# ORIGINAL ARTICLE

# An Assessment of Alternate Fertilizer Potential of Glauconite Deposits in India using Simple Beneficiation Methods

Tathagata Roy Choudhury<sup>1</sup>, P.V. Sunder Raju<sup>2</sup>, Tehreen Shaikh<sup>1</sup> and Santanu Banerjee<sup>1,\*</sup>

<sup>1</sup>Department of Earth Sciences, Indian Institute of Technology Bombay, Powai, Mumbai - 400 076, India <sup>2</sup>CSIR-National Geophysical Research Institute, Uppal Road, Hyderabad - 500 007, India \**E-mail:* santanu@iitb.ac.in

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## ABSTRACT

This study presents an assessment of alternate fertilizer potential of glauconite deposits in India with precise stratigraphy, dimension of the deposit, and its  $K_2O$  contents for understanding their alternate potash fertilizer potential. Further, it provides simple beneficiation methods to separate glauconite from the rest of the sediments. Many of the glauconite deposits, particularly those of Precambrian age, are considerably thick and are laterally extensive. Although the content of  $K_2O$  is low in the bulk rock, it is moderate to high in the glauconites. The glauconite content of the original deposits is low, mostly in the range of 10 to 20 wt%. Inexpensive and simple methods such as sieving and electromagnetic separation enhance the glauconite content up to 57 wt% in selected samples. This study is crucial for planning alternatives of conventional potash fertilizer, which are expected to be exhausted in the near future.

## **INTRODUCTION**

Potassium (K) is one of the essential nutrients for plants growth. Marine evaporite deposits such as slyvite and other KCl salts are the most commonly used potassium fertilizers. Till date, India meets its entire demand of agricultural potash fertilizers through imports from countries such as Canada, Russia, Belarus, Germany, Brazil, Israel and Jordan. As the world reserve of potash fertilizer is depleting fast; it is necessary to search for indigenous alternatives. Glauconite is emerging as alternate potassium fertilizer in many countries like Argentina, Russia, Egypt and Congo (Rudmin et al., 2017). Glauconite is a 2:1 dioctahedral mica that forms a continuous series from glauconitic-smectite to glauconitic-mica. Unlike K-feldspars, the K content of the glauconite occupies the interlayer sites, which is removed by simple techniques. The transition from glauconitic smectite to glauconitic mica is accompanied by the addition of K into the interlayer sites. The direct application of glauconite-rich soil to agricultural field boosts the production of crops (Rudmin et al. 2017, 2020; Shekhar et al., 2017). Glauconitic soil avoids the problem of early salinization in agriculture fields, releases nutrients slowly, and enhances soil fertility (Rudmin et al., 2017). Alternatively, the K content of glauconite is extracted as potash salts by the roasting-leaching method using concentrated acids (Rudmin et al., 2017). As the glauconite content of the whole rock rarely exceeds 20%, it is necessary to enhance its concentration before direct application to soil. Glauconite is weakly magnetic and often occurs as silt- to sand-sized pellets. Therefore, glauconites may be concentrated by granulometric and magnetic separation techniques (Rudmin et al. 2017). Although a few studies indicate the occurrence of glauconite deposits in India, stratigraphy, dimension of the deposit, and its  $K_2O$  content are yet to be evaluated. The objectives of this study are: (a) to present physical and chemical characteristics of major glauconite deposits in India and (b) to study the effectiveness of sieving and magnetic separation on enriching the glauconite content of whole rock sample.

