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Clay-mineral suites, sources, and inferred dispersal routes: Southern California continental shelf

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Abstract

Clay mineralogy is useful in determining the distribution, sources, and dispersal routes of fine-grained sediments. In addition, clay minerals, especially smectite, may control the degree to which contaminants are adsorbed by the sediment. We analyzed 250 shelf sediment samples, 24 river-suspended-sediment samples, and 12 river-bed samples for clay-mineral contents in the Southern California Borderland from Point Conception to the Mexico border. In addition, six samples were analyzed from the Palos Verdes Headland in order to characterize the clay minerals contributed to the offshore from that point source. The <2 μm-size fraction was isolated, Mg-saturated, and glycolated before analysis by X-ray diffraction. Semi-quantitative percentages of smectite, illite, and kaolinite plus chlorite were calculated using peak areas and standard weighting factors. Most fine-grained sediment is supplied to the shelf by rivers during major winter storms, especially during El Niño years. The largest sediment fluxes to the region are from the Santa Ynez and Santa Clara Rivers, which drain the Transverse Ranges. The mean clay-mineral suite for the entire shelf sediment data set (26% smectite, 50% illite, 24% kaolinite + chlorite) is closely comparable to that for the mean of all the rivers (31% smectite, 49% illite, 20% kaolinite + chlorite), indicating that the main source of shelf fine-grained sediments is the adjacent rivers. However, regional variations do exist and the shelf is divided into four provinces with characteristic clay-mineral suites. The means of the clay-mineral suites of the two southernmost provinces are within analytical error of the mineral suites of adjacent rivers. The next province to the north includes Santa Monica Bay and has a suite of clay minerals derived from mixing of fine-grained sediments from several sources, both from the north and south. The northernmost province clay-mineral suite matches moderately

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well that of the adjacent rivers, but does indicate some mixing from sources in adjacent provinces.
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Keywords: Southern California; Clay minerals; Shelf sediments; River sediments; Source areas; Dispersal routes

1. Introduction

Clay mineralogy is useful in determining the distribution, sources, and dispersal routes of fine-grained sediments, from which current patterns can be inferred. The fine-grained component is that sediment fraction with which most contaminants are transported and within which they are hosted after deposition. In addition, clay minerals may control the degree to which contaminants (heavy metals, organic molecules) are incorporated into the sediment via both adsorption and absorption processes (House, 1998; Jackson, 1998). Detailed and systematic clay-mineral studies of shelf and slope sediments and adjacent rivers have been completed for much of the continental margin of the western United States, for example central and northern California (Griggs & Hein, 1980), Oregon and Washington (Duncan, Kulm, & Griggs, 1970; Karlin, 1980), Gulf of Alaska (Hein, Bouma, Hampton, & Ross, 1979; Molnia & Hein, 1982; Naidu & Mowatt, 1983), and the Bering Sea shelf (Moser & Hein, 1984; Naidu, Creager, & Mowatt, 1982). However, such a systematic study has not been done for the Southern California Borderland where sediment sources and sinks, transport pathways, and contaminant processes are critical issues for a region that encompasses huge population centers, major harbor facilities, offshore petroleum fields, and important marine recreational activities.

Only a few previous studies of Borderland clay mineralogy have been published, most dealing with sediments from the deep offshore basins, from small areas of the shelf, or from suspended and bottom sediments of individual rivers. Grim, Dietz, and Bradley (1949) analyzed about 30 sediment samples distributed throughout the Borderland as far west as the Patton Escarpment for clay-mineral content in the <2 μm size fraction. However, they did not present the compositions for individual samples, or estimate percentages of the various clay-minerals. Fleischer (1972) presented clay-mineral compositions of the <2 μm size fraction for sediments from a Santa Barbara Basin core, river-bed samples from the Ventura River and Gaviota Canyon Creek, and suspended sediment samples from the Ventura, Santa Clara, and Santa Ynez rivers. These suspended-sediment samples were collected during the major floods of February and March, 1969. He concluded that the Santa Clara River is the dominant source of sediment to the Santa Barbara Basin and that distinct layers were deposited during flood events. These same data had been presented earlier in a report to the Office of Naval Research, which also included clay-mineral suites for a core from each of Santa Monica, Santa Cruz, Catalina, and Tanner Basins, continental-rise sediments, and river-bed samples from San Gabriel, Santa Ana, San Onofre, and Santa Margarita rivers (Fleischer, 1970). McMurtry and Fan (1974) analyzed the clay-mineral content in the <2 μm size fraction of river-bed

samples from the Santa Ana River drainage basin and a few samples from the shelf immediately offshore from that river. They showed that the clay-mineral suite of the lower drainage basin is similar to that of the shelf sediments. Rateev, Timofeev, and Grechin (1981) determined clay-mineral suites in the <1 μm size fraction of sediments from Deep-Sea Drilling Project cores collected from Borderland basins. They concluded that a small amount of the smectite in the sediments is authigenic and that a variety of mixed-layer smectite–illite and chlorite–smectite mixed-layer clay minerals occur in the sediments.

The most extensive study of clay-mineral suites in the Borderland was based on analysis of the uppermost 2 cm of 392 box cores from six small areas sampled on a 2-km grid, three areas of which include part of the continental shelf, and three areas sampled on a 20 km grid (Berry & Nocita, 1977; Nocita, 1977). They analyzed the <4 μm size fraction of surface sediments collected along the margin from about Newport Beach to Point Mugu and another area north of Santa Barbara, as well in deep water basins west of Santa Catalina Island, south of San Nicolas Island, and south of San Miguel Island. They concluded that offshore clay minerals consist predominantly of smectite and illite with minor chlorite and kaolinite and reflect the mineralogy of soils on the adjacent continental margin. They also concluded that there is no regional pattern in clay-mineral distributions or dominant regional control on the distribution of nearshore clay-mineral suites, although various controls were suggested for local distributions.

For this study, we determined the clay-mineral contents of 249 surface sediment samples collected on the shelf from Ventura to the US–Mexico border, and one sample located on the shelf west of Santa Barbara (Fig. 1). In addition, we analyzed samples from sources of sediment to the Borderland shelf, including bed and suspended sediments from rivers and samples from the Palos Verdes Headland including the Portuguese Bend landslide.

2. Setting and sediment sources

The Southern California Borderland has many characteristics that are important to understanding the sources and dispersal of fine-grained sediment on the shelf. Southern California has a semi-arid climate and consequently most streams are small and ephemeral. There was a clear change from a wet to a dry climate in 1944 and then a change back to a wet climate in 1968–1969, based on stream-flow records from 1928 to 1995 (Inman & Jenkins, 1999).

The vast majority of sediment that has accumulated on the shelf and in deeper waters was supplied during major winter storms during El Niño years. For example, the suspended sediment delivered to the coast during the 1969 El Niño floods exceeded the input for the entire preceding 25-year dry period for most of the rivers draining the Borderland margin (Inman & Jenkins, 1999). Even during the wet periods (such as 1969–present), the amount of sediment supplied during El Niño years far exceeded that supplied during other years (Fig. 2). The vast majority of sediment was supplied during the months of January and February during El Niño years and November–January during other years (Fig. 2).

