Raman Spectroscopic Data of the Quenching Phases of a Pt Solution in a Low Water Reduced Carbonic Fluid at P = 200 and T = 950-1000 °C

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Abstract—Raman spectroscopic data of quenching phases in experiments on the dissolution of Pt in reduced carbonic fluid, containing about 30 mol % of CO, both with and without chlorine at P = 200 MPa and $T = 950-1000^{\circ}$ C are presented. Water content in the fluid was no more than 4.5 mol %. The only soluble form of Pt determined in the acetone solution of the quenching phases and in the experimental products is platinum carbonyl. Low concentrations of carbonyl (no more than a few ppm) become detectable using Raman spectroscopy due to the SERS effect (Surface-Enhanced Raman Scattering), which is possible in the presence of Pt nanoparticles in the objects under study. Platinum nanoparticles, formed at the decomposition of carbonyls, generates specific photoluminescence (PL) peak approximated by Gaussian with parameters FWHM = $1050-1300 \text{ cm}^{-1}$, $k_{max} = 2050-2100 \text{ cm}^{-1}$ both in acetone solution and experimental samples. The spectra of CO (main band $k \approx 2050 \text{ cm}^{-1}$) adsorbed on Pt nanoparticles supported on glassy carbon, formed during the decomposition of excess CO relative to the CCO buffer, corresponded to nanoparticle sizes of about 2 nm. No convincing evidence of a mixed chloride-carbonyl composition of platinum was found in the spectra, which may reflect the lower thermodynamic stability of these mixed complexes at high *P*-*T* parameters. Large concentrations of platinum Pt on carbon (up to 2000–3000 ppm) can be explained by the formation of the Pt-C matrix bond and the weakening of the Pt-CO bond in carbonyls, causing their decomposition. Unusual PL peaks were detected in samples from experiments with chlorine-containing fluids, very reminiscent of the PL background of noble metal nanoparticles and attributed to the effect of carbon nanoparticles.

Keywords: Raman spectroscopy, platinum, carbonyl, SERS, PGE deposits **DOI:** 10.1134/S0869591124700188

INTRODUCTION

A connection between low-sulfide igneous PGE deposits and fluids is often inferred (Boudreau et al., 1986; Barnes and Campbell, 1988), and in some cases obvious, when platinum mineralization is millions to tens of millions of years younger than the host intrusion (Mochalov et al., 2021). The composition of the magmatic fluid at the cumulus parameters of ultramafic mafic intrusions parental to PGE deposits is generally unknown. Usually (Stillwater, Bushveld) the only source of information on fluid composition is aqueous fluid and multiphase salt-gas-aqueous fluid inclusions in secondary quartz (Boudreau, 2019). However, these inclusions of aqueous fluids and brines may form at lower temperatures when mostly solidified mafic intrusions are incorporated into crustal fluid reservoirs. The parent magmas of ultramafic and mafic intrusions are of mantle plume origin and are often associated with LIPs (Ernst, 2014). The initial CO₂ content in such magmas is usually high (Black et al., 2021; Hernandez et al., 2021). Decarbonization (Mivano and Beukes, 1997) and mobilization of organic carbon (Rodriguez Monreal et al., 2009) at the lower thermal contact of the intrusion may become additional sources of CO₂ and hydrocarbons filtering through the cumulates into the magma. The composition of a high-temperature magmatic or post-magmatic fluid may be a reduced carbonic fluid with a low water content, as also suggested by Fleet and Wu (1993) and Mathez (1989). In the presence of graphite, a mineral typical of the Bushveld intrusion, at moderate pressure P = 200 - 300 MPa and T = 900 -1000°C, the $CO/(CO_2 + CO)$ ratio (CCO buffer conditions) is in the range of 0.15-0.30. This means that at a high mole fraction of CO₂ $X_{CO_2} = 0.7-0.8$, the mole fraction of carbon monoxide $X_{CO} = 0.11-0.24$ is high enough for the formation of carbonyls (Simakin et al., 2021). Because the carbonyl complexes contain

Run	Fluid source	NaCl	Trap	Object	λ_L , photo luminescence PL_C/PL_{Pt}	CO region	C, ppm
O89bub	FeCO ₃ MgC ₂ O ₄	Yes	Albite glass	Ab trap	514 nm, PL _{Pt}	2006/2051/ <u>1960</u> (3.5-4 s)	Pt = 79.1 Au = 2.0
O91vn	MgC ₂ O ₄	Yes	No	Oxide matrix (OM)	632.8 nm, PL _C /PL _{Pt}	not evident	$Pt = 839 \pm 317$
O98vn*	$MgC_2O_4 + Mgt$	Yes	Albite glass	ОМ	632.8 nm, PL _C /PL _{Pt}	2035/1940 (8 s) 2026/ <u>1927;</u> 2033/ <u>1931</u> 2043/ <u>1974</u>	$Pt = 162 \pm 33$
<i>Chrm</i> 1**	$MgC_2O_4 + Chrm$	Yes	No	ОМ	632.8 nm, PL _C	_	Au≤dl
<i>Ab</i> ₈₆	FeCO ₃	No	Albite glass	ОМ	514 nm, no	2049/2170	Pt = 5140, mech. contamination
Qz ₉₈	MgC ₂ O ₄	No	Sintered quartz glass	ОМ	514 nm, no	2044/2159	n.d.
O56	MgC ₂ O ₄	No	na	Acetone solution	1064 nm, PL _{Pt}	1760/1949/2117	Pt = 0.25 (max 0.714)
O57	MgC ₂ O ₄	No	na	Acetone solution	1064 nm, PL _{Pt}	1774/1944/2122	Pt = 0.016 (max 0.025)

