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Characteristics and genesis of phillipsite grains in a sediment core from the Central Indian Ocean Basin

Sridhar D. Iyer[1], Shannon Meryl Pinto[2] & Areef A. Sardar[1]

[1]CSIR-National Institute of Oceanography, Dona Paula, Goa 403004, India

[2]Earth Science and Resource Management, Department of Studies in Earth Science, University of Mysore, Mysore 570005, India

[E.Mail: iyer@nio.org; shannonmeryl@gmail.com; areef@nio.org]

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Present study is the phillipsite grains present in a siliceous sediment core (water depth 5100 m) recovered near a seamount from the Central Indian Ocean Basin (CIOB). Phillipsite occurs as single grains, cruciform crystals and as simple to complex twinned forms. Chemical composition (av SiO_2 56 wt%, Al_2O_3 19 wt%, Na_2O 3 wt%, K_2O 9 wt%) and the Si/Al ratio (av 2.58) of the phillipsite are comparable with those reported from the Pacific Ocean. The formation of phillipsite depends on parameters such as the availability and type of precursors, the pH-Eh conditions, formation time and temperature, and type of processes. Low temperature halmyrolysis of precursors such as altered basaltic fragments and palagonite resulted in intra-sedimentary diagenesis and formation of abundant phillipsite grains.

[**Keywords:** zeolite, phillipsite, origin, intrasedimentary genesis, Central Indian Ocean]

Introduction

Zeolites, hydrated aluminosilicates with alkaline and alkali elements, are common in deep-sea sediments[1]. The zeolite, phillipsite was first recognised in the Pacific Ocean sediments during the expedition of the H.M.S. Challenger (1872-76)[2]. These were confirmed by Dekov et al[3] who reported the presence of zeolites in the SE Pacific metalliferous sediments that were recovered during the said expedition.

Phillipsite crystals are abundant in Miocene and younger sediments of the Indian and Pacific oceans than in the Atlantic Ocean[4-6]. Phillipsite in the SE Pacific Ocean and in some areas of the Indian Ocean ranges from 3 to 12% (by weight) in siliceous sediments while in calcareous sediments phillipsite could be up to 50% (by weight)[7]. It was opined that phillipsite and clinoptilolite may comprise up to 80% (by weight) of the oceanic and volcanoclastic sediments[8].

Phillipsite and volcanogenic sediments co-exist at Deep Sea Drilling Sites (DSDP) 382 (Nashville Seamount) and 385 (Vogel Seamount) in the Western North Atlantic Ocean[9]. Several types of zeolites nearly cover the entire outcrop of Late Cretaceous Cayo Formation of Coastal Ecuador[10].

Phillipsite crystallizes in the monoclinic system as colourless to yellowish prismatic crystals and is between 8 and 250 mm long[11]. Generally, volcanic glass, montmorillonite and palagonite are the most commonly reported precursors for phillipsite formation[12-14]. Detailed crystal chemistry of phillipsite has been presented by Gatta and co-workers[15,16]. Studies have revealed that the diagenetically remobilized rare earth elements (REE) and thorium are incorporated by phillipsite crystals by the processes of particulate inclusion and solution and ion-exchange[13].

Generally, phillpsite occurs in deep-sea sediments as individual crystals but there are reports of cemented/consolidated slabs of phillipsite and harmotome (barium-rich phillipsite) in the Society Ridge, South Pacific[17], as cavity filling of tuff as at the Sylvania Guyot, Pacific Ocean[18], as fracture filling in basalts of Leg 17 and replacement of the volcanic debris with nearly 50% of phillipsite[19]. Phillipsite could replace plagioclase crystals[19] and also occur in the nucleus of ferromanganese (FeMn) nodules[2,20,21]. It was reported that the authigenic phillipsite within the FeMn nodules, collected from Clarion-Clipperton Zone (NE Equatorial Pacific Ocean), formed at <10 ^{o}C, at a pH of about 8 and at <0.7 kbar pressure[22].

Four discrete stages of mineralization have been identified within the volcanic-hosted mineral deposits of the Dead-Sea-Transform Fault Systems[23]. Of these four stages, phases such as siliceous gels, smectite, analcime and phillipsite formed due to hypogene syneruptive alteration of pyroclastic rocks. Deep-sea mud at several sites in the eastern South and Central North Pacific Ocean contains high concentrations of REE and Yttrium (REY)[24] that are hosted by hydrothermal iron-oxyhydroxides and phillipsite. The mud contains phillipsites and biogenic apatite (fish debris) and the strong correlation between total REY content and apatite abundance indicate the latter to host the REY[25].

Based on the reported enrichment of REY in the deep-sea mud in the Pacific Ocean and considering the abundant presence of zeolite-claystone[26,27], perhaps the likelihood of a similar occurrence cannot be ruled out in the CIOB. Although simple acid leaching method would release the REY (except cerium) from the mud but the great water depth (4000-5000 m) is a major constraint to mine the REY-rich mud[24].

Cavalazzi et al.[28] examined the pillow basalts from the Ampere-Coral Patch Seamounts (eastern North Atlantic) for potential microbial life. Phillipsite is reported to occur in an eolian silicate dust of a 328 cm long piston core collected from the northeast equatorial Pacific[29].

