Precambrian Research 294 (2017) 214–229

Contents lists available at ScienceDirect

Precambrian Research

journal homepage: www.elsevier.com/locate/precamres

# Formation of shallow-water glaucony in weakly oxygenated Precambrian ocean: An example from the Mesoproterozoic Tieling Formation in North China

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ARTICLE INFO

*Article history:*
Received 20 December 2016
Revised 18 March 2017
Accepted 21 March 2017
Available online 22 March 2017

*Keywords:*
Glaucony
Seawater redox conditions
Mesoproterozoic
Tieling Formation
North China platform

ABSTRACT

Authigenic glaucony precipitation in Phanerozoic oceans takes place mostly in middle shelf to upper slope environments with low depositional rate or sediment starvation. Precambrian glaucony, however, is more common in stratigraphic successions deposited from shallower-water environments with high and variable depositional rates. This phenomenon has long been noticed in literature, but the controlling factors of shallow-water glaucony precipitation in Precambrian oceans have not been adequately investigated. To better understand the glauconitization processes in Precambrian oceans, we have conducted an integrated study of the glaucony in stromatolitic carbonates of the Mesoproterozoic Tieling Formation (ca. 1437 Ma) in North China, using sedimentological, mineralogical, and geochemical data obtained from field observations, petrography, XRD, SEM, quantitative EDS and ICP-MS analyses. Macro- and microscopic observations show that the Tieling glaucony fills voids of varying sizes and shapes, and records different maturation stages of glauconitization. Geochemical analyses show that the Tieling glaucony has high $K_2O$ (avg. > 8%) but low and variable total $Fe_2O_3$ ($TFe_2O_3$) contents (1.92–13.65 wt%). The $TFe_2O_3$ contents increase with maturation of glaucony. Titration results show that the Tieling glaucony contains both $Fe^{3+}$ and $Fe^{2+}$ ions, but has $Fe^{2+}/Fe^{3+}$ ratios much higher than that of the Phanerozoic glaucony. REE results of glaucony-hosting carbonates show weak negative and positive Ce anomalies with average Ce/Ce* ratio close to 1.0, suggesting carbonate precipitation near the redoxcline of Fe-Mn oxides. All these features suggest that the Tieling glaucony was precipitated in seawater around the Fe-redoxcline, where both $Fe^{2+}$ and $Fe^{3+}$ were available throughout the glaucony maturation stages. High $Fe^{2+}/Fe^{3+}$ ratios in the depositional environments led to $Fe^{2+}$ occupation at octahedral sites of glaucony and negative charges on octahedrons, which resulted in high K content (to balance the negative charges on octahedrons) and low $TFe_2O_3$ (limited by dioctahedral structure). The formation of the Tieling glaucony and other similar Precambrian glauconies is likely controlled by low oxygen concentration in seawater and a shallow redoxcline that controls the availability of Fe and K cations during initial precipitation and maturation of glaucony. The shift of authigenic glaucony precipitation from shallow water in the Precambrian to deep water in the Phanerozoic may record the deepening of ocean chemocline in response to increased ocean oxygenation.



## 1. Introduction

Glauconite [$(K,Na)(Fe,Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$] refers to a phyllosilicate mineral of dioctahedral mica group with 2:1 + interlayer ion structures, while the term glaucony is used to represent a series of green clay minerals with a wide range of chemical/mineralogical compositions including glauconitic mica, glauconitic smectite, and ferric illite (Banerjee et al., 2015, 2016; Odin and Létolle, 1980). Glaucony typically occurs as 60–1000 μm green clay aggregates formed through marine authigenesis in sedimentary rocks (e.g., Banerjee et al., 2015, 2016). Although detrital and reworked glaucony is sporadically present in both modern and

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http://dx.doi.org/10.1016/j.precamres.2017.03.026
0301-9268/

ancient records (Amorosi, 1997), most autochthonous glauconies form in depositional environments with low sedimentary rate or sediment starvation where persistent chemical exchange between sediments and seawater promotes fixation of potassium (K) and iron (Fe) into mineralogical structures (e.g., Amorosi, 1997; Odin and Matter, 1981). Based on K-contents and morphological attributes, Odin and Matter (1981) divided glaucony into four evolution stages: nascent (2–4% $K_2O$), slightly evolved (4–6% $K_2O$), evolved (6–8% $K_2O$), and highly evolved (8–10% $K_2O$). Most Phanerozoic evolved and highly-evolved glauconies are found in transgressive deposits and/or condensed sections, and they are spatially distributed in low-energy depositional environments from middle continental shelf to upper slope with water depths between 50 and 500 m (Amorosi, 1997; Baldermann et al., 2017; Banerjee et al., 2008, 2012a, 2012b; Bansal et al., 2017; Chattoraj et al., 2009; Chafetz and Reid, 2000; Giresse and Wiewióra, 2001; Harris and Whiting, 2000; Hesselbo and Huggett, 2001; Kitamura, 1998; Meunier and El Albani, 2007; Odin and Matter, 1981).