## SAMPLES AND METHODS

The present study incorporates physical, chemical and mineralogical data of glauconite deposits in India (see Banerjee et al., 2015, 2016 and references therein for routine methods). The bulk rock composition of the sample was carried out by the energy dispersive X-Ray fluorescence analyzer at National Geophysical Research Institute, Hyderabad. Granulometric analysis and magnetic separation were carried out on two glauconitic shale samples of Oligocene Maniyara Fort Formation of Kutch (sample A) and Eocene Cambay Shale Formation of Vastan lignite mines (sample B). The original glauconite content of shales varies from 10 to 20 %. The samples were gently crushed using agate mortar. Granulometric analysis was carried out by dry sieving the samples for collecting three different size fractions viz. coarse (>500 µm), medium (between 500 and 250  $\mu$ m) and fine (< 250  $\mu$ m). The glauconite content of each fraction was enriched by using a Frantz magnetic separator (LB-1) with 15° slope and 15° lateral tilt at IIT Bombay. Samples were initially processed with 1.8 A current to distinguish between 'magnetic' and 'nonmagnetic' concentrates. The magnetic concentrate was reprocessed at 0.4 Å, to collect the 'sub-magnetic' concentrate (cf. Tóth et al., 2010). The magnetic, sub-magnetic and non-magnetic concentrates of coarse, medium and fine fractions were analysed separately using the X-ray diffraction technique to identify mineral phases. All samples were powdered to  $<75 \,\mu m$  mesh before scanning from 4° to 30° with the step size of 0.026° 20, using nickel filtered copper radiation at a scan speed of 96 s/step in an Empyrean X-ray diffractometer with Pixel 3D detector at IIT Bombay. Mineral phases were semiquantitatively identified using the database library of the International Centre for Diffraction Data (ICSD, 2013).

## RESULTS

#### **Glauconitic Deposits in Indian Sedimentary Basins**

Glauconite occurs within transgressive sedimentary deposits in basins ranging in age from Precambrian to Cenozoic in India. Table 1

Sedimentary basin/ Location	Stratigraphic unit	Thickness and lateral extent of deposit	K <sub>2</sub> O wt% of glauconite (range and average wt%)	$K_2O$ wt% of whole rock (range and average wt%)	Fe <sub>2</sub> O <sub>3</sub> wt% of glauconite (range and average wt%)
Kutch Basin, Gujarat	Maniyara Fort Formation Harudi Formation Naredi Formation	4 m x 15 km 5.5 m x 10 km 6.5 m x 5 km	5.5 to 7 (av 6.5%) 3 to 7 (av 4.5%) 3.5 to 5 (av 4.5%)	1.0 to 2.5 (av. 1.5%) 0.5 to 1.5 (av. 0.7%) 0.5 to 1.5 (av. 0.8%)	23.5 to 28 (av 25%) 23 to 29 (av 26.5%) 16 to 25 (av 20.5%)
Jaisalmer Basin, Rajasthan	Bandah Formation Khuiyala Formation	1.5 m x 40 km 0.5 m x 30 km	4.8 to 7 (av 6.1%) 5.1 to 8.7 (av 7.1%)	0.5 to 1.5 (av. 0.9%) 1.0 to 2.0 (av. 1.5%)	20 to 25.5 (av 22%) 15.7 to 24 (av 20.4%)
Cambay Basin, Gujarat	Cambay Shale	2m x 5 km	3.1 to 6.4 (av 4.2%)	0.5 to 1.5 (av. 1.1%)	12.8 to 24 (av 19.7%)
Himalayan foreland Basin, Jammu	Kalakot Formation	2.5 m x 10 km	3 to 6 (av 4.5%)	0.5 to 1.5 (av. 0.7%)	15 to 23.5 (av. 18%)
Cauvery Basin, Tamil Nadu	Karai Shale	145 m x 20 km	4 to 7.5 (av 5.5%)	1 to 2.2 (av. 1.3%)	17 to 31 (av 26.5%)
Narmada Basin, Madhya Pradesh	Lameta Formation Bryozoan Limestone	5 m x 15 km 0.5 m x 5 km	5.5 to 8 (av 7.5%) 6 to 8 (av 7.5%)	1.5 to 2.5 (av. 2.1%) 1.5 to 2.5 (av. 1.7%)	12.5 to 19 (av 16.5%) 13.5 to 20 (av 16.5%)
Kutch Basin, Gujarat	Ukra Member	6.5 m x 20 km	5.5 to 8 (av 7.5%)	1 to 2.2 (av. 1.8%)	19 to 29.5 (av 27%)
Assam Basin, Meghalaya	Mahadek Formation	2.5 m x 10 km	3.8 to 9.3 (av 6.5%)	0.5 to 2.5 (av. 1.5%)	7.9 to 26.7 (av 27%)
Bhima Basin, Telengana	Rabanpalli Formation	4.5 m x 20 km	8.4 to 9 (av 8.5%)	2 to 3 (av. 2.5%)	6.5 to 9 (av 8%)
Chhatisgarh Basin, Chattishgarh	Bhalukona Formation	6 m x 20 km	8.5 to 9 (av 8.7%)	0.4 to 2.4 (av. 0.9%)	5.5 to 10.2 (av 8%)
Pranhita Basin, Telengana	Ramgundam Sandstone Pranhita Sandstone	15 m x 20 km 20 m x 15 km	8.3 to 8.9 (av 8.6%) 7.5 to 9.8 (av 8.5%)	2 to 3.5 (av. 2%) 2 to 3.5 (av. 2%)	5.7 to 10.2 (av 6.5) 3.5 to 10.5 (av 7.5%)
Cuddapah Basin, Telenagana	Gandikota Quartzite	15 m x 15 km	7.3 to 9.6 (av 8.6%)	1.5 to 3.5 (av. 2.2%)	4.6 to 17.1 (av 9.3%)
Vindhyan Basin, Madhya Pradesh	Bhander Formation Kaimur Formation Kheinjua Formation Deoland Formation	5 m x 10 km 30 m x 40 km 45 m x 40 km 35 m x 45 km	6.7 to 8.3 (av 7.5%) 6.7 to 8 (av 7.5%) 6 to 9.5 (av 8%) 6 to 8.5 (av 7.5%)	2 to 5 (av. 2.5%) 2 to 5 (av. 2.5%) 2 to 5 (av. 2.5%) 2 to 5 (av. 2.5%) 2 to 5 (av. 2.5%)	4.5 to 9.6 (av 9.3%) 4.5 to 9.5% (av 7.5%) 3 to 7 % (av 6%) 4 to 10% (av 7%)

