

Mineralogy and paragenesis of “pocket” clays and associated minerals in complex granitic pegmatites, San Diego County, California

EUGENE E. FOORD, HARRY C. STARKEY,¹ JOSEPH E. TAGGART, JR.

U.S. Geological Survey, Denver, Colorado 80225

ABSTRACT

The gem- and specimen-bearing, complex granitic pegmatite and aplite dikes and bodies of Cretaceous age emplaced into the Southern California batholith locally contain fractures and cavities (“pockets”) that are usually clay filled. Some pockets, however, contain only a thin coating of cookeite or sericite, deposited as “snow on the roof.” Other pockets contain pseudomorphs of lepidolite after elbaite, bavenite after beryl, and clays and micas after spodumene. Pseudomorphism took place under nearly closed system conditions at temperatures similar to those at the time of pocket formation. Most pockets contain fragmented primary minerals enclosed in a matrix of Ca-Na zeolites; white, pink, or red beidellite; Li-tosudite; Ca-Mg montmorillonite; and rare calcite. Paragenetic relationships indicate a decrease in Na relative to Ca during the crystallization of zeolites and a decrease in Li and Al—concomitant with an enrichment of Ca, Mg, and Si—for the layer silicates. The most prevalent minerals found are stilbite, laumontite, cookeite, Li-tosudite, beidellite, Mg-Ca montmorillonite, palygorskite, and calcite. Sparse amounts of nontronite, heulandite, and todorokite have also been identified. Deposition of zeolites, clays, and carbonates in open pockets took place subsequent to crystallization of the primary pocket minerals, under hydrothermal conditions with temperatures ranging from approximately 400 to 150°C. The major amounts of Ca and Mg, represented by as much as 8.4 wt% MgO in palygorskite and more than 10 wt% CaO in minerals such as laumontite and bavenite, were provided by hydrothermal alteration of gabbro-norite and/or tonalite host rocks. Red-brown (iron-stained) kaolinite is locally present as a final phase of deposition in some pockets and is probably indicative of a transition from an alkaline to an acidic environment.

INTRODUCTION AND STATEMENT OF PROBLEM

The gem-bearing complex granitic pegmatites of San Diego and Riverside Counties, California, have been objects of study since their discovery in the 1870s. Exploitation, initially for gems and later for specimen-quality minerals, began in 1898 with the discovery of the Himalaya dike system in the Mesa Grande district (Rynerson, 1967; Foord, 1976). Scientific studies of the pegmatites began about 1903 and include those of Kunz (1905), Schaller (1925), Jahns and Wright (1951), Hanley (1951), Jahns (1954), Simpson (1965), and Foord (1976). Jahns (1979) presented a summary of the Stewart and Himalaya mines. From the time that mining first began, it was noted that the best-quality minerals occurred in specific portions of pegmatite dikes and bodies and were frequently concentrated in crystal-lined, clay-filled, or open voids and cavities referred to as “pockets” by the miners. These cavities range from several centimeters across to extensive, multiply-projecting, and branching cavities as much as 3 m or more in maximum dimension. Many pockets contain fragments of minerals that were once attached to

the pocket walls but are now “floating” in a matrix of clays, zeolites, and other low-temperature minerals. A few pockets, referred to as “dry pockets,” contain no clays, zeolites, or carbonates, but do contain small amounts of cookeite as a coating on the minerals present. Coatings of cookeite, with or without associated minerals, that are found only on the top surfaces of various primary pocket minerals such as quartz, feldspars, micas, and tourmaline, and not underside or overhanging surfaces are known as “snow-on-the-roof” coatings. Pockets in the Himalaya dike system are strongly controlled vertically by dike geometry and zonation, but they may extend laterally, in the plane of the dike, for 3 to as much as 30 m or more. Additional details on the Himalaya dike system and the pockets themselves are given in Foord (1976, 1977) and Jahns (1979). Some pocket clays appear to be partial or complete replacements (pseudomorphs) of pre-existing minerals, most frequently beryl, elbaite, and Nb-Ta oxides (Himalaya dike system) and spodumene and phosphates (Pala district). Apart from that of Herbert (1982), little or no specific attention has been devoted to the detailed clay mineralogy of the pocket clays. Most of the earlier studies were done prior to use of X-ray powder diffraction for identification purposes. Of the early work, only that of Schaller (1905, 1925) and Lauder milk and Woodford

¹ Present address: 1636 South Yarrow Court, Lakewood, Colorado 80226.

(1934) included chemical analyses of pocket clays from pegmatites in the Southern California batholith. As early as 1880, however, Brush and Dana (1880) had examined clays and other minerals pseudomorphous after spodumene in pegmatites at Branchville, Connecticut. The pink clay analyzed by Schaller (1905) was termed "halloysite" by Ross and Shannon (1926) after optical study. Kaolinite pseudomorphs after spodumene were described by Schwartz (1937) from the Etta mine, Black Hills. Both Schaller (1925) and Laudermilk and Woodford (1934) attributed the origin of the pocket clays to weathering rather than to hydrothermal action.

Schaller (1925) identified two types of pocket clay in the Pala district: (1) a white, gray, or pink clay, derived from decomposition of the pegmatite minerals, and (2) a deep red-brown, sticky clay, derived in part from the surrounding gabbro-norite. Jahns and Wright (1951) attributed their formation to both hypogene and supergene processes. The hypogene clays contained members of both the smectite and kaolinite groups; the supergene clays contained only members of the kaolinite group. Foord (1976, 1977) found white to pink Mg-Ca montmorillonite in pockets within the Himalaya dike system, Mesa Grande district. Red-brown, disordered kaolinite was also described, and was clearly deposited later than the lighter-colored montmorillonite.

