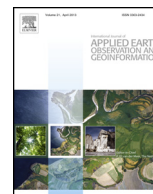




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Application of visible and infrared spectroscopy for the evaluation of evolved glauconite

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ABSTRACT

The Oligocene Maniyara Fort Formation in western India exhibits two distinct glauconite types with different maturation states, which are characterized by their spectral response in the visible to infrared spectrum of electromagnetic radiation. Spectral signatures of Maniyara Fort glauconites display absorption features at approximately 0.77, 1.08, 1.9, 2.3 μm in the visible-short-wave infrared (SWIR) and 2.8 and 10 μm in the mid-infrared (MIR) region which vary with K_2O content of glauconite. The spectra of glauconite varies significantly as a function of its cationic contents and substitution in different sites. The maturity is found to increase in tandem with the metal–metal charge transfer (CT) and the Fe^{2+} dd absorption band respectively at 1.08 and 0.77 μm . H_2O and OH^- signatures at the NIR region reflect differences in the sensitivity of glauconites with different molecular H_2O content. In the MIR region, a gradual shift of the Si–O stretch at 10 μm towards lower wavelengths indicates the dominance of smectite layers in glauconites. This study demonstrates a strong correlation between the proportion of expandable layers in the glauconite structure with variations in characteristic band position, depth and symmetry in reflectance and emissivity.

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1. Introduction

Glauconite mostly occurs as pellets of 50–1000 μm in diameter and it consists of dioctahedral sheet silicates similar to biotite in terms of structure, but compositionally akin to muscovite (Deer et al., 2013; Jarrar et al., 2000; Odin and Matter, 1981). Glauconitic smectite and glauconitic mica are the two end members of glauconitic minerals, the proportion of expandable layer contents dominates the former (Odin and Matter, 1981). The origin of glauconite is explained by two popular hypotheses. The ‘verdissement theory’ considers initial precipitation of glauconitic smectite within pores of bioclasts and faecal pellets, which subsequently matures into glauconitic mica by the addition of K_2O at a constant $\text{Fe}_2\text{O}_{3(\text{total})}$ (Odin and Matter, 1981). The ‘layer lattice theory’, on the other hand, considers the formation of glauconite from degraded layer silicates, which involves the simultaneous increase of both K_2O and $\text{Fe}_2\text{O}_{3(\text{total})}$ (Burst, 1958a,b). On the basis of K_2O content glau-

conite may be classified into four types, i.e. nascent (2–4%), slightly evolved (4–6%), evolved (6–8%) and highly evolved (>8%) (Amorosi, 1995, 1997; Odin and Matter, 1981). As the state of maturation of glauconite depends on the sedimentation rate, a highly evolved glauconite (>8% K_2O) indicates significant stratigraphic condensation (Amorosi, 1995; Banerjee et al., 2016a,b, 2015; Odin and Fullagar, 1988; Odin and Matter, 1981). The origin of K-rich glauconite is related to its higher degree of maturation (Amorosi et al., 2007; Odin and Matter, 1981). Additionally, evolved glauconites are considered as important datable material in a sedimentary sequence (Odin and Fullagar, 1988; Stille and Clauer, 1994).

The spectral properties of phyllosilicate minerals in the 0.4–2.5 μm region have been studied extensively because the diagnostic absorptions can provide crucial information on the chemical composition and crystal structure (Bishop et al., 2002, 2008; Clark, 1983, 1999; Post and Noble, 1993).

Various investigators have investigated the qualitative and quantitative relationships between the structure of a clay/mica group of minerals and the number, depth and position of absorptions employing both visible and infra-red spectroscopy (Aines and Rossman, 1984; Besson and Drits, 1997; Bishop et al., 2002, 2008; Buckley et al., 1978; Crowley and Vergo, 1988; Hunt and Turner, 1953; Nahin, 1955; Rossman, 1988a). While the absorptions due to

