Solubility of Palladium (Pd) in Hydrocarbons: Application to Ore Genesis

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In natural systems, the platinum group elements (PGE) are commonly associated spatially with hydrocarbons. For example, pyrobitumen in the Kupferschiefer, Poland, has been shown to have high concentrations of Pd and Pt [1]. Black shales in South China likewise have been shown to contain elevated Pd and Pt (0.4 ppm Pd and 0.3 ppm Pt in the Zunyi deposit) [2]. These observations and preliminary experiments showing that crude oils can dissolve metals to potentially exploitable concentrations, suggest that liquid hydrocarbons could constitute important ore fluids [3]. The objective of this research is to experimentally determine the solubility of Pd in selected organic compounds known to be important constituents of natural liquid hydrocarbons, and thereby contribute to the body of knowledge on ore forming processes involving hydrocarbons. Approximately 40 to 50% of crude oil is composed of paraffins, including straight chain alkanes. In view of this and the fact that Pd is known to have a strong affinity for sulphur (some crude oils contain appreciable sulphur), we have investigated the solubility of Pd in dodecane and dodecanethiol.

Our experiments were performed in light-weight titanium autoclaves treated with nitric acid to produce an inert internal surface coated with TiO_2, and involved measuring the solubility of palladium metal in dodecane and dodecanethiol at 150 °C. The durations of the experiments ranged from 15 to 60 days. After completion of an experiment, the autoclave was quenched, and samples of the quenched solutions, and solutions used to wash the autoclaves (Pd commonly precipitated on the surface of the autoclave), were analyzed for Pd using NAA.

The concentration of Pd in dodecane was 0.33 ppm ± 0.18 ppm and in dodecanethiol was 0.90 ppm ± 0.45 ppm. These data show that that Pd is very soluble in these simple analogues of natural liquid hydrocarbons at temperatures commonly encountered in oil reservoirs, and that its solubility may be increased by complexation with thiol groups. We therefore conclude that liquid hydrocarbons could be very effective agents of Pd transport. This and the observed close spatial association of Pd with hydrocarbons in some PGE deposits suggest that liquid hydrocarbons could be important ore fluids for these deposits.

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Exploration and enhancement of Sm/Nd carbonate geochronology

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Carbonate mineralization occurs across a broad spectrum of Earth’s environment. Direct dating of carbonate minerals has become an important goal. Prior work has used the ^{14}C, U-series, and U/Pb isotope systems, but all have limtations. The Sm-Nd system has rarely been attmepted because most carbonate has very low ^{147}Sm/^{144}Nd ratios (<0.2), indicating limited geochronologic potential. A handful of published studies [e.g. 1,2,3] suggest that some high (0.2 to >1.0) ^{147}Sm/^{144}Nd carbonates do exist and that meaningful age information can potentially be extracted. These studies use mild acids to extract multiple carbonate separates from a single vein or deposit.

Our preliminary work has focused on three samples: a metamorphic calcite vein from Vermont, a hydrothermal dolomite from an ultramafic hosted talc deposit, also from Vermont, and a siderite from the Copper Chief Mine in Arizona. All three samples were put through an 8-step sequential extraction procedure (5.0, 4.2, 3.9, 3.5pH acetic, glacial acetic, 1.5N HCl, conc. HNO_3, HF) to isolate a high ^{147}Sm/^{144}Nd reservoir within the carbonates. All leachates were analyzed for Sm/Nd isotopes and major and trace element concentrations. Differences in Ca, Mg, Mn, Fe, and Sr between each leachate show that they represent different reservoirs. Electron microprobe data confirms there is subtle compositional zoning within the carbonate, at the micron scale, in all three samples.

As with previous studies, there is scatter in our “isochron” data. A 9-point isochron for the Vermont calcite vein shows a ^{147}Sm/^{144}Nd range of 0.09884-0.21180 yielding an age of 386 ± 34 Ma (MSWD 4.7). The high MSWD implies that some leached material did not form in isotopic equilibrium with the concordant carbonate fractions and therefore does not belong on the isochron. Assuming most of the carbonate is dissolved in the pH-controlled acetic leachates, and discarding the stronger acid extractions, we calculate a 4-point isochron age of 353 ± 27 Ma (MSWD 1.17). This age agrees with a published monazite age of 352.9 ± 8.9 Ma from the same outcrop [4]. The same effect is seen with the Vermont dolomite sample: when all leachates are considered the isochron yields an age of 508 ± 93 Ma (MSWD 41), but if we eliminate the stronger acid leachates the age becomes 657 ± 62 Ma (MSWD 1.05). The low MSWD implies this is a reliable “isochron”, however the age is clearly older than Taconic or Acadian metamorphism expected for this sample. The siderite sample from Arizona shows a ^{147}Sm/^{144}Nd range of 0.21105-0.44711 and gives a reasonable Proterozoic age.

Our data shows that there are multiple chemical and isotopic domains present within each sample and our leaching procedure has begun to successfully isolate them. To refine sample selection and improve the reliability and precision of the carbonate ages, we are combining major and trace element data with electron microprobe images to identify the origin of the compositional variations and determine which acid extractions should be included in the isochron.

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