Natrolite has been reported to occur in the Indian Ocean[20,31]. Venkatarathnam and Biscaye[8] concluded that alterations of basic and silicic volcanic materials in the Indian Ocean could result in the formation of phillipsite and clinoptilolite, respectively. The rate of formation of authigenic phillipsite in the CIOB and the Equatorial Pacific Ocean was calculated by Czyscinski[5]. In the Indian Ocean, clinoptilolite is dominant (59%), followed by phillipsite (22%) and analcime (17%)[ref 32]. Phillipsite occurs in various sedimentary facies in the DSDP sediment cores from the Indian Ocean[33]. In the CIOB, well-developed and diagenetically formed phillipsite crystals occur within FeMn micronodules[34], macronodules[35, 36] and in a red-clay sediment core[37]. In the above reports phillipsite occurs as small-sized grains but there are also widespread occurrences of zeolitic slabs (also termed as zeolitic clay-stones) that are dominantly composed of phillipsite and possibly harmotome (Ba-rich phillipsite)[26]. Iyer et al.[27] attributed the formation of these zeolitic slabs to the transformation and halmyrolysis of precursors (glass, palagonite) under the influence of low-temperature conditions.

The CIOB, the largest basin (~5.6 x10^6 sq km) in the Indian Ocean, extends from 0^0 S to 25^0 S latitude and 70^0 E to 90^0 E longitude and has two distinct regions: the highly deformed north (north of 9° S) and northeastern part and the relatively undeformed southern region (south of 9° S). The average water depth is 5100 m and it increases from west to east. Several studies exist concerning the CIOB such as its sediment characteristics (types, minerals, geochemistry[38]), bathymetry and morpho-tectonic features (fracture zones, seamounts, hills[39]), occurrence of a variety of mafic and silicic volcanics[40,41], FeMn deposits (nodules, crusts[38, 42]), probable hydrothermal activity[43] and the relation between volcanics and the FeMn deposits[38, 44]. Baddeleyite (ZrO_2) grains have been noted in FeMn nodules of the CIOB. These occur as single isolated sub-rounded to elliptical grains or in clusters forming fine subhedral crystals (<3 μm). Their mode of occurrence, textural features and composition suggest a detrital and possibly an authigenic origin[45].

We investigated a siliceous sediment core recovered from the Central Indian Ocean Basin (CIOB). The coarse fraction (> 63 μm) contained phillipsite grains, glass shards, pumice pieces, FeMn micronodules, mafic rock fragments, microtektite, mineral fragments, palagonite grains and biogenic matter in the sediment core. These materials have been described and their sources have been deciphered[30]. Of these components phillipsite grains are one of the major authigenic phases. Therefore, the characteristics and composition of phillipsite crystals were studied to decipher their genesis in an intra-sedimentary environment i.e., an open hydrologic system[15].

Materials and Methods

We studied a sediment core collected during the 10th cruise of *MV Skandi Surveyor*. Initially, a Van Veen core (SS 10/655 A) was recovered but since the sampler came back nearly empty another operation was carried out. The sample (SS 10/655 B) was lifted from a water depth of 5190 m at latitude 13˚58.773' S and longitude 75˚ 57.990' E (Fig. 1). The core is located near a seamount and the adjacent microtopography is flat. The core SS 10/655 is close to those of SS-89 and SS 10-657 (Fig. 2) from which volcanogenic-hydrothermal materials (vhm) were recovered that helped to ascertain the timing (~10 ka) of the volcanic events[46].

The sampler was filled with siliceous sediments and the weight of the sediment was 56 kg. The

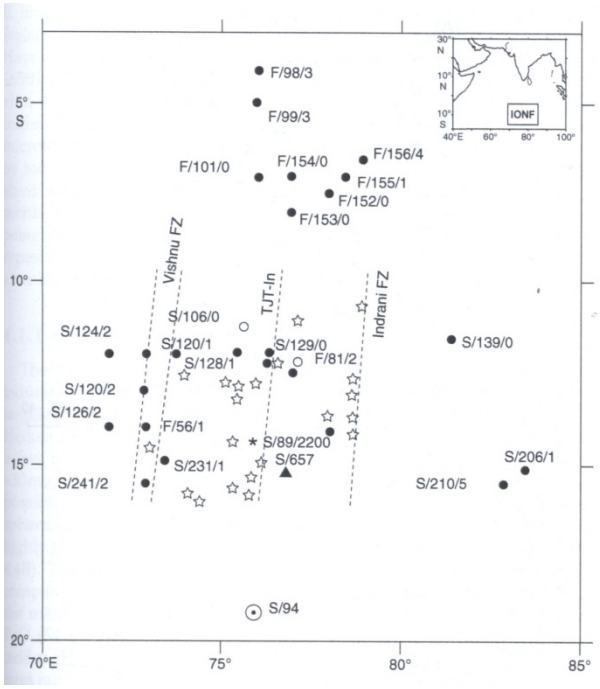

Fig. 1 — Distribution of volcanogenic sediments in the CIOB (Open star = seamounts, solid dots = sediments examined for volcanogenic hydrothermal material; solid triangle = S657 and asterisk = S89 are near a large seamount). The last numerals after station number represent magnetic particles present in 1 g of the sediments coarse fraction e.g. S/124/2 means "cruise Skandi Surveyor, station 124 and 2 is the number of magnetic particles." F = Farnella ship (after Iyer at al.[46]).