 Table 1. Experimental conditions

* Experiment at $T = 1000^{\circ}$ C; ** experiment in Au capsule.

several CO molecules, the carbonyls are stabilized by pressure at high temperatures, allowing them to exist in a dilute state in the fluid and providing Pt solubility of up to 150 ppm at P = 200 MPa and $T = 950^{\circ}$ C (Simakin et al., 2021). Such a high level of solubility is achieved in carbon-free aqueous fluids with chlorine only at high fO2 values. Sullivan et al. (2022) estimated the solubility of 100 ppm platinum in brine at fO_2 close to QFM + 2, improving on semi-quantitative data obtained by Hanley (2005). Solubility of 200-300 ppm in chlorine-containing hydrous fluids at fO_2 around QFM + $4\div5$ was reported in (Orlova et al., 1987; Blaine et al., 2011). However, mineralization in the mafic intrusions occurs at low oxygen fugacity $fO_2 <$ OFM, when the solubility of Pt in brines and more dilute aqueous fluid can be extrapolated (according to Sullivan et al., 2022) to a value of only about 1 ppm. In water-poor fluids containing chlorine, mixed PGE carbonyl chlorides become possible, which can increase PGE solubility. Here we present Raman spectroscopy data of Pt-containing quench phases, indicating the presence of platinum carbonyl and not confirming the stability of mixed chloride-carbonyl in the fluid at temperatures close to magmatic temperatures ($T = 900 - 1000^{\circ}$ C) and upper crustal depths (P =200 MPa).

MATERIALS AND METHODS

689

In our experiments fluid was generated due to the decomposition of MgC_2O_4 or $FeCO_3$ (see Table 1) added to the small (diameter of 3 mm) open capsule, which was placed in the welded larger capsule (diameter of 5 mm and length of 40 mm) loaded with fluid trap.

Starting materials. We use chemically pure MgC₂O₄ (Onyxmet reagent). By XRF data it is dihydrate MgC₂O₄·2H₂O (C_{H₂O} = 24.3 wt %). Water content after drying at $T = 100^{\circ}$ C for 4 h by KFT analysis becomes 10.4 wt %. After drying at 260°C for 4 h is lowered to 1.5%. To minimize water contamination all equipped capsules were additionally heated at 220°C for 1-1.5 h before experiment, flashed with argon and then welded. Sintered optical quartz (Lytkarino, Russia) glass was used in the fluid trap and has the concentrations of all impurities below detection limit for microprobe. Dry albite glass was prepared by the melting of the natural albite mineral from Kolba massif (Kazakhstan). Siderite was used as the CO source: monomineral FeCO₃ (10 mol % MnCO₃). The runs with pure oxalate also involved magnetite (Kovdor massif, Kola Peninsula) and chromite (Rai-Iz massif, N. Ural). In the second series of experiments (see Table 1), chlorine was added in the form of chemically pure NaCl.

Experimental setup. The experiments were carried out in a high-pressure gas apparatus with Ar as a working fluid at the Institute of Experimental Mineralogy of the Russian Academy of Sciences. The temperature during the experiments was measured by a Pt-Rh thermocouple, the gradient-free zone was 40–50 mm. Pressure was measured using piezoelectric sensors accurate to 5%. Temperature was controlled with an accuracy of $\pm 2.5^{\circ}$ C, pressure with an accuracy of $\pm 1\%$. Quenching was performed by turning off the furnace at a cooling rate of 150°C/min. The experiments were carried out at a pressure of 200 MPa and a temperature of 950°C, the duration of the experiments was 4 h. The amount of MgC_2O_4 oxalate was selected to ensure that a large capsule was filled with fluid and solid components by 20-25% of the maximum internal volume. After quenching, the residual pressure of non-condensable CO₂ was estimated to be approximately 30 bar. The experimental conditions are described in more detail in (Simakin et al., 2021, 2024).

Chemical Analyses. Water content in the starting $Mg_2C_2O_4$ was measured by the Karl–Fischer titration (KFT) on an Aqua 40.00 system with a high-temperature HT 1300 unit at IEM RAS (Chernogolovka, Russia). Range of detectable water mass (m_W) : 1 µg–100 mg, reproducibility: ±3 µg at the m_W 1–1000 mg, 3% at the $m_W > 1$ r

To prepare for analysis by ETAAS method, the samples were decomposed by heating to 120°C in a mixture of strong HF + HNO₃ in Savillex screw vessels, and then dried to wet salt. Then the sample was treated with Aqua Regia (HCl : $HNO_3 = 3 : 1$) to obtain wet salts, and then it was treated with concentrated HCl to convert the salts into chlorides. After complete dissolution of the salts, the solution was cooled and filtered in a 5-10 mL flask. Determination of the nanograms quantities of Pt was carried out using a Solaar MQZ (Thermo Electron Corp. UK) ETAA spectrometer with a Zeeman background correction (Kubrakova et al., 2020). The measurements were conducted on the most sensitive line of $\lambda = 265.9$ using pyrolytically coated graphite furnaces. The sample was introduced automatically or manually with a micropipette with disposable plastic tips (5 to $20 \,\mu$ L). The signal was measured using the height of the peak and its area. The analytical inaccuracy of ETAAS analysis within the concentration range of 1-100 ng/mL is no higher than 4 relative %. Detection limit is 2.5 ppb for Pt. To analyze the forms of platinum dissolved in acetone, an organic phase was introduced directly into the ET-AAS graphite furnaces. The measurement was performed using water calibration solutions.

