

## 13 $\alpha$ (*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 $\alpha$ (*n*-alkyl)-tricyclic terpanes (C<sub>18</sub>~C<sub>33</sub>) (13 $\alpha$ 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 C<sub>15</sub>) in 13 $\alpha$ 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 $\alpha$ NATTs may have originated from prokaryotes, given the robust evidence of steranes being undetectable in the shales [3].

The fact that 13 $\alpha$ NATTs have not been detected from the post-Mesoproterozoic sedimentary sequences in China, may suggest that 13 $\alpha$ 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 $\alpha$ 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<sup>+</sup>, Cd<sup>2+</sup>//Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O at 298 K were studied by an isothermal solution saturation method. Experimental results indicate that there are seven univariant curves F<sub>2</sub>E<sub>2</sub>, F<sub>4</sub>E<sub>2</sub>, E<sub>2</sub>E<sub>1</sub>, F<sub>3</sub>E<sub>1</sub>, E<sub>1</sub>E<sub>3</sub>, F<sub>3</sub>E<sub>3</sub>, F<sub>1</sub>E<sub>3</sub>, three invariant point: E<sub>1</sub>, E<sub>2</sub> and E<sub>3</sub> and five crystallization fields in the reciprocal quaternary system. There is double salt Cd<sub>3</sub>KCl<sub>7</sub>·4H<sub>2</sub>O existing in the reciprocal quaternary system. The crystallization zones of equilibrium solid phases are K<sub>2</sub>SO<sub>4</sub> (F<sub>2</sub>E<sub>2</sub>F<sub>4</sub>), KCl (F<sub>4</sub>E<sub>2</sub>E<sub>1</sub>F<sub>3</sub>), CdCl<sub>2</sub>·H<sub>2</sub>O (F<sub>3</sub>E<sub>3</sub>F<sub>1</sub>), Cd<sub>3</sub>KCl<sub>7</sub>·4H<sub>2</sub>O (F<sub>3</sub>E<sub>1</sub>E<sub>3</sub>F<sub>3</sub>), 3CdSO<sub>4</sub>·8H<sub>2</sub>O (F<sub>1</sub>E<sub>3</sub>E<sub>1</sub>E<sub>2</sub>F<sub>2</sub>), respectively. The point E<sub>1</sub> represents the equilibrium of three solid phase KCl, Cd<sub>3</sub>KCl<sub>7</sub>·4H<sub>2</sub>O, and 3CdSO<sub>4</sub>·8H<sub>2</sub>O. The eutectic point E<sub>2</sub> represents the equilibrium of three solid phase K<sub>2</sub>SO<sub>4</sub>, KCl and 3CdSO<sub>4</sub>·8H<sub>2</sub>O. The other eutectic point E<sub>3</sub> represents the equilibrium of three solid phase Cd<sub>3</sub>KCl<sub>7</sub>·4H<sub>2</sub>O, CdCl<sub>2</sub>·H<sub>2</sub>O and 3CdSO<sub>4</sub>·8H<sub>2</sub>O. Potassium Sulfate has the biggest crystallization field while Cadmium Chlorine has a smaller crystallization region than others.