The following questions are addressed in this paper: (1) What were the sources of the elements incorporated into the pocket-filling clays and pseudomorphous minerals? (2) How, when, and under what conditions were the minerals formed? (3) What is the paragenesis? Samples of late-stage secondary minerals and pocket fillings were collected from four of the major pegmatite districts in San Diego County for mineralogical and petrologic study. In addition, samples of the host norite were collected from the Himalaya dike system for chemical and mineralogical study.

SAMPLES AND ANALYTICAL METHODS

Thirty-nine of fifty-three samples examined (Table 1)² are from the Himalaya pegmatite-aplite dike system. Two samples of clay pseudomorphous after spodumene, variety kunzite, were examined from the Katrina mine, on Hiriart Mountain; five samples of pseudomorphous and pocket clays are from the Ocean View (Elizabeth R) mine on Chief Mountain; one sample of deep purple-red clay is from the White Queen mine, Hiriart Mountain; and one sample of red-brown pocket-filling clay is from the Tourmaline Queen mine, Queen Mountain. All are from the Pala district. Four samples of pocket clay from the main dike and one from the "garnet dike" on the Little Three mine, Ramona district, and one sample of material coating pocket minerals from the Maple Lode mine, Aguanga Mountain, were examined as well. Locations of the four districts, as well as the individual mines, are given in Jahns and Wright (1951), Jahns (1979), Simpson (1965), and Foord (1976).

All samples were prepared for X-ray diffraction analysis ac-

ording to accepted clay mineral procedures (Starkey et al., 1984). Bulk splits of samples were first X-rayed as unoriented packs. Then the clay-sized (<2 μm) fraction was removed by settling in water or centrifuging and run as air-dried, randomly oriented patterns. Oriented patterns were made after air-drying at 25°C, after glycolation at 60°C, and heating at 400 and 550°C for 0.5 h each. Other size fractions for approximately 30 samples, such as >2, 1–2, 0.5–1, 0.2–0.5, and <0.2 μm , were also examined by X-ray diffraction. Some samples were examined at other temperatures and conditions when necessary (e.g., Greene-Kelly test or treatment with glycerol). Many of the samples were examined with a petrographic microscope to confirm mineral identifications and estimate relative amounts of individual minerals in mineral mixtures.

Twenty mineral separates and rock samples were analyzed for major elements by X-ray fluorescence spectroscopy using a Philips³ PW1600 simultaneous wavelength-dispersive spectrometer according to the method of Taggart et al. (1981). Samples were incorporated in lithium tetraborate fusion discs prepared by the methods of Taggart and Wahlberg (1980a, 1980b). Because of the difficulty of purifying the clay fractions, most of the mineral separates were analyzed as a half-weight sample (0.4 g); rock samples and some of the more abundant clay separates were analyzed as normal full-weight samples (0.8 g). Six-step semi-quantitative emission spectrographic analyses were made of fifteen samples of clay and other minerals. Rare alkalis (Li, Rb, Cs) were spectrographically determined for three samples. Li_2O was determined by induction-coupled plasma spectroscopy for five selected samples known to contain Li.

BACKGROUND INFORMATION AND OBSERVATIONS

In the Pala and Mesa Grande districts, pegmatite dike emplacement was along nearly flat lying planes of weakness in the oldest unit of the Southern California batholith, the San Marcos Gabbro (Krummenacher et al., 1975; Foord, 1976). In the Ramona district, the slightly younger Green Valley Tonalite is the host to pegmatite-aplite dikes. The older, higher-temperature units of the batholith behaved as brittle media with development of sheet-structure in response to a combination of intrusive pressures from below and tectonic unloading.

A "snow-on-the-roof" coating of cookeite, $\text{Li-Al}_4(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$, and/or fine-grained K-feldspar with or without albite is found usually only covering minerals on the bottom of pocket cavities. Pocket roofs are generally completely free of these coatings. Deposition from stagnant and rest, subcritical liquids may be inferred from this widespread material because of its physical distribution as described above, the very fine grain size, and in some cases, an unusual chemical composition, as at the Little Three mine where in one large pocket a boron-rich K-feldspar possibly representing a pressure-quench product was deposited. Furthermore, rotation to the west of the batholith as a whole is indicated by the distribution of the "snow-on-the-roof" on the pocket minerals, which was deposited under a vertical gravity gradient, and by the present average 30° dips of the pegmatite-aplite dikes in that direction (Foord, 1976).

² To receive a copy of Table 1, order Document AM-86-296 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006. Please remit \$5.00 in advance for the microfiche.

³ Use of brand names is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

Crystallization temperatures of primary minerals in the Himalaya and Little Three pegmatite-aplite dike systems are thought to have ranged from approximately 700°C (basal aplite) down to 520–540°C at the central pocket zone and at pressures of 2 kbar (Taylor et al., 1979; Stern et al., 1986). Temperature and pressure estimates of 450–500°C and 2–3 kbar for pocket formation have been made by London (1986).

So-called "dry pockets" form less than 1% of all pockets and are best developed in the Himalaya dike system. These pockets contain their primary minerals in varying states of preservation, coated with cookeite or muscovite. Crystals of tourmaline, quartz, feldspar, mica, beryl, apatite, and Nb-Ta oxides that have been broken off during pocket rupture are all loosely or compactly cemented together in the bottoms of such pockets. The cement may consist only of cookeite and rarely of muscovite, but more frequently of both primary minerals and the micas. Pockets of this type, and particularly "clay-filled" pockets, may contain a lower-temperature and lower-pressure assemblage of zeolites, clay minerals, micas, borates, and carbonates.

