A new conceptional model: Reconstruction of freshwater incursions in stratified marine paleoenvironments in Late Devonian extinctions

S. TULIPANI[1], K. GRICE[1]*, P. GREENWOOD[1,2], L. SCHWARK[1,3] AND R. SUMMONS[4]

[1]WA-Organic & Isotope Geochemistry Centre, Curtin University, GPO Box U1987, Perth, WA 6845, Australia (*correspondence: k.grice@curtin.edu.au)

[2] Centres for Exploration Targeting & Biogeochemistry, University of Western Australia, 35 Stirling Highway, Crawley WA 6009Australia

[3] Institute of Geoscience, Kiel University, Ludewig-Meyn Str. 10, 24118 Kiel, Germany

[4] Department of Earth, Atmospheric & Planetary Sciences, MIT, E25-633, 45 Carleton Street Cambridge, MA 02139 USA

One of the biggest mass extinctions in Earth's history took place in the Late Devonian. The most well know event occurred at the Frasnian – Famennian boundary, but there were also major biodiversity crises towards the end of the Givetian and Famennian time periods.

Here we present a novel biomarker approach using methyltrimethyltridecylchromans (MTTCs) as indicators of freshwater incursions and terrigenous input to a Late Givetian/Early Frasnian marine palaeoenvironment [1]. The abundance of gammacerane and *Chlorobi* biomarkers furthermore indicated persistent water-column stratification and prevailing photic zone euxinia. MTTCs are isoprenoid substituted aromatic compounds which are established palaeosalinity indicators [2]. Nevertheless, their source and formation pathway remain unknown. Our data would be consistent with an origin from early diagenetic condensation reactions of phytol with alkyl phenols (from higher plant sources) as it has been suggested previously by Li *et al*. [3].

[1] Tulipani *et al*. (2013) *Geology*, in prep. [2] Schwark *et al*. (1998), *Org. Geochem*. 29, 1921-1952. [3] Li *et al*. (1995) *Org. Geochem*. 23, 159-167.

Recent groundwater circulation of U at Forsmark, eastern Sweden

E-L. TULLBORG[1]*, J. SUKSI[2], B. SANDSTRÖM[3], A. B. MACKENZIE[4], J. SMELLIE[5], L. KRALL[6] AND I. PUIGDOMENECH[6]

[1]Terralogica AB, Gråbo, Sweden, *(evalena@terralogica.se)

[2]Laboratory of Radiochemistry, Helsinki University, Finland

[3] WSP Group, Gothenburg, Sweden,

[4]SUERC, East Kilbride, Scotland, UK

[5]Conterra AB, Stockholm, Sweden

[6]SKB, Stockholm, Sweden

Uranium in groundwaters commonly shows a trend of decreasing concentration with depth due to the chemical reactivity of recharging waters, rich in O_2 and CO_2, which promotes U mobility by oxidising U(IV) to U(VI) and by carbonate complexation. Towards depth, the redox potential drops, U is increasingly reduced to the more insoluble U(IV) form, and U concentrations decrease. However, carbonate complexation may enable dissolved U(VI) to exist to greater depths in even mildly reducing conditions. Such is demonstrated in the crystalline bedrock aquifer of the Forsmark area, where elevated U concentrations (10 to 170 μg/L) are found in several borehole sections at depths down to 600 metres. These concentrations are generally associated with Brackish-type groundwaters which are not oxidising but show Eh > −190 mV and bicarbonate contents >30 mg/L. It can, however, be concluded that this water has not transported U into the bedrock aquifer, but rather has mobilised an easily dissolvable uranium phase present along some of the water conducting fractures. The $^{234}U/^{238}U$ activity ratios (AR) in the groundwaters are within the range 2 to 6 and the samples with the highest U contents tend to show the lowest $^{234}U/^{238}U$ AR ($\leq$ 3). Annual sampling (from 2005 to 2012) in some borehole sections with elevated U, has shown the $^{234}U/^{238}U$ AR to be very stable and unique for each specific fracture groundwater and most probably also for the dissolved phase. Because the suspected source is hosted in the fracture fillings, the water/fracture mineral interaction is also studied using U-series measurements on the mineral phase. The results support a complex pattern of leaching and redeposition of U in many of the studied fractures during the last 1.5 Ma, whereas others show only small or insignificant deviations from equilibrium. Together these results support the very inhomogeneous distribution of flow paths typical for crystalline bedrock and previously interpreted in the Forsmark area.

An understanding of the geologically late (<1.5 Ma) behaviour of U in the groundwater can help to interpret the groundwater circulation and find the most important water pathways during this period. The changes in groundwater composition and redox conditions have caused both mobilisation and deposition of U, and it is possible to trace both processes in one and the same fracture sample.

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