



## News &amp; Views

# Hydrothermal conversion of hydrocarbons to heterocyclic compounds by geological supercritical CO<sub>2</sub> volatiles

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In order to assess the dynamics of molecular conversion, scientists simulated the low-temperature synthesis of polycyclic aromatic hydrocarbons (PAHs) in Titan's atmosphere [1], and noticed the transformation (hydrogenation, oxygenation, and hydroxylation to complex molecules) of PAHs under interstellar medium conditions. Geological hydrothermal systems have also drawn attention as potential key sites for various organic synthesis and transformation reactions [2,3]. Thus the formation of abiotic CH<sub>4</sub> [4], which has proven to be an important component of deep hydrothermal fluids that are generated outside the temperature regime envisaged for thermogenic gases, have long been reported in a range of global hydrothermal sites, including mid-ocean ridges, continental rifts, pre-orogenic and subduction zones, back-arcs, hot springs, and volcanically-active areas. These transformation processes have been suggested to occur at the water-mineral interface. There is compelling evidence for the generation of C–H chain molecules from inorganic chemicals via abiotic reactions (e.g., Fischer-Tropsch synthesis of CH<sub>4</sub>) in laboratory and field studies [5,6]. However, a huge gap remains in the understanding of carbon and hydrogen evolution and heterocyclization from C–H chain molecules to complex heterocyclic materials and then possible hydrophobic or hydrophilic macromolecules, and the corresponding reaction mechanism(s). The occurrence of abundant and complex heterocyclic molecules formed through abiotic processes is rare in natural regions associated with deep fluid movement and activity.

Recently, organic molecules in liquid hydrocarbons and rocks associated with deep-sourced CO<sub>2</sub>-rich gases have been reported in the Huangqiao region of the Tancheng-Lujiang deep-faulted area of eastern China. These samples have distinct unresolved complex mixture (UCMs) and abundant heterocyclic molecules, which increase in abundance with increasing hydrothermal effect (Fig. 1), in stark contrast to normal thermogenic organic molecules. Indeed, their distribution patterns resemble those observed in other known submarine hydrothermal systems. Hydrothermal