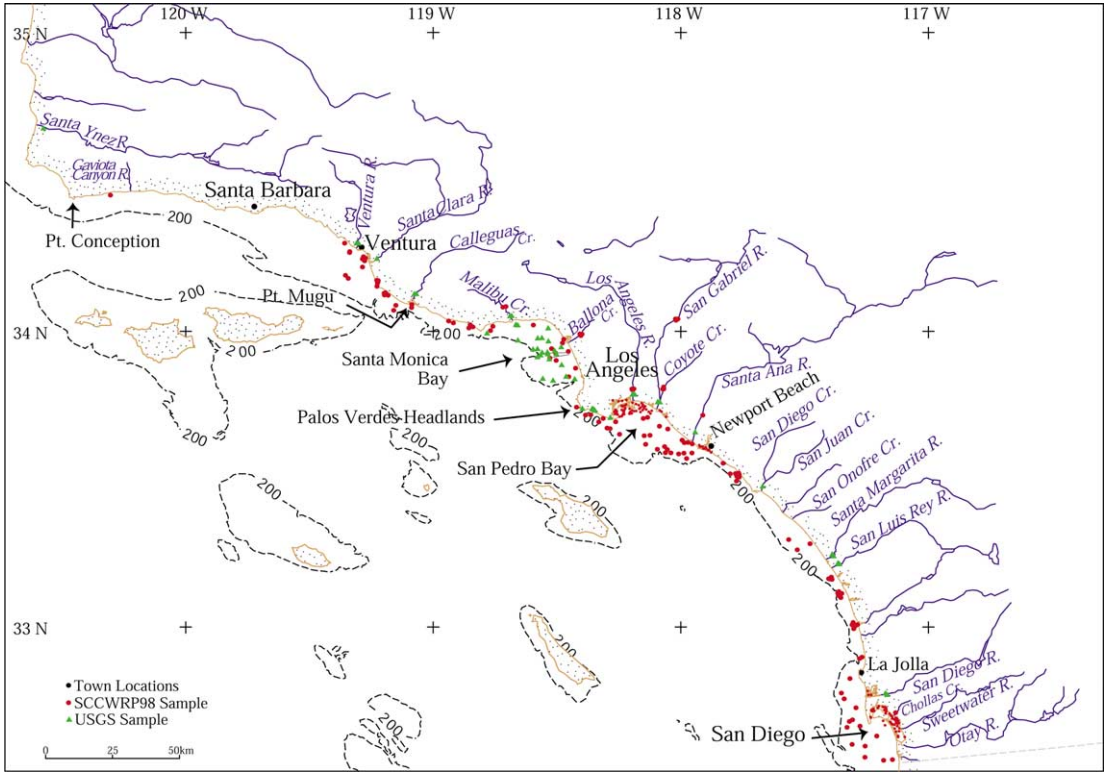

Fig. 1. Location of Southern California Borderland sampling sites (green triangles, red dots), river names (blue), and place names (black); the coastline is brown and the coastal area and islands are stippled; the 200 m isobath is a dashed black line.

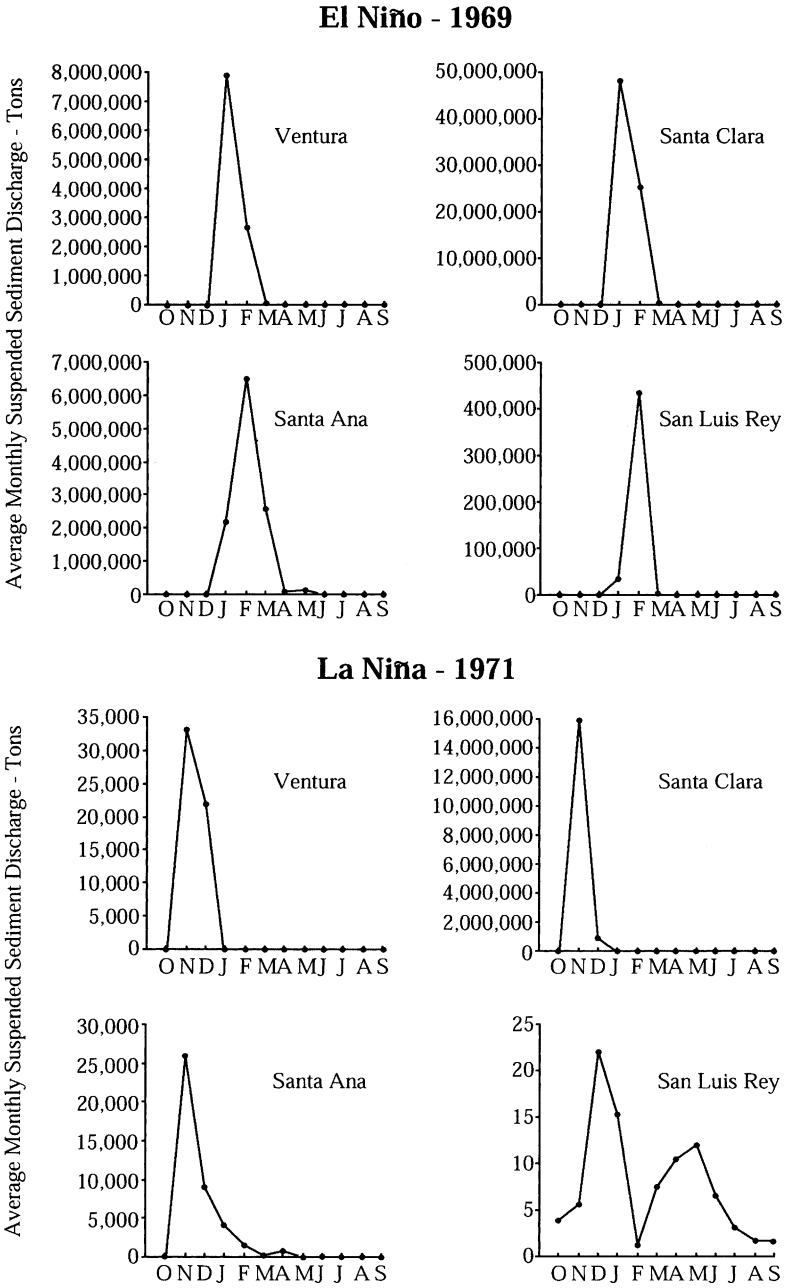

Fig. 2. Average monthly suspended-sediment discharge from four rivers draining Southern California during the large floods of the 1969 El Niño year and the subsequent La Niña year; note that all discharge scales are different and vary by about six orders of magnitude; compiled from U.S. Geological Survey data base found on http://webserver.cr.usgs.gov/sediment.

Sediment on the shelf is generally relatively coarse grained consisting of sand and silt, with rarely more than 20% consisting of clay-size particles (Emery, 1960), the size fraction studied here. In places, the sediment does not have a fine fraction at all, and in other places, the seafloor consists of rock outcrops.

The largest source of sediment input directly into the Borderland is the Santa Clara River (Fig. 3; Table 1), which has contributed more sediment annually during the last 40 years than it did during previous years. The Ventura, Calleguas, Malibu, and Santa Ana rivers have become more important sources of sediment during the past 40 years, primarily due to modification of the drainage basins and increased rainfall since 1969 (Fig. 4). Just north of the Borderland, the Santa Ynez River is a relatively large source of sediment that creates a plume that moves south and east around Point Conception and into the Borderland (Griggs & Hein, 1980). Even though the above mentioned rivers are the largest sediment sources for the Borderland, their combined annual load of sediment is small compared to that of the large rivers of Northern California, such as the combined load of the Eel, Smith, Russian, etc. rivers (Griggs & Hein, 1980).

The large floods of 1969 were the first major flush-events for the Southern California drainage basins and ended nearly 25 years of dry climate. Those events delivered a larger proportion of fine-grained sediment to the offshore than did subsequent floods during the 1969–1995 wet period (Inman & Jenkins, 1999). Rivers and creeks (Santa Ynez, Ventura, Santa Clara, Calleguas) that drain the Transverse Ranges occur in the northern part of the study area and contribute significantly larger amounts of sediment to the shelf than do rivers to the south. This large sediment contribution from northern Borderland rivers is the result of higher rainfall

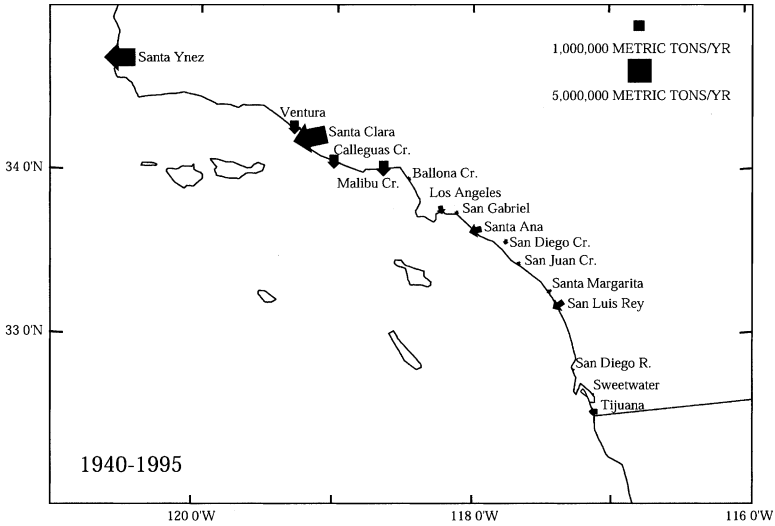

Fig. 3. Graphic representation of mean annual sediment supply from rivers to the Southern California Borderland, based on 55 years of data; the area of the arrow shaft is proportional to the sediment discharge as shown in the key; compiled from Inman, Jenkins, and Wasyl (1998).

