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# Compositional variation of glauconites in Upper Cretaceous-Paleogene sedimentary iron-ore deposits in South-eastern Western Siberia

Maxim Rudmin [a,*], Santanu Banerjee [b], Aleksey Mazurov [a]

[a] Department of Geology and Mineral Exploration, Institute of Natural Resources, National Research Tomsk Polytechnic University, 634050 Tomsk, Lenin Avenue, 30, Russia
[b] Department of Earth Sciences, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, Maharashtra, India

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ABSTRACT

Glauconite occurs either as unaltered greenish or as altered brownish variety in Upper Cretaceous-Palaeocene sediments in the southeastern corner of Western Siberia. Studied section within the Bakchar iron-ore deposit includes Ipatovo, Slavgorod, Gan'kino and Lyulinvor formations, which are represented by sandstones, siltstones, claystones and oolitic ironstones of coastal-marine facies. The origin of unaltered glauconite is explained by the "verdissement theory". Transgressions during Lower Coniacian, Santonian and Campanian favored the formation of unaltered glauconites in dysoxic to anoxic conditions. Subaerial exposure of glauconite resulted in leaching of potassium, oxidation of iron and formation of iron hydroxides in Upper Coniacian, Maastrichtian and Palaeocene. Glauconite ultimately converts to leptochlorite and hydrogoethite by this alteration. Abundant microscopic gold inclusions, besides sulphides, sulphates, oxides and silicates characterize this glauconite. Mineral inclusions include precious, rare metals and non-ferrous metals. The concentration of gold in glauconite may be as high as 42.9 ppb. Abundant inclusions of various compositions in glauconites indicate enrichment of marine sediments in precious and non-precious metals. While major element composition of glauconites is affected by subaerial exposure, the broadly similar micro-inclusions in both altered and unaltered varieties are possibly related to the comparatively immobile nature of REE and trace elements.



## 1. Introduction

Glauconite is a foliated hydrous aluminosilicate of variable composition, with a general formula $(K, Na, Ca)(Fe, Al, Mg, Mn)_2(Si, Al)_4O_{10}(OH)_2$ (Odin and Matter, 1981). Glauconite is considered to be an efficient indicator of marine authigenesis (Kossovskaya and Drits, 1970; McRae, 1972; Odin and Matter, 1981; Van Houten and Purucker, 1984; Amorosi, 1997; Drits, 1997; Meunier and El Albani, 2007; Wigley and Compton, 2007; Baldermann et al., 2012; Banerjee et al., 2015, 2012; Sylvestre et al., 2017). It is significant from industrial point of view because of its molecular-sorption and ion-exchange properties (Smith et al., 1996; Karimi et al., 2012; Franzosi et al., 2014; Rahimzadeh et al., 2015; Yapparov et al., 2015). Absorption of other elements into the glauconite structure may lead to the formation of new minerals during diagenesis forming metal-rich zones (Miledstkii, 2012). The detailed investigations regarding the origin of glauconite in sedimentological and stratigraphical context facilitates the reconstruction of geochemical facies (Amorosi, 1997; Amorosi et al., 2007; Wigley and Compton, 2007; Baioumy and Boulis, 2012b; Baldermann et al., 2013; Banerjee et al., 2016; Bansal et al., 2017).

Glauconite as well as phosphorite are associated with the Upper Cretaceous transgressive deposits of passive continental margins (Delamette, 1989; Garzanti et al., 1989; Jimenez-Millan et al., 1998; Amorosi, 2012), including Western Siberian territories. Pshenichkin and Domarenko (2011) indicated the presence of gold (ranging from 0.3 to 5.0 and 10 to 50 ppb) and platinum (ranging from 0.5 to 3 and 10 to 40 ppb) in oolitic ironstone. However, precious minerals were not reported. Sub-micrometer gold has been identified in hydromica of different localities (Guo et al., 2001; Cline et al., 2005; Zhmodik et al., 2012), including southeastern Western Siberia (Nesterenko et al., 2013). However, the wide variation in chemical composition of micro-inclusions within glauconite is yet to be investigated. Therefore, the aim of this study was to investigate microscopic mineral inclusions in glauconites of Upper Cretaceous-Palaeocene sediments within Ipatovo, Slavgorod, Gan'kino and Lyulinvor formations. The study focuses on chemical composition, mineralogy and mineral micro-inclusions of glauconite for the reconstruction of paleo-environmental condition.

