

# X-ray Diffraction (XRD) Analysis of *Gile armani* (Armenian bole)

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## Abstract

*Gile Armani* (Armenian bole) is a mineral origin drug used in *Unani* system of medicine as astringent, desiccative and antiseptic. Its origin in *Unani* classical text is said to be Armenia. Different clay / minerals are sold under the name of *Gile Armani*. Keeping in consideration the controversy over its identification this study was carried out. Three different samples of *Gile Armani* were collected from crude drug market of different cities. X-ray diffraction (XRD) for crystallographic study was undertaken with powder method of diffraction. A thorough review was undertaken from various classical as well as contemporary literature for its identity and it was compared with the XRD analysis. Intensity of the peaks in XRD pattern showed that all three samples were crystalline. Sample No.1 and sample No. 3 consisted of similar constituents i.e.  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  - Kaolinite,  $\text{CaCO}_3$  and  $\text{Fe}_2\text{O}_3$ - hematite with no evidence of silica (quartz alpha). Sample No. 2 consisted of  $\text{Fe}_2\text{O}_3$ -Hematite; Silica ( $\text{SiO}_2$ )-Quartz alpha;  $\text{CaCO}_3$  and  $\text{TiO}_2$ -Titanium Oxide, Anatase with no evidence of Kaolinite. The common view from literature that it is usually prepared by mixing pipe-clay or common chalk with oxide of iron or red ochre seems in consonance with XRD analysis findings in sample No.1 and 3; Sample No. 2 resembled Red Ochre. The findings suggested that among the various samples available in the market, the one that resembles with Red Ochre appears to be genuine drug.

**Keywords:** *Gile Armani*, Armenian bole, X-RAY diffraction, Clay, *Geru*

## Introduction

*Gile-Armani* (*Amenian bole*) is a mineral origin drug used in *Unani* system of medicine. Various clay / mineral material are sold under the name of *Gile Armani* (GA). External features of the different market samples are very similar but are slightly differing in colour and shape. Keeping in consideration the controversy over its identification, this study was carried out.

Literature regarding its identity reveals that it is blackish red coloured clay having slender pleasant odour and insipid taste. It is soft, greasy and sticks on tongue. It is described to be brought from country *Armenia and Iran* (Kabiruddin, 2007). The clay which is found in *Armenia* is considered to be a better clay (Rafeequddin, 1985). Important pharmacological actions and uses of GA, are *Qabiz* (Astringent), *Mugharri* (Mucilaginous), *Mujaffif* (Desiccative), *Habis-i-ishal* (Anti Diarrhoeal), *Habis-i-nazf al-dam* (Anti haemorrhagic) / *Habis-i-Dam* (Haemostyptic), *Mudammil Qarhae Ama* and *Qarhae Raham* (heals intestinal and uterine ulcers), *Dafe-i-taffun* (Antiseptic), etc. (Kabiruddin, 2007;

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Rafeequddin, 1985; Ghani, YNM; Hakeem, 2002). It is one of the ingredients of various important Unani formulations such as *Qurse Tabasheer* etc. (Kabeeruddin, 1935). Ibn Baitar by reference of *Jalinoos* mentioned that it is obtained from Armenia which is situated near country of *Balad* and *Qabad* (Ibn Baitar, 1999). *Armenian bole* was commonly used in the formulations of Abulcasis (*Abul Qasam Zahrawi*) (Duffin *et al.*, 2013). It is also called as *Rubrica Synopica* (due to its presence in the city of Synope). The name *Rubrica synopica* was given by *Dioscorides* as this was taken usually to Synope to be sold in market. It was also named as Roman earth, Cyprus earth or *Terra sigillata rubra* also called as *sealed earth* (shaped into the coin and stamped) (Duffin *et al.*, 2013; Foulk and Pickering, 1935).

