Chemical Geology 356 (2013) 76–93

Contents lists available at ScienceDirect

Chemical Geology

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

Minor and trace element and Re–Os chemistry of the Upper Devonian Woodford Shale, Permian Basin, west Texas: Insights into metal abundance and basin processes

Nicholas B. Harris [a,b,*], Cheryl A. Mnich [b,1], David Selby [c], Dieter Korn [d]

[a] Department of Earth and Atmospheric Sciences, University of Alberta, 1-26 ESB, Edmonton, Alberta T6G 2E3, Canada
[b] Department of Geology and Geological Engineering, Colorado School of Mines, Golden, CO 80401, USA
[c] Department of Earth Sciences, Durham University, Durham DH1 3LE, UK
[d] Museum für Naturkunde, Leibniz Institute at the Humboldt University Berlin, Invalidenstraße 43, D-10 115 Berlin, Germany

ARTICLE INFO

Article history:
Received 29 July 2012
Received in revised form 19 July 2013
Accepted 22 July 2013
Available online 31 July 2013

Editor: U. Brand

Keywords:
Black shales
Hydrocarbon source rocks
Paleoceanography
Redox conditions
Trace elements
Frasnian–Famennian boundary

ABSTRACT

The trace and minor element and Re–Os geochemistry of the Upper Devonian Woodford Shale are analyzed in order to characterize elemental abundances, to identify associations among trace elements and to constrain paleoceanographic conditions and depositional processes. This organic-carbon-rich mudstone in the Permian Basin, west Texas, is a major source of hydrocarbons in the basin and is coeval with many other Upper Devonian shales in North America.

The Woodford lacks enrichment in many trace metals. Only Mo, U, S and Se are significantly enriched. Other redox sensitive elements are depleted or similar to average shale composition, including Pb, Bi, Cr, Ti, Cu, Zn, Co, and V. Elements associated with granitic sources such as rare earths, Th, Ce, and TiO_2 are also depleted relative to average shale; this appears to be related to be a source control. A strong basin reservoir effect is noted among several redox sensitive elements, including Mo, Cu and Ni, which largely accounts for the depletion. Dilution by biogenic silica had an additional effect on metal concentrations. Multivariate factors analysis identified associations between elements, including groupings of: rare earth elements; elements enriched in granitic crust; silica, varying antithetically with elements in carbonate minerals; organic carbon, Mo and U; V; phosphate; Fe and S. Noteworthy among the results are the different behavior of redox-sensitive elements, suggesting different precipitation mechanisms or varying dependence on reservoir effects.

A strong redox effect is noted in the TOC/P_{tot} ratio at approximately the Frasnian–Famennian boundary, indicating an abrupt transition to an anoxic column boundary that coincides with a short-term significant fall in sea level. This suggests that anoxia was induced by isolation of the basin from the global ocean. However with the exception of the uppermost Famennian, initial $^{187}Os/^{188}Os$ values determined from Re–Os geochronology for the Permian Basin are similar to correlative sections of the Appalachian and Peace River Basins of North American and the Rhenohercynian basin of Europe. This indicates that although the Permian Basin became restricted during the upper Devonian and early Mississippian, ocean connectivity remained between regional and global basins.

1. Introduction

Organic-carbon-rich mudstones, so-called 'black shales', are generally regarded as enriched in many trace metals and, in fact, are significant economic resources of U, Mo, Ni, Mn, V, Hg, Sb, Au, and W. Enrichment results from the potent reduction capacity associated with high reactive organic carbon content and the decreased solubility and increased reactivity of metals under reducing conditions; organic matter also provides reaction pathways for fixing metals. However, metal abundance in mudstones also depends on sources of metals, which may be derived from the global ocean through hydrothermal processes at mid-ocean spreading centers or from detrital or chemical weathering and transport from continental sources. Where exchange of water masses between a basin and the global ocean is restricted, possibly the case in some black shale basins, that may be indicated by anomalously low trace metal concentrations.

We examine trace element abundances and associations in the Woodford Shale, an Upper Devonian to Lower Mississippian organic carbon-rich mudstone in the Permian Basin, west Texas. The Late

* Corresponding author at: Department of Earth and Atmospheric Sciences, University of Alberta, 1-26 ESB, Edmonton, Alberta T6G 2E3, Canada.
E-mail addresses: nharris@ualberta.ca (N.B. Harris), cheryl.mnich@conocophillips.com (C.A. Mnich), david.selby@durham.ac.uk (D. Selby), dieter.korn@mfn-berlin.de (D. Korn).
[1] Now at: ConocoPhillips (United Kingdom), Rubislaw House, Anderson Drive, Aberdeen AB15 6FZ, Scotland.