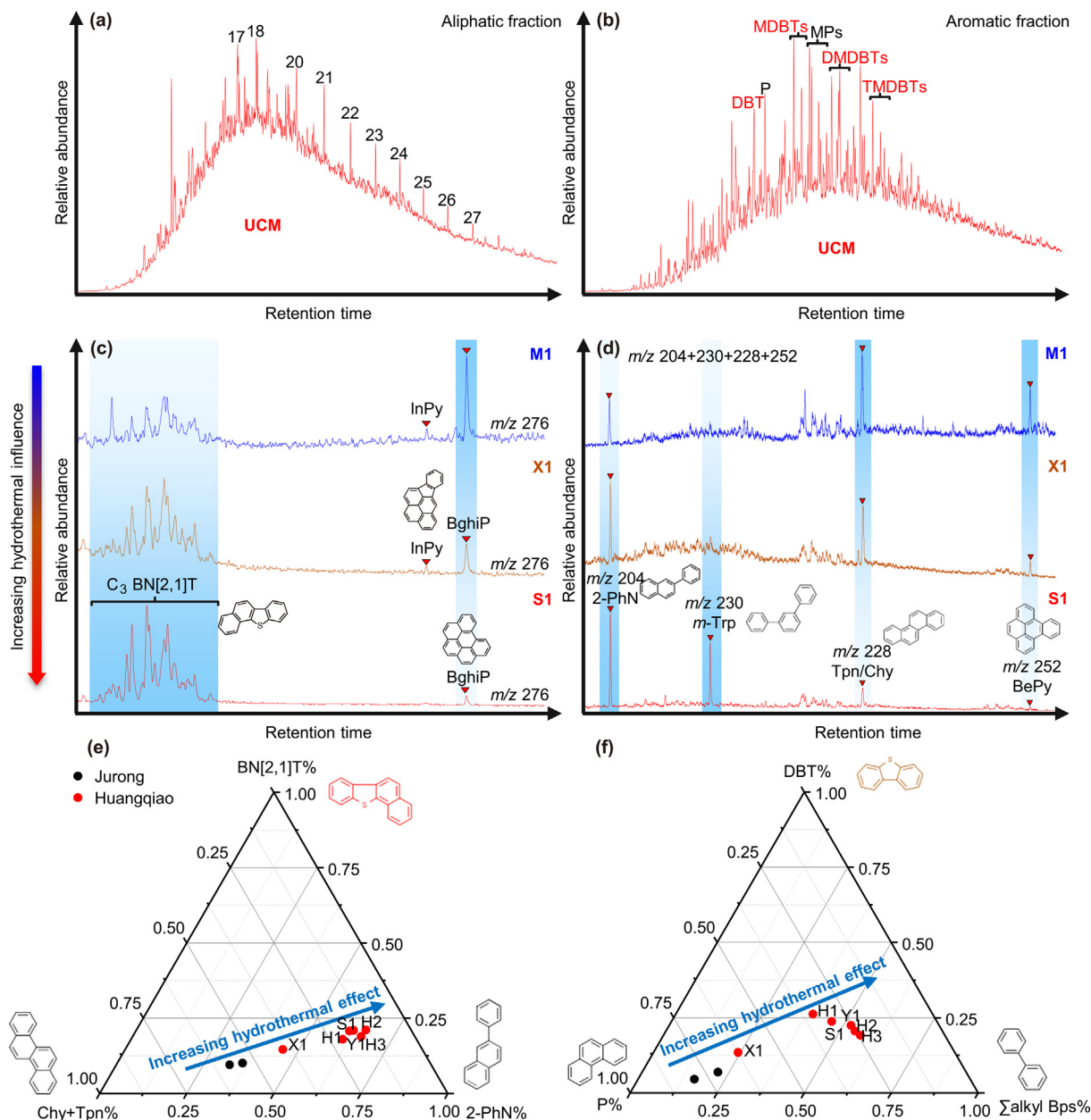
alteration of organic molecules is well known, but the complex reaction pathways in natural hydrothermal environments remain largely elusive. The trends showing higher relative abundance of PAHs in the surrounding areas, and higher relative abundance of phenyl derivatives (termed PDs) and sulfur-containing polycyclic aromatic hydrocarbons (SPAHS) in the hydrothermal area (Fig. 1c, d), along with differences in the magnitude of the UCMs, were most likely caused by proximity to and/or the intensity of hydrothermal activity, confirming the hydrothermal effect.

PAHs are signature compounds of extreme conditions in the universe and the Earth, such as submarine hydrothermal environments, meteorites [7], or even the atmosphere of Saturn's moon Titan [1]. Their formation and transformation need no combustion systems if phenyl radicals are available, even at temperatures of 70–180 K [1,8,9]. Abundant SPAHs such as dibenzothiophene (DBT) and benzo[*b*]naphtho[2,1-*d*]thiophene (BN[2,1]T) have previously been observed in hydrothermal systems. The formation mechanisms of SPAHs in geological environments remain unclear. The incorporation of H<sub>2</sub>S into molecular compounds after microbial sulfate reduction during early diagenesis may produce sulfur-rich organic compounds, as does sulfurization under high thermal stress. Alternatively, the interaction between indigenous adsorbed organosulfur species and deep hydrothermal fluids may be responsible for the increase in the relative abundance of SPAHs. Free radical reactions involving sulfur would lower the homolytic cleavage temperature of C–C bonds during early thermal maturation, enhancing the formation of SPAHs. Moreover, S, N, and P-containing compounds may be inherently more stable than C–H–O compounds at elevated temperatures [10].