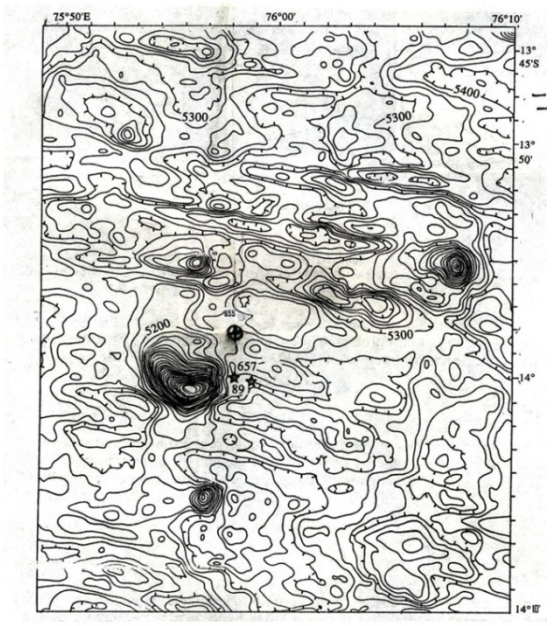

Fig. 2 — Bathymetry of the study area. Sample SS X/655B is in the vicinity of a seamount while cores SS 2/89, SS 10/657 are from the base of the seamount. This seamount has a pronounced bulge in an approximately E-W direction. Contour interval = 100 m (after Iyer at al.[46]).

sediment hosted 15 buried FeMn nodules that have a rough surface feature. The core was divided into top (up to 5 cm), centre (5-10 cm) and bottom (10-15 cm) portions. The sediments were thoroughly washed with distilled water and the clays were dispersed using 20 ml of 10% Na-hexameta-phosphate and later passed through a 63 μm sieve. The coarse fraction was oven dried at 60-70 °C, weighed and stored in vials.

Several phillipsite crystals were impregnated in epoxy mounts. These were polished, cleaned in an ultrasonic bath, dried and later coated with carbon. Mineral composition was determined with a CAMECA SX5 electron probe micro analyzer (EPMA) at an operating voltage of 15 kV, a beam current of 12 nA and a beam diameter of 1 μm. Mineral standards were used to check the accuracy of the analysis and the data were subjected to ZAF corrections. Water content was calculated by totaling the oxides and subtracting from 100.

Results

The core sediment is siliceous and has low contents of coarse fraction ranging from 1% to 1.25 wt%. Dominant phases are FeMn and silicic glass shards of variable shapes and morphology such as platy, Y-shaped, ridge-like etc. There are also small-sized pumice, altered rock fragments, palagonite, biotite and quartz[30]. Biogenic matter includes fish teeth (whole and fragments), agglutinated foraminifers and radiolarians. Several of the agglutinated foraminifers have their test wall made of phillipsite crystals (Fig. 3).

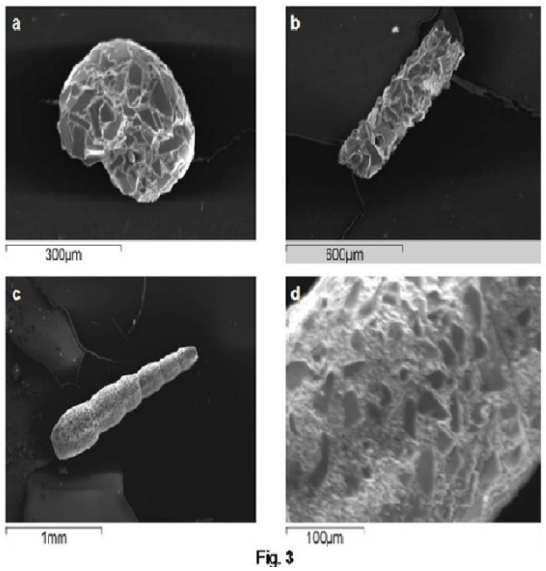

Fig. 3 — Electron micrographs of agglutinated foraminiferal test made of phillipsite and glass shards, (d) magnified portion of c

In general, the average content of phillipsite crystals is 14% (10.7 to 16.5% in the three sub-section of the core). Crystals are fresh and have no pores or pits while a few show features of dissolution. The colourless to yellowish prismatic phillipsite grains are 128 to 282 µm long (Fig. 4). Typical cruciform crystals are very common as also single crystals, twinned (simple interpenetrative to complex sector types) and ball-shaped aggregates (Figs. 4, 5). Some of the crystals have an overgrowth of smaller phillipsite crystals (Figs. 4, 5) and/or a thin coating of FeMn oxides. Phillipsite may undergo rapid dissolution (Fig. 6) that results in etched crystal faces or complete disappearance of the crystal form.

Microprobe analysis of 58 phillipsite grains (Table 1) shows the following variations in the major oxides: SiO_2 (52-61%), Al_2O_3 (18-21%), FeO (1-4.5%), MgO (0.10-1.4%), Na_2O (1-4.5%), and very low CaO (<0.3%) and BaO (<0.6). Minor amounts of TiO_2 (0.12-0.3), P_2O_5 and MnO are present in a few grains. The H_2O varies from 3.39 to 13.5%. The phillipsite grains can be called as K-rich phillipsites due to the considerable content of potassium (K_2O 4.8-12.5%). Similar K-rich (8-10%) phillipsites occur in the Neapolitan Yellow Tuff, Italy[9] and at DSDP Sites 382 and 385 (6-10% K_2O)[15]. The ratios of Si/Al and Na/K in the CIOB phillipsites range from 2.4 to 2.8 (av 2.58) and 0.12 to 0.4 (av 0.28), respectively. A comparison of the composition of the CIOB phillipsite with those at the other