Raman spectroscopy. Spectroscopic study of fluid trapped in the albite glass and oxide matrix coated with carbon was carried at the Institute of Geology,

RAS (Syktyvkar). The samples were analyzed with a high-resolution Raman spectrometer LabRam HR800 (Horiba, Jobin Yvon) using external Ar + laser (514.5 nm, 1.2 μ W). One series of measurements was carried out with He-Ne (red) laser (632.8 nm, 2 μ W). The spectrometer is coupled with an Olympus BX41 optical microscope with a 50× object lens. Spectra were recorded in the 100–4000 cm⁻¹ range using a spectrometer grating of 600 lines/mm. A confocal hole size is 300 μ m and a slit is 100 μ m. The size of analyzed region was about 5 μ m. Each spectrum was the result of three accumulations with a 10 s exposure. The spectra were recorded at room temperature.

Raman spectra of quenching platinum phases dissolved in acetone were measured in Institute of Experimental Mineralogy RAS (Chernogolovka, Russia). Ram II module for Fourier spectrometer VERTAX 70 (Bruker) was used to record Fourier-Raman spectra with excited line 1064 nm line of infrared laser with an output power of 500 μ W. The spectrometer was equipped with semi-conductive Ge detector.

RESULTS

Run products. From numerous observations, several experiments with spectral data worthy of attention were selected (see Table 1). The products of the selected experiments include an oxide matrix formed during fluid generation and an albite glass trap used to capture the experimental fluid in bubbles. The oxide matrix consists predominantly of MgO, formed during the decomposition of MgC₂O₄:

$$MgC_2O_4 = MgO + CO + CO_2.$$
(1)

In experiments with chlorine, the oxide matrix also contains magnetite (chromite), NaCl and their reaction products, including $FeCl_2$ and $FeCl_3$. The fugacity of chlorine was buffered by the reaction:

$$FeCl_3 = FeCl_2 + 1/2Cl_2,$$
 (2)

at a level 3-4 orders of magnitude lower than the value at the Pt-PtCl₂ equilibrium (Simakin et al., 2024). Periclase is often coated with carbon produced by the disproportionation of excess CO:

$$2CO = C + CO_2, \tag{3}$$

so that the CO content approaches the equilibrium dictated by the CCO buffer. Raman spectrum of the experimental fluid trapped in the albite glass trap of the O89 experiment with CO₂ and CO bands is Supplementary 1, Fig. 1S. The CO/(CO₂ + CO) ratio estimated with μ -Raman spectroscopy is 0.3 (the value constrained by the CCO buffer at $T = 1000^{\circ}$ C and P = 200 MPa is 0.31). The initial water content in the fluid was about 4.5 mol %, however, due to the reaction with chlorine, HCl is formed. Part of the hydrogen is spent on the synthesis of bitumen, which is an amorphous carbon containing H (Ferrari and Robertson,



Fig. 1. SEM image of platinum whiskers deposited from fluid in a MgO oxide matrix from experiment O57, image width is 25 mkm.

2004) characterized by high luminescence in Raman spectra (e.g., Stokes et al., 2022). Due to these two reactions, the mass of water decreases. At the same time, when CO is disproportioned (equation (3)), the mass of the carbonaceous components of the fluid also decreases, so that the actual mole fraction of water remains low. More information on the fluid composition is in (Simakin et al., 2021; Simakin et al., 2024).

ETAAS analyzes show high platinum content in test products (see Table 1). Relatively large crystals of platinum and Fe-Pt alloys were observed on the surface of the bubble walls, on the oxide matrix and on the capsule walls (for examples in a chlorine-free system, see (Simakin et al., 2021)). These crystals often have a thread-like morphology with aspect ratios up to 100 : 1 (Fig. 1). The lowest concentrations of Pt in fluid traps correspond to platinum dissolved in the fluid, located in the pore space and precipitated during quenching. Nano-sized platinum can also be expected to appear, which cannot be detected in SEM images.

