

## Origin of Opal-CT in Lower Eocene Tallahatta Formation, Mississippi, USA and Pleistocene Barind Clay Formation in Bangladesh: A Comparative Study

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**Abstract.** Opal-CT mineral in the lower Eocene Tallahatta formation in Mississippi, USA and the Pleistocene Barind clay formation in Bangladesh is of volcanogenic origin. X-ray diffraction patterns of claystones in the former indicated more ordered condition of the older sediments than those of the latter, which may be due to higher burial temperatures and longer time interval for transformation from volcanic ash to opal-CT of the former. Glass shards, present in the latter sediments, were not identified in the former, which may be due to transformation of glass shards of volcanic ash to opal-CT over the time.

**Keywords:** opal-CT, glass shards, Tallahatta formation, Barind clay formation, Bangladesh

### Introduction

Opal-CT mineral of the lower Eocene Tallahatta formation is present throughout the Gulf and Atlantic coastal plains from Mississippi to Georgia and South Carolina states of USA. Opal-CT in Mississippi is suggested to be of volcanogenic origin (Kabir and Panhorst, 2004). Very recently this mineral was identified in the Barind clay formation of Pleistocene age in Bangladesh (Kabir, 2001; Kabir *et al.*, 2001). A volcanic ash bed within this formation, a precursor of opal-CT, is reported from other localities in Bangladesh (Islam and Parveen, 1997; Abdullah and Hasan, 1991) and in India, which has been identified as Toba ash (Acharyya and Basu, 1993; Rose and Chesner, 1987). Kabir (2003) reported the chemical and mineralogical similarities of opal-CT-rich sediment of Bangladesh with Toba ash (75,000 BP) in India.

The present paper describes the evolutionary development of opal-CT in response to the depth of burial and age of sediments of the Tallahatta formation in USA and the Barind clay formation in Bangladesh.

**Opaline silica—a brief review.** Opal-CT, natural hydrous silica, is rarely studied mineral in the subcontinent. Opal and opaline silica can be grouped as opal-A, opal-CT and opal-C (Jones and Segnit, 1971). Opal-A is a highly disordered, nearly amorphous silica phase precipitated from solution either organically or inorganically. Marine organisms such as diatoms, radiolarians and sponges can extract silica from seawater at concentrations well below saturation levels with respect to amorphous silica. The sequence of change from

opal-A contained in diatoms to opal-CT found in diatomite is well established. According to Hein *et al.* (1978), in the first 300 to 400 metres of burial, diatom frustules are fragmented, which increase the surface area available for the associated mild dissolution. By 600 m, the dissolution of opal-A is advanced and opal-CT precipitates abundantly between 600 and 700 m depth. The temperature required for transformation of opal-A to opal-CT is 35 to 55 °C (Calvert, 1983). Because the temperature is relative to the depth of burial, Hein *et al.* (1978) suggested that 500 m of diatomaceous sediment might be required at the base of the siliceous section for conversion of opal-A to begin. Murata *et al.* (1977) estimated that complete transformation of opal-A to disordered opal-CT occurred at a temperature of about 55 °C and at a burial depth of 900 to 1000 m. Nühr *et al.* (1998) showed a transition from opal-A to opal-CT in deep-sea sediments at depth of 340 to 370 m. Issacs (1982) and Williams *et al.* (1985) indicated that several hundred metres of burial and mildly elevated temperatures were required for conversion of opal-A to opal-CT when deposited with other types of sediments containing detrital materials. Inorganically precipitated opal-A is formed when a solution becomes saturated with respect to silica, causing silicic acid polymer to precipitate. These polymers then grow by the Ostwald ripening process to form colloidal sols and gels (Iler, 1979). Opal-CT can develop from opal-A as a solution-reprecipitation process (Williams and Crerar, 1985).

Opal-A produces an X-ray diffraction (XRD) pattern of a single diffuse band extending from about  $19^{\circ} 2\theta$  to  $25^{\circ} 2\theta$  ( $4.67\text{\AA}$ - $3.56\text{\AA}$  d-spacing) for  $\text{CuK}\alpha$  radiation (Murata and Larson, 1975).

Opal-CT is a disordered variety of low cristobalite that contains randomly interstratified tridymite (Flörke *et al.*, 1975; Jones and Segnit, 1971; Flörke, 1955). It has an X-ray diffraction pattern characterized by two broad reflections at  $22^\circ 2\theta$  (4.04–4.12 Å d-spacing) and  $36^\circ 2\theta$  (2.50 Å d-spacing) and a single small reflection at  $20.5^\circ 2\theta$  (4.25–4.12 Å d-spacing). Opal-C is well ordered  $\alpha$  (low) cristobalite. It closely resembles cristobalite and is recognized by major XRD reflections occurring as sharp, symmetrical peaks centered at  $22.2^\circ 2\theta$  (4.04 Å),  $28.5^\circ 2\theta$  (3.13 Å),  $31.5^\circ 2\theta$  (2.84 Å) and  $35.9^\circ 2\theta$  (2.50 Å).