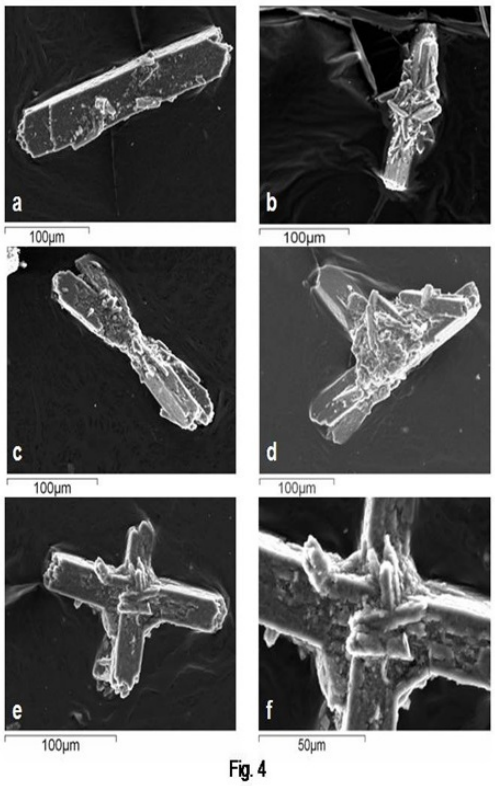

Fig. 4 — Electron micrographs of phillipsite crystals, a-Single crystal, b-Single crystal with over growths, c and d-twinned crystals, e-Typical cruciform, f- magnified view to show the overgrowth of small grains of phillipsite over a large crystal.

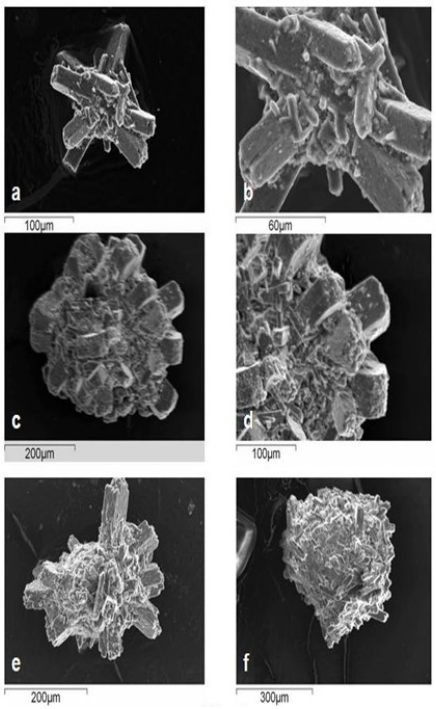

Fig. 5 — Electron micrographs of multiple twinned phillipsite

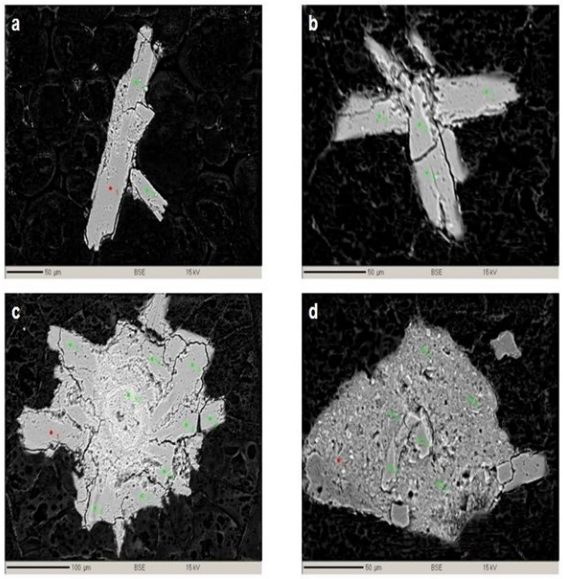

Fig. 6 — Electron micrographs of polished phillipsite crystals exhibiting dissolution features at the termination of the crystal faces.

Table 1 — Microprobe analysis of 58 grains of phillipsite from a sediment core recovered from the Central Indian Ocean Basin. bd =below detection limits, H_2O is by difference

Oxides (wt %)	1	2	3	4	5	6	7	8	9	10
SiO_2	57.78	59.19	59.02	59	59.7	58.96	57.07	59.81	58.99	58.18
Al_2O_3	19.36	19.8	19.71	20.5	20.00	19.55	19.09	19.83	19.98	19.18
FeO	1.54	0.89	1.60	1.05	0.99	1.07	1.04	1.35	1.25	1.77
MgO	0.61	0.27	0.3	0.24	0.27	0.28	0.18	0.25	0.29	0.47
CaO	0.11	0.12	0.19	0.1	0.11	0.11	0.05	0.1	0.1	0.26
Na_2O	2.21	1.93	2.10	1.78	2.22	2.58	2.28	2.12	2.04	2.07
K_2O	11.02	10.19	9.61	10.56	10.81	10.64	11.24	12.05	11.23	10.23
P_2O_5	0.14	bd	0.16	bd	bd	0.14	bd	bd	bd	0.16
BaO	0.15	0.34	bd	0.14	bd	0.2	0.28	0.12	bd	0.21
H_2O	7.08	7.27	7.31	6.63	5.90	6.47	8.77	4.37	6.11	7.47
Si/Al	2.64	2.64	2.64	2.54	2.65	2.66	2.64	2.66	2.61	2.68
Na/K	0.18	0.17	0.20	0.15	0.18	0.22	0.18	0.167	0.16	0.18

