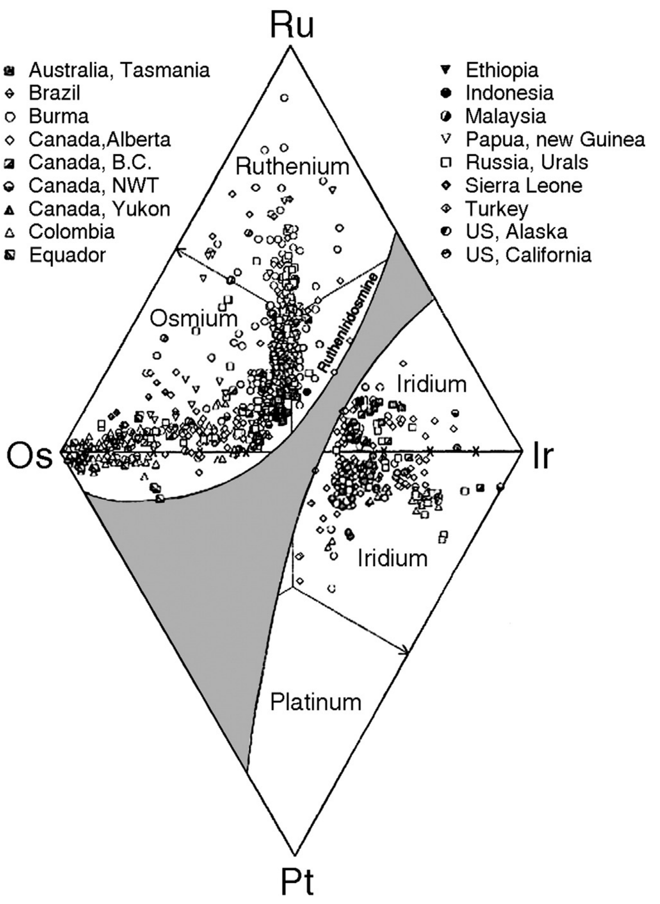

Fig. 4. The quaternary system Ru–Os–Ir–Pt–Ir depicting the composition of PGE alloys from worldwide placer deposits.
After Cabri et al. (1996) and Brenan (2008).

of complexing of ligands in soils, sediments, surface- and groundwaters (Southam and Saunders, 2005; Reith et al., 2008; Gadd, 2010). Consequently the surface cycling of many metals, e.g., chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pd), tungsten (W), vanadium (V), uranium (U) and zinc (Zn), is driven by microbiota (e.g., Ehrlich and Newman, 2009; Gadd, 2010). Gold is an example of a metal with an active biogeochemical cycle that until recently was considered to be inert, immobile and not biologically active under Earth surface conditions (Reith et al., 2007; Southam et al., 2009). Microbial weathering contributes to the mobilization of Au by releasing elemental Au trapped within minerals and by solubilizing Au via oxidation-promoting complexation with ligands, e.g., thiosulfate, amino acids and cyanide (Reith and McPhail, 2006, 2007; Fairbrother et al., 2009). Subsequent microbial destabilization of Au(I/III)-complexes coupled with bio-precipitation and -reduction, which is actively catalyzed by a number of groups of microbiota, e.g., Fe- and S-oxidisers, SRBs, cyanobacteria, and metallophillic bacteria as well as thermophilic and hyperthermophilic archaea, leads to the biomineralization of secondary gold (e.g., Lengke and Southam, 2005, 2006, 2007; Reith et al., 2006, 2007, 2009a). Secondary Au is widespread in surface environments, where Au can be very pure (>99 wt.% Au), finely crystalline (0.01 to 5 μm), and occurring as nano-particulate, bacteriomorphic, sheet-like and wire Au as well as euhedral, hexagonal, octahedral and pseudotriangonal octahedral crystals and secondary grains (Reith et al., 2006, 2010; Falconer and Craw, 2009; Fairbrother et al., 2012).

While research has shown that Pt is mobile and bioavailable in surface environments, the processes, pathways and especially the influences of (micro)biota on Pt cycling are little understood. Hence, the aims of this review are to: (1) provide an accurate evaluation of the current knowledge of Pt dispersion and concentration mechanisms in supergene environments; (2) develop a process model for the cycling of Pt in surface environments; and (3) uncover gaps in our knowledge in order to highlight areas where future research needs to be focussed.

2. Physical and chemical properties of platinum

Platinum is a dense, malleable, ductile, silvery-white, transition metal (Table S1). It was known to pre-Hispanic Columbians, who mined Pt grains from placer deposits (Figs. 1 and 3). Unlike Au it was not widely used for the production of artifacts. It has been referenced in European writings since the 16th century, but its discovery and scientific description are credited to de Ulloa and Wood/Brownrigg, who worked independently on the metal during the 18th century (Watson and Brownrigg, 1750). The name platinum is derived from the Spanish term *platina* meaning “little silver”. Platinum has a density of $21.45\ \mathrm{g \cdot cm^{-3}}$ and comprises six natural isotopes: ^{190}Pt, ^{192}Pt, ^{194}Pt, ^{195}Pt, ^{196}Pt, and ^{198}Pt; the most abundant of these is ^{195}Pt constituting 33.83 wt.% (Table S1; Bond, 1991). Platinum occurs with a maximum

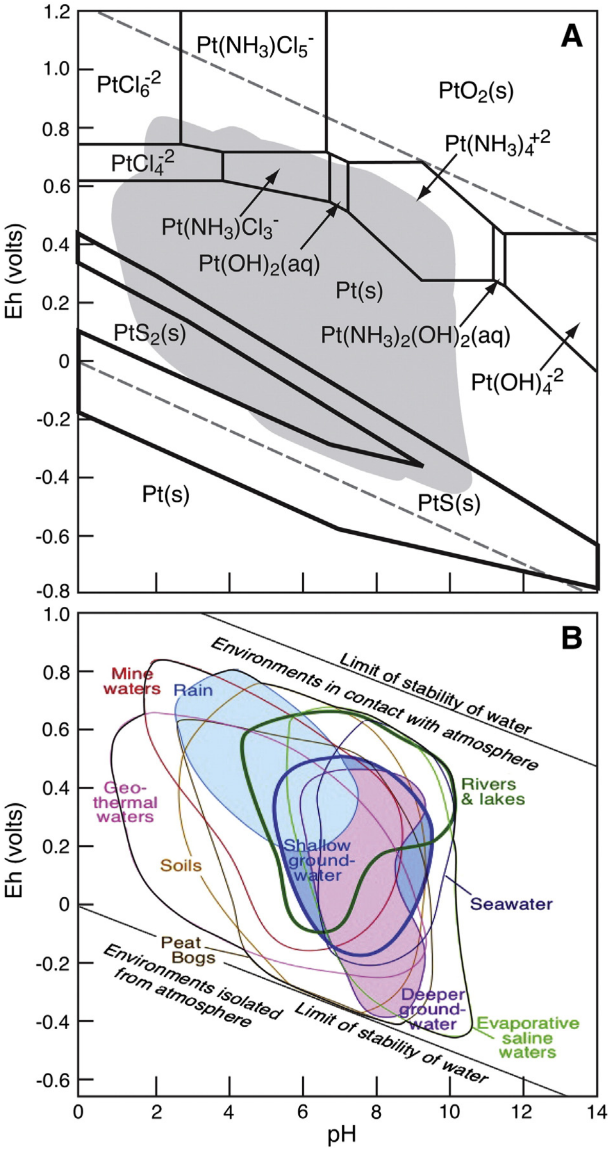

Fig. 5. (A) Eh–pH diagram for Pt in aqueous solution containing a mixed ligand system consisting of $[\sum \mathrm{Pt}] = 10^{-9}$ M, $[\sum \mathrm{S}] = 10^{-3}$ M, $[\sum \mathrm{N}] = 5 \times 10^{-4}$ M, $[\sum \mathrm{Cl}] = 0.5$ M; (B) Range of Eh–pH conditions in aquatic environments.
Panel A is after Colombo et al. (2008a,b). Panel B is after Baas-Becking et al. (1960) and Railsback (2012).

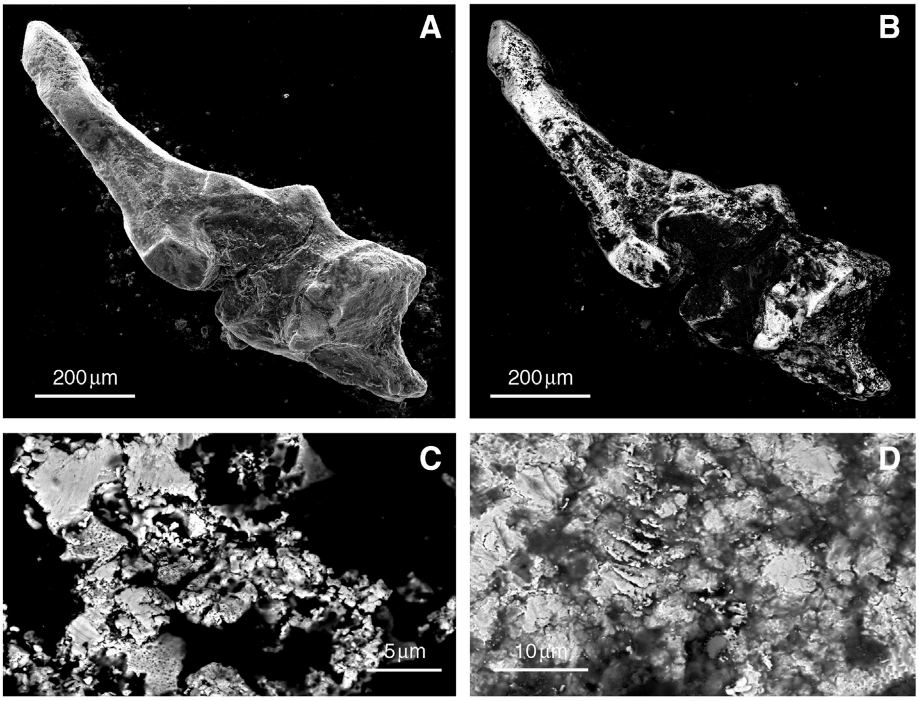

Fig. 6. (A) Secondary- and (B–D) backscatter electron micrographs of a surface transformed Pt grains from the Kars eluvial placer system, Fifield, New South Wales, Australia; (C) deeply pitted grain surface indicative of Pt dissolution; (D) adjacent surface area rich in nano- and micro-particulate Pt particles indicative of re-precipitation.

oxidation state of +6, yet oxidation states +2 and +4 are the most stable under surface conditions (Bond, 1991). It is the least reactive metal in the periodic table and exhibits a remarkable resistance to corrosion. This is the result of a very high oxidation potential, which makes it stable in air even at high temperatures. Platinum is insoluble in hydrochloric and nitric acid, but dissolves in hot *aqua regia*; in addition, surface corrosion occurs with halogens, cyanides, thiosulfate, other sulfur compounds and potentially organic acids (Bond, 1991). An important property that makes Pt the metal of choice for its use as automobile catalytic converters is its ability to chemosorb simple gaseous molecules, such as O_2 and CO. This results in significant coverage of the metal surface, but adherence is not strong enough for surface reaction rates to be retarded (Koek et al., 2010).