Table 1. Stratigraphic thickness and K<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub> of glauconites in different stratigraphic units

presents a summary of glauconite occurrences in India incorporating precise stratigraphy, the thickness of the deposit, its strikeparallel lateral continuity, the K,O content of the glauconite and the K<sub>2</sub>O in whole rock (Table 1). Glauconitic sandstones are abundant in Precambrian deposits of Vindhyan, Chattisgarh, Cuddapah, Bhima and Pranhita basins. The Thickness of the glauconite deposits varies from 4.5 m to 45 m. These deposits are laterally extensive, often traceable up to 45 km along strike-parallel sections. Glauconitic shales occur in Mesozoic Cauvery, Kutch, Narmada and Assam basins, the thickness of which varies from a few cm to up to 145 m, as in the case for Karai Shale Formation. The lateral extent of the glauconite deposits varies from 5 to 20 km. Glauconitic shales are also found in Cenozoic Kutch, Jaisalmer, Cambay and Assam basins (Table 1). The K<sub>2</sub>O of content of the whole rock samples is low, ranging from 0.5 to 2.5%. The average  $K_2O$  and The Fe<sub>2</sub>O<sub>3</sub> content of glauconite ranges from 4 to 8 wt% and 6 to 27 wt%, respectively.

### **Mineralogy of Selected Samples**

Two glauconitic shale samples of Maniyara Fort (sample A) and Cambay Shale Formation (sample B) were chosen for electromagnetic and granulometric analysis for easy availability on the outcrop. The whole rock X-ray diffraction pattern of samples A and B show a broad and asymmetric peak of ~10 Å, representing the basal (001) reflection of glauconite, along with other characteristic peaks of 4.5 Å, 3.3 Å and 1.51 Å. Whole-rock XRD pattern also reveals the presence of other minerals, including kaolinite, quartz, feldspar, calcite, and montmorillonite in both samples. Besides, pyrite and siderite occur in sample A and sample B, respectively. The contents of glauconite in the whole rock are ~15% and ~20% for samples A and B, respectively.