A significant enrichment of SPAHs may be a geochemical signature showing the effect of deep hydrothermal fluids on organic molecules and chemical reactions involved during hydrothermal events. The addition of H and OH radicals and then other heteroatoms to pre-activated PAHs becomes barrierless. Hydrothermal energy breaks the C–C bond to produce phenyl radicals. Transition metals in ascending hydrothermal fluids can aid as catalysts [11], and here are hypothesised to have converting “stubborn” PAHs to “reactive” PDs. Subsequent catalytic surface reactions between

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**Fig. 1.** Total ion chromatograms of the aliphatic (a) and aromatic (b) fractions in the hydrothermal sample S1 from the Huangqiao hydrothermal system, showing the *n*-alkanes, phenanthrene and alkylphenanthrenes, and sulfur-containing polycyclic aromatic hydrocarbons (SPAHS; labelled in red). The S1 sample has a marked unresolved complex mixture (UCM) in both fractions. The aromatic fraction of the S1 sample shows an abundant dibenzothiophene (DBT) series, and a shift towards low molecular weights compared to the aliphatic fraction. Progressive changes with increasing hydrothermal influence in the relative abundance and distributions of SPAHS (c) and phenyl derivatives and unsubstituted PAHs (d) in the aromatic fractions of three representative samples (M1, X1, and S1; denoted by blue, brown, and red traces, respectively) from the Huangqiao hydrothermal system. The partial *m/z* 276 mass chromatogram shows C<sub>3</sub> benzo[*b*]naphtho[2,1-*d*]thiophene (BN[2,1]T), 6 ring indeno[1,2,3-*cd*]pyrene (InPy), and benzo[*ghi*]perylene (BghiP). From surrounding areas to the Huangqiao hydrothermal system, the relative amounts of SPAHS (e.g., the C<sub>3</sub> BN[2,1]T series) increase, and the relative amounts of unsubstituted 6-ring PAH (InPy and BghiP) decrease. The summed partial *m/z* 204 + 230 + 228 + 252 mass chromatograms show 2-phenylnaphthalene (2-PhN), *meta*-terphenyl (*m*-Trp), coeluting chrysene (Chy) and triphenylene (Tpn), and benzo[*e*]pyrene (BePy). From surrounding areas to the Huangqiao region, the relative amounts of 2-PhN and *m*-Trp increase, and the relative amounts of the unsubstituted 4–5 ring PAH decrease. Numbers on peaks in (a) are *n*-alkane carbon numbers. P: phenanthrene, MP: methylphenanthrene, MBDT: methyl dibenzothiophene, DMBT: dimethyl dibenzothiophene, TMBT: trimethyl dibenzothiophene. The relative abundances of key compounds are highlighted with blue shading and by red triangles. (e) Ternary diagram showing the relative contents of chrysene + triphenylene (Chy + Tpn), 2-phenylnaphthalene (2-PhN), and benzo[*b*]naphtho[2,1-*d*]thiophene (BN[2,1]T). (f) Ternary diagram showing the relative contents of phenanthrene, Σalkylbiphenyls (Bps) and dibenzothiophene (DBT). The trends reflect the transformations between three different compounds with proximity to and/or an intensity of hydrothermal activity. The samples from Jurong and Huangqiao are denoted by black and red solid circles, respectively.

adsorbed heteroatoms (e.g., S) and phenyl linkages would have contributed to the formation of SPAHS or the addition of aromatic rings. Transformations between these complex molecules are most likely present in subsurface hydrothermal environments (Fig. 1e, f).

In addition to the C<sub>27–29</sub> 8,14-secosteranes, a group of four low molecular weight (C<sub>21–24</sub>) 8,14-secosteranes is tentatively identified here (Supplementary materials online). 8,14-Secopregnane

(isomer A) has been observed to form under hydrothermal conditions in the subsurface. The C<sub>21–24</sub> and C<sub>27–29</sub> 8,14-secosteranes progressively increase in abundance relative to pregnanes and steranes from surrounding locations to the hydrothermal area, demonstrating their formation and stability during hydrothermal events.