3. Platinum mineralogy and deposits

To date more than 120 primary and secondary minerals, in which PGEs are essential components, have been described (Cabri, 2002). In addition, more than 500 unidentified PGE-phases have been recorded (Daltry and Wilson, 1997; Mindat, 2012). Principal Pt minerals found in the supergene zone are listed in Table 1; note that Table 1 contains only minerals that occur as primary phases at more than one locality. Platinum has a wide range of valence states and the ability to form complexes and alloys with other PGEs (Fig. 3), semi-metals (Te, Sb, As), metals (Pb, Ni, Cu) and non-metals (particularly S), but rarely with O; note however that O-bearing phases of Pd and possibly Pt have been described (Auge and Legendre, 1995; Cabral et al., 2004).

Platinum shares properties with both siderophile and chalcophile elements. Like the siderophile elements Fe and Ni, Pt has the tendency to form metallic rather than ionic bonds. But like all PGEs and metals including Cu, silver (Ag) and Au, it shares a tendency to form covalent bonds with S in preference to ionized bonds with O; this places it with the chalcophile elements (Goldschmidt, 1954). Therefore, the fundamental controls on the behavior and distribution of the Pt on Earth are determined by the presence/absence of metallic and sulfidic phases (Macdonald, 1987; Mungall and Naldrett, 2008).

On Earth Pt is an extremely rare and occurs at an average concentration of 0.4 $ng \cdot g^{-1}$ (Table 2; Wedepohl, 1995). In order to be mined profitably, Pt deposits require a 1000 to 10,000-fold enrichment over background concentrations (Mungall and Naldrett, 2008; Koek et al., 2010). Consequently, economically prospective deposits are hard to pinpoint and few large deposits have been identified. Primary Pt deposits are formed by orthomagmatic processes, including mixing and wallrock contamination of magma as well as deuteric processes (Mungall and Naldrett, 2008). These processes commonly form stratiform Pt-bearing layered reefs within large, mantle-derived, mafic and ultramafic intrusions, which contain average grades between 5 and 20 $g \cdot t^{-1}$ of Pt of ore (Maier, 2005; Koek et al., 2010). In these economically most important deposits Pt is associated with chromite or disseminated in sulfides, e.g., in pyrrhotite, pentlandite and pyrite, and occurs as sulfide minerals and PG alloys (Campbell et al., 1983; Oberthuer, 2002). Important examples of reef-type Pt include the Merenskey Reef, UG2 Chromitite Layer and Platreef of the giant Bushveld Complex (South Africa), the Stillwater Complex (USA), and the Main Sulfide Zone of the Great Dyke (Fig. 3; Zimbabwe; Cawthorn, 1999; Oberthuer, 2002; Maier, 2005; Mudd, 2012).

Other important primary deposits are Ni–Cu deposits resulting from mafic sill-like intrusions. Here Pt mineralization occurs as accessory minerals and can be refined as a by-product during the production of Cu and Ni (Naldrett, 1997; Maier, 2005). In these sulfide-rich deposits, PGEs occur as sulfides (e.g., (Pt,Pd)S), tellurides (e.g., PtBiTe), antimonides (PdSb), arsenides (e.g., $PtAs_2$), or alloyed to Ni and Cu (Melcher, 2000; Lesher and Keays, 2002). The most important examples of these types of deposits are at Norilsk (Russia) and Duluth (USA; Fig. 3; Naldrett, 1997). Other primary deposits include large mafic, possibly impact-related meltsheets, e.g., the Sudbury Igneous Complex (Canada), tholeiitic mafic intrusions, e.g., Voisey's Bay (Canada), and komatiitic volcanic flows, e.g. Kambalda (Australia; Fig. 3; Naldrett, 1997; Fiorentini et al., 2010). Although poorly understood, hydrothermal, chloride-rich brines can cause the mobilization, transport and subsequent re-precipitation of Pt. This leads to the formation of polymetallic deposits of PGEs, Au, Ag and Cu under appropriate pressure/temperature and geological conditions (Mungall and Naldrett, 2008). Currently, the only economically-relevant hydrothermal Pt deposits are Lac des Iles (Canada) and Sukhoi Log (Russia; Fig. 3; Bruegmann et al., 1989; Distler and Yudovskaya, 2005).

Enrichment of PGEs has also been described in lateritic environments. For instance in the Yilgarn Craton in Western Australia hundreds of millions of years of surface weathering associated with element redistribution have led to the formation of Ni-rich laterites containing economical concentrations of Pt (Fig. 3; Hoatson, 1998). Platinum also occurs in numerous eluvial and alluvial placers (Fig. 3). Placer grain mineralogy is dominated by the occurrence of native elements and alloys (Weiser, 2002). The most important alloy compositions lie in the Pt–Fe– and Ru–Os–Pt–Ir systems (Fig. 4). In the Pt–Fe alloy system three phases are defined as natural minerals. These are native Pt (Pt) and isoferroplatinum (Pt_3Fe), which are the most abundant, as well as tetraferroplatinum (PtFe; Weiser, 2002). In the Ru–Os–Pt–Ir ternary system, Ir and Pt dominant minerals are cubic, whereas Os and Ru dominant minerals are hexagonal (Auge and Legendre, 1995; Cabral et al., 2004). This division is illustrated in the ternary plot (Fig. 4), which shows a large gap in the compositional fields that extend from the Os–Pt joint across the ternary to the Ru–Ir joint and crosses the Os–Ir joint at mid-point (Cabri et al., 1996). Composite grains and intergrowths between Pt–Fe and Os–Ir–Ru–Pt alloys are very common in placer deposits (Cabri et al., 1996; Cabri, 2002). Placer deposits currently contribute approximately 1% to the global production and are consequently of little economic significance. However, until the middle of the 20th century most of the world's Pt was derived from placer deposits, with the largest and best-described placers located in the central Ural mountains (Russia) yielding more than 300 t of Pt (Fig. 3; Weiser, 2002). Due to more recent discoveries of large (>100 t) placers in Kamchatka (Russia), placer deposits may in the future regain some of their global economic significance (Weiser, 2002).

4. Linking platinum mobility to surface processes

Platinum occurs in surface environments in different forms. These include: (1) complexes and nano-particles in surface- and groundwaters; (2) complexes and nano-particles associated with mineral- and organic phases in naturally platinoferrous soils, sediments and other weathered materials; (3) nano- and micro-particles associated with mineral- and organic phases in anthropogenically polluted soils and sediments in urban and industrialized areas; (4) detrital and secondary grains in eluvial and alluvial placer deposits and (5) nano-particles and organic complexes in microorganisms, plants and animals (reviewed in Section 5). Consequently, in the following sections Pt occurrences are reviewed and linked to the processes leading to its (bio)geochemical cycling.

4.1. Platinum in aqueous solutions

For (bio)geochemical cycling to occur, Pt needs to be mobilized and transported in solution, either as free ion, complex or stabilized colloidal nano-particles. However, Pt speciation and complexation has not been directly measured in surface solutions due to its extremely low solubility under standard conditions. Hence, to assess how Pt occurs in aqueous solutions, the thermodynamic solubility of Pt (-complexes), the availability of suitable complexing ligands and kinetic factors are discussed. At surface conditions Pt may only be transported as free aqueous ion in extremely oxidizing and acidic environments (Mountain and Wood, 1988a, b). Consequently under most conditions occurring in surface environments, the aqueous chemistry of Pt compounds is dominated by coordination complexes with inorganic and organic ligands or Pt occurs as stabilized colloids/nano-particles (Fig. 5; Mountain and Wood, 1988a,b; Wood, 2002; Wood and van Middlesworth, 2004). The concentrations of many possible ligands, e.g., I^-, Br^-, F^-, S^{2-} or Te^{2-}, are commonly very low in surface waters, are hence unlikely to affect Pt mobility and are further discussed in this review.

Several studies agree that Pt is mobile under most surface conditions based on the wide and overlapping stability fields of environmentally relevant Pt-ligand systems reviewed below (Fig. 5; Wood, 2002; Ek et al., 2004; Colombo et al., 2008a). The predicted oxidation state for Pt in most surface waters is Pt(II), see Eq. (1). Pt^{2+} is a “soft” ion, which forms stable linear complexes with “soft” ligands, e.g., chloride, cyanide, amines, thiosulfate, bisulfide and with some “hard” ligands, including hydroxyl groups, ammonium and carboxylic acids, e.g., acetate and oxalate (Mountain and Wood, 1988a,b; Wood, 2002). Note that based on Lewis' acid–base concept “hard” ions are small, compact and non-polarizable, whereas “soft” ions are larger with a more diffuse distribution of electrons (Lewis, 1923).

$$Pt_{(s)} + {}^{1}\!/_{2}O_2 + 2H^+_{(aq)} \leftrightarrow Pt^{2+}_{(aq)} + H_2O. \tag{1}$$