Table 1
Mean fluvial sediment fluxes (10^6 tons/year) calculated from data in Inman et al. (1998), which are shown graphically in Figs. 3 and 4

	1940–1995	1945–1950	1990–1995
Santa Ynez	2.77	0.45	5.08
Ventura	0.59	0.05	1.24
Santa Clara	4.07	0.43	11.17
Calleguas	0.66	0.13	1.18
Malibu	0.75	0.01	1.45
Ballona	0.01	0.004	0.02
Los Angeles	0.24	0.04	0.43
San Gabriel	0.04	0.01	0.09
Santa Ana	0.44	0.01	0.99
San Diego	0.10	0.03	0.19
San Juan	0.05	0.0002	0.09
Santa Margarita	0.10	0.01	0.30
San Luis Rey	0.53	0.01	0.63
San Diego	0.01	0.0002	0.02
Sweetwater	0.005	0.0004	0.01
Tijuana	0.25	0.03	0.32

and the greater erodability of sedimentary rocks there compared to erosion of granitic and metamorphic rocks to the south. The Transverse Range comprises 25% of the Southern California drainage area, but supplies more than half of the suspended sediment to the coast (Inman & Jenkins, 1999). This is true even though those four rivers have intermediate-size drainage basins and water discharge for Southern California watersheds.

Weathering of the different rock types that comprise the various drainage basins produce different clay-mineral suites for each basin. Erosion and runoff transport those clay-mineral suites to the rivers that deliver them to the coast, where they may mix with suites carried by other rivers.

Contributions of sediment to the offshore from seacliff erosion is minor, except in the vicinity of the Palos Verdes Headland where the huge Portuguese Bend Landslide has conveyed significant amounts of sediment to the offshore (Kayen, Lee, & Hein, 2002). Shepard and Grant (1947) estimated that erosion of Borderland cliffs during the first half of the twentieth century had a maximum average of about 6–10 mm/year. This would translate into about 0.054 million tons/year of sediment, which is about 10% of the amount of sediment contributed to the Borderland as wind-blown debris (Emery, 1960). These cliff retreat and erosion rates have likely changed during the later half of twentieth century as the result of both extensive development of the region, which increases erosion rates, and armoring of the coast, which decreases cliff retreat.

Southern California and the coastal zone have been extensively modified. Those modifications have changed the amounts and types of materials input to the offshore. For example, rivers draining the Los Angeles area have a relatively high water discharge, but low suspended-sediment load because much of the drainage basin has

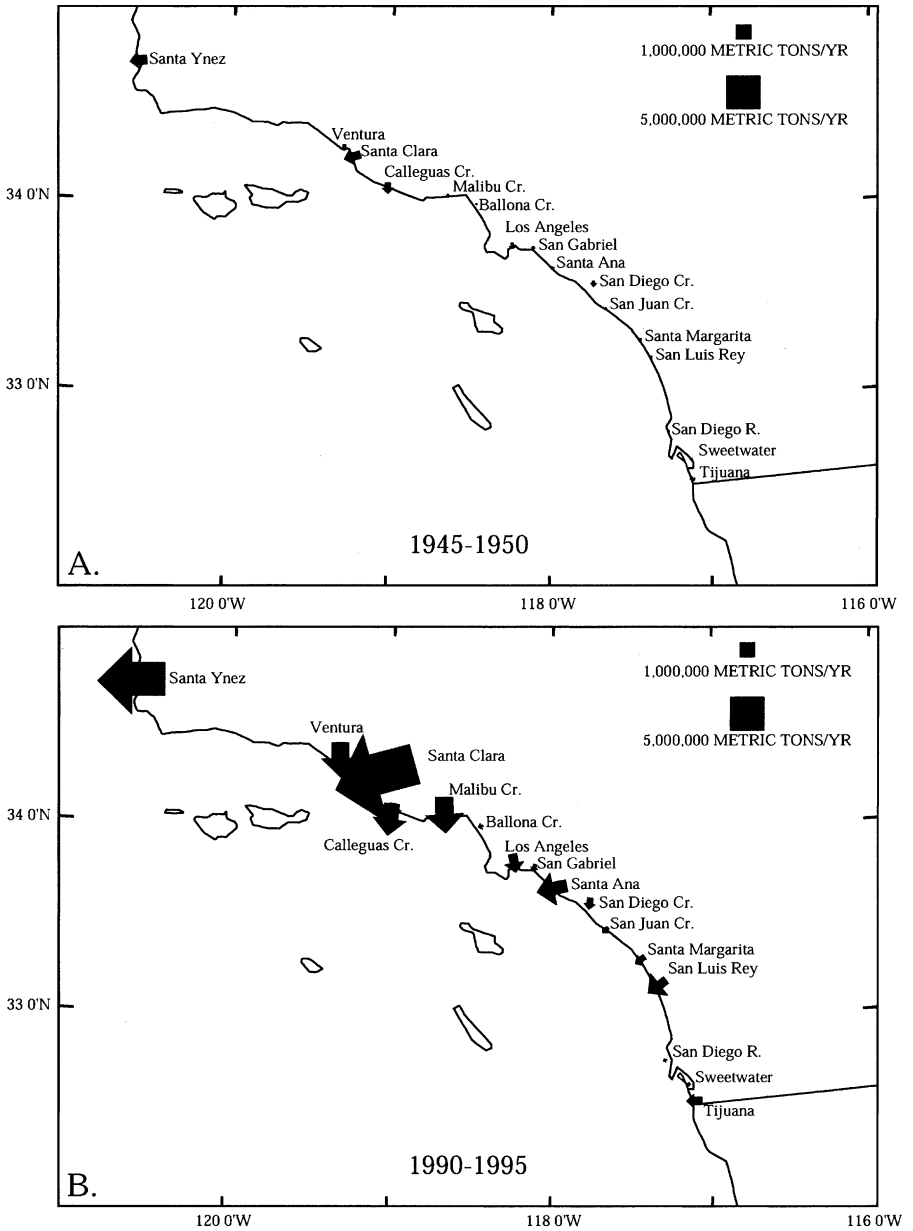

Fig. 4. Graphic representation of mean annual sediment supply from rivers to the Southern California Borderland, for two 5-year periods: A. 1945–1950, part of a 25-year dry period; and B. 1990–1995, part of a 30-year wet period; compiled from Inman et al. (1998).

been paved, including the river channels. Nearly all streams in Southern California have one or more dams that impound sediment, whereas in agricultural areas, sediment supply to rivers is enhanced. Much of the agricultural chemicals that had accumulated in the Southern California drainage basins, including those chemicals that had been banned, were transported to the offshore during the first major flush event (1969), which occurred after 25 years of relatively dry climate. Storm-water runoff from the urban areas of Southern California has proven to be toxic to offshore biota and disruptive to the ecosystems (Bay, Jones, & Schiff, 1999).