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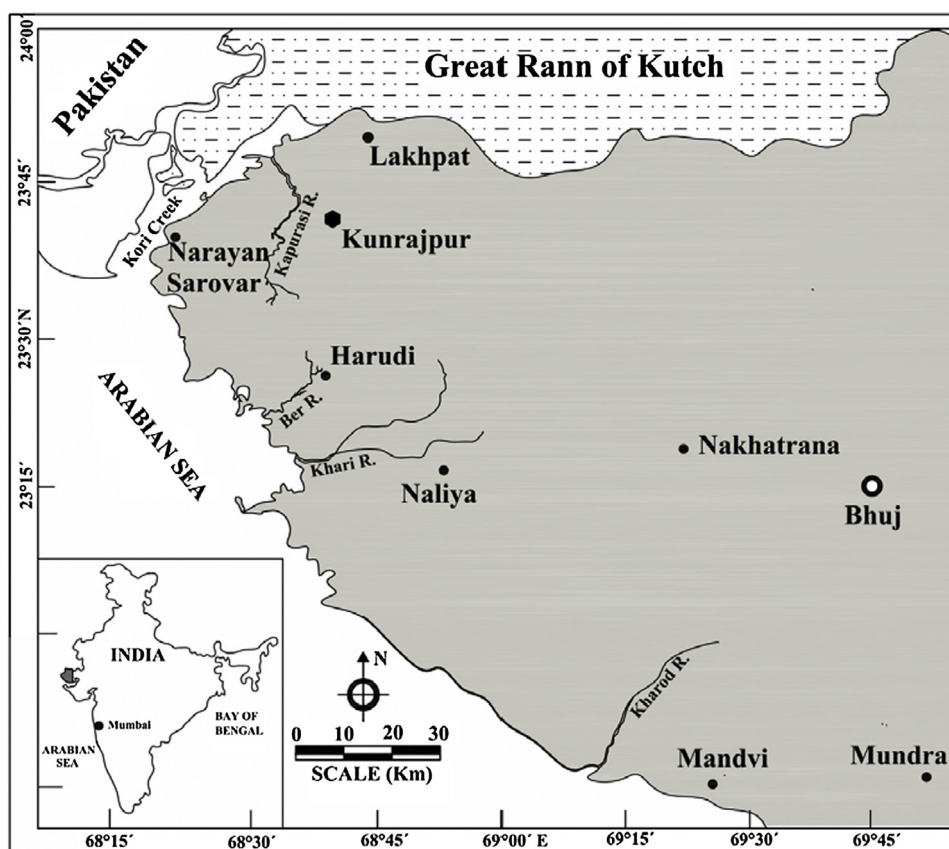


Fig 1. Location map of the study area showing the western part of the Kutch District, India (Grey shaded area in inset shows the same).

OH-stretching of clay/mica group of minerals have drawn attention over decades, characteristic absorptions due to presence of combinations of H—O—H bend, metal (Al, Mg)—OH bend in addition to OH stretch in the VIS-NIR region have also been studied (Burns, 1993; Clark et al., 1990; Mitra, 1996; Slonimskaya et al., 1986; Petit et al., 1998, 1999; Rossman, 1988b). Optical spectroscopy, additionally, enables determination of the presence of Fe^{2+} and Fe^{3+} , both of which are octahedrally coordinated in mica group of minerals like glauconite.

To date few studies report on the maturity of glauconites and its possible imprints on spectral signatures. Manghnani and Hower (1964a,b) reported Si—O absorptions in the mid infrared region and related to expandable layers in glauconite and tetrahedral ionic substitution and charge. Sanchez-Navas et al. (2008) correlated colour of glauconites as a maturation indicator and calibrated spectral absorption features due to presence of H_2O at different bands in the VIS-NIR range with maturity. Lyon and Tuddenham (1960) linked the shape of absorption spectra of mica in the 9–10 μm region to the amount of aluminum substitution in the silicon tetrahedral site. Pertinently, glauconitic minerals have ubiquitously been reported from all formations of the Palaeogene succession of Kutch (Chatteraj et al., 2008a,b, 2009; Chatteraj, 2011, 2016; Biswas, 1992; Singh, 1978) which is the focus of the study. Chatteraj (2011) studied stratigraphic implications of the glauconite rich green shales from the Kunrajpur area and presented a detailed geochemical database of the glauconites. However, there is no previous work reported on the identification and characterization of the maturation state of these otherwise well illustrated glauconites using spectroscopic methods. This study envisages the spectroscopic characterization of the Maniyara Fort glauconites, of the Kutch district in India, for understanding glauconite maturation and explores the relationship between geochemical characteristics

Table 1

Oligocene stratigraphy and lithological variations in Maniyara Fort Formation (after Biswas, 1992).

Age	Formation	Member	Lithology
Neogene Formations			
Oligocene	Maniyara Fort	Bermoti	Foraminiferal limestone
		Coral limestone	Foraminiferal and Coralline limestone
		Lumpy Clay	Grey shale
		Basal Member	Green, red shale and limestone

Paleocene to Eocene Formations resting on Deccan Basalt basement

and the spectral response of glauconite. Banerjee et al. (2012a) presented a geological and geochemical database of the glauconites as well as stratigraphic implications of Maniyara Fort glauconites. The central theme of the present investigation involves recognition of spectral signatures of different types of glauconites approximately at 0.7, 1.08, 1.9, 2.3 μm in the Visible-SWIR and 2.8 and 10 μm in the IR region. Further, the paper presents a variation of spectral characteristics in response to the presence of 1) octahedral Fe^{2+} , Mg^{2+} and Al^{3+} , 2) tetrahedral Al^{3+} and Si^{4+} , 3) molecular H_2O and 4) associated smectitic expandable layer.

2. Geological background

One of the major glauconitic intervals in the Paleogene (~65–23 My) of the Kutch district was investigated around the Kunrajpur village (Fig. 1; Table 1 Banerjee et al., 2012a,b; Biswas, 1992; Chatteraj et al., 2008a; Burns, 1993; Clark et al., 1990; Mitra, 1996). The study area near Kunrajpur (23°43'28.80"N, 68°43' 43.20"E) exposes two Palaeogene formations, viz., the Fulra Limestone (av.

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