In magmatic and hydrothermal fluids Pt is chemically mobile as complexes with sulfide and bisulfide $Pt(HS)_{2(aq)}$; deposition from these fluids leads to the formation of Pt-bearing sulfides (Wood, 2002; Maier, 2005). Chemical mobility of Pt in the supergene zone is linked to the weathering of these sulfides, native Pt and Pt-alloys, followed by the oxidation and complexation of Pt. Hence, thiosulfate complexation may be important during the weathering of PGE-bearing sulfide ores and an important driver of Pt mobility in and around primary deposits (Anthony and Williams, 1994). When sulfides are oxidized under micro-aerophillic conditions, thiosulfate that has been shown to readily dissolve metallic Pt is produced by Fe- and S-oxidizers, e.g., *Acidithiobacillus thioparus* and *Acidithiobacillus ferrooxidans* (Eq. (2); Mountain and Wood, 1988a,b; Anthony and Williams, 1994). Sulfate reducing bacteria (SRB), which commonly occur in anoxic metal-rich sulfate-containing zones, also form thiosulfate during the reduction of sulfite with H_2 and formate (Fitz and Cypionka, 1990). *Streptomyces fradiae*, a common soil actinobacterium, produces thiosulfate as a result of the metabolization of S from cystine (Kunert and Stransky, 1988). The resulting Pt(II)-thiosulfate complexes are stable from mildly acid to highly alkaline pHs and moderately oxidizing to reducing conditions (Wood, 2002).

$$Pt + 4S_2O_3{}^{2-}{}_{(aq)} + 2Fe^{3+} \leftrightarrow \left[Pt(S_2O_3)_4\right]^{6-}{}_{(aq)} + 2Fe^{2+}. \tag{2}$$

When Pt reaches saline ground-, estuarine-, marine- or roadside environments subject to salting during the winter months, chloride complexes are likely to control Pt mobility (e.g., Wood, 2002; Colombo et al., 2008b). Chloride anions can form stable complexes with Pt^{2+} and Pt^{4+} (Fig. 5; Fuchs and Rose, 1974; Bowles, 1986; Wood, 2002). These reactions are shown in Eqs. (3) and (4) (Colombo et al., 2008a). While the aqueous complexes $PtCl^+$, $PtCl_2$, and $PtCl_3^-$ are also known to exist, $PtCl_4^{2-}$ likely is the dominant anion at 25 °C (Azaroual et al., 2001; Wood, 2002). In addition, Pt may exist as Pt(IV)-chloride and hydroxychloride complexes in highly oxidizing, acidic and chloride-rich surface waters (Wood, 2002). Chloride is an ubiquitous component in all natural waters and far more abundant in surface waters than F^-, I^- and Br^-, with chloride concentrations ranging from 10^{-4} M to 0.8 M in freshwater and seawater, respectively, and reaching up to 5 M in hypersaline brines (Feth, 1981).

$$Pt^{2+}{}_{(aq)} + 4Cl^-{}_{(aq)} \leftrightarrow Pt(Cl_4)^{2-}{}_{(aq)} \tag{3}$$

$$Pt^{4+}{}_{(aq)} + 6Cl^-{}_{(aq)} \leftrightarrow Pt(Cl_6)^{2-}{}_{(aq)}. \tag{4}$$

In halide-limited, highly oxidizing environments complexation with hydroxides may occur (Azaroual et al., 2001; Colombo et al., 2008a). Eq. (5) shows a simplified reaction (Wood, 1991). Hydroxyl ions, which are always present in water especially at neutral and basic pH, and Pt-hydroxide complexes may dominate over Pt-chloride complexes even when chloride is not limiting (Mountain and Wood, 1988a,b).

Aqueous Pt(II)-hydroxide compounds include $PtOH^+$, $PtOH_2$, and $Pt(OH)_4^{2-}$, and as pH increases the predominance of complexes may shift to more hydroxylated species (Mountain and Wood, 1988a,b; Wood, 1991).

$$Pt^{2+}{}_{(aq)} + nOH^-{}_{(aq)} \leftrightarrow Pt(OH)_n{}^{2-n}{}_{(aq)}. \quad (5)$$

Pt(II) also forms strong complexes with ammonium (Fig. 5; Eq. (6)). The formation of ammonium in surface environments is controlled by bacteria, yeast, filamentous fungi, algae and plants through the decomposition of urea via the urease enzyme (Follmer, 2008). Urea is continuously released into the environment, because it is a product of the degradation of amino acids, purines, pyrimidines and uric acid, which is excreted by birds, reptiles and most terrestrial insects as their primary detoxification product (Millo et al., 2012). In addition, ammonium is co-emitted in substantial amounts in vehicle exhaust. Hence, Pt solubilization from emitted particles is likely associated with the formation of Pt(II)-ammonium complexes (Fraser and Cass, 1998). Pt(II)-ammonium complexes are likely important for transport under near-neutral to basic oxidizing conditions.

$$Pt^{2+}{}_{(aq)} + 4NH_3{}^-{}_{(aq)} \leftrightarrow Pt(NH_3)_4{}^{2+}{}_{(aq)}. \quad (6)$$

Mixed hydroxyl–chloride, thiosulfate–chloride, ammonia–chloride complexes are also assumed to occur and therefore may also contribute to the transport of Pt in surface solutions (Fig. 5; Colombo et al., 2008a).

Cyanide forms very stable complexes with Pt(II) under reducing and oxidizing conditions (Eq. (7)), and consequently may be an important driver of Pt mobility (Wood, 2002). Cyanide compounds are ubiquitous in surface environments especially in soils (Wong-Chong et al., 2006), where cyanide is produced by many microorganisms, i.e., bacteria (e.g., *Chromobacterium violaceum*; *Pseudomonas fluorescens*, *P. aeruginosa*, *P. putida*, *P. syringae* and *Bacillus megaterium*), algae (e.g., *Chlorella vulgaris*), fungi (e.g., *Marasmius oreades*, *Stemphylium loti*, *Gloeocercospora sorghi* (Knowles, 1976), as well as numerous plants (Wong-Chong et al., 2006). Cyanide concentrations of up to several $\mu g \cdot g^{-1}$ have been measured in soils, which could lead to the formation of mobile cyanide complexes with metals such as Pt, Pd, Au, Co and Fe (Dzombak et al., 2006).

$$Pt^{2+}{}_{(aq)} + 4CN^-{}_{(aq)} \leftrightarrow Pt(CN)_4{}^{2-}{}_{(aq)}. \quad (7)$$

Pt(II) also readily forms complexes with LMWOAs, e.g., acetate, oxalate and amino acids (Wood, 1990; Wood, 1996; Wood and van Middlesworth, 2004). LMWOAs, e.g., carboxylic acids, are some of the most abundant organic molecules in soils, sedimentary systems and deeper regolith materials and constitute more than 10% of the dissolved organic matter (DOC) in soil solutions (Fox and Comerford, 1990). The most abundant carboxylic acids are mono-carboxylic acids, e.g., acetate, di- and tri-carboxylic acids, e.g., oxalate and citrate, respectively, which have been detected in soil solutions in concentrations of up to 50 μM (Kuesel and Drake, 1999; Reith et al., 2002). Amino acids commonly occur in soil humus, where they can account for up to 50 wt.% of organic N (Wood, 2002). Concentrations of free amino acids range from 20 to 250 $\mu g \cdot L^{-1}$ in seawater, from 50 to 1000 $\mu g \cdot L^{-1}$ in river water, and from 500 to 10,000 $\mu g \cdot L^{-1}$ in soil solutions (Thurman, 1985).

Dissolved humic and fulvic acids also form complexes with Pt (Wood, 1990, 1996, 2002). Humic and fulvic substances are main components of soil organic matter (SOM) and constitute the majority of dissolved organic matter (DOM). They commonly make up to 95% of DOC, and concentrations in natural waters and soil solutions can be as high as 100 $\mu g \cdot g^{-1}$ (Reuter and Perdue, 1977). The relevance of many of these humic substances for metal mobility lies in the functional groups they contain, which can form complexes with heavy metals such as Pt (Wood, 2002). Carboxyl functional groups in humic acids contain abundant O. When they are dissolved in neutral waters, carboxylic acids become negatively charged and can react with Pt to form soluble Pt-organo complexes or stabilized Pt-organic colloids (Eq. (8); Wood, 1990; Wood et al., 1992).

$$Pt^{2+}{}_{(aq)} + 2CH_3COO^-{}_{(aq)} \leftrightarrow Pt(CH_3COO)_{2(aq)} \quad (8)$$

Humic substances have been shown to increase the stability of amorphous $Pt(OH)_2$ (Wood, 1990; Hanley, 2005). However, it is not known if interactions of Pt(II/IV) with humic and fulvic acids lead to the formation of true complexes or stabilized colloids or nano-particles (Wood, 2002). Platinum nano-particles have been observed on the surface of natural Pt grains (Fig. 6), but their most important source in surface environments is anthropogenic pollution from the exhaust of vehicles with catalytic converters. Generally, nano-particle mobility in the supergene environment is a function of surface charge, pH–Eh conditions as well as clay and organic matter contents of soils and sediments. Negatively charged nano-particles are considered to be highly mobile in soils and sediments, especially when these soils and sediments are C-limited and sandy (Cornelis et al., 2012).

Data reviewed above are largely the result of thermodynamic equilibrium calculations showing that reactions (1) to (8) are thermodynamically possible (Fig. 5). Little information is available of the kinetics of these reactions, which may be so slow that geologic time may be required for their catalysis (Westland, 1981). However, experimental studies conducted with Pt foils, nano- and micro-particles of Pt and mixed particles derived from automotive catalysts suggested that Pt mobilization occurs at much higher rates (e.g., Freiesleben et al., 1993; Zereini et al., 1997; Butt et al., 2001; Moldovan et al., 2002; Ek et al., 2004; Bowles and Gize, 2005; Colombo et al., 2008b; Brugger et al., 2013). While most studies have been conducted with concentrations of ligands that are unlikely to occur in natural environments, they have shown that substantial quantities of Pt can be dissolved within days to weeks, rather than years or millennia. One study, using 0.1 M thiosulfate solutions, incubated at 25 °C, under oxic conditions, at pH values ranging from 6 to 9 showed that up to 23 $\mu g \cdot mL^{-1}$ of Pt were dissolved from Pt micro-particles after 46 days (Butt et al., 2001). Another study has shown that L-methionine, pyrophosphate, adenosinetriphosphate and humic acids were capable of rapidly mediating the dissolution of substantial concentration of metallic Pt (Lustig et al., 1998).

4.2. Platinum in naturally platinoferrous soils and sediments

Aqueous Pt compounds and nano-particles are transported by surface-, soil- and groundwaters until they encounter conditions that favor (bio)geochemical transformation or precipitation. The destabilization of Pt complexes and stabilized nano-particles leads to their sorption onto mineral phases and dead organic matter or their accumulation by (micro)biota (e.g., Butt et al., 2001; Lengke et al., 2006). Subsequent passive or active electron transfer leads to the reduction of Pt complexes and the formation of metallic Pt particles (Fig. 7; Lengke et al., 2006). As a result Pt enrichment zones form in soils, regolith materials and sediments, where Pt is then finely dispersed within organic- and mineral phases (Gray et al., 1996).