Raman spectra, SERS effect. Summary of the spectral data acquired on the solid samples used in this study is in the Supplementary 1, Figs. 2S-5S. Solutions of quenching phases in acetone were also studied, obtained by washing the walls of capsules that were in contact with the fluid during the experiment and filtering a suspension of the oxide matrix in acetone. In a solution of organometallic compounds (carbonyls) in acetone, the Pt content can reach 0.2 ppm. Within a few hours, the dissolved carbonyls decompose to form platinum nano-particles distributed in acetone. An ensemble of conductive noble metals nanoparticles (Ag (Yang et al., 2007), Au (Lin et al., 2017), Pt (Gómez et al., 2005) has a specific background photoluminescence (PL) signal formed due to the interaction of laser light with conductive particles smaller than the wavelength of light that produces surface plasmons. PL spectra have a Gaussian shape with the relatively small width (full width at half maximum FWHM = 1000–1300 cm⁻¹) and a maximum at k = $1000-3000 \text{ cm}^{-1}$ (Lin et al., 2017), depending on the size, shape and composition of nanoparticles (see Supplementary 1, Fig. 6S).

Spectral data for a colloidal solution of Pt in acetone produced from quenching phases were previously reported in (Simakin et al., 2021). The study of these



Fig. 2. Raman spectra of acetone extracts of oxide matrices from experiments O56, O57, and O63 (see Table 1), the spectrum of acetone is subtracted. (a) background Raman photoluminescence (PL) bands in the spectra of partially decomposed solutions of quenching Pt carbonyls forming Pt nano-particles; for comparison, the PL band of Au nano-particles (Lin et al., 2017) is shown with an off scale intensity; (b) Due to the SERS effect caused by the presence of Pt nanoparticles, carbonyl bands can be recognized in the deconvoluted spectra of sample O56 (PL band was subtracted). The position of the main bands of Chini complex (Pt₃(CO)₆)^{2–} (Longoni and Chini, 1976) is shown by vertical dotted lines in (a) and crosshatched bars in (b). The range of stretching vibration band of CO adsorbed on Pt nano-particles is shown by the dashed line in (a).

spectra (see Fig. 2a) demonstrated that the PL background is approximated by a Gaussian with parameters characteristic of the PL band of a nanosized ensemble of noble metals: $056 - k_{\text{max}} = 2057.0$, FWHM = 1055 cm⁻¹; O57 $- k_{max} = 2028.8$, FWHM = 1068 cm⁻¹; O63 $- k_{max} = 2158.7$, FWHM = 1335 cm⁻¹. The Raman signal of molecules adsorbed on the surface of nanoparticles is amplified up to 10^5 times through interaction with plasmons (surface-enhanced Raman scattering or SERS), allowing single-molecule detection. The Pt concentration in the acetone solution of the quenching phases from experiments O56, O57 is low, less than 1 ppm. Obviously, such low concentrations are below the detection limit of Raman spectroscopy. Only due to the SERS effect, it was possible to deconvolute the Pt carbonyl bands after subtracting the background PL and acetone spectra. The fresh solution obtained immediately after opening the capsule does not contain Pt nanoparticles and the corresponding PL band. Exposure to air for several hours leads to oxidation of CO and partial decomposition of carbonyl with the formation of Pt nanoparticles. With the appearance of a typical PL background, the spectrum of Pt carbonyl appears (see Fig. 2b and Supplementary 1, Fig. 7S). In the carbonyl spectrum there is a distinct band with $k \approx 1945 \text{ cm}^{-1}$, which corresponds well to the main band of the multinuclear Chini com-

plex. $Pt_3(CO)_6^{2-}$ (Longoni and Chini, 1976).

The PL background of the Raman spectra of our experimental samples is usually a broad band with a maximum at wavenumbers above the observation limit of 4000 cm⁻¹ due to the presence of bitumen (see Supplementary 1, Figs. 2S, 3S). When bitumen exhibits strong luminescence, the spectra of other compounds are often suppressed. In samples free of chlorine and bitumen, carbon particles with low crystallinity showed a weak PL background (almost flat spectrum). In some bitumen-free samples of runs with chlorinecontaining fluid, the PL has a Gaussian peak with parameters close to the peaks of the ensemble of noble metal nanoparticles (Fig. 3). We tentatively associated these Gaussian components of the background PL in the spectra of the *Chrm*1 (no noble metals, see Table 1), O91 and O98 runs with the effect of an ensemble of carbon nanoparticles (see details of interpretation below in section). Such features of the PL background were encountered in the Raman spectra of oxide matrices in experiments with chromite (*Chrm*1): $k_{max} =$ 992, FWHM = 2400 cm^{-1} and magnetite (O91, O98): $k_{\text{max}} = 1367 \text{ FWHM} = 1300 \text{ cm}^{-1}$. On the top of the PL band, a pair of main carbon peaks can be identified at $k \approx 1333 \text{ cm}^{-1}$ (D1) and 1576–1591 cm⁻¹ (G). In the spectra of oxide matrices of experiments O91, O98, performed in Pt capsules, additional Gaussians were deconvoluted from the carbon PL peak with parameters $k_{\text{max}} = 2547 \text{ cm}^{-1}$, FWHM = 1434 cm⁻¹ in O91-3; $k_{\text{max}} = 2172 \text{ cm}^{-1}$, FWHM = 1451 cm⁻¹ in O98-4.



Fig. 3. Relatively narrow, red-shifted background PL peaks in the spectra of various types of oxide matrices from experiments: *Chrm*1, caused by carbon nano-particles and O98, and O91, Pt nanoparticles (see text for explanations). For comparison, the background PL peak caused by the interaction of laser radiation with Pt nanoparticles in acetone from experiment O57 (intensity not in scale) is also shown.