# Sieving of Glauconite

Contents of glauconite in fine, medium and coarse fractions of

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sample A are 15%, 12% and 16%, respectively (Fig. 1). Therefore, the glauconite content remains broadly same in all size fractions in sample A. In case of sample B, the content of glauconite increases in medium and coarse fractions and decreases in the fine fraction compared to its original value. The pyrite content is high in coarse fractions of both samples A and B. Fine and medium fractions of samples A and B show high contents of montmorillonite and siderite, respectively.

#### **Electro-magnetic Separation**

In the case of sample A, the content of glauconite in magnetic concentrate of the fine fraction increases from an initial 15% to 35%. Sub-magnetic and non-magnetic concentrates are entirely devoid of glauconite (Fig. 1). Apart from glauconite, the magnetic fraction comprises montmorillonite, pyrite, ilmenite and rutile, besides quartz and calcite impurities. The submagnetic and non-magnetic fractions consist chiefly of quartz, feldspar and calcite. Additionally, minor montmorillonite occurs in the sub-magnetic fraction. Within the medium fraction of sample A, the magnetic concentrate comprises ~54% glauconite along with montmorillonite, pyrite and ilmenite besides quartz and calcite impurities. The sub-magnetic concentrate contains ~22% glauconite besides calcite, feldspar and montmorillonite, while the non-magnetic concentrate contains negligible glauconite and is chiefly comprised of calcite, quartz and feldspar (Fig. 1). The coarse fraction of sample A shows ~41% glauconite besides minor pyrite, ilmenite, rutile and montmorillonite in the magnetic concentrate, besides quartz and calcite impurities (Fig. 1). The sub-magnetic concentrate exhibit ~28% glauconite besides calcite, quartz, feldspar and minor montmorillonite. The non-magnetic concentrate is entirely devoid of glauconite, comprised of calcite quartz, feldspar besides minor gypsum and kaolinite.

Within the fine fraction of sample B, the content of glauconite increases marginally in the magnetic concentrate while it records a significant increase within the sub-magnetic concentrate (Fig. 1).



**Fig. 1.** Pie-diagrams representing the relative abundance of minerals within the fine (A-1), medium (A-2) and coarse (A-3) fractions of Maniyara Fort Formation and fine (B-1), medium fraction (B-2) and coarse (B-3) fractions of Cambay Shale Formation. Small pie-diagrams provide the mineralogy of the magnetic, sub-magnetic and non-magnetic concentrates of each fraction.

Besides glauconite, the magnetic concentrate includes siderite, montmorillonite, calcite quartz, pyrite, ilmenite and rutile in order of decreasing abundance. The content of glauconite increases to ~34% in the sub-magnetic concentrate, besides kaolinite, quartz and siderite with minor pyrite, montmorillonite and ilmenite. The non-magnetic concentrate is completely devoid of glauconite, consisting dominantly of kaolinite and quartz with feldspar and calcite. Within the medium fraction of sample B, the content of glauconite increases to ~41% and 31% in the magnetic and sub-magnetic concentrates, respectively. Along with glauconite, montmorillonite, siderite, pyrite, quartz, kaolinite, minor ilmenite and rutile occur within the magnetic and submagnetic concentrates. The non-magnetic concentrate comprises chiefly of quartz besides calcite and feldspar. The coarse fraction of the Cambay Shale Formation exhibits the highest content of glauconite within the magnetic concentrate. The content of glauconite increases to ~57% in the magnetic concentrate while the rest of the magnetic concentrate is dominated mostly by montmorillonite and pyrite along with quartz impurities (Fig. 1). The sub-magnetic concentrate records ~19% glauconite with pyrite and montmorillonite besides minor quartz impurity. The nonmagnetic concentrates of the coarse fraction are completely devoid of glauconite and mostly contain kaolinite, quartz, calcite, feldspar and gypsum in order of decreasing abundance.