Turner et al. (2006) found that adsorption of Pt(IV) to river sediments preceded rapidly via a first order reversible reaction. Kubrakova et al. (2011) found that Fe-oxyhydroxides formed in supergene environments may preferentially scavenge inorganic PGE species, and precipitate or adsorb them to their positively charged surfaces. To further constrain the sorption behavior of aqueous Pt complexes onto natural mineral- and organic phases, Fe- and Mn-oxide-rich, organic matter-rich and carbonate-rich soils and peat moss were amended with Pt-humic-acid-complexes, Pt(II)-thiosulfate and Pt(II)-chloride complexes (Butt et al., 2001). The study showed that: (1) secondary Fe-minerals were more efficient in sorbing Pt complexes than organic matter;

(2) Pt-chloride complexes were adsorbed at lower rates compared to corresponding Au- and Pd-complexes; this suggests that Pt-chloride complexes are more stable and transportable in surface environments; and (3) Pt(II)-chloride and Pt-humic-acid-complexes were sorbed to mineral phases at lower rates than Pt(II)-thiosulfate, which were irreversibly adsorbed to Fe- and Mn-oxides.

The occurrence of zones of secondary Pt enrichment seems to be largely a function of the weathering time. So have studies of weathered materials overlying the Pt– and Ni–Pt deposits in the Yilgarn Craton (Western Australia) shown substantial enrichment of Pt in surface materials compared to the primary Pt hosting rock (Gray et al., 1996; Butt et al., 2001). For instance, at the Mt. Keith-, Perseverance-, Mt. Carnage- and Ora Banda Pt deposits (Western Australia) several hundred millions of years of weathering and biogeochemical cycling of Pt have led to enrichment profiles, in which Pt concentrations in ferruginous-, clay-rich- and in calcareous horizons increase steadily towards the surface (Fig. 3; Table 2; Butt et al., 2000; Gray et al., 1996). Similar results were obtained at other sites with extended weathering histories, e.g. in Cameroon, Sierra Leone, New Caledonia and South Africa (Bowles et al., 1994; Evans et al., 1994; Traoré et al., 2006, 2008; Ebah-Abeng et al., 2012). At sites, where weathering (and lateritization) histories are shorter or different climates prevail, e.g., at the Lac des Iles, Ferguson Lake and Tulameen deposits (Canada), Pt has not been biogeochemical enriched in soil minerals overlying the deposits (Fig. 3; Fuchs and Rose, 1974; Wood and Vlassopoulos, 1990; Cook and Fletcher, 1994; Fletcher et al., 1995).

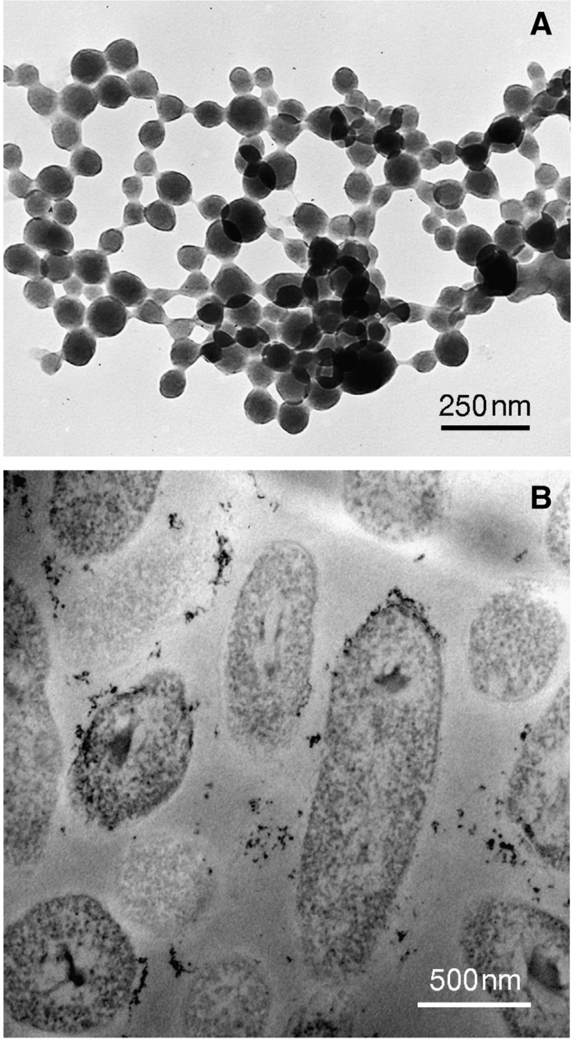

Fig. 7. (A) TEM micrographs of whole mounts of amorphous spherical Pt nano-particles forming long beadlike chains in cyanobacteria—Pt(IV)—chloride systems (Lengke et al., 2006); (B) Ultra-thin section TEM micrographs of *C. metallidurans* exposed to Pt(II)-chloride showing immobilized nano-particulate Pt in the cytoplasm and periplasm

Important examples of Pt enrichment in supergene environments also occur in marine sediments (Table 2); in particular, during the formation of carboniferous sediments (coal) in shallow marine basins. These deposits, which have formed throughout the Earth's history, especially during the Carboniferous and Cretaceous, have resulted in large reservoirs of Pt. Burning of this coal and other fossil fuels now leads to a large scale redistribution of Pt throughout the environment. Enrichment of Pt has also been reported in deep seafloor sediments with enrichment factors of up to 10,000 times compared to the surrounding seawater (e.g., Hodge et al., 1985). In a recent Japanese study 284 marine sediments of terrigenous, hemipelagic and pelagic origin were collected (Table 2; Terashima et al., 2002). The authors found that average abundances of Pt were markedly higher in pelagic sediments compared to terrigenous sediments with hemipelagic sediments showing intermediate abundances. They suggested that this enrichment of Pt in pelagic sediments may result from the very low sedimentation rates and strongly oxidizing environments. Authors of another Japanese study argued that Pt are most likely supplied to marine sediments in complexed form and/or as nano-particles from river outflows (Terashima et al., 1993). They suggested that Pt and Pd complexes and particles that are dissolved or suspended in seawater, respectively, are precipitated as hydroxides and sulfides and/or adsorbed onto mineral phases, e.g., ferromanganese nodules (Fig. 8). Platinum concentrations in ferromanganese nodules of more than 1 $\mu g \cdot g^{-1}$ material have been detected (Hodge et al., 1985).

4.3. Anthropogenic dispersion of platinum

In the last 300 years, dispersion of Pt from anthropogenic sources linked to the production, utilization and disposal of Pt has significantly added to the amount of Pt being cycled in surface environments from geogenic sources (Table 2; Niskavaara et al., 2004). The single largest anthropogenic use of Pt is for automobile catalysts, which were first introduced in the mid 1970s and now account for approximately 50% of the annual global production of Pt alone (Fig. 2; Rauch and Morrison, 2008). Automobile catalysts are also regarded as one of the main sources of Pt emitted into the environment. During the catalytic conversion, where Pt is used to remove gaseous pollutants from the exhaust gas, small quantities of Pt (predicted to be in the order of 1–3 $ng \cdot km^{-1}$ for petrol catalysts) are released through emission of airborne particles and deposition in the roadside environment (Table 2; Moldovan et al., 2002). Actual measurements of Pt in exhausts have recorded emissions of up to 0.8 $\mu g \cdot km^{-1}$ (Table 2; Helmers, 1997; Helmers and Mergel, 1997); the discrepancy between estimated and actual concentrations of Pt is thought to be due to issues such as ignition problems, age of the catalytic unit and driving habits (Artelt et al., 2000). From this an annual global emission from automotive catalyst approximating 6 t of Pt has been calculated (Rauch et al., 2005). The sizes of Pt-containing particles from automotive catalysts range from less than 1 μm to over 63 μm (mass = approx. 2.8 μg for a spherical Pt nano-particle), suggesting that emission is due to thermal and chemical aging, with soluble Pt representing up to 40% of emissions (Sutherland et al., 2008). Anthropogenic Pt emissions also originate from the burning of fossil fuels, especially coal. Coal has been reported to contain between 0.005 and 170 $\mu g \cdot kg^{-1}$ (Table 2; Flier-Keller, 1991; Kabata-Pendias and Mukherjee, 2007), which led to a substantial environmental dispersion (Klee and Graedel, 2004). Nickel smelters, particularly in Russia have been identified as another important source of Pt emissions (Niskavaara et al., 2004), although actual rates of emission have not been calculated. Because many Pt particles are small and airborne, their residence time in the atmosphere is sufficient for Pt to be globally dispersed. The discovery of increasing levels of Pt at remote sites supports this theory, with increasing concentrations being recorded in snow

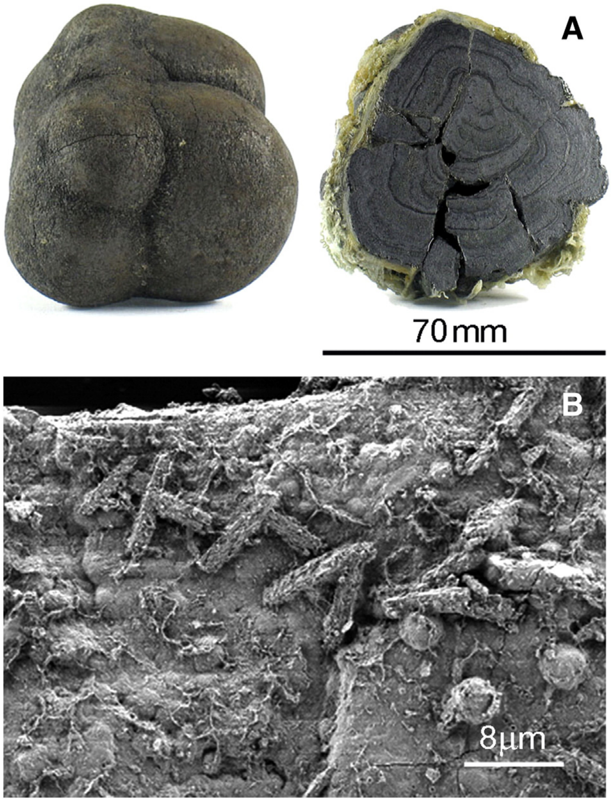

Fig. 8. (A) Optical image of a typical deep-sea polymetallic ferromanganese nodule, (B) secondary electron micrograph of bacterial biominerals forming the seeds for the biogenic/abiogenic mineralization of polymetallic ferromanganese nodule in deep-sea environments.
Images W.E.G. Mueller and Wang and Mueller (2009).

from Alpine glaciers near Monte Rosa and from central Greenland (Table 2; Barbante et al., 1999, 2001). Platinum is also a component of a range of medical products, including cisplatin and carboplatin (diamine 1,1-cyclobutanedicarboxylato-Pt(II)). These are commonly used in cancer therapy, resulting in the dispersion of Pt through hospital waste disposal systems and general sewage (Kuemmerer et al., 1999). Platinum emitted by hospitals is estimated to be between 3 and 12% of the amount emitted from automobile catalysts. However, these Pt compounds and their transformation products after excretion by patients are commonly highly bioavailable and toxic (Kuemmerer et al., 1999).