**Opal-CT in the Tallahatta Formation, Mississippi, USA.** The Lower Eocene Tallahatta formation in Mississippi consists of Basic City Shale Member (lower member) and Nesoba Sand Member (upper member). The Basic City Shale Member consists mainly of grey to dark grey glauconitic claystone. It can be divided into four units (Kabir, 1998). The lowermost unit consists of claystone (clinoptilolite and smectite clay) and sandstone. The second unit is clinoptilolite-rich claystone, whereas the third unit is opal-CT-rich claystone, and the uppermost unit consists of claystone (mainly clinoptilolite with smectite clay), siltstone, mudstone and sandstone. The thickness of the Basic City Shale Member averages 45 to 50 meters.

From XRD data, the two claystone facies minerals opal-CT and clinoptilolite are identified (Fig. 1). One or both of these two minerals comprise of about 80% of all samples (Kabir, 1998). Scanning Electron Microscope (SEM) microphotographs indicate that the opal-CT is typically massive and structureless. It can also be formed within cavities as spherical crystal aggregates. Using chemical analyses, the high abundance of  $\text{SiO}_2$  (70 to 90%) in opal-CT-rich samples confirms the abundance of the mineral (Table 1). The assemblage of opal-CT, clinoptilolite, smectite group minerals and quartz indicates that the original sediment is unlikely to have been

the high purity opal-A material, seemingly required to produce early diagenetic opal-CT under low-temperature conditions (Bohrmann *et al.*, 1994). The Tallahatta Formation never achieved burial depth great enough for transformation of opal-A to opal-CT (Kabir and Panhorst, 2004). With increasing diagenesis, the structural disorder decreases according to the reaction path: non-crystalline opal (opal-A)  $\rightarrow$  opal-CT  $\rightarrow$  opal-C  $\rightarrow$  quartz in sea floor deposits of silica (Williams *et al.*, 1985; Calvert, 1977). Out of 577 samples analyzed from the Tallahatta formation, not a single sample contained any opal-A and the d-spacing (mostly 4.11 to 4.12 Å) signifies opal-CT (Kabir and Panhorst, 2004). In volcanically derived deposits of silica, opal-C and opal-CT seem to be formed directly without the initial development of opal-A (Flörke *et al.*, 1991; Ijima, 1978).

**Opal-CT in the Barind Clay Formation, Bangladesh.** The volcanic ash bed is confined within the Barind clay formation. The ash bed is about 10 to 30 cm thick and light grey to white in colour. This horizon is comprised mostly of quartz with very minor feldspar and glassy materials. Muscovite and dark-colour minerals are also present (Kabir, 2001). X-ray analyses of ash bed samples from Rajshahi and Bogra Districts of Bangladesh indicate the presence of opal-CT (Kabir, 2001, Kabir *et al.*, 2001). Illite, smectite and chlorite clay minerals are also present. Glass shards are identified through microscopic study of opal-CT-rich samples, which indicates the presence of volcanogenic sediments. The glass shards are larger than the surrounding minerals (Kabir, 2003). The presence of volcanic glass shards are considered as precursor of opal-CT identified in the sediments. Opal-CT might be formed from the glass shards by solid-solid inversion (Calvert, 1983; Hein *et al.*, 1978; Murata *et al.*, 1977) or by solution-reprecipitation (Williams and Crerar, 1985). The solid-solid inversion is thought to be responsible for the transformation of volcanic ash to opal-CT

