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Applied Geochemistry

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

The stable isotope composition of vanadium, nickel, and molybdenum in crude oils



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ARTICLE INFO

Article history:

Available online 15 April 2015

Editorial handling by M. Kersten

ABSTRACT

Crude oils often have high concentrations of transition metals including vanadium (V), nickel (Ni), iron (Fe), and to a lesser extent molybdenum (Mo). Determining the conditions under which these metals enter into crude oil is of interest for the understanding of biogeochemical cycles and the pathways leading to oil formation. This study presents the first high precision measurements of V, Ni, and Mo stable isotopes determined for a set of globally distributed crude oils as a first examination of the magnitude of potential stable isotope fractionation. Vanadium stable isotope compositions are presented for crude oils formed from different source rocks spanning a range of geologic ages (Paleozoic–Tertiary) and are complemented by Ni and Mo stable isotope compositions on a subset of crude oils produced from lacustrine source rocks in the Campos Basin, Brazil. The crude oils span a wide range of V and Mo isotope compositions, and display more restricted Ni stable isotope signatures. Overall, the stable isotope composition of all three systems overlaps with previously determined values for igneous and inorganic sedimentary materials. Comparisons between vanadium concentration and stable isotope composition yield distinct clusters associated with crude oils predominantly derived from terrestrial/lacustrine or marine/carbonate source rocks. The Ni stable isotope signatures of studied crude oils are similar to that of carbonaceous shales. The Mo stable isotope signatures of the lacustrine sourced crude oils are similar to what is observed for rivers. This indicates trace metal stable isotopic composition of crude oils are unlikely to result from mass dependent fractionation associated with the generation, expulsion, and migration of petroleum and are instead primarily inherited from the initial sedimentary organic matter or metal bearing fluids present during metalation. In contrast, although Mo stable isotopes also span a wide range of values, they do not appear to be correlated with source rock lithology, perhaps suggestive of a greater role for secondary processes. Finally, both V and Ni stable isotope compositions co-vary with $V/(V + Ni)$, a commonly used parameter in determining crude oil grade. Since $V/(V + Ni)$ ratios reflect redox conditions, the correlation implies that stable V and Ni isotope compositions may also respond to the redox conditions of the depositional environment. The contrasting behavior of these three isotope systems in this initial dataset provides fundamental guidance for future investigation to fully exploit the potential of these new isotopic tracers. These isotope tracers can be developed to determine a broad range of factors fundamental to the formation and preservation of petroleum source rocks that spans from provenance evaluation to paleoredox chemistry.

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1. Introduction

Carbon, hydrogen, nitrogen, and sulfur isotopic compositions are commonly used to provide information about the source, maturity, and age of crude oils. More recently, radiogenic isotopes techniques including Re–Os and Sm–Nd have also been used to

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determine oil migration, geochronology and/or fingerprinting (e.g., Manning et al., 1991; Selby and Creaser, 2005). Crude oils are commonly enriched in transition metals such as V, Ni, and Mo (Aleshin et al., 1984; Amorim et al., 2007). Technical advances now allow the exploration of stable isotope compositions for these three elements in crude oils. Crude oils are ideal substrates to investigate transition metal isotope biogeochemistry due to their accessibility and extensive global occurrence. They represent the most pervasive reservoir of ancient marine and lacustrine sedimentary organic matter and serve as a window to the past with existing crude oils having been formed from sedimentary rocks as old as the Neoproterozoic (e.g. Fowler and Douglas, 1987).

A long research history surrounds the elemental analysis of transition metals in crude oils and considerable progress has been made in understanding how these metals become incorporated into carbonaceous materials (Treibs, 1934, 1936; Hodgson, 1954; Yen, 1975; Lewan and Maynard, 1982; Lewan, 1984; Barwise and Roberts, 1984; Barwise, 1990; Louda et al., 1998; Premovic et al., 2000a; Duyck et al., 2007; Amorim et al., 2007). Vanadium, Ni, and to a lesser extent Mo are the best understood of these metals (Williams and Fraústo da Silva, 2002; Bellenger et al., 2008). Vanadium, Ni, and Mo enter the hydrosphere through continental weathering, volcanic ash and aerosols, and from hydrothermal vent systems (Fig. 1; e.g. Wedepohl, 1971, 1991; Tribouillard et al., 2006). These metals naturally form a variety of metal complexes in terrestrial and marine environments (Wehrli and Stumm, 1989) that are mediated by the valence state and therefore redox conditions of the water column and sedimentary pore water (Fig. 1; Emerson and Huestes, 1991) or as a function of biological respiratory processes (e.g. Rehder, 2000).

Vanadium, Ni, and Mo have different oxidation states in surface or near surface environments (Fig. 1). Vanadium mainly occurs as a quadrivalent metal in the form of a vanadyl (VO^{2+}) ion in environments that are moderately reducing (0.5 to -0.2 Eh Volts) and within normal pH (4–7) conditions typical for environments where carbonaceous sediments accumulate. Under these conditions the cation is readily hydrolyzed and strongly adsorbs onto particles to form stable complexes with humic acids and porphyrins (Wehrli and Stumm, 1989). Nickel and Mo are also preferentially concentrated in organic-rich sediments under reducing conditions. Nickel speciation is primarily Ni^{2+} or as NiS within sulfidic environments. Under oxic conditions at oceanic pH levels, Mo is present as soluble molybdate (MoO_4^{2-}). With reducing conditions in the presence of low sulfide concentrations, Mo is converted to particle-reactive thiomolybdate complexes, which leads to the primary mechanism for authigenic Mo enrichment in reducing

sediments (Fig. 1; Erickson and Helz, 2000; Helz et al., 1996; Manheim, 1974; Emerson and Huestes, 1991). For euxinic settings, when H_2S concentrations in the water column exceed $11 \mu\text{mol L}^{-1}$ $\text{H}_2\text{S}_{\text{aq}}$, Mo is completely transformed into Mo-sulfide (+4) (Neubert et al., 2008a,b). However, these differences in oxidation chemistry only partially control organic matter metalation.

