INVESTIGATION OF A THERMAL EFFECT ON REARRANGED HOPANES

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Hopanes are ubiquitous compounds in sediments and crude oils, and are widely applied as biomarkers for geochemical studies on petroleum source rocks and oils. Rearranged hopanes (including Ts, C_{29}Ts, and C_{29} and C_{30} 17α-diahopanes; Fig 1) have not only been used to distinguish various petroleum source rock facies, especially those with clay-mediated acid catalysis, but are also regarded as thermal maturity parameters for hydrocarbon source rocks and crude oils (Moldowan et al., 1991; Farrimond and Telnæs, 1996). However, it is still controversial how their concentrations are affected by depositional environment (fresh, brackish or saline water), thermal maturity (immature, oil-window or over-mature), organic input (e.g., red algae or bacteria) and clay catalysis (illite, montmorillonite or kaolinite). There are four series of rearranged hopanes that have been identified in hydrocarbon source rocks and crude oils from several basins in China, e.g. Songliao Basin, Tarim Basin, Sichuan Basin, Bohai Bay Basin and Erdos Basin (Zhang et al, unpublished data). Investigation of vitrinite reflectance (R_o) and rearranged hopane abundance for hydrocarbon source rocks from Songliao, Tarim and Erdos basins showed that these have a Gaussian relationship (Fig. 1a). In general, the abundance of rearranged hopanes increases in concentration from immature samples to a peak in the oil window, corresponding to Ro = ~0.8-0.9%, followed by a decrease with further increasing thermal maturity. In order to investigate the thermal effect on rearranged hopanes, an immature mudstone source rock in Well PL-1 (Depth: 3265m; R_o: 0.44%; TOC: 1.97%; HI: 564.47mg/g) from Bohai Bay Basin was chosen to conduct a thermal simulation experiment in an open system (experimental conditions were as Li et al., 2007). The laboratory temperatures chosen were 250, 275, 300, 325, 350 and 400°C, corresponding to R_o values of approximate 0.74, 0.83, 0.95 1.05, 1.25 and 1.78% respectively. Aliphatic hydrocarbons separated from both the expelled oils and the residual oils on different temperatures were analysed by gas chromatography-mass spectrometry.

The ratios of rearranged hopanes to hopanes in the residual oils fluctuate with temperature (Fig. 1b, top). Their ratios increase slightly from the starting composition to 275°C, drop to a minimum at 325°C, and then increase from 325 to 350°C, and further increase very markedly to 400°C. Similar trend is noted for the expelled oils (Fig. 1b, bottom). Apart from a slight drop for Ts/Tm from 250 to 275°C, the ratios of rearranged hopanes to hopanes generally increase slightly to 275°C and then decline to 300°C. At higher temperatures the ratios for the expelled oils are variable and then increase to 400°C, although a lesser degree than for the residual oils.

Combined with variations in the absolute concentrations, the aliphatic and aromatic thermal maturity parameters and R_o analyses, it is reasonable to draw the conclusion that thermal maturity has a considerable effect on the abundance of rearranged hopanes. Rearranged hopanes can be formed both during the immature to oil window stage, as well as at higher mature stage, but the former is their dominant formation stage in which alteration of hopanoid precursors probably contribute to their abundance. Nevertheless, the increase in

their abundance in the over-mature stage is possibly attributed to the products from the pyrolysis of hydrocarbons and the rearrangement of regular hopanes. Interestingly, the increasing rate of the relative concentrations is more obvious in the residual oils than in the expelled oils within over-mature stage. The hypothesis that clay minerals could act as catalysts in their formation is consistent with the data from R_o and these heating experiments, but more researches needs to be carried out.

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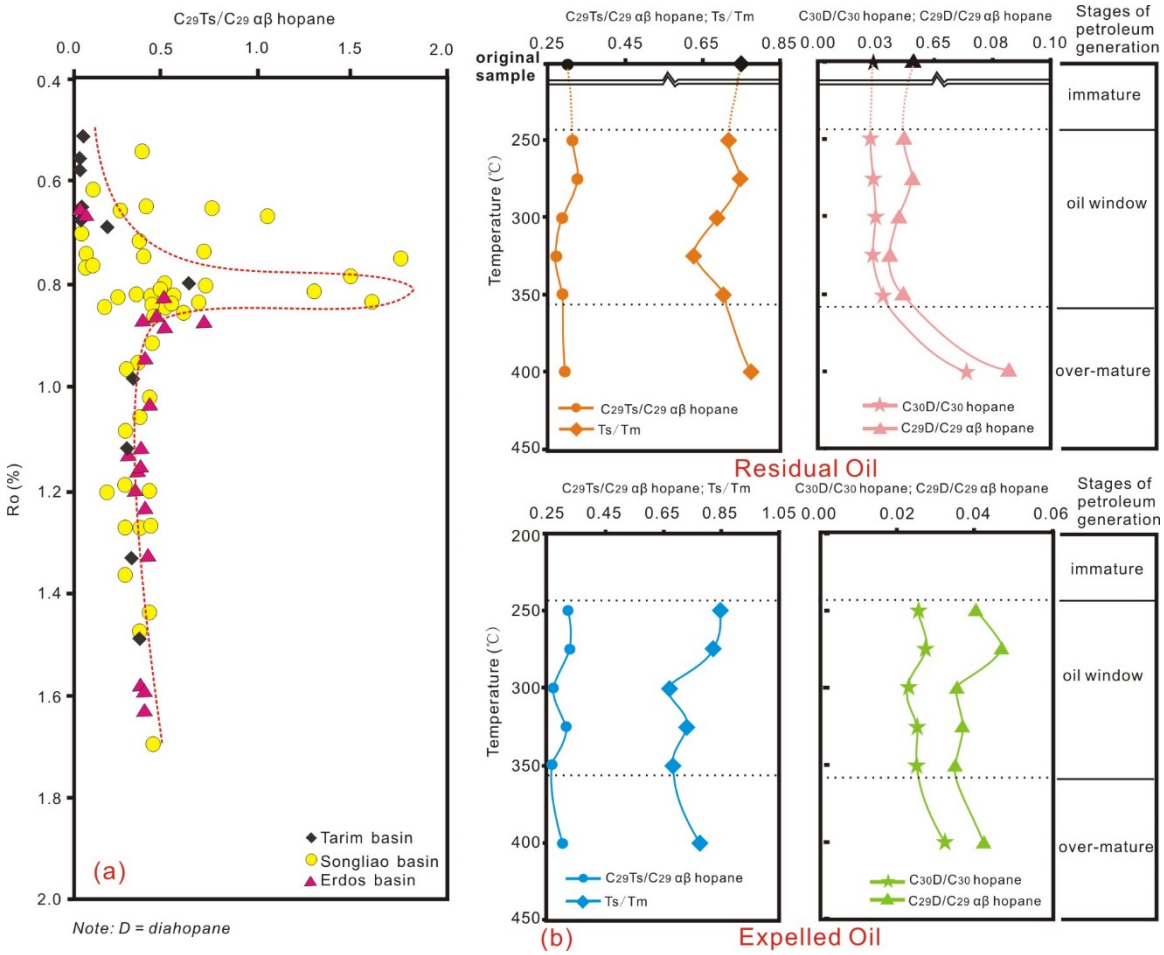

Fig. 1 The variation of ratios of rearranged hopanes to hopanes in the residual and expelled oils with increasing temperature