## 2. Material and methods

This study investigated twelve well core samples within the Bakchar deposit (Figs. 1, 2). Cores recovered from 180 to 240 m depth in the Bakchar area were available for the study. Wet screening was carried

* Corresponding author.
*E-mail addresses:* rudminma@tpu.ru (M. Rudmin), santanu@iitb.ac.in (S. Banerjee), akm@tpu.ru (A. Mazurov).

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out with help of standard stainless steel sieves (mesh openings of 1000, 500, 200 and 100 μm) to classify glauconite into five granulometric fractions: coarser than 1000 μm, 1000 to 500 μm, 500 to 200 μm, 200 to 100 μm and finer than 100 μm. Each granulometric fraction was separated into non-magnetic (more than 4 A), low magnetic (4 to 2 A) and magnetic (<2 A) fractions using an electromagnetic separator (ECM 10/5) at current of 4 to 2 A. Glauconite fractions were finally separated under binocular microscope manually picking from each magnetic and low magnetic fraction. Polished pellets were produced from these fractions using diamond paste which included numerous glauconite grains bound in an epoxy matrix (fim balsam Russian GOST 2290-76).

Pellets were studied under scanning electron microscope (SEM) TESCAN VEGA 3 SBU and energy-dispersive adapter OXFORD X-Max 50 with 20 kV accelerating voltage. Chemical compositions of glauconite grains were determined at 116 points in about 12 samples of polished sections using SEM-EDS. X-ray diffraction patterns of these specimens were obtained using a Bruker D2 Phaser X-ray diffractometer. The generator settings were 40 kV and 40 mA.

The gold content in the samples was determined by the atomic-absorption analysis method. Samples of glauconite pellets were thoroughly crushed into powders. 1 g of ore was placed in a corundum crucible and calcined in a muffle furnace at 600 to 650 °C for an hour. The sample was cooled in air and treated with 15 ml of hydrofluoric acid. Subsequently the sample was evaporated in an electric furnace at 180 °C to a wet residue. Freshly prepared aqua regia (15 ml) was added to the residue and the mixture was evaporated up to the volume of 2 to 4 ml at 180 °C. Concentrated hydrochloric acid (10 ml) was added to the mixture and it was evaporated up to the volume 2 to 4 ml at 100 °C. The mixture was then cooled and diluted to the volume of 10 ml of 4 M hydrochloric acid. The obtained aqueous solution with 1 ml of 5% di-n-octyl sulfide in toluene was extracted for determining the concentration of gold (cf. Oskina et al., 2014).

Rare earth elements (REEs) were assayed using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) at Tomsk Polytechnic University, Russia. About 0.5 g of the powdered sample was fused using 0.8 g of $LiBO_2/Li_2B_4O_7$ at 1050 °C for 15 min. After fusion, the glass beads were dissolved in a mixture of 5:4:1.5 HF, $HNO_3$ and $HClO_4$ at 120 °C in a platinum crucible for 6 h. The acids were evaporated at 160 °C and the rest was dissolved in 10 mL of 5 N HNO3. The resultant solutions were filtered and analyzed for rare earth elements. Detailed methodologies are provided in El-Habaak et al. (2016).