0009-2541/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemgeo.2013.07.018

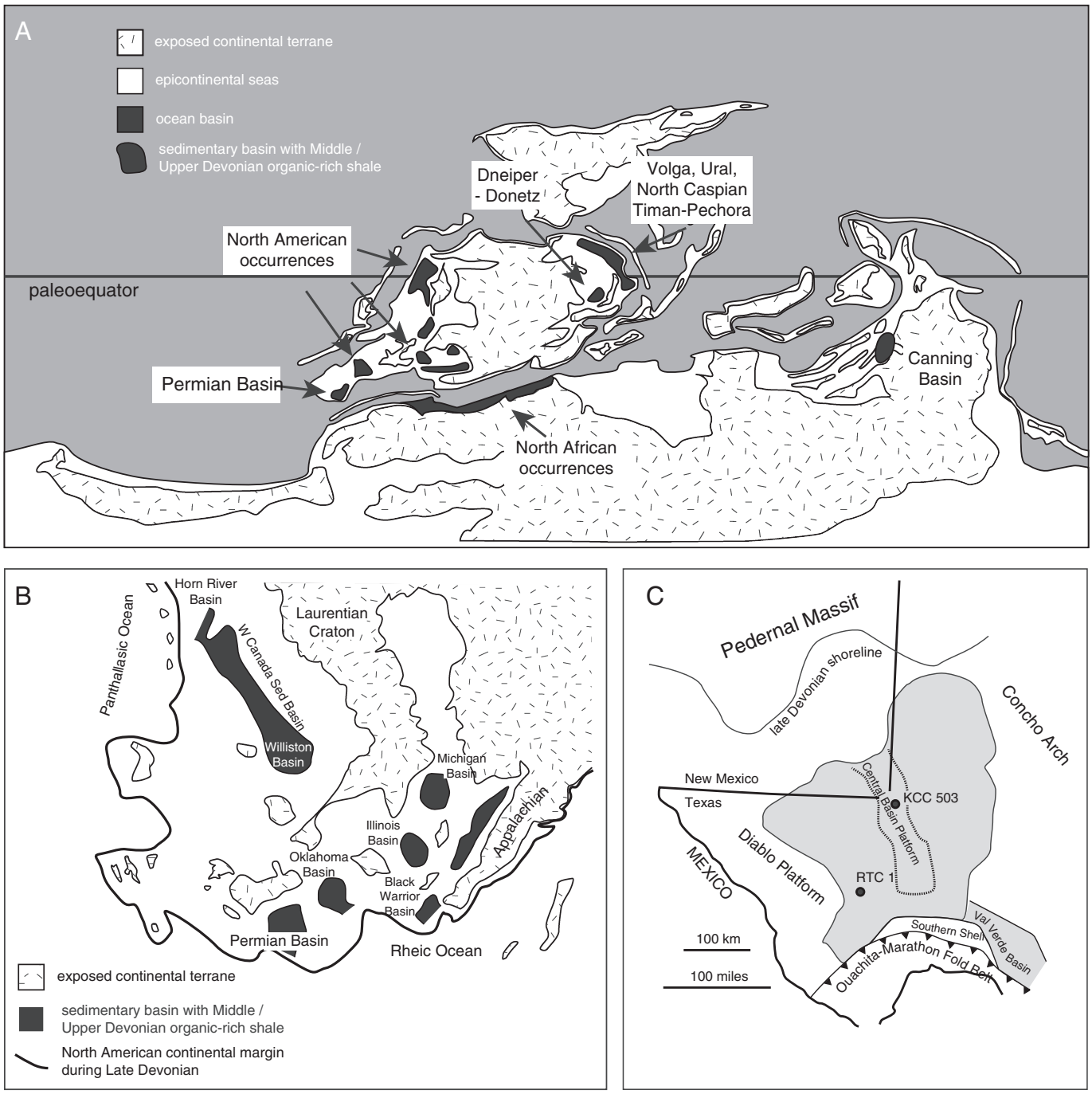

Fig. 1. A. Map of configuration of the continents at 370 Ma, modified after Colorado Plateau Geosystems Inc. (2012a), showing locations of Middle and Upper Devonian organic-rich shale formations. Location of North African shale formations from Lüning et al. (2003) and Australian and eastern European occurrences after Klemme and Ulmishek (1991). B. North American continent at 365 Ma, modified after Colorado Plateau Geosystems Inc. (2012b). Sedimentary basins with Middle or Upper Devonian organic-rich shale formations are highlighted. C. Map of the Permian Basin, showing the locations of the two cores described here. Modified after Comer (1991).

Devonian was noteworthy both for the global deposition of organic-carbon-rich shales (Fig. 1A) and for instability in a number of marine geological and geochemical parameters. It includes the famous Frasnian–Famennian boundary, which marks one of the great extinction events in the Phanerozoic (Hallam and Wignall, 1997), although Schindler (1993) noted that the 'crisis' may in fact comprise a series of extinctions spaced over a period of one million years. Geochemical fluctuations have been documented during this time, including positive perturbations of +4 to +6‰ in $\delta^{13}C_{carb}$ (Saltzman, 2005), interpreted to be the result of enhanced phosphate (nutrient) flux to the photic zone due to extreme anoxia. The Late Devonian also had a distinctive paleogeography, with large areas of epicontinental seaways and continental sags in present-day North America (Algeo et al., 2007), Europe and Australia. In this configuration, even relatively small sea level fluctuations could have had a profound effect on both the stratigraphy and geochemistry of sediments deposited in these basins.

In this study, we compare analyses from two long cores to average shale values to determine which metals are, in fact, enriched. We then apply factor analysis, a multivariate statistical technique, to the whole rock geochemical data to identify associations between elements that aid in interpretations of redox conditions, metal fixation and metal sources. Factor analysis seeks to reduce the dimensionality of a data