Griggs and McCrory (1975) showed that the amount of discharge of industrial, domestic, and thermal effluents to the ocean off Southern California is much greater than the water discharged from streams. These anthropogenic effluents include such contaminants as agricultural chemicals, petrochemicals, chemical wastes and heavy metals, radioactive wastes, domestic sewage, and heat from power plants. The effluents are transported offshore through outfall pipes and profoundly influence the marine environment in terms of water quality, clarity, and chemical composition. Not only are effluents discharged through outfall pipes, but sludge has also been discharged in some areas, for example from the Hyperion Treatment Plant into central Santa Monica Bay from 1957 to 1987, which contributed to sedimentation in the bay.

The role of clay minerals as carrier phases for inorganic and organic contaminants is well known (e.g. House, 1998; Jackson, 1998). The clay minerals smectite and vermiculite are capable of adsorbing contaminants as the result of expansion (swelling) of the basal spacing of their crystal lattice; they also have a high cation-exchange capacity (about 50–120 milliequivalents/100 g) compared with the other common clay minerals, illite, kaolinite, and chlorite (10 meq/100 g). All of these clay minerals can absorb contaminants onto surface edge faces.

3. Methods

We analyzed 250 shelf sediment samples for clay-mineral contents, as well as 24 suspended-sediment samples and 12 bed samples from rivers. The suspended-sediment samples from the rivers were collected in February, April, and June of 2000, except for one sample that was collected in February 1998. In addition, six samples were analyzed from the Palos Verdes Headland in order to characterize the clay minerals contributed to the offshore from that point source. That headland is more significant as a sediment source than others in the Borderland because of the large Portuguese Bend landslide that feeds sediment to the shoreline (Kayen et al., 2002). The sediment that settled from 15 gallons of effluent collected on 17–18 May 1999 from the Hyperion Treatment Plant in Santa Monica Bay was also analyzed for mineralogy, but the sediment was nearly all organic matter without a measurable quantity of minerals.

The procedure to determine clay-mineral contents includes the following steps. (1) About 5–15 cc of sediment were soaked for two days in a combination of Morgan's solution (sodium acetate, glacial acetic acid, and water) to remove carbonate and

30% hydrogen peroxide to remove organic matter. The samples were then washed several times with Morgan's solution and removed from suspension by centrifugation. (2) The washed sediment was suspended again with a magnetic stirrer in 0.01% sodium carbonate solution and the <2 μm size fraction (clay-size fraction) was isolated by centrifugation. (3) The clay-sized material was concentrated by centrifuging; magnesium saturated by washing four times with 1 M magnesium chloride; and excess salts were removed by washing with distilled water. (4) The clay was spread evenly over a plastic or glass insert of an aluminum sample holder and dried in a desiccator, after which the sample was placed over a bowl of ethylene glycol in an oven at 65 °C for 1 h and then in a desiccator for 1 day to expand the smectite clay-mineral lattice so that smectite could be distinguished from chlorite and vermiculite.

The glycolated samples were analyzed using a Philips X-ray diffractometer with carbon monochromator and Cuk_α radiation. Continuous scans were run from 3 to 70° 2Θ using a step size of 0.02° 2Θ at 1 s/step, yielding a scan speed of 0.02° 2Θ/s. A second scan was run from 24 to 26° 2Θ using a step size of 0.02° 2Θ at 5 s/step, yielding a scan speed of 0.004° 2Θ/s. This second scan was used to attempt to distinguish chlorite from kaolinite (Biscaye, 1964), which was generally unsuccessful, so kaolinite and chlorite percentages are listed together in the tables. Semi-quantitative estimates of relative clay-mineral percentages were obtained from measurement of diffractogram peak areas, which were multiplied times the weighting factors of Biscaye (1965): four times the illite peak area, two times the kaolinite + chlorite peak area, and one times the smectite peak area, then normalized to 100%. This procedure allows us to compare our results with other studies of marine clay minerals that use those same weighting factors; especially important in this regard is comparisons with the Central and Northern California shelf clay-mineral suites determined by Griggs and Hein (1980). Vermiculite does not occur in most samples analyzed, and is a very minor component, less that 2–3%, in the others. Smectite listed in the tables is a smectite–illite mixed-layer clay mineral and the amount of expandable layers (the smectite portion) was calculated based on the difference in the height of the base line from the high and low 2Θ sides of the 5.2° 2Θ peak (see Perry & Hower, 1970; Reynolds and Hower, 1970). Clay-mineral contents of all samples used in this study, including a non-weighted data set, can be found on the USGS Web site http://geopubs.wr.usgs.gov/open-file/of01-077/ (Hein & Dowling, 2001).

Duplicate analyses were run on 10% of the samples in order to measure analytical precision. Reproducibility was within three percent for 80% of the duplicate samples and within five percent for 90% of the samples. Samples with total peak areas less than about 550 mm^2 had poor reproducibility and those data are not used; those samples are listed in the tables as LCMC, low clay-mineral content. A <2 μm fraction exists for those LCMC samples, but the clay minerals are either absent or very poorly crystalline; this phenomenon needs further study. Because of these 16 LCMC samples, the total number of samples used in analyses include 130 shelf sediment and 111 harbor sediment samples for a total of 241 offshore samples; and 29 river sediment samples (see first paragraph in Methods section).

4. Results

4.1. Clay-mineral suites

Clay-mineral suites will be presented first for three different groups of samples: shelf, harbor, and river samples. Harbor samples are considered separately from shelf samples because harbors have a greater potential to be disturbed by anthropogenic activities, such as dredging. The variability in clay-mineral contents is large within each of these three groups of samples. For example, for shelf samples, smectite contents vary from 0 to 54%, illite from 25 to 89%, and kaolinite + chlorite (k + c) from 7 to 46%. However, the mean clay-mineral suites for the three groups are remarkably similar, especially for the shelf and river samples (Table 2). For 130 shelf samples, the clay-mineral suite is 26% smectite, 50% illite, and 24% k + c, similar to the mean for 29 river samples of 31% smectite, 49% illite, and 20% k + c. Thus, the Borderland clay minerals are dominated by illite, with smectite somewhat more abundant than k + c.

Because k + c contents are relatively uniform, smectite and illite contents of samples for each of the three groups and for all three groups combined have a strong inverse relationship, with a correlation coefficient of −0.87 (Fig. 5). Smectite contents of shelf sediments have weak, but statistically significant positive correlations with the silt (2–62 μm size fraction)- and clay-size (< 2 μm) fractions as percentages of the bulk sediment and a negative correlation with the sand (> 62 μm)-size fraction. In contrast, illite contents show the opposite correlations with sand, silt, and clay contents of the bulk sediment samples. Q-mode factor analysis (Klovan & Imbrie, 1971) shows these same relationships, placing smectite content, silt-size fraction, and clay-size fraction in one factor and illite content, sand-size fraction, as well as k + c content in a second factor. This means that there is a weak tendency for the coarser-

Table 2
General statistics for Borderland clay-mineral suites

	N[a]	Mean	S.D.[a]	Min.[a]	Max.[a]
Shelf					
Smectite	130	26	13	0	54
Illite	130	50	14	25	89
Kaolinite & chlorite	130	24	7	7	46
Rivers					
Smectite	29	31	19	0	73
Illite	29	49	13	19	75
Kaolinite & chlorite	29	20	9	3	44
Harbors					
Smectite	111	22	10	5	53
Illite	111	57	9	37	75
Kaolinite & chlorite	111	21	6	8	40

[a] *N* is number of samples; S.D. is standard deviation; Min. is minimum. Max. is maximum.

