Palladium complexation in chloride- and bisulfide-rich fluids: Insights from *ab initio* molecular dynamics simulations and X-ray absorption spectroscopy

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Abstract

Palladium (Pd) is the most mobile element of the platinum group elements (PGE) in hydrothermal fluids. The characterization of the nature and stability of Pd(II) complexes in geofluids is essential in understanding the formation of hydrothermal PGE deposits and the remobilization of PGE during hydrothermal and metamorphic overprints of magmatic deposits. However, the aqueous speciation of this metal in a range of geologically relevant conditions remains controversial. A number of experimental studies of Pd solubility and speciation in hydrothermal fluids suggest that chloride and bisulfide are the major ligands responsible for carrying Pd as Pd(II)–Cl and Pd(II)–HS complexes, but different experimental studies predicted different predominant chloride and bisulfide complexes and their relative strengths. Hence, we conducted *ab initio* molecular dynamics (MD) simulations to predict the speciation of Pd–Cl and Pd–HS complexes at 300 °C. The simulations predicted that all complexes share fourfold square-planar structures, which is consistent with X-ray absorption spectroscopy measurements of Pd(II) in chloride-rich solutions. The stability constants for the stepwise formation of Pd(II)–Cl and Pd(II)–HS complexes were determined using thermodynamic integration. The predicted formation constants of Pd(II)–Cl complexes show excellent agreement (within $\sim$1 order of magnitude for $PdCl^+$, within 0.3 for $PdCl_{2(aq)}$ and $PdCl_3^-$, within 0.1 for $PdCl_4^{2-}$) with the recent experimental study of Tagirov et al. (2013). However, our results suggest that the $Pd(HS)_4^{2-}$ complex predominates in HS^--rich hydrothermal fluids, whereas interpretation of previous experimental studies neglected this species. Modeling of Pd solubility in chloride- and sulfur-rich hydrothermal fluids demonstrated that Pd is mainly carried as the $Pd(HS)_4^{2-}$ hydrosulfide complex at neutral-alkaline and reduced (pyrite/pyrrhotite stable) conditions, and as the $PdCl_4^{2-}$ chloride complex at acidic and oxidized conditions. At 300 °C, significant Pd mobility at ppb level as Pd bisulfide complexes is predicted under fluid-buffered conditions (e.g., pH $\sim$7 to 8, near $HS^-/H_2S(aq)$ pH buffer), but only limited Pd solubility is predicted under rock-buffered conditions (e.g., pH $\sim$4 to 5, quartz–feldspar–muscovite buffer).

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1. INTRODUCTION

Aqueous metal speciation plays an important role in controlling metal transport and deposition in hydrothermal fluids in both natural and man-made environments (Seward and Driesner, 2004; Brugger et al., 2010). Characterizing the speciation and solubility of platinum group elements (PGE) in hydrothermal fluids is useful in understanding and critically evaluating (1) the formation of hydrothermal PGE deposits (e.g., Boudreau et al., 1986; Mernagh et al., 1994; Farrow and Watkinson, 1996; Wood, 2002); (2) the significance of PGE as petrogenetic indicators in hydrothermal settings (e.g., porphyry copper deposits; Xiong and Wood, 2000); and (3) the mobility of PGE during hydrothermal and/or metamorphic overprint of magmatic Ni–Cu-PGE deposits, leading to the formation of secondary enrichments or alteration halos that may enlarge the footprint of these deposits (e.g., Willmore et al., 2000; Barnes, 2004; Barnes and Liu, 2012; Djon and Barnes, 2012; Le Vaillant et al., 2014).

The distribution of PGE, in particular palladium, has long been recognized as a marker for ore-forming processes (e.g., Fiorentini et al., 2010; Barnes et al., 2013; Locmelis et al., 2013) and hydrothermal alteration of magmatic nickel deposits (e.g., Keays and Davison, 1976; Le Vaillant et al., 2014). Recently, Barnes and Liu (2012) observed that magmatic Pd/Pt ratios were preserved within metamorphosed komatiite-hosted Ni ores where the S-contents were low, but varied greatly around S-rich ore bodies. Based on available thermodynamic data, they suggested that this pattern of Pd mobility was due to the fact that bisulfide complexes, rather than chloride complexes, dominate Pd speciation at $T \geqslant 300\ °C$ in moderately reduced, S-rich aqueous fluids in the Earth's crust.