ETAAS analyzes give the total Pt content in the matrixes of experiments $O91-839 \pm 317$ ppm and $O98-162 \pm 33$ ppm (see Table 1). The high Pt content suggests that the second Gaussian components of PL background may be interpreted as the presence of some Pt deposited on MgO in the form of nanoparticles. In the spectrum of the oxide matrix of the Chrm2 experiment, only one Gaussian band with the param-eters k_{max} = 986, FWHM = 2420 cm⁻¹ of carbon nanoparticles is identified, which is consistent with ETAAS data on the absence of noble metals in the matrix. Our interpretation of the second Gaussian peak of the PL background in the O98 spectrum as an effect of nanoparticles of Pt is supported by the observation of polynuclar carbonyls peaks at 1940 and 1937 cm⁻¹ (see Fig. 4 and Table 1), made possible by the SERS effect.

In addition, in all spectra of the O98 experiment there is a peak at 1502 cm⁻¹, enhanced by the SERS effect. According to the database of Raman and IR spectra of organic compounds (Lin-Vien et al., 1991), the wave number at $k \approx 1500$ cm⁻¹ can be explained by C=C stretching in some aromatic hydrocarbons, e.g. to symmetrical tension under vibration in cyclopentadiene (C₅H₆). In the spectra of the oxide matrix of the O91 experiment, no lines enhanced by the SERS effect were detected, which can be interpreted as the complete decomposition of carbonyls (Fig. 3).

A PL peak with parameters $k_{\text{max}} = 1843$, FWHM = 982 cm⁻¹, compatible with nano-sized Pt, was observed in the spectrum of an albite glass trap from



Fig. 4. Raman spectra of MgO with admixture of MgCO₃ from the O98 experiment with the subtraction of the background consisting of two PL bands due to conducting carbon and platinum nanoparticles (for the full spectrum, see Fig. 3); Due to the SERS effect, the bands of carbonyl ($k \approx$ 1940 cm⁻¹; the grey bar indicates the position of the main band of the Chini complex) and CO adsorbed on platinum ($k \approx 2035$ cm⁻¹) became noticeable.

experiment O89 with a platinum content of 79 ppm. After subtracting this peak, the spectrum takes the form of a typical bitumen-containing sample with a broad PL band with $k_{\text{max}} \approx 4000 \text{ cm}^{-1}$ (Fig. 5a). The poorly resolved signal in the CO-related region, enhanced by the SERS effect, can be deconvoluted as a sum of Gaussians with the main contribution of the band at $k = 2002 \text{ cm}^{-1}$ (Fig. 5b and Supplementary 1, Fig. 7S (c)).

Characterization of carbon phase. The structural type of amorphous carbon formed by CO disproportionation in our experiments can be characterized based on Raman spectra (Fig. 6 and Supplementary 1, Figs. 8S, 9S). An example of deconvoluted first-order bands of disordered carbon from the Chrm1 experiment is shown in Fig. 6. Band D1 reflects the contribution of carbon in the state of sp3 hybridization (as in diamond), while G is the band of carbon in the state of sp2 hybridization (as in graphite). Single-crystal diamond is characterized by one D1 band with k =1331 cm⁻¹, and well-ordered graphite is characterized by one G band with $k \approx 1580 \text{ cm}^{-1}$ (for example, Ferrari, 2007). Range k = 1323 - 1334 cm⁻¹ for D1 is characteristic of commercial high pressure and high temperature (HPHT) synthetic nanodiamond powders (Ruiz-Valdez et al., 2018). Different types of amorphous carbon with different degrees of crystallinity and hydrogen content have spectra with different positions and FWHM of the D1 and G bands (Ferrari and Robertson, 2004). Well-ordered crystalline solids and molecular compounds have a fixed Raman spectrum that does not depend on the wavelength of the exciting laser, while for disordered substances the position of the bands can depend on λ_L . Robertson (2002) showed that the position of the G-band of glassy carbon (a form very similar to amorphous carbon in our experiments) remains essentially fixed near 1600 cm⁻¹ when the laser excitation wavelength (λ_{I}) is varied in the range 200–700 nm, while the position of the D1 band is strongly red-shifted with increasing λ_1 (from 1353 at $\lambda_{\rm L} = 514$ nm to 1324 cm⁻¹ at $\lambda_{\rm L} = 632.8$ nm or $\Delta k \approx$ 29 cm⁻¹). Figure 7 shows the positions of the D1 and



Fig. 5. Raman spectra of the albite glass trap from experiment O89. (a) full spectrum (black line) with the deconvoluted Gaussian band of the Pt nanoparticles located at the bottom, the spectrum obtained after subtracting this Gaussian band is shown by the gray line; albite glass bands are expressed at $k < 1500 \text{ cm}^{-1}$; (b) deconvolution of the part of the spectrum associated with CO: bands with k = 2002 and 2080 cm^{-1} can be attributed to terminal CO adsorbed on Pt nanoparticles. The assignment of the band with $k = 1877 \text{ cm}^{-1}$ is unclear; it may be bridged CO bonded to multiple Pt atoms.