Nadkarni (2009) mentioned that “Gile Armani is a calcareous mineral often made into small cakes and stamped with certain impression. It occurs in powder or irregular pieces of reddish brown or variegated colours, it is soft and somewhat heavy. On section it is granular and sprinkled with white particles, and the cut portion resembles a piece of rhubarb”. He further describes its property that “When exposed to the air, it absorbs moisture very rapidly, If thrown into the water it readily crumbles into atoms, when put in the mouth it sticks firmly to the tongue” He further stated that “It is usually prepared by mixing pipe-clay or common chalk with oxide of iron or red ochre” But on the contrary, Unani texts mention that it is brought from Armenia or Iran. Since long time, there is controversy on identification of this drug. It was up to the extent that Ibn Sina in the introduction of *Gile Armani* in *Alqanoon* mentioned a substitute drug resembling the action of *Gile Armani* (Ibn Sina, 980-1037A.D.). Keeping all these factors in consideration different market samples of *Gile Armani* were studied with the help of XRD (X-Ray diffraction) in an attempt to resolve the controversy.

## Materials and Methods

### X-Ray Diffraction study

Different samples of *Gile Armani* (Armenian Bole) were collected from crude drug market of Bangalore and other cities in India. Three differently appearing samples processed from Bangalore, Delhi and Malegaon (MS.) were subjected, for identification and determination of constituents by X-Ray diffraction (XRD) method for crystallographic study. XRD was conducted at the Department of Material Engineering, Indian Institute of Sciences, Bangalore.

### Material and sample preparation

Powder method of diffraction was adopted in this study. Fine powder of the three different samples was prepared and passed through 300 mesh sieve for its



- Sample no. 1 and sample 3 contained Kaolinite, CaCo<sub>3</sub> and hematite with no evidence of silica (quartz alpha). (Fig. 4, Fig. 6). On the other hand Sample 2 contained hematite, CaCo<sub>3</sub> and quartz alpha with no evidence of Kaolinite (Fig. 5).
- Sample no. 1 and 3 showed presence of Fe<sub>2</sub>O<sub>3</sub>-Hematite; Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> (OH)<sub>4</sub> Kaolinite, Aluminium silicate; CaCo<sub>3</sub>-Vaterite syn. The constituents of sample 1 and 3 appeared similar to that of common chalk (Fig. 4, Fig. 6).
- Sample no. 2 (*Geru*) showed presence of Fe<sub>2</sub>O<sub>3</sub>-Hematite; Silica (SiO<sub>2</sub>)-Quartz alpha; CaCo<sub>3</sub>- Calcite form and TiO<sub>2</sub>- Titanium Oxide, Anatase, Sample no. 2 is different from 1 and 3 (Fig. 5, Fig.7).