**Table 1.** Major oxides of field samples from different locations

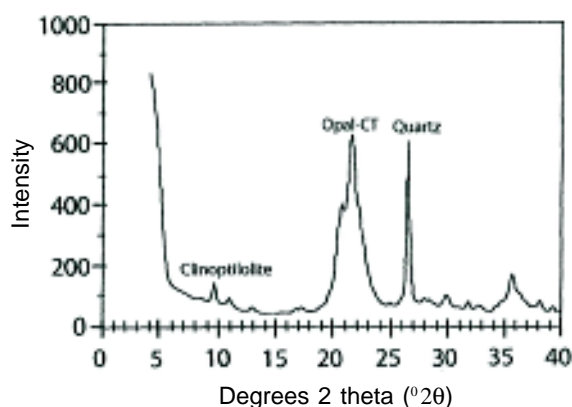
Oxides	Volcanic <sup>a</sup> ash, Rajshahi (BD)	Volcanic <sup>a</sup> ash, Bogra (BD)	Toba ash <sup>b</sup> Narmada, India	Toba ash <sup>b</sup> Son, India	Toba ash <sup>c</sup> Deep Sea Core	Toba ash <sup>d</sup> Tampan, Malaysia	Opal-CT <sup>e</sup> Mississippi, USA
$\text{SiO}_2$	68.16	61.21	68.18	73.97	77.04	70.46	80.45
$\text{Al}_2\text{O}_3$	10.12	18.65	15.90	13.59	14.24	13.51	5.23
$\text{Fe}_2\text{O}_3$	3.47	5.90	5.01	2.62	0.84	1.12	1.89
MgO	1.94	3.10	0.57	0.27	0.10	0.26	0.86
CaO	1.1	nil	5.58	2.29	1.05	1.70	0.68
$\text{Na}_2\text{O}$	0.93	1.50	1.82	2.29	2.52	3.82	0.17
$\text{K}_2\text{O}$	2.99	1.95	2.28	4.42	5.07	5.26	1.00
$\text{TiO}_2$	0.24	0.64	0.67	0.29	0.06	0.14	0.38

Ref: <sup>a</sup> = Kabir, 2001; <sup>b</sup> = Acharyya and Basu, 1993; <sup>c</sup> = Rose and Chestner, 1987; <sup>d</sup> = Ninokovitch *et al.*, 1978; <sup>e</sup> = Kabir and Panhorst, 2004

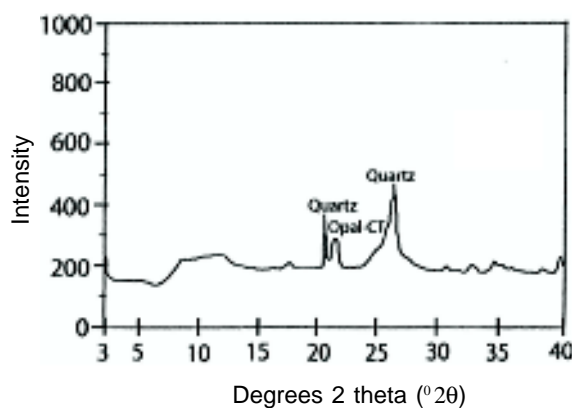
in Bangladesh as inferred from optical analysis. The presence of smectite minerals also confirmed the alteration of glass to smectite (Kabir, 2003). The XRD signature (Fig. 2) of these samples is more likely to be opal-CT than opal-C as classified by Jones and Segnit (1971). During increasing temperatures, Opal-CT changes its internal structure to opal-C at the expense of tridymite. Chemical analyses of the Barind clay volcanogenic sediments are listed in Table 1, along with analyses of Toba ash (75,000 BP) found in India (Acharyya and Basu, 1993), Malaysia (Ninokovitch *et al.*, 1978) and deep sea core (Rose and Chestner, 1987).

## Results and Discussion

XRD signatures of minerals in the Tallahatta samples (Fig. 1) are more distinct than those of the Barind clay samples (Fig. 2). The patterns of the Barind clay samples are diffused with less well-defined peaks. The opal-CT and quartz peaks



**Fig. 1.** XRD pattern of sample MCH 6-54 of Tallahatta formation showing opal-CT with clinoptilolite and quartz (modified from Kabir and Panhorst, 2004).



**Fig. 2.** XRD pattern of Barind clay sample SSOO-03A showing opal-CT with quartz (modified from Kabir *et al.*, 2001).

are much shorter relative to the background in the Barind clay samples than those of the Tallahatta samples. For the same mineral, relatively higher and sharper peaks indicate more ordered crystalline phase than the diffused peaks. The opaline phase of silica has changed to more crystalline phase in the course of time. The depth of burial of the Barind clay formation is about 1 m (Alam and Paepe, 1996) and that of the Tallahatta formation is more than 250 m (Merrill, 1985). The maturity depends on the age along with the depth of burial that is responsible for level of heating. These criteria indicate the difference in maturity between the opal-CT in the two formations. The volcanic ash in the Barind clay formation is in the process of transformation from opaline silica to opal-CT. The diffused nature and less intense peak height of opal-CT and quartz in the Barind clay samples indicate the presence of less silica minerals and more other minerals within it than the Tallahatta sample. There is a correlation between  $Al_2O_3$  and  $Fe_2O_3$ , both of which are probably contained within aluminosilicate minerals such as clinoptilolite, smectite and muscovite in the Tallahatta formation and smectite, illite and muscovite in the Barind clay formation. Presence of glass shards in the Barind clay formation is an obvious indication of volcanogenic origin of opal-CT within the sediments. Glass shards were not identified in the Tallahatta formation. Probably all glass shards in this older sedimentary unit were converted to opal-CT over the time.

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