## 3. Geological background

The study area is located in Western Siberia in Bakchar-Kolpashevo area (Fig. 1). Oolitic ironstone deposits occur as isolated accumulations. Glauconitic sediments occur at depths from 170 to 235 m, intimately associated with oolitic ironstone (Podobina, 1998; Podobina and Kseneva, 2005) (Fig. 2). Glauconitic sediments, ranging in age from

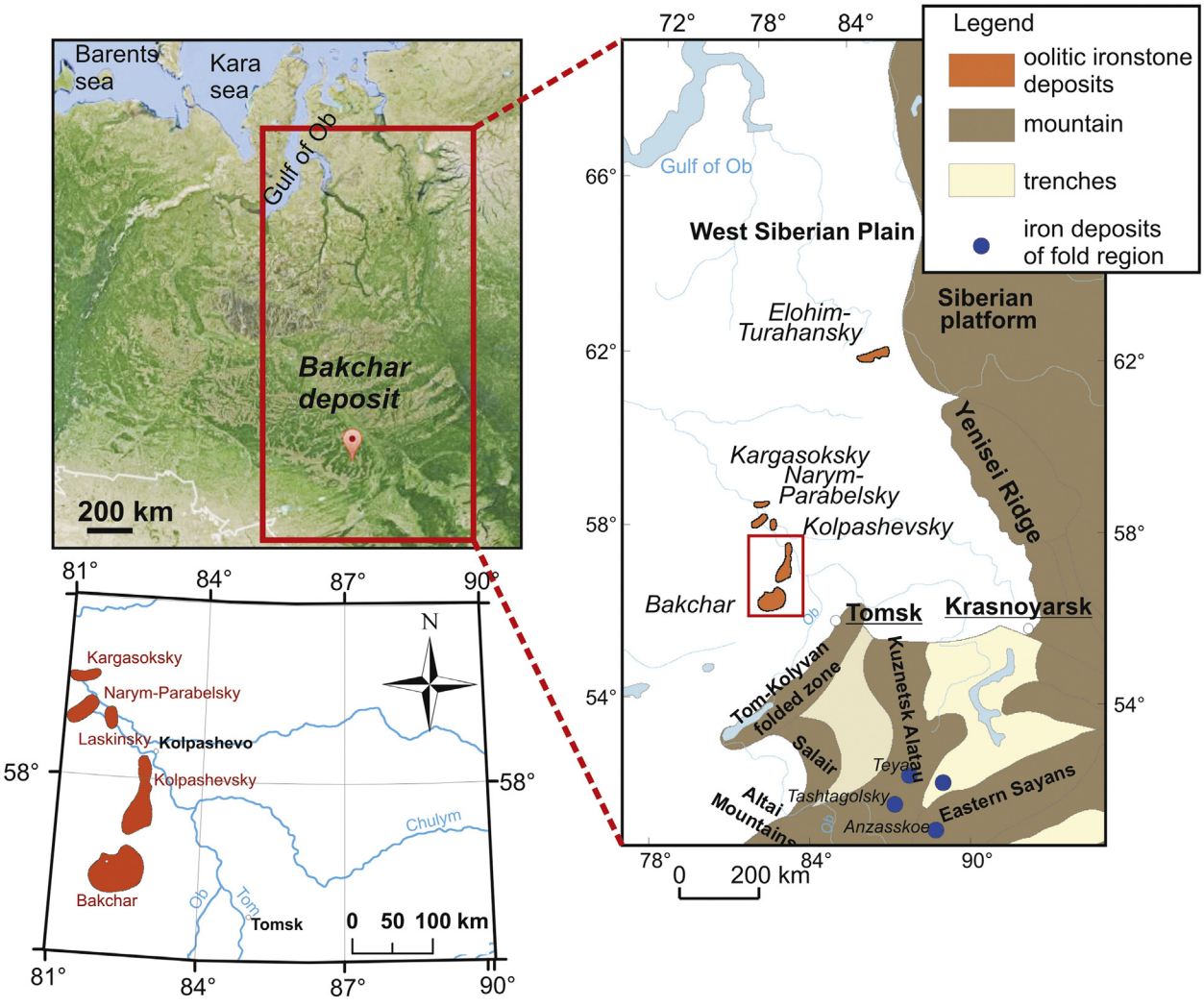


**Fig. 1.** Study area and location of oolitic ironstone deposits in S-E Western Siberia (modified after Rudmin et al., 2015b). Study area marked by rectangle.