Center Width Height

D1 1200 G 56.516 613.81 43477 1585.1 D1 62.286 62320 1328.7 798.33 D2 74041 1459.3 252.43 234.03 1000 D3 43486 167.13 207.60 1268.7 G 800 Intensity 600 400 D3 200 0 -2001000 1200 1400 2000 1600 1800 Raman shift, cm⁻¹

Peak Area

Fig. 6. Raman spectra of a carbon-coated oxide matrix from the Chrm1 experiment with Gaussian background PL subtracted (full spectrum in Fig. 3), the graph shows the first-order carbon bands D and G. The use of an excitation laser with a wavelength of 632.8 nm causes a shift in the position of the D1 band to an unusual (diamond-like) wave number $k = 1329 \text{ cm}^{-1}$



Fig. 7. Diagram of the positions of the main Raman bands (D1 and G) of carbon formed by disproportionation of CO in experiments with reduced carbonic fluid with and without chlorine, acquired at different exciting laser wavelength λ_L . With increasing λ_L , one can note a systematic shift in the position of the D1 band towards lower wave numbers. The gray arrow shows the shift value for glassy carbon according to (Robertson (2002)).



Fig. 8. Raman spectra of a carbon-coated MgO matrix from the Ab_{86} experiment. (a) spectra obtained at laser powers of 1 (black line) and 10 μ W (red line); at higher powers only second-order carbon peaks are retained; (b) deconvolution of the Raman spectra of gases chemically adsorbed on Pt in the Ab_{86} experiment; the band with k = 2044 cm⁻¹ is attributed to CO adsorbed on Pt, with $k = 2160 \text{ cm}^{-1}$ presumably to CO adsorbed on MgO or carbon, the band with $k = 2346 \text{ cm}^{-1}$ can presumably be attributed to CO₂ adsorbed on carbon with loss of symmetry.

G bands for experimental amorphous carbon measured at $\lambda_L = 514$ and 632.8 nm. Our observations demonstrated a slightly smaller than expected red shift of glassy carbon from 1332 ± 4 to 1352 ± 4 cm⁻¹ ($\Delta k \approx$ 20 cm^{-1}). However, according to Robertson (2002), the $k_{D1}(\lambda_{I})$ dependence is not fixed and depends on the degree of carbon disorder. At the same time, the position of the D-band of the diamond does not depend on λ_{I} .

The Supplementary 1, Fig. 10S shows an example of Raman spectra obtained at $\lambda_L = 514$ nm of diamond-like (D1 = 1327 cm^{-1}) and glassy amorphous forms of carbon ($D1 = 1342 \text{ cm}^{-1}$) in the Au14 experiment with chlorine-containing reduced carbon diox-



Fig. 9. Raman spectrum of Au ore from the Suzdal deposit, Eastern Kazakhstan (green line), the red line shows the main Gaussian component of the spectrum with $k_{max} =$ 1024 cm⁻¹, FWHM = 1538 cm⁻¹. For comparison, the background PL spectrum recorded in the Au-TERS setup from (Lin et al., 2017) with parameters $k_{max} =$ 1018.6 cm⁻¹, w = 1314 cm⁻¹. The close similarity of these spectra suggests the presence of nano-sized gold in the Suzdal ore sample.

ide fluid, not used in this publication (for experimental conditions, see Simakin et al., 2024). Diamondlike carbon is a film deposited on FeCl₂ and FeCl₃, and glassy carbon is a macrophase (5–10 μ m in size) formed on MgO. The red shift of the Raman peak position of diamond-like carbon is ca. 10 cm⁻¹ (1132 to 1324 cm⁻¹) may be due to the small film thickness of less than 10 nm (Ramsteiner et al., 1988).

In some of the experiments described above, the spectra of carbon are characterized by a relatively narrow PL band (see Fig. 3), similar to the PL bands of an ensemble of conducting metal nanoparticles. This feature is known for carbon nanoparticles (carbon dots or CDs with a size of 2-3 nm) (Dolenko et al., 2015; Zhang et al., 2021), see Supplementary 1, Fig. 11S. Carbon dots, along with detonation nanodiamonds, are widely used as luminescent materials in biological sciences (Dolenko et al., 2015).

Raman spectra of CO chemically adsorbed on Pt. In the Raman spectra of oxide matrices from experiments without chlorine, no signature of Gaussian PL was observed that could be associated with carbon conducting nanoparticles (Fig. 8). At high platinum concentrations, usually in the range of 1000–3000 ppm, clear spectra of CO chemically bound to platinum are found in some cases. A total of three spectra were measured for samples Ab_{86} and Qz_{98} . When exposed to a laser power of 10 μ W, all bands in the range of 2000– 2600 cm⁻¹ disappear (see Fig. 8a), which indicates the

PETROLOGY Vol. 32 No. 5 2024

easy release of chemically adsorbed gases. Two bands with k = 2040 - 2050 and k = 2160 - 2170 cm⁻¹ can be attributed to CO chemically bonded to platinum and matrix (MgO or carbon), respectively (Fig. 8b). The additional adsorbed gas is characterized by a band with a maximum at k = 2305 - 2346 cm⁻¹ (Fig. 8b). We presumably interpret this gaseous compound as adsorbed CO₂, a product of the in-situ oxidation of CO catalyzed by Pt on a carbon support. Our spectra are very similar to observations of CO oxidation on a TiO₂supported Au catalyst using Fourier transform infrared diffuse reflectance spectroscopy (Raphulu et al., 2010). In the CO_2 gas phase, the symmetric stretch at 2349 cm⁻¹ is the main IR band, absent in the Raman spectrum. Having attached to the active centers of Pt, the linear CO_2 molecule loses its symmetry, which can probably lead to the activation of Raman mode with a similar wave number.

