



## Paleoenvironmental reconstruction of a saline lake in the Tertiary: Evidence from aragonite laminae in the northern Tibet Plateau

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### ABSTRACT

The origin of aragonite has long been debated because it is precipitated and preserved under specific conditions. Aragonite laminae, first found from Eocene to Miocene strata in the western Qaidam Basin, northern Tibet Plateau, contain much information on paleolake signatures. Mineralogical and geochemical analyses were conducted on alternating yellowish and grayish aragonite layers. The yellowish layers are mainly composed of aragonite crystals, while the grayish layers contain less aragonite and fewer organic remnants that accumulate among debris with sporadic framboidal pyrite. The  $\delta^{13}\text{C}$  values of yellowish layers are remarkably positive by approximately 4.01‰ (VPDB), and the  $\delta^{18}\text{O}$  values are slightly negative compared with base data of the Qaidam Basin. Considering the  $^{12}\text{CO}_2$  absorption of algal blooms, positive excursions of  $\delta^{13}\text{C}$  shown in aragonite indicate high  $^{13}\text{C}$  values in depositional water. Therefore, a seasonal algal-influenced inorganic origin is proposed to explain the formation of aragonite laminae. During warm seasons, Mg/Ca ratios are elevated because of evaporation effects. The algal blooms decrease the  $\text{CO}_2$  content, leading to high pH values. These conditions promote the rapid crystal growth of aragonite instead of other carbonate minerals. Slightly negative  $\delta^{18}\text{O}$  values in yellowish layers are interpreted as the result of intense inflow during warm seasons, which leads to less precipitation of organic matter and debris. The grayish layers in cold seasons are the opposite. From the Eocene to Oligocene, the progressively decreasing  $\delta^{18}\text{O}$  values of aragonite reflect global cooling during this time. A conspicuously positive step in  $\delta^{18}\text{O}$  values indicates an arid environment coinciding with the uplift of the Himalaya, from the Oligocene to Lower Miocene. The results from this study show that understanding of aragonite in the Qaidam Basin is essential to reconstruct the high-resolution paleoenvironment and to reveal the Tertiary evolution of paleoclimates in the northern Tibet Plateau.

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### 1. Introduction

Most lacustrine carbonates are limited in distribution (Zhao 2015). However, these deposits serve as important archives of depositional conditions, such as climate and resident ecosystems (Alonso-Zarza 2010). Aragonite, an unstable polymorph of calcite, contains considerable information about paleoclimate and paleoenvironment especially in nonmarine setting (Huang et al. 2014). Aragonite is easily transformed into other carbonate minerals, because it is highly sensitive to ambient conditions (Sondi and Juracic 2010).

Determining whether aragonite is of inorganic or biological origin has been a long-lasting dilemma in many typical marine (e.g., Mediterranean)

and nonmarine (e.g., Bear Lake) environments (DeGroot 1965; Shinn et al. 1989; Boss and Neumann 1993; Milliman and Friedman 1993; Morse et al. 2003; Sondi and Juracic 2010; Paction et al. 2015). Experimental research has mainly focused on the chemical conditions that affect the precipitation of aragonite (Bischoff 1968; Bischoff and Fyfe 1968; Berner 1975; Xyla and Koutsoukos 1989; Tai and Chen 1998). Increasing Mg/Ca ratios probably promote the precipitation of aragonite instead of other carbonate minerals (Muller et al. 1972; Kelts and Hsu 1978; Riccioni et al. 1996; Peckmann et al. 1999; Prasad et al. 2009; Baoumy et al. 2011; Murphy et al. 2014). Some researchers hypothesize that aragonite may precipitate from whittings (Shinn et al. 1989; Morse and He, 1993), drifting clouds of milky water, that contain suspended carbonates originating from the direct chemical precipitation of calcium carbonate (Robbins et al. 1997; Sondi and Juracic 2010). Others (e.g., Thompson et al. 1997; Hodell et al. 1998; Kim et al. 2013; Cangemi et al. 2016) propose that the formation of carbonates could be related to biological activity, compared with the