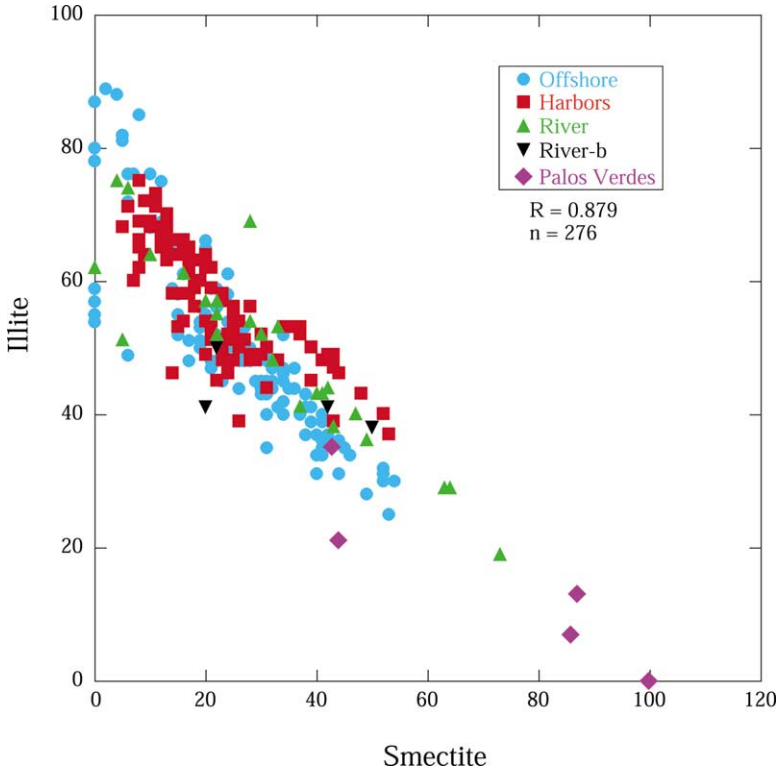

Fig. 5. Strong statistical correlation between smectite and illite contents from clay-mineral suites of fine-grained sediments; River-b points are for the four large rivers (Santa Ynez, Ventura, Santa Clara, Calleguas) that drain the Transverse Range; Palos Verdes is the clay-mineral composition of rocks that comprise the Palos Verdes Headland.

grained bottom sediments to have higher illite and k + c contents than finer-grained sediments. This is consistent with smectite generally having a smaller mean grain size than illite, kaolinite, and chlorite.

The Palos Verdes Headland is a point source for a smectite-dominated clay-mineral suite. The mudstones that comprise part of the Portuguese Bend landslide have a mean clay-mineral suite of 79% smectite, 14% illite, and 7% k + c, based on four samples. That landslide comprises 1.06 km^2 of the southwestern part of the headland and has contributed 12.1 million metric tons of sediment to the shelf since 1956 (Kayen et al., 2002). A composite sample composed of a spot sample taken every meter through about 40 stratigraphic meters of the Monterey Formation that comprises much of the headland has a clay-mineral suite of 44% smectite, 21% illite, and 35% k + c, and in this regard is also a point source for k + c. Sediment produced from the alteration of basalt on the headland is 100% smectite. The amount of material delivered to the offshore by the landslide is significantly greater than that provided by erosion of cliffs that front the peninsula.

The clay-mineral composition of rivers can vary dramatically for suspended samples collected at different times and between suspended- and bottom-sediment samples, even those collected at the same time (Table 3). A bottom-sediment sample may or may not be representative of the river clay-mineral suite as a whole, whereas a suspended-sediment sample should be representative for the period of flow during which the sample was collected. The clay-mineral suite of the bottom-sediment sample from the San Diego River (Table 3) indicates that it may represent a local deposit because it is so different from the suspended-sediment clay-mineral suite; consequently, we do not use that sample in calculations of mean river clay-mineral suites. Illite content is commonly 10–13% less in bottom sediment than in suspended sediment; whereas the smectite content of suspended sediment is commonly less than it is in bottom sediment. Suspended and bottom sediment k + c contents are generally the same within analytical error.

4.2. Regional distribution

The clay-mineral content of the river sediment varies along the coast. The rivers and creeks that drain the Transverse Range (Santa Ynez, Ventura, Santa Clara, Calleguas) have a mean illite content of 43% (range 38–50%; all bottom sediment samples), whereas the smectite and k + c contents are highly variable for those rivers. Smectite contents are low for the Santa Ynez and Ventura Rivers (mean 21%) and relatively high (mean 46%) for the other two rivers. K + c contents decrease steadily to the south, from 39% for the Santa Ynez River to 12% for the Calleguas Creek and decrease still further to 8% for Malibu Creek.

Mean illite contents increase steadily to the south, from Malibu Creek (24%) to Ballona Creek (41%) to Los Angeles, San Gabriel, and Santa Ana Rivers (mean 51%), to San Juan, Santa Margarita, San Luis Rey, and San Diego Rivers (mean 66%). Then, illite contents decrease farther south to 48%. Smectite contents have the opposite trend and decrease to the south from Malibu Creek (mean 69%) to Ballona Creek (mean 41%), to Los Angeles through San Juan Rivers (30%), to Santa Margarita through San Diego Rivers (mean 8%). Smectite then increases to 32% farther south. K + c contents fluctuate in rivers moving south from a mean of 20% for Ballona Creek through the Santa Ana River to 3% for San Juan Creek, then back to about 20% for the Santa Margarita River, to 44% for San Luis Rey River, back to about 20% again for San Diego River and Chollas Creek.

In order to delineate trends in the clay-mineral contents of shelf sediments, we divided data for each mineral into three sub-equal groups (Figs. 6–8). The boundaries of the percentage groups were chosen where there is a relative paucity in the sequence of percentage values. This analysis shows that there is a zone of low-illite contents in central and northern Santa Monica Bay, immediately seaward of the Palos Verdes Headland, and in a few other small areas (Fig. 6). In contrast, high illite contents occur in many areas in the nearest-shore samples and in a large area off of San Diego where the seafloor is covered by coarse-grained sediments and outcrops with sparse and discontinuous sediment cover. These high illite areas are consistent with the statistics (Q-mode and correlation coefficients) that indicate an association of illite with sediments with relatively higher sand contents.

Table 3
Clay-mineral suites of Borderland river samples and Palos Verdes Headland (first six) samples; rivers listed from north to south

	Smectite (%)	Illite (%)	k + c (%)	Expandable layers (%)
05-1C-10-99	44	21	35	70
06-1E-10-99	100	0	0	50
06-3B-10-99	43	35	22	58
06-3C-10-99	87	13	0	49
06-3D-10-99	100	0	0	52
06-3E-10-99	86	7	7	65
Santa Ynez R. 1975B	28	38	34	–
Santa Ynez R. 061300 B	20	41	39	50
Ventura R. 061300 W	LCMC	LCMC	LCMC	LCMC
Ventura R. 061300 B	22	50	28	56
Santa Clara R. 061400 B	42	41	17	56
Calleguas R. 061300 W	LCMC	LCMC	LCMC	LCMC
Calleguas R. 061300 B	50	38	12	63
Malibu Cr 022400 W	73	19	8	75
Malibu Cr 041800 W	64	29	7	70
Malibu R. 061300 W	LCMC	LCMC	LCMC	LCMC
Malibu R. 061300 B	LCMC	LCMC	LCMC	LCMC
Ballona Cr 022400 W	41	43	16	62
Ballona Cr 022800 W	43	38	19	59
Ballona Cr 041800 W	40	43	17	60
LA River 022400 W	22	55	23	55
LA River 022800 W	0	62	38	0
LA River 041900 W	20	57	23	46
LA River 061300 W	47	40	13	65
LA River 061300 B	42	44	14	55
San Gabriel R 022400 W	30	52	18	65
San Gabriel R 022800 W	49	36	15	78
San Gabriel R 041900 W	33	53	14	65
San Gabriel R. 061400 W	LCMC	LCMC	LCMC	LCMC
San Gabriel R. 061400 B	22	57	21	51
Coyote Cr 022400 W	10	64	26	50
Coyote Cr 022800 W	28	54	18	52
Coyote Cr 041900 W	LCMC	LCMC	LCMC	LCMC
Santa Ana R 020998 W	22	52	26	70
Santa Ana R. 061400 B	37	41	22	59
San Juan Cr. 061400 B	28	69	3	65
S. Margarita R. 061400 W	6	74	20	43
S. Margarita R. 061400 B	16	61	23	55
San Luis Rey R. 061400 W	LCMC	LCMC	LCMC	LCMC
San Luis Rey R. 061400 B	5	51	44	41
San Diego R. 061400 W	4	75	21	50
San Diego R. 061400 B	63	29	8	65
Chollas Cr 021200 W	32	48	20	65

