MINERALOGICAL NOTES

The clay component of the Columbia River palagonites

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Abstract

Palagonite from four localities within the Columbia River Group was studied to determine mineralogy of the clay component. X-ray analysis, differential thermal analysis, and optical study defined the mineralogy of the palagonite as a mixture of nontronite, fresh sideromelane with plagioclase crystals, and accessory minerals. The nontronite identification is based on the spacing of the (001) peak at 14.7 Å which expands to 18 Å upon glyceration, and the temperature of the second endothermic peak at 525 and 550°C. Nontronite identity was confirmed by the partial chemical analyses and the glycerol expandability of heated Li-saturated material.

Introduction

Palagonite is commonly associated with pillow basalts of the Columbia River Group. Four samples from different stratigraphic horizons and physical settings were examined. Sample A, found on Highway 23 north of St. John, Washington, is part of an extensive pillow horizon in eastern Washington of late Middle Yakima age (Don Swanson, personal communication, 1974). The palagonite occurred as rinds around the pillows. Sample G, from a rubble breccia zone on Highway 95 north of Whitebird, Idaho, is part of the Imnaha basalts. Sample I is part of an extensive pillow horizon in central Washington, the Gingko Flow of early Middle Yakima age (Mackin, 1961). This particular sample was obtained at a roadcut on Highway 26, southeast of Vantage, Washington. The palagonite is found both as rinds and in between the pillows. Sample J was taken from a roadcut on Highway 28 near Crescent Bar, Washington. The palagonite is mostly interpillow material of Lower or Middle Yakima age.

Methods

The palagonite samples were analyzed for mineralogy and chemical composition. Methods used were X-ray analysis by powder camera and diffractometer, differential thermal analysis, and examination of thin sections. The palagonite samples were pre-treated before X-ray and thermal analysis to iso-

late the clay fractions, using a procedure based on Kittrick and Hope (1963). Interferences such as iron oxides, carbonates, and amorphous Si and Al were removed, using a procedure modified from Hashimoto and Jackson (1960) and Kittrick and Hope (1963). The material was size-separated into $>5\mu$, $2-5\mu$, $0.2-2\mu$, and $<0.2\mu$ fractions. Basally-oriented slides were prepared of variously saturated clays (Mg^{2+}, Li^+, or K^+) and X-rayed on a diffractometer using $CuK\alpha$ radiation. Randomly-oriented samples of the $2-5\mu$ size fraction using gelatin fiber mounts (Sorem, 1960) were run on a powder camera with $FeK\alpha$ radiation.

Petrology

Palagonite is composed of fresh, light brown sideromelane, clay minerals, and plagioclase crystals (An_{60-80}), with accessory minerals such as calcium-rich clinopyroxene, opal, calcite, iron oxides, and zeolites. Three stages of alteration from fresh glass to palagonite are seen in thin-section. These stages are as follows: a yellow-fibrous, isotropic phase, possibly equivalent to fibro-palagonite (Peacock and Fuller, 1928); a yellow-nonfibrous, isotropic phase, possibly gel-palagonite (Peacock and Fuller, 1928); and a brown or orange, anisotropic phase, corresponding to Phase Y (Stokes, 1971). The alteration appears first along cracks and edges of vesicles, suggesting that percolating fluid or steam aids formation.

X-ray analysis

The clay portion of palagonite in all four samples was identified as belonging to the smectite group

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TABLE 1. Comparison of DTA peaks of samples with published values of smectites

Type of Peak	Temperature Range of Peaks for Samples and Standards (°C)						
	1	2	3	4	5	A	G
1st Endothermic	125-250	125-260	100-200	120-280	125-250	124	105
2nd Endothermic	400-600	625-750	600-700	600-700		550	525
3rd Endothermic		800-925	800-900	850-925	725-925		
1st Exothermic	825-925	900-980	900-925	920-980	900-980	870	870

1-Nontronite (De Bruyn and Van der Marel, 1954, p. 407).
2-Montmorillonite (De Bruyn and Van der Marel, 1954, p. 407).
3-Fe-Montmorillonite (Sudo, 1952, p. 235).
4-Beidellite (De Bruyn and Van der Marel, 1954, p. 407).
5-Saponite (De Bruyn and Van der Marel, 1954, p. 407).
A-Sample A.
G-Sample G.

from the following evidence. The (001) peak of the Mg^{2+} saturated clay at 14.7 Å expanded to 18 Å upon glyceration. After heating the Mg^{2+} saturated and glycerated clay to 300°C the (001) peak collapsed to 10 Å, as expected for a smectite mineral. After heating the K^+ saturated clay to 500°C, the (001) peak collapsed to 10 Å. No other clay mineral groups were detected in any of the samples. The (hkl) lines on the powder camera patterns confirmed the smectite identification. In addition, the occurrence of the (060) line at 1.51 Å implies that the clay is composed of dioctahedral layers. More lines are common to nontronite (ASTM No. 2-004) than to other smectite minerals. As an additional test for montmorillonite, a modification of the Greene-Kelley test (Greene-Kelley, 1955) was run. The Li^+ saturated samples did re-expand after glyceration, suggesting that the clays have a negative charge arising from substitutions mostly in the tetrahedral layer, and are not montmorillonite.

DTA analysis

Differential thermal analysis was used to distinguish between high-Fe montmorillonite, montmorillonite, and nontronite (Sudo, 1952). The peak temperatures are listed in Table 1. The presence of the low second endothermic peak, found when iron is the primary cation in the octahedral layer, the absence of the third endothermic peak present in montmorillonite and saponite, and the temperature of the exothermic peak all support the identification of the clays as nontronite. Sudo (1952) examined high-Fe montmorillonites from Japan which had an exothermic peak in the nontronite range but a second endothermic peak in the montmorillonite range. Not enough clay was available to permit a DTA analysis of Samples I and J, but the close similarities of the X-ray data suggest that similar results would be expected for the DTA analysis.

Chemical composition

To confirm the identification made by X-ray and DTA analyses, partial chemical analyses were made of the separated clays. The samples were analyzed for Fe and Mg using 3:1 lithium tetraborate-to-clay pellets on a Philips X-ray spectrograph. Analyses were also made of the bulk samples. Results are given in Table 2. The MgO content is in the nontronite range. The iron content is higher than the range considered to be for high-Fe montmorillonite, according to the usage of this term. The Al content is higher than expected for nontronite, but most of it is probably present in plagioclase. The much higher iron content of Sample G in bulk than in the clay sample is due to the abundance of hematite.

Conclusions

The composition of palagonite is influenced by several factors, including lava composition, chemical composition of surrounding medium at time of extrusion, type of surface drainage, and groundwater conditions. From the present study and one by Allen and Scheid (1946), it appears that palagonite from the Columbia River Group basalts contains nontronite as the predominant clay mineral. Other areas of palagonite may have another smectite as the predominant clay component, such as montmorillonite in the palagonite tuffs of the Honolulu Group in

TABLE 2. Partial chemical analyses of clays

Sample	Al_2O_3 *	MgO #	MgO *	Fe #	Fe *
A	14.23	2.9	2.76		13.16
G	15.88	1.2	1.3	25.69	31.26
I	13.38	4.1	4.2	19.78	14.08
J	14.34	3.2	3.3	13.10	13.31

*Bulk sample
#Separated sample

Hawaii (Hay and Iijima, 1968) and saponite in tuffs of Palagonia, Sicily (Honnorez, 1972).

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