A particular phenomenon noticed in literature is that most Precambrian glaucony, in contrast to its Phanerozoic counterparts, tends to concentrate in shallow-water environments (e.g., Banerjee et al., 2015, 2016; Chafetz and Reid, 2000; Mei et al., 2008; Zhou et al., 2009). Yet the mechanism behind this favorable glauconitization in shallow-water environments during the Precambrian has not been adequately addressed. To better understand the controlling factors of shallow-water glauconitization during the Precambrian, we have conducted a comprehensive study of the glaucony in stromatolitic carbonates of the Mesoproterozoic Tieling Formation (ca. 1437 Ma) in North China (Figs. 1 and 2), using integrated sedimentological, mineralogical, and geochemical data obtained from field observations, petrography, XRD, SEM, quantitative EDS and ICP-MS analyses. With the integrated dataset, we discuss the potential seawater control on the source of Fe and K required for glauconitization in shallow-water environments.

## 2. Geological setting

### 2.1. Regional stratigraphy and age constraints

The Proterozoic succession of the North China platform was deposited in rift and post-rift basins associated with the tectonic evolution from the breakup of supercontinent Columbia to the assembly of supercontinent Rodinia. Paleoproterozoic to Neoproterozoic strata in North China have a total thickness of ~9 km and are regionally well preserved with low metamorphic grade below prehnite–pumpellyite phase (Chu et al., 2007; Li et al., 2003). The Proterozoic succession consists of three groups (Fig. 2), in ascending order, the Changcheng Group (1660–1600 Ma, $Pt_1$), the Jixian Group (1600–1400 Ma, $Pt_2$), and the Qingbaikou Group (1000–800 Ma, $Pt_3$). A hiatus of up to 400 Ma occurs at the unconformity between the Jixian and Qingbaikou groups (Gao et al., 2009).

The Jixian Group comprises six formations including, in ascending order, the Gaoyuzhuang, Yangzhuang, Wumishan, Hongshuizhuang, Tieling, and the Xiamaling formations. This group is predominated by carbonates with a total thickness of ~6000 m, recording shallow-water deposits of an extensional epicontinental sea. The Jixian Group is unconformably overlain by sandstones of

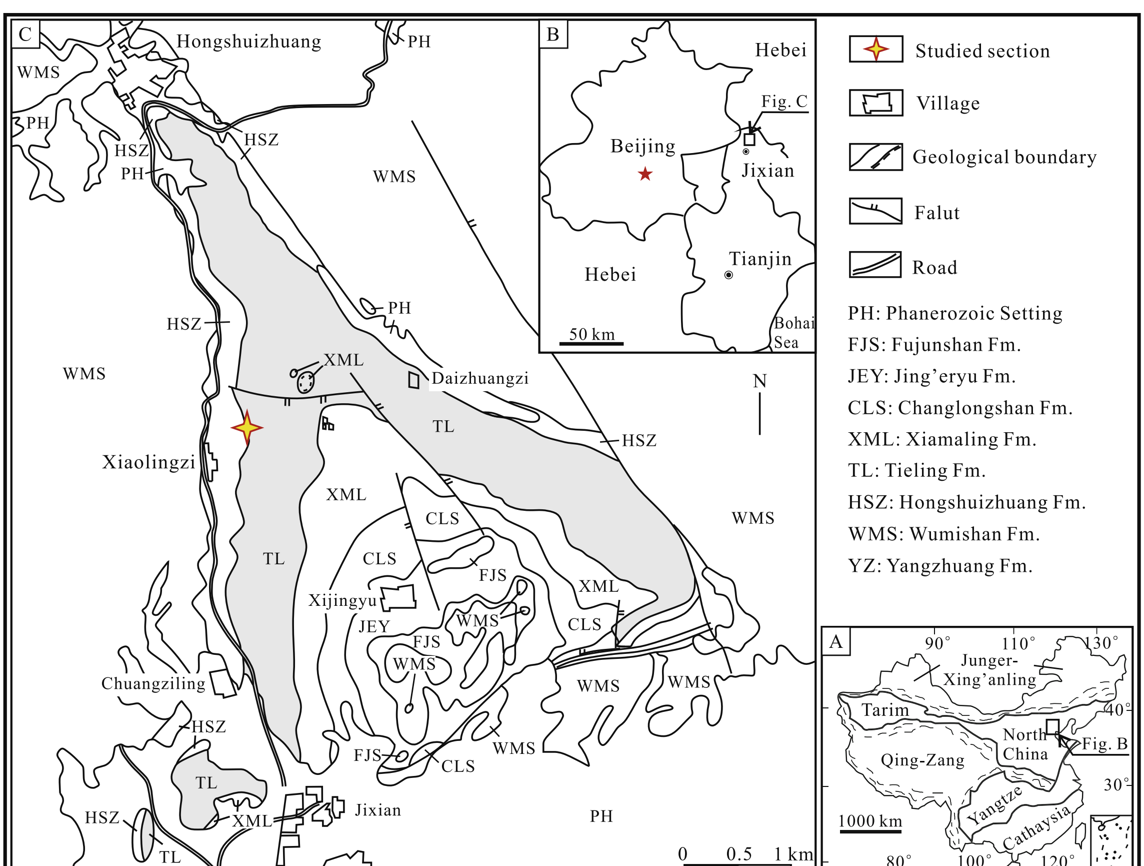


**Fig. 1.** Simplified geological map of the study area (modified after Xie and Zhou, 2005). (A) Major tectonic subdivisions of China. (B) Location of the study area. (C) Simplified geological map showing distribution of the Tieling Formation (in grey color) and location of the studied section (star).