Oxides (wt %)	11	12	13	14	15	16	17	18	19	20
SiO_2	58.22	58.54	58.32	59.24	60.11	53.87	58.5	61.35	60.91	56.96
Al_2O_3	19.08	20.48	19.2	20.06	19.91	18.81	19.45	20.07	20.15	19.38
FeO	1.45	1.04	1.03	1.18	1.15	1.91	1.67	1.74	1.2	0.94
MgO	0.35	0.22	0.2	0.22	0.34	0.27	0.35	0.37	0.25	0.12
CaO	0.15	bd	0.1	bd	bd	0.23	bd	0.13	bd	bd
Na_2O	1.77	2.77	2.08	2.21	2.45	2.52	2.01	2.46	1.88	2.43
K_2O	10.67	11.61	11.7	11.36	11.42	10.95	10.95	10.15	10.92	10.79
P_2O_5	0.10	bd	bd	bd	bd	0.15	bd	bd	bd	bd
BaO	bd	0.21	bd	0.33	0.16	0.22	0.29	0.34	bd	bd
H_2O	8.21	5.13	7.37	5.4	4.45	11.07	6.77	3.39	4.69	9.38
Si/Al	2.69	2.52	2.68	2.61	2.68	2.52	2.70	2.70	2.70	2.60
Na/K	0.15	0.21	0.16	0.17	0.19	0.21	0.16	0.22	0.15	0.20

Oxides (wt %)	21	22	23	24	25	26	27	28	29	30
SiO_2	58.48	59.82	58.82	60.22	56.11	58.43	59.68	58.62	58.41	55.17
Al_2O_3	20.28	20.47	19.74	20.05	19.66	19.62	19.93	20.52	19.73	18.25
FeO	2.03	1.12	1.55	0.99	1.48	1.33	1.41	1.61	1.55	2.2
MgO	0.46	0.25	0.27	0.23	0.24	0.24	0.25	0.22	0.30	0.44
CaO	bd	0.27	0.15	0.13	bd	0.12	0.15	0.11	bd	bd
Na_2O	2.2	1.84	1.98	2.19	2.31	3.35	2.43	2.41	2.76	3.04
K_2O	12.07	10.92	10.59	10.83	10.31	9.7	8.87	8.61	11.97	11.92
P_2O_5	bd	0.24	0.1	bd	bd	bd	bd	bd	bd	bd
BaO	0.18	0.13	0.21	0.31	0.24	bd	bd	0.17	0.22	0.13
H_2O	4.3	4.9	6.59	5.05	9.65	7.21	7.27	8.18	5.06	8.84
Si/Al	2.55	2.59	2.63	2.65	2.52	2.64	2.64	2.52	2.61	2.67
Na/K	0.16	0.15	0.17	0.18	0.20	0.31	0.24	0.26	0.21	0.23

Oxides (wt %)	31	32	33	34	35	36	37	38	39	40
SiO_2	52.83	56.36	54.96	56.60	56.22	54.95	58.71	53.24	60.55	57.18
Al_2O_3	19.2	19.32	19.29	18.97	18.39	17.98	19.29	18.34	19.94	18.65
FeO	4.34	2.01	2.87	1.51	1.04	1.2	1.16	1.29	0.62	0.76
MgO	0.43	0.32	0.36	0.21	0.21	0.18	0.23	0.29	0.14	0.18
CaO	0.27	bd	0.16	0.1	0.1	0.1	0.1	3.62	bd	bd
Na_2O	3.46	1.97	3.09	2.39	1.95	1.99	2.96	2	2.72	2.55
K_2O	8.27	11.6	8.1	10.25	9.92	10.98	11.12	10.69	12.24	10.87
P_2O_5	0.21	bd	0.13	0.1	bd	bd	bd	2.65	bd	bd
BaO	0.69	0.48	0.49	0.20	bd	bd	0.24	bd	0.12	bd
H_2O	10.3	7.94	10.55	9.67	12.17	12.92	6.19	7.87	3.67	9.80

(*Contd.*)

Table 1 — Microprobe analysis of 58 grains of phillipsite from a sediment core recovered from the Central Indian Ocean Basin. bd =below detection limits, H_2O is by difference (*Contd*.)

Oxides (wt %)	31	32	33	34	35	36	37	38	39	40
Si/Al	2.43	2.57	2.53	2.63	2.70	2.70	2.69	2.56	2.68	2.71
Na/K	0.37	0.15	0.34	0.21	0.18	0.16	0.24	0.17	0.20	0.21
Oxides (wt %)	41	42	43	44	45	46	47	48	49	50
SiO_2	60.00	58.81	57.42	56.96	54.97	57.53	51.13	57.72	56.91	57.71
Al_2O_3	19.87	19.56	20.2	19.34	18.65	19.6	17.94	20.06	19.15	18.83
FeO	0.12	1.21	1.41	1.06	1.42	2.67	5.4	1.42	1.01	0.87
MgO	0.18	0.22	0.3	0.22	0.28	0.5	0.89	0.32	0.18	0.91
CaO	0.10	0.11	bd	bd	0.11	0.11	0.12	bd	bd	bd
Na_2O	2.25	2.47	2.2	3.31	2.55	2.37	1.31	2.22	2.57	2.49
K_2O	11.19	10.95	11.46	11.06	12.93	10.48	9.04	11.32	10.14	9.70
P_2O_5	bd	bd	bd	bd	bd	0.12	0.2	bd	bd	bd
BaO	bd	bd	0.31	0.25	0.15	0.24	0.49	0.22	bd	0.25
H_2O	6.28	6.67	6.69	7.8	8.94	6.38	13.48	6.72	10.04	9.24
Si/Al	2.67	2.66	2.51	2.60	2.60	2.59	2.52	2.54	2.62	2.71
Na/K	0.18	0.20	0.17	0.27	0.18	0.20	0.12	0.18	0.23	0.23