Increases in Pt emissions have resulted in increasing environmental concentrations (Table 2). For example, the concentration of Pt in airborne particles near an urban road in Germany increased 46 fold over a 10-year period from 1988 to 1998 (Table 2; Zereini et al., 2001). During rainfall events Pt particles are transported to rivers, where they can be trapped and accumulated in sediments. For instance, Pt concentrations in sediments of the river Rhine (Germany) have reached values of 31.2 $\mu g \cdot g^{-1}$, which is an enrichment of 10,000 compared to the natural background of 0.5–4 $ng \cdot g^{-1}$ of sediment (Dissanayake et al., 1984). In the US, up to 8-fold increases in Pt levels were detected in sediments following the introduction of automobile catalysts (Table 2; Tuit et al., 2000). Platinum containing particles can be transported in open water bodies, groundwater or in the soil solution. Similar to Pt particles from geogenic sources, they may be (bio)geochemically transformed, dispersed as complexes and nano-particles and taken up by plants (Schaefer et al., 1998; Ravindra et al., 2004; Rauch and Morrison, 2008; Wiseman and Zereini, 2009). Generally, the transformation of Pt compounds in soils and sedimentary systems depends on many factors, including pH, redox potential, soil salinity, organic matter content and structure, presence of complexing agents, and the activity of macro- and microbiota (e.g., Wiseman and Zereini, 2009; Soborova et al., 2012). Additionally, they may be adsorbed by microorganisms or mineral grains and co-transported (Yee and Fein, 2002). A number of experimental studies shown that natural or synthetic Pt compounds are strongly adsorbed by organic matter and biota (e.g., Lustig et al., 1996, 1998; Plyusnina et al., 2000; Kalbitz et al., 2008; Ljubomirova et al., 2008). For instance, a study by Lustig et al. (1998) showed that different Pt-complexes as well as particles originating from vehicle catalysts underwent rapid and highly complex biogeochemical transformations, e.g., oxidation and re-complexation with DOM in soils, leading to their precipitation and therefore decreasing their mobility.

4.4. Platinum in placer deposits

Assessing the (trans)formation of Pt grains and nuggets from placer deposits can also provide valuable evidence for the existence of (bio)geochemical mobilization and precipitation processes in surface environments. Placer grains are typically tens of micrometers to several millimeters in diameter (Fig. 1). Larger nuggets have also been discovered, e.g., a nugget weighing 11.6 kg was recovered in Colombia and several nuggets of more than 6 kg were recovered from Ural placers (Weiser, 2002). The origin of Pt grains in placers is the subject of an ongoing debate. Some authors suggest that their sizes and morphologies depend entirely on their original sizes, as derived from the primary mineralization, and the type and length of transport. So smaller, more rounded or flattened grains are commonly recovered further from their proposed source (Wyssotzky, 1913). Consequently, the origin of Pt grains in placers was assumed to be purely detrital, resulting from the weathering of host materials and physical enrichment of primary grains (e.g., Koen, 1964; Cabri and Harris, 1975; Slansky et al., 1991; Hattori and Cabri, 1992). Apparent chemical transformations observed on grains from many locations were assumed to originate from the

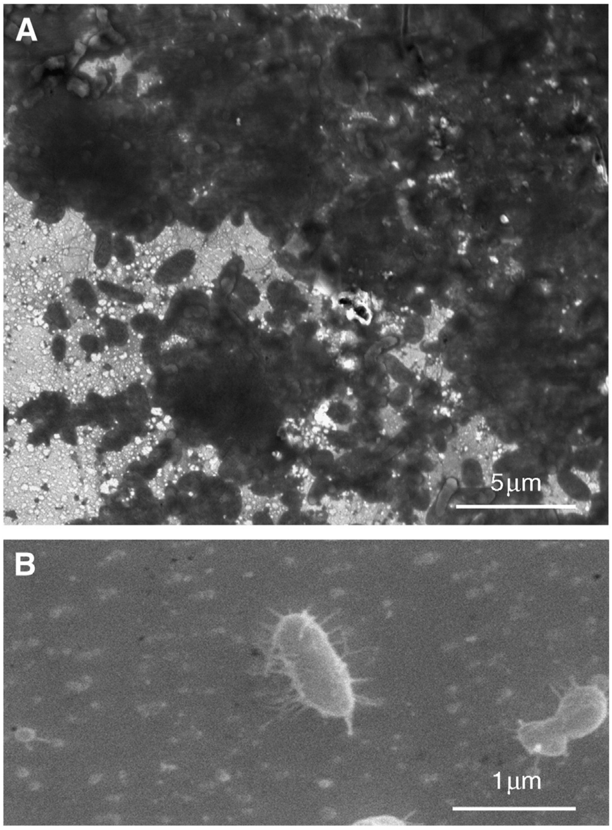

Fig. 9. Scanning electron micrographs a biofilms (A) and an individual cell (B) of the cyanide-producing bacterium *Chromobacterium violaceum* forming on the surface of ultraflat Pt (A) and Au (B) surfaces (Fairbrother et al., 2009).

dissolution of primary PGE and Fe minerals, rather than from the neoformation of secondary Pt due to accretionary processes.

Other authors argue that, in addition to a detrital origin, Pt grains may also originate from secondary processes occurring in placers and soils (Augustithis, 1965, 1998; Ottemann and Augustithis, 1967; Stumpfl, 1974; Stumpfl and Tarkian, 1976; Bowles, 1986, 1995). They suggested that transported Pt-complexes and pure and alloyed nano-particles form nucleation zones leading to the growth of secondary Pt-metal-alloy grains through continual accretion. Nano-particles and microcrystal aggregates and layers of secondary Pt have been observed on the surface of primary grains from sites in Australia, Brazil, Zimbabwe and Ethiopia (Fig. 6; Augustithis, 1965; Bowles, 1995; Mogessie et al., 1999; Oberthuer et al., 1999; Cabral et al., 2011). Cousins (1973) and Cousins and Kinloch (1976) noted that sizes, shapes, compositions and microtextures of many eluvial and alluvial Pt grains from the Witwatersrand system differed from those in associated primary ores. Bowles (1986) and Melcher et al (2005) pointed out that PGE grains in host rocks are commonly smaller than 50 μm, but that placer grains can measure up to several centimeters, suggesting that secondary mineralization of Pt-alloys might lead to the growth of grains under supergene conditions.

The occurrence of zoned grains possessing unconstrained 3-D growth and/or corrosion features on mineral faces, plating of mineral faces, porous and spongy Pt–Fe textures and overgrowths of one phase by another is considered direct evidence for secondary accretion of Pt in low-temperature environments (Hussak, 1906; Leake et al., 1991; Bowles, 1995; Cabral et al., 2011). Probably the best described example for this type of secondary PGE grains are the botryoidal, zoned Pt–Pd nuggets from the Brazilian diamantiferous alluvial deposit Bom Sucesso, Minas Gerais (Cassedanne and Alves, 1992). Hussak (1906) was the first to recognize that the delicate arrangements of the Pt–Pd aggregates, including arborescent varieties, resulted from precipitation of aqueous Pt and Pd within the alluvium. Hussak's hypothesis of a supergene origin of the Pt–Pd aggregates is strongly supported by recent research that demonstrated that accretionary processes in surface environments linked to biological activities play a direct role in the formation of these grains (Cabral et al., 2009a, 2011). Two lines of evidence have been presented in these studies: (1) The presence of organic matter within arborescent Pt–Pd aggregates; and (2) the high concentrations of iodine (I), which is a strongly biophilic element, in the grains. The concentrations of I detected in grains range from 10 to ~120 $\mu g \cdot g^{-1}$ and are compatible to those measured in peat bogs, where I is stored as organo-I in humified plant tissue (Keppler et al., 2004). Additional studies using scanning electron microscopy combined with electron backscatter diffraction and energy dispersive X-ray (SEM-EBSD-EDX) analyzes on focussed-ion-beam (FIB)-milled sections have shown a layered zoning of Pt, Pd and Ti in the grains, which resembled growth structures common in minerals formed by surface processes, e.g., speleothems or pisoliths (Cabral et al., 2012). Unlike the larger crystals of Pd–Hg–Au intermetallic compounds, which form the core of most Córrego Bom Sucesso grains and are possibly of hydrothermal origin, Pt in these zones is highly pure and finely crystalline (Fleet, 2002; Cabral et al., 2009a). In addition, the association of secondary Pt with secondary poorly-crystalline secondary Ti-oxide nano-particles further supports the hypothesis of their secondary origin resulting from biogeochemical cycling (Cabral et al., 2012).

5. Geobiology of platinum

The previous chapters suggest that biological processes might play an important role in the cycling of Pt in surface environments. However, many aspects of biological, and especially microbial, processes affecting Pt cycling are not well studied. Therefore, in this chapter the field- and experimental data for biomediated Pt transformations, i.e., (1) bioaccumulation, (2) biosolubilization, (3) biomineralization and (4) effect of Pt on biota, are reviewed.