Very few papers have been published on secosteranes, and none on secopregnane in the geosciences. The formation mechanism of

“seco” compounds remains a “lingering mystery” in organic geochemistry, because the cleavage of a C–C single bond in recalcitrant organic molecules requires fairly harsh conditions, and the three six-membered rings in the core structure of steranes make the C–C bonds even more inert. Two possible known routes for the formation of “seco” compounds are chemical/thermal breakdown and microbial oxidation [12], which are processes that can potentially overcome the large activation barrier necessary for C–C bond cleavage. However, only the former could be acting in the present study, due to the correlation of UCM abundance with SPAH abundance, phenyl abundance, and thermal maturity parameters, together with the absence of 25-norhopanes, and the presence of increasingly abundant compounds that are not resistant to biodegradation, such as S-bearing DBT and phenyl-derivative 2-phenylnaphthalene (largely excluding the effect of in-reservoir mixing). Secosteranes have also been reported to correlate with temperature, but not with the level of microbial reworking. Pregnane and homopregnane are highly thermally-stable and biodegradation-resistant molecules in the subsurface. Thus, the most promising route for the formation of more recalcitrant secopregnane is the involvement of hydrothermal fluids and mineral surfaces in facilitating the cleavage of the C–C bond. Transition-metal catalysed activation of C–C bonds is well established in the field of organic synthesis. Transition metal atoms with expandable valence shell electrons are accessible to electron exchange reactions, and their ion pairs can serve well as oxidation catalysts.

With the proximity to and/or the intensity of hydrothermal activity in the Huangqiao region, it is hypothesised that transition metals (e.g., Fe, Cu, and Au) in ascending hydrothermal fluids induced by deep faults mediated C–C bond cleavage in the pregnane ring. The 8,14-bond is inherently weak, since it is markedly longer than other C–C single bonds [13], and therefore it may possess the lowest energy in the sterane core structure, so that C-ring cleavage (to form 8,14-secosteranes) occurs prior to cleavage in other rings. Cleavage of the C-ring in pregnane by hydrothermal catalytic oxidation is feasible, and would be accomplished by a subsequent reduction process with energy release, such as hydrogenation, oxygenation, and hydroxylation. In summary, the presence of secosteranes in the Huangqiao CO<sub>2</sub> hydrothermal system, especially of secopregnane, is consistent with hydrothermal activity, which increases the possibility of the transformation of PAHs and the creation of new molecular structures in the subsurface.

Generation of biogenic C–H molecules is usually an irreversible process in geology, and is a function of time, temperature, the presence of catalysts, and the inventory of biological precursors. Heat is the major factor in the incongruent decomposition of insoluble organic matter under geothermal regimes. However, metastable equilibrium between molecular compounds can be attained through hydrothermal organic–inorganic interactions in laboratories. The oxidation of organic carbons accelerates the mineralization of metal salts (e.g., UO<sub>2</sub>, Cu, Zn, and Pb). Both the reduction products of low molecular weight molecules and the oxidation products of complex peri-condensed compounds are at metastable equilibrium under hydrothermal conditions.

In the Huangqiao CO<sub>2</sub> hydrothermal system, the combination of heat, deep-sourced CO<sub>2</sub>, various transition metals, and H<sub>2</sub>O, induced by deep faults, is interpreted to have promoted the formation of complex molecules that are oxidized and contain polar functional groups such as double-bonded alkenes, ketones, cyclic alkanes, and benzene rings. Hydrothermal alteration may also catalyse the cleavage of C–C bonds and reversed reactions (i.e., hydrogenation, oxygenation, and hydroxylation) to yield simple, reduced and nonpolar molecules. Examples include the transformation of alkenes to alkanes, ketones to alcohols, decyclization of cycloalkanes to alkanes, and dearomatization of benzene rings

to phenyl linkages. Alcohols and carboxylic acids can be formed in solution and on mineral catalyst surfaces during hydrothermal abiotic organic synthesis in laboratory experiments at elevated temperatures and pressures. This was previously observed in laboratory studies between PAHs and PDs under hydrothermal conditions of 120–180 °C and 2–3 MPa with transition metal catalysts [14,15]. The number of PAH rings that are cracked by catalysts can be up to 10, i.e., ovalene. This suggests that catalyst-rich hydrothermal fluids may be the key factor controlling both thermogenic and abiotic reactions.