The individual Himalaya and Little Three dikes, which may be from several centimeters to 2 m thick, are thinner by an order of magnitude or more than many of the dikes at Pala such as the Stewart (20 m thick), the Katrina (16 m thick), and the Ocean View (10–13 m thick). Depth and temperature of emplacement of all of these dikes was about the same, 7 km and 730–700°C (Taylor et al., 1979) and under structural conditions as presented above. The more competent and thicker (>2 m) dikes were not able (or incompletely able) to release their elevated internal vapor pressures in areas of final crystallization, and as a result the final crystallizing products "stewed in their own juices" (Jahns and Burnham, 1969; Jahns, 1982, pers. comm.). Thinner dikes (<2 m), such as the Himalaya and Little Three dikes, generally were able to release their internally derived vapor pressures and pocket fluids (Jahns, 1981, pers. comm.). Thus, pocket cavities are well developed in the Himalaya and Little Three dikes, and a minimum of mineral replacement has occurred, whereas in the Stewart, Katrina, and Ocean View dikes, pockets are not as well developed, and mineral replacement has taken place in both the pockets and the rest of the dikes themselves.

Mineral replacement producing pseudomorphs of pocket minerals, such as clay minerals after spodumene (kunzite) in some of the pegmatite bodies in the Pala district, appears to have occurred either prior to or in the absence of pocket rupture. Large, thick, competent dikes—such as the Stewart, the Ocean View, and the Katrina in the Pala district—contain spodumene, some of it as gem-quality kunzite. In all of these dikes, the spodumene and/or kunzite is commonly etched and chemically corroded and is in a matrix of white, pink, or red clays and micas. The matrix often perfectly preserves the cleavage of the pre-existing kunzite, and a sponge-like network is frequently developed with splinters and fragments of kunzite surrounded by pure clays and micas. Both Ca-Mg mont-

morillonite and cookeite or kaolinite have been observed to form as pseudomorphs after spodumene (Herbert, 1982).

Most replacement appears to be post-rupture and thus at temperatures of less than 500°C, as in the case of the Himalaya dike system, where pseudomorphs of lepidolite after elbaite, bavenite after beryl, rynersonite and fersmite after stibiotantalite, as well as others have been found. Pollucite is found sparingly in the pocket zone of the Himalaya dike system (Foord, 1976) and is often associated with montmorillonite and other minerals, but most pollucite does not appear to be altered to illite, kaolinite, quartz, and montmorillonite (see, e.g., Černý, 1978). K-feldspars are frequently corroded and solution etched and have partial coatings of minerals such as cleavelandite, lepidolite, and cookeite. Some K-feldspar crystals have a sharp and distinctive overgrowth of glassy ordered orthoclase (Prince et al., 1973; Horsky and Martin, 1977). Elbaite crystals in some pockets are found partially etched (never a mixture of unetched and etched together) and corroded. Corrosion has occurred on the prism faces but not the pyramidal or pedion faces. Some doubly terminated pink crystals of elbaite tipped by green tourmaline have the pink portion nearly completely removed, but the green ends are essentially untouched, lustrous, and smooth. Figure 1 shows a crystal of pink-green elbaite coated by muscovite. The green cap is unattacked, and the termination beneath the muscovite coating is sharp and lustrous. Other tourmaline crystals show some corrosion on all parts, but the ends are much less affected. This is believed to be a function of the chemical and structural character of tourmaline. Most crystals are partially or completely coated with cookeite or later-formed zeolites and clays. The corrosion of the feldspar and tourmaline (and sometimes beryl) is believed to take place in pockets that have released their internal vapor pressure by rupturing or slower release and then resealed themselves by subsequent crystallization. All of these phenomena have occurred prior to deposition of cookeite from the final stagnant rest liquid. Some pockets show evidence of having adjusted to altered chemistry three or more times (Foord, 1976).

Ruptured pockets may contain only zeolites and calcite that cement previously crystallized minerals, or they may contain some clay minerals as well. Usually, laumontite and beidellite-montmorillonite are the dominant matrix minerals; however, some ruptured pockets appear to contain only cookeite and clay minerals, with little or no zeolites. In a few pockets, the presence of fibrous palygorskite, $(\text{Mg,Al})_2\text{Si}_4\text{O}_{10}(\text{OH})\cdot 4\text{H}_2\text{O}$, indicates a dominance of Mg as the divalent cation. An analysis of pure, white, elastic palygorskite from the Himalaya mine is given in Table 2 (analysis 10). Pure masses of palygorskite several centimeters thick or more and several meters in extent were found during mining in 1984.

Rare todorokite, $(\text{Mn}^{2+}, \text{Ca, Mg, Ba, Sr})\text{Mn}_3^+\text{O}_7\cdot \text{H}_2\text{O}$, occurs either as a coating on nearly all other minerals or as concretionary pellets (Foord, 1976). Only red-brown kaolinite appears to be younger on the basis of textural

relationships. The todorokite is the only mineral found in the Himalaya dike system to contain >0.1 wt% each of Sr, Ba, and Cu. Analysis 13 (Table 3) shows that 500 ppm Ni, 150 ppm V, and 150 ppm Co are also present; these latter elements were probably derived from hydrothermal alteration of the host sulfide-bearing norite-gabbro as they are present in the host and not the dike system.

Pseudomalachite, $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$, and cryptomelane, $\text{K}(\text{Mn}^{4+}, \text{Mn}^{2+})_8\text{O}_{16}$, two late-stage minerals from the Ocean View mine, were identified as new to the San Diego County pegmatites. The pseudomalachite occurs as sparse, thin, discontinuous green fracture coatings in feldspar and quartz and as cleavage fillings in muscovite. Cryptomelane occurs in the pocket zone as compact, dense, blue-black masses several centimeters or more across. Sparse malayaite, CaSnSiO_3 , was identified from the Himalaya mine. The mineral occurs as tiny white hemispheres and rosettes, <0.2 mm across, on top of elbaite, quartz, cleavelandite, and K-feldspar.

