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**Natural Occurrence of Higher Thiadiamondoids and Diamondoidthiols in a Deep
Petroleum Reservoir in the Mobil Bay Gas field: Indication of Thermochemical Sulfate
Reduction**

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Thermochemical sulfate reduction (TSR) involves a complex series of redox reactions that occurs in hot (~ >120°C) carbonate reservoirs whereby petroleum is oxidized by sulfate forming primarily H₂S, CO₂, and an insoluble, highly sulfur-enriched and largely polynuclear aromatic organic solid. Incomplete and back reactions between hydrocarbons and the generated sulfide form organic sulfur compounds including thiophenes (Cai et al., 2003) and reactive sulfur species, such as mercaptans (thiols) and sulfides (Zhang et al., 2008a, 2008b; Amrani et al., 2008). In particular, tricyclic sulfides with diamondoid structures, called thiadiamondoids, are formed during this process. TSR is thought to be the only process that can generate significant quantities of thiadiamondoids via sulfurization of their parent diamondoids (Wei et al., 2007). As a result, thiadiamondoids are molecular indicators of TSR.

Like diamondoids, thiadiamondoids and diamondoidthiols also have a series of compound clusters with different numbers of adamantane cages. Lower thiadiamondoids (thiaadamantanes, thiadamantanes and thiatriamantanes) are generally orders of magnitude more abundant than higher forms. In this study, a series of higher thiadiamondoids and diamondoidthiols, including thiatetramantanes, tetramantanethiols, thiapentamantanes, pentamantanethiols, thiahexamantanes, hexamantanethiols and thiacyclohexamantane, was discovered in a gas condensate produced from a very deep petroleum reservoir in the Mobile Bay gas field, located offshore Alabama in the northern Gulf of Mexico, USA. This appears to be the first reported natural occurrence of these compounds. Several isomers of higher thiadiamondoids and diamondoidthiols were identified using full scan gas chromatography-mass spectrometry (GC-MS) coupled with GC-sulfur chemiluminescence detection (GC-SCD) and GC×GC-time of flight mass spectrometry (GC×GC-TOFMS). These higher thiadiamondoids and diamondoidthiols are associated with abundant lower homologues including thiaadamantanes, thiadamantanes, thiatriamantanes and their thiol groups. It is speculated that similar to lower thiadiamondoids and diamondoidthiols, higher ones are possibly formed from the sulfurization of their precursor diamondoids during TSR, a conclusion supported by the occurrence of open-cage higher diamondoidthiols and sulfur isotopic data of higher thiadiamondoids and diamondoidthiols isolated from the Mobile Bay condensate. The presence of higher thiadiamondoids and diamondoidthiols is indicative of the occurrence of TSR and can be used to predict sour gas production. In addition, higher thiadiamondoids and diamondoidthiols have the potential to serve as markers for liquid phase migration of TSR-related oil where the lower

species may be perturbed by phase fractionation and differential migration of the gas and liquid phases.

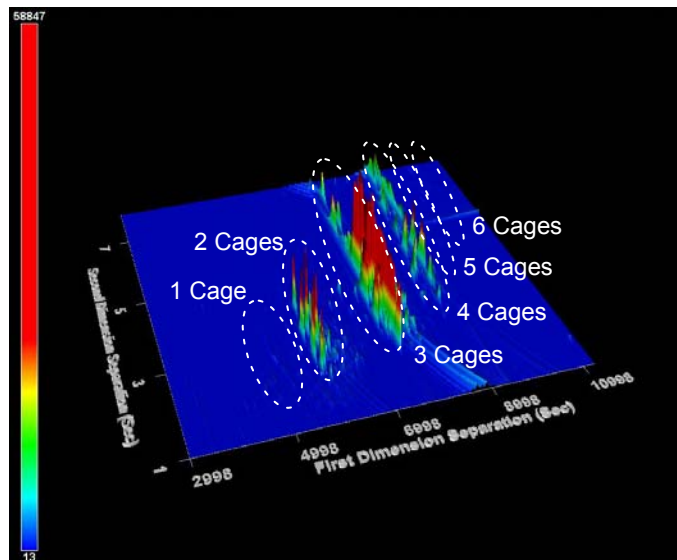


Figure 1. GCxGC-TOF/MS surface image of thiadiamondoids and diamondoidthiols ranging from one to six cages in a concentrated Mobile Bay condensate.

- 1 Cage: thiaadamantanes and adamantanethiols;
- 2 Cages: thiadamantanes and diamantanethiols;
- 3 Cages: thiatriamantanes and triamantanethiols;
- 4 Cages: thiatetramantanes and tetramantanethiols;
- 5 Cages: thiapentamantanes and pentamantanethiols;
- 6 Cages: thiahexamantanes, thiacyclohexamantane and hexamantanethiols.

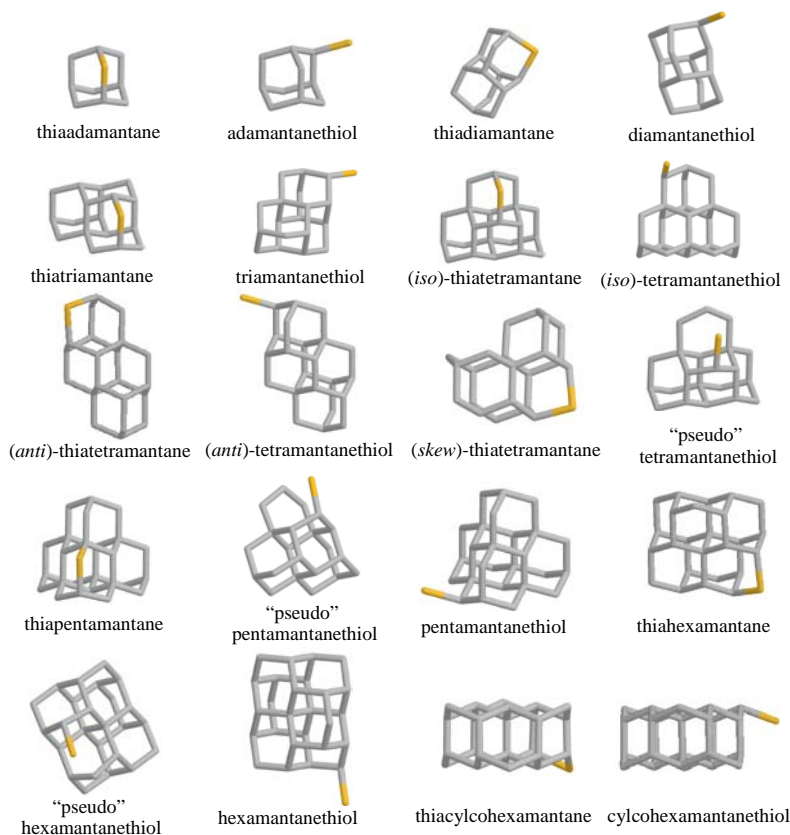


Figure 2. Chemical structures of lower and higher thiadiamondoids and diamondoidthiols.

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