Transformations of the unsubstituted PAHs, PDs, and SPAHs are observed in the Huangqiao CO<sub>2</sub> hydrothermal system. Indeed, metastable equilibrium is present under these hydrothermal conditions, which plays a role in controlling the relative content of the observed molecular compounds (various PAHs, including those containing oxygen [OPAHs], PDs, and SPAHs). Hydrothermal effects dynamically mimic the molecular processes of condensation, breakups, and incorporation of sulfur, contributing to the increase in molecular complexity.

The ubiquitous PAHs are key molecules in all prebiotic terrestrial and astronomical environments, including in cosmic dust, icy satellites, carbonaceous chondrites, meteorites [7], comets, Titan's and Earth's atmosphere, hydrothermal systems, and oceanic and continental crust. PAHs and related heterocyclic compounds can function as light energy absorbers, energy transducers, containers, and precursors of carboxylic acids under hydrothermal conditions [7]. Phenyl and PAH systems are closely involved in the synthesis of heterocyclic monomeric molecules [16].

Hydrothermal systems contain molecules ranging from simple molecules (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, etc.) to biopolymers. The Huangqiao CO<sub>2</sub> hydrothermal system provides an excellent example showing the contribution of deep catalyst-rich hydrothermal fluids to the transformation of C–H molecules (e.g., PAHs) to heterocyclic compounds [17], and also the metastable existence of these organic molecules. The functionalised intermediate products PDs and OPAHs not only possess the necessary amphiphilicity, but also play important roles incorporating heteroatoms under moderately hydrothermal conditions (~200 °C). These processes are important driving forces of heteroatom addition to C–H molecules, e.g., generating complex S-bearing macromolecules. In addition, the presence of tentatively-identified secopregnane expands the transformation conditions of organic molecules into the deep subsurface, and supports the hydrothermal transformation of complex molecules in nature. The hydrothermal hydrogenation, oxygenation, and hydroxylation to form complex molecules and the prevalent alteration and metastable existence of PAHs, PDs, and SPAHs in the presence of hot fluids in the Huangqiao CO<sub>2</sub> hydrothermal system illustrate a crucial mechanism for introducing essential elements to the starting materials of macromolecules. This is a complementary information to the hydrothermal transformation of PAH-type species, in comparison to the low temperature transformation of PAHs induced by stellar irradiation and cosmic rays in the interstellar medium [8].

Phenyl radicals are the key intermediates in the formation of complex molecules both in hydrothermal and astronomical environments [1]. The metastable equilibria of these compounds are the foundation for the concentration of more complex molecules and heterocyclic compounds. Similar reactions other than abiotic reactions could diversify the inventory of organic molecules not readily formed from abiotic syntheses, and even contributing to the polymerization of macromolecules. This finding in the Huangqiao CO<sub>2</sub> hydrothermal system provides a natural laboratory that partly mimics organic synthesis and the modification of aromatic materials of monomeric molecules. The transformation of these molecules serves as an intermediary step, bridging the gap between chains of organic chemicals and heterocyclic

macromolecules. With element availability, CO<sub>2</sub> hydrothermal systems may result in the diverse forms of complex molecules [18].

Geological evidence from the Huangqiao region in eastern China demonstrates that organic molecules were continuously modified by the presence of deep CO<sub>2</sub> hydrothermal fluids. It was shown that PAHs, phenyl derivatives, and S-bearing PAHs increased the likelihood of the formation of new complex molecules in the crust. The ability of hydrothermal alteration to collect sulfur and the metastability of molecular compounds are crucial for introducing essential elements (such as oxygen, phosphorus, and even nitrogen) and permitting the concentration of more complex molecules.

### Conflict of interest

The authors declare that they have no conflict of interest.

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### Appendix A. Supplementary materials

Supplementary materials to this news & views can be found online at <https://doi.org/10.1016/j.scib.2023.07.013>.

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