In the entire set of spectra, the bands of metal particles-CO are concentrated at k = 2033 - 2035 cm⁻¹ (O98); 2000–2006 cm⁻¹ (O89); 2044–2049 cm⁻¹ (Ab_{86}, Qz_{98}) . Due to the SERS effect, redshifts of up to 10 cm⁻¹ have been reported (Grabhorn and Otto, 1990), so values of $k = 2033 - 2035 \text{ cm}^{-1}$ may correspond to k = 2043 - 2045 cm⁻¹ of the unmodified spectra in the O98 experiment. The values of 2040-2045 cm⁻¹ can be explained by the particle size of Pt (on carbon support) of c.a. 2 nm (Rice et al., 2000) or according to the coordination number of Pt in neutral clusters 6-7 (Alexandrov et al., 2016). Much lower wave numbers of 2000–2006 cm^{-1} can be associated with adsorption on mini-clusters (n = 8) on an oxide matrix (Alexandrov et al., 2016), which in our case is represented by albite glass of the fluid trap in run O89.

DISCUSSION

Carbonyls as potentially important components of natural fluids. We are aware of only one publication with Raman spectroscopic observation of iron carbonyl dissolved in lunar basaltic glass, experimentally produced at $fO_2 \le IW-0.55$ (Wetzel et al., 2013). Volatile carbonyls of PGE were previously noted to have the potential to be transport species in magmatic fluids, but were rejected due to their low thermal stability (Fleet and Wu, 1993). Moreover, simple platinum and palladium carbonyls ($Pt(CO)_4$ and $Pd(CO)_4$) are unstable even under ambient conditions (Darling and Ogden, 1972; Kundig et al., 1973). Polynuclear carbonyls Pt and Pd are more stable (Bradford, 1972; Sachtler and Zhang, 1993). It has been experimentally established that stable polynuclear carbonyls Ru, Re, Rh, Os thermally decompose at temperatures above 200-300°C (Connor et al., 1973). However, PtCl₂ (and the $PtCl_4^{2-}$ complex), currently accepted as the main substance in the high-temperature fluid, is also unstable as a phase at magmatic T and fCl_2 (Simakin et al., 2024) and can only form in dilute solution. Carbonyls are also stabilized by dilution and especially by increased pressure to high temperatures. In this regard, our observations of carbonyls in quenching phases provide important evidence supporting the formation of carbonyls under high *P*-*T* conditions.

The possible participation of organometallic compounds, including carbonyls and mixed carbonyl chlorides (Distler, Yudovskava, 2005), was assumed in the process of the formation of the giant Au deposit Sukhoi Log in black shales (Irkutsk region, Russia). However, the authors' attempts to identify organometallic compounds of noble metals in a carbonaceous matter failed. Given our experimental data demonstrating the decomposition of quenched carbonyls within a few days, it is not unusual for organometallic compounds to decompose within ca. 300 million years (Distler and Yudovskaya, 2005) since ore formation. Therefore the absence of organometallic compounds in the studied rock samples does not mean the denial of their participation in the transport of noble metals during the process of ore formation.

Raman spectra of the natural nano-sized Au? As our data showed, the SERS effect can operate at relatively low concentrations of Pt nanoparticles (less than 0.2 ppm in acetone) and, therefore, can be expected in Raman studies of native metal nano assemblages in nature. The PL peak associated with nano-gold can be anticipated in the Raman spectra of Carlin-type gold mineralization in the Suzdal deposit of Eastern Kazakhstan (Moroz et al., 2015) (Fig. 9). The maximum gold content in carbon-rich rocks ranges from 2–54 ppm (Kovalev et al., 2009). The example spectrum from (Moroz et al., 2015) can be deconvoluted into two Gaussian peaks, the parameters of the stronger of which are very close to the approximation of the PL peak in the gold TERS spectrum (tip-enhanced Raman scattering, similar to SERS) from (Lin et al., 2017). It follows that some gold particles have nanosizes smaller than the resolution of the SEM used to characterize Suzdal gold (Kovalev et al., 2009). It is assumed that the nanoparticles rapidly coarse and may therefore represent a transitional form of gold mineralization resulting from weathering or bacterial action (Hough et al., 2008).