Deposition of zeolites commenced with stilbite, $\text{Na-Ca}_2\text{Al}_3\text{Si}_{13}\text{O}_{36} \cdot 14\text{H}_2\text{O}$, and/or heulandite, $(\text{Na}, \text{Ca})_{2-3}\text{-Al}_3(\text{Al}, \text{Si})_2\text{Si}_{13}\text{O}_{36} \cdot 12\text{H}_2\text{O}$ (sparse), followed by laumontite, $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$. Both stilbite and laumontite are common in the dike system, but do not always occur together. These same three zeolites were first reported as occurring in pegmatite pockets in San Diego County by Rogers (1909) from the Victor pegmatite at Rincon and were later described as widespread but minor constituents of fracture fillings and pockets, associated with clay minerals in the Pala district by Jahns and Wright (1951). Stilbite is also present, coating pocket minerals at the Maple Lode mine, Aguanga Mountain (Table 1, ML-1). In some pockets in the new Himalaya workings (1980–1984), early clear rhombohedral calcite was followed by platy, opaque, nearly pure calcite contemporaneous with the deposition of laumontite. Table 3 is a compilation of semiquantitative emission spectrographic analyses of these late-stage pocket-filling minerals including stilbite, laumontite, calcite, cookeite, montmorillonite, Li-tosudite, beidellite, palygorskite, todorokite, pseudomorphous bavenite and rynersonite (Foord and Mrose, 1978), fine-grained, locally porcelaneous aggregates of B-containing K-feldspar, and finally the orthoclase-sanidine(?) and albite that coat primary pocket minerals. The three feldspar coatings (analyses 1–3, Table 3) represent very late precipitates on all pocket minerals on the floors of the pockets. The B-rich K-feldspar from the Little Three mine is unusual and not completely characterized. The two samples of stilbite and laumontite (analyses 4 and 5) are typical for the species and contain trace amounts of other metals. There is little difference in the chemistry of the two generations of calcite (analyses 6 and 7) from the Himalaya mine; traces of Mn, Sr, and Y are present in both. The two beidellites and two montmorillonites (analyses 8–11) contain varying amounts of different elements that reflect details of their origin and some contamination. An analysis of thoroughly water-washed palygorskite (analysis 12) confirms that major (about 2.4 wt% Na_2O)



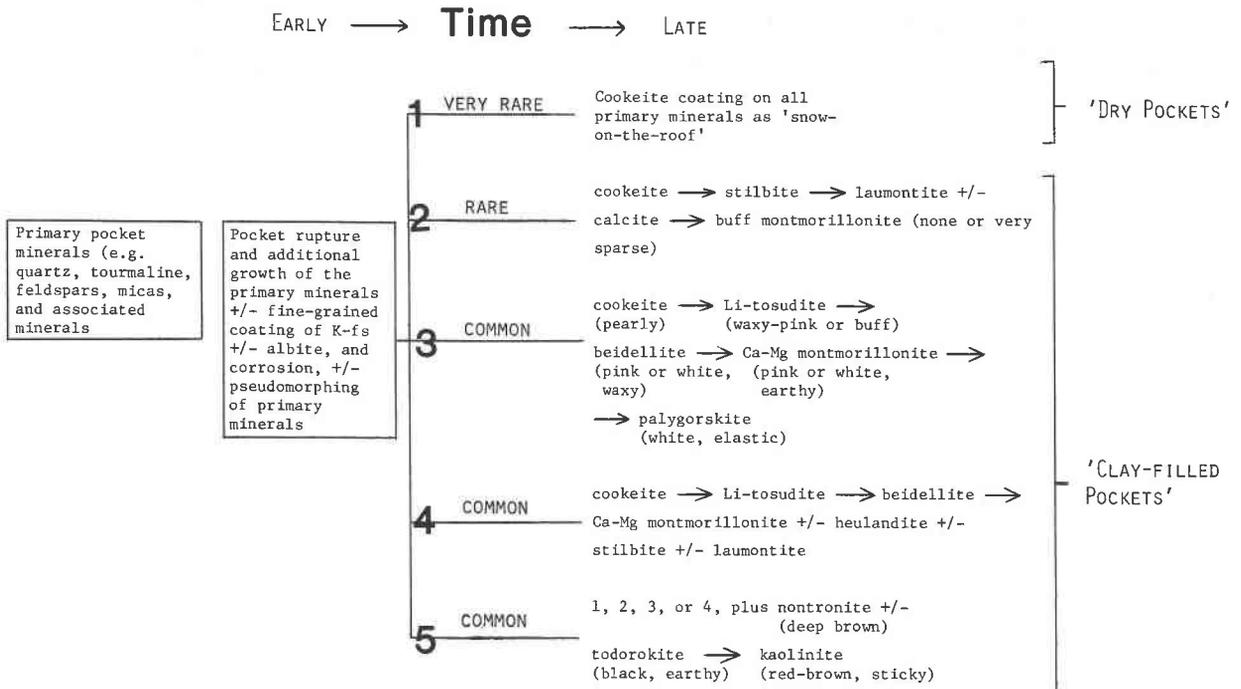
Fig. 1. Etched and corroded tourmaline crystal showing preferential dissolution of the prism zone and coating of muscovite.

sodium was removed. The todorokite (analysis 13), the first occurrence to be reported from granitic pegmatites (Foord, 1976), contains 1.5% Ba, 1.5% Mg, 0.3% Cu, 0.05% Ni, 0.15% Sr, and 0.03% Zn. The pseudomorphous bavenite after beryl (analysis 14) contains a trace amount of stibiotantalite. The rynersonite (analysis 15), pseudomorphous after stibiotantalite, contains negligible REE.

Ca and Mg, which form major components in the clays, zeolites, and calcite encountered in pockets that have released their internal vapor phase, are not present in any of the other pocket minerals, having been depleted by fractional crystallization. Therefore, they must have come from some other source than the pockets. The source is not the pegmatites but principally their host rocks. Abundant Ca and Mg are present in the host norite-gabbro or tonalite. The composition of the montmorillonite developed in the altered envelopes of rock adjacent to the dikes is extremely similar to that of the montmorillonite found in the pockets. For many pockets, the source of the Si, Al, and Fe in the contained clays and pocket fillings is also the host rocks. A progressive and continuous mineralogic and geochemical sequence has been observed in the pegmatite pocket contents (Figs. 2 and 3). The first mineral to be deposited as "snow-on-the-roof" is cookeite, indicative of availability of Li and Al. If a given pocket continued to interact with circulating hydrothermal solutions and did not become closed, depletion of Li but continued availability of Al resulted in crystallization of Li-tosudite and subsequently beidellite (Table 2). Continued fluid circulation and alteration of the norite adjacent to the aplite and pegmatite dikes resulted in an increase of Ca and Mg and formation of Ca-Mg montmorillonite, palygorskite, zeolites, and calcite. Still later, sparse amounts of todorokite and nontronite were deposited, and final deposition of Fe-stained kaolinite occurred after a significant hiatus in time and at low temperatures and pressures. The textural observations are consistent with the observed chemical trends.

Table 2. Chemical analyses of pocket clays from the Katrina mine, Pala district, and Himalaya dike system, Mesa Grande district, California

	1	2	3	4	5	6	7	8	9	10					
Wt. % Oxide															
	K-F ⁺ dominant pink-purple clay pseudomorphous after spodumene.	K-W white clay find on apodumene	SDFM-0 light pink waxy clay	SDFM-5 tan to white waxy clay pseudomorphous after ebatite	BEF-75-16 ⁺⁺ tan-buff waxy clay, San Diego Mine.	SDFM-1974Fol white clay, San Diego Mine.	SDFM1975PP pink clay, San Diego Mine.	SDFM1975NP white clay, San Diego Mine.	SDFM197424,8 pink pocket clay, San Diego Mine.	HM-10 ⁺⁺⁺ white, fibrous, elastic clay.					
	uncorr. corr.	A B C D	A B C D	uncorr. corr.	uncorr. corr.		a b	a b		uncorr. corr.					
SiO ₂	51.5	56.3	44.7	54.7	43.0	51.6	43.9	42.3	49.5	51.9	54.4	55.1	54.3	59.5	61.0
Al ₂ O ₃ **	25.5	20.0	37.8	27.4	38.0	27.9	34.2	35.9	27.7	24.6	19.6	19.9	19.2	15.7	16.1
Fe ₂ O ₃ **	1.05	1.32	0.85	0.14	0.27	0.43	0.19	0.38	0.21	0.41	<0.04	<0.04	<0.04	<0.04	0.73
MgO	2.09	2.63	3.74	0.84	1.65	0.99	1.39	2.77	2.58	3.55	4.98	4.92	5.12	8.16	8.36
CaO	0.60	0.75	0.84	1.00	1.96	0.99	0.92	1.71	1.30	1.29	1.80	1.82	1.84	0.41	0.42
Na ₂ O	0.55	0.69	<0.15	<0.15	<0.15	<0.15	0.50	0.12	0.31	<0.15	<0.15	<0.15	<0.15	<0.15	2.42
K ₂ O	0.41	0.52	<0.02	0.98	1.92	0.57	3.21	0.42	0.21	0.13	0.29	0.47	0.06	0.46	0.47
TiO ₂	<0.02	---	<0.02	<0.02	<0.02	<0.02	0.20	0.40	0.11	<0.02	<0.02	<0.02	<0.02	<0.02	---
P ₂ O ₅	<0.05	---	<0.05	0.26	<0.05	---	<0.05	---	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	---
H ₂ O	1.10	1.38	0.06	0.06	0.12	0.11	0.04	---	<0.02	<0.02	<0.02	0.02	0.03	0.09	0.09
LOI (920°C)	16.1	16.4	19.7	13.4	11.3	15.2	12.3	16.0	17.0	18.0	18.4	17.7	18.9	11.7	12.0
Li ₂ O (ICP)			1.7	0.2	1.5	---									
Li ₂ O (E-spec.)							1.5		0.03						none
Totals	98.90	100.0	99.89	100.88	100.0	100.58	100.0	98.35	100.0	99.88	99.47	99.93	99.45	99.23	99.25
Name	mont.	beid.	Li-tosud.	Li-tosud.	Li-tosud.	Li-tosud.	beid.	beid.	beid.	beid.	mont.	mont.	mont.	mont.	paly.
Notes---	** - All Fe expressed as Fe ₂ O ₃ . A, C are bulk analyses; B, D are recalculated to obtain the amesite component by subtracting 50% wt. % of ideal cookeite, LiAl ₂ (Si ₂ Al)O ₆ (OH) ₂ and normalizing to 100%. + - analysis corrected for 20 wt. % admixed cookeite. ++ - analysis corrected for 30 wt. % admixed lepidolite. 10 wt. % gibbsite, and 10 wt. % cookeite. a, b - replicate analyses on two splits of the same sample. +--- analysis recalculated to correct for the presence of soluble NaCl not normalized to 100%. Amounts of admixed minerals determined by X-ray diffraction. mont. - montmorillonite, beid. - beidellite, Li-tosud. - Li-tosudite, paly. - palygorskite.														



Note- In any of the five assemblages, not all minerals listed may be developed. Herderite and/or hambergite may be present in all of them and pre-date deposition of cookeite.

Fig. 3. Mineralogical assemblages and evolution of pocket clays in the Himalaya dike system.

dikes are present, the norite is frequently completely altered between the dikes.

Locally, the presence of tourmaline (schorl-dravite series) in the host norite suggests the introduction of B (Foord, 1976). Small dikelets of fine-grained (<0.1 mm) "pressure-quench" aplite emanate from the pocket zone and extend either upward or downward toward the margins of the pegmatite-aplite dikes. These stringers have intruded the norite and resulted in its tourmalinization, with concomitant development of hornblende, biotite, vermiculite, and montmorillonite. An analysis (Table 4, no. 3) shows decreased amounts of CaO and MgO and increased amounts of Na₂O, B₂O₃, K₂O, and H₂O. The areas of B-metasomatized host rock are all spatially and temporally related to formation of the pocket zone of the Himalaya dike system. This metasomatism occurred earlier and in an environment of higher temperature and pressure than the hydrothermal alteration involving the formation and deposition of the pocket clays.

The bulk chemistry of two samples (Table 4, nos. 1 and 2) of equigranular and porphyritic varieties of nearly fresh norite was determined. Six analyses of the highly altered norite, in the form of three pairs of samples from three different locations in the San Diego mine, were also performed (Table 4, nos. 4–9), along with one sample (Table 4, no. 3) of B-metasomatized norite. At two of the three locations, samples were taken above and below the dike. The analyses have been recalculated on a dry-weight basis to account for water in hydrous minerals formed during

alteration (LOI, 5.73–9.15 wt%). The content of Fe₂O₃ remains essentially unchanged when comparing fresh and altered norite. Significantly, however, the content of MgO decreases from 10 to 7 wt%, and that of CaO from 11 to 6 wt%. The contents of SiO₂, Al₂O₃, Na₂O, K₂O, TiO₂, P₂O₅, and MnO increase slightly. All of these observations provide strong evidence that the pocket clays were derived from the host norite.

DISCUSSION

Structural formulas for the ten analyzed clays, which include Mg-Ca montmorillonite, beidellite, Li-tosudite, and palygorskite, are shown in Table 5.

The analyses of the beidellites and particularly the Mg-Ca montmorillonites and the Mg-poor montmorillonite are similar to the results given for two pink montmorillonites from pegmatite pockets from the Pala district (Wells, 1937; Ross and Hendricks, 1945) and to montmorillonites from Greenwood, Maine (Wells, 1937), Branchville, Connecticut (Brush and Dana, 1880), Claremont, California (Laudermilk and Woodford, 1934), and Embudo, New Mexico (Ross and Shannon, 1926). Schaller (1905) described pink halloysite from the Stewart mine at Pala. The purity of this material and its X-ray properties are unknown. The Li-tosudite (Table 2, analyses 3 and 4) is a combination of di-trioctahedral cookeite and dioctahedral beidellite. Li-tosudite was first described by Rusinova et al. (1976) and discussed by Eberl (1978b). Synthetic Li-tosudite, along with kaolinite and quartz, was

Table 4. X-ray fluorescence analyses of fresh, B-metasomatized, and hydrothermally altered norite adjacent to the Himalaya dike system

	1	2	3	4	5	6	7	8	9
Weight percent oxides (raw weight)	unaltered porphyritic norite	unaltered norite	boron metasomatized norite	red line and above upper slope	below red line upper slope	hanging wall lower dike, present working area	footwall lower dike, present working area	hanging wall upper dike, right of junction 10'	footwall upper dike, right of junction 10'
SiO ₂	49.6	50.4	50.7	46.5	46.9	48.9	50.3	49.9	54.1
Al ₂ O ₃	19.1	16.0	22.1	22.1	21.0	16.5	18.7	16.6	17.1
Fe ₂ O ₃	8.93	9.69	7.68	10.50	9.39	9.63	9.30	10.2	7.87
MgO	8.96	11.3	4.14	5.30	5.13	10.0	9.37	6.14	2.91
CaO	12.1	10.3	3.14	6.83	6.77	7.26	2.99	6.58	4.57
Na ₂ O	1.12	1.03	2.06	1.12	1.28	0.72	0.72	1.17	1.80
K ₂ O	0.11	0.14	2.54	0.22	0.87	0.28	0.16	0.54	1.33
TiO ₂	0.43	0.24	0.93	1.42	1.34	0.84	0.14	1.14	1.03
P ₂ O ₅	<0.05	<0.05	0.21	0.23	0.22	<0.05	<0.05	0.11	0.17
MnO	0.15	0.17	0.17	0.17	0.17	0.17	0.19	0.21	0.27
LOI (920°C)	0.65	0.98	2.63	5.75	7.33	5.73	8.64	8.25	9.15
Totals	101.2	100.3	96.3 [†]	100.1	100.4	100.1	100.6	100.8	100.3
Weight percent oxides (dry weight)									
SiO ₂	49.9	50.9	52.1	49.3	50.6	51.9	55.0	54.3	59.5
Al ₂ O ₃	19.2	16.1	22.7	23.4	22.7	17.5	20.5	18.1	18.8
Fe ₂ O ₃	8.99	9.78	7.90	11.1	10.1	10.2	10.2	11.1	8.66
MgO	9.02	11.4	4.26	5.62	5.53	10.6	10.3	6.69	3.20
CaO	12.2	10.4	3.33	7.25	7.30	7.70	3.27	7.17	5.02
Na ₂ O	1.13	1.04	2.12	1.19	1.38	0.76	0.79	1.27	2.00
K ₂ O	0.11	0.14	2.61	0.23	0.94	0.18	0.18	0.59	1.46
TiO ₂	0.43	0.24	0.96	1.51	1.45	0.89	0.15	1.24	1.13
P ₂ O ₅	<0.05	0.05	0.21	0.24	0.24	<0.05	<0.05	0.12	0.19
MnO	0.15	0.17	0.17	0.18	0.18	0.18	0.21	0.23	0.30
LOI (920°C)	---	---	---	---	---	---	---	---	---
Totals	101.2	100.3	96.3 [†]	100.1	100.4	100.1	100.6	100.8	100.3

Notes - All Fe determined as Fe₂O₃. + - Difference is 4% B₂O₃, 40 wt. % schorl-draavite.

Table 5. Calculated structural formulas for analyzed clays and palygorskite

1.	$(Al_{1.62}Mg_{0.28}Fe_{0.07})_{\Sigma 1.97}(Si_{3.96}Al_{0.04})_{\Sigma 4.00}O_{10}(OH)_2[Na_{0.09}Mn_{0.08}Ca_{0.06}K_{0.05}]_{\Sigma 0.28}$ • 2.8H ₂ O
2.	$(Al_{1.73}Fe_{0.05}Mn_{0.01}Mg_{0.21})_{\Sigma 2.00}(Si_{3.69}Al_{0.31})_{\Sigma 4.00}O_{10}(OH)_2[Mg_{0.20}Ca_{0.07}]_{\Sigma 0.27}$ • 3.8H ₂ O
3.	$(Al_{1.83}Mg_{0.16}Fe_{0.01})_{\Sigma 2.00}(Si_{3.67}Al_{0.33})_{\Sigma 4.00}O_{10}(OH)_2[K_{0.16}Ca_{0.14}Mg_{0.01}]_{\Sigma 0.31}$ • 1.5H ₂ O
4.	$(Al_{1.85}Mg_{0.13}Fe_{0.02})_{\Sigma 2.00}(Si_{3.57}Al_{0.43})_{\Sigma 4.00}O_{10}(OH)_2[Ca_{0.15}K_{0.10}Mg_{0.07}Mn_{0.01}]_{\Sigma 0.33}$ • 2.4H ₂ O
5.	$(Al_{2.01}Fe_{0.02})_{\Sigma 2.00}(Si_{3.00}Al_{1.00})_{\Sigma 4.00}O_{10}(OH)_2[Mg_{0.30}Ca_{0.13}Na_{0.02}K_{0.04}]_{\Sigma 0.49}$ • 2.8H ₂ O
6.	$(Al_{1.87}Mg_{0.12}Fe_{0.01})_{\Sigma 2.00}(Si_{3.54}Al_{0.46})_{\Sigma 4.00}O_{10}(OH)_2[Mg_{0.16}Ca_{0.11}Na_{0.04}K_{0.02}]_{\Sigma 0.33}$ • 3.0H ₂ O
7.	$(Al_{1.76}Mg_{0.24})_{\Sigma 2.00}(Si_{3.69}Al_{0.31})_{\Sigma 4.00}O_{10}(OH)_2[Mg_{0.14}Ca_{0.10}K_{0.01}]_{\Sigma 0.25}$ • 3.3H ₂ O
8.	$(Al_{1.57}Mg_{0.43})_{\Sigma 2.00}(Si_{3.91}Al_{0.09})_{\Sigma 4.00}O_{10}(OH)_2[Mg_{0.10}Ca_{0.14}K_{0.03}]_{\Sigma 0.27}$ • 3.3H ₂ O
9.	$(Al_{1.56}Mg_{0.44})_{\Sigma 2.00}(Si_{3.92}Al_{0.08})_{\Sigma 4.00}O_{10}(OH)_2[Mg_{0.11}Ca_{0.15}K_{0.01}]_{\Sigma 0.26}$ • 3.6H ₂ O
10.	$(Al_{1.11}Mg_{0.80}Fe_{0.04}K_{0.04}Ca_{0.03})_{\Sigma 2.03}(Si_{3.89}Al_{0.11})_{\Sigma 4.00}O_{10}(OH)_2$ • 2.05H ₂ O

Notes - Numbering is as given in Table 2. Smectite formulas calculated on the basis of 22 (O,OH), palygorskite on 21 (O,OH), Li-tosudite by subtracting 50 wt.% of cookeite (ideal) and calculating the formula for the smectite component on the basis of 22 (O,OH). The structural formula for the montmorillonite (no. 1) is after correction for 20 wt. % admixed cookeite. The structural formula for the beidellite (no. 5) is after correction for 30 wt. % admixed lepidolite, 10 wt. % cookeite and 10 wt. % elbaite. The structural formula for the palygorskite (no. 10) is after subtraction of Na₂O as water-soluble NaCl.

generated from Wyoming bentonite saturated with LiCl and reacted at 400 °C for 30 d, but was not produced after 30 d at 300 °C (Eberl, 1978a). The Li-tosudite in the Himalaya dike system may not necessarily have formed in this temperature range because the experiments were not reversed. However, these temperatures are reasonable on the basis of oxygen isotopic and fluid-inclusion data (Taylor et al., 1979) obtained on higher temperature and pressure primary pocket minerals and lower-temperature fluid inclusions in later secondary calcite.