5.1. Bioaccumulation of platinum

Elevated concentrations of Pt in plants have been reported from remote localities before the recent anthropogenic dispersion through automotive catalysts was of much concern (Table 2; Fuchs and Rose, 1974; Riese and Arp, 1986). Elevated concentrations of Pt in leaves, twigs bark and wood have been used in biogeochemical exploration to pinpoint underlying deposits (Dunn, 1986). For instance, analyses of more than 25,000 plant samples from remote Siberia resulted in the discovery of several new PGE deposits (Table 2; Kovalevsky, 2001). Here ashed stumps of Scots pine (*Pinus sylvestris*) growing over mineralization contained up to 5000 ng of Pt g^{-1} of ash compared to background levels of <1 ng of Pt g^{-1} of ash. A Canadian study using dwarf birch (*Betula glandulosa*) and Labrador tea (*Ledum palustre*) from a mineralized zone near Lake Ferguson, reported Pt contents of up to 1350 $ng \cdot g^{-1}$ of ash from stems (Coker et al., 1991). Prior to commencement of mining operations, Fuchs and Rose (1974) and Riese and Arp (1986) collected samples of Limber pine (*Pinus flexilis*) and Douglas-fir (*Pseudotsuga menziesii*) from sites overlying the Stillwater Complex in Montana and reported concentrations of up to 3000 $ng \cdot g^{-1}$ of Pt in the ash (Table 2). Douglas-fir twigs and bark collected over the Alaskan-type Tulameen Complex in British Columbia contained up to 17 ng of Pt g^{-1} in the ash and in another North American example, conducted over 1000 km^2 encompassing the Pt prospective Duluth Gabbro, maxima of 40 ng of Pt g^{-1} in ash of white spruce twigs were recorded (Buchheit et al., 1989).

Anthropogenic dispersion of Pt through airborne particles leads to the deposition of nano- and micro-particles onto plants and soils (Ek et al., 2004; Ravindra et al., 2004; Wiseman and Zereini, 2009). Numerous studies have demonstrated elevated concentration of Pt in plants (up to 5670 $\mu g \cdot g^{-1}$) from urban areas and along motorways, with concentrations of Pt increasing steadily since studies began in the early to mid 1990s (Table 2; e.g., Zereini et al., 2001; Dongarra et al., 2003; Ravindra et al., 2004). Up to 150 $ng \cdot g^{-1}$ of Pt was detected in soils collected near motorways in Perth (Australia; Table 2; Whiteley and Murray, 2003). At sites across Europe, North America and China up to 1000 $ng \cdot g^{-1}$ of Pt was detected in roadside dust and soils (Table 2; Farago et al., 1998; Zereini et al., 1997, 2001; Schaefer and Puchelt, 1998). When this Pt is solubilized, up to 30% (by weight) can become bioavailable, leading to its uptake by plants (Alt et al., 1998; Lustig et al., 1998; Djingova et al., 2003). Platinum also enters the food chain via inhalation of airborne particles (Alt et al., 1993).

To experimentally constrain Pt uptake in plants, calculate transfer coefficients and assess uptake mechanisms, experiments with a number of different plant species were performed (Farago and Parsons, 1994; Lustig et al., 1997a,b; Klueppel et al., 1998; Schaefer et al., 1998; Verstraete et al., 1998; Ravindra et al., 2004). These studies were conducted in a greenhouse environment and the results showed that: (1) a measurable transfer of Pt from contaminated soils to plants occurred; (2) transfer coefficients of Pt from soils into plants were in the same as other moderately mobile elements, e.g., Cu; (3) *dicotyledons* have higher ability to accumulate Pt than *monocotyledons*; and (4) the majority of the Pt taken up was not metabolized, but stored in the roots, the phloem or the xylem or deposited in vacuoles.

Through direct deposition and runoff, Pt complexes and Pt particles accumulate in freshwater-, estuarine- and marine environments and therefore may lead to accumulation in aquatic organisms. Studies with a range of fresh- and saltwater animals have been conducted to assess the bioavailability and accumulation of Pt (Veltz et al., 1996; Moldovan et al., 2001; Sures et al., 2001, 2002, 2003; Zimmermann et al., 2002, 2005) These studies have shown that: (1) mobile Pt complexes are bioavailable; (2) 20–30 (w/w) % of Pt from particles emitted from vehicle exhausts are easily mobilized; and (3) mobile Pt is readily accumulated, with highest concentrations detected in the liver and kidneys. Uptake depended on exposure times and occurred through ingestion as well as potentially through direct absorption through the

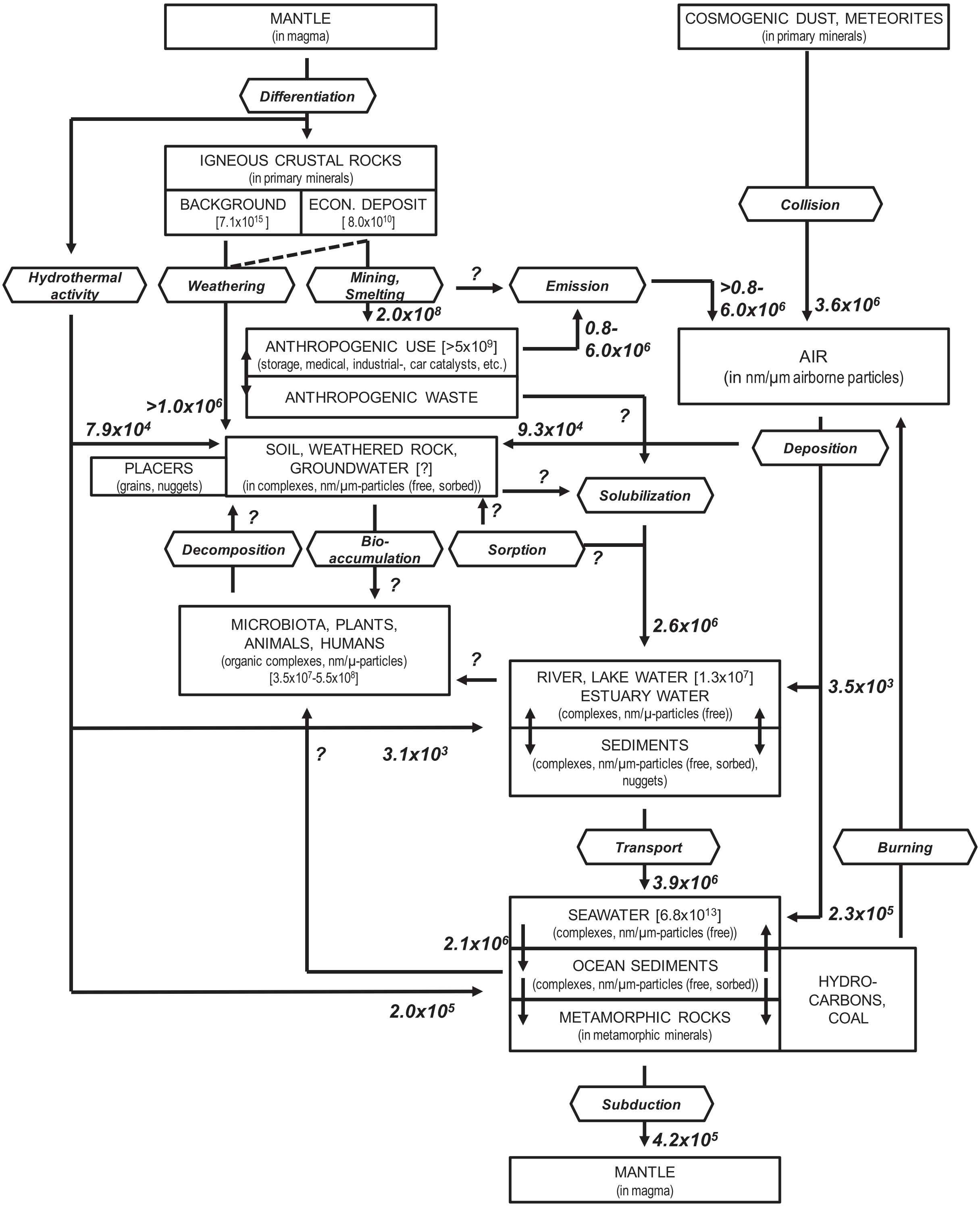

Fig. 10. Semi-quantitative model merging geogenic, biogenic and anthropogenic Pt cycling in surface environments. Masses [g] of Pt transferred between environmental compartments (square boxes with estimated total mass [g] of Pt in the compartment given in square brackets) by surface processes (in hexagonal boxes are the masses of Pt currently turned over annually [g]). For typical concentrations of Pt in materials from different environmental compartments see Table 2. Additional data used for calculations are as follows: Earth radius: 6.371 km; distribution of ocean, land and lakes/river surfaces: 70.8%; 28.1% and 1.1% of the total surface area; crustal mass 1.913×10^{25} g distribution of igneous and sedimentary/metamorphic rocks in the crust 95% and 5%, subduction rate 20% of sedimentation rate given in Soyol-Erdene and Huh (2012); distribution and density of oceanic and terrigenous crustal rock 70%, 3 g · cm^{-3} and 30%, 2.7 g · cm^{-3}, respectively. Biomass estimates are based on dry organic C of 3.5–5.5 × 10^{17} g (Whitman et al., 1998); biomass was assumed to contain 0.1 and 1.0 ng · kg^{-1} of Pt (WHO, 2000; Kabata-Pendias and Mukherjee, 2007).
Calculations are based on data given WHO (2000), Klee and Graedel (2004), Dubiella-Jackowska et al. (2007), Kabata-Pendias and Mukherjee (2007), Rauch and Morrison (2008), Butler (2012); Mudd (2012), Soborova et al. (2012) and Soyol-Erdene and Huh (2012).

gills. Elevated concentration of Pt from ingestion of food and inhalation were also observed in land animals (Jensen et al., 2002). Platinum levels in feathers, blood, eggs, feces, liver and kidney of the Swedish peregrine falcon (*Falco peregrinus*) living in their natural habitat were in the range of 0.1–3.4 ng·g^{-1} dry weight (Table 2; Jensen et al., 2002). While detectable in most body fluids and tissues, e.g., blood, urine, hair, spleen and adrenal gland tissue, the highest concentration of Pt in humans and other animals are commonly detected in the kidneys and the liver (Ravindra et al., 2004). Here Pt is assumed to bind to metallothionein through the replacement of Zn and Cd on sulfhydryl groups. Studies in Australia suggested that the major pathway of Pt into the human body is via the diet, with an average dietary intake of 1.44 μg Pt day^{-1} for adults (Table 2; Vaughan and Florence, 1992).