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hypothesis of inorganic precipitation. Phototrophic cyanobacteria, a type of algae, could promote aragonite precipitation via controlling alkalinity, which is regarded as a biologically-influenced origin of aragonite (Kelts and Hsü 1978; Koschel et al., 1983; Koschel, 1997; Cangemi et al. 2016). Aragonite can also originate from the process of biomineralization, as bacterial metabolism and its by-products might affect the microenvironment and promote aragonite formation (Braissant et al. 2003; Bontognali et al. 2013). Further, extracellular polymeric substances (EPS) might play an important role during this process as it could both alter the precipitation kinetics of carbonates (Balci et al. 2016) and impact the crystal shape of aragonite (Pacton et al. 2015; Balci et al. 2016). In addition, aragonite is relatively common in disintegrated skeletal material or mollusks (Lowenstam and Epstein 1957), which have an organic origin (Neumann and Land 1975). Aragonite may form during diagenesis and recrystallization in caves and tufa (Zhang et al. 2014). Although the origin of aragonite has long been debated, it typically associated with warm, shallow and tropical zones (Weyl 1963). Aragonite in cold and high-elevation environments is highly unusual, but it has been found in pre-Quaternary formations in the western Qaidam Basin, northern Tibet Plateau.

The Qaidam Basin, located at the intersection of climatic systems in China (Huang et al. 2016), is sensitive to Asian climate change (Mao et al. 2014). The Qaidam Basin existed as a brackish-saline water lake in the Paleogene and Neogene with primary carbonate distribution (Zhao 2015). Previous studies of lacustrine carbonates in the Qaidam Basin primarily focused on the petrography, sedimentary microfacies, and geochemistry of calcite and dolomite (Zhang et al. 2004; Song et al. 2010; Jian et al. 2014; Yuan et al. 2015; Huang et al. 2015, 2016). However, research on aragonite is still an untouched area in the Qaidam

Basin. Primary lake signatures are well preserved in aragonite laminae under specific conditions, which will be helpful for reconstructing paleoenvironments and paleoclimates.

In this contribution, mineralogical and geochemical studies were conducted to elucidate the formation mechanism of aragonite laminae. We attempt to reveal environmental changes of aragonite laminae in different strata and to reconstruct the pre-Quaternary evolution of paleoclimates in the northern Tibet Plateau.

## 2. Geological setting and climate background

The Qaidam Basin, bounded by the Qilian Shan-Nan Shan Thrust Zone (Yin, Dang, Wang et al., 2008; Yin, Dang, Zhang et al., 2008), the Altyn Tagh Fault Zone (Yin et al. 2002; Wu et al. 2012) and the Eastern Kunlun Fault Zone (Cheng et al. 2014), is the largest Cenozoic basin in the Tibet Plateau (Fig. 1). The basin center has an average elevation of 2800 m while the surrounding mountains (Altyn, Kunlun/Qimantagh and Qilian) reach heights in excess of 5000 m (Rieser et al. 2009). The western sector of the Qaidam Basin, in which the lacustrine environment was found (Liu et al. 1998; Duan and Hu 2001), records the evolution of the region, north of the Tibet plateau.

In the early Eocene, the area covered by lake water in the western Qaidam Basin began to expand, around which braided delta front sediments were deposited across a large region (Huang et al. 2015). In the late Eocene, after the collision of India with Eurasia (Qiu 2002; Gradstein et al., 2004), the water area continued to expand, based on the previous braided delta system (Liu et al. 1998), which contributed to the large area of lake deposition in the entire basin. As the Himalayas have acted as a barrier for precipitation since the latest Oligocene (Sun