Palladium is the most mobile PGE element in geofluids (Cabral et al., 2012; Tagirov et al., 2013). The thermodynamic models and properties for aqueous PGE complexes have been estimated by a number of studies (Wood et al., 1989; Sassani and Shock, 1990, 1998; Wood and Mountain, 1991). Chlorine and sulfur are the main elements involved in the complexing of metals in natural hydrothermal fluids (e.g., Seward and Barnes, 1997). Consequently, a number of experimental studies have investigated Pd speciation and solubility in chloride and hydrosulfide solutions under hydrothermal conditions up to 700 °C (Hsu et al., 1991; Wood et al., 1992; Gammons et al., 1992, 1993; Pan and Wood, 1994; Gammons, 1995; Seward et al., 2002; Boily and Seward, 2005, 2007; Tagirov and Baranova, 2009; Tagirov et al., 2013; Bazarkina et al., 2014).

Despite this extensive amount of work, large discrepancies still exist among different studies and the resulting thermodynamic models. For example, Xiong and Wood (2000) noted that the Pd and Pt solubility calculated using the available thermodynamic properties are several orders of magnitudes lower than expected from mass balance considerations and from experimental values for porphyry copper environments (350–500 °C). Two main groups have provided extensive experimental work, with the results and preferred thermodynamic properties summarized in Wood et al. (1992) and Tagirov et al. (2013), respectively.

In general, the formation constants ($\log \beta_n$) for the Pd chloride complexes ($PdCl_n^{2-n}$) up to 300 °C and the solubility predicted by both models in chloride brines are in reasonable agreement (predicted solubilities within one order of magnitude). However, at 300 °C the formation constant of $PdCl_4^{2-}$, a dominant complex in moderately saline fluids, are about two orders of magnitude higher according to Tagirov et al. (2013) than in the earlier study of Wood et al. (1992). The situation is much worse for Pd–bisulfide complexes, due to the scarcity of experimental data and the variety of experimental challenges encountered. Both groups proposed different predominating Pd–HS species. Consequently, if Pd solubilities in sulfur-rich solutions calculated on the basis of the earlier experimental studies by Gammons and Bloom (1993) and Pan and Wood (1994) are in reasonable agreement, those predicted using the data of Tagirov and Baranova (2009) are several orders of magnitude lower. Furthermore, the absence of $Pd(HS)_4^{2-}$ in the interpretation of experimental data (Wood et al., 1992; Tagirov et al., 2013) poses an interesting (geo)chemical conundrum, since the $PdCl_4^{2-}$ complex is acknowledged by all studies to be the most important complex in chloride brines (see also Bazarkina et al., 2014).

These discrepancies severely hinder our understanding of PGE mobility in hydrothermal fluids and the reliability of the predictions of numerical reactive transport modeling. For example, the conclusion of Barnes and Liu (2012) that the disturbance of Pd/Pt ratios in komatiite-hosted massive sulfide ores is due to bisulfide complexing of Pd during hydrothermal overprint is not consistent with the model of Tagirov et al. (2013); this illustrates that even first order predictions depend on the choice of the model. Consequently, it is desirable to use alternative experimental and/or theoretical approaches to investigate PGE speciation and solubility in hydrothermal fluids to confirm the available experimental data.

The geometrical properties of Pd–Cl complexes have been investigated by X-ray absorption spectroscopy (XAS) (Seward et al., 2002; Seward and Driesner, 2004; Bazarkina et al., 2014). Several theoretical studies have also investigated the structure of Pd(II) complexes using *ab initio* calculations on gas-phase molecules (Boily and Seward, 2005; Boily et al., 2007). Metal–ligand interactions (e.g., bond lengths) are generally well reproduced using Density Functional Theory (DFT) with current generalized-gradient exchange–correlation functionals. *Ab initio* MD was employed extensively to investigate the hydration of Pd^{2+} ions (e.g., Martínez et al., 2004; Hofer et al., 2007; Beret et al., 2008a,b; Bowron et al., 2011; Vidossich et al., 2011). The studies listed above found good agreement between the predicted and experimental structural properties investigated. The difference of Pd–O bond distances between theoretical studies and experiments (e.g., 2.01–2.04 Å from experiments versus 2.052/2.065 Å from *ab initio* calculation with B3LYP exchange–correlation functional, Boily and Seward, 2005) are inline with the expected accuracy of the DFT approach (e.g., Bühl et al., 2006).

Using *ab initio* MD simulations, we can also explore the thermodynamics of metal complexation at hydrothermal