5.2. Biologically-driven solubilization of platinum

Few studies have directly assessed the microbial influence on Pt solubilization. One study has shown that the bacterium *Pseudomonas plecoglossicida* was capable of mobilizing 0.2% (w/w) Pt, as Pt(IV)-cyanide, from Pt-containing catalytic converters after 10 days of incubation (Brandl et al., 2008). The authors hypothesized that this limited solubilization was due to the coating of surfaces by unreactive oxide layers, which may also be the reason Lustig et al. (1997a) did not observed elevated Pt mobilization in bacterial incubations compared to sterile controls.

A study directly comparing Pt and Au mobility in samples from sites in Fifield Au/Pt-field in New South Wales, Australia was conducted by Brugger et al. (2013). The results showed that in spite of similar chemical properties of Au and Pt, environmental cycling of these elements in surface environments occurred at vastly different rates (Brugger et al., 2013). The study compared μm-scale dispersion of Pt and Au within a rare, 10 mm-sized fragment of ferruginous palaeochannel material from Fifield (New South Wales, Australia), which contained both native Au- and isoferroplatinum grains. Gold grains in the aggregate displayed complex morphologies and wide (up to 100 μm) secondary enrichment/depletion rims indicative of supergene, biogenic transformations, whereas isoferroplatinum grains were smoother and rounded. Secondary enrichment/depletion zones on Pt grains from this site reached width of up to of 2 μm. Gold grains were surrounded by a diffuse layer of high purity Au particles (<10 nm to 10 μm in size), whereas Pt particles were not observed. In addition, Pt concentrations in surrounding groundwater were below detection, but up to 1 $\mu g \cdot L^{-1}$ of Au was detected. However, eluvial Pt grains collected from soils at the nearby Kars Pt mineralization displayed wider secondary enrichment/depletion zones nano- and micro-particulate Pt particles, suggesting that Pt dissolution and re-precipitation can also occur in this environment (Fig. 6).

A series of incubation experiments was conducted to investigate the hypothesis that these differences in mobility are driven by interactions with microbiota. Ultraflat Au and Pt foils were incubated with the cyanogenic bacterium *Chromobacterium violoaceum and C. metallidurans* CH34, which formed biofilms on their surfaces (Fig. 9). After removal of the biofilms the surface roughness of the foils had increased and originally sharp FIB-milled markings into the surface appeared diffuse, suggesting that limited dissolution and possibly re-precipitation of Pt had occurred. Gold surfaces were significantly rougher and the FIB-milled markings had completely disappeared, suggesting a much higher microbial turnover of Au compared to Pt. Minimal inhibitory concentrations for Au-complexes are more than an order of magnitude lower than those measured for Pt-complexes in *C. metallidurans* cells (Brugger et al., 2013). This higher cell-toxicity of mobile Au- compared to Pt-complexes can lead to toxic levels of mobile Au in the vicinity of Au grain surfaces. The elevated toxicity likely drives the formation of Au-detoxifying biofilms that catalyze the biomineralization of spheroidal nano-particulate and bacteriomorphic Au (Reith et al., 2010; Wiesemann et al., 2013). In contrast, the toxicity of platinum complexes around isoferroplatinum grains was not sufficient to drive an analogous response, which according Brugger et al. (2013) may explain the contrast in Au and Pt mobility.

A number of other studies have presented indirect evidence for the geomicrobial mobilization of Pt during the weathering of sulfides: The oxidation of pyrite, which in surface environments is biomediated through the activity of Fe- and S-oxidizing bacteria, leads to the formation of aqueous sulfuric acid (H_2SO_4) and ferric sulfate ($Fe_2(SO_4)_3$. This may enable the dissolution of PGE-sulfides and lead to the formation of Pt(II)-thiosulfate complexes (Bowles, 1986). When the dissolved metals are transported away by acidic and oxidizing waters, a “leached cap” that lacks the target metals is left behind in the mineral. This gap is commonly filled by an insoluble mixture of Fe-minerals, e.g., jarosite, goethite and hematite, giving it the characteristic rusty-red appearance (Suárez et al., 2008). Iron-oxide and -oxyhydroxide coatings on Pt nuggets are assumed to be the result of this process (Bowles, 1986; Suárez et al., 2008).

Several other studies have shown that Pt is mobilized in solutions containing ligands commonly formed by geobiological processes (Freiesleben et al., 1993; Bowles et al., 1995; Lustig et al., 1996, 1998; Butt et al., 2001; Ek et al., 2004; Bowles and Gize, 2005; Colombo et al., 2008b). Significant solubilization of primary Pt and Pt particles from catalytic converters occurred in solutions and in polluted or spiked soils, when they were incubated with thiosulfate, siderophores, L-methionine, adenosine, humic and fulvic acids, ammonium and acetate (Lustig et al., 1997a, 1998). In a study by Butt et al. (2001) more than 20 $\mu g \cdot g^{-1}$ of Pt was mobilized from powdered metallic Pt in aqueous solutions containing 0.1 M thiosulfate. In another study, aqueous solutions containing L-methionine displayed the highest capability to mobilize metallic Pt and Pt oxides (Lustig et al., 1998). A study by Dahlheimer et al. (2007), showed that the addition of the siderophore desferrioxamine to powdered Pt led to a significant solubilization of Pt. This suggests that siderophores, which are compounds produced by biota to increase the bioavailability of metals required for cell growth, have the potential to increase the environmental mobility of Pt. Other studies have shown that volatile methylated Pt-complexes were formed in experimental studies using microbiota, and some authors suggest that these complexes may contribute to the mobility of Pt particularly in organic matter rich soils and sediments (Peterson and Minski, 1985; Wei and Morrison, 1994). While methylated Pt-complexes are thermodynamically stable under ‘abiotic’ surface conditions they have not been observed in natural environments, suggesting that they may be rapidly transferred back to their solid inorganic state, and thus immobilized giving rise to only limited Pt dispersion.

5.3. Biomineralization of platinum

Early studies using the Gram-negative bacterium *E. coli* amended with cisplatin showed that cisplatin inhibits cell division, causing filamentous growth (Rosenberg et al., 1965). A similar effect was observed with other Gram-negative bacteria, whereas Gram-positive bacteria responded only at near-toxic levels of the metal (LeRoy, 1975). While these studies indicated that Pt-complexes enter bacterial cells, the fate of intracellular Pt was not assessed. However, accumulation of Pt(IV)-chloride and subsequent formation of Pt nano-particles has been observed in a range of bacteria, e.g., *Pseudomonas* spp., *E. coli* and sulfate reducing bacteria (SRB), and fungi, e.g., *Neurospora crassa* and *Fusarium oxysporum* (e.g., Lengke et al., 2006c; Rashamuse and Whiteley, 2007; Syed and Ahmad, 2012). In another study Lengke et al. (2006c) assessed interactions of a cyanobacterium (*Plectonema boryanum* UTEX 485) with aqueous Pt(IV)-chloride. The study showed that the addition of $PtCl_4^0$ to the cyanobacterial culture promoted the formation of amorphous spherical Pt(II)-organic nano-particles (≤300 nm) dispersed within cells and in solution. The Pt(II)-organic nanoparticles were connected into long beadlike chains by a continuous coating of organic material derived from the cells, and transformed into crystalline nanoparticles of metallic Pt with increasing temperatures and reaction times (Fig. 7A). In another study, a mixed consortium of SRBs was used to investigate enzymatic mechanisms for the bioreduction of Pt(IV)-complexes to Pt^0 nano-particles (Riddin et al., 2009). This study established that two different hydrogenase enzymes were involved in Pt reduction; Pt(IV) was initially reduced to Pt(II) by a two-electron bioreduction catalyzed by an O-sensitive cytoplasmic hydrogenase. Once all Pt(IV) had been reduced to Pt(II), Pt(II) was reduced to metallic nano-particles by another two-electron bioreduction involving an O-tolerant or protected periplasmic hydrogenase. The authors also showed that no exogenous electron donors were required, as the cytoplasmic hydrogenase regulated the endogenous production of H^+/electrons via the oxidation of metabolites. In the absence of sulfate, these endogenous electrons were used for the reduction of Pt(II) by the periplasmic hydrogenase. In another study using SRB a pH-dependent rate of Pt removal from aqueous solution was observed, indicating that metal speciation is a main factor controlling the bioaccumulation of Pt by bacteria (Rashamuse and Whiteley, 2007). These results suggest that active biochemical mechanisms can lead to the formation of Pt nano-particles in surface environments.

In addition to directly mediating the immobilization and biomineralization of Pt-complexes and nano-particles via bio-accumulation and -reduction, (micro)biota are also important for the formation of secondary, Au and potentially Pt sequestering minerals, e.g., Mn-/Fe-oxides and carbonates (e.g., Schmidtmumm and Reith, 2007; Reith et al., 2009b, 2011). So has the important role of bacteria and archaea in the biomineralization of secondary ferromanganese nodules in terrestrial and marine sediments now been established (Fig. 8; Wang and Mueller, 2009; Wang et al., 2009). Recent Russian studies have shown that enrichment of Pt in oceanic ferromanganese nodules may be the result of bioaccumulation and biomineralization of Pt(II)-complexes by resident microbiota, especially micro-fungi, which may use Pt(II) as catalyst for the activation of methane (Zhmodik et al., 2009; Kubrakova et al., 2010).

