

13 α (*n*-alkyl)-tricyclic terpanes: A series of biomarkers for the unique microbial mat ecosystem in the middle Mesoproterozoic (1.45~1.30Gyr) North China Sea

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Anoxygenic photosynthesis may have modulated Proterozoic oxygen production and sustained an intermediate redox state in the oceans for the Earth's middle age [1, 2]. A special biomarker assembly indicates that a unique prokaryotic microbial mat ecosystem may have contributed to the major primary production in the middle Mesoproterozoic (1.45~1.30Gyr) North China sea [3]. However, we know little about the microbial structures of the Mesoproterozoic microbial mats. Here, we report for the first time that the series of 13 α (*n*-alkyl)-tricyclic terpanes (C₁₈~C₃₃) (13 α NATTs) occurs in the organic-rich shales from this middle Mesoproterozoic sequence, including Hongshuizhuang Fm, Tieling Fm and Xiamaling Fm. We infer the long straight-chain substitution (up to C₁₅) in 13 α NATTs to be originally of *n*-alkyl-substituted chain, while not of demethylated isoprenoid chain [4]. This scenario is probably just like that of hopanes. Thus, 13 α NATTs may have originated from prokaryotes, given the robust evidence of steranes being undetectable in the shales [3].

The fact that 13 α NATTs have not been detected from the post-Mesoproterozoic sedimentary sequences in China, may suggest that 13 α NATTs could be a unique series of biomarkers for some special Mesoproterozoic prokaryotes, which probably disappeared from the late geological record. The remaining key question is to reveal what kinds of prokaryotes may have contributed to 13 α NATTs?

[1] Johnston *et al.* (2009) *PNAS* **106**, 16925–16929. [2] Lyons *et al.* (2009) *PNAS* **106**, 18045–18046. [3] Wang (2010) *GCA* **74**, A1099-A1099. [4] Wang and Simoneit (1995) *Chem. Geol.* **120**, 155–170.

Phase equilibrium of the Cd-bearing quaternary reciprocal system at 298 K

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Solid-Liquid Equilibrium of reciprocal quaternary system K⁺, Cd²⁺//Cl⁻, SO₄²⁻-H₂O at 298 K were studied by an isothermal solution saturation method. Experimental results indicate that there are seven univariant curves F₂E₂, F₄E₂, E₂E₁, F₃E₁, E₁E₃, F₃E₃, F₁E₃, three invariant point: E₁, E₂ and E₃ and five crystallization fields in the reciprocal quaternary system. There is double salt Cd₃KCl₇·4H₂O existing in the reciprocal quaternary system. The crystallization zones of equilibrium solid phases are K₂SO₄ (F₂E₂F₄), KCl (F₄E₂E₁F₃), CdCl₂·H₂O (F₃E₃F₁), Cd₃KCl₇·4H₂O (F₃E₁E₃F₃), 3CdSO₄·8H₂O (F₁E₃E₁E₂F₂), respectively. The point E₁ represents the equilibrium of three solid phase KCl, Cd₃KCl₇·4H₂O, and 3CdSO₄·8H₂O. The eutectic point E₂ represents the equilibrium of three solid phase K₂SO₄, KCl and 3CdSO₄·8H₂O. The other eutectic point E₃ represents the equilibrium of three solid phase Cd₃KCl₇·4H₂O, CdCl₂·H₂O and 3CdSO₄·8H₂O. Potassium Sulfate has the biggest crystallization field while Cadmium Chlorine has a smaller crystallization region than others.