05-1C is composite of Monterey Fm; 06-1E is sediment produced from weathering of basalt; 06-3B-3E are from toe of Portuguese Bend Landslide; numbers following river names are dates of collection (mmddyy); the first sample from Santa Ynez R. is from Griggs and Hein (1980); LCMC means low clay-mineral content, below semi-quantifiable limits; shelf sample data are available on the Web (Hein & Dowling, 2001)

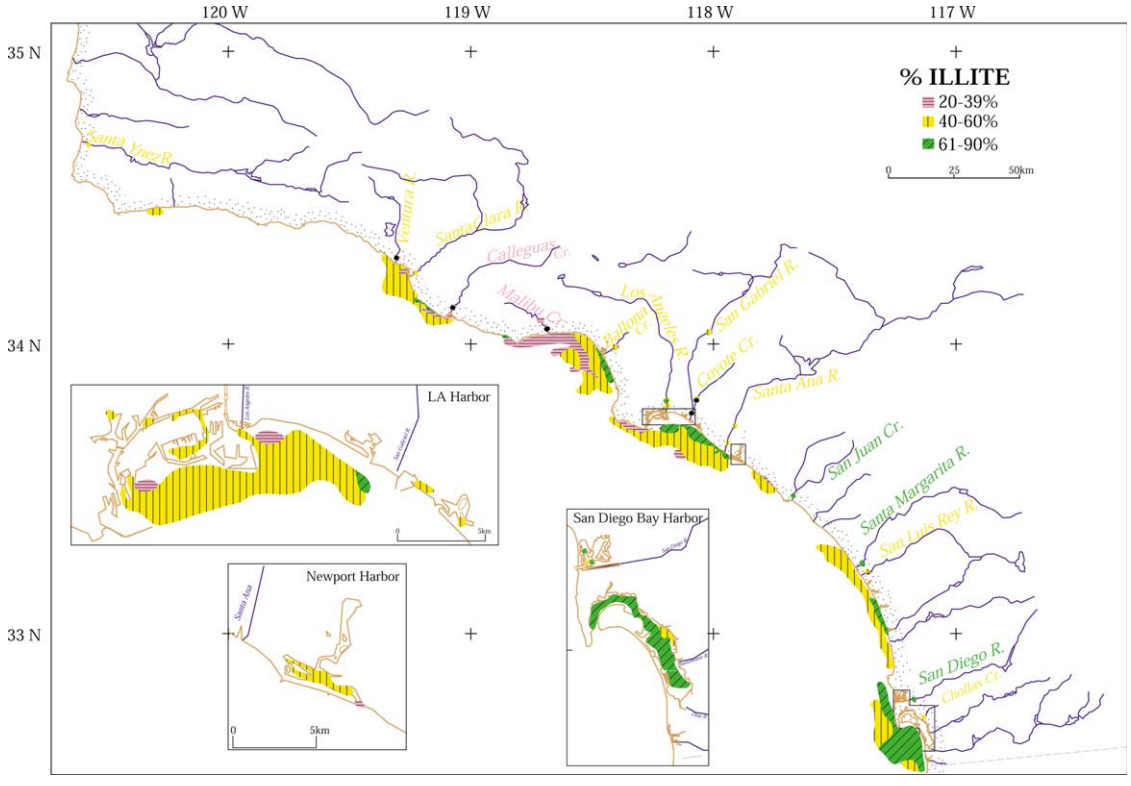

Fig. 6. Distribution of three percentage ranges of illite contents of fine-grained sediment fraction from shelf and harbor sediment samples, and suspended and bottom sediment samples from rivers; the color of the river names also corresponds to percentage illite as defined in the key.

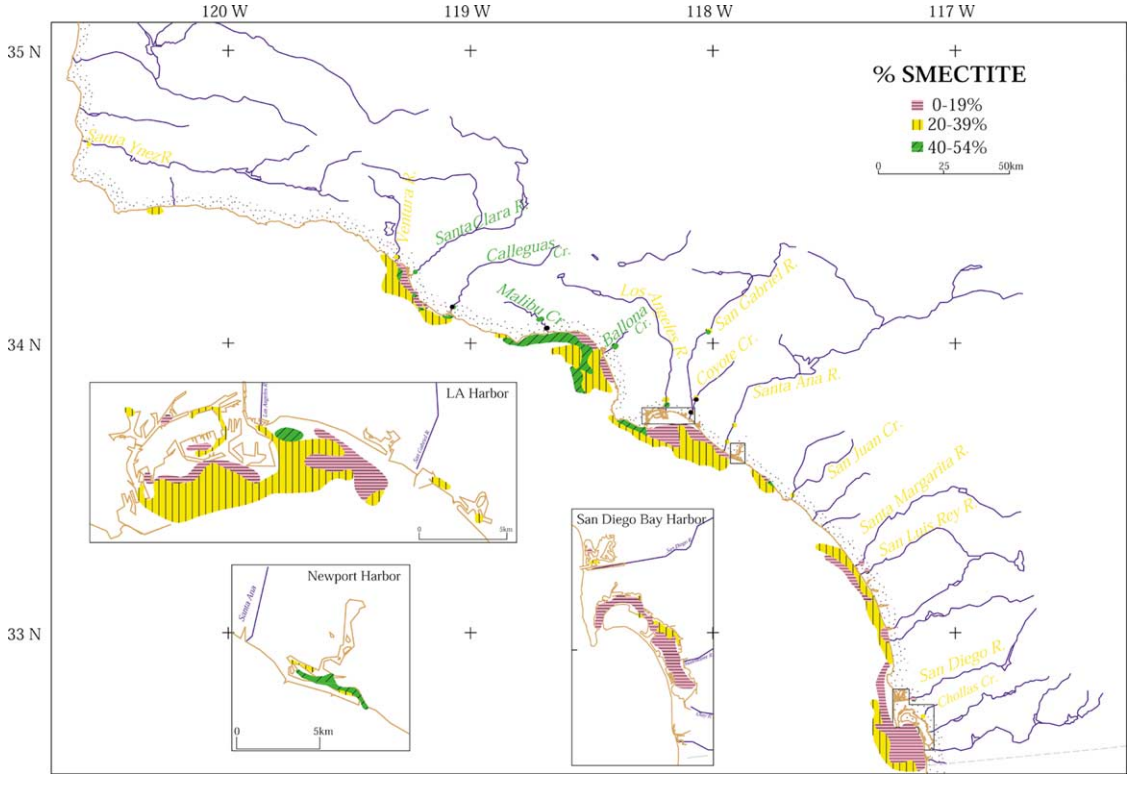

Fig. 7. Distribution of three percentage ranges of smectite contents of fine-grained sediment fraction from shelf and harbor sediments, and suspended and bottom sediment samples from rivers; the color of the river names also corresponds to mean percentage smectite as defined in the key.

