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# Crocetane a marker for photic-zone euxinia in Devonian source rocks (Duvernay Formation, Western Canada Sedimentary Basin) and crude oils

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Crocetane, an irregular $C_{20}$ isoprenoid in sediments associated with gas hydrate settings, methane vent ecosystems and methane-rich-mud volcanic sediments, is a molecular indicator for the anaerobic oxidation of methane. This compound has been detected in sediments comprising archaea mediating oxidation by reverse methanogenesis in co-operation with sulfate reducing bacteria (e.g. Thiel et al., 1999). In anoxic environments, crocetane has a $^{13}$C depleted carbon isotopic signature (e.g. -150$\%_{,}$) consistent with a biogenic methane source. Moreover, crocetane has been previously reported in Western Australian crude oils from the Canning Basin (Devonian age) (Barber et al., 2001 and Greenwood & Summons, 2003). However, the discrete source of crocetane in Devonian samples and especially crude oils remains uncertain.

Photosynthetic green/brown sulfur bacteria (GSB) are the ultimate source for aromatic carotenoids (e.g. isorenieratane) in sedimentary environments. They are strict anaerobes that require light and hydrogen sulfide in stratified water columns to carry out photosynthesis. Aromatic carotenoids with $^{13}$C enriched isotopic signatures are accepted as indicative markers for photic-zone euxinia (PZE) in depositional environments. Biomarkers derived from GSB in sediments spanning the P/Tr event (Western Australia) have been recently reported (Grice et al., 2005).

The present study comprises a detailed molecular study of crocetane and GSB-derived

carotenoids in Devonian sediments (Duvernay Formation) of the Western Canada Sedimentary Basin (WCSB, Devonian) covering a range of thermal maturities. In addition, a series of oils generated from Devonian source-rocks of the basin have been analysed for crocetane. Crocetane was found to be present throughout the WCSB and all crude oils of Devonian age of the basin and of Canning basin in WA. Its abundance was found to increase with thermal maturity.

Crocetane is proposed to be as a diagenetic product of isorenieratane/ene from GSB based on its structural similarities to carotenoids of GSB. Crocetane is therefore a new marker of these specialised conditions. Crocetane can still be identified in samples that have undergone significant thermal maturity and provides evidence for PZE conditions in highly matured samples, especially those spanning the Frasnian/Fammenian boundary. Interestingly, the highest abundances of PZE markers are recorded in the Larapintine petroleum system, Australia, which includes Late Devonian reef complexes. There appears to be a relationship between the origin of the biomarker crocetane and the pervasiveness of PZE conditions throughout certain periods of geological time.

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