Oxides (wt %)	51	52	53	54	55	56	57	58
SiO_2	60.91	43.52	57.47	55.45	56.63	57.62	57.46	56.79
Al_2O_3	20.00	14.05	19.84	19.17	18.90	18.12	19.27	19.32
FeO	1.04	10.26	1.14	1.87	1.50	1.36	1.66	1.52
MgO	1.04	1.90	0.24	0.31	0.23	0.26	0.24	0.20
CaO	bd	0.34	bd	0.10	0.10	0.22	0.15	0.28
Na_2O	2.06	0.56	3.99	4.24	4.17	3.76	3.76	4.05
K_2O	10.92	6.06	6.92	6.83	6.71	6.44	7.35	7.17
P_2O_5	bd	0.39	bd	bd	bd	bd	bd	bd
BaO	bd	1.05	0.11	0.26	0.16	0.19	0.74	0.14
H_2O	4.02	21.87	10.29	11.71	11.6	12.03	9.37	10.53
Si/Al	2.68	2.74	2.56	2.55	2.65	2.81	2.63	2.60
Na/K	0.16	0.08	0.52	0.55	0.56	0.52	0.46	0.50

deep-sea sites[6,7,47] shows a close similarity in the contents of Si, Al, Na and K while the Si/Al and Na/K ratios are also on par with the reported values (Table 2).

Besides phillipsite grains we also examined several palagonite grains, clay-like material and altered basaltic fragments. The electron micrographs are shown in figure 7 and their compositions in table 3 (a to d). Palagonite grains display dehydration cracks (Fig. 7a) and are have enriched Si and Fe, high K and low K and Ca (Table 3a). Several of the palagonite grains are encrusted by FeMn oxides (Fig. 7b; Table 3b). Clay-like materials (Fig. 7c) have a composition corresponding to a mixture of montmorillonite/ smectite and zeolite (Table 3c). This material is similar to the indurated zeolitic claystones that occur as slabs and fragments on the seafloor sediments of the CIOB[27]. In addition to the above, we noted the presence of a few basaltic fragments (Fig. 7d) that are highly altered and oxidized as seen from the loss of Mg and high Fe (Table 3d). A few of the fragments are encrusted by FeMn oxides.

On a plot of SiO_2 vs Na/K ratio (Fig. 8) are included the data of the CIOB phillipsite (Table 1) and the average values of phillipsite grains from the CIOB and Indian and Pacific oceans (Table 2). We observed that a majority of the samples cluster between 50 and 60 wt% SiO_2 and have Na/K <0.4 while some have between 0.4 and 0.6 Na/K, the exception being the phillipsite from the Pacific Ocean[7] that has the highest Na/K (>1) for similar SiO_2 values.

Discussion

In the present study phillipsite occurs as single grains, multiple-twinned grains and ball-like structures which might have formed due to the aggregation of several single or multiple-twinned

Table 2 — Analysis of phillipsite grains (1) & (2) Stonecipher[6], (3) Sheppard et al.[47], (4) Goldberg[7], (5) Present work (Average of 55). bd = below detection limits, na = not available.

Oxides (wt %)	1	2	3	4	5	7	8	9	10
SiO_2	56.21	58.28	54.06	53.47	56.5	43.17	29.75	65.52	52.90
TiO_2	na	na	na	na	na	1.99	0.50	0.62	1.20
Al_2O_3	18.38	17.21	17.71	16.62	19.5	6.56	6.73	15.47	14.16
FeO	0.42	0.35	na	na	2.75	37.58	13.98	9.65	22.62
MnO	na	na	na	na	na	5.63	37.41	1.33	1.35
MgO	0.19	na	0.50	0.06	0.75	1.15	4.04	0.96	bd
CaO	3.17	0.27	1.29	0.29	0.26	2.16	2.79	3.72	2.48
Na_2O	2.35	4.72	3.82	7.41	2.75	na	0.20	0.59	1.86
K_2O	7.17	6.72	6.78	6.41	8.84	1.87	2.00	2.73	2.93
H_2O	12.11	12.54	15.63	na	8.48	-	-	-	-
Si/Al	2.69	2.99	2.71	2.84	2.58	-	-	-	-
Na/K	0.29	0.63	0.50	1.03	0.28	-	-	-	-

Table 3 — EDS analysis of palagonite grains, mixture of clay and zeolite and altered basaltic fragments. bd = below detection limits. A = Palagonite ; B = Palagonite with FeMn Oxides.