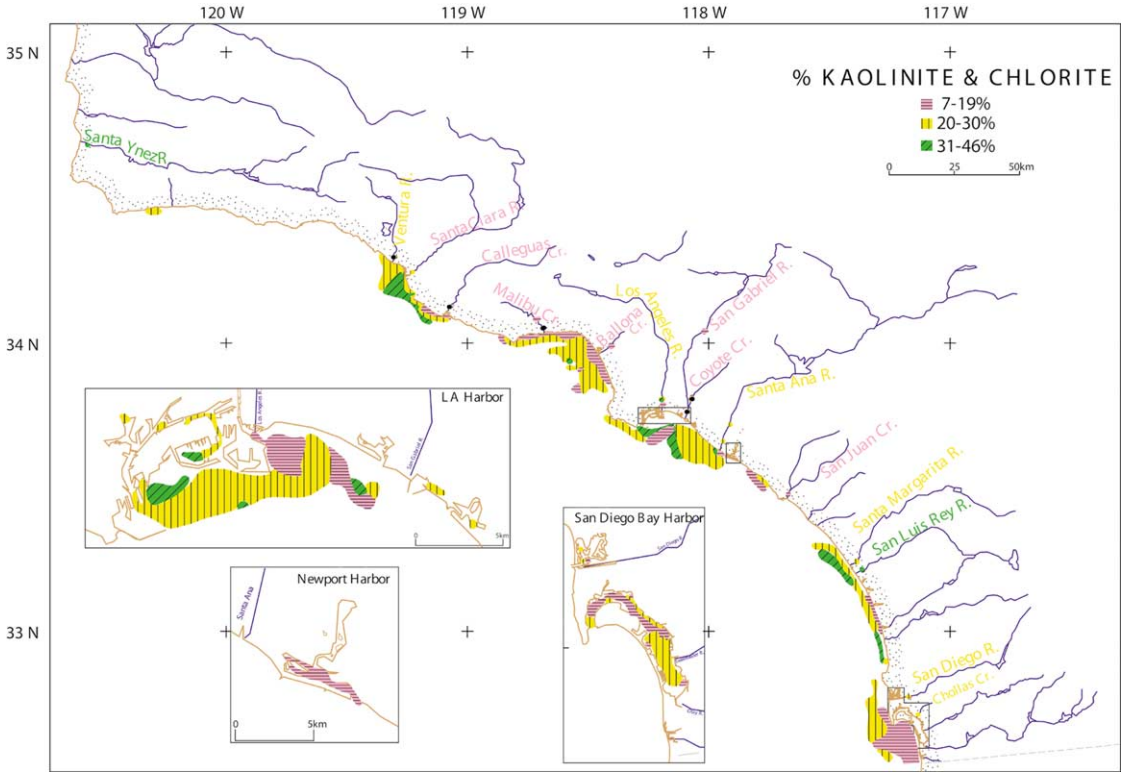

Fig. 8. Distribution of three percentage ranges of k + c contents of fine-grained sediment fraction from shelf and harbor sediments, and suspended and bottom sediment samples from rivers; the color of the river names also corresponds to percentage k + c as defined in the key.

Smectite shows the opposite trend of that of illite with low contents in the nearest-shore sediments and off San Diego and highest contents in central and northern Santa Monica Bay and immediately offshore Palos Verdes Headland (Fig. 7). K + c contents are also lowest in the nearest-shore samples (Fig. 8). The highest k + c contents generally occur in samples that are farthest from shore throughout much of the region.

Clay-mineral contents of harbor sediments are generally similar to those of sediments on the shelf seaward of the harbors. However, there are some differences, for example the high smectite contents in sediments in Newport Harbor do not match the contents for sediment just outside the harbor.

4.3. Clay-mineral suites and provinces

Clay-mineral suites on the Borderland shelf can be divided into four provinces based on mean clay-mineral contents of groups of samples. The suites are not sharply defined because of the high variability of smectite and illite contents of samples within regions and the small variability of k + c contents overall. The high variability of smectite and illite contents is the result of local sediment and seafloor conditions, such as sediment mixing, winnowing, or sampling of relict deposits, etc. that modify the clay-mineral suite in some samples within each Province relative to the majority of samples that characterize each province. The northern province (A) occurs from Point Conception south to Point Mugu and has a mean content of 23% smectite, 49% illite, and 28% k + c (Table 4). The next province south (B) encompasses Santa Monica Bay and offshore Palos Verdes Headland with a clay-mineral suite of 35% smectite, 43% illite, and 22% k + c. The next province south (C) includes San Pedro Bay south to just north of La Jolla with a clay-mineral suite of 24% smectite, 52% illite, and 24% k + c. The southernmost province (D) extends from just north of La

Table 4
Mean clay-mineral suites for divisions of the Borderland shelf and adjacent rivers

	Smectite (%)	Illite (%)	k + c (%)	Location
Province A	23	49	28	Pt. Conception–Pt. Mugu
Province A rivers	34	42	24	
Province A rivers[a]	32	41	27	
Province B	35	43	22	Pt. Mugu–N. San Pedro Bay
Province B rivers	52	34	14	
Province B rivers[a]	68	24	8	
Province C	24	52	24	San Pedro Bay–N. La Jolla
Province C rivers	21	57	22	
Province C rivers[a]	18	52	30	
Province D	15	67	18	N. La Jolla to US–Mexico border
Province D rivers	18	62	20	

[a] Normalized to mean (1940–1995) suspended-sediment flux in rivers; data not available for Province D rivers.

Jolla to the Mexico border with a clay-mineral suite of 15% smectite, 67% illite, and 18% k + c. The mean composition of characteristic samples from adjacent provinces are distinct within one standard deviation (Fig. 9).

Basically, smectite contents decrease south through Provinces B–D, whereas illite contents increase. Province A occurs off rivers that drain the Santa Ynez Mountains of the Transverse Range; Province B occurs off rivers that drain primarily the Santa Monica Mountains, and also part of the Los Angeles Basin and Palos Verdes Headland; Province C lies off rivers that drain the Peninsular Ranges and Los Angeles Basin; and Province D lies off a region with little river input.

The mean clay-mineral content of rivers entering each province matches that of the mean for the shelf sediments very well for Provinces C and D, moderately well for Province A, and poorly for Province B, especially smectite contents (Table 4). The clay-mineral percentages for each river in a given province were normalized to the mean suspended-sediment flux (55 year mean) for each river in order to give the clay minerals of larger rivers more weight in determining the mean clay-mineral suites (Table 4; the percent of the total province sediment flux that each river contributes to a province is multiplied by the percentage of each clay mineral for that river and those values summed for all rivers in that province, which provides the weighted province mean). The normalized clay-mineral suites change significantly only for Province B rivers compared to the non-weighted suite, but do slightly improve the match between the shelf suite and river suite for Province A. Suspended

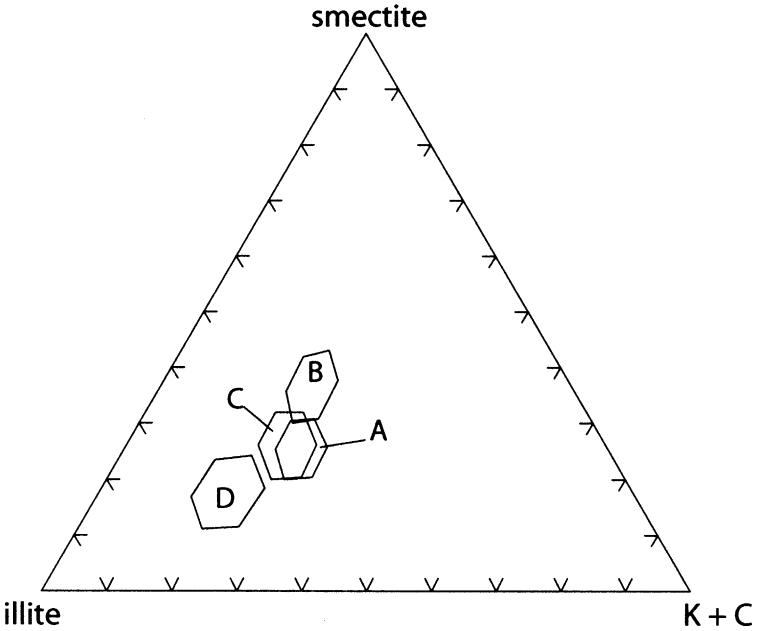

Fig. 9. Ternary plot of clay-mineral suite standard deviation fields for the mean composition of characteristic samples from the four clay-mineral provinces (Table 4), showing little overlap between geographically adjacent provinces; Province B lies geographically between Provinces A and C.

sediment data are not available to normalize river clay-mineral suites of Province D, but the normalized suite is unlikely to vary much from the suite given because all the rivers there have similarly small discharge.

