

Estimation and application of the thermodynamic properties of aqueous phenanthrene and isomers of methylphenanthrene at high temperature

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Abstract

Estimates of standard molal Gibbs energy (ΔG_f°) and enthalpy (ΔH_f°) of formation, entropy (S°), heat capacity (C_p°) and volume (V°) at 25 °C and 1 bar of aqueous phenanthrene (P) and 1-, 2-, 3-, 4- and 9-methylphenanthrene (1-MP, 2-MP, 3-MP, 4-MP, 9-MP) were made by combining reported standard-state properties of the crystalline compounds, solubilities and enthalpies of phenanthrene and 1-MP, and relative Gibbs energies, enthalpies and entropies of aqueous MP isomers from published quantum chemical simulations. The calculated properties are consistent with greater stabilities of the β isomers (2-MP and 3-MP) relative to the α isomers (1-MP and 9-MP) at 25 °C. However, the metastable equilibrium values of the abundance ratios 2-MP/1-MP (MPR) and (2-MP + 3-MP)/(1-MP + 9-MP) (MPI-3) decrease with temperature, becoming <1 at ~375–455 °C. The thermodynamic model is consistent with observations of reversals of these organic maturity parameters at high temperature in hydrothermal and metamorphic settings. Application of the model to data reported for the Paleoproterozoic Here's Your Chance (HYC) Pb–Zn–Ag ore deposit (McArthur River, Northern Territory, Australia) indicates a likely effect of high-temperature equilibration on reported values of MPR and MPI-3, but this finding is contingent on the location within the deposit. If metastable equilibrium holds, a third aromatic maturity ratio, $1.5 \times (2\text{-MP} + 3\text{-MP}) / (\text{P} + 1\text{-MP} + 9\text{-MP})$ (MPI-1), can be used as a proxy for oxidation potential. Values of $\log a_{\text{H}_2(\text{aq})}$ determined from data reported for HYC and for a sequence of deeply buried source rocks are indicative of more reducing conditions at a given temperature than those inferred from data reported for two sets of samples exposed to contact or regional metamorphism. These results are limiting-case scenarios for the modeled systems that do not account for effects of non-ideal mixing or kinetics, or external sources or transport of the organic matter. Nevertheless, quantifying the temperature dependence of equilibrium constants of organic reactions enables the utilization of organic maturity parameters as relative geothermometers at temperatures higher than the nominal limits of the oil window.

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1. INTRODUCTION

Hydrocarbons, in particular aromatic compounds, can persist in hydrothermal conditions and in the early stages

of rock metamorphism. Price (1993) reported the presence of naphthalene and biphenyl at 450 °C in aqueous–pyrolysis experiments and predicted that aromatic hydrocarbons might be found at low concentrations at higher temperatures, possibly preserved as inclusions in minerals that have undergone the early stages of rock metamorphism, potentially making organic compounds useful as geothermometers. Indeed, the relative abundances of specific aromatic compounds, known as maturity parameters, can

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be used to infer effects of past igneous and hydrothermal activity on organic-rich systems (George, 1992) and the history of possible ore-forming fluids (Püttmann et al., 1989; Chen et al., 2003; Mackenzie et al., 2008; Williford et al., 2011), but observed reversals or unexpectedly low values of these ratios at high maturity and/or temperature (George, 1992; Raymond and Murchison, 1992; Bechtel et al., 1995; Brocks et al., 2003a, and others) are not accounted for by existing theoretical models. The goal of the present study is to better understand the applications of the aromatic maturity ratios of phenanthrene (P) and methylphenanthrene (MP) in hydrothermal systems by estimating the high-temperature standard Gibbs energies of the species involved and comparing predictions made by thermodynamic calculations with published observations.