## DISCUSSION AND CONCLUSIONS

Glauconite, a K-bearing silicate mineral, can be a good alternative of existing potash fertilizers for its readily exchangeable interlayer K<sup>+</sup> ion. Thick glauconite deposits exist in most Precambrian basins of India. Precambrian glauconites contain higher K<sub>2</sub>O compared to those in Phanerozoic. However, Precambrian glauconite occurs predominantly in partially cemented sandstones and thus harder to be processed for glauconite separation. In contrast, glauconitic shales and siltstones in Phanerozoic are weakly consolidated for the easy separation of glauconites. Glauconite occurs as pellets, mostly of 100–600 µm of grain diameter. Reworking and breakage of glauconite may cause its enrichment in finer fractions.

Although the glauconite is evenly distributed within fine and medium fractions of sample A, it increases in coarser fractions after sieving. Magnetic separation effectively removes glauconite from the non-magnetic fraction. In the case of sample B, glauconite tends to concentrate more in medium and coarse fraction which is further concentrated after electromagnetic separation. Depending on the occurrence of other Fe minerals, including pyrite, siderite and Fe-smectite, glauconite may concentrate either in the magnetic or submagnetic fractions. Therefore, using a combination of sieving and magnetic separation glauconite content of whole-rock sample may be increased to a maximum of ~57%. The main conclusions of the present

study are as follows. Further experiments are desirable with a large volume of samples using a strong magnetic field to evaluate the fertilizer potential of Indian glauconite deposits.

- a) While the Precambrian deposits are rich in K<sub>2</sub>O and are significantly thick and laterally extensive, Mesozoic and Cenozoic glauconites are potential reserves in places, e.g., the Karai shale. The Meso-Cenozoic deposits of Kutch are also rich in glauconite in several horizons.
- b) The content of glauconite increases marginally in coarse fractions compared to that of fine Maniyara Fort and Cambay Shale Formation record a significant increase in glauconite content within both the medium and coarse fractions after magnetic separation. A combination of sieving and magnetic separation is useful for enriching the content of glauconites in glauconitic shales.

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# References

- Banerjee, S., Bansal, U., Pande, K. and Meena, S.S. (2016) Compositional variability of glauconites within the Upper Cretaceous Karai Shale Formation, Cauvery Basin, India: implications for evaluation of stratigraphic condensation. Sediment. Geol., v.331, pp.12-29.
- Banerjee, S., Mondal, S., Chakraborty, P.P. and Meena, S.S. (2015) Distinctive compositional characteristics and evolutionary trend of Precambrian glaucony: example from Bhalukona Formation, Chhattisgarh basin, India. Precambrian Res., v.271, pp.33-48.
- Rudmin, M., Banerjee, S. and Makarov, B. (2020) Evaluation of the effects of the application of glauconitic fertilizer on oat development: A two-year field-based investigation. Agronomy, v.10(6), pp.872.
- Rudmin, M., Banerjee, S., Makarov, B., Mazurov, A., Ruban, A., Oskina, Y., Tolkachev, O., Buyakov, A. and Shaldybin, M. (2019) An investigation of plant growth by the addition of glauconitic fertilizer. Applied Clay Science, 180, 105178.
- Rudmin, M., Banerjee, S., Mazurov, A., Makarov, B. and Martemyanov, D. (2017) Economic potential of glauconitic rocks in Bakchar deposit (SE Western Siberia) for alternate potash fertilizer. Applied Clay Science, v.150, pp.225-233.
- Shekhar, S., Mishra, D., Agrawal, A. and Sahu, K.K. (2017) Physical and chemical characterization and recovery of potash fertilizer from glauconitic clay for agricultural application. Applied Clay Science, v.143, pp.50-56.
- Tóth, E., Weiszburg, T.G., Jeffries, T., Williams, C.T., Bartha, A., Bertalan, É. and Cora, I. (2010). Submicroscopic accessory minerals overprinting clay mineral REE patterns (celadonite–glauconite group examples). Chemical Geol., v.269(3-4), pp.312-328.