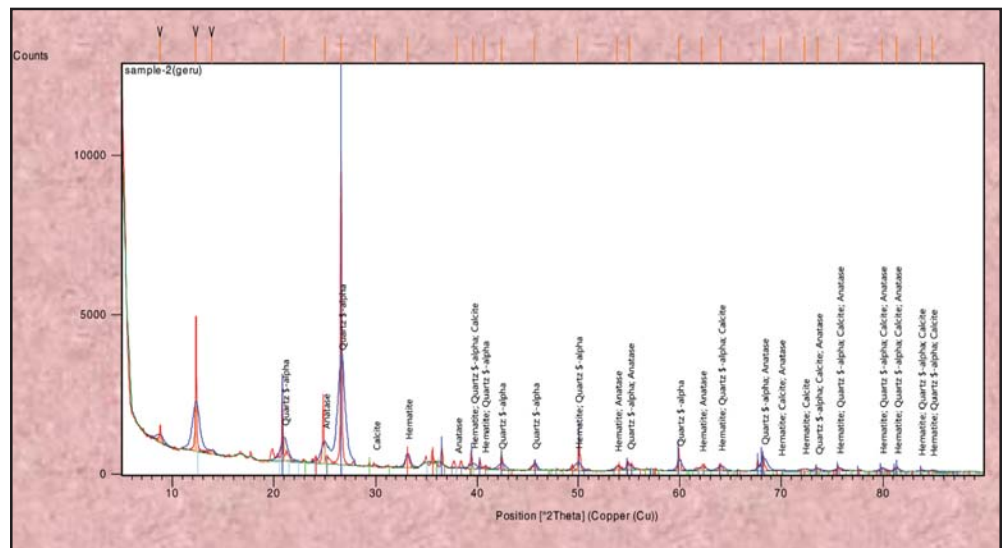


Fig. 5: Graph XRD for Sample No. 2

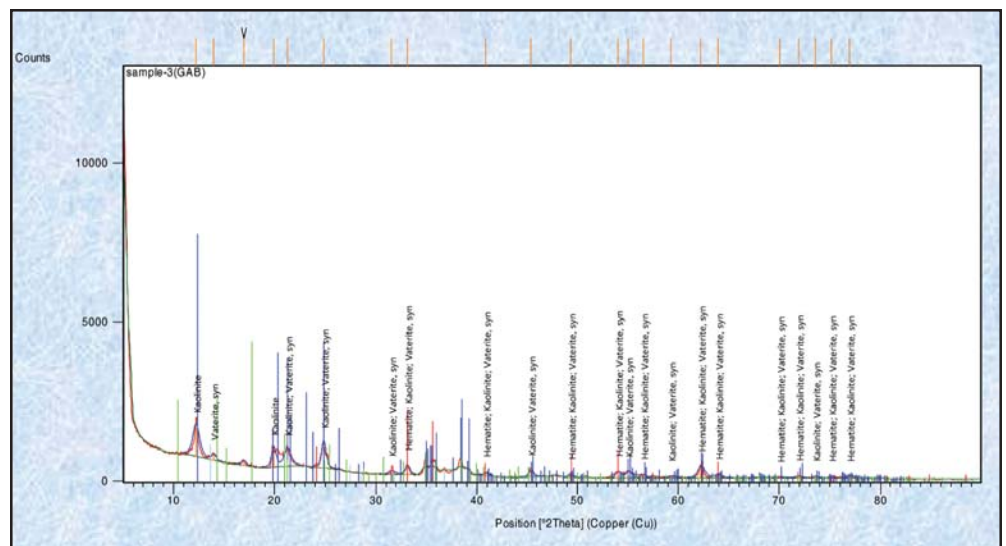
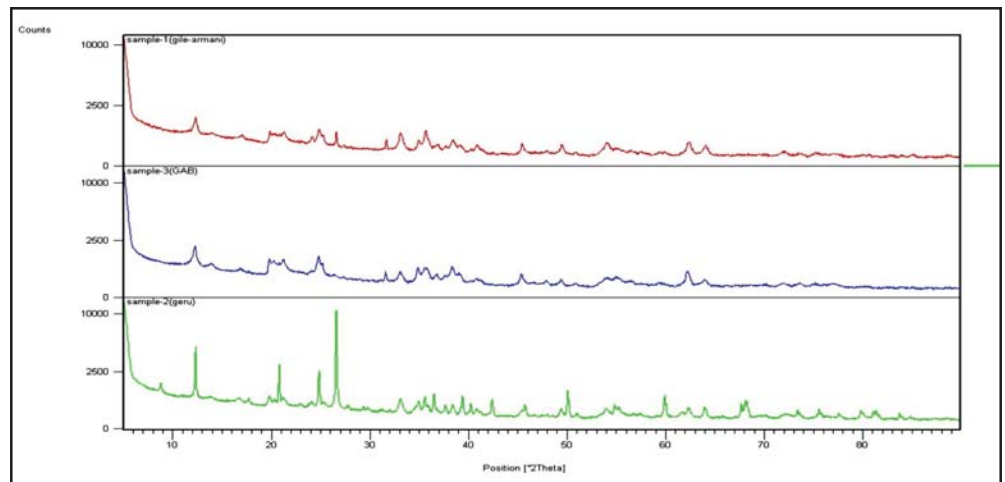


Fig. 6: Graph XRD for Sample No. 3



**Fig. 7:** Combined Graph of sample no. 1", 2" and 3"

## Discussion

Sample no. 2 was slightly yellowish red and soft, and sample no. 1 and 3 were red and soft. XRD findings of sample no. 1 and no 3 showed presence of  $\text{Fe}_2\text{O}_3$ -Hematite;  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  Kaolinite, Aluminium silicate;  $\text{CaCO}_3$ -Vaterite syn. form, common chalk. Sample no. 1 appears to have the similar constituents as that of the sample no. 3 and therefore both have great degree of resemblance in morphology. The description in the Literature that *Gile armani* is usually prepared by mixing pipe-clay or common chalk with oxide of Iron or red ochre (Nadkarni, 2009) was somehow confirmed by the findings of the present study as in the XRD analysis the presence of iron oxide ( $\text{Fe}_2\text{O}_3$ ) pipe clay (Kaolinite) and common chalk ( $\text{CaCO}_3$ ) has been shown in sample no. 1 and 3. Sample no. 2 shows presence of  $\text{Fe}_2\text{O}_3$ -Hematite; Silica ( $\text{SiO}_2$ )-Quartz alpha;  $\text{CaCO}_3$ - Calcite form and  $\text{TiO}_2$ - Titanium Oxide, Anatase. Its appearance looked like Yellow Ochre. Intensity of the peaks in XRD pattern shows that all three samples are crystalline but Sample no. 2 was having finer crystal structure as compared to sample 1 and sample 3. Sample no. 2 is different from 1 and 3, and its constituents resembled like Red Ochre as per its constituents mentioned in Ayurvedic Pharmacopeia (Anonymous, 2009).