Conventionally accepted pre-oil forming metalation pathways involve the sequestration of transition metals into specific classes of compounds called metallo-porphyrins, the most well recognized being vanadyl and Ni porphyrins (Treibs, 1934, 1936; Barwise and Roberts, 1984; Louda et al., 1998). These structurally labile geoporphyrins are initially derived from bacterial and plant pigments such as Chlorophyll *a* (e.g. Treibs, 1934, 1936; Baker and Palmer, 1978; Louda et al., 1998; Lipiner et al., 1988). The Mg^{2+} ion of Chlorophyll *a* is replaced by hydrogen during transport through the water column. During early to late diagenesis Ni and V become ligated to the tetrapyrrole structure (Louda et al., 1998). In this way, upwards of 50% of the total vanadium content can be locked within porphyrins (Premovic et al., 2000a, 2002) with the remaining chelates likely being comprised of cracked porphyrins, metal-binding non-porphyrin species (Filby, 1975, 1994; Fish and Komlenic, 1984; Fish et al., 1984), and naphthenic acid salts (Marquez et al., 1999; Varadaraj and Brons, 2007).

The initial metal source of porphyrins is unclear. Incorporation of VO^{2+} and Ni^{2+} into porphyrins may result from diffusion into organic-rich sediments from the overlying water column (Lewan and Maynard, 1982) or through oil–rock and/or water–rock interactions within the subsurface (Yen, 1975; Barwise, 1987, 1990). Potential sources may also extend to deposition of sedimentary organic matter enriched in organisms that preferentially extract these metals from the environment. For example, Mo is a common respiratory pigment in nitrogen fixation (Williams and Fraústo da Silva, 2002; Bellenger et al., 2008), while Ni forms a part of urease, an enzyme necessary for organisms utilizing urea as a nitrogen source (Ragsdale, 2007). Vanadyl may initially come from the vacuoles of certain marine tunicates, which accumulate V to a level that is more than 100 times greater than what is naturally present in seawater (Macara et al., 1979; Oltz et al., 1988).

Post-oil forming pathways for enrichment include metals sourced from microscopic inclusions of sediment and brines or by direct scavenging from the bedrock via fluid/rock, oil/rock, and oil/fluid interactions. These processes can occur during burial, catagenesis, migration, and entrapment within the reservoir (Fig. 1; Hodgson, 1954; Witherspoon and Nagashima, 1957; Al-Shahrastani and Al-Atyia, 1972). Elevated transition metal concentrations may also be due to volumetric losses of aliphatic

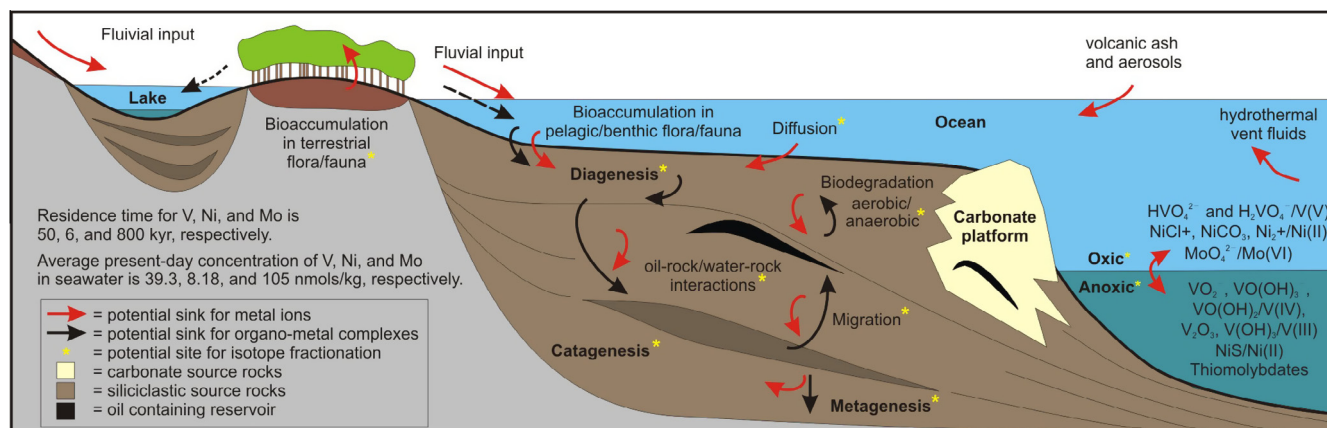


Fig. 1. Sources and sinks of metal ions and organometallic complexes as organic matter becomes buried, cracked to oil, migrated and then biodegraded. Arrows indicate potential sites of metal enrichment. Stars denote potential sources of isotope fractionation. Residence time and average concentration data from Tribouillard et al. (2006).

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