Occurrence of nontronite in amygdales of Deccan basalts at Nagewadi basalt quarry, Satara, Maharashtra

The smectite group includes dioctahedral smectite, such as montmorillonite and nontronite \((\text{Ca}_{(2-4)}\text{Mg}_{(3-6)}\text{Al}_{(2-4)}\text{Si}_{(3-4)}\text{O}_{(10)}\text{OH}_{2})_{4}\) and trioctahedral smectite -- saponite \((\text{Ca}_{2}\text{Na}_{3}\text{Fe}^{3+})_{3}(\text{Si}_{7}\text{Al}_{8}\text{Fe}^{2+})_{7-8}\text{O}_{20}(\text{OH})_{4})\) and trioctahedral smectite -- beidellite series from fine clay separated from 354 cm deep sediment core in the southeastern Pacific Basin, Okinawa Trough, Japan. Singer et al. recorded smectite close to the pure Fe end-member or the nontronite–beidellite series from fine clay separated from a 354 cm deep sediment core in the southeastern Pacific Basin. A sediment core containing a yellowish-green bed was recovered from an area of extensive hydrothermal deposition on the southeastern slope of the Eolo Seamount, Tyrrhenian Sea. The clay bed is composed of pure nontronite, which appears to be the most aluminous nontronite ever found among the seafloor hydrothermal deposits. Study of the occurrence of nontronite in Washington, Idaho and Oregon of the Columbia River region by Victor and Veron suggests that the nontronite has formed by weathering of basaltic glass, palagonite, iddingsite and augite under conditions of poor drainage in the presence of alkalis, magnesium and probably ferrous iron.

There are several quarries in the Deccan Traps at Nagewadi (17°45′24.39″N–73°59′24.31″E) on the Pune–Bangalore Highway. One such quarry located about 7.62 km north of Satara, Maharashtra exposes the basaltic lava flows in a 73.5 m deep cut. Here, a 40.5 m thick, vertically jointed compact basalt is overlain by 10 m thick, grey, amygdaloidal basalt. The amygdales are made up of greenish-grey clay mineral (Figure 1). The amygdales range in size from 0.11 to 0.16 cm and the average size is 0.75 cm. In general, the amygdales are rounded to sub-rounded in form. Rarely, other minerals found as amygdales include quartz and opaques. Overlying this flow is an approximately 3 m thick reddish, tuffaceous horizon with an appreciable concentration of secondary minerals. The tuffaceous horizon is overlain by another flow. The lower 10 m zone of this flow is grey, compact and amygdaloidal. The uppermost 10 m of the upper flow is highly weathered forming a typical soil horizon.

The greyish-green clayey mineral was carefully scooped out from the amygdales using a steel pocket knife. Its physical, optical and geochemical characterization has been carried out. The clay mineral exhibits a waxy luster and has a relative hardness of about 1.5–2.0. It yields a greenish-grey streak. Host basalt reveals intergranular and interstitial texture; sometimes glomeroporphyritic aggregates of plagioclase are seen. Plagioclase feldspar, pyroxene, olivine and opaques are primary minerals, whereas palagonite and iddingsite are secondary alteration products. Under the microscope, the clayey mineral appears opaque (Figure 2) and is traversed by randomly oriented undulating cracks.

**Figure 1.** Field photograph of the Deccan Trap exposure at Satara quarry. Note the vesicles entirely filled with greyish-green nontronite.
Figure 2. Photomicrograph of the vesicle with greyish-green nontronite exhibiting cracks (scale – 600 μm).

Figure 3. Scanning electron photomicrograph exhibiting delicate aggregates of spheroids with well-crystallized dioctahedral sheets of nontronite (scale – 50 μm).

Scanning electron photomicrograph of the clay mineral was obtained using JOEL SEM–EDX using the JSM-6360 Scanning Electron Microscope at the Department of Physics, University of Pune. The SEM reveals the presence of delicate aggregates of spheroids with well-crystallized dioctahedral sheets of nontronite (Figure 3). Partial chemical analysis of the photographed phases is given in Table 1.

The compact, clay-like matter was hand-ground in an agate mortar and was subjected to X-ray diffraction analysis using CuKα radiation at the PA Nautical X’Pert PRO XRD System in RASA, (AMSE Wing), Geological Survey of India (GSI), Bangalore. The XRD of the random oriented sample reveals a double peak at 5.87° 2θ (15 Å) and 6.01° 2θ (14.69 Å; Figure 4a), indicating the presence of two types of smectite minerals, a mixed layer mineral with smectite and chlorite or vermiculite. For confirmation of the clay mineral species, an oriented mount was prepared and was also subjected to XRD analysis. A major peak is observed at 5.87° 2θ (15 Å) suggesting the presence of nontronite. The broad peak at 12.3° 2θ indicates trace amounts of chlorite (Figure 4b).