By correlation of XRD findings with authentic literature it can be concluded that this clays sample appears to be of natural combination. Beside this, review of classical / relevant literature showed that Red Ochre was sold in the name of *Armenian Bole*, and also mixture of English Red Ochre or kind of pale red ochre and pipe-makers clay formed into cakes and dried are sold in the name of *Arminan bole*. Generally other clays were given the name of Bole Armenia but the fact is that true Bole Armenia is almost not available in the shops (Pomet *et al.*, 1570).



The characters mentioned in Unani literature of *Gile Armani* such as red coloured, multilayer, soft, slippery, sticks to the tongue etc. (Kabeeruddin, 2007; Ghani, YNM; Ibn Sina [980-1037A.D.]; Mustehasan and Ali, 2004; Anonymous, 2003) matches with several clays including a type of Red ochre (*Geru*) used internally. Review of *Geru* (Red Ochre) enable us better understanding of relation of *Gile Armani* with *Geru*. *Geru* contains oxide of iron, it is a natural mineral pigment found with other iron-titanium oxide minerals in igneous and metamorphic rocks as accessory hematite mineral, associated with magnetite, which is generally found mixed with clay and some other impurities (Anonymous, 2009). Two types of ochre are found in the country, one is red ochre (*Gairika, geru*) contain anhydrous iron oxide  $Fe_2O_3$ . 15-65% and other one is yellow ochre containing hydrated iron oxide 15-30% (Nadkarni, 2009; Anonymous, 2003, 2009). According to other classification *geru* is of two types, one is *Pasana* (hard) and other is *Swarna* (soft) and latter is preferred for medicinal use (Vohora and Athar, 2008). One which is red and pure, is called *Soun geru*, second one is light red and impure, commonly known as simply *geru* (Ghani, YNM). *Geru* has been mentioned as a substitute of GA. while GA has also been mentioned as the substitute of *Geru* (Kabiruddin, 2007; Ghani, YNM; Hakeem, 2002). Red ochre is widely distributed in India whereas GA is not found. *Geru* contains silicate of aluminium and iron oxide whereas GA mainly contains silicate of aluminium, magnesium and iron oxide (Vohora and Athar, 2008), *Geru* may also contain 1% Magnesium and 1% Titanium (Anonymous, 2009). In some recent literature *Geru* is even mentioned as an Indian type of *Gile Armani* (Mustehasan and Ali, 2004). Majority of pharmacological actions of *Gile Armani* and *Geru* have also been described to be similar (Kabiruddin, 2007; Rafeequddin, 1985; Ghani, YNM; Hakeem, 2002).

Findings of the present work and review indicates that *Armenian Bole* sold in the market is either (*Geru*) Red Ochre or dried cakes formed by mixture of Red Ochre and pipe maker's clay. To some extent drug name *Armenian bole* is a case of shift from a locality-related name to a general type mark '*Armenian bole*', which was later used for any clayey red material (Hradila *et al.*, 2003). Probably no such clay is available in market that is brought from *Armenia*. Sample no. 2 of GA can be taken as a genuine substitute of *Gile armani*.

## Conclusion

It can be established by review of *Gile Armani* and XRD findings of the samples studied that clay available in market in the name of *Gile Armani* is doubtfully associated to be procured from Armenia. Clay sample no 2 looks closer to the natural combination and its constituents resemble component of Red Ochre. Therefore, it can be concluded that among the various sample of GA available

in the market only sample no. 2 can be said to be the genuine one. None of the available samples have been updated for Armani.

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