The thermodynamic modeling of maturity parameters actually invokes a metastable equilibrium, in which transformations are limited to certain classes of compounds, for example between P and MP. In a metastable equilibrium scenario (Shock, 2000), the organic molecules persist and react with each other over the time scale of interest, instead of transforming to the globally more stable methane, carbon dioxide, water and graphite in the system C–H–O (Shock and Helgeson, 1990; Holloway, 1984). It has already been established that metastable equilibrium states are attainable in hydrothermal systems containing organic molecules (Helgeson et al., 1993, 2009; Shock, 2000; Seewald, 2001). The thermodynamic parameters reported in this study can be used to predict the metastable equilibrium abundances of isomers of MP as a function of temperature as well as the abundance ratios for metastable equilibrium among P and isomers of MP by specifying oxidation–reduction potential in addition to temperature. The hypothesis of metastable equilibrium between isomers is tested using aromatic maturity ratios reported in bitumens extracted from the mineralized zones of the Here's Your Chance (HYC) Pb–Zn–Ag deposit at McArthur River, Northern Territory, Australia (Chen et al., 2003; Williford et al., 2011) and in samples from unmineralized but heated areas associated with regional metamorphism (Brocks et al., 2003a), near igneous intrusions (George, 1992), or in deeply buried sediments (George and Ahmed, 2002).

The metastable equilibrium model that is proposed provides a potential explanation for observed reversals of some aromatic maturity parameters at high temperature; to our knowledge such a model and its applications have not been described before. The equilibrium model is not applicable to all situations. For example, migration and transport from different sources and mixing of fluids on time scales shorter than those required for metastable equilibrium may be more important in particular samples. Even at high temperatures, alteration of the aromatic compounds during thermal cracking of reservoir petroleum may be primarily kinetically driven (Fusetti et al., 2010a,b). Where equilibration is possible, attainment or progression toward metastable equilibrium can occur through multiple mechanisms. It must be emphasized that the predictions of the equilibrium model carry no implications for mechanisms. Besides interconversion between isomers (transmethylation), preferential degradation or demethylation are other possible

pathways by which a metastable equilibrium distribution can be obtained.

The organic matter in some ore deposits, including the HYC deposit, likely results from hydrothermal alteration and transport in aqueous fluids, including potential ore-forming fluids (Brocks et al., 2003b; Chen et al., 2003; Williford et al., 2011; Greenwood et al., 2013). Despite the condensed or surface-bound nature of much sedimentary organic matter, quantifying the behavior of aromatic compounds dissolved in high-temperature aqueous fluids is important for understanding the sources and reactions of organic species in hydrothermal fluids (Price, 1993; Konn et al., 2012), the formation of petroleum in some environments by hydrothermal alteration of organic matter (Kawka and Simoneit, 1990; Ventura et al., 2012), possible formation via abiotic processes on other planets (Zolotov and Shock, 1999), and reactions occurring in hydrous pyrolysis experiments (Kawka and Simoneit, 1994; McCollom et al., 2001, 1999) and in industrial processes (Karásek et al., 2007). Therefore, the thermodynamic properties of aqueous solute species of P and MP are considered in this study. “High temperature” is used here to refer to temperatures exceeding the maximum for the oil window, which in this study is nominally taken to be 130–160 °C, as no single value is applicable to all systems (Hunt, 1996; Gize et al., 2000). Existing estimates of the high-temperature thermodynamic properties of pure crystalline and liquid isomers of MP are limited to the isomers denoted as 1-MP, 2-MP and 4-MP (Richard and Helgeson, 1998), but recent quantum chemical results for the aqueous species (Szczerba and Rospondek, 2010) also include 3-MP and 9-MP. Based on these and other available data, a compilation of thermodynamic parameters is presented here that may be used for estimates to ~500 °C of the aqueous-species standard Gibbs energies.

2. BACKGROUND

The structures of the species of interest in this study are shown in Fig. 1. In studies of organic maturation, these aromatic hydrocarbons are sometimes referred to as geomarkers (Simoneit, 2005), because the methylated products are formed through geosynthetic pathways, even though the precursor compounds may ultimately be derived from biological sources. Fig. 1 includes a simplified depiction of the major geosynthetic pathways. Geosynthetic pathways of methylation and isomerization of phenanthrene depend to varying extents on mineral catalysts and the energetics of the different isomerization reactions (Smith et al., 1995); in most cases the starting material is likely to be an α -methylated isomer (1-MP or 9-MP). 9-MP is an initial product of some geosynthetic pathways (Alexander et al., 1995). Application of the free valence number technique of Burkitt et al. (1951) shows that alkylation at position 1 is highly kinetically favored over 2 and 3 (Karr et al., 1967). 2-MP and 3-MP follow either by rearrangement (methyl shift) or are more susceptible to being formed by methylation at higher temperatures (Alexander et al., 1995; Smith et al., 1995).

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