Oxides	S1M1	S2M2	S2M4	S2B4	S7T3	S7M3
SiO_2	65.93	29.27	41.42	52.52	39.84	30.05
TiO_2	1.85	2.06	2.75	2.32	bd	2.96
Al_2O_3	13.59	9.93	9.14	bd	bd	6.72
FeO	14.9	43.90	36.63	40.29	45.72	44.06
MnO	0.33	7.02	5.03	1.44	9.64	10.33
MgO	bd	4.25	2.66	bd	bd	bd
CaO	0.5	2.28	2.42	2.79	-	4.97
K_2O	2.94	0.81	1.15	0.62	4.79	0.93
TOTAL	100.04	99.52	101.2	99.98	99.99	100.02

Oxides	S1T1	S1T2	S1M1	S1M2	S1M3	S2T1	S2M2	S6T1	S6T1	S6M1	S6M1	S7B3
SiO_2	30.24	31.89	29.22	27.21	27.42	15.01	30.95	31.54	34.34	32.01	33.62	33.6
TiO_2	0.48	0.4	0.52	0.52	0.41	0.43	0.34	0.53	0.54	bd	0.63	1.23
Al_2O_3	10.45	10.99	9.9	9.16	7.71	5.69	10.65	bd	4.94	bd	bd	11.27
FeO	5.14	5.72	6.74	6.38	5.59	4.42	6.89	25.07	20.51	33.05	23.13	25.12
MnO	40.07	36.58	41.63	38.36	42.89	57.16	33.89	36.02	35.91	29.6	37.72	19.17
MgO	6.51	7.03	4.37	4.98	8.12	7.35	6.24	bd	bd	bd	bd	3.84
CaO	1.86	1.72	2.49	8.31	2.45	3.22	3.56	1.93	1.99	1.7	1.88	2.39
Na_2O	bd	bd	bd	bd	bd	bd	bd	0.92	bd	1.49	bd	bd
K_2O	2.35	2.33	2.37	2.06	2.61	1.9	2.63	1.9	1.54	1.36	1.00	1.97
CuO	0.78	0.79	1.29	0.76	0.7	1.35	0.78	0.74	0.87	0.78	1.21	bd
NiO	1.88	1.97	1.97	2.25	1.75	3.81	2.16	0.79	0.78	bd	0.82	1.39
ZnO	bd	0.28	0.45	0.48	bd	0.62	0.41	bd	0.33	bd	bd	bd
TOTAL	99.76	99.7	100.95	100.47	99.65	100.96	98.5	99.44	101.75	99.99	100.01	99.98

small-sized phillipsite grains. Abundance of phillipsite in the studied sediment core (SS 10/655 B) could be due to the nucleation and growth of phillipsite crystals not only at the sediment/water interface but also because of their continued growth within the sediment column[22,33]The processes of rapid growth and dissolution of phillipsite (Fig. 6) indicate that its formation is kinetically controlled and forms metastably[22]. The phillipsite grains observed by us are generally devoid of dissolution features (Fig. 5) and this attests to the freshness and well-preserved nature of the grains.

We now discuss the source of the precursors for and the formational process of phillipsite present in the core SS 10/655 B of the CIOB. The most common precursors for phillipsite formation are volcanic glass andpalagonite[14,32,47].

Besides these factors, the composition of zeolites depends on reaction time for devitrification, crystallochemical transformations of glass of different Si/Al ratios at low temperature and pressure, sedimentation rates, sediment type, Eh-pH conditions and formational time[26,27 and refs therein]. A study of the stability field of phillipsite and the depth and age

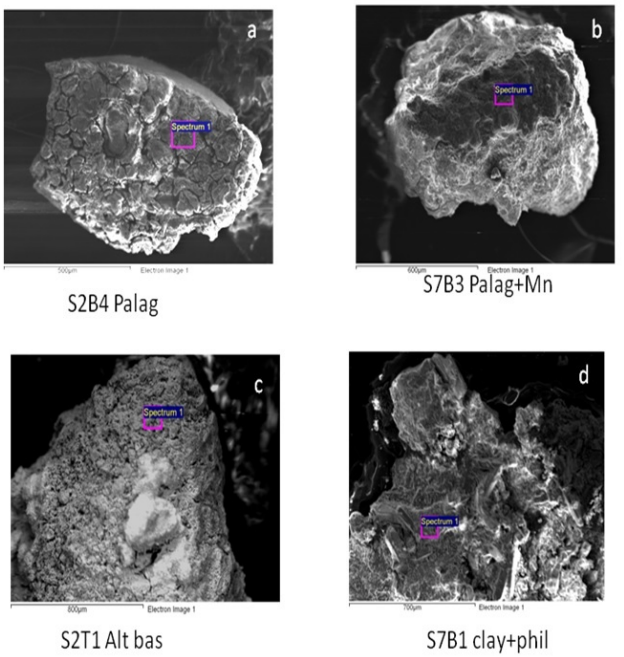

Fig. 7 — Electron micrographs of (a) palagonite grains with dehydration cracks, (b) palagonite grains with ferromanganese oxides, (c) altered and oxidized basaltic fragment, (d) part of a grain of clay + phillipsite. The sample numbers correspond to those in Table 2 (a to d)

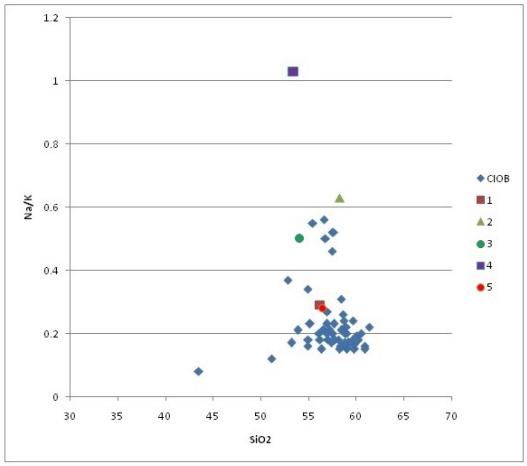

Fig. 8 — Plot of SiO_2 vs Na/K ratio of phillipsite from the CIOB (Table 1) and other oceans (Table 2). Please see the explanation in the text.

relations of phillipsite and clinoptilolite, show that phillipsite does not form a thermodynamically stable phase in the deep-sea environment; instead kinetic factors control their rapid nucleation and growth[33].