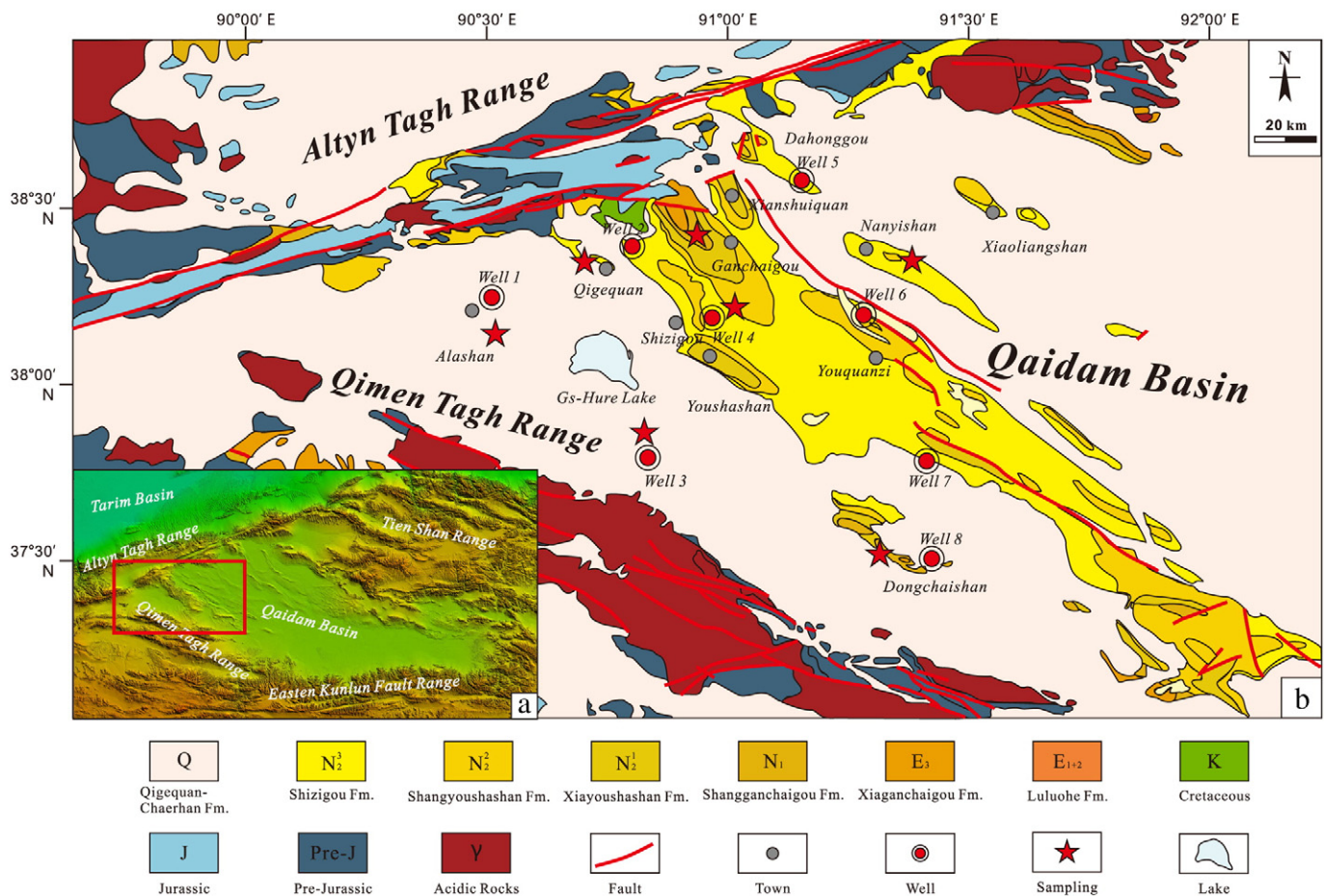


Fig. 1. Location of the Qaidam Basin, the northwest of China: (a) Remote-sensing image of full basin. (b) The simplified geological map of the study area, the western Qaidam Basin, with carbonate sampling sites.

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