5.4. Effect of platinum on biota

Bioaccumulation and transformation of Pt occur not only in the environment but also higher organisms, e.g., in the bowel of higher animals (Ravindra et al., 2004). This can lead to enrichment along the food chain and elevated PGE concentrations in human and other mammalian tissues (Table 2; Soborova et al., 2012). Studies have shown that Pt compounds are highly cytotoxic, have mutagenic potential in microbial and mammalian cells and may trigger toxic and allergic reactions in humans (Ward et al., 1976; Gebel et al., 1990; Cristaudo et al., 2005; Gagnon et al., 2006). Some Pt compounds can bind to N- and S-containing groups in proteins producing a reduction in enzymatic activity of enzymes such as glyceraldehyde-3-phosphate dehydrogenase, glucose-6-phosphate dehydrogenase, dihydrofolate reductase, fructose-l,6-bisphosphate aldolase, catalase and tyrosinase, which are inhibited by K_2PtCl_4 (Aull et al., 1979). While the impact of Pt compounds on ecosystem functioning of complex ecosystems at environmentally relevant concentration is lacking, studies suggest that Pt enrichment in urban environments may adversely affect ecosystems experiencing high Pt loads (e.g., Ravindra et al., 2004). So have bioaccumulation experiments with plants and animals shown adverse effects on some of the tested species (Ravindra et al., 2004; Gagnon et al., 2006; Soborova et al., 2012). For instance, Gagnon et al. (2006) used two different species, i.e., a wild wetland common *Sphagnum* moss and six week old rats as models to study the effect of Pt compounds on plants. Both species were exposed, in controlled environments, to different concentrations of the Pt. Results on the uptake of Pt by *Sphagnum* showed significant decreases in plant length and biomass as Pt concentration increased (Gagnon et al., 2006). Histological and pathological analysis of the rats revealed vacuolization, eosinophil inclusion bodies in adrenal glands, shrinkage of glomeruli in the kidney, and enlargement of white pulp in the spleen (Gagnon et al., 2006). In addition, in both species DNA damage was detected. This suggests that population-wide health issues in the human population may arise from elevated Pt concentrations accumulating along the food chain (Vaughan and Florence, 1992; Moldovan et al., 2002; Wiseman and Zereini, 2009). To date, toxicological effects of Pt in humans are generally confined to Pt-halide and -ammonium complexes, and to the anti-tumor agent cisplatin and its analogs (LeRoy, 1975; Hughes, 1980; Farago et al., 1998). They include sensitization, irritation of the respiratory tract, asthmatic symptoms and contact dermatitis. Chemotherapy treatment using cisplatin has given rise to severe nausea and vomiting, nephrotoxicity, with both tubular and glomerular lesions, ototoxicity, with tinnitus and hearing loss, as well as sensory peripheral neuropathy (Hughes, 1980; Schultze-Werninghaus et al., 1985). In contrast, metallic Pt, unless mobilized in bodily fluids, is considered non-toxic to humans (Gomez et al., 2002).

6. A process model for platinum cycling-towards a global budget

The knowledge of the abiotic as well as biotic processes driving the cycle of Pt in surface environments, integrated with the results of a number of recent studies allows us now to develop a process model for Pt cycling in surface environments capable of quantifying the global Pt turnover before and after the occurrence of large scale anthropogenic influences (Klee and Graedel, 2004; Soyol-Erdene and Huh, 2012). The dispersion of Pt in surface environments occurs via physical and (bio) geochemical weathering of crustal rocks and was estimated to be in the order of one metric $t \cdot a^{-1}$ (Fig. 10; Klee and Graedel, 2004). Additional inputs to the geogenic surficial Pt cycle are derived from hydrothermal activity (i.e., deep sea- and terrestrial hydrothermal vents) and cosmogenic sources (i.e., dust and meteorites) and are also in the order of a few $t \cdot a^{-1}$ (Fig. 10; Soyol-Erdene and Huh, 2012). Over geological periods these processes have led to the enrichment of Pt in surface environments, especially in oceanic waters and sediments, which are the main surficial sinks for Pt. For instance, at an estimated average concentration of Pt in seawater of approximate 0.5 $ng \cdot kg^{-1}$, 6.8×10^7 t of Pt are stored in seawater alone, where it is likely to exist as Pt-oxohydroxy-chloride complexes (Fig. 10; Wood, 2002; Soyol-Erdene and Huh, 2012). Platinum is withdrawn from the oceans and hence from the surface environment by the subduction of sedimentary and metamorphic rocks, which is estimated to lie in the order of $t \cdot a^{-1}$. Soyol-Erdene and Huh (2012) estimated that the main continental input of Pt to the oceans occurs via dissolved and particulate Pt from rivers. Concentrations of dissolved Pt in 11 east Asian river systems, i.e., the Salween-, Mekong, Chiang Jian-, Hong-, Huang He-, Duman-, Mt. Baekdu-, Amur-, Lena-, Yana-, Indigirka- and Kolyma Rivers, were between >0.27 and 1.1 $ng \cdot kg^{-1}$ (based on more than 200 samples). The authors estimated the river and estuary input of Pt into the oceans to approximate 4 $t \cdot a^{-1}$ and oceanic residence times between 16 and 45 ka were calculated. These data suggest that annual pre-anthropogenic turnover of Pt between different surface compartments lay in the order of tens of tonnes.

Since the large-scale utilization of Pt for industrial processes and in automobile catalytic converters began in the 1960s and 1970s, thousands of tonnes of Pt have been mined from primary deposits and released into surface environments. Due to anthropogenic activities quantities in the order of hundreds of tonnes of Pt a^{-1} are currently dispersed into surface environments (Klee and Graedel, 2004). Initial dispersion and transport occur mostly via the emission of Pt containing particles through mining and smelting, car exhausts and the burning of fossil fuels. This is likely going to increase given that more and more coal fired power plants are commissioned and more cars are equipped with Pt containing catalytic converters. Airborne particles are dispersed around the globe and have reached the most remote corners of the planet, e.g., snow and glacier ice in Greenland and Antarctica (e.g., Soyol-Erdene et al., 2011). Estimates by Klee and Graedel (2004) suggest that the biogeochemical cycle of Pt is one of the most anthropogenically dominated cycles, with a ratio of anthropogenic mobilization from mining, industrial utilization (200 $t \cdot a^{-1}$) and burning of coal (500 $t \cdot a^{-1}$) to natural mobilization from crustal weathering (1 $t \cdot a^{-1}$), upwards of 1000. The dramatically increasing concentrations of Pt in surface environments are then likely to lead to an accelerated transformation of Pt at the Earth's surface (Southam, 2012). Here Pt is (bio) geochemically transformed and transferred between the different compartments, including soils, ground-, lake-, river- and seawaters, terrestrial and oceanic sediments and biota, as detailed in sections above. However, the available concentration data as well as data on sorption and mobilization behavior of Pt in the environment, especially mediated by biogenic mechanisms, are too few and most likely skewed towards highly polluted environments to reliably estimate transfer coefficients and quantities.

7. Conclusions and further research

To understand the transformations of Pt in surface environments, this review assessed geological, geochemical as well as biological and most recently anthropological processes that are strongly interlinked in driving the biogeochemical cycling of Pt in Earth' supergene environments. Specifically this review has highlighted that: (1) Pt is mobile and can become bioavailable in surface environments; (2) bioavailable forms can be present at contaminated and geogenic 'natural' sites; (3) complexes of Pt with chloride and hydroxide play an important role for the mobility of Pt in surface environments; (4) microbiota are likely to contribute to the mobilization of Pt in geogenic and anthropogenically polluted environments via the release of complexation ligands, e.g., thiosulfate, LMWOAs, ammonium and cyanide; (5) microbiota, plants, higher aquatic and land animals as well as humans accumulate Pt; (6) the main factors influencing the uptake of Pt by plants from both geogenic and anthropogenic sources are: the plant species, the physicochemical soil properties and the resident microbial communities, which determine the transformation of Pt-(complexes), as well as the local geology/lithology and the climate; (7) SRB, cyanobacteria and other metallophillic bacteria actively precipitate Pt nano-particles after amendment with Pt-complexes; (8) Pt compounds, e.g., cisplatin, as well as other environmentally relevant Pt complexes can induce toxic effects in bacteria, plants, animals and humans, whereas toxicity of Pt nano-particles at an environmentally relevant concentration has not been reported; (9) Pt is accumulated in marine Mn-oxide rich sediments and nodules; (10) subduction of sediments links the surface and the magmatic cycle of Pt; (11) Pt forms a wide range of primary and secondary mineral phases, including grains and nuggets; (12) primary economical deposits are commonly restricted to deposits in mafic and ultramafic intrusive settings; (13) Pt cycling in surface environments is dominated by anthropogenic activities; (14) due to anthropogenic activities the volume of Pt cycled in surface environments has increased more than 100 fold compared to the Pt cycle prior to large scale anthropogenic Pt production and utilization; and (15) this led to an accelerated turnover of Pt in surface environments.

The current understanding of the interactions of Pt with biogenic and abiogenic phases can now drive research required to experimentally confirm the cycling of Pt proposed in this review. While it is likely that many environmentally relevant groups of biota are involved in the biogeochemical cycling of Pt in geogenic and anthropogenic environments, experimental evidence for the proposed mechanisms needs to be obtained. (Bio)geochemical processes mediating Pt mobility and re-precipitation need to be experimentally verified and the kinetics of these processes, e.g., solubilization-, transport- and re-precipitation rates need to be established, especially in areas of geogenic enrichment. Of particular interest in this regard are processes leading to the formation of secondary Pt minerals and nano-particles as well as Pt grains and nuggets, because accelerated Pt turnover is expected in these environments, which may be triggered by, or itself, trigger biochemical reactions. Hence, assessment of the ultra-fine structures and compositions of primary and secondary Pt grains and nuggets from numerous field sites need to be conducted. These analyses should include the assessment of presence and composition of microbial biofilms associated with Pt grains and nuggets. Furthermore, the biochemical pathways leading to Pt toxicity and possible detoxification mechanisms in environmentally relevant organisms need to be studied, and Pt turnover needs to be linked to functions and activities of complex microbial communities from geogenic or anthropogenically polluted Pt containing soils. Hence, studies using genomic, transcriptomic, proteomic and metabolomic approaches, need to be conducted to understand the biochemistry of Pt turnover in environmentally relevant microbiota. These molecular approaches can be combined with field-, microcosm- and culturing studies to link microbial community structures and functions with the turnover processes of Pt in surface environments. In addition, synchrotron-radiation based experiments, such as μXRF, μXANES-mapping and EXAFS of Pt in mineral and organic phases, microbial cells, plants and animal/human cells/tissue need to be conducted to assess bioaccumulation and transformation processes. In combination, these studies will provide evidence for the impact of biogenic vs. abiogenic processes on the mobility of Pt in surface environments. In order to differentiate anthropogenic Pt contributions in areas of geogenic Pt enrichment isotope studies of Pt and associated PGE should be conducted. Understanding these pathways will then open new routes for the exploration processing of Pt ores and the remediation of polluted sites. Finally, quantitative analyses of a wide range of air, soil, plant and animal samples will need to be conducted to be able quantify Pt content in these key compartments, in order to calculate the global turnover rates between these environmental compartments more accurately.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.earscirev.2014.01.003.

Acknowledgments

Funding was provided by the Australian Research Council (DP20106946 to Reith, Ball and Southam). We acknowledge the following colleagues for contributing materials and images, J. Budd, Dr. A.R. Cabral, L. Fairbrother, J. Kaminski, Dr. M. Lengke, Prof. W.E.G. Müller, C. Plumridge and S.S. Said. The paper benefited from suggestions by the editor Shuhab Khan and the three anonymous reviewers.

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