The Si/Al ratio of the marine phillipsite is 2 to 3, which is intermediate between the mafic volcanic and silicic tuff. Since the alkali cations are dominant and K predominates over Na[47] hence, phillipsites were presumed to form in a chemical environment with lower activity of silica and higher activity of alumina and potassium[33]. The Si/Al ratio of the phillipsite grains in our samples is between 2.4 and 2.8 (av 2.58) and indicates the phillipsite to have an intermediate composition between those formed from the mafic igneous rocks and the silicic tuffs as in saline lacustrine deposits[33]. The Si/Al ratio is perhaps related to the buffering capacity of seawater which, in the form of interstitial water, tends to maintain the seawater's pH between 7.2 and 7.7 and a Si concentration of 20 to 50 ppm[48].

The enhanced silica and potassic contents of the CIOB phillipsites (Table 1) may be due to their association with montmorillonites-illite clays that are common in the CIOB sediments[49] and the K-rich palagonite derived from the alteration of the basaltic glass[50]. According to Houghton et al.[9] a decrease in montmorillonite and an increase in illite would involve uptake of potassium with a result that there is insufficient potassium in the sediments to form clinoptilolite. This mechanism could help explain the scarcity of clinoptilolite in the CIOB sediments.

Phillipsite could form by the reaction between basaltic glass and dissolved silica (primarily biogenic)[8]. Further, phillipsite may coexist with smectite, Fe-oxyhydroxides and FeMn oxides and almost always with basaltic glass[33]. According to Honnorez[51] diagenesis or alteration of volcanic debris, glass and palagonite (that are present in the surrounding sediments), may be transformed to zeolites. This fact is attested in the CIOB by an abundance of volcanic material that is present in the form of altered basaltic glass and palagonite[50] and rhyolitic glass shards[52,53,54].

In the core SS 10/655 B we observed a significant amount of palagonite grains (av 7.5%; range 5.3-9 %). The factors that influence the rate, formation, composition of palagonite and dissolution of primary material and precipitation of secondary phases are: temperature, structure, porosity, permeability, and reactive surface of the primary material, the structure of the secondary phases, time and fluid properties (Eh, pH, ionic strength, oxygen fugacity fO_2)[14]. Besides these aspects, microbial activity could also breakdown the volcanic glass to produce authigenic phases and result in elemental redistributions[55,56].

Deep-sea phillipsite may form by the processes of: diagenesis, hydrothermal, metamorphism and halmyrolysis[32]. It was reported that the basaltic lava

of ~60 Ma in the CIOB chilled to form pillow with a quenched glassy exterior and a polycrystalline interior. Constant interaction with the seawater produced palagonite and phillipsite in a low oxidative alteration environment[50]. In a similar manner the basaltic fragments in the core SS 10/ 655 B may have been altered to result in palagonite and this in turn was slowly transformed to phillipsite. This mechanism is similar to intranodule diagenesis within manganese nodules wherein phillipsite crystallises[21].

Investigations have revealed that phillipsite more commonly forms as a result of diagenesis because of its regional occurrence and dominant appearance in younger and somewhat shallower sedimentary column. In the case of the phillipsite crystals present in the studied sediment core, we rule out the influence of low-temperature hydrothermal and metamorphism as there are no substantial evidences for these processes.

The presence of phillipsite with palagonitic muds of the seafloor suggests that hydrolysis of palagonitised glass to smectite creates an environment essential for phillipsite formation. This is attested by the higher content of phillipsite crystal (14%) as compared to that of palagonite grains (7.5%) in the studied core. Further, an increase in the amount of zeolites formed after the initial stages of alteration to palagonite suggests removal of Al from the glass[14]. Prevalence of montmorillonite and phillipsite grains in the core SS10/655 B suggests their derivation from altered volcanic glasses. This fact is evident from table 3 (a to d) that depict the different stages of alteration and palagonitisation of basaltic fragments and subsequent formation of a mixture of clay and zeolite. Such a transformation is plausibly the result of intra-sedimentary diagenesis brought about by halmyrolysis of precursors at a low temperature.

Therefore, we ascribe the formation of phillipsite to a process of halmyrolysis of the mafic rock fragments that initially result in the formation of palagonite which was later diagenetically altered to produce authigenic phillipsite grains. The co-occurrence of mafic rock fragments, palagonite and phillipsite attests to the intra-sedimentary formation of phillipsite crystals in the sediment core.

Conclusions

The composition of the CIOB phillipsite is similar to those from the other oceanic counterparts. Intermediate Si/Al ratio (2.4-2.8, avg 2.58) indicates the phillipsite grains to have formed by a process of intra-sedimentary halmyrolysis and diagenesis of altered mafic volcanic and palagonite that are present in the core.

Phillipsites are common in volcanogenic sediments and are relatively resistant to weathering and alteration in contrast to the other authigenic phases such as FeMn nodules, which are readily affected by a change in the redox conditions. Therefore, the ubiquitous occurrence of phillipsites could be used to understand the sedimentary processes and sediment accumulation rates.

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