Chemical analysis of clay minerals obtained by XRF at Geological Survey of India, Bangalore shows SiO₂ – 41.82%, Al₂O₃ – 7.10%, Fe₂O₃ – 25.92%, MnO – 0.17%, MgO – 12.54%, CaO – 4.89%, Na₂O – 0.84%, K₂O – 0.05%, TiO₂ – 0.74%, P₂O₅ – 0.05%, Cr₂O₃ – 2.3% and LOI (loss of ignition) – 0.36%. The composition is similar to that of iron-rich nontronite. However, it has higher percentage of magnesium.

Occurrence of nontronite in Deccan basalts is rare. Its occurrence at Nagewadi, Satara District, is important from the genetic point of view. As discussed earlier, the occurrence of nontronite in basalts is associated with deep marine sedimentary environment⁵ and deuteritic alterations of basalt along mid-oceanic ridges⁶. Powers et al.⁷ have observed that glassy tuffs in Hawaii weather more rapidly than lava flows characterized by crystalline material. Peacock⁸ distinguished two main varieties of palagonite–gel-palagonite and fibro-palagonite, a distinction considered valid till now. According to him, the palagonite formation is accompanied by oxidation of Fe, uptake of H₂O, and loss of CaO and Na₂O. Gel palagonite, which forms next to unaltered glass surface, is clear and transparent, isotropic, smooth and commonly concentrically banded. The more intensely coloured fibro-palagonite develops during the later stages of palagonitization on the outer surface of the gel-palagonite⁹. Fibro-palagonite is a mixture of gel-palagonite and crystallizing smectite, developing during the aging of gel-palagonite⁹. Eggleton and Keller¹⁰ noted, on the basis of high resolution transmission electron microscopic studies, occurrence of spherical structures even in gel-palagonite. Apparently, exfoliation of 10 Å (2 : 1) clay layers from these spheroids results in the development of small, dioctahedral smectite crystals (30–60 Å), which ultimately form a tangled network of sub-micron sized bent flakes.

Sarbadhikari and Bhattacherjee¹¹ have reported green, yellow and brown secondary minerals occurring in amygdalas, irregular infillings and replacements in Rajmahal basalts of eastern India. According to them, the secondary constituents were found to be chlorophaeite and palagonite, which essentially consists of common clay minerals, particularly montmorillonite and vermiculites. Parthasarathy et al.¹² have recorded a green-coloured, iron-rich saponite in the amygdalas and fractures in the Deccan Traps at Killari, Maharashtra. Their finding suggests that the ferrous saponite has the capability of absorbing and reducing toxic hexavalent chromium to the trivalent state. Studies of the core samples of the Lonar crater, Maharashtra by Hagerty and Newsom¹³ suggest that the basaltic impact breccias were found to be altered by the post-impact hydrothermal processes to form secondary alteration products. Microprobe and XRD analysis of the altered mineral assemblage revealed the presence of saponite, with minor amounts of celadonite and carbonate.

At the Nagewadi basalt quarry, the reddish tufaceous horizon above the nontronite-bearing basaltic flow contains appreciable devitrified glass containing palagonite. The weathering of palagonite in a semi-arid environment released substantial amounts of highly mobile oxides.
Table 1. Partial chemical analysis of clay obtained by SEM–EDX for the photographed phases

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<th>SEM: 1 elements</th>
<th>Mass (%)</th>
<th>Atomic (%)</th>
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</table>

and aided in the formation of clay. The ease of alteration of basaltic glass to nontronite varies with the conditions and the composition of the reacting solutions. The formation of nontronite is favoured by conditions of poor surface drainage and by the presence of alkalies, alkaline earths, magnesium and probably ferrous ions in the precipitating groundwaters at the quarry site.

In general, the clay mineral montmorillonite is formed during weathering of basalt and many soil profiles contain montmorillonite as the dominant clay mineral. In the present case, it is envisaged that the volcanic glass from the tuffaceous layer rather than the basalt itself, weathered releasing the alkali and alkali earth elements along with the other oxides (SiO$_2$, MgO, CaO, etc.) and got deposited as nontronite within the empty gas vesicles of the underlying flow.


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