Why no signs of mixed chloride-carbonyls of Pt in our quenching phases? Under the conditions of our experiment during quenching, the exsolved carbonyls decompose, and only a small part of them survives and is recorded in the quenching products: in an acetone solution of the experimental products (O56, O57, O59), in the oxide matrix (O98) or albite trap (O89). It is important to note that the Raman spectra of both chlorine-containing and chlorine-free systems in the region of chemically bound CO of ca. 1850–2200 cm⁻¹ are characterized by bands of platinum carbonyl and CO chemically adsorbed on Pt nanoclusters of different sizes. No significant signals were detected in the range characteristic of mixed platinum chloride carbonyls. Mixed complexes of noble metals have the following parameters: CO stretching wave number in Pd₂Cl₄(CO)₂ $k_{CO} = 2160 \text{ cm}^{-1}$, in PtCl₂(CO)₂ $k_{CO} =$ 2120, 2167 cm⁻¹, in Pt₂Cl₄(CO)₂ $k_{CO} = 2128 \text{ cm}^{-1}$ 1 and in AuCl(CO) $k_{CO} = 2163 \text{ cm}^{-1}$ (Calderazzo, 1990). The weaker Pt-C(O) π -bonding of the metal cation in these complexes is reflected in a stronger C-O bond and a blue shift of the C-O stretching vibration (relative to CO gas with $k_{CO} = 2138 \text{ cm}^{-1}$). A similar shift is expected during the adsorption of CO on the PtO phase and on Pt-O centers of the platinum surface (Alexandrov et al., 2016). Spectroscopic data indicate that the PtCl₂(CO)₂ complex is less thermodynamically stable than Pt₃(CO)₆, and even if it forms at high *P-T*, it completely decomposes during quenching.

Carbonyls decomposition at the interaction with carbon and PGE accumulation in carbonaceous rocks. Our observations can explain well known association of carbon and PGE in nature. This relationship is probably best expressed in regionally graphitized Upper Proterozoic and Cambrian metamorphic rocks enriched in platinum up to 62 ppm in the Khankai terrain in the Russian Far East (Khanchuk et al., 2013). A deep (mantle) source for carbon was suggested for the fluid and probably PGE. In natural fluids, the concentrations of PGE are negligible, which leads to negligible equilibrium concentrations of PGE adsorbed on carbon. However, carbonyls adsorbed on carbon have been decomposed, so in the spectra of samples from experiments Ab_{86} and Qz_{98} only bands of terminal CO bound to Pt nano-particles are detected. X-ray absorption spectroscopy (Torigoe et al., 2000) has provided data on the mechanism of interaction of carbonyls with the carbon support. When polynuclear platinum carbonyls $(Pt_3(CO)_6)_n$ are adsorbed on a carbon support, they first transform into a single-layer complex $(Pt_3(CO)_6)$ in contact with carbon. The bridging CO molecules are then gradually lost and Pt-C bonds to carbon are created. The interaction of Pt with carbon weakens the π -bond Pt-CO (Ma et al., 2012; Oh et al., 2010), which leads to irreversible decomposition of the carbonyl. Thus, Pt accumulates and can reach high grades despite the low content of Pt carbonyls in the fluid.

CONCLUSIONS

At moderately high pressures of 200–300 MPa, corresponding to the typical level of formation of PGE bearing mafic-ultramafic intrusions, the solubility of Pt in low-water reduced carbonic fluid can be quite high, limited by CO content and temperature. Platinum carbonyls, presumably the main soluble compounds, were registered in the quenching products of experiments carried out at P = 200 MPa and $T = 950-1000^{\circ}$ C. The most convincing evidence for the pres-

ence of Pt carbonyls was obtained by Raman spectroscopy of a solution of quenching phases in acetone. Partial decomposition of carbonyl creates colloidal suspension of Pt nano-particles. Due to the SERS effect caused by these nano-particles, low concentrations of carbonyls adsorbed on the surface give a highly amplified Raman spectrum with two main bands: k =1945 and k = 1740 cm⁻¹ of the Chini complex

 $Pt_3(CO)_6^{-2}$. In the spectrum of oxide matrices from our experiments, background photoluminescence (PL) peaks are observed with parameters close to the PL peaks in an acetone solution with Pt nanoparticles. We interpret these PL peaks in the spectra of the solid experimental products as a manifestation of nanoplatinum deposited from the fluid. In some solid samples, bands associated with Pt carbonyl were observed, enhanced by the SERS effect, as in the acetone solution. The presence of carbon nanoparticles presumably of quench origin is suggested by the observation of compact PL peaks with parameters close to the PL peaks of nanoplatinum in the sample not containing noble metals. The presence of chlorine in our experimental fluid with fugacity controlled by the FeCl₂-FeCl₃ buffer did not lead to the appearance of signs of mixed carbonyl chlorides in the Raman spectra of the quench products. In some experiments with chlorine-free fluid, the carbon coated oxide matrix has Pt contents up to 3000 ppm (may be higher due to mechanical contamination). Some Raman spectra of such samples have strong bands with a maximum at $k \approx 2050 \text{ cm}^{-1}$. corresponding to the stretching vibrations of CO adsorbed on Pt nanoparticles with a size of about 2 nm. The extremely high concentration of platinum in the oxide matrix can be explained by the adsorption of carbonyls on the coating carbon. Further interaction of platinum with carbon leads to a weakening of Pt-CO π -bonds and the decomposition of carbonyls. This mechanism may explain the enrichment of carbonaceous rocks with PGE in nature to grades well above the equilibrium adsorption limit in the presence of fluid containing noble metals at ppb level.

SUPPLEMENTARY INFORMATION

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PETROLOGY Vol. 32 No. 5 2024

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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