5. Discussion

5.1. Fine-grained sediment sources and inferred dispersal routes

The clay-mineral contents of rivers change during storms (e.g. Weaver, 1967). However, a systematic study of storm-induced variations in intermittent or small coastal streams like those that occur in southern California has not been published. The best representation of the clay minerals delivered to the offshore by rivers would be those carried by the rivers during major storms; for the Borderland that especially would have been the 1969 floods that occurred after a 25-year dry period and which produced an initial flush of the river drainage basins. We do not have samples from those floods, but most of the river samples analyzed here were collected during a winter of large storms in 2000. Fleischer (1970) provides data for the clay-mineral content of suspended sediment samples from the Santa Ynez, Ventura, and Santa Clara Rivers collected during the 1969 floods. However, it is difficult to compare those results with ours because of different analytical techniques.

The variability of clay-mineral contents is very high in both Borderland shelf sediments and river samples. That regional variability in shelf sediments is controlled by local and regional factors such as mixing of clay minerals from different rivers by along-shore drift and currents; topography (headlands, canyons, wide and narrow shelves, etc.); sediment type, especially grain size; major and enduring landslides; modification of rivers and their drainage basins; urbanization of the coastal zone. Despite all these variables, it is clear from the nearly identical mean clay-mineral suites for the shelf and rivers that the primary source of clay minerals to the Borderland shelf is rivers draining the adjacent region. This is especially true for the southern part of the region where the clay-mineral suites of shelf sediments and rivers match within analytical error. For the northern part of the region, the match is not as good, especially for Province B, and several sources are likely providing sediments to those regions.

The long-distant transport to the Borderland of sediment from rivers in Northern California, which have huge sediment fluxes, is unlikely because their clay-mineral suites (Griggs & Hein, 1980) are much different than those found in the Borderland. This is especially true of the k + c contents, which are much higher in Northern California rivers. In addition, the north-flowing Davidson current dominates circulation during winter months when the greatest amounts of sediment are being discharged into coastal waters. Consequently, the lack of correspondence between shelf and river clay-mineral suites in Province B, and to a lesser extent in Province A, must be due to mixing of various Southern California sources.

Province B includes Santa Monica Bay and offshore Palos Verdes Headland. The clay-mineral suite in Santa Monica Bay must be a composite of clay minerals derived from the adjacent rivers as well as from other sources. Though Malibu

Creek is the predominant source of fine-grained sediment for an arcuate band of low-illite and high-smectite contents that is centered on the river (Figs. 6 and 7), the mean clay-mineral content for the Bay is much different than that of Malibu Creek. Illite contents are lower in Santa Monica Bay sediment than in the adjacent rivers and may have been added by the Los Angeles River, which prior to 1884 (began in 1825 and became permanent in 1884; Emery, 1960), emptied into Santa Monica Bay, whereas now it empties into San Pedro Bay. In addition, sediment from the Los Angeles River and rivers to the south in Province C, may be presently transported north along the coast and into Santa Monica Bay. Littoral drift is to the south in that region, but the California Current has a strong shoreward component in the southern Borderland, which bifurcates and the poleward component flows along shore (Hendershott & Winant, 1996). Illite may also be derived from rivers draining the Transverse Ranges via near-shore transport to the south (Griggs & Hein, 1980), or by a more circuitous route with the California Current (Thornton, 1981). Smectite contents in Santa Monica Bay are much lower than they are in adjacent rivers, which can be explained by: (1) preferential transport of smectite into deeper water because of its finer grain size than the other clay minerals (Gibbs, 1977); (2) transport of a low-smectite, high-illite suite south from the Santa Ynez and Ventura Rivers; (3) transport of clay minerals via the Los Angeles River directly into Santa Monica Bay prior to 1884; and/or (4) transport of clay minerals into Santa Monica Bay from the Los Angeles and other rivers of Province C via northward flowing currents. There does not appear to be an enrichment of smectite in deeper water sediments (Fleischer, 1970), so the first explanation is probably not important. An exception to this may be the high-smectite suite being delivered to the offshore from the Palos Verdes Headland, which is abundant in a narrow near-shore zone, but overall, may be transported off the very narrow shelf that occurs in that area. The 7-mile long outfall pipe dumped large quantities of sludge onto the shelf in central Santa Monica Bay for three decades; the clay-mineral content of that sludge is not known. Relatively low-smectite contents (compared to adjacent Bay sediments) just northwest of the outfall pipe may reflect contributions from that sludge.

Province A fine-grained sediments are derived predominantly from the relatively large rivers that drain the Transverse Range, with the small differences between shelf and river mean clay-mineral contents being due to the relative contributions from rivers north of Point Conception versus those in the Ventura area.

5.2. Smectite and the environment

Smectite is the only clay mineral that occurs in abundance in the Borderland that can adsorb large quantities of organic and inorganic chemicals via expansion of its basal spacing, although the other clay minerals present can absorb contaminants onto surface sites, such as edge faces (House, 1998; Jackson, 1998). Smectite is the name used for a group of clay minerals (montmorillonite, nontronite, saponite, etc.) that have both very high cation-exchange capacities and the ability to expand (swell) the basal spacing. This means that heavy metals and organic molecules can be incorporated between the expandable layers of the smectite lattice (adsorption), in

addition to absorption on surface faces, and through ion-exchange; the incorporated contaminants can be thereby assimilated into the sediment. Relatively high-smectite contents occur in sediments in Santa Monica Bay, immediately offshore the Palos Verdes Headland, and in Newport Harbor. These are all places where toxic effluents have been discharged in the past and the smectite may be instrumental in adsorbing some of those toxicants. However, in general, sediment on the Borderland shelf contains $<20\%$ clay-size material, so the overall cation-exchange capacity of the bulk sediment and expandable component of the sediment may have a small overall influence on contaminant storage and transport.

6. Conclusions

Smectite contents in Borderland shelf samples vary inversely with illite contents because k + c contents are relatively uniform. Statistical analyses shows that there is a weak tendency for coarser-grained bottom sediments to have higher illite and k + c contents and finer-grained sediments to have higher smectite contents. This means that grain-size in part determines the sediment clay-mineral suite, but that other factors have a more dominant control, for example the clay-mineral suite of sediments from the many rivers that deliver sediment to the shelf during storms. In fact, most fine-grained sediment is supplied to the Southern California Borderland shelf by rivers during major winter storms, especially during El Niño years. The largest sediment fluxes to the region are from the Santa Ynez and Santa Clara Rivers, which drain the Transverse Ranges. The mean clay-mineral suite for the entire shelf sediment data set (26% smectite, 50% illite, 24% kaolinite + chlorite) is closely comparable to that for the mean of all the rivers (31% smectite, 49% illite, 20% kaolinite + chlorite), indicating that the main source of shelf fine-grained sediments is the adjacent rivers. However, regional variations exist and the shelf is divided into four provinces with characteristic clay-mineral suites. Santa Monica Bay in Province B is a region of mixing of fine-grained sediments derived from Province A rivers (especially the Santa Ynez, Santa Clara, and Ventura Rivers) to the north, Province B rivers (especially Malibu Creek), and Province C rivers (especially the Los Angeles, San Gabriel, and Santa Ana Rivers) to the south. In contrast, the clay-mineral suites from the two southernmost provinces, C and D, are derived predominantly from the adjacent rivers. Province A fine-grained sediments are derived predominantly from the relatively large rivers that drain the Transverse Range, with the small differences between shelf and river mean clay-mineral contents being due to the relative contributions from rivers north of Point Conception versus those in the Ventura area.

Clay minerals, especially smectite, may play an important role in the transport and storage of contaminants in local areas, for example in Newport Harbor. However, because sediments on the Borderland shelf generally contain $<20\%$ clay-size material and only moderate amounts of smectite, clay minerals may have only a small overall influence on contaminant distributions.

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