X-ray diffraction data indicate that the palygorskite (Table 1, Him-10) is pure, but the analysis of several samples indicates 2.42 wt% Na₂O. By omitting Na from the analysis, a more reasonable structural formula is obtained (Table 5, analysis 10). To determine whether the Na was present as a residual salt from an intragranular brine solution in the palygorskite, a 4.07-g sample was disaggregated in triply distilled ultrapure water and centrifuged. The supernatant liquid was analyzed semiquantitatively for Na and qualitatively for Cl. Cl was determined by adding AgNO₃ solution, which forms a dense precipitate of AgCl if Cl ions are present; Na was determined by atomic absorption spectrophotometry. These determinations indicate that most of the Na is present in a water-soluble form. The residue was dried and analyzed by XRF spectrometry, and the decrease in Na₂O from 2.42 to 1.26

wt% confirmed that much of the Na was removed by the single washing.

A chemical analysis of a sample of cookeite, containing some microcline, albite, and stibiotantalite, confirmed the optical and X-ray diffraction identification of cookeite. All of the samples of beidellite and Ca-Mg montmorillonite are dioctahedral and have d_{060} spacings of 1.49–1.51 Å. Beidellite cannot be distinguished visually from the Ca-Mg montmorillonite in the pockets and must be identified by complete chemical analysis or by the Greener-Kelly test (Starkey et al., 1984). The mineral may be much more widespread in this and other pegmatites than realized at present. The one sample of nontronite (Table 1, SDTM 4C) examined was trioctahedral with a d_{060} of 1.53 Å. Nontronite and todorokite are both uncommon minerals in the Himalaya dike system and represent deposition from locally specialized environments with the availability of the necessary Fe and/or Mn. Both occur late in the crystallization history, and only the red-brown kaolinite postdates them.

As noted in Table 1, three samples (SDTM-2EV; SDTM-2EJ, pink and white) of montmorillonite collapse on heating at 400 °C to a d_{001} spacing of 9.2 Å rather than the normal 9.8 Å spacing. The reason for this smaller spacing has not been determined, but may be due to substitution of F for OH in the 2:1 layer resulting in a thinner octa-

hectahedral sheet. An XRF analysis of a split of SDTM-2EV (Table 1) gave (in weight percent) SiO₂ 58.7, Al₂O₃ 19.1, Fe₂O₃ <0.04, MgO 3.76, CaO 1.63, Na₂O 0.19, K₂O 4.27, TiO₂ <0.02, MnO <0.02, P₂O₅ <0.05, LOI (920°C) 12.7, Total 100.35. After taking into account the admixed 20–30 wt% K-feldspar, the bulk chemistry of this montmorillonite is similar to that of the two montmorillonites given in Table 2 (analyses 8 and 9).

Two of the pocket clays examined (Table 2, analysis 1; Table 3, analysis 11) were a striking purplish red, whereas all others were either white, pink, brown, or red brown. The purplish-red color correlates with a significant content of Mn, >1% MnO, in both samples. Much of the Mn in pink pegmatite clays from New England is present as Mn³⁺, based on optical spectroscopy studies (D. Sherman and N. Vergo, 1985, pers. comm.).

Calcite has been found locally in pockets in the Himalaya dike system associated with laumontite, as a pocket cement. Only small amounts of later, buff-colored montmorillonite were associated with the calcite. Calcite has been reported from orogenic and anorogenic granitic pegmatites (Gillson, 1927; Hurlbut, 1958; Foord and Martin, 1979). A specimen (no. 15614) in the Denver Museum of Natural History, collected by H. Truebe, was identified as calcite by R. R. Cobban. The calcite occurs in beryl and smoky quartz pocket cavities in the anorogenic Mount Antero granite of Oligocene age (Switzer, 1939). Quartz, feldspar, beryl, and fluorite are associated with the calcite. The calcite itself closely resembles the calcite from the Himalaya dike system, having a platy habit, clear yellow cores, and opaque tan-buff rims that are solution-etched. The transition from early, clear, yellow, rhombohedral calcite to later, opaque, cream-colored, platy calcite parallels the observed development of habits of calcite from hydrothermal veins and Mississippi Valley-type deposits (A. V. Heyl, 1984, pers. comm.). Five measurements of fluid-inclusion-filling and/or homogenization temperatures for the platy calcite yielded pressure-uncorrected temperatures of 205–215°C. Freezing-point-depression temperatures between –15 and –18°C were also determined. Salinities, expressed as equivalent weight percent NaCl, range from 8 to 12.

CONCLUSIONS

We confirm the observations by Schaller (1925) and Jahns and Wright (1951) that there are two distinct types of pocket clays—hypogene and supergene. The source for many of the elements incorporated in the zeolite-clay-carbonate pocket-filling assemblage is the immediately adjacent norite. The pocket minerals were deposited under moderate- to low-temperature hydrothermal conditions at some time after the crystallization of the primary pocket minerals. A sharp discontinuity between the white-pink hydrothermal smectite clays and the red-brown supergene kaolinite is apparent in all the pegmatites. Kaolinite is currently being deposited in some of the fractures and pockets that have access to meteoric waters. The hydrothermal smectites were probably deposited in an al-

kaline environment, whereas the supergene kaolinite was deposited in an acid or less alkaline environment, on the basis of general knowledge of depositional conditions (Krauskopf, 1967). Many of the pegmatites show a consistent and widespread trend of changing depositional environment, reflected in both chemistry and mineralogy. Li-tosudite and palygorskite are first reported here from a pegmatite. This study and others of the complex pegmatites of San Diego County, California, indicate the existence of a